

UNIVERSITY OF SOUTHAMPTON

STUDIES OF CdTe ELECTRODEPOSITION.

by

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ABSTRACT

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The electrocrystallization and growth of Te and CdTe under potentiostatic conditions have been studied using the theories developed for the electrocrystallization of metals on foreign substrates. The electrodeposition of Te on glassy carbon and of CdTe on tin oxide coated glass take place by progressive nucleation / three dimensional growth under diffusion control, whereas the electrodeposition of CdTe on monocrystalline silicon takes place by instantaneous nucleation / two dimensional growth under kinetic control. From considerations of progressive nucleation / three dimensional growth under diffusion control, a new analytical equation to express increase in current with deposition time is proposed. The dependence of saturation nuclear number density on temperature is also discussed. Computer simulations of instantaneous nucleation / hemispherical growth under diffusion control have been carried out using the three dimensional diffusion limited aggregation technique. The simulated current transients are compared to analytical expressions. Photoeffects during electrodeposition have also been studied. The results show that the CdTe deposit behaves as an amorphous insulator with a high density of bandgap states.

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CHAPTER 1.

INTRODUCTION.

- 1.1 Solar cells.
 - 1.2 Semiconductor properties of CdTe.
 - 1.3 Electrodeposition of CdTe.
- References.

1.1 Solar cells.

The energy problem is one of the major scientific challenges facing the world today. We depend on fossil fuels for 66% of electricity. However, fossil fuels will deplete in the next 200 years. As a more urgent problem, the environmental impact of electricity generation must be considered. Electricity is a highly refined form of energy, but in the conversion process from fossil fuels, gases and heat are emitted to the atmosphere. The emission of combustion products has been causing air pollution and global warming. In addition to the scientific reasons, political pressure is also increasing to achieve the solution of the energy problem. Reliance on other countries for fossil fuels reserves can give rise to difficulties which are illustrated by the Arab oil embargo in 1973.

Recognition of the limitations of fossil fuels and environmental and political factors have stimulated the search for clean sources of electricity with plenty of reserves. The use of plutonium is a high risk strategy and a decrease of nuclear power should be considered as a desired direction. The growth of hydropower is limited. It is expected that the electricity generation with wind and tidal power will grow and supply several percent of electricity requirements. In this situation, solar electricity generation is expected to become increasingly important.

In order to contribute to large scale electrical supply, the solar cell is required to be cost effective, easily scalable and reliable. Silicon single crystal solar cells and $\text{GaAs/Ga}_x\text{Al}_{(1-x)}\text{As}$ solar cells with high energy conversion efficiencies have been developed. However, in terms of the material cost, these solar cells are not

satisfactory for large scale electrical generators and, therefore, they have not been used except for limited purposes like satellites.

In the 1970s, the US Energy Research and Development Administration launched the terrestrial Photovoltaic (PV) program and the US government has been funding terrestrial PV development for about 20 years. In this program, the following goals of PV material were defined [1,2].

- 1) Manufacture : million square meters per year or more.
- 2) Durability : 20 years.
- 3) Electricity cost : less than 2 dollars per peak watt.
- 4) Module cost : 30 dollars and 50 dollars per square meter for single- and two-junction cells, respectively.
- 5) Efficiency : 15 percent or greater for single-junction and 20% or greater for two-junction.

(These desired goals are changed regularly)

For achieving the above PV materials requirements, efforts have concentrated on polycrystalline thin film photovoltaic technologies. In the late 1970s, the PV research and development program investigated several polycrystalline thin film materials including CuInSe₂ (CIS), cadmium telluride (CdTe), indium phosphide (InP), zinc phosphide (Zn₃P₂), copper selenide (Cu₂Se), tungsten diselenide (WSe₂), gallium arsenide (GaSe) and zinc silicon arsenide (ZnSiAs₂). As the result of the investigations, CuInSe₂-based alloy (CIS) and CdTe were developed for the market. The conversion efficiency of solar cells with polycrystalline thin films of these materials has been improved to achieve an efficiency beyond 20%. In 1984, the

highest efficiency was 9.15% [3] in the published data, however an efficiency as high as 15.8% has been recently achieved in a 1.047cm² CdTe/CdS solar cell by the university of South Florida [4]. Figure 1.1 shows the configuration of the CdTe/CdS solar cell which has achieved the highest efficiency.

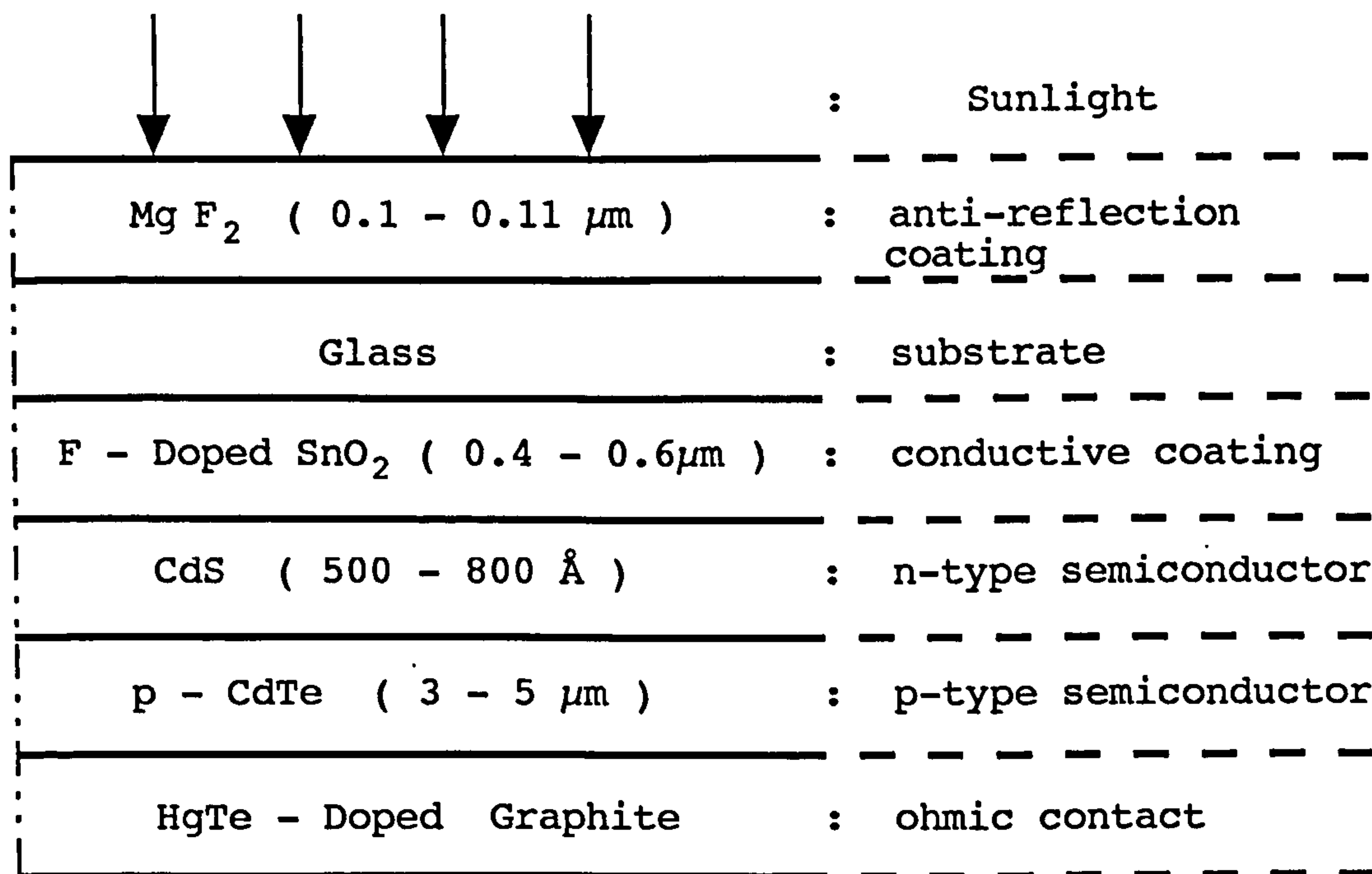


Figure 1.1 Configuration of a CdS / CdTe solar cell with a conversion efficiency of 15.8% [4].

Highly efficient thin film CdS/CdTe heterojunction solar cells have been prepared by the successive deposition of a CdS film, a p-CdTe and an ohmic contact onto a fluoride-doped tin oxide coated glass. For large scale solar cells with CdTe, it was reported that BP Solar has already fabricated a 30 x 30 cm² CdTe/CdS solar cell with an efficiency close to 10% [5] and that Solar Cell Incorporated and Photon Energy have developed 0.7m² size CdTe modules.

For CIS solar cells, efficiency of 14.8% was reported by EUROCIS. Siemens Solar achieved an efficiency of 10% on a 0.4m² CIS modules. Another remarkable thin film material is a-Si [6]. a-Si thin film solar cells are the only modules which have already been commercialised to be used for small power supplies. The commercial modules have an efficiency of around 5 percent.

Thus, thin film solar cells have been considered as candidates which have the opportunity to contribute to a solution of the energy problem. Especially, CdTe/CdS solar cells and CIS solar cells can be expected to be introduced into the market in the near future and to become a new source of large electric supply because of their high energy conversion efficiency, low material cost and scaling possibilities.

1.2 Semiconductor properties of CdTe.

The stable form for CdTe at room temperature is the zinc blende structure with a lattice parameter of 6.48Å. The zinc blende structure is shown in Figure 1.2. In crystalline CdTe, each Cd atom is surrounded by four nearest-neighbour Te atoms and, on the other hand, each Te atom is also surrounded by four Cd atoms. The distance between the nearest neighbours is $\sqrt{3}a/4$, namely 2.8Å. The hexagonal form has been reported as the other structure of CdTe. The occurrence of the phase transition from the hexagonal form to the cubic one in the process of natural ageing suggests that the hexagonal structure is not stable. However, the hexagonal structure of thin CdTe films is more stable. It may be suggested that the substrate material and its orientation make the hexagonal structure of CdTe films more stable.

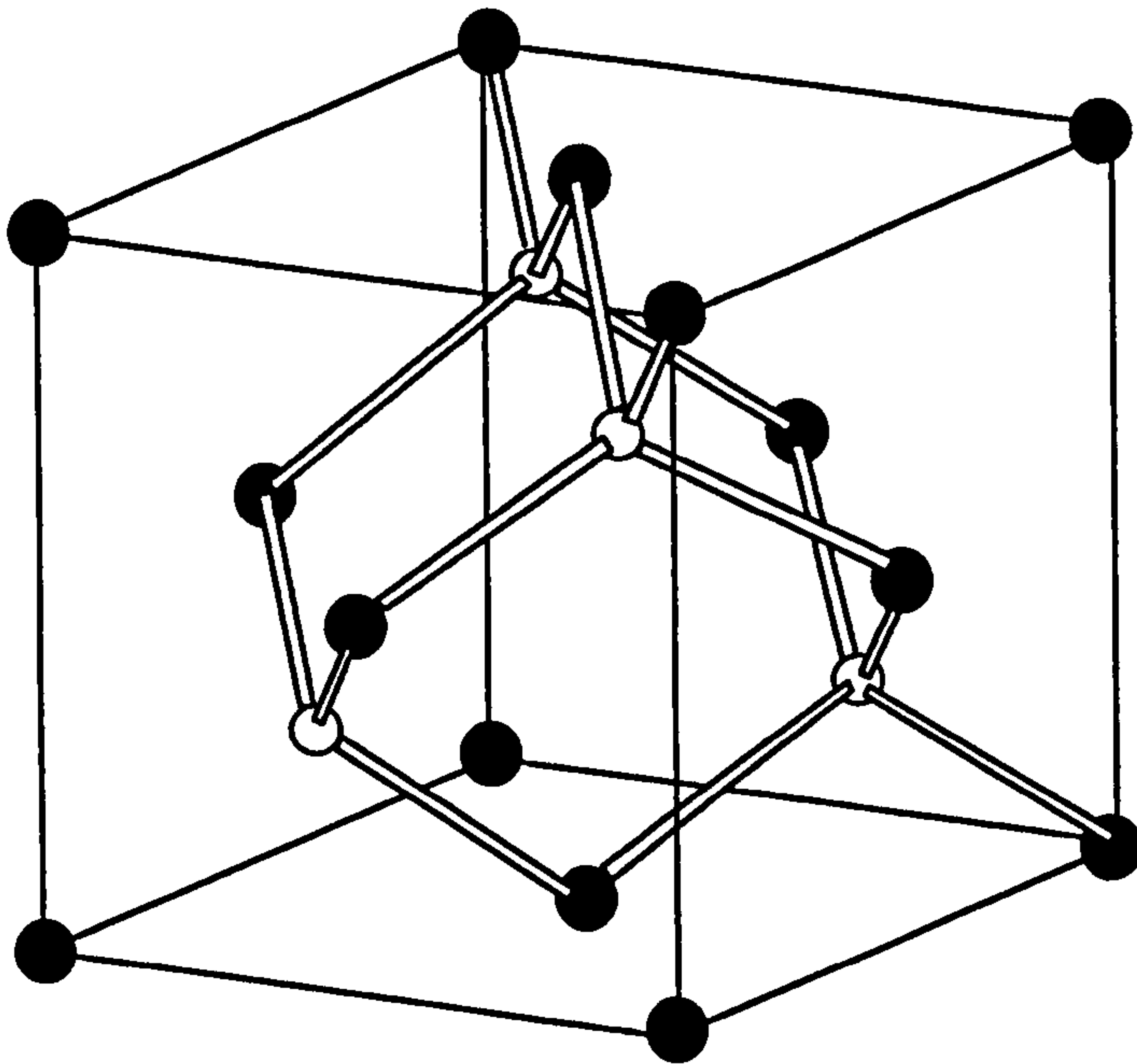


Figure 1.2 Zinc blende structure (stable form for CdTe at room temperature).

(If the black sites and the white sites are occupied by the same kind of atoms, the structure is referred to as "Diamond structure")

CdTe is one of the group II-VI compound semiconductors, and it has a band-gap of 1.44eV at a room-temperature [7]. The band-gap is the near-ideal value for solar energy conversion. CdTe also has high optical absorption coefficients [8]. Therefore, CdTe is considered to be a promising candidate for thin film solar cell applications. In addition, CdTe can be doped both n-type (In,Al,Cl) and p-type (P,As,Li,Na).

Single crystal CdTe has applications in nuclear radiation detectors, electro-optical modulators, infrared windows, solar cells, etc. Single crystal CdTe can be grown from the melt, from Te-rich solution at lower temperature than the melting point and from the vapour phase [9,10].

Although both monocrystalline CdTe [11~13] and polycrystalline CdTe [14,15] have been investigated for solar cell applications, it is obvious that the lower material cost makes polycrystalline CdTe more attractive. Polycrystalline CdTe can be produced by vacuum evaporation [16~18], sputtering [19], chemical vapour deposition [20], close-spaced sublimation [21,22], liquid phase epitaxial growth [23], spray printing [24] and electrodeposition [25,26]. Among the techniques, electrodeposition [27], spray printing [28] and close-spaced sublimation [29] have produced CdS/CdTe solar cells with greater than 12 % efficiency. In many of these techniques, the electrical resistivity control which determines the electric properties of solar cells remains a problem.

1.3 Electrodeposition of CdTe films.

Production of thin film materials by electrodeposition has many advantages:

In general,

1) Low cost [25]

Electrodeposition does not require specialised expensive equipment. Furthermore, the electrolyte temperature can be maintained low, so that the operating cost is cheaper than with other physical techniques.

2) Easy large-scale production [30]

Electrodeposition is a relatively simple technique and is suitable for large-scale production.

3) Control of thickness [31]

The thickness of the film can be controlled easily by monitoring the quantity of charge passed during the deposition.

For the particular case of CdTe electrodeposition, additional advantages are

4) Production of n-type and p-type [32,33].

Both n-type and p-type material can be obtained by a mere change of deposition potentials.

5) Simple way of doping [34].

Doping is a very useful technique to improve properties of semiconductors. Doping can be carried out just by addition of impurities (eg. CuSO_4) to electrolytes.

Thus, since electrodeposition is a very attractive method, there have been many investigations of the electrodeposition of CdTe and of the properties of electrodeposited CdTe films.

The first article on electrodeposition of II-VI compound semiconductors was published in 1975 [35]. This article was about the electrodeposition of ZnSe from two kinds of molten salts. After this publication, articles on the electrodeposition of CdSe [36], CdS [37], Bi_2S_3 [37], CdTe [25], CdS_xSe_y [38], CuInSe_2 [39], appeared in succession.

Many kinds of electrolytes have been reported as suitable for CdTe electrodeposition. Most CdTe co-deposition processes make use of an aqueous solution containing cadmium sulphate, tellurium dioxide and sulphuric acid as the electrolyte [25,26,40]. Due to the possibility of unexpected effects caused by hydrogen evolution during

electrodeposition from aqueous solutions, nonaqueous solutions for CdTe deposition have been also developed. Darkowski et al.[41] reported the use of propylene carbonate electrolyte containing tri-n-butylphosphine telluride, cadmium perchlorate, lithium perchlorate and tri-fluoromethane sulfuric acid as an alternative electrolyte. Dimethylformamide saturated with tellurium and containing CdCl₂ and KI has also been used as an electrolyte for CdTe deposition [42]. Skyllas-Kazacos [43] has used alkaline solution and has investigated CdTe electrodeposition from tellurocyanide (KTeCN) and CdCl₂. Pandey et al.[44] have obtained CdTe films from ethylene glycol electrolytes containing TeCl₄ and CdCl₂. The above-described electrolytes were used for cathodic deposition. On the other hand, Rajeshwar et al.[45] have investigated the anodic electrosynthesis of CdTe thin films. They reported that CdTe films were obtained on a cadmium anode from an alkaline electrolyte containing Te²⁻ species. As an electroless bath, Bhattacharya et al.[46] have used 10% sulfuric acid solution containing tellurium dioxide and cadmium acetate. Buckley [47] has studied CdTe thin film deposition from a electroless bath containing ammonia solution, CdCl₂, TeO₂, triethanolamine and hydrated hydrazine.

Since aqueous solutions can be handled easily, most of the research on CdTe deposition has been done using aqueous solutions containing TeO₂, CdSO₄ and H₂SO₄. In acid media, tellurium dioxide is protonated and exists as HTeO₂⁺. The solubility of tellurium dioxide is very poor, and the solubility data have been reported by Pourbaix [48] and Lyons [49]. According to Pourbaix, the solubility of tellurium dioxide in an acid media is given by

$$\log_{10} [\text{Te}] = -1.0\text{pH} - 2.0 \quad (1.1)$$

Lyons showed that equation (1.2) is applicable for this process in the pH range 1.2 to 2.6.

$$\log_{10} [\text{Te}] = -0.84\text{pH} - 2.5 \quad (1.2 < \text{pH} < 2.6) \quad (1.2)$$

The limiting (mass transfer controlled) current density for electrodeposition is proportional to the bulk concentration of depositing species. As the solubility of CdSO_4 is much higher than that of TeO_2 , the limiting current density for CdTe deposition depends on the TeO_2 concentration. In order to achieve high productivity, the concentration of TeO_2 should be maintained as high as possible. Although this can be achieved by the use of a low pH electrolyte, it has been reported [50] that deposits obtained from low pH electrolytes tend to include excess tellurium which can result in poor properties for solar energy conversion. Consequently, Lyons et al. [40] have recommended an electrolyte in the pH range of 1.5 to 2.5.

Figure 1.3 shows the potential - pH diagrams for the Cd-Te- H_2O system, the Te- H_2O system and the Cd- H_2O system. These diagrams were calculated for the concentrations of HTeO_2^+ (10^{-4} M) and Cd^{2+} (0.5M). The thermodynamic data have been taken from references [48] and [51]. CdTe is the thermodynamically stable product at more negative potential than +0.065V vs. SHE. Since bulk Cd deposits at -0.412V vs. SHE, the potential range for CdTe deposition lies between +0.065 and -0.412V vs. SHE.

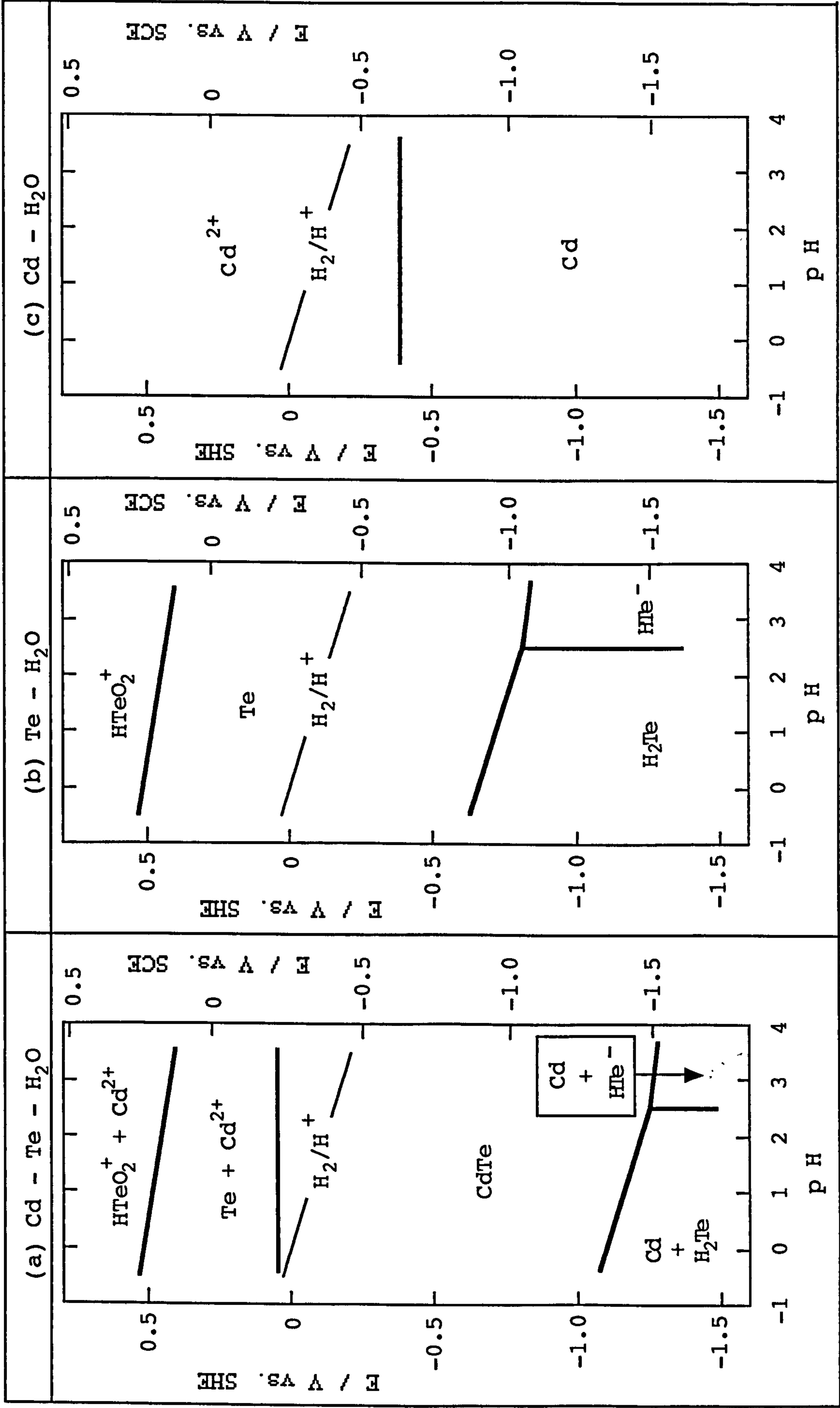


Figure 1.3 Potential - pH diagrams for (a) Cd-Te-H₂O, (b) Te-H₂O and (c) Cd-H₂O.

These diagrams were calculated using $H_2TeO_2^+ = 2 \times 10^{-4}M$, $Cd^{2+} = 0.5M$,

$H_2Te = HTe^- = 10^{-4}M$ and temp. = 25°C. The thermodynamic data were

Various mechanisms for CdTe electrodeposition have been proposed. The most commonly proposed mechanism is that the first step involves the $4e^-$ reduction of HTeO_2^+ to Te.

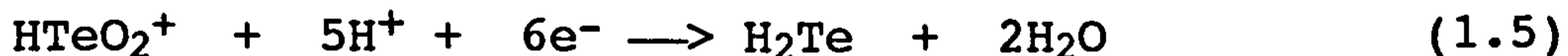


This reaction is followed by Cd deposition and reaction to form CdTe.



This mechanism suggests that the cadmium ion can deposit only on deposited Te atoms and the process is similar to under-potential deposition.

A different mechanism involving a more complicated route has also been reported. The mechanism involves the formation of H_2Te as the first step, and CdTe is then formed by the oxidation-reduction chemical reaction between H_2Te and Cd^{2+}



This particular route has been proposed only when Pt [40] and Au electrodes [50] were used, and there is no report of this route operating on inert electrodes like glassy carbon. It may indicate that the $6e^-$ reduction of HTeO_2^+ occurs on only high catalytic surfaces, although Dennison et al.[52] have discounted the possibility of this six electron reduction of HTeO_2^+ even on Au electrodes.

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CHAPTER 2.

THEORY OF ELECTROCRYSTALLIZATION.

- 2.1 Introduction.
- 2.2 Nucleation theory.
 - 2.2.1 Classical theory.
 - 2.2.2 Atomistic theory.
- 2.3 Electrochemical growth of nuclei.
 - 2.3.1 Instantaneous and progressive nucleation.
 - 2.3.2 Two dimensional growth.
 - 2.3.3 Three dimensional growth.
- References.

2.1 Introduction.

Thin films are very important in many technological applications. They have been used for optical coating (e.g., titanium nitride film for imitation of gold), corrosion protection (e.g., tin coated steel for can materials and zinc coated steel for car bodies) and semiconductor devices. Since thin films have further possibilities to become new functional materials, studies of thin films have been carried out extremely widely and there is no doubt that interest in thin films will continue to increase. In order to develop thin films and to improve their properties, fundamental studies on deposition processes are very important.

The first fundamental study of "nucleation" was made by Volmer and Weber in 1925 [1]. They studied the condensation of liquid droplets from the vapour phase, and their studies were applied subsequently to nucleation of solid crystals. In terms of electrochemical nucleation (i.e., electrocrystallization), the initial articles appeared in the 1930s [2,3]. Since electrocrystallization shares many features which are observed in the solid formation process from its supersaturated vapour, the theory of electrocrystallization has been established as an extension of vapour deposition theory [3].

Electrocrystallization on a foreign surface involves several steps. The steps of electrocrystallization and growth of nuclei are shown schematically in figure 2.1. The steps are :

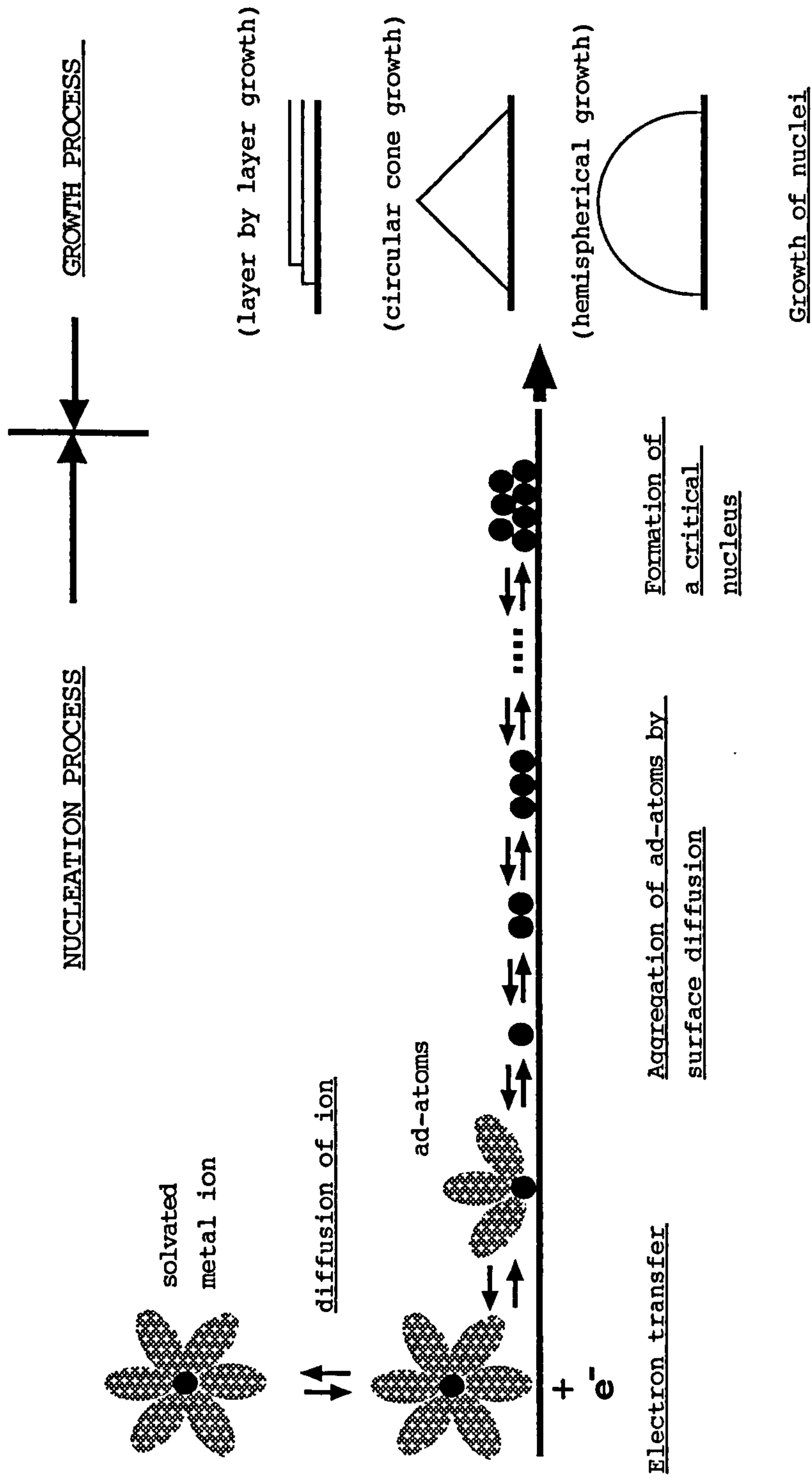


Figure 2.1 Schematic diagram of the process of electrocrystallization and growth on an electrode.

- (1) diffusion of ions (e.g., aquo-ions in aqueous solution) to the electrode surface.
- (2) electron transfer on the electrode surface and formation of adsorbed-atoms (ad-atoms) which may still hold some ligands.
- (3) surface diffusion of ad-atoms and formation of pairs of ad-atoms.
- (4) growth of clusters by surface diffusion (or by direct deposition on clusters).
- (5) formation of supercritical nuclei (stable clusters).
- (6) growth of nuclei (mono-layer growth as typical two dimensional growth, hemispherical or circular cone growth as three dimensional growth).

In this chapter, theories of nucleation and electrocrystallization are described. In 2.2.1, the so-called "classical nucleation theory" is interpreted. This is followed in section 2.2.2 by a discussion of the atomistic nucleation theory. In terms of growth theory, two-dimensional growth and three dimensional growth are explained in 2.3.2 and 2.3.3, respectively. As current-time responses with growth of nuclei depend on the morphology of deposits and the rate determining step, useful information of growth behaviour can be obtained by measurements of the current responses to potential steps. Therefore, in section 2.3, quantitative treatment of the current transients is demonstrated theoretically.

The terms, cluster and nucleus have similar meanings and they are sometimes confused. In order to avoid the confusion in the following discussion, it is defined that nuclei are "stable clusters" and clusters are unstable seeds of nuclei which have possibility of disappearing.

2.2 Nucleation theory.

Firstly, the thermodynamics and kinetics of nucleation are described before interpretation of the classical theory and the atomistic theory. These are fundamental concepts of nucleation, and both the classical theory and the atomistic theory are based on these concepts. The classical theory and the atomistic theory are discussed individually after discussion of the concepts shared by the two theories.

Thermodynamics of nucleation.

When a n-atomic cluster is formed in a supersaturated phase, the thermodynamic potentials of the system before and after formation of the cluster are given by

$$G_{\text{ before }} = N \cdot \mu_1 \quad (2.1)$$

$$G_{\text{ after }} = (N - n) \cdot \mu_1 + G_n \quad (2.2)$$

where μ_1 is the free energy of an isolated atom, N is the total number of atoms in the system and G_n is the free energy of the n-atomic cluster. The free energy change of the formation of n-atomic cluster, ΔG , is

$$\Delta G = G_{\text{ after }} - G_{\text{ before }} = G_n - n \cdot \mu_1 \quad (2.3)$$

ΔG is considered as the work of the formation of a n-atomic cluster. Equation 2.3 can be rewritten as

$$\Delta G = -n \cdot (\mu_1 - \mu_2) + (G_n - n \cdot \mu_2) \quad (2.4)$$

where μ_2 is the free energy of an atom in the cluster (bulk). $(\mu_1 - \mu_2)$ is driving force of nucleation, sometimes called the supersaturation, $\Delta\mu$ [e.g. 4]. When nuclei grow, $\Delta\mu$ must be positive (i.e. $\Delta G < 0$). $(G_n - n \cdot \mu_2)$ is the excess energy required for the formation of new phase. The excess energy corresponds to surface energy of the new phase (i.e.

surface energy of the n-atomic cluster). The surface energy term is often written using $\emptyset(n)$. The free energy change of cluster formation, the so-called work of nucleation, is finally given by the following equation.

$$\Delta G(n) = - n \cdot \Delta \mu + \emptyset(n) \quad (2.5)$$

This is a basic equation which is used for both the classical theory and the atomistic theory. However, the treatment of $\Delta \mu$ is different in each theory, i.e., in the case of the classical theory, $\Delta \mu$ is independent of the number of atoms consisting of a cluster, whereas for the atomistic theory, $\Delta \mu$ depends on it.

Kinetics of nucleation.

Figure 2.2 shows nucleation on an active site of a substrate schematically.

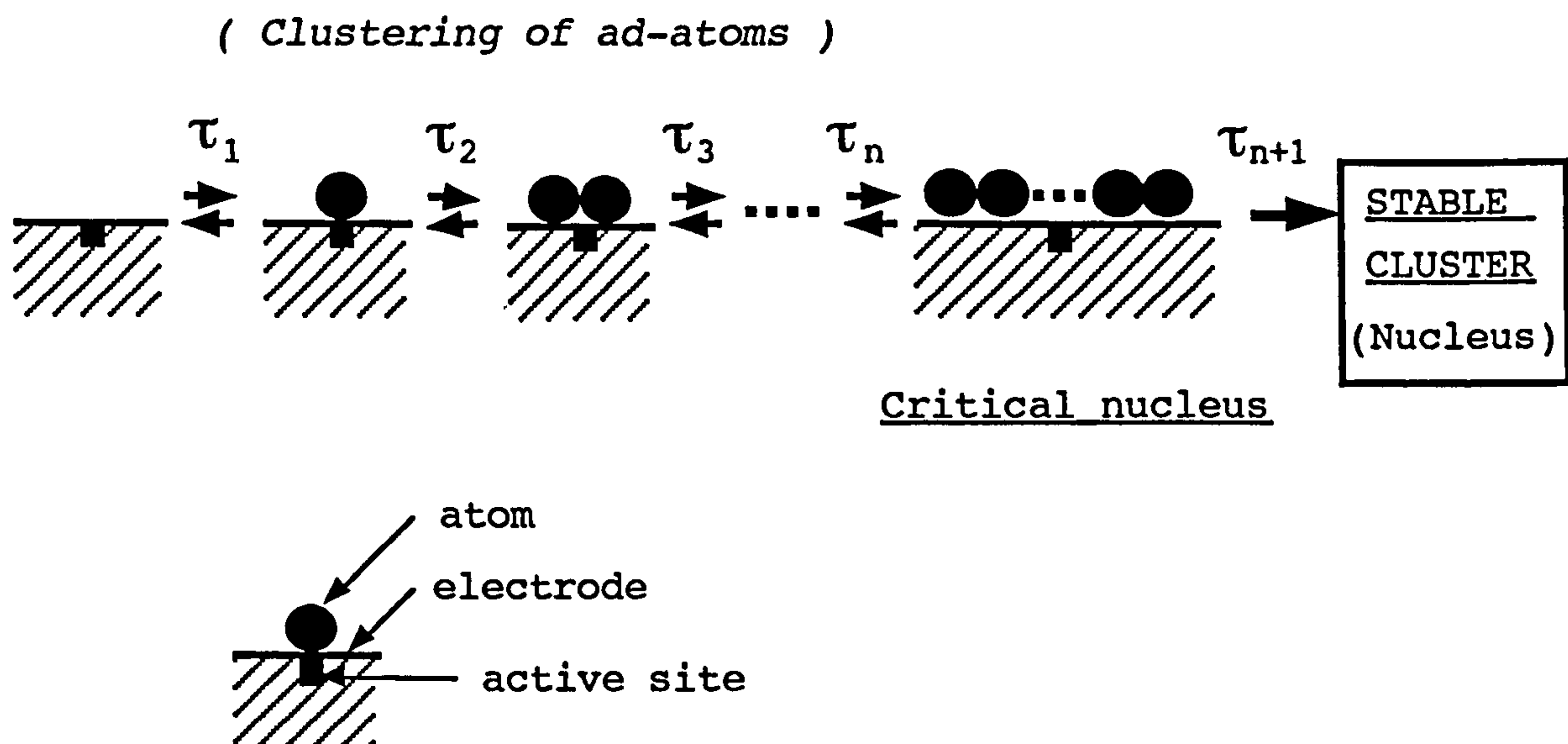


Figure 2.2 Nucleation process occurring on an active site of electrode. (two-dimensional nucleation)

The single step of aggregation of ad-atoms can be expressed by the reaction



where a is an ad-atom, a_{n-1} and a_n are clusters consisting of $(n-1)$ and n atoms respectively. Just after the nucleation starts, the reaction in the right direction is much faster than the opposite reaction and the number of clusters increases. The rate of the formation of n -atomic clusters $\partial N_n(t)/\partial t$ is given by

$$\begin{aligned} \partial N_n(t)/\partial t = & \omega_{+n-1}N_{n-1}(t) + \omega_{-n+1}N_{n+1}(t) \\ & - (\omega_{+n} + \omega_{-n}) N_n(t) \end{aligned} \quad (2.7)$$

where $N_n(t)$ is the number of clusters consisting of n atoms at time t , ω_{+n} and ω_{-n} are the frequencies with which a single atom attaches to and detaches from a n -atomic cluster respectively. However, the formation and growth of clusters causes the decrease of ad-atoms, and a steady state is established at a certain time. In the situation, the clustering rates at every step, τ_1 , τ_2 , τ_n and τ_{n+1} shown in figure 2.2, should be the same and the clustering rate is called "steady state nucleation rate, τ_{st} ".

$$\tau_{st} = \omega_{+0} \cdot N_0 - \omega_{-1} \cdot N_1 \quad (2.8.1)$$

$$= \omega_{+1} \cdot N_1 - \omega_{-2} \cdot N_2 \quad (2.8.2)$$

$$= \omega_{+2} \cdot N_2 - \omega_{-3} \cdot N_3 \quad (2.8.3)$$

.
.
.

$$= \omega_{+n-1} \cdot N_{n-1} - \omega_{-n} \cdot N_n \quad (2.8.n)$$

N_0 is the number of active sites on the substrate. When clusters become large enough, they do not lose the atoms in their clusters again and they are regarded as "nuclei". In particular, the n -atomic nucleus shown in figure 2.2

corresponds to the so-called critical nucleus (see figure 2.4 for the thermodynamic explanation of critical nuclei). For the critical nucleus, the steady state nucleation rate is given by

$$\tau_{st} = \omega_{+n} \cdot N_n \quad (2.8.n+1)$$

Substituting equations (2.8.1), (2.8.2), ..., and (2.8.n) into (2.8.n+1) gives the general form of the steady state nucleation rate [5,6].

$$\tau_{st} = \frac{N_0}{\frac{1}{\omega_{+0}} + \frac{\omega_{-1}}{\omega_{+0}\omega_{+1}} + \dots + \frac{\omega_{-1}\omega_{-2} \dots \omega_{-n-1}\omega_{-n}}{\omega_{+0}\omega_{+1}\omega_{+2} \dots \omega_{+n-1}\omega_{+n}}} \quad (2.9)$$

$$= N_0 \left(\sum_0^{s-1} \frac{1}{\omega_{+n}} \cdot \frac{\omega_{-1}\omega_{-2} \dots \omega_{-n-1}\omega_{-n}}{\omega_{+0}\omega_{+1} \dots \omega_{+n-2}\omega_{+n-1}} \right) \quad (2.10)$$

Since nucleation on active sites of a substrate is discussed in this chapter, the numbers between 0 and n are used for the subscripts of N. In terms of nucleation on a uniform substrate without any active sites, the number should be 1 to n, as described in references [5,6].

The general equations for ΔG (equation 2.5) and for τ_{st} (equation 2.10) are used by the classical theory and the atomistic theory and have been modified to allow comparison with experimental results. In the next two sections, the modification of these equations by the two theories are described.

2.2.1 Classical theory.

The classical nucleation theory was proposed primarily to explain the experimental results on homogeneous nucleation of liquid droplets from the vapour phase [1].

This theory has been extended and applied to heterogeneous nucleation of liquids and solids on a foreign substrate from the vapour phase [4,7~13] as well as to electrochemical nucleation [2,14~17]. The classical nucleation theory and its application to electrocrystallization are described below.

According to the classical theory, the nucleation process is considered from macroscopic view point. The classical theory originally assumed that clusters have a hemispherical shape. If the surface free energy of clusters is isotropic, the clusters should be cap-shaped as shown in figure 2.3.

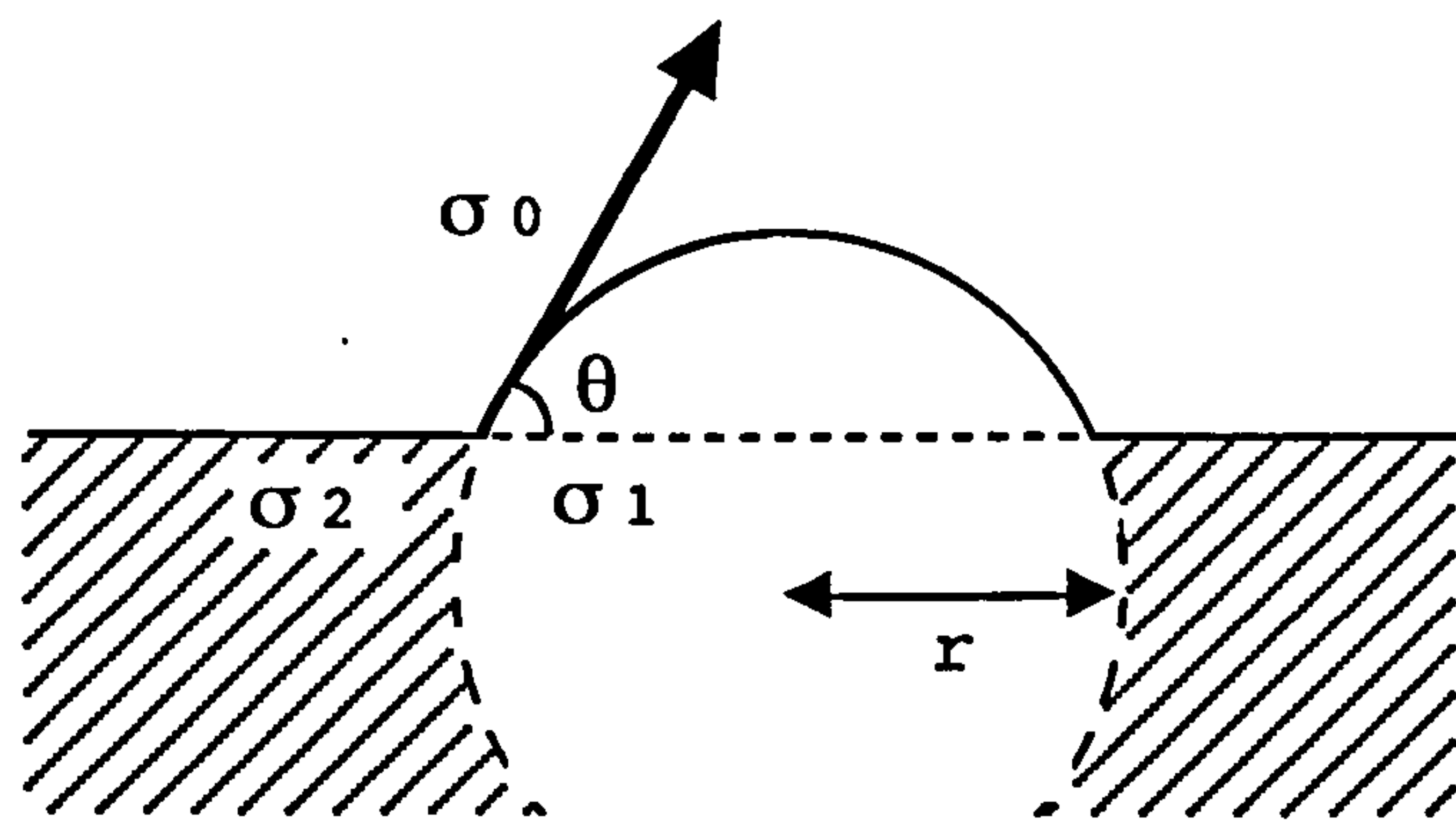


Figure 2.3 Cross - section of a cap-shaped cluster on substrate.

In this section, it is assumed that clusters have a cap-shape which is more general than a hemisphere. The equilibrium contact angle (or wetting angle) θ is given by Young's law.

$$\sigma_2 = \sigma_1 + \sigma_0 \cdot \cos\theta \quad (2.11)$$

σ_2 , σ_1 and σ_0 are the specific interfacial free energies (surface tension) of the substrate-solution, the cluster-substrate and the cluster-solution. The excess surface free energy due to the formation of a new phase (an n -atomic cluster) is given by

$$\phi(n) = S_{cl} \cdot \sigma_0 + S_{sub} \cdot (\sigma_1 - \sigma_2) \quad (2.12)$$

where S_{cl} is the surface area of the cluster and S_{sub} is the area of substrate covered with the cluster. Equation (2.12) can be rewritten as a function of radius of the cluster.

$$\phi(r) = 2\pi r^2(1-\cos\theta) \cdot \sigma_0 + \pi r^2 \sin^2\theta \cdot (\sigma_1 - \sigma_2) \quad (2.13)$$

Substituting equation (2.11) into equation (2.13) gives

$$\phi(r) = \pi r^2 \sigma_0 \cdot (2 - 3\cos\theta + \cos^3\theta) \quad (2.14)$$

Since the volume of a spherical cap is $1/3 \cdot \pi r^3(2-3\cos\theta + \cos^3\theta)$, the relationship between radius and the number of atoms in the cluster is given by

$$n \cdot V_{atom} = 1/3 \cdot \pi r^3(2-3\cos\theta + \cos^3\theta) \quad (2.15)$$

where V_{atom} is the volume of an atom. Finally, the surface free energy can be derived as a function of n .

$$\phi(n) = [9\pi V_{atom}^2 \cdot (2-3\cos\theta + \cos^3\theta)]^{1/3} \times n^{2/3} \quad (2.16)$$

The work of nucleation given by equation (2.5) is therefore rewritten as

$$\Delta G(n) = -n\Delta\mu + [9\pi V_{atom}^2 \cdot (2-3\cos\theta + \cos^3\theta)]^{1/3} \cdot n^{2/3} \quad (2.17)$$

Figure 2.4 is a schematic diagram of the dependence of work of nucleation on the number of atoms in a cluster. As shown in this figure, the work of nucleation has a maximum value. The peak is located at the boundary between the stable and the unstable region of the clusters (the cluster on this boundary is a critical nucleus). For the formation

of nuclei, clusters are required to go over the energy peak, $\Delta G(n_k)$. The clusters consisting of less than n_k atoms have not gone over the barrier and, therefore, they are not stable and have possibility of extinction. On the other hand, the clusters consisting of more than n_k atoms are stable and their growth is thermodynamically in a favourite direction.

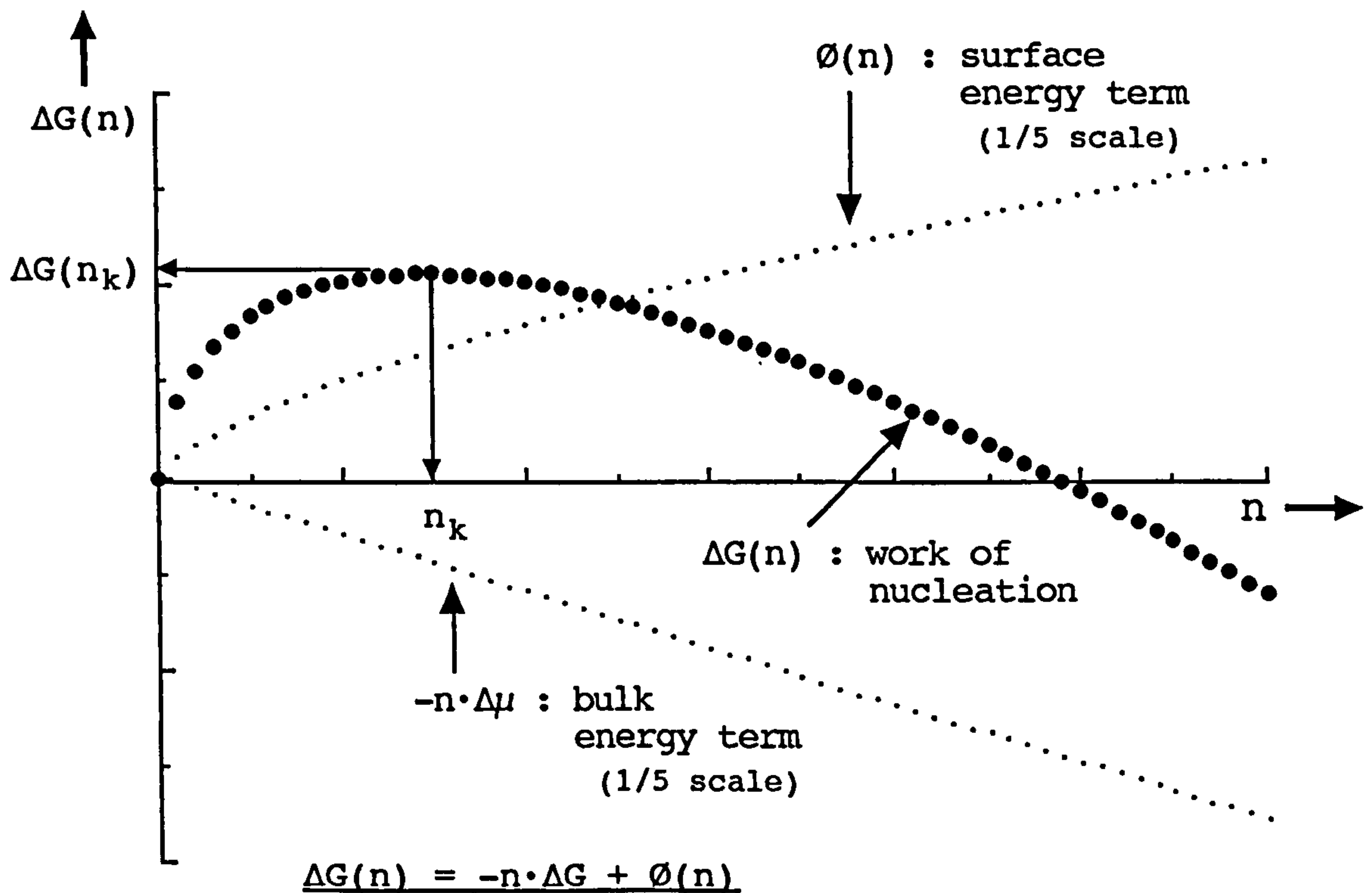


Figure 2.4 Schematic work of nucleation as a function of the number of atoms in a cluster. n_k is the number of atoms in a critical nucleus.

At $n = n_k$, the following differential equation is established.

$$\left(\frac{d\Delta G(n)}{dn} \right)_{n_k} = 0 \quad (2.18)$$

Solving this equation with equation (2.17) gives both the number of atoms in the critical nucleus, n_k , and the work of nucleation, $\Delta G(n_k)$.

$$n_k = 8\pi V_{\text{atom}}^2 \cdot (2 - 3\cos\theta + \cos^3\theta) / 3\Delta\mu^3 \quad (2.19)$$

$$\Delta G(n_k) = 4\pi V_{\text{atom}}^2 \cdot (2 - 3\cos\theta + \cos^3\theta) / 3\Delta\mu^2 \quad (2.20)$$

If the number of critical nuclei is given by the Boltzmann expression,

$$N_{n_k} = N_0 \cdot \exp(-\Delta G(n_k)/kT) \quad (2.21)$$

As given by equation (2.8.n+1), the steady state nucleation rate is the product of frequency of attachment of an atom to a critical nucleus multiplied by the number of critical nuclei. Substituting equations (2.21) and (2.20) into equation (2.8.n+1) gives the steady state nucleation rate.

$$\begin{aligned} \tau_{\text{st}} &= \omega_{+n_k} \cdot N_0 \cdot \exp(-\Delta G(n_k)/kT) \\ &= \omega_{+n_k} \cdot N_0 \cdot \exp[4\pi V_{\text{atom}}^2 (2 - 3\cos\theta + \cos^3\theta) / 3\Delta\mu^2 kT] \end{aligned} \quad (2.22)$$

Although this equation is obtained by assuming equilibrium, nucleation process occurs obviously in non-equilibrium because of increase in the nuclear number. Therefore, in order to improve equation (2.22), Becker and Doering [5] and Kaishev [6] solved equation (2.9) by replacing the sum in the equation with an integration. As the result, they obtained the following steady state nucleation rate.

$$\tau_{\text{st}} = \omega_{+n_k} \cdot \Gamma \cdot N_0 \cdot \exp(-\Delta G(n_k)/kT) \quad (2.23)$$

Thus, they introduced a new factor, Γ to equation (2.22). The factor Γ is called the "Zeldovich factor" and has a

value of $(\Delta G(n_k)/3\pi kTn_k^2)^{1/2}$ for a liquid droplet. The typical value of the Zeldovich factor was obtained experimentally and is an order of 10^{-2} [18~20]. The Zeldovich factor works to compensate the difference between the number of critical nuclei given by equation (2.21) and the actual number. The difference may be due to the depletion of the cluster population with increase in nuclei.

The driving force of electrocrystallization is the difference between the equilibrium potential and the electrode potential, i.e. overpotential, η . The electrochemical potential change is expressed by

$$\tilde{\Delta\mu} = ze\eta \quad (2.24)$$

where z is the valency of depositing ions and e is the quantity of charge on the electron. The relationship between steady state nucleation rate and overpotential is derived by substitution of equation (2.24) into equation (2.22) or (2.23).

$$\ln (\tau_{st}) \propto 1/\eta^2 \quad (2.25)$$

note : The Zeldovich factor is given by $(\Delta G(n_k)/3\pi kTn_k^2)^{1/2}$ and is a function of overpotential. However, the effect of overpotential in the Zeldovich factor on the nucleation rate is much weaker than overpotential in the exponential term and, therefore, equation (2.25) can be obtained as the result of the approximation.

Since the relationship between the number of nuclei and overpotential can be obtained experimentally, equation (2.25) has been often used to compare the classical theory

with experimental results. As the result of the comparison between the classical theory and the experimental results, good agreement between them is obtained at relatively low supersaturation. However, the classical theory does not show a good fit with experiment results obtained at high supersaturation. Hirth and Pound pointed out [7,8] that the classical theory is only valid when the critical nuclei consist of approximately 100 atoms or more. As the reason of this disagreement at high supersaturation, they considered that wetting angle, surface area and surface energy lose their physical meaning for small cluster. Cahn et al.[21] and Hirth [22] tried to compensate this disagreement by developing the classical theory. However, the compensation did not work well in many cases. Therefore, this disagreement led to the conclusion that a *microscopic* theory is required to discuss the nucleation at high supersaturation.

2.2.2 Atomistic theory.

The atomistic nucleation theory was proposed by Walton [23,24]. He established the new nucleation theory for the range of very small critical nuclei by considering the forces of atomic interaction. He explained the dependence of nucleation rate on supersaturation without use of any macroscopic concept. In terms of the atomistic theory of electrocrystallization, Kaishev, Stoyanov and Milshev extended Walton's theory and have published many articles [25~32]. In this section, the atomistic theory of electrocrystallization on active sites is described.

The general equation of the steady state nucleation rate is given by equation (2.9). When the supersaturation is large and the critical nucleus is comparatively small,

all terms in the denominator of equation (2.9) except for the largest term are negligible and the general form can be written as

$$\tau_{st} = \frac{\omega_{+n} N_0}{\frac{\omega_{-1}\omega_{-2} \cdots \omega_{-n-1}\omega_{-n}}{\omega_{+0}\omega_{+1}\omega_{+2} \cdots \omega_{+n-1}\omega_{+n-1}}} \quad (2.26)$$

For electrodeposition, Butler proposed that the deposition rate, $v_{+\infty}$, and dissociation rate, $v_{-\infty}$ [33] are given by

$$v_{+\infty} = p_{+}c \cdot \exp[-(W_{+\infty} - (1-\alpha)zeE) / kT] \quad (2.27)$$

$$v_{-\infty} = p_{-} \cdot \exp[-(W_{-\infty} + \alpha zeE) / kT] \quad (2.28)$$

where E is the potential difference between the electrode and the electrolyte, α is the transfer coefficient, c is the concentration, $p_{+\infty}$ and $W_{+\infty}$ are a constant of deposition and an energy barrier of deposition, respectively. The minus sign means the direction of dissociation. Since the deposition rate is equal to the dissociation rate at equilibrium, dividing equation(2.28) by equation (2.27) gives

$$\gamma_{\infty}/c \cdot \exp(-\varphi_{\infty}/kT) \cdot \exp(-zeE_0/kT) = 1 \quad (2.29)$$

where $\gamma_{\infty} = p_{-}/p_{+}$, and $\varphi_{\infty} = W_{-\infty} - W_{+\infty}$ is the work of separation of one atom from the infinitely large crystal. Equations (2.27) and (2.28) were also applied to the frequencies of attachment and detachment of an atom to and from a cluster. For the attachment and detachment of the i th atom,

$$\omega_{+i} = K_{+i}c \cdot \exp[-(U_{+i} - (1-\alpha)zeE) / kT] \quad (2.30)$$

$$\omega_{-i} = K_{-i} \cdot \exp[-(U_{-i} + \alpha zeE) / kT] \quad (2.31)$$

where K and U have the same meaning as P and W in equations (2.27) and (2.28). From equations (2.30) and (2.31), $\omega_{-n} / \omega_{+n-1}$ is given by

$$\frac{\omega_{-n}}{\omega_{+n-1}} = \frac{K_{-n}}{K_{+n-1}} \cdot \frac{1}{c} \cdot \exp\left(-\frac{\varphi_n}{kT}\right) \cdot \exp\left(-\frac{ze(E_0+\eta)}{kT}\right) \quad (2.32)$$

where $\varphi_n = U_{+n} - U_{-n}$ is work of separation of one atom from a n-atomic cluster. The series of equation (2.32) gives

$$\frac{\omega_{-1}\omega_{-2} \cdots \omega_{-n-1}\omega_{-n}}{\omega_{+0}\omega_{+1}\omega_{+2} \cdots \omega_{+n-1}\omega_{+n-1}} = \frac{K_{-n}}{K_{+0}} \prod_{i=1}^{n-1} \gamma_i \cdot \frac{1}{c^n} \cdot \exp\left(-\frac{\sum_{i=1}^n \varphi_i}{kT}\right) \cdot \exp\left(-\frac{nze(E_0+\eta)}{kT}\right) \quad \cdots (2.33)$$

where γ_i is K_{-i}/K_{+i} . Equation (2.26) can be rewritten by substitution of equation (2.33), then, substitution of c obtained from equation (2.29) and, finally, substitution of equation (2.30).

$$\tau_{st} = \frac{(\gamma_\infty)^n}{\prod_{i=1}^n \gamma_i} K_{+0} \cdot N_0 \cdot c \cdot \exp\left(\frac{U_n - (1-\alpha)zeE_0}{kT}\right) \times \exp\left(-\frac{-(n+1-\alpha)ze\eta + n\varphi_\infty - \sum_{i=1}^n \varphi_i}{kT}\right) \quad (2.34)$$

When this equation is compared with equation (2.23), it is noticed that work of nucleation for the atomistic theory is given by

$$\Delta G(n) = -(n+1-\alpha)ze\eta + n\varphi_\infty - \sum_{i=1}^n \varphi_i \quad (2.35)$$

The term $\emptyset(n)$ in equation (2.5) which is considered as the surface energy of a cluster in the classical theory can be represented by

$$\phi(n) = n\varphi_\infty - \sum_{i=1}^n \varphi_i \quad (2.36)$$

In the atomistic theory, $\emptyset(n)$ is effectively the difference between the energy of n atoms in a infinitely large crystal and the energy of n atoms in a small cluster.

Stoyanov calculated equation (2.35) by assuming a simple model [34]. He considered only the interaction of atoms between first next-neighbours. In figure 2.5, the relationship between dimensionless energy $\Delta G/\psi$ and 'n' is shown. Here ψ is the binding energy between the nearest atoms in a cluster. It should be noticed that this relationship is similar to one for the classical theory shown in figure 2.4.

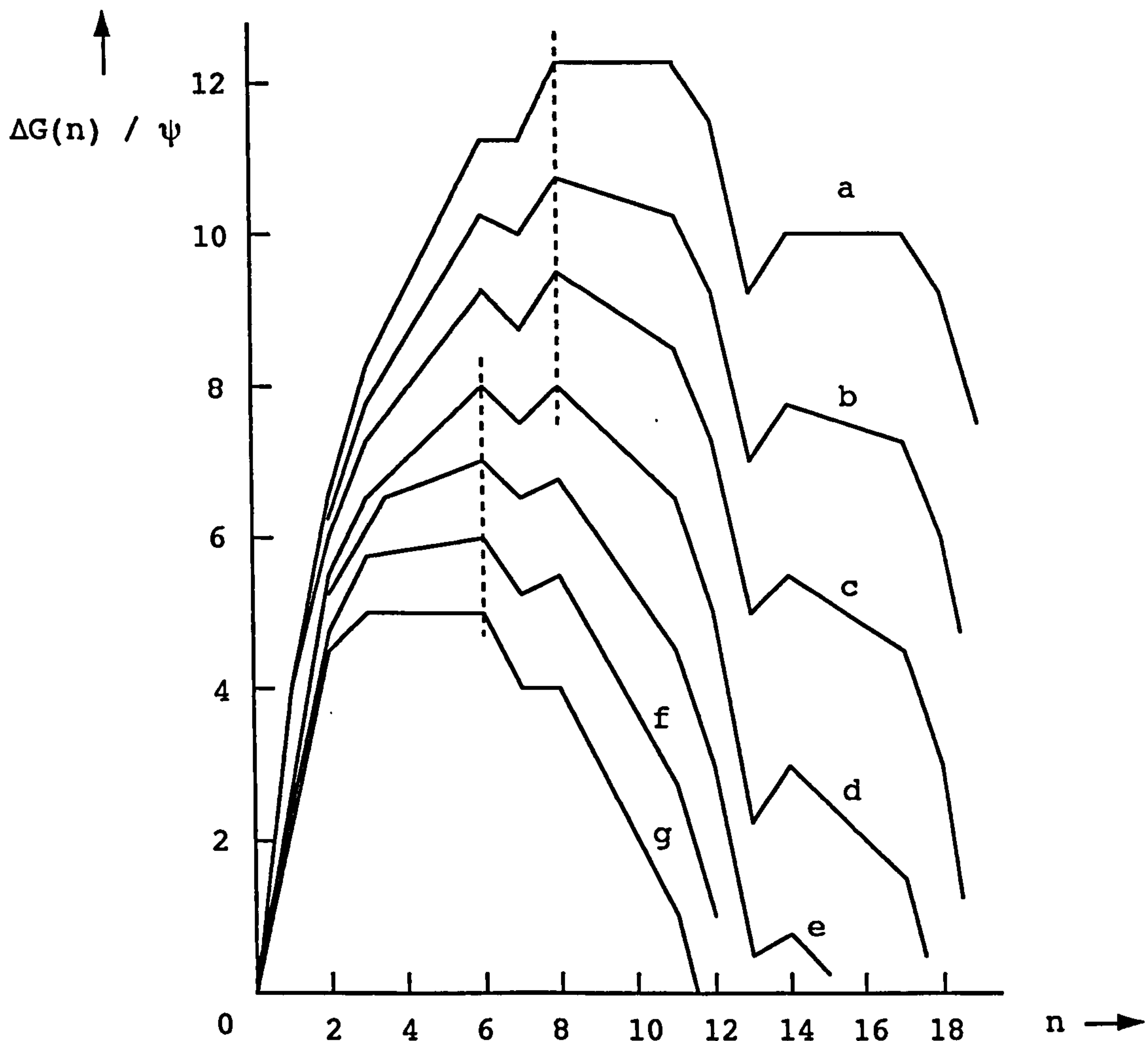


Figure 2.5 Dependence of work of nucleation, $\Delta G(n)$ on the number of atoms in a cluster, according to the atomistic theory. The supersaturation increases from a to g [30]. The cluster consisting of 13 atoms shows relatively low ΔG because of the stable structure of the cluster under the assumptions employed to obtain these relations.

The curves also have a maximum value of energy. The number of atoms which gives the highest work of nucleation corresponds to the number of atoms in the critical nucleus at the supersaturation $\Delta\mu$. With increase of $\Delta\mu$, the number of atoms in critical nuclei decreases step by step.

The equation used most commonly to compare the atomistic theory with experimental results is equation (2.34). This equation can be rewritten simply as

$$\tau_{st} = K' \cdot \exp\left(\frac{-\phi(n)}{kT}\right) \cdot \exp\left(\frac{n_k + (1-\alpha)}{kT} \cdot ze\eta\right) \quad (2.37)$$

This suggests that logarithm of nucleation rate is proportional to overpotential.

$$\ln(\tau_{st}) \propto \eta \quad (2.38)$$

The relation of τ_{st} vs. η is different from the one expected by the classical theory (equation 2.25). The number of atoms in critical nuclei can be obtained from equation (2.37).

$$n_k = \frac{kT}{ze} \cdot \frac{\ln(\tau_{st})}{\eta} - (1-\alpha) \quad (2.39)$$

In the paper written by Kashchiev [35], α was used instead of $(1-\alpha)$ in equation (2.39) because the direction of the symmetry factor was opposite to the direction described above (note that $\alpha_+ + \alpha_- = 1$).

Equation (2.39) suggests that the slope of $\ln(\tau_{st})$ vs. η changes if the size of critical nuclei changes. Figures 2.6 (a) and (b) show the $\tau_{st} - \eta$ curves predicted by the atomistic theory (equation 2.37) and by the classical theory (equation 2.25), respectively. Figure 2.6 (a) shows that with decrease of overpotential, the length of broken

straight lines is getting shorter and the relationship of $\ln(\tau_{st})$ vs. η becomes like a smooth line. According to Milchev, in this range of overpotential (region of the pseudo-smooth line), the supersaturation is small enough that the classical theory can be applied [29].

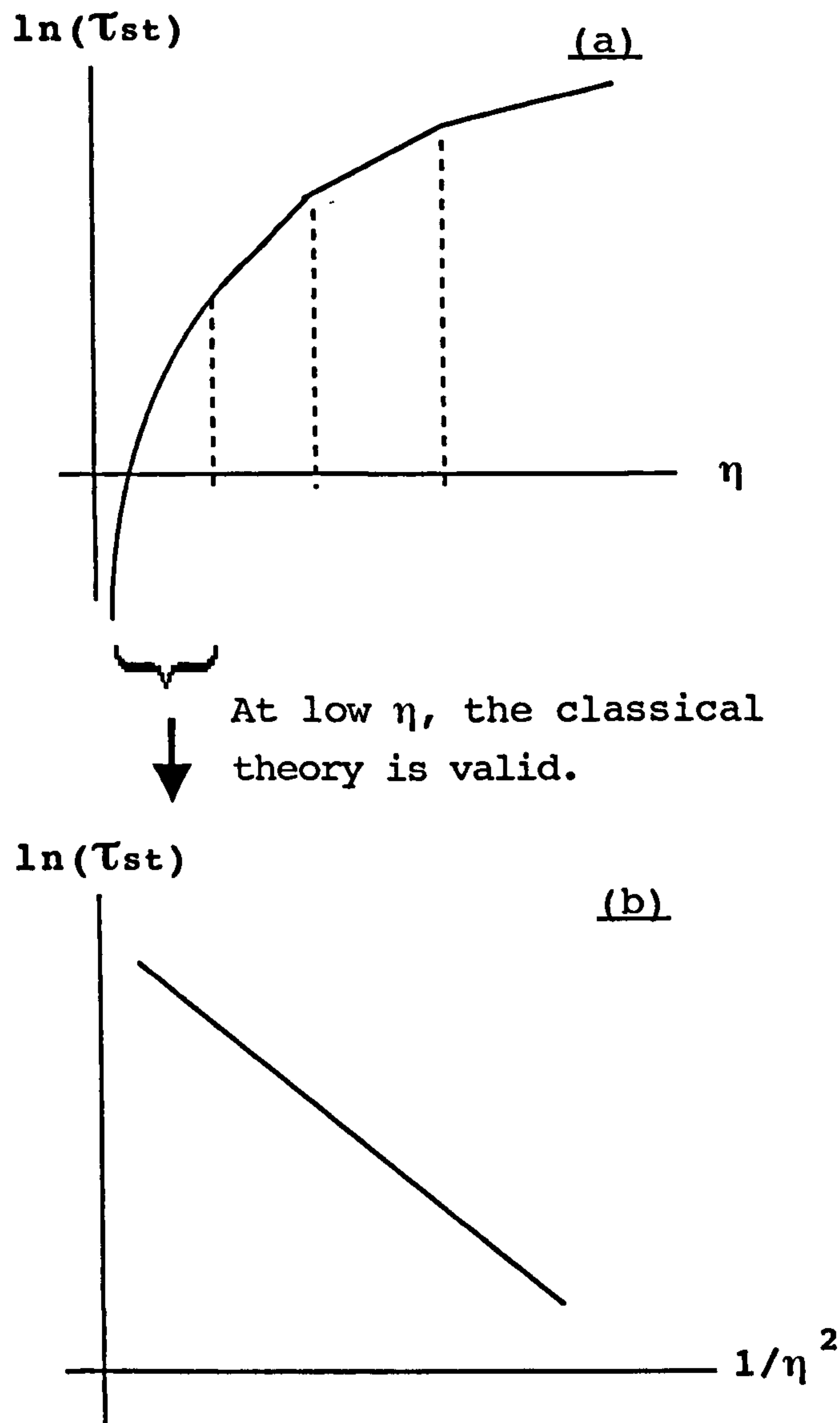


Figure 2.6 Relationships between steady state nucleation rate τ_{st} and overpotential, η .

(a) predicted by the atomistic theory,
(b) predicted by the classical theory.

2.3 Electrochemical growth of nuclei.

As shown in figure 2.1, after formation of critical nuclei, the nuclei grow two-dimensionally or three-dimensionally. As a result of the growth, they develop a morphology (e.g. hemisphere, cone or layer) which may be determined by the interactions among the deposited material, the electrode material and the solution. The growth of nuclei increases the active area where electron transfer from electrode to depositing ions can occur. With this spread of the active area, the deposition current also increases. The deposition current therefore gives information on growth. The theoretical treatments of the deposition current have been dominated by geometric considerations concerned with the shape of growing centres.

Deposition currents are often measured by potential step method and the theoretical equations of current transient curves involving potential steps have been proposed. In section 2.3.2 and 2.3.3, the current transient curves for two-dimensional growth and for three-dimensional growth are described. In order to make the theoretical treatment simple, new limiting cases have been introduced. These new concepts (i.e. instantaneous nucleation and progressive nucleation) are explained in section 2.3.1.

2.3.1 Instantaneous and progressive nucleation.

If the nucleation rate is proportional to the number of free active sites (i.e. if nucleation is a first-order reaction),

$$- dN_{\text{free}}(t) / dt = A \cdot N(t)_{\text{free}} \quad (2.40)$$

where $N_{\text{free}}(t)$ is the number of free active sites at time t and A is the first-order rate constant. Integrating equation (2.40) gives

$$N(t) = N_0 \cdot \{ 1 - \exp(-At) \} \quad (2.41)$$

where $N(t) = N_0 - N_{\text{Free}}(t)$. $N(t)$ and N_0 are the number of nuclei and the number of active sites per unit electrode area respectively [36]. Figure 2.7 shows the relationship between $1 - \exp(-At)$ and time, t , at $A = 0.2$ and 20 .

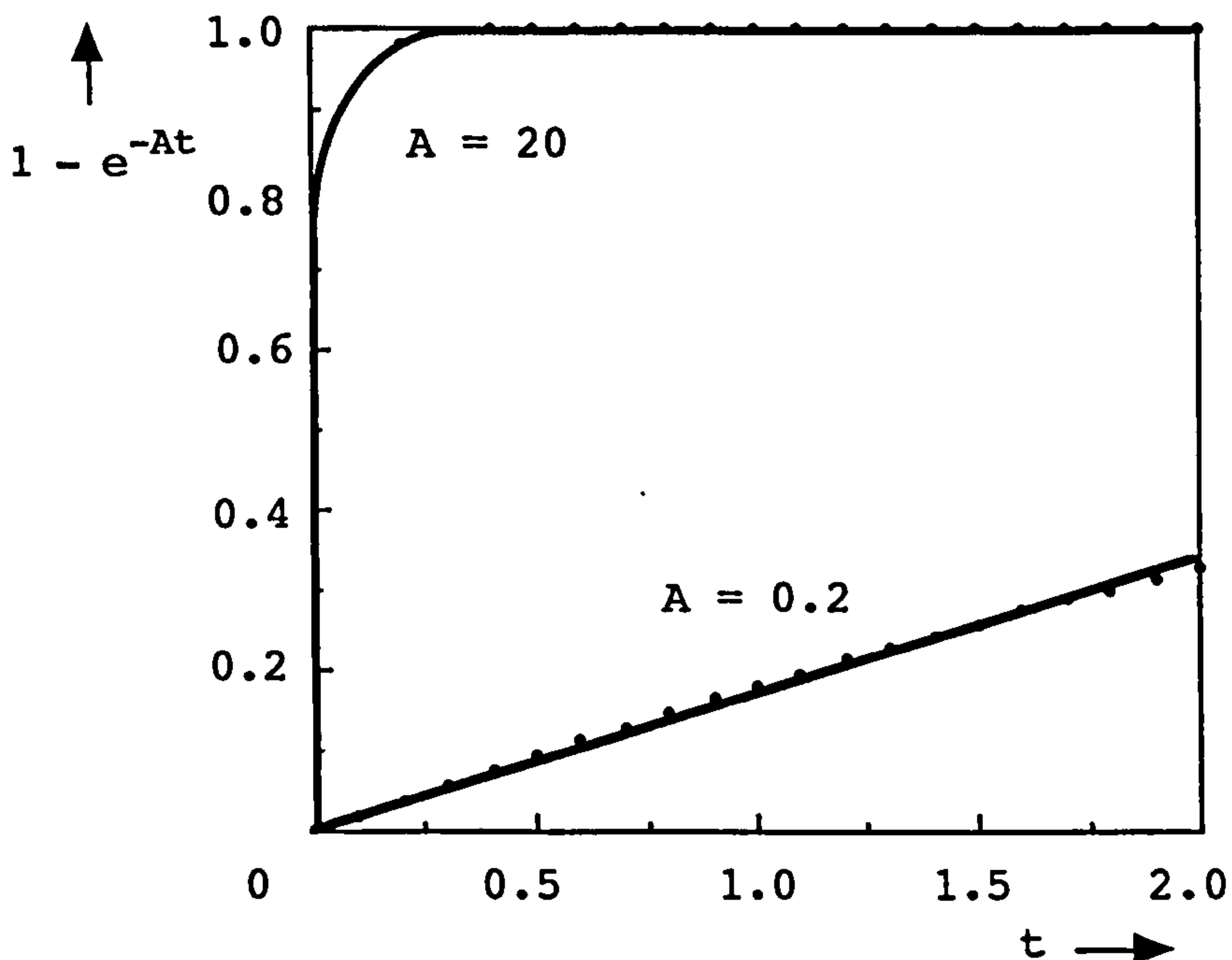


Figure 2.7 Effect of values of A on $[1 - \exp(-At)] - t$ curves. Equation : $y = 1 - \exp(-At)$

At $A = 0.2$, the $[1 - \exp(-At)] - t$ curve can be regarded as a straight line. This suggests that, for small values of A , equation (2.41) can be approximated to

$$N(t) = AN_0 \cdot t \quad (2.42)$$

On the other hand, at higher values of A , all of active sites are occupied by nuclei within a very short time. In

this case, i.e. $At \gg 1$, it can be considered that the formation of nuclei completes in an instant and equation (2.41) can be rewritten as

$$N(t) = N_0 \quad (2.43)$$

These limiting cases described by equations (2.42) and (2.43) are referred to as "progressive nucleation" and "instantaneous nucleation" respectively.

These limiting cases have the following apparent features. In the case of instantaneous nucleation, the sizes of growing centres are the same, because they are formed simultaneously and also grow at the same rate. However, for progressive nucleation, as the nuclei are formed continuously, the sizes differ from each other.

2.3.2 Two dimensional growth.

Two dimensional mono-layer (or thin layer) growth under kinetic control [36~40].

Figure 2.8 illustrates an cylindrical centre growing two-dimensionally. The incorporation of atoms can occur only at the edge of the cylindrical centre.

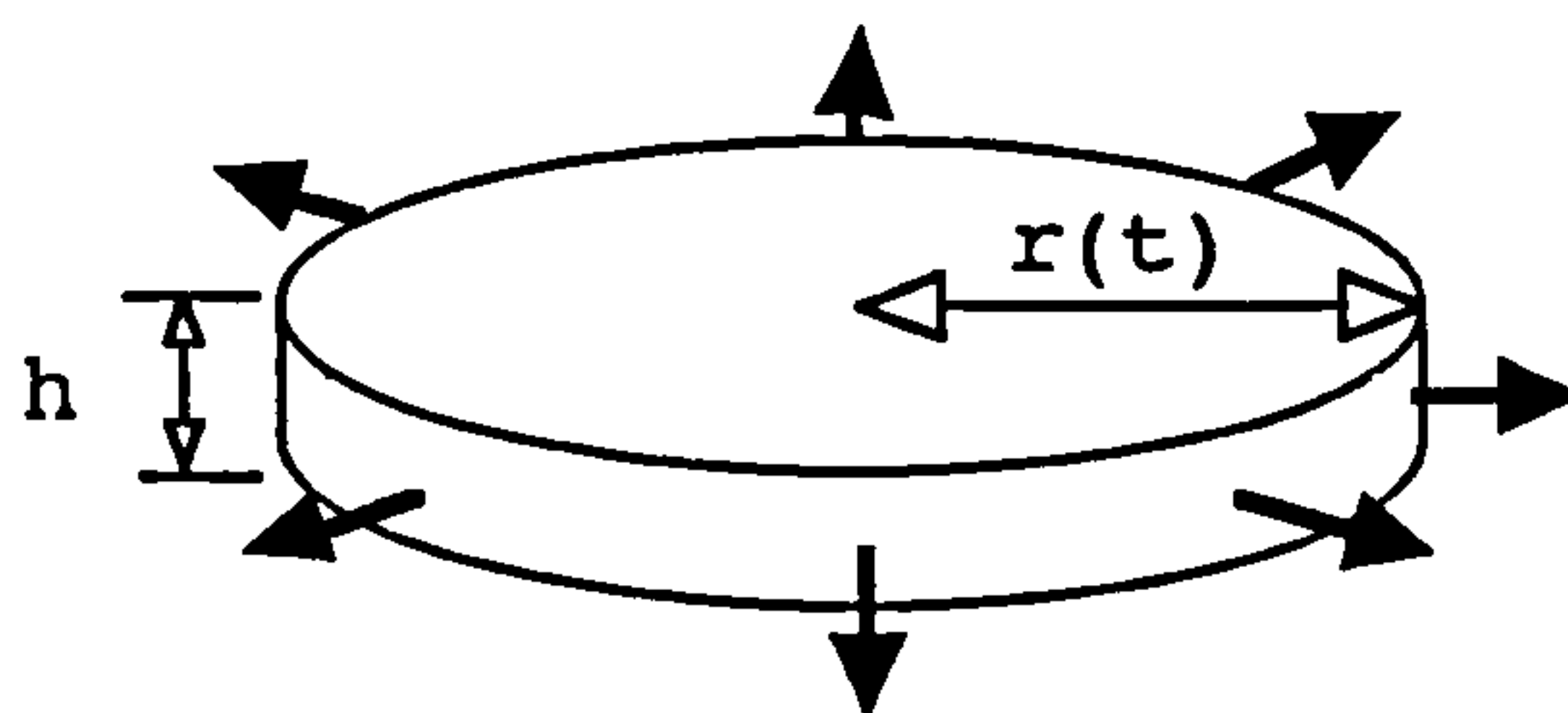


Figure 2.8 Two-dimensional cylindrical growth.
($\longleftarrow$ Growth direction)

Here the rate determining step of the growth is assumed to be the incorporation of atoms (i.e. kinetic control). As the deposition current, $i(t)$, is proportional to the area where the incorporation of atoms can occur,

$$i(t) = nFk \cdot (2\pi hr(t)) \quad (2.44)$$

where k is the rate of incorporation and $r(t)$ and h are expressed in figure 2.8. n and F have the usual meanings. The charge required to form a cylindrical centre is given by

$$Q(t) = nF\rho V(t) / M = nF\rho r(t)^2 \pi h / M \quad (2.45)$$

where ρ is the density of the deposit, M is the molecular weight. The charge can be also obtained by integrating equation (2.44) with respect to time.

$$Q(t) = \int_0^t i(t) dt = 2\pi hnFk \int_0^t r(t) dt \quad (2.46)$$

From equations (2.45) and (2.46), the following differential equation is derived.

$$\frac{nF\rho\pi h \cdot r(t)^2}{M} = 2\pi hnFk \int_0^t r(t) dt \quad (2.47)$$

Solving this equation gives

$$r(t) = (kM / \rho) \cdot t \quad (2.48)$$

The current associated with the growth of a cylindrical centre can be obtained by substitution of equation (2.48) into (2.44).

$$i(t) = \frac{2\pi nFk^2 hM}{\rho} \cdot t \quad (2.49)$$

In the case of instantaneous nucleation, the deposition current density, $j(t)$, is considered as the sum of the currents flowing into N_0 cylindrical centres.

$$j(t) = \frac{2\pi F k^2 h M N_0}{\rho} \cdot t \quad (2.50)$$

In the case of progressive nucleation, the number of nuclei formed for a short time, du , is given from equation (2.42).

$$dN = AN_0 \cdot du \quad (2.51)$$

The current density into nuclei formed at time u , $j(t)_{t=u}$ is given as a function of t .

$$j(t)_{t=u} = \frac{2\pi F k^2 h M}{\rho} \cdot (t-u) \cdot \frac{dN}{du} \quad (2.52)$$

Integrating equation (2.52) from $u=0$ to $u=t$ yields the current density at time, t .

$$\begin{aligned} j(t) &= \int_0^t \frac{2\pi F k^2 h M}{\rho} \cdot (t-u) \cdot \frac{dN}{du} \cdot du = \frac{2\pi F k^2 h M A N_0}{\rho} \int_0^t (t-u) du \\ &= \frac{\pi F k^2 h M A N_0}{\rho} \cdot t^2 \quad (2.53) \end{aligned}$$

(NOTE : In some articles, this integration has been done incorrectly and different (wrong?) equations have been reported. [37] for 2-D growth, [41~43] for 3-D growth)

These equations can be applied to the growth of isolated cylindrical nuclei. However, as nuclei grow, they begin to overlap each other. In this situation, equations (2.50) and (2.53) need to be modified. This modification has been achieved by using the Avrami theorem [44].

According to the Avrami theorem, the normalised area covered with the cylindrical centres, S , is related to the normalised extended area, S_{ext} by the expression.

$$S = 1 - \exp(-S_{ext}) \quad (2.54)$$

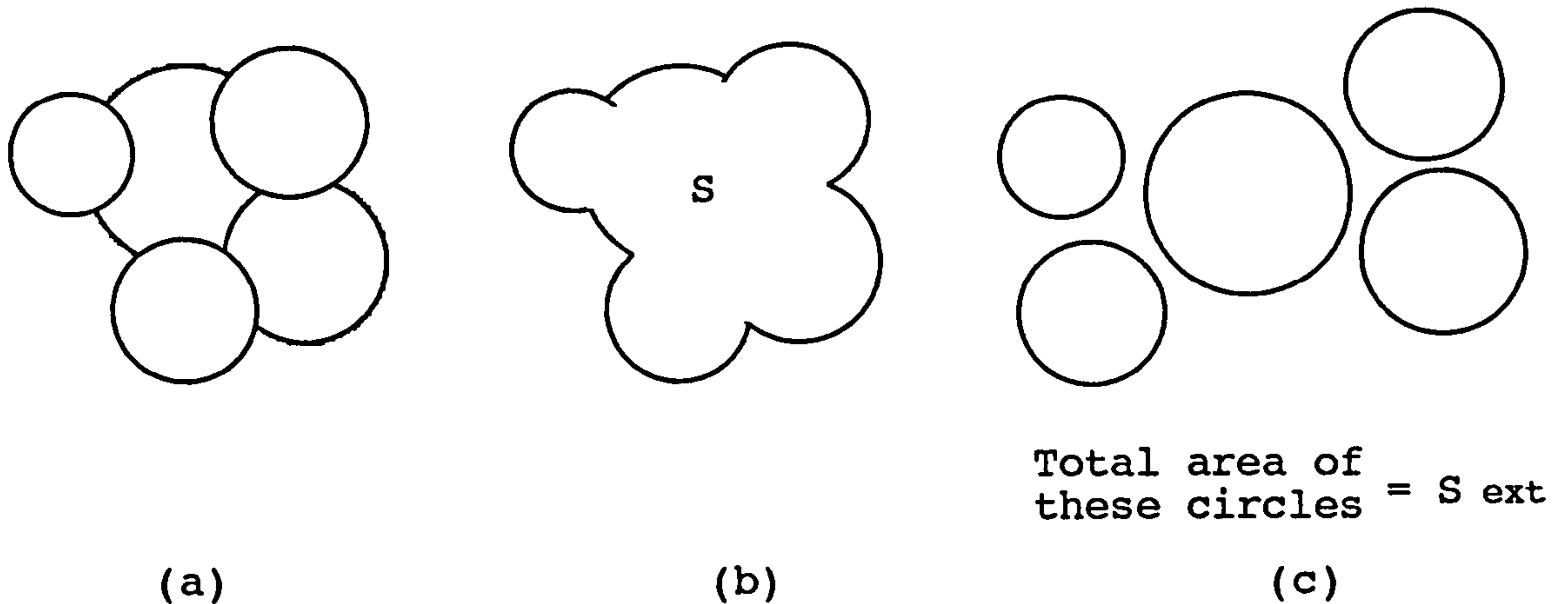


Figure 2.9 Overlap of cylindrical centres growing on a surface (a). (b) is the real area, S , and (c) is the extended area, S_{ext} , used in Avrami theorem (equation 2.54).

This equation means that at small values of S_{ext} , the area increases linearly with S_{ext} and at large values of S_{ext} , it tends toward 1. From the Avrami theorem, the relationship between current density, j , and extended current density, j_{ext} , is given by

$$j = j_{ext} \cdot \exp(-S_{ext}) \quad (2.55)$$

because $j = k' \cdot dS/dt$, $j_{ext} = k' \cdot dS_{ext}/dt$.

In the case of instantaneous nucleation, the extended area can be expressed as

$$S_{ext}(t) = N_0 \cdot r(t)^2 \cdot \pi \quad (2.56)$$

Substituting equation (2.48) yields

$$S_{\text{ext}}(t) = N_0 \cdot \pi \cdot (kM/\rho)^2 \cdot t^2 \quad (2.57)$$

The current can be derived by substituting equations (2.57) and (2.50) into (2.55).

$$j(t) = \frac{2\pi F k^2 h M N_0 t}{\rho} \cdot \exp\left(-\frac{\pi N_0 M^2 k^2 t^2}{\rho^2}\right) \quad (2.58)$$

For progressive nucleation, $S_{\text{ext}}(t)$ is expressed as

$$\begin{aligned} S_{\text{ext}}(t) &= A N_0 \int_0^t \pi \{r(t-u)\}^2 du \\ &= \frac{A N_0 \pi M^2 k^2 t^3}{3\rho^2} \end{aligned} \quad (2.59)$$

The current is, therefore, given by

$$j(t) = \frac{\pi F k^2 h M A N_0 t^2}{\rho} \cdot \exp\left(-\frac{\pi A N_0 M^2 k^2 t^3}{3\rho^2}\right) \quad (2.60)$$

Thus, the current transients for instantaneous and progressive nucleation / 2-D kinetic control are derived by equations (2.58) and (2.60) respectively. The current changes with the deposition time as follows. Before overlap of the nuclei, the current is linearly proportional to the deposition time for instantaneous nucleation and is proportional to the square of the deposition time for progressive nucleation. When the overlap becomes significant, the currents reach a maximum value and then begin to decrease.

Two dimensional layer-by-layer growth.

Figure 2.10 shows an expected current transient for two-dimensional layer-by-layer growth under kinetic control

[17]. The current transient is given by the sum of currents associated with growth of each layer. The feature of two-dimensional layer-by-layer growth is the oscillation observed before the steady state current and therefore current oscillations may be interpreted as evidence of this growth regime.

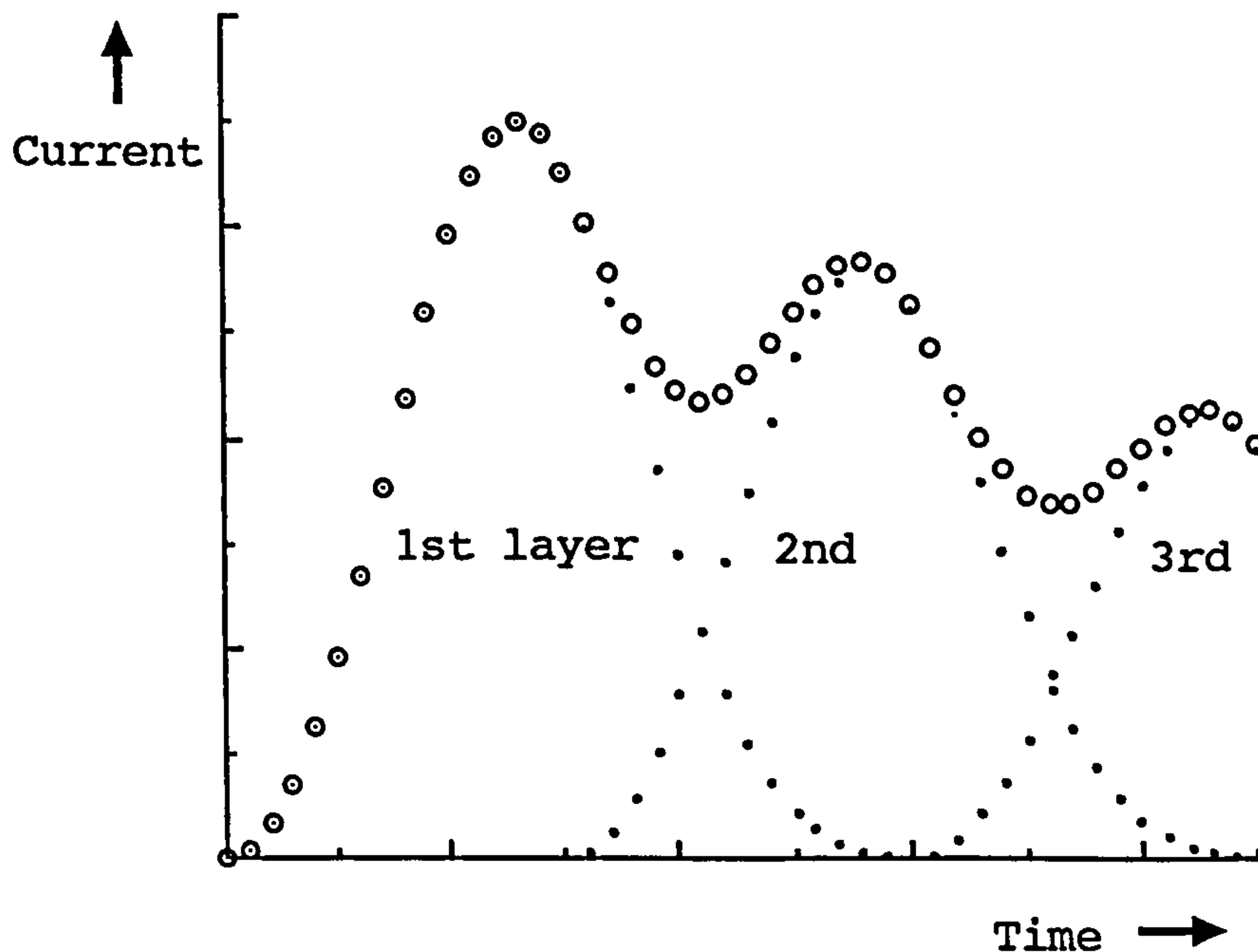


Figure 2.10 An expected current transient for two-dimensional layer-by-layer growth under diffusion control.

Two dimensional growth under diffusion control.

A theory of two dimensional growth under diffusion control has not appeared yet, because the deposition sites move rapidly with the growth of nuclei and it is therefore very difficult to make a model for this growth system.

However, it is expected that the current transient obeys the Cottrell relation at long deposition times (equation 2.70).

2.3.3 Three dimensional growth.

Theoretical current-time curves have been derived for hemispherical and cone-shaped growth under both kinetic and diffusion control. In this section, hemispherical growth under diffusion control is described. For cone-shaped growth [38,45,46], the relationships between current and time are shown in table 2.1, though the derivations of the relationships are omitted.

Growth of an isolated hemispherical nucleus.

The theoretical current-time response for diffusion controlled growth was derived initially by Astley et al.[47]. They assumed that the transfer of depositing ions to isolated nuclei was by planar diffusion. However, Hills et al.[41] proposed that the diffusion zone is more likely to be hemispherical as illustrated in figure 2.11.

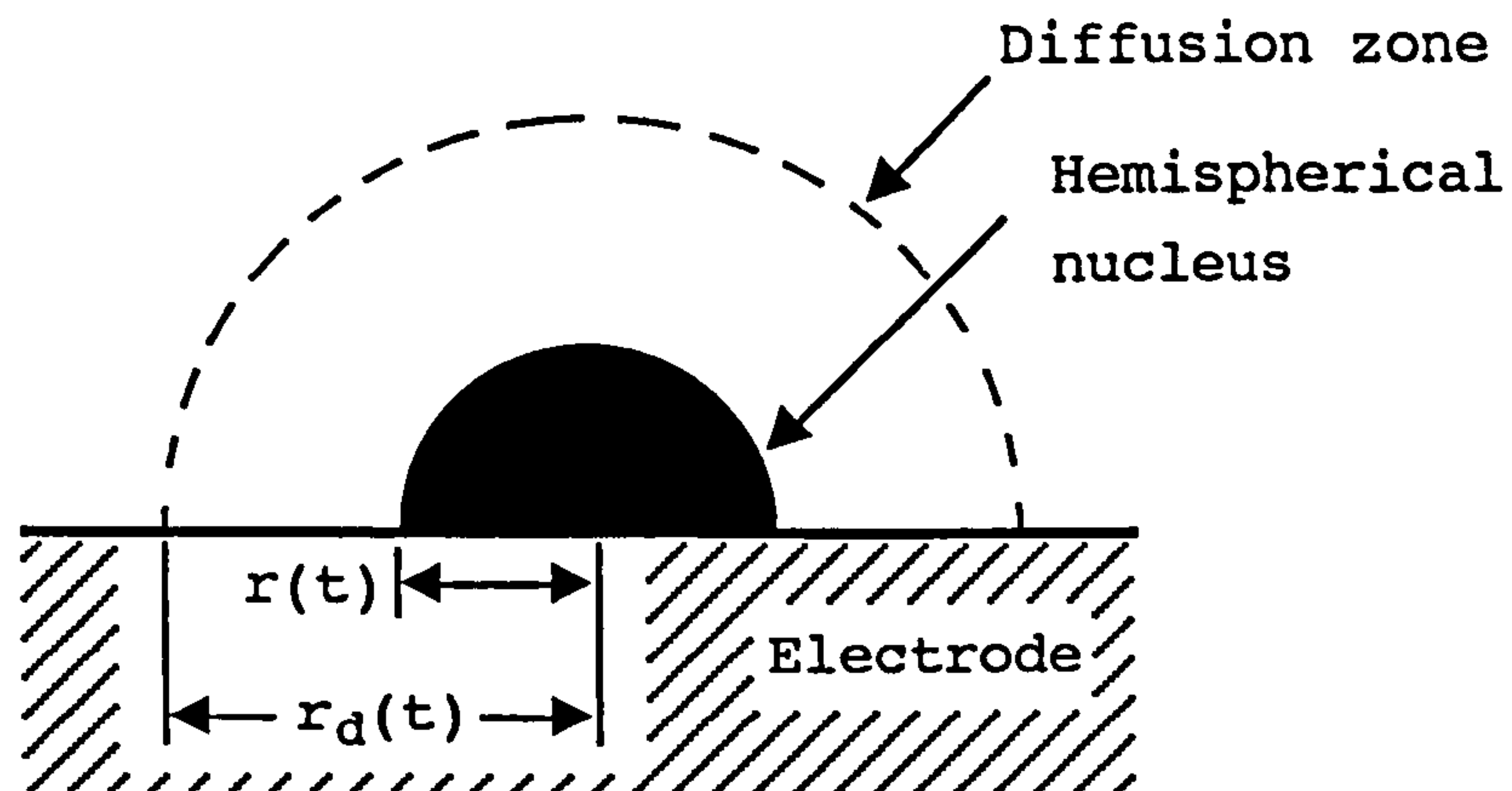


Figure 2.11 Schematic diagram of hemispherical growth under diffusion control.

At a spherical electrode, the diffusion limiting current density, $j(t)$, is given by [e.g.37]

$$j(t) = nFC_b \cdot (D/\pi t)^{1/2} + nFDC_b / r \quad (2.61)$$

where C_b is the bulk concentration of depositing element, r is the radius of a spherical electrode. If the radius, r , is sufficiently small,

$$j \approx nFDC_b / r \quad (2.62)$$

The current flowing into a hemispherical centre is given by multiplying equation (2.62) by the surface area of the hemispherical centre, $2\pi r^2$.

$$i(t) = nFDC_b \cdot 2\pi \cdot r(t) \quad (2.63)$$

Here the radius is a function of time because of growth of the hemispherical centre. The current can be also obtained from the rate of increase in the volume of the centre.

$$i(t) = nF\rho/M \cdot dV/dt \quad (2.64)$$

Here ρ is the density of the deposit and V is the volume. dV can be given as a function of radius.

$$dV = 2\pi r(t)^2 \cdot dr \quad (2.65)$$

From equations (2.63), (2.64) and (2.65), $r(t)$ is expressed as

$$r(t) = (2MDC_b \cdot t / \rho)^{1/2} \quad (2.66)$$

Substituting equation (2.66) into (2.63) yields the diffusion limiting current at an isolated hemispherical nucleus.

$$i(t) = \frac{nF\pi(2DC_b)^{3/2}M^{1/2}}{\rho^{1/2}} \times t^{1/2} \quad (2.67)$$

In the case of instantaneous nucleation, the current density is given by

$$j(t) = \frac{nF\pi N_0 (2DC_b)^{3/2} M^{1/2}}{\rho^{1/2}} \cdot t^{1/2} \quad (2.68)$$

For progressive nucleation, the current density is derived by the same integration as equation (2.53).

$$\begin{aligned} j(t) &= AN_0 \int_0^t \frac{nF\pi (2DC_b)^{3/2} M^{1/2}}{\rho^{1/2}} \cdot (t-u)^{1/2} du \\ &= \frac{2nF\pi AN_0 (2DC_b)^{3/2} M^{1/2}}{3\rho^{1/2}} \cdot t^{3/2} \end{aligned} \quad (2.69)$$

Thus, the current transients for instantaneous and progressive 3-D nucleation / hemispherical growth under diffusion control are given by equations (2.68) and (2.69), respectively. These relations are expected to be observed before significant overlap of diffusion zones occurs. However, at long times, the current-time curves are modified by the overlap. Figure 2.12 shows the schematic diagrams of hemispherical growth and expected relationships between current and time at different stages. The current transient curve expected is also shown schematically in figure 2.13. These figures are illustrated for progressive nucleation. At short times, the diffusion zones are isolated and the nuclei grow independently. During this period, the current is proportional to $t^{1.5}$. Then, the diffusion zones begin to overlap each other. At a certain time of the intermediate term, the current reaches a maximum. Finally, the diffusion regime changes from hemispherical to planar diffusion and the current-time relationship is expressed by the Cottrell equation (i.e. j is proportional to $t^{-0.5}$).

$$j(t) = nFD^{1/2}C_b \cdot (\pi t)^{-1/2} \quad (2.70)$$

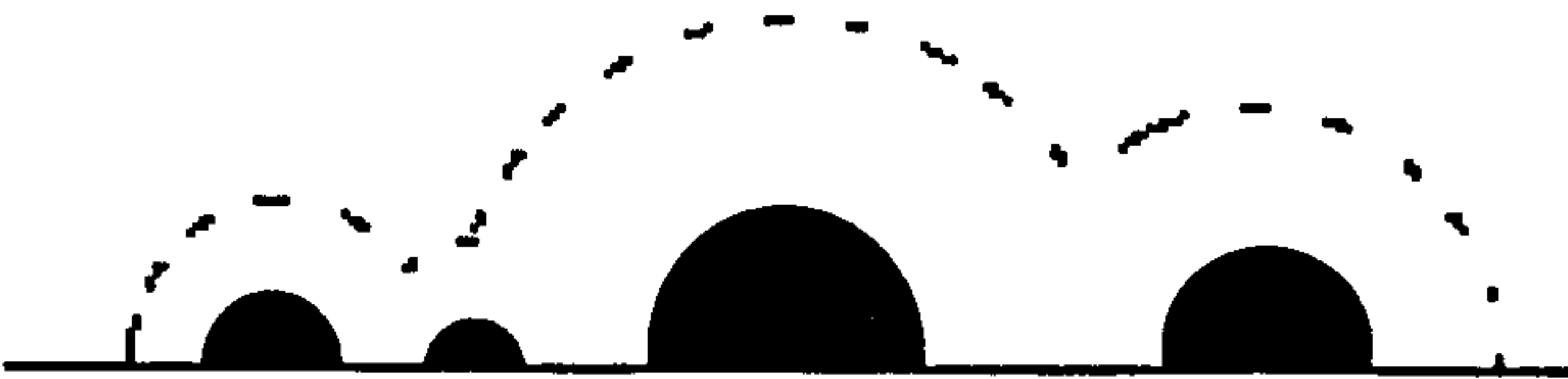
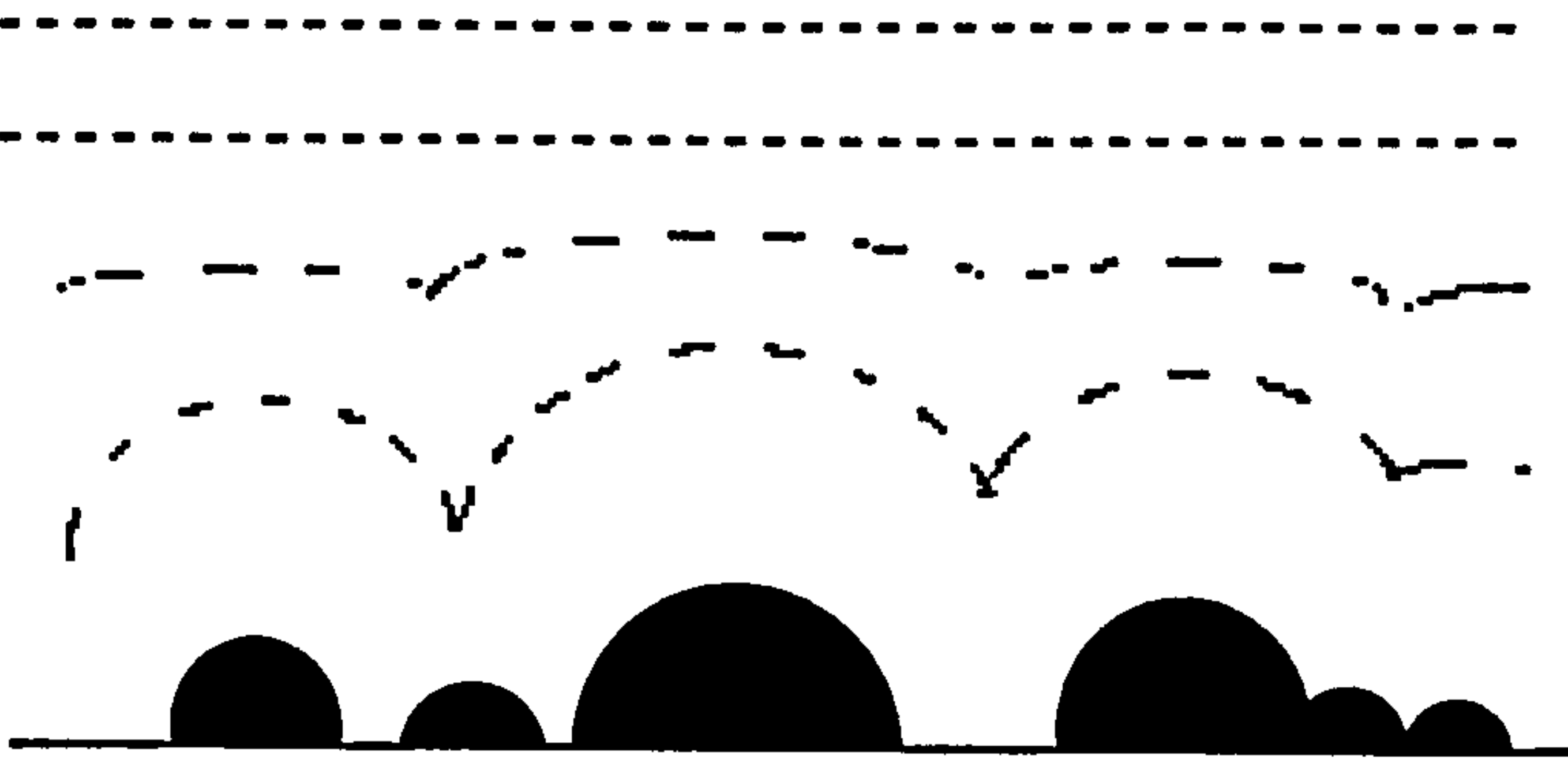
Diagrams of hemispherical growth.	i-t curves expected at each step.
	
	$i \propto t^{1.5}$
	
	
	Intermediate between $i \propto t^{1.5}$ and $i \propto t^{-0.5}$ $i \propto t^{-0.5}$

Figure 2.12 Schematic diagrams of progressive nucleation / hemispherical growth under diffusion control.

 : nucleus ---- : diffusion zone

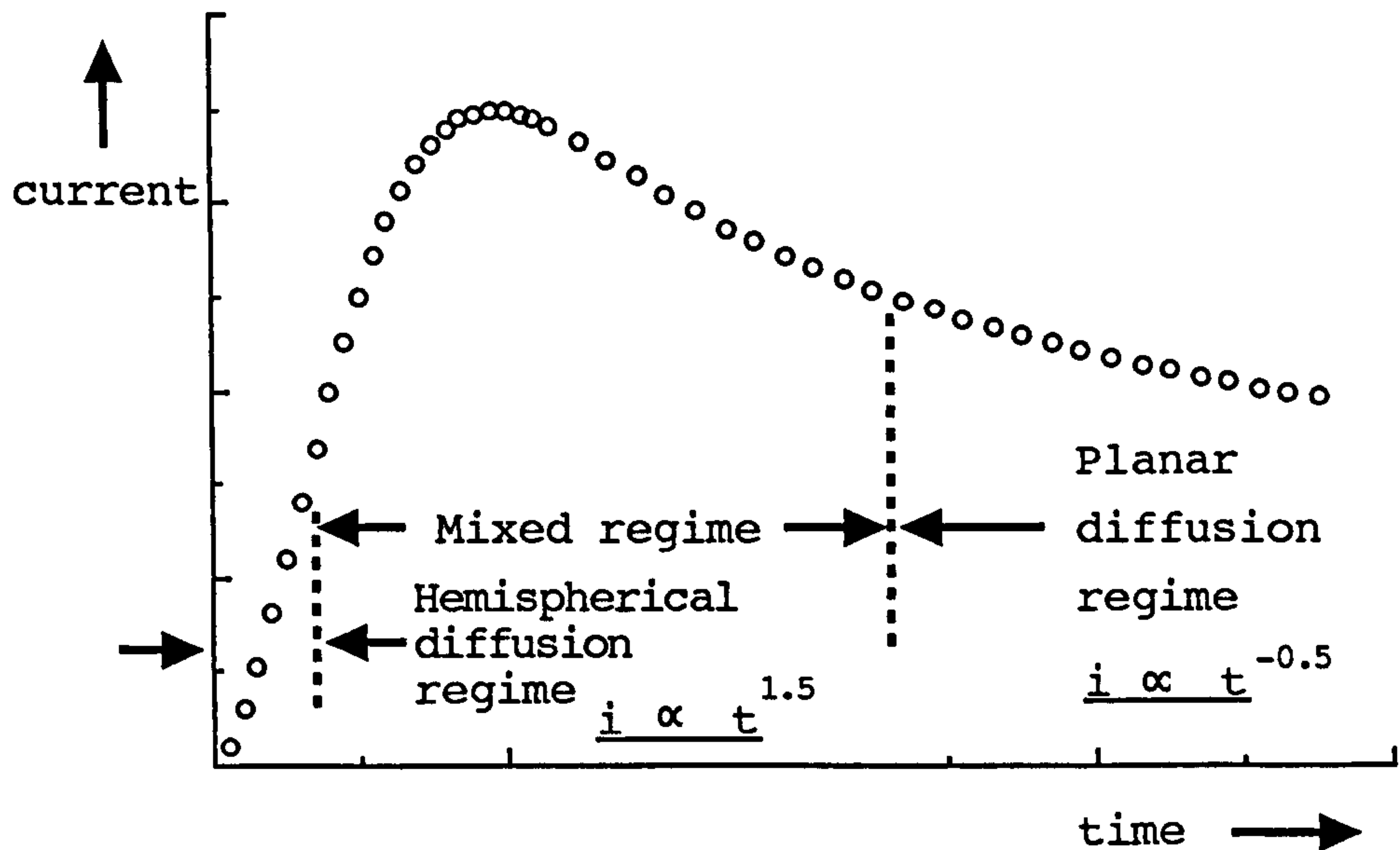


Figure 2.13 A schematic current transient for progressive nucleation / hemispherical growth under diffusion control.

Overlap of diffusion zones.

Some equations to explain whole range of the transient have been proposed. The first equation was derived by Gunawardena et al.[48]. They assumed that overlap of hemispherical diffusion zones can be estimated by the Avrami theorem. Their idea was improved by Scharifker et al.[49] and Sluyters et al.[50]. Through different approaches, Bosco et al.[51] and Bobbert et al.[52] have also proposed theoretical equations for the current transient. As the equations proposed by Gunawardena, Scharifker and Sluyters are quoted most often to compare with experimental results [42,53~55], their approaches are described in this section.

Gunawardena's approach [48].

In order to estimate the overlap of diffusion zones, the sizes of diffusion zones (i.e. radii of the hemispherical diffusion zones) must be calculated first. Gunawardena et al. considered "the equivalent area of plane surface towards which diffuses, by linear diffusion, the same amount of material that would be transferred, through hemispherical diffusion, to a hemispherical growing centre [48]". This assumption means that the diffusion zones are cylindrical in shape and the depositing material diffuses vertically from the top of the cylindrical diffusion zones to the electrode surface. As the depositing material flows through a circular plane surface under diffusion control, it can be considered that the deposition current is given by the Cottrell equation.

$$i(t) = \frac{nFD^{1/2}C_b \cdot \pi r_d(t)^2}{\pi^{1/2}t^{1/2}} \quad (2.71)$$

Here $r_d(t)$ is the radius of an equivalent cylindrical diffusion zone. From equations (2.63), (2.66) and (2.71), the radius, $r_d(t)$, can be expressed as

$$r_d(t) = (\lambda Dt)^{1/2} \quad (2.72)$$

where $\lambda = (8\pi C_b M / \rho)^{1/2}$. For instantaneous nucleation, the extended diffusion area is given by

$$S_{ext} = N_0 \cdot \pi \lambda Dt \quad (2.73)$$

Gunawardena et al. took account of establishment of the Cottrell relation at long times and have obtained the following equation with Avrami theorem (2.54).

$$j(t) = \frac{nFC_b D^{1/2}}{(\pi t)^{1/2}} \cdot [1 - \exp(-N_0 \pi \lambda D \cdot t)] \quad (2.74)$$

Since the exponential term in equation (2.74) can be regarded as $N_0 \cdot \pi \lambda D t$ at short times, equation (2.74) can be rewritten as equation (2.67). Therefore, it is expected that, for instantaneous nucleation, equation (2.73) can explain not only the current transients after overlap, but also before overlap of diffusion zones.

For progressive nucleation, the extended diffusion area is given by

$$S_{\text{ext}}(t) = \int_0^t \pi \{r_d(t-u)\}^2 \cdot \frac{dN}{du} \cdot du \quad (2.75)$$

Substituting equations (2.51) and (2.72) yields

$$S_{\text{ext}}(t) = 1/2 \cdot A N_0 \cdot \pi \lambda D \cdot t^2 \quad (2.76)$$

As well as for instantaneous nucleation, the current for progressive nucleation is given by

$$j(t) = \frac{n F C_b D^{1/2}}{(\pi t)^{1/2}} \cdot [1 - \exp(-\frac{1}{2} A N_0 \pi \lambda D \cdot t^2)] \quad (2.77)$$

However, this equation yields a different equation from equation (2.69) at short times.

$$\begin{aligned} j(t)_{\text{small } t} &\approx n F C_b D^{1/2} \cdot (\pi t)^{-1/2} \cdot (1/2 \cdot A N_0 \pi \lambda D \cdot t^2) \\ &= \frac{n F \pi A N_0 (2 D C_b)^{3/2} M^{1/2}}{2 \rho^{1/2}} \cdot t^{3/2} \end{aligned} \quad (2.78)$$

Here $(8 \pi C_b M / \rho)^{1/2}$ is substituted into λ . In order to compensate for the difference between equation (2.69) and (2.78), Gunawardena et al. have changed the value of ' λ ' in equation (2.77) to $(4/3)(8 \pi C_b M / \rho)^{1/2}$. Of course, this method for the compensation is an undesirable one. Giving different values of λ to equations (2.74) and (2.77) leads to the strange situation that diffusion zones spread at

different rates for instantaneous and progressive nucleation, even before overlap of diffusion zones. Gunawardena et al. did not justify this difference. However, this difference is compensated by Sluyters's equation (2.87) and by a new equation proposed in this thesis (see section 5.5).

Scharifker's approach [49].

As described above, Gunawardena et al. obtained the theoretical transients for the limiting cases of nucleation (i.e. instantaneous and progressive nucleation). Scharifker et al. have used a more general form of nucleation rate and tried to get a current-time equation to express the whole range of nucleation system (i.e. from instantaneous nucleation to progressive nucleation). The general form applied for nucleation rate is

$$dN(t) / dt = AN_0 \cdot \exp(-At) \quad (2.79)$$

This equation can be obtained by differentiation of equation (2.41). The equation for the extended diffusion area (2.75) is rewritten by

$$\begin{aligned} S_{\text{ext}}(t) &= \int_0^t \pi \lambda D (t-u) \cdot AN_0 \cdot \exp(-Au) \cdot du \\ &= N_0 \pi \lambda D \cdot \left(t - \frac{1 - \exp(-At)}{A} \right) \end{aligned} \quad (2.80)$$

The current transient can be expressed as well as equation (2.74).

$$j(t) = \frac{nFC_b D^{1/2}}{(\pi t)^{1/2}} \cdot \left[1 - \exp\left(-N_0 \pi \lambda D \cdot \left(t - \frac{1 - e^{-At}}{A} \right) \right) \right] \quad (2.81)$$

This equation was obtained simply by modifying the nucleation rate term in Gunawardena's equations. Therefore, this equation has the same problem as Gunawardena's equation (namely, values of ' λ '). As Gunawardena obtained an equation for instantaneous nucleation and another equation for progressive nucleation, he could give the different value of ' λ ' to each equation ($(8\pi C_b M / \rho)^{1/2}$ for instantaneous nucleation, $(4/3)(8\pi C_b M / \rho)^{1/2}$ for progressive nucleation). However, Scharifker tried to get a current-time equation valid for any cases of nucleation system. Therefore, if $(8\pi C_b M / \rho)^{1/2}$ is given as the value of ' λ ', the equation can be applied to only nucleation system close to instantaneous nucleation. If the equation is applied to progressive nucleation, it gives smaller currents than the currents expected by equation (2.69) at short times (3/4 times smaller).

Sluyters's approach [50].

Sluyters et al. pointed out that the cylindrical diffusion zones proposed by Gunawardena et al. have different heights. This situation is shown in figure 2.14. They considered that the height of all diffusion zones should be the same and tried to improve Scharifker's equation (2.81).

The current which flows through the equivalent plane surface is given by the Cottrell equation (2.71). Although Gunawardena and Scharifker modified t to $(t-u)$ for nuclei formed at $t=u$, Sluyters has not done this modification in order to give $(\pi D t)^{1/2}$ as the height of all diffusion zones. The Cottrell equation and equation (2.63) yield

$$i(t) = \frac{n F D^{1/2} C_b \cdot \pi r_d(t)^2}{\pi^{1/2} t^{1/2}} = n F C_b \cdot 2\pi \cdot \{r(t-u)\} \quad (2.82)$$

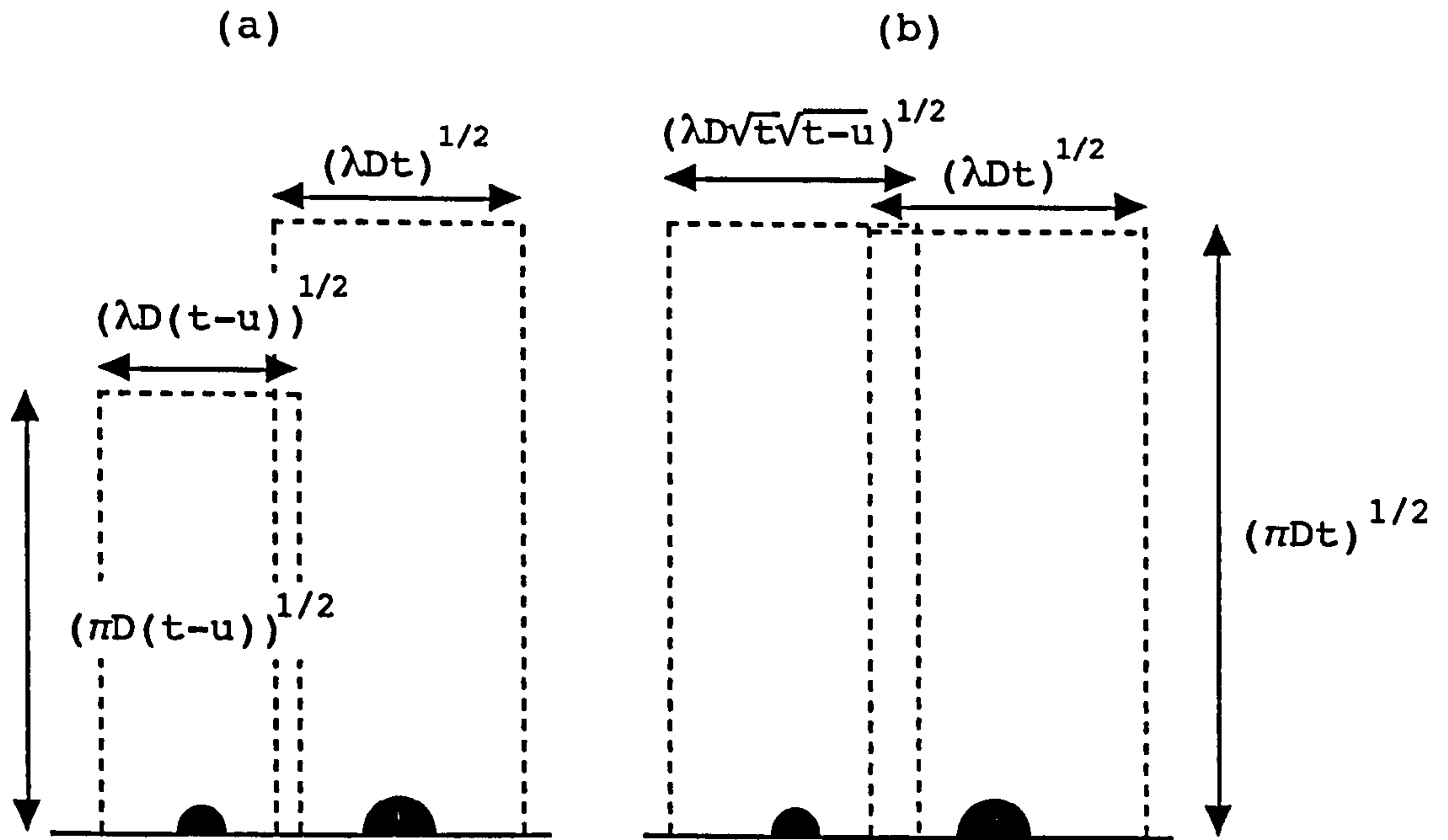


Figure 2.14 Schematic representation of the hypothetical cylindrical diffusion zones around nuclei.

(a) : the model of Gunawardena[45].

The height depends on the time when the nuclei form, u .

(b) : the model of Sluyters[47].

The height is independent of u .

The smaller nuclei are formed at $t = u$ and the larger nuclei are formed at $t=0$.

◐ : Nucleus [] : Diffusion zone

for nuclei formed at $t=u$. From this equation, the plane diffusion area, $\pi r_d(t)^2$ is given by

$$\pi r_d(t)^2 = 2\pi^{3/2} \cdot D^{1/2} \cdot t^{1/2} \cdot \{r(t-u)\} \quad (2.83)$$

and substituting equation (2.66) gives

$$\begin{aligned} \pi r_d(t)^2 &= (2\pi)^{3/2} \cdot (C_b M / \rho)^{1/2} \cdot D \cdot t^{1/2} \cdot (t-u)^{1/2} \\ &= \lambda \pi D \cdot t^{1/2} \cdot (t-u)^{1/2} \end{aligned} \quad (2.84)$$

where λ is $(8\pi C_b M/\rho)^{1/2}$ as given by Gunawardena. By substituting equations (2.84) and (2.79) into (2.75), the extended diffusion area is given by

$$S_{\text{ext}}(t) = AN_0\lambda\pi Dt^{1/2} \int_0^t (t-u)^{1/2} \cdot \exp(-At) \cdot du \quad (2.85)$$

or as $h = (A \cdot (t-u))^{1/2}$,

$$S_{\text{ext}}(t) = 2A^{1/2}N_0\lambda\pi Dt^{1/2} \exp(-At) \int_0^{(At)^{1/2}} h^2 \cdot \exp(h^2) \cdot dh \quad (2.86)$$

The equation for the current transient is given with the Avrami theorem as well as Gunawardena's and Scharifker's equations.

$$j(t) = \frac{nFC_b D^{1/2}}{(\pi t)^{1/2}} \cdot [1 - \exp(-AN_0\lambda\pi Dt^{1/2} \int_0^t (t-u)^{1/2} \cdot \exp(-At) \cdot du)] \quad \dots (2.87)$$

In the case of instantaneous nucleation, at short times (i.e. before overlap of diffusion zones), the current transient should be expressed by equation (2.68). For instantaneous nucleation, it can be considered that Sluyters's approach is the same as Gunawardena's. The similarity between the two approach is obvious when $u=0$ is substituted into the radii and the heights of diffusion zones shown in figure 2.14. This means that, at short times, equation (2.87) can be rewritten as equation (2.68). As defined initially, $(8\pi C_b M/\rho)^{1/2}$ can be used as the value of ' λ '.

On the other hand, in order to rewrite equation (2.87) to obtain the equation for progressive nucleation, $dN/du = AN_0$ instead of $AN_0 \cdot \exp(-Au)$ is substituted into equation (2.85). The substitution gives

$$\begin{aligned} S_{\text{ext}}(t) &= AN_0 \lambda \pi D t^{1/2} \int_0^t (t-u)^{1/2} \cdot du \\ &= 2/3 \cdot AN_0 \lambda \pi D t^2 \end{aligned} \quad (2.88)$$

The current at short times can be expressed by

$$\begin{aligned} j(t)_{\text{small } t} &\approx n F C_b D^{1/2} \cdot (\pi t)^{-1/2} \cdot (2/3 \cdot AN_0 \pi \lambda D \cdot t^2) \\ &= \frac{2 n F \pi AN_0 (2 D C_b)^{3/2} M^{1/2}}{3 \rho^{1/2}} \cdot t^{3/2} \end{aligned} \quad (2.89)$$

where $(8\pi C_b M/\rho)^{1/2}$ is substituted for the value of ' λ '. It should be noticed that this equation is the same as equation (2.69). Therefore, for Sluyters's equation, the compensation which Gunawardena et al. have done for the value of λ is not required and $(8\pi C_b M/\rho)^{1/2}$ can be used for the whole range of nucleation system (i.e. from instantaneous to progressive nucleation).

Summary.

(1) As a conclusion of section 2.3, current transients for some growth models are shown in table 2.1. In order to study electrocrystallization, it is obvious that measurement of the time dependence of deposition current is very powerful method.

(2) For three dimensional hemispherical growth under diffusion control, Gunawardena et al., Scharifker et al. and

Sluyters et al. have proposed current-time responses. The three approaches are compared below.

(I) Gunawardena's approach.

Theoretical current transients for instantaneous nucleation (equation 2.74) and progressive nucleation (2.77) have been proposed. As a value of ' λ ', they have used $(8\pi C_b M/\rho)^{1/2}$ for instantaneous nucleation and $(3/4)(8\pi C_b M/\rho)^{1/2}$ for progressive nucleation. At short times, their equations correspond to the equations (2.68,69) which Hills et al. have proposed to explain the current transients observed before overlap of diffusion zones. However, the theory has a contradiction that the growth rate of diffusion zones depends on the nucleation rate law.

(II) Scharifker's approach.

A theoretical current transient applied for the whole range of nucleation system (i.e. from instantaneous to progressive nucleation) has been proposed (equation 2.81). However, if λ is set equal to $(8\pi C_b M/\rho)^{1/2}$, the equation can be expressed only for nucleation system close to instantaneous nucleation. If λ is set equal to $(3/4)(8\pi C_b M/\rho)^{1/2}$, the equation can be used only for systems near progressive nucleation. Therefore, in fact, the equation cannot be applied for the whole range of nucleation systems.

(III) Sluyters's approach.

Following Scharifker, Sluyters has tried to derive an equation applicable to any nucleation system. In both cases of instantaneous and progressive nucleation, for short times, equation (2.87) corresponds to Hills's equations (2.68,2.69), when λ is given the value $(8\pi C_b M/\rho)^{1/2}$. Since the equation can explain both of the limiting cases without any modification of λ , it can be probably applied to the

whole range of nucleation system. It should be noticed that Sluyters's equations modified for instantaneous and progressive nucleation are the same equations as Gunawardena's equations (2.74, 2.77). This means that Sluyters has normalised Gunawardena's equations from equations for two limiting cases to equations for the whole range of nucleation.

Table 2.1 Current transients expected for the various nucleation/ growth models.

Growth model			Initial transient	Whole transient
2-D	Single layer	K	I	$\frac{2\pi Fk^2hMN_0t}{\rho} \cdot \exp(-\frac{\pi N_0M^2k^2t^2}{\rho^2})$
			P	$\frac{\pi Fk^2hMAN_0t^2}{\rho} \cdot \exp(-\frac{\pi AN_0M^2k^2t^3}{3\rho^2})$
	D	No equations proposed		At long times, the Cottrell relation?
3-D	Cone	K	I	$nFk_v[\pi M^2k_h^2N_0 \cdot t^2]$
			P	$nFk_v[\pi M^2k_h^2AN_0 \cdot t^3]$
	Hemi-sphere	K	I	$nFk_r[1-\exp(-\frac{2\pi M^2k_r^2N_0 \cdot t^2}{\rho^2})]$
			P	$nFk_r[1-\exp(-\frac{2\pi M^2k_r^2AN_0 \cdot t^3}{3\rho^2})]$
	D		I	$\frac{nFC_bD^{1/2}}{(\pi t)^{1/2}} \cdot [1-\exp(-N_0\pi\lambda_1D \cdot t)]$
			P	$\frac{nFC_bD^{1/2}}{(\pi t)^{1/2}} \cdot [1-\exp(-\frac{1}{2}AN_0\pi\lambda_2D \cdot t^2)]$

K, D : Kinetic, Diffusion control. I , P : Instantaneous, Progressive nucleation.
k, k_h, k_v, k_r : Constants. λ₁ = (8πC_BM/ρ)^{1/2}, λ₂ = (3/4)•λ₁.

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CHAPTER 3.

EXPERIMENTAL.

- 3.1 Reagents and electrolytes.
 - 3.2 Electrochemical cells and instruments.
 - 3.3 Electrodes and surface preparation.
- References.

3.1 Reagents and electrolytes.

Water purified by a "Milli-Q" system ($10^8 \Omega \cdot \text{cm}$) was used for all electrolyte solutions. The chemicals used are shown below.

TeO ₂	:	ALDRICH CHEMICALS.	5N grade (99.999%).
CdSO ₄	:	KOCH-LIGHT LTD.	A.R. grade.
		or BDH CHEMICALS.	Arista <u>a</u> R grade.
H ₂ SO ₄	:	BDH CHEMICALS.	A.R. grade.
Na ₂ SO ₄	:	BDH CHEMICALS.	A.R. grade.
NH ₄ F	:	BDH CHEMICALS	Arista <u>a</u> R grade.

Three kinds of electrolytes were used mainly for CdTe electrodeposition. Table 3.1 shows composition of the electrolytes. Sodium sulphate was added to solution (a) as a supporting electrolyte, because the concentration of cadmium sulphate was much lower than that in solution (b) and (c). The pH of solution (a) was adjusted to a value of 1.5 with a ORION pH meter (MODEL 520A), by addition of sulphuric acid.

Table 3.1 Composition of electrolytes.

Electrolyte	(a)	(b)	(c)
TeO ₂	$2 \times 10^{-4} \text{ M}$	$2 \times 10^{-3} \text{ M}$	$2 \times 10^{-3} \text{ M}$
CdSO ₄	0.02 M	0.5 M	0.5 M
H ₂ SO ₄	$\approx 0.016 \text{ M}$	0.5 M	0.5 M
Na ₂ SO ₄	0.1 M	—	—
NH ₄ F	—	—	0.5 M
pH	1.5	≈ 0.5	≈ 0.5

Electrolyte(a) was used for studies of Te electrodeposition on glassy carbon. Electrolytes(b) and (c) were used for studies of CdTe electrodeposition on tin oxide coated glass and on n-type silicon, respectively. Electrolyte(c) for CdTe electrodeposition on silicon included ammonium fluoride to prevent formation of silicon dioxide on the silicon surface.

As described in chapter 1, the solubility of tellurium dioxide depends on pH. Both equations (1.1) [1] and (1.2) [2] have been proposed to describe the relationship between the solubility and pH. From these equations, it is found that the TeO_2 concentration of each electrolyte is adjusted close to the solubility limit (2×10^{-4} M of TeO_2 at pH 1.5 and 2×10^{-3} M at pH 0.5).

The electrolytes in the electrochemical cell were deoxygenated with oxygen-free nitrogen gas for 2 hours before measurements and then the measurements were carried out under a nitrogen blanket. The temperature of the electrolytes was 24 ± 1 °C (room temperature), unless otherwise stated.

3.2 Electrochemical cells and instruments.

All measurements were carried out with a standard three-electrode system. Glassy carbon rotating disk, tin oxide coated glass and n-type monocrystalline Si were used as the working electrodes. Details of these working electrodes are described in section 3.3. The reference electrode employed was a saturated calomel electrode. All potentials are quoted against this reference electrode. A large-area platinum foil (or wire) was used as the counter electrode. For the purpose of minimising noise, the

electrochemical cells were kept in a Faraday box during measurements.

Glassy carbon rotating disk electrode.

Glassy carbon rotating disk electrodes were used for studies of Te electrodeposition on glassy carbon, which is described in chapter 4. Figure 3.1 shows the electrochemical cell used for the rotating electrodes. A sintered glass frit was put between the counter electrode and the main cell, to avoid contamination of solution in the main cell. The distance between the working electrode and the Luggin capillary was about 5 mm. The distance of 5 mm was chosen from the consideration of the following two points.

- : influence of the Luggin capillary on diffusion of reactant.
- : IR drop between the working electrode and the Luggin capillary.

Figures 3.2 and 3.3 show the experimental arrangements for a standard rotating electrode and for a hydrodynamically modulated rotating disk electrode (HMRDE). A fast-rise potentiostat (home made) was used in connection with a HI-TEK INSTRUMENTS PPR1 function generator. Cyclic voltammograms and current transient curves were recorded directly on a BRYANS INSTRUMENTS X-Y-t recorder. A TACUSSEL rotating electrode system was employed. The HMRDE [3,4] was used to investigate the influence of linear diffusion on nucleation current. An ORTEC BROOKDEAL lock-in amplifier and a LEVELL ELECTRONICS oscillator (MODEL TG200D) were added to the standard system shown in figure 3.2.

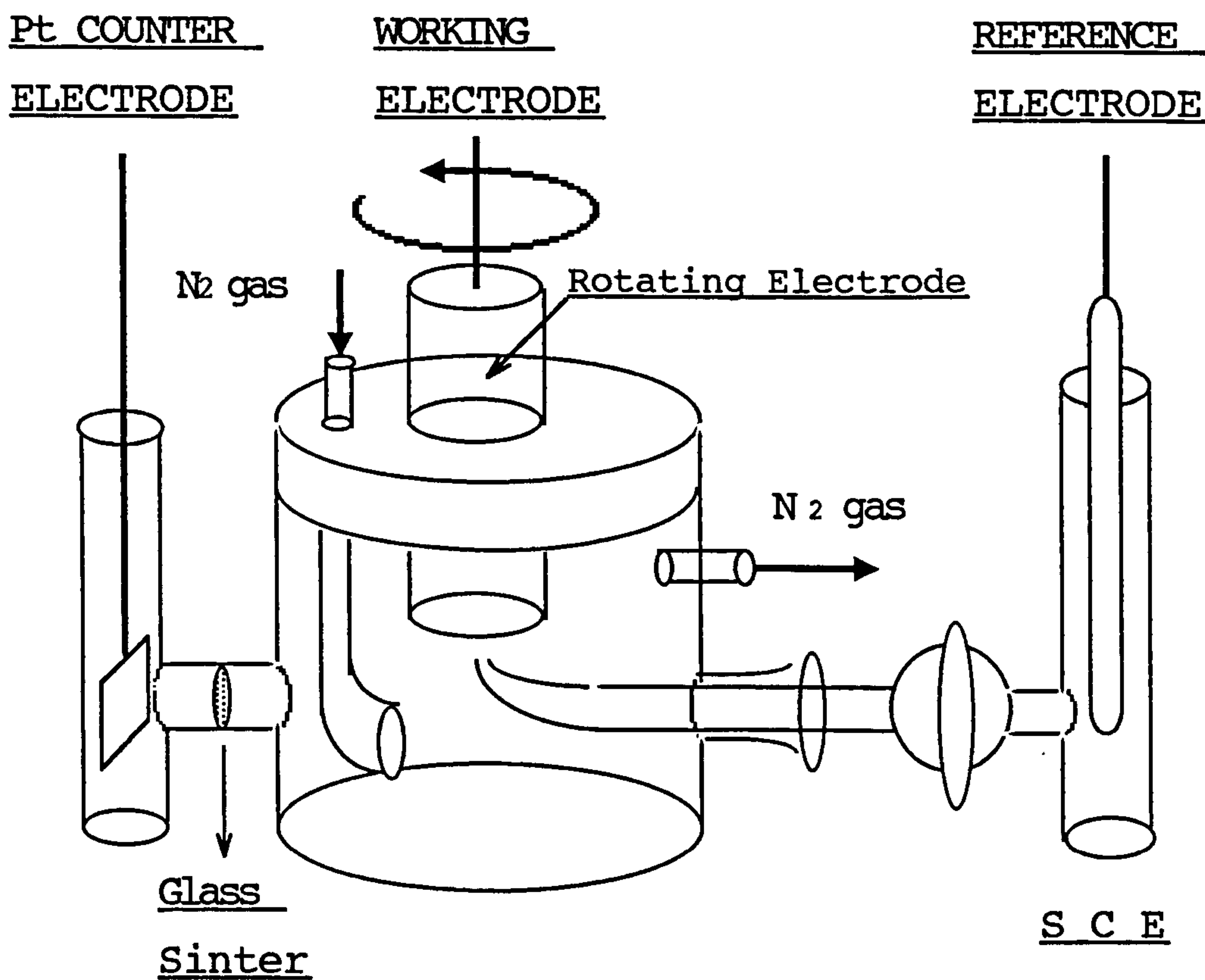


Figure 3.1 Electrochemical cell for glassy carbon rotating disk electrode.

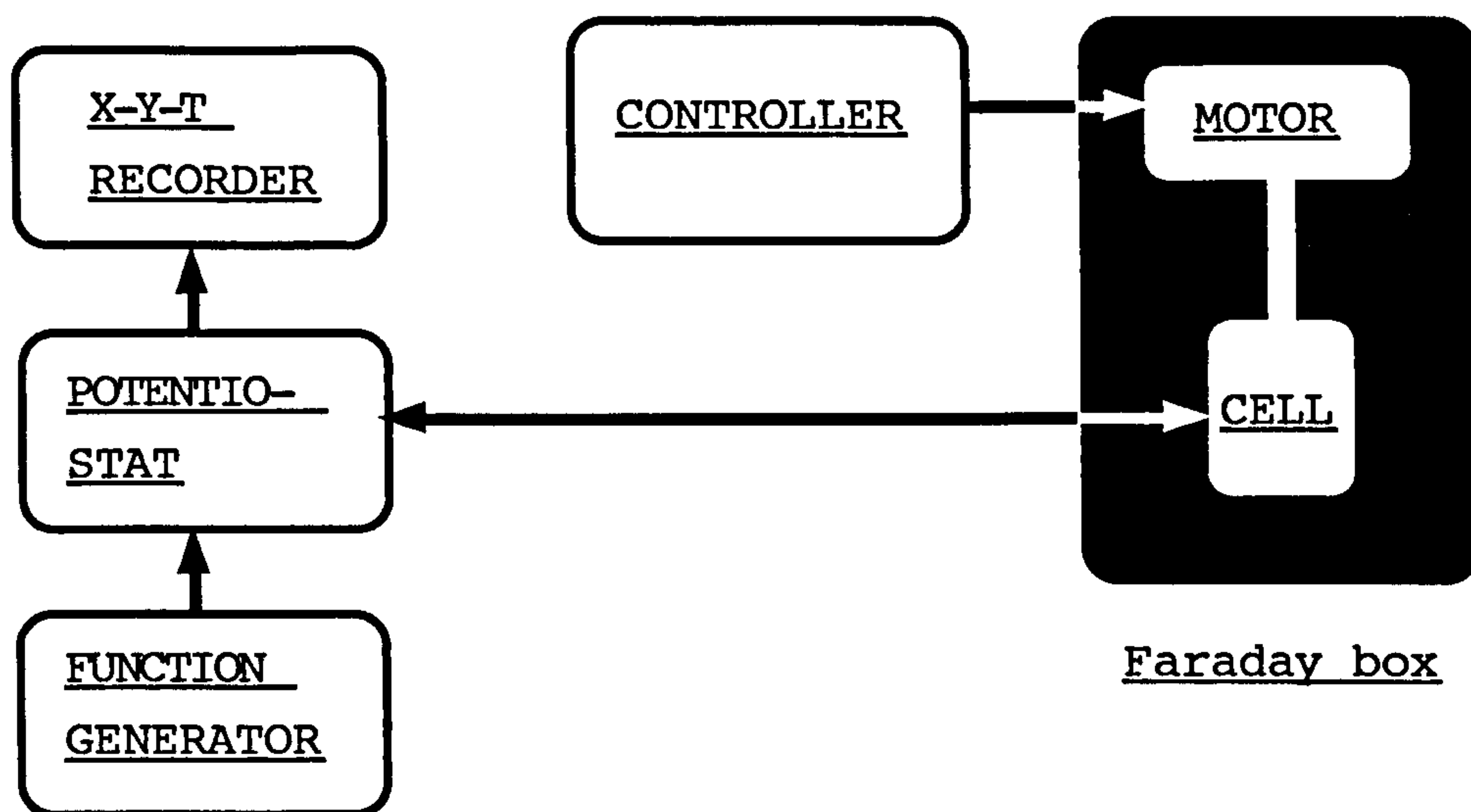


Figure 3.2 Experimental arrangement for a glassy carbon rotating disk electrode.

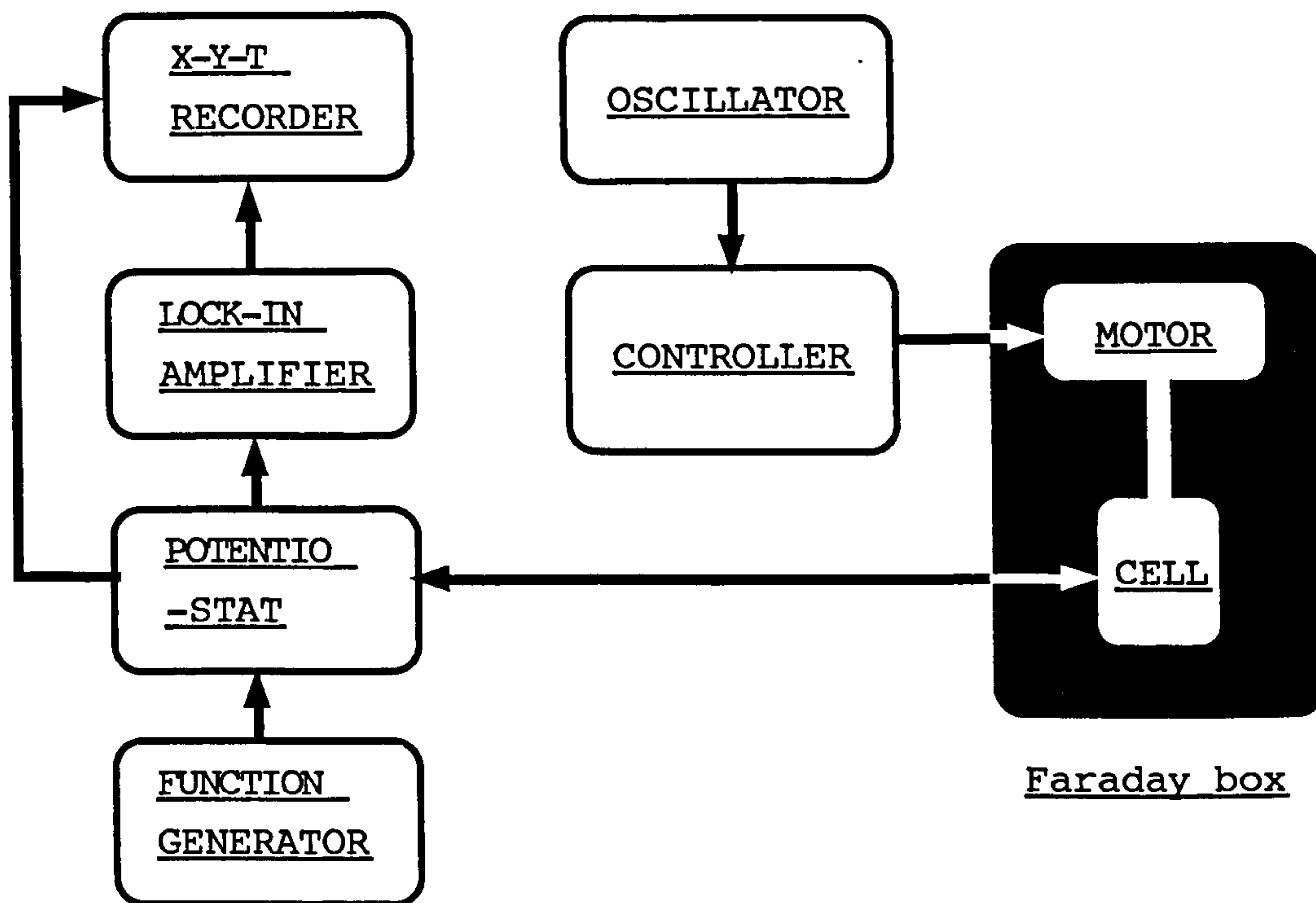


Figure 3.3 Experimental arrangement for a hydrodynamically modulated rotating disk electrode (HMRDE).

Tin oxide coated glass electrodes.

Tin oxide coated glass was used for studies of CdTe electrodeposition at several temperatures. Figure 3.4 shows the thermostatted electrochemical cell.

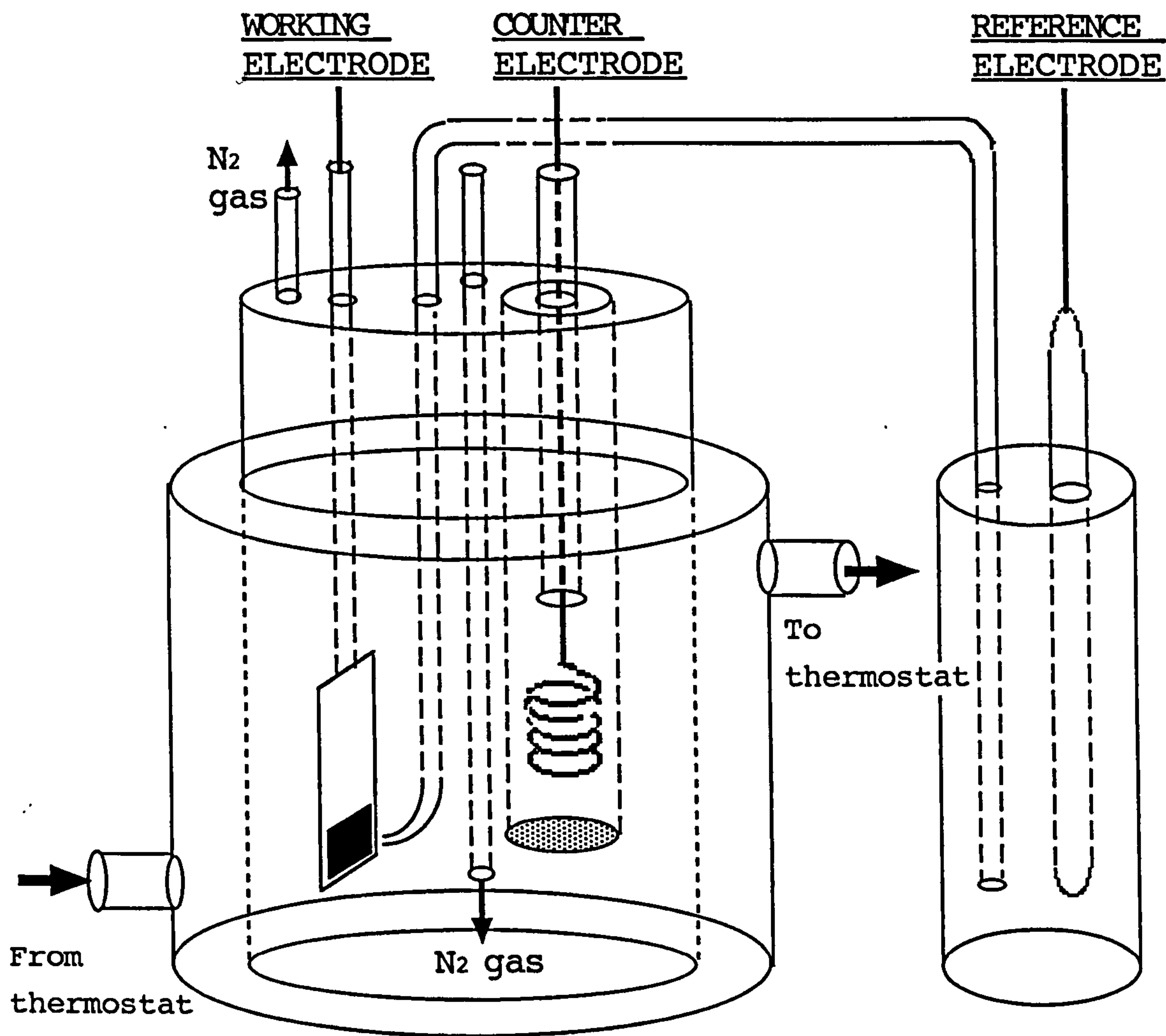


Figure 3.4 Electrochemical cell for a tin oxide coated glass electrode.

The experimental arrangement is shown in figure 3.5. In order to observe fast nucleation processes, a HITACHI digital storage oscilloscope (MODEL VC-6265) was used. The current transient curves were saved with the storage oscilloscope and then plotted with a HEWLETT PACKARD plotter. The temperature of the electrolyte was varied in a range of -6 to $+50$ °C with a HAAKE thermostat. The temperatures were controlled within an error of ± 1 °C. Silicone oil was used as the thermal fluid for the thermostat.

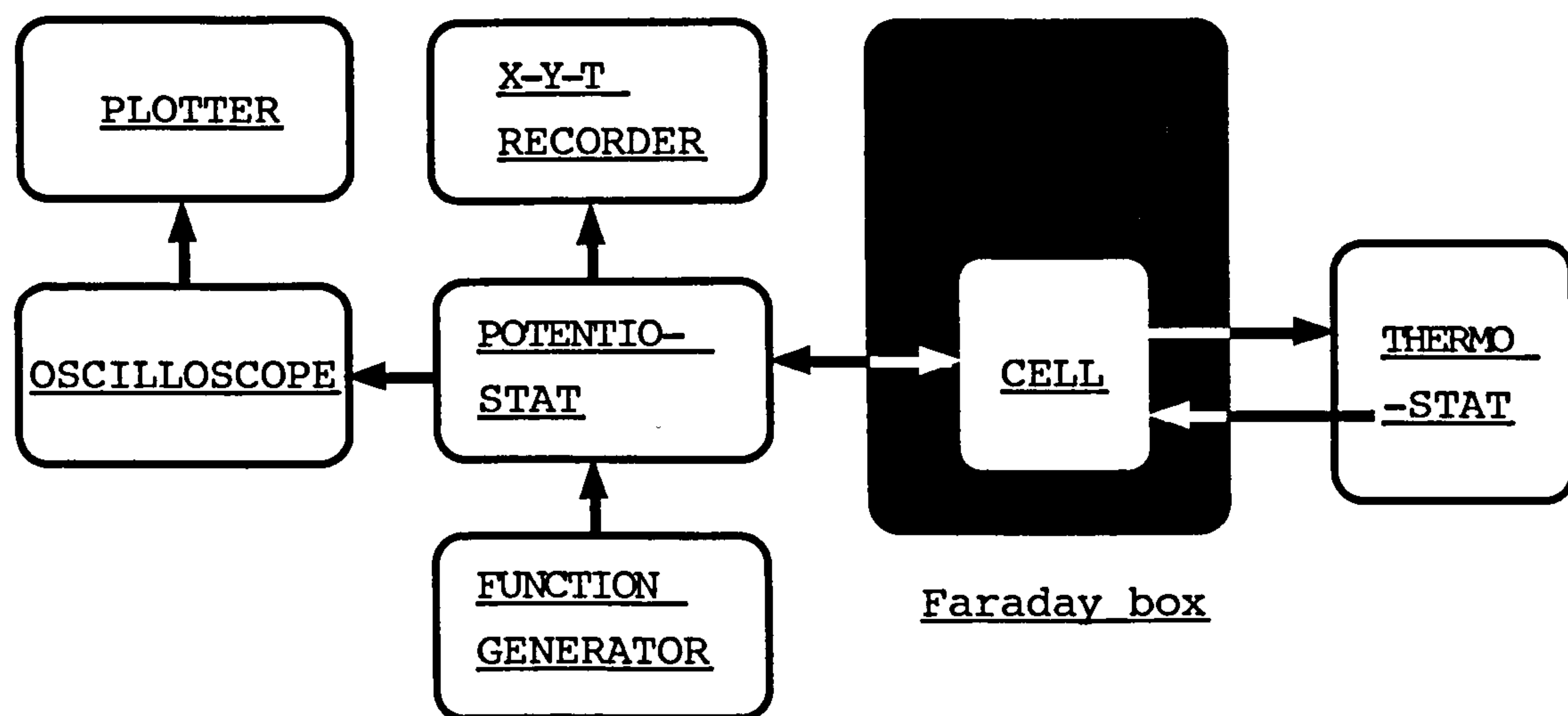


Figure 3.5 Experimental arrangement used for tin oxide coated glass electrodes.

N-type monocrystalline Si electrodes.

The experimental arrangement for tin oxide coated glass shown in figure 3.5 was also used for studies of CdTe electrodeposition on monocrystalline silicon. Photoeffects during electrodeposition of CdTe were studied with the set-up shown in figure 3.6. As the light source, a 5mW UNIPHASE

He-Ne laser was used. The intensity was controlled with a set of neutral density filters. The incident photon flux was measured using a LICONIX calibrated laser powermeter (MODEL 45PM). The illumination period was controlled using a home-made programmed high speed electromechanical shutter. A magnetic stirrer was used to quicken deposition and to investigate the effect of stirring on photocurrent. Although a quartz window is often used for photoelectrochemical measurements, a conventional glass electrochemical cell without a quartz window was found to be satisfactory in the present case.

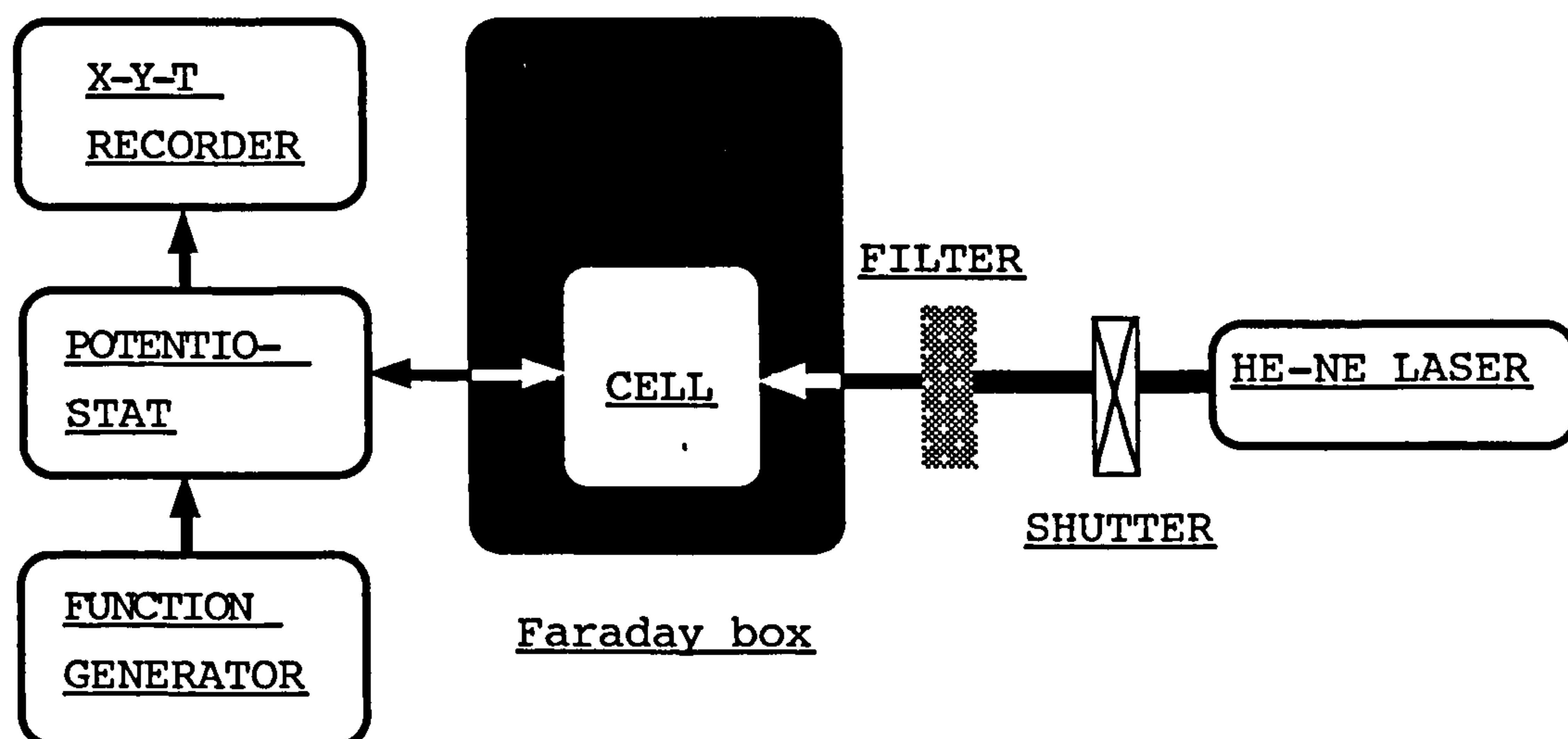


Figure 3.6 Experimental arrangement used for measurements of photoeffects.

Observation of deposits.

The morphology and composition of the deposits were determined by a JEOL JSM-6400 scanning electron microscope with energy dispersive analytical x-ray (Tracor Series II EDAX system). The morphology was also investigated by profilometry (Three dimensional tally surf). An X-ray

diffractometer D5000 (SIEMENS) was used to take X-ray diffraction data.

3.3 Electrodes and surface preparation.

Glassy carbon rotating electrode.

Figure 3.7 shows a glassy carbon rotating disk electrode schematically. Cylindrical glassy carbon (TOKAI CARBON) of 6 mm diameter was mounted in a plastic tube with epoxy resin. Then, the electrode was polished with emery paper and alumina to get a flat and mirror surface. The smallest size of alumina used was $1\mu\text{m}$. Prior to every measurement, the following pre-treatments for the electrode were carried out.

- 1) Cleaning with 30% nitric acid, followed by water rinse.
- 2) Polishing with $1\mu\text{m}$ -alumina sheet (3M).
- 3) Cleaning with purified water in an ultrasonic bath for 1 minute.

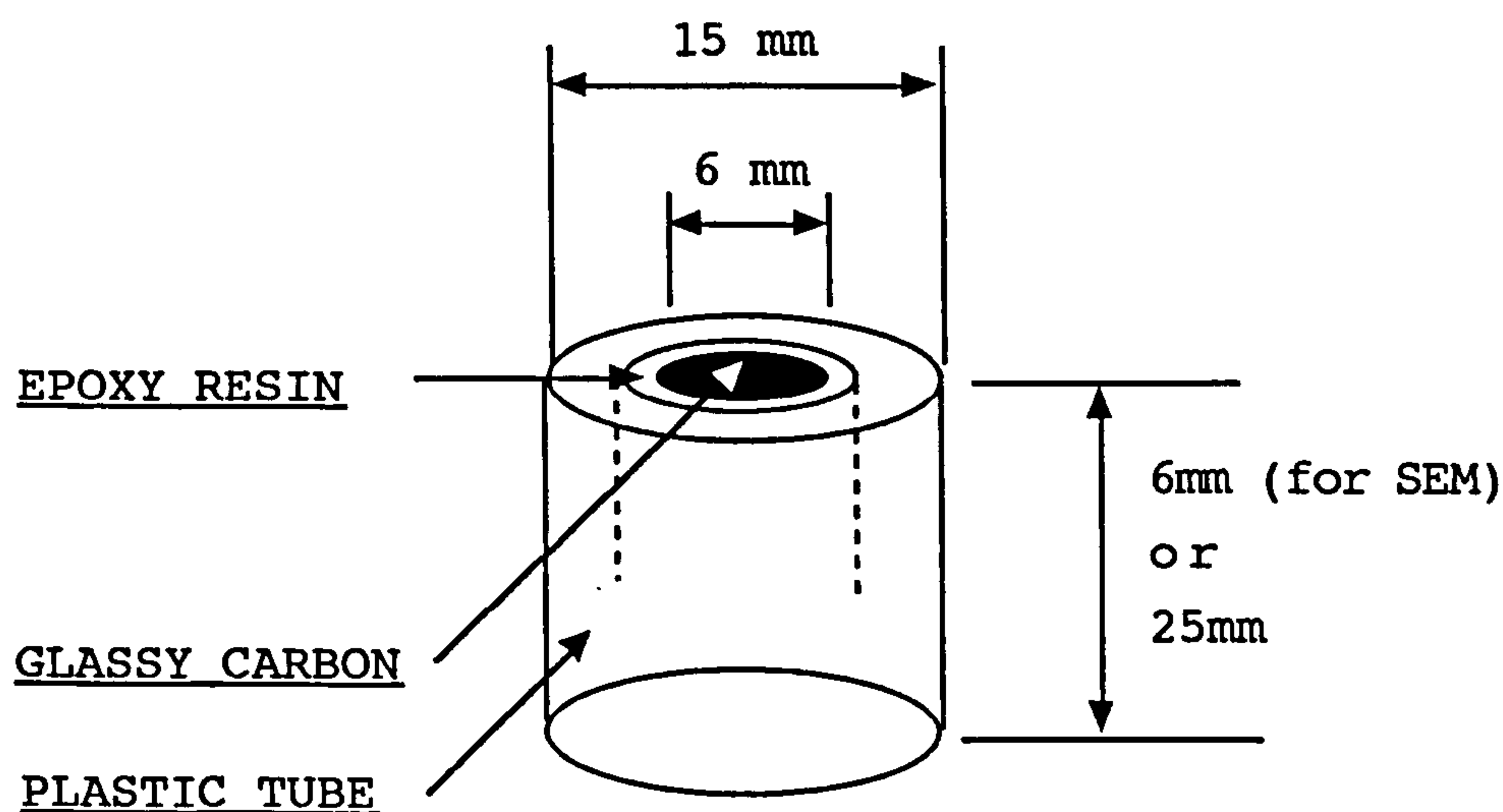


Figure 3.7 Schematic diagram of the glassy carbon rotating disk electrode used.

Tin oxide coated glass electrode (TO).

The TO electrode is illustrated schematically in figure 3.8. The tin oxide glass was supplied by BP Solar. Before assembly as shown in figure 3.8, the tin oxide glass was degreased carefully with acetone. For the electric contact between the electrode and the crocodile clip, silver paint (supplied by RS) was used. The edges of the electrode and the crocodile clip were covered with epoxy resin for insulation.

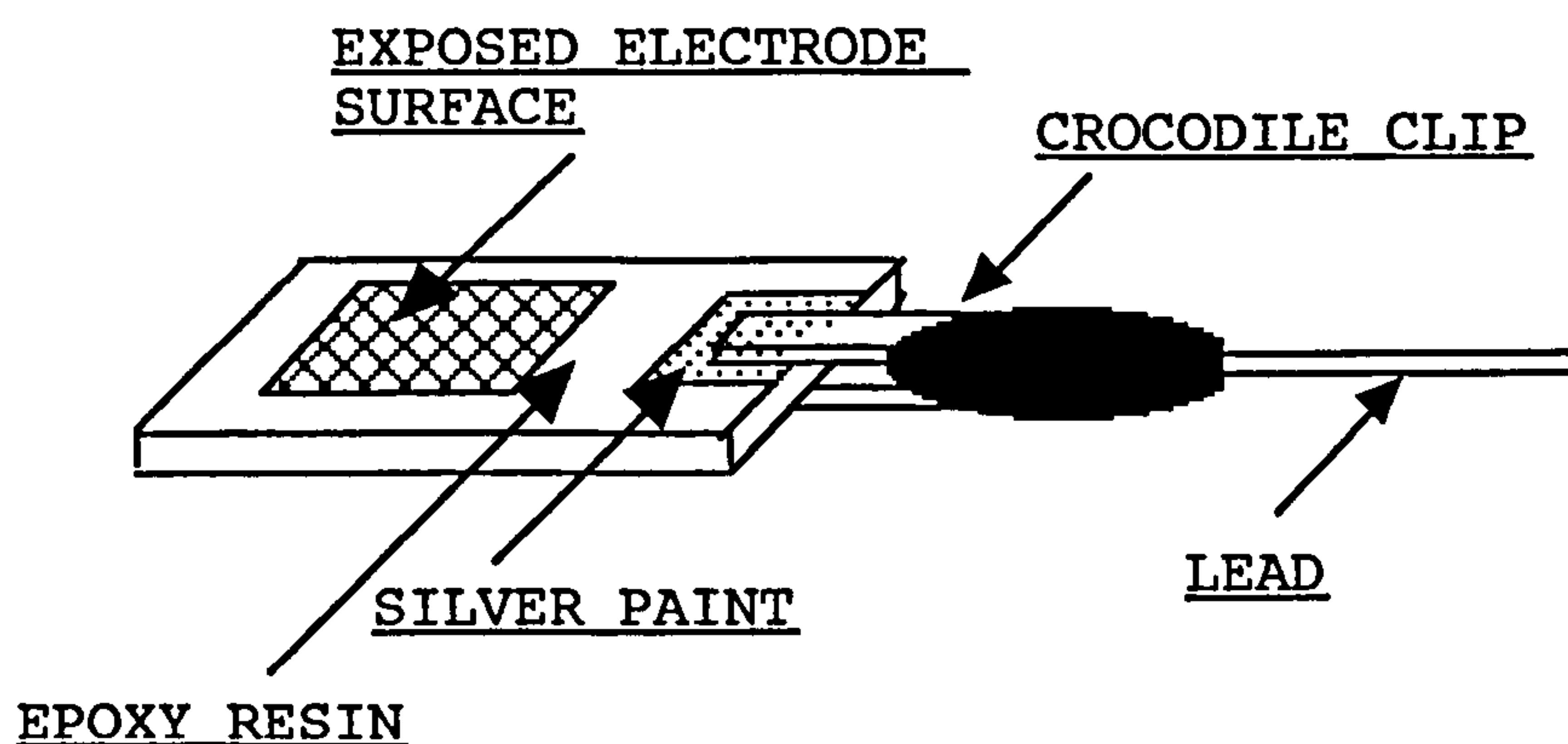


Figure 3.8 Illustration of the tin oxide coated glass electrode (TO).

N-type monocrystalline silicon electrode.

N-type monocrystalline silicon with (100), (110) and (111) orientations was used. The doping density was about 10^{15} cm^{-3} . Figure 3.9 is a drawing of a silicon electrode.

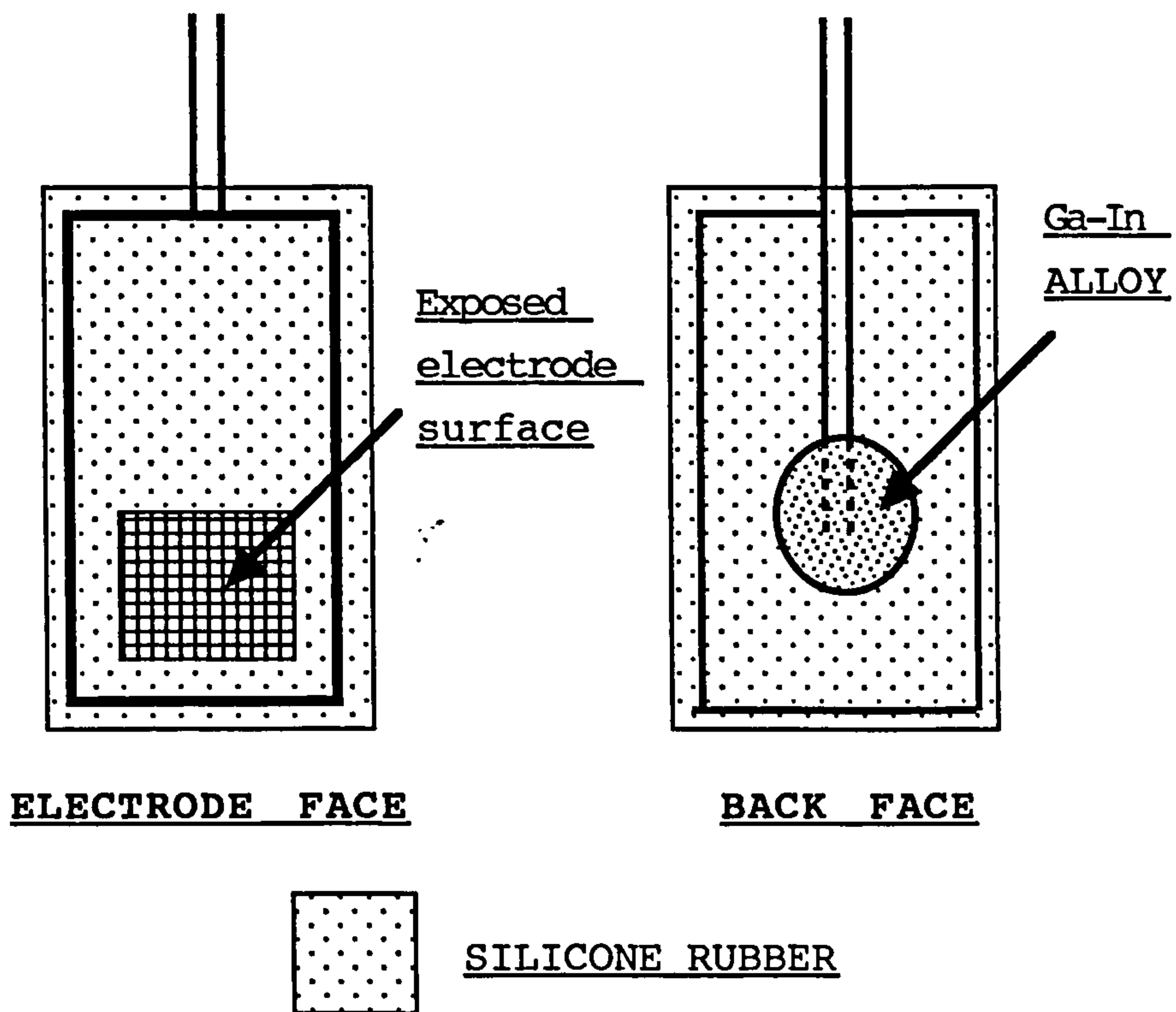


Figure 3.9 Schematic diagram for n-type silicon electrode.

The following pre-treatments for the silicon electrodes were carried out.

- 1) Degreasing by iso-propanol vapour cleaning for 2 hours.
- 2) Removal of silicon dioxide on the back face of the silicon wafers with 2M NH_4F (pH 4.5) for 2 hours.
(See reference [5,6] for the influence of concentration of NH_4F and pH).
- 3) Water rinse followed by drying with N_2 gas.
- 4) Making electric contact from the back face with Ga-In alloy (Ga/In = 7/3).
- 5) Coating the edges of the wafers and In-Ga alloy with silicone rubber.

Furthermore, before electrochemical measurements,

- 6) Cleaning with H_2O_2 -HCl solution at 80°C for 15 minutes, to remove metallic impurities [6,7].
($\text{H}_2\text{O}_2 : \text{HCl} : \text{H}_2\text{O} = 2 : 1 : 8$)
- 7) Removal of silicon dioxide on the electrode surface for 15 minutes with 2M NH_4F (pH 4.5).

After these pre-treatments, measurements were carried out as soon as the silicon electrode was moved to an electrochemical cell.

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CHAPTER 4.

ELECTRODEPOSITION OF Te
ON GLASSY CARBON.

- 4.1 Introduction.
- 4.2 Voltammetric studies.
- 4.3 Nucleation studies.
 - 4.3.1 Nucleation and growth model.
 - 4.3.2 Hydrodynamically modulated rotating disk electrode (HMRDE) studies.
 - 4.3.3 Nucleation rates.
- 4.4 Conclusions.
- Appendix 4.I Discussion of the initial 'charging' current.
- References.

3.1 Introduction.

As the first part of the study, an investigation of electrodeposition of pure tellurium was carried out. Since the first step of CdTe electrodeposition is considered to be electrodeposition of pure Te, several reports dealing with pure Te electrodeposition [1~7] have appeared as interest in CdTe semiconductors has increased. Most of these reports have discussed the electrodeposition mechanism. This work has shown that the reaction is complex and involves adsorption of Te on electrode surface, reduction of Te^{4+} to H_2Te , and chemical reaction between HTeO_2^+ and H_2Te . The reduction of $\text{Te}(+4)$ is expressed as



in acid solution and



in strongly alkaline solution. Since acid solutions are often used as the solutions for CdTe and Te electrodeposition, reactions (4.1) and (4.2) should be considered as the route of H_2Te formation. In terms of the nucleation and growth during Te electrodeposition, two papers have been published by Vittori et al.[4] and Mori et al.[8]. Vittori et al. used an acid solution containing TeO_2 and HClO_4 and measured the current transients on glassy carbon and on gold. They compared their results with the electrocrystallization theory proposed by Hills [9] and reached the conclusion that the nucleation is progressive. Although they did not describe the growth of nuclei, it appeared that they expected 3-D growth under diffusion control as the growth regime. Mori et al. studied the nucleation and growth of Te on glassy carbon from $\text{TeO}_2/\text{H}_2\text{SO}_4$

solution. They concluded that the nucleation and growth is instantaneous nucleation/2-D growth under kinetic control. Thus, the two articles have deduced different nucleation and growth models and, therefore, it seems that reliable conclusion about the nucleation and growth of Te have not been reached yet. In addition, since our interest is CdTe electrodeposition, it was thought that the solution for CdTe deposition should be also used for studies of Te deposition. From these viewpoints, the nucleation and growth of Te have been investigated carefully from the same solution that was used for CdTe electrodeposition.

The solution used for the experiments described in this chapter is a typical solution for CdTe electrodeposition, shown in table 3.1 (a). For the purpose of avoiding cadmium co-deposition, relatively low deposition potentials were employed. The deposition regimes were determined initially from cyclic voltammetric studies. The current transient curves for Te electrodeposition were then measured by the double-potential step method. The nucleation and growth transients were compared with the forms predicted by the electrocrystallization theories described in chapter 2. Although these electrocrystallization theories have been derived for stationary electrodes, rotating disk electrodes were used for the experiments discussed in this chapter. The reason for the use of rotating electrodes is that electrodeposition of Te did not occur to any significant extent on a stationary electrode in the potential region. The effect of rotation was investigated with the hydrodynamically modulated rotating disk electrode.

4.2 Voltammetric studies.

Cyclic voltammetric studies were carried out to investigate the macroscopic CdTe electrodeposition behaviour and to determine the potential region where deposition of pure Te occurred. The first cycle of cyclic voltammograms was recorded to investigate deposition of CdTe on a fresh electrode surface. Figure 4.1 shows a cyclic voltammogram recorded for a glassy carbon rotating electrode (rotation rate = 2000 rpm, scan rate = $5\text{mV}\cdot\text{sec}^{-1}$, solution as shown in table 3.1(a)). The cyclic voltammogram is similar to the result reported by Mori et al. [8].

Four characteristic features were observed in the cyclic voltammogram. These peaks are discussed by reference to the thermodynamic data (potential-pH diagram) shown in figure 1.3.

(1) At about -220mV vs. SCE, a cathodic current wave was observed. According to the potential-pH diagram, CdTe deposition as well as Te deposition can occur at this potential. The mechanism of CdTe electrodeposition can be expressed by the reactions.



Kröger et al.[10] has proposed that the rate of CdTe formation is controlled by formation of Te. The reason was explained by the large Gibbs energy of CdTe formation from $\text{Te}(0)$ and $\text{Cd}(0)$ ($\Delta G_{298}^\circ = -107\text{kJ}\cdot\text{mol}^{-1}$). This means that pure Te deposition cannot occur from solutions containing Cd^{2+} and HTeO_2^+ . From this idea, Mori et al.[8] assumed that CdTe could be obtained at around -230mV vs. SCE and discussed their results as electrodeposition of CdTe. However, it is not certain that Cd deposition on Te occurs

close to the thermodynamic deposition potential, though it is obvious that reaction (4.4) occurs at the potential.

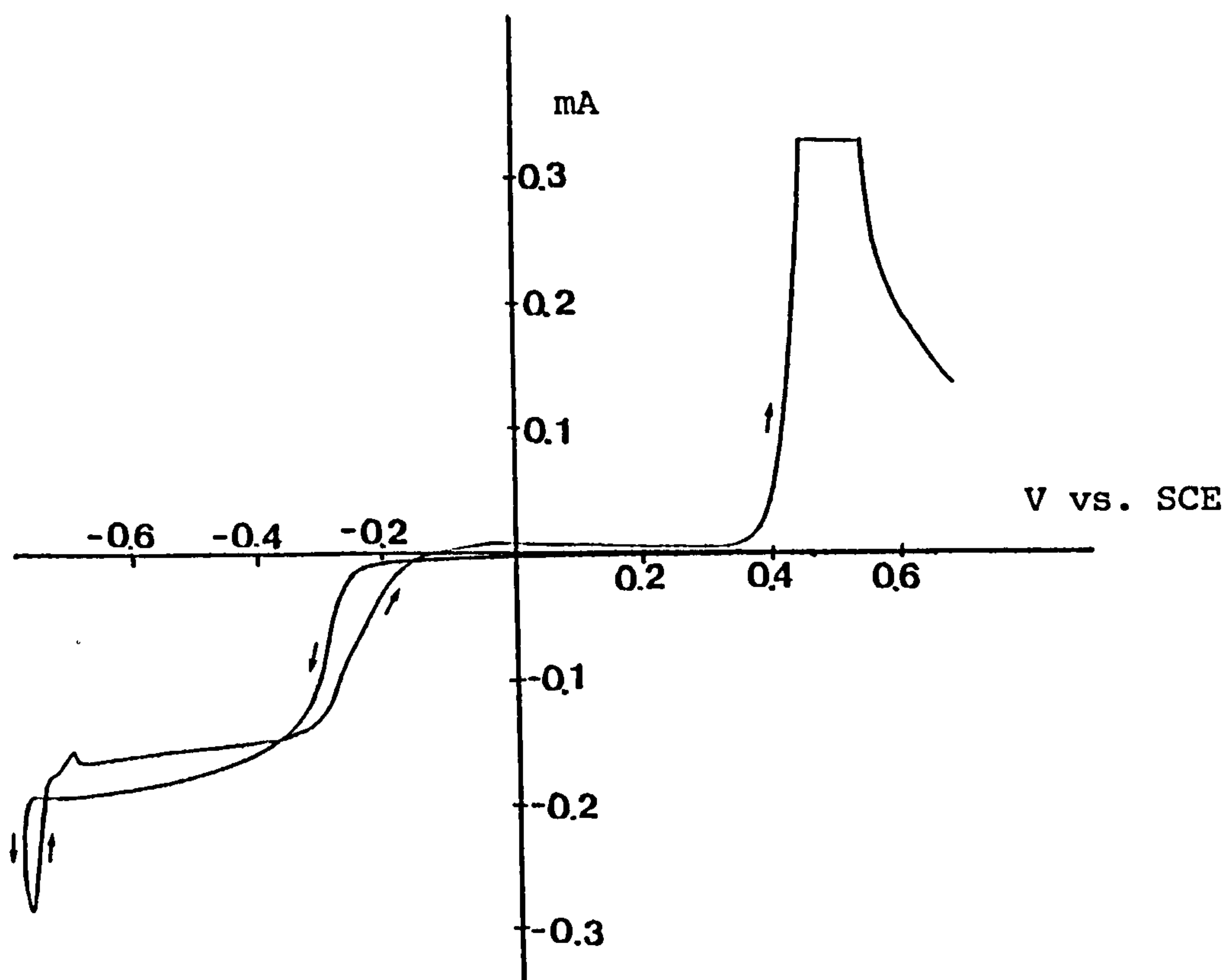


Figure 4.1 Cyclic voltammogram of a glassy carbon disk electrode in $\text{TeO}_2 + \text{CdSO}_4 + \text{Na}_2\text{SO}_4$ solution shown in Table 3.1(a).
Scan rate = 5mv / sec,
Rotation rate = 2000 rpm.

Further experiments were carried out to clarify whether CdTe or Te deposition takes place in this potential region. These results are discussed at the last part of this section. It should be noticed that the deposition of Te on glassy carbon needs a large overpotential (the deposition potential expected from thermodynamic data is +266 mv vs. SCE at pH 1.5, $[\text{HTeO}_2^+] = 2 \times 10^{-4}\text{M}$). The large overpotential is observed on platinum [11] and on indium-tin oxide coated glass [12] as well as on glassy carbon. The reduction mechanism of metal oxides such as TeO_2 is usually very complicated and the reduction consists of several single steps. Since a large overpotential was also observed on platinum, it seems unlikely that the overpotential is due to the poor electrocatalysis of glassy carbon for the reduction of HTeO_2^+ .

(2) A cathodic peak was observed at -700mV. This peak is attributed to pure Cd deposition. Just before the pure Cd deposition peak, the current reaches a constant value. In this potential region, the CdTe deposition rate is controlled by the diffusion of deposition species (the current is proportional to the square root of the rotation rate). Since the concentration of HTeO_2^+ is 100 times smaller than that of Cd^{2+} , it is expected that the deposition rate is determined by HTeO_2^+ diffusion.

(3) The stripping peak of pure Cd was observed at -680mV on the anodic sweep. The stripping charge was much smaller than the deposition charge. This probably indicates that pure Cd was partly covered with a CdTe film before the stripping.

(4) Stripping of all deposits occurred at +400mV. The stripping charge and the cathodic charge observed at the potential range between -200mV and -700mV were measured and it was found that the cathodic charge was nearly equal to the stripping charge. This suggests that hydrogen evolution scarcely occurred. According to thermodynamic data (see figure 1.3), the potential of H₂Te formation by reduction of Te is approximately -0.95 V vs. SCE (this value was calculated with [H₂Te] = 10⁻⁴ M, pH 1.5). Traore et al.[5] and Dennison et al.[6] observed the formation of H₂Te at -700mV vs. SCE and -800mV vs. Ag/AgCl, respectively. If H₂Te is formed, a new route for Te deposition should be considered (reaction (4.6)) and this makes the deposition mechanism complicated.



Fortunately, the formation potential of H₂Te can be expected to be equal to or more negative than that of pure Cd deposition. Therefore, as the deposition route, just reactions (4.4) and (4.5) are considered below.

Although there is no doubt that CdTe deposition occurs just before pure Cd deposition, it is not clear whether CdTe deposition can occur in the more positive potential region. For the purpose of making the electrodeposition behaviour clear, steady-state currents were measured over the potential region -500 to -60mV. The measurement was carried out from -500mV in steps of 25mV or 10mV. The interval to obtain the steady-current at each potential was 2 minutes to 15 minutes. The rotation rate was 2000 rpm. Figure 4.2 shows this result.

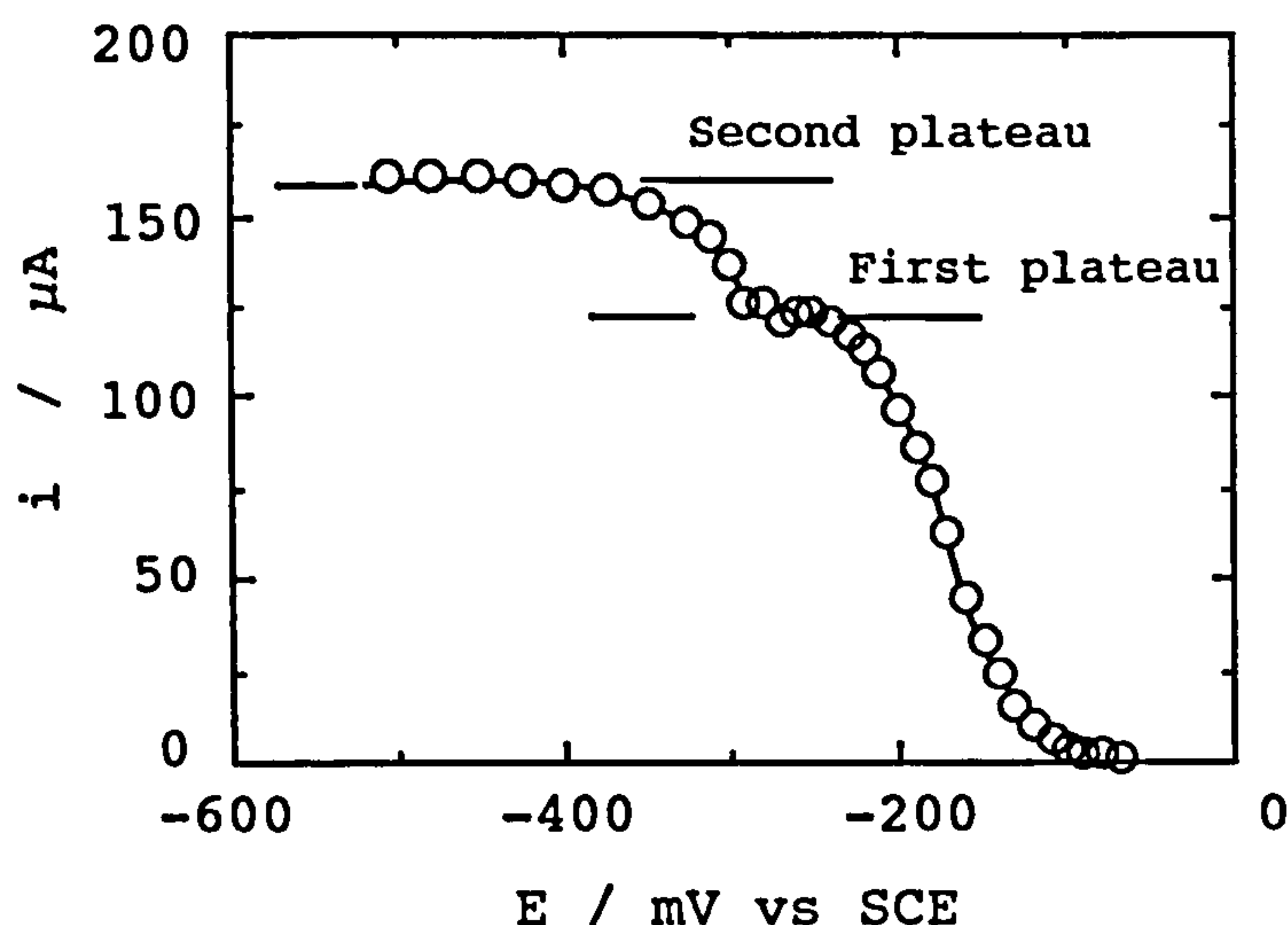


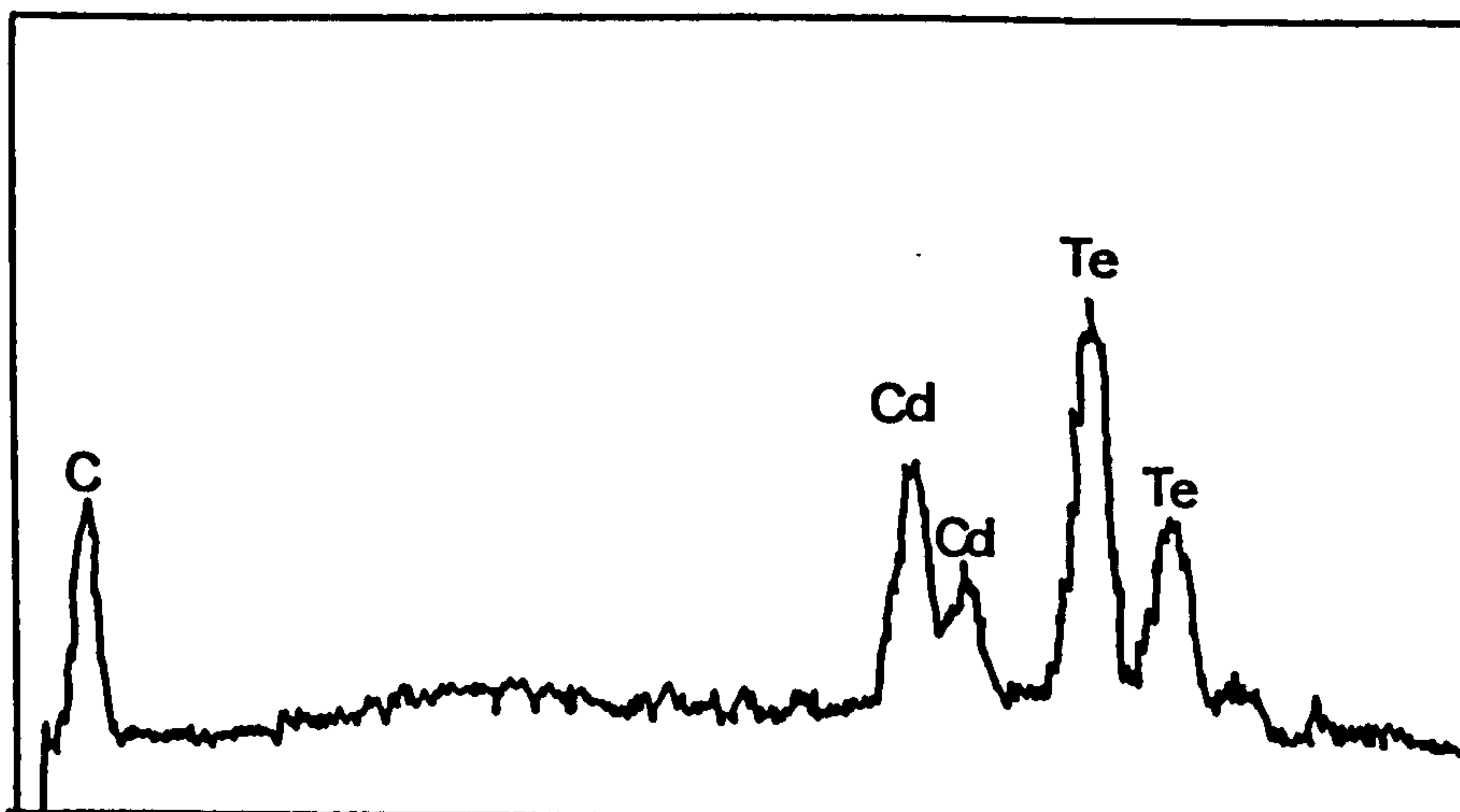
Figure 4.2 Steady-state polarization curve measured in $\text{TeO}_2 + \text{CdSO}_4 + \text{Na}_2\text{SO}_4$ solution shown in Table 3.1(a).
Rotation rate = 2000 rpm

Two plateau currents were observed clearly. The first plateau and the second plateau are shown over the potential ranges of -250 to -280mV and -400 to -500mV, respectively. The two plateau currents suggest the existence of two kinds of diffusion controlled deposition. The ratio of plateau currents suggests that (1) at the first plateau potential or at more positive potentials than the first plateau, pure tellurium deposits. At the first plateau potential, Te deposition is controlled by diffusion of HTeO_2^+ . (2) the percentage of Cd in deposits increases as the deposition potential is shifted to negative values and (3) finally, the

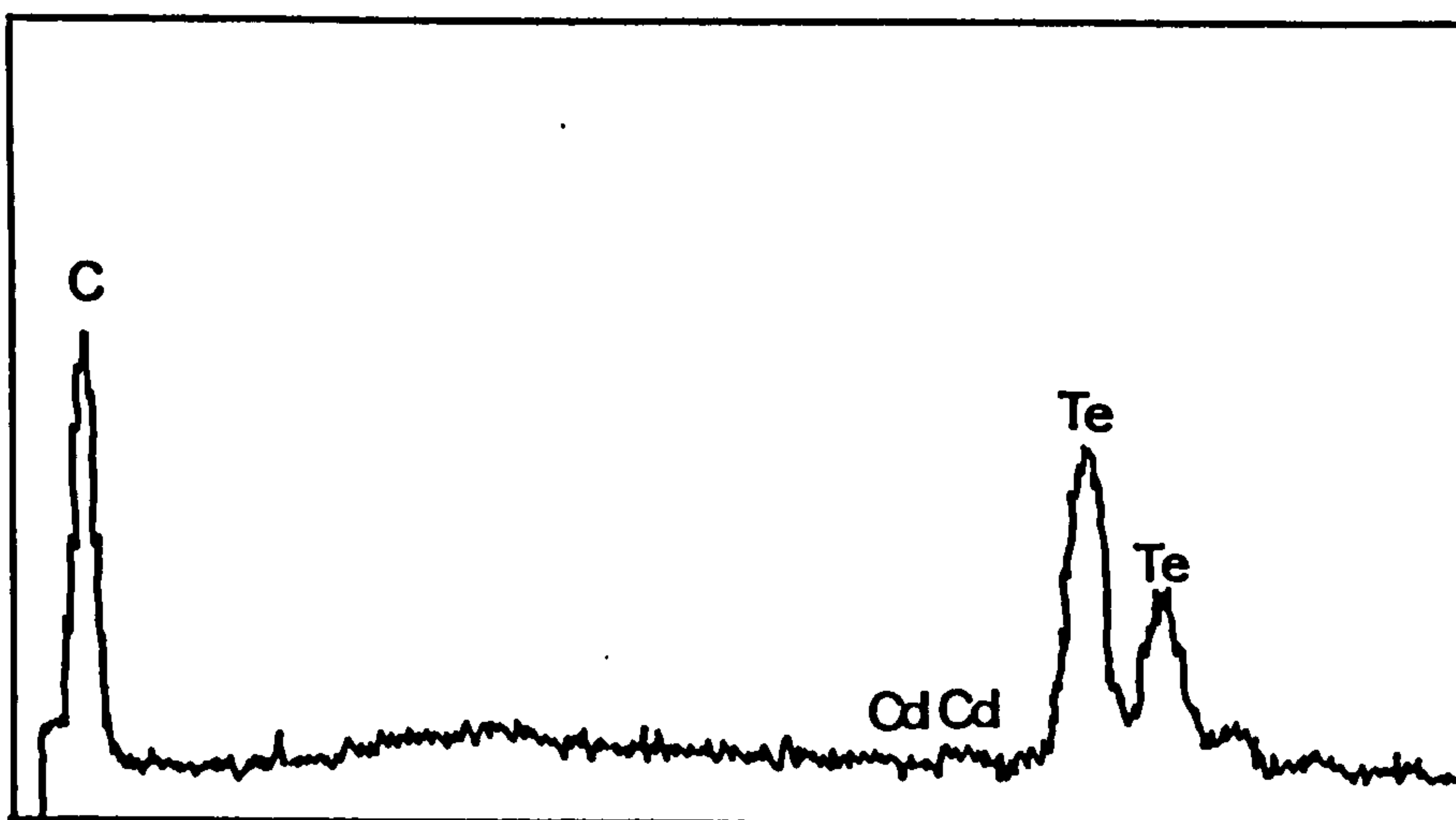
ratio of Cd to Te in deposits reaches a constant value at approximately -400mV.

In order to make sure that pure Te deposits at the first plateau region, the deposit obtained at -250mV (1st plateau) was analysed by EDAX. Figure 4.3 (a) shows the result. As expected from the polarization curve, the deposit obtained at the first plateau did not contain Cd. Figure 4.3 (b) shows the analytical result of the deposit obtained at -500mV. The deposit obtained at the second plateau potential consisted of Te and Cd. According to the quantitative analysis of EDAX, the ratio of Cd to Te was 40:60 approximately. Thus, it was confirmed that pure tellurium deposits at the first plateau potential or at more positive potential. In addition, it was found that Cd content increases with the negative change of potential and the value reaches about 40%.

As the electron number of CdTe deposition is 6 (Reactions 4.4 and 4.5) and that of Te deposition is 4 (Reaction 4.4), the limiting current of CdTe deposition should be 1.5 times bigger than pure Te deposition. However, since the atomic ratio of Cd to Te obtained by EDAX is 4/6, the ratio of the second plateau current to the first plateau current should be 1.33. Figure 4.2 shows that the ratio (current at the second plateau / current at the first plateau) obtained experimentally is 1.33, and therefore it is suggested that the ratio of two diffusion limited currents is equivalent to the ratio expected from the quantitative analysis of the deposits.



(a) Deposition potential = -500mV vs.SCE



(b) Deposition potential = -250mV vs.SCE

Figure 4.3 Analysis of deposits on a glassy carbon rotating disk electrode (2000 rpm) by EDAX.
The deposits were covered with vapour deposited carbon to prevent an occurrence of halation.

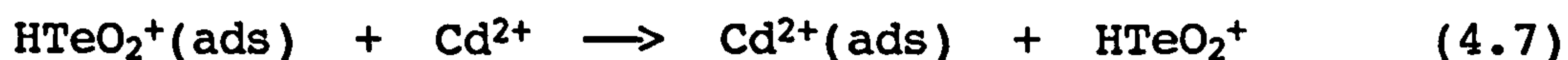
As the result of these investigations, it can be concluded that there are three stages in the electrodeposition process.

- (1) At more positive potentials than -280mV , a pure Te deposit can be obtained. In the first plateau potential region, the deposition occurs under diffusion control.
- (2) As the deposition potential is shifted to more negative values, the Cd content in the deposits increases.
- (3) At more negative potentials than -400mV , a CdTe film containing some excess Te (the atomic ratio of Cd/Te is 4/6) can be obtained. The ratio of Cd to Te in deposits seems to be determined by the competition between deposition of Cd ions on Te atoms and of Te ions on Te atoms.

4.3 Nucleation studies.

Pure Te deposition from acid HTeO_2^+ solution containing no Cd^{2+} has been studied by Dennison et al.[6]. They reported that dendritic Te deposits were produced. In order to investigate the effect of Cd^{2+} on the morphology of the Te deposit, the deposition with solutions having no cadmium as well as those having cadmium were carried out. The solution containing no cadmium was adjusted to the composition shown in table 3.1 (a) except that CdSO_4 was absent. The deposit obtained from the electrolyte without Cd^{2+} showed a black colour and the surface appeared to be very rough. On the other hand, Te obtained from the electrolyte with Cd^{2+} showed a silver-grey colour and had a semi-bright surface. This difference indicates that Cd^{2+} ions play an important role in the Te deposition process. Since a semi-bright surface can be obtained by addition of Cd^{2+} ions, Cd^{2+} ions can be considered to work as a so-called levelling agent. The levelling mechanism is described in some general remarks

[e.g. 13]. One of the most important processes for levelling is adsorption of reagents on the electrode surface. Sella et al.[14] hinted at the possibility of Cd^{2+} adsorption on the electrode surface to explain that a HTeO_2^+ adsorption peak on cyclic voltammograms disappears with the addition of Cd^{2+} into the electrolyte. Reactions (4.7) and (4.8) describe the Te deposition mechanism proposed by Sella et al.. Namely, by the addition of Cd^{2+} into the electrolyte, adsorbed HTeO_2^+ is displaced by Cd^{2+} (reaction 4.7) and then the deposition of Te occurs (reaction 4.8).



Thus, since Cd^{2+} is considered to have a considerable effect on Te deposition, it can be expected that studies of Te deposition from solution containing HTeO_2^+ and Cd^{2+} are useful to understand CdTe deposition.

4.3.1 Nucleation and growth model.

A series of potential step experiments was conducted and the current transient curves were monitored. To avoid the overlap between deposition current and electrode charging current, current transient curves were measured by a double potential step method. The potential step diagram is shown in figure 4.4.

Figure 4.5 shows the typical current transient curves which were measured at different potentials. In all experiments, the rotation rate was 2000 rpm. Large 'charging' currents were observed just after the potential step.

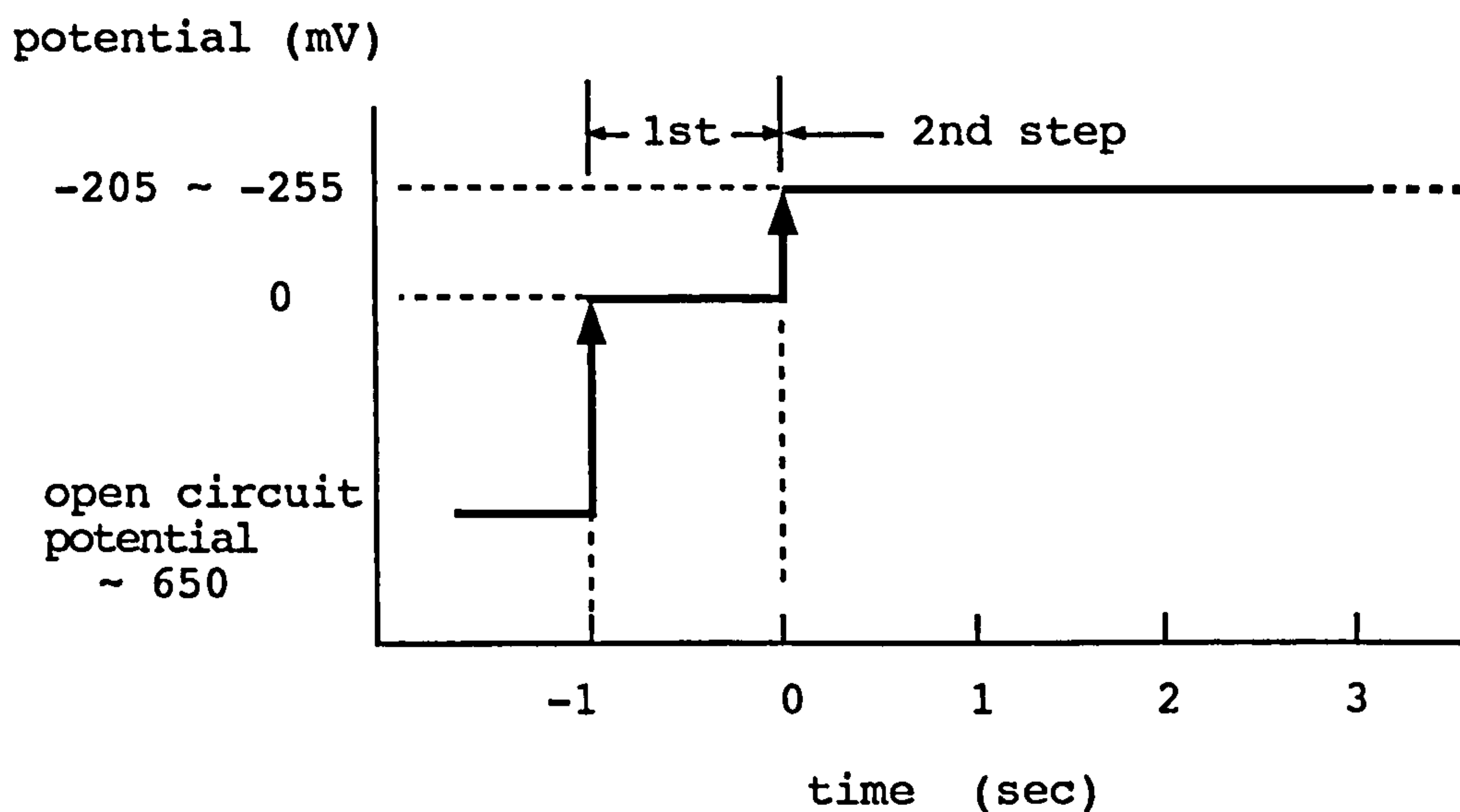


Figure 4.4 Wave form of double potential step employed for current transient measurements.

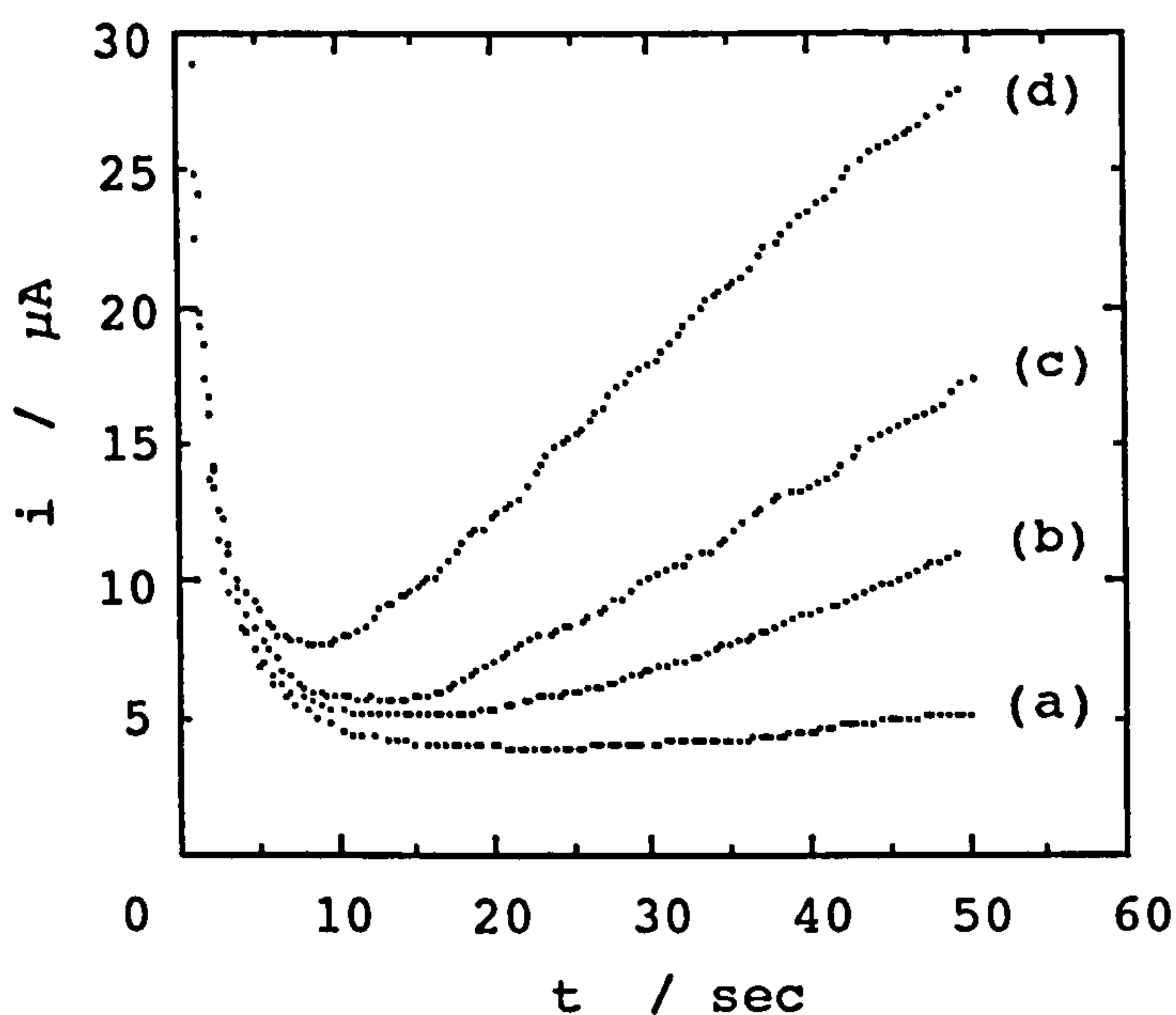


Figure 4.5 Typical current transient curves for Te deposition on a glassy carbon rotating disk electrode (2000 rpm) (a) at -205, (b) at -220, (c) at -230 and (d) at -240mV vs. SCE.

In general, since charging the double layer should require only a few milliseconds, the spike observed in the experiments is not a pure double layer charging current. From these curves, the charge of the spike was measured and found to be approximately 1.2mC/cm^2 . The charge required for formation of a Te monolayer on the electrode surface was derived by assuming that the Te-Te distance is $2.64\text{\AA}$ and that the monolayer deposits as a hexagonal closed lattice on the electrode surface. This theoretical value (1.06mC/cm^2) is almost equal to the charge obtained experimentally. Consequently, it is possible that the current spikes correspond to the deposition of a Te monolayer. (For further discussion of the large current spike, see Appendix 4.I)

After an induction time (t_0), the current increases showing that nuclei are formed and that they grow with deposition time. As shown in table 2.1, the relationships between current and deposition time are given by the general form.

$$i(t) = k \cdot t^n \quad (4.9)$$

where k is a constant and n is given a particular value for each nucleation system shown in table 2.1 (see initial transients in table 2.1). This relationship is valid in the short-time regime (i.e., in the absence of significant overlap of nuclei or diffusion zones). The current transients as functions of t^n were plotted using different values of n (0.5, 1, 1.5, 2 and 3). For these tests, $(t-t_0)$ was used instead of t , because $(t-t_0)$ shows the real deposition time. t_0 is referred to as induction time and is considered in this chapter as the time when the minimum current is observed. Discussion about methods to obtain t_0 is made in section 5.3.1. As the result of the analysis, it can be shown that the best fit of the transients is given as

a function of $(t-t_0)^{1.5}$. Figure 4.6 shows the $i-(t-t_0)^{1.5}$ plots. The good fit to the experimental data implies that deposition takes place by progressive nucleation and three dimensional diffusion controlled growth.

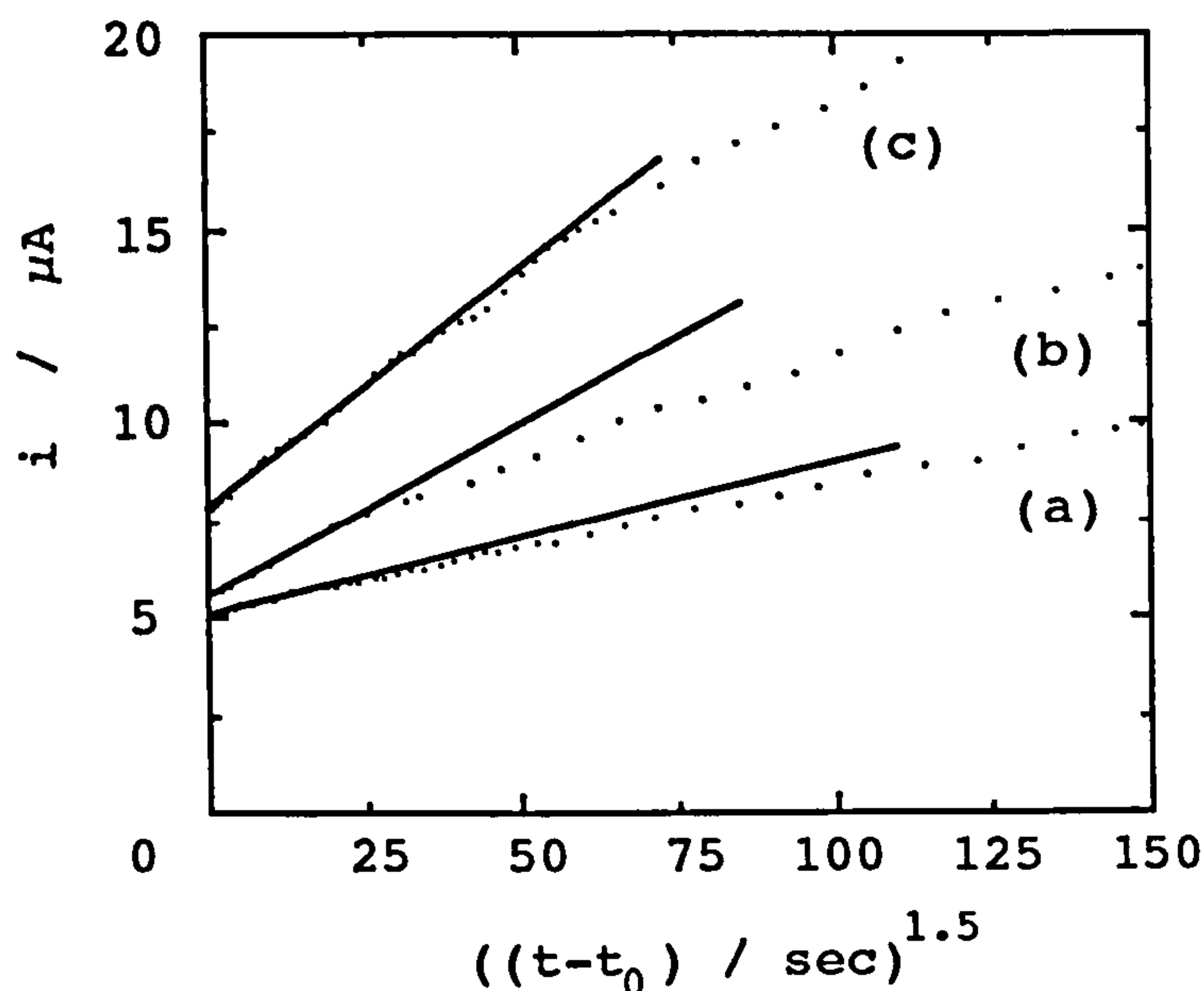


Figure 4.6 $i-(t-t_0)^{1.5}$ plots of current transient curves shown in figure 4.5.
(a) -220, (b) -230 and (c) -240mV vs. SCE.

This conclusion supports the analysis given by Vittori et al.[5]. However, as described in section 4.1, Mori et al. reported [8] that the nucleation and the growth for Te deposition on glassy carbon occurs by instantaneous nucleation and two dimensional growth under kinetic control. The conclusion was obtained from the result that the current is linearly proportional to the deposition time. However, the authors also show that, at longer times, the deposition current is proportional to $t^{-0.5}$, indicating a diffusion

controlled reaction. This result is obviously in contradiction to the conclusion obtained for initial transients. From the apparent Cottrell relation, it should be considered that the growth is controlled by diffusion. This contradiction, therefore, may be due to the analysis of the initial current transient curves. Mori et al. regarded background currents of their transient curves as constant values and showed that $i - t^1$ plots had good linearity. However, it can be expected that, from their transient curves, the background currents decay with the time. If the background currents decay with time, the value of n in equation (4.9) should be bigger than 1 suggesting a different nucleation/growth mechanism from their conclusion. In the case of progressive nucleation / 3-D growth under diffusion control, the value of n is 1.5 and, at long times, the current obeys the Cottrell relation. Therefore, it seems that the nucleation and growth model is more likely to be progressive nucleation / 3-D growth under diffusion control than instantaneous nucleation / 2-D growth under kinetic control. In the results obtained here, the background currents in the transients obtained at -205 and -220mV (figure 4.5 (a) and (b)) can be considered to be almost constant and the linear $i - t^{1.5}$ relations are confirmed by the transients. Although the transients measured at higher overpotentials show that background currents decay, it is considered the nucleation and growth model does not change from progressive nucleation / diffusion controlled three dimensional growth to others (especially to kinetic control as reported by Mori et al.) by slight increase in overpotential.

4.3.2 Hydrodynamically modulated rotating disk electrode (HMRDE) studies.

In the current transient experiments, the rotating disk electrode was used, although the theories for electrocrystallization have been derived for stationary electrode systems. The reason for the use of rotating electrodes is that the current transient curves could not be obtained on a stationary electrode in the potential region employed (the details are shown in 4.3.3.). Theoretically, electrode rotation only influences the linear diffusion regime. As the initial 3-D growth theory under diffusion control is obtained by assuming that hemispherical diffusion zones are formed around the nuclei, there should be no effect of the linear diffusion regime (i.e. no effect of electrode rotation) on the current transients, while the currents have linear relations with $(t-t_0)^{1.5}$.

In order to make sure that the linear diffusion regime has no effect on the current transients while the linear relation between i and $(t-t_0)^{1.5}$ can be obtained, the hydrodynamically modulated rotating electrode (HMRDE) was used [15~18].

Theory of HMRDE.

This technique can distinguish diffusion currents from kinetically controlled currents. This feature is sometimes used to analyse ions at submicromolar concentration level, even in the presence of large kinetically controlled currents [16].

When an electrochemical reaction takes place under diffusion control, the limiting current density can be expressed as a function of rotation rate, ω .

$$j_{lim} = 0.62nFD^{2/3}\omega^{1/2}\nu^{-1/6} \cdot (C_b - C_s) \quad (4.10)$$

Here ν is the kinematic viscosity, C_b and C_s are the bulk and surface concentration of material controlling the current. When the reaction rate is controlled completely by diffusion ($C_s = 0$), expression (4.10) becomes the well-known Levich equation. For the HMRDE, a sinusoidal modulated rotation rate, $\Delta\omega^{1/2} \cdot \sin(\delta t)$, is added to the constant rotation rate, $\omega_0^{1/2}$. The modulation of the rotation rate is given by

$$\omega^{1/2} = \omega_0^{1/2}(1 + \Delta\omega^{1/2}/\omega_0^{1/2} \cdot \sin(\delta t)) \quad (4.11)$$

where δ is the radial frequency (if the modulation frequency is 3Hz, δ is 6π). The value of $\Delta\omega$ is typically about 1% of ω_0 . By substituting equation (4.11) into (4.10), the current associated with the modulation of rotation rate is expressed as

$$\Delta i(t) = 0.62nFAD^{2/3}\nu^{-1/6} \cdot (C_b - C_s) \cdot \Delta\omega^{1/2} \cdot \sin(\delta t) \quad (4.12)$$

If a reaction occurs under complete kinetic control, modulation of current associated with $\Delta\omega$ is not observed because the bulk concentration is equal to the surface concentration ($C_b - C_s = 0$). If the reaction has an influence of diffusion ($C_b - C_s \neq 0$), the modulation of current can be observed. Therefore, the existence of $\Delta i(t)$ proves that the planar diffusion of reactance to electrode surface influences the current. The amplitude of $\Delta i(t)$, $\Delta\omega$ and the average current (i_{ω_0}) are defined as shown in figure 4.7.

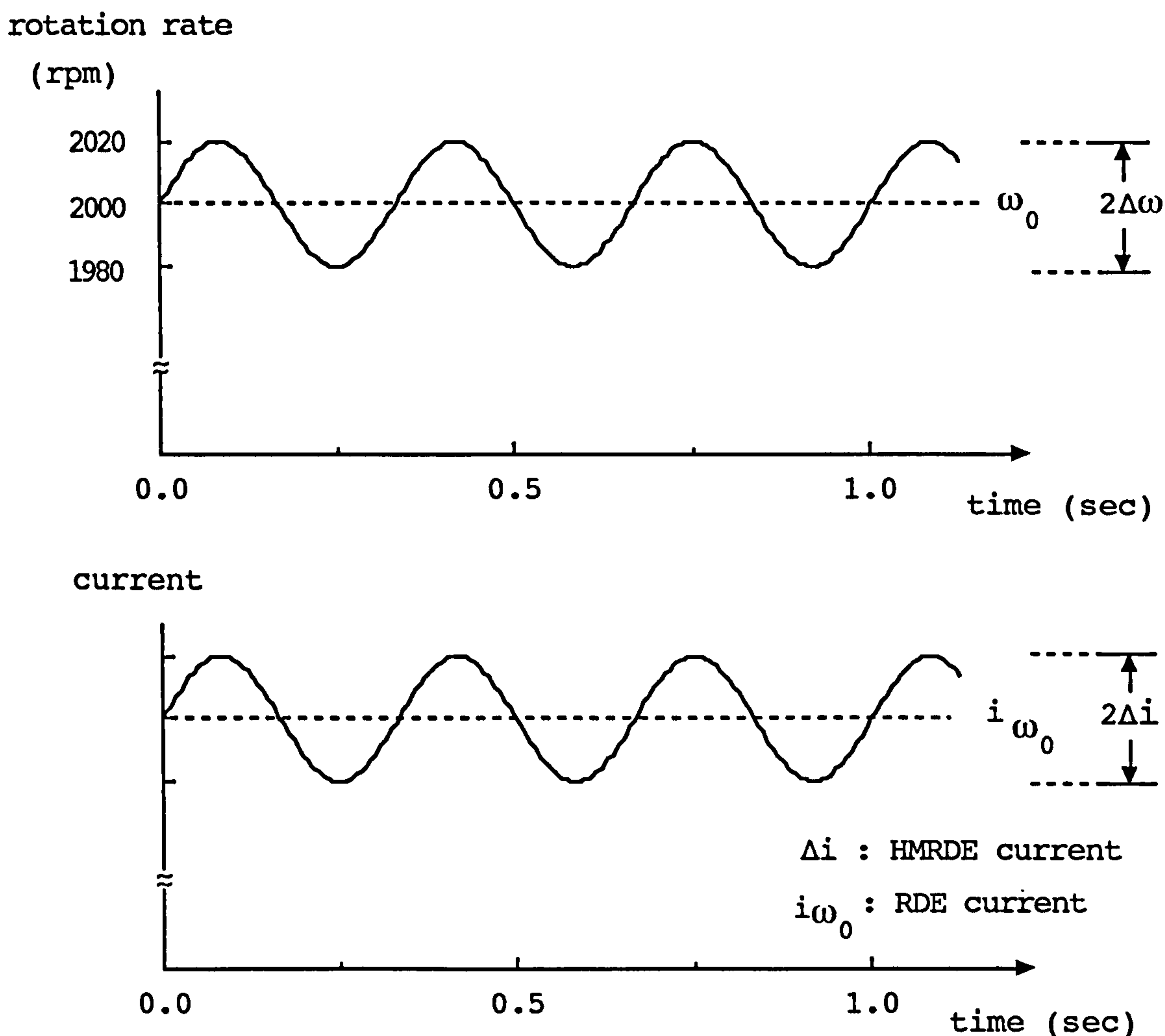


Figure 4.7 Representation of $\Delta\omega$ and Δi for a sinusoidal HMRDE. The conditions of HMRDE experiments are also described in this figure.

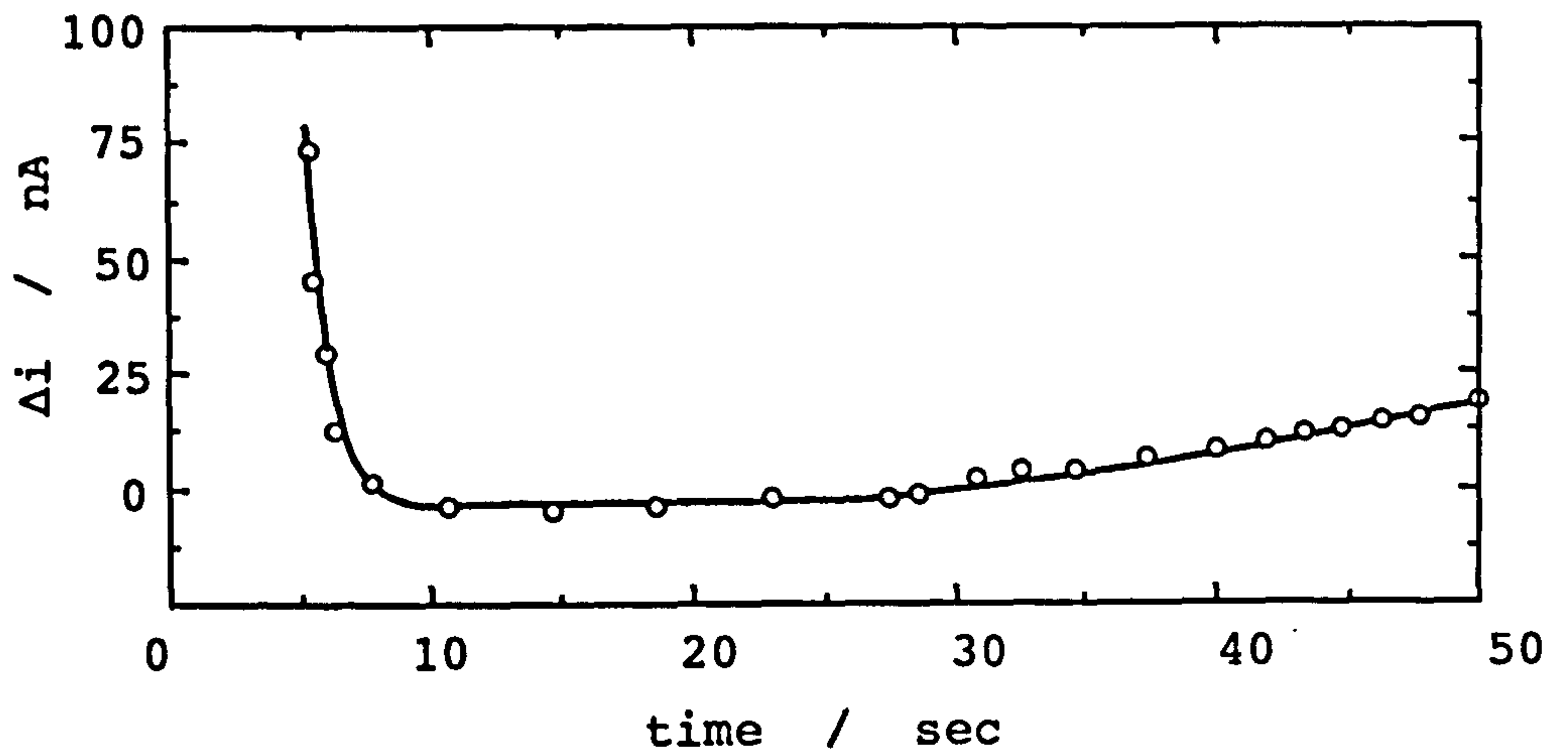
Results of HMRDE experiments.

If there is an influence of electrode rotation (i.e., influence of linear diffusion) on current transients, the deposition current should exhibit a small modulation synchronous with the rotation modulation. The small modulation of current was measured by a lock-in amplifier.

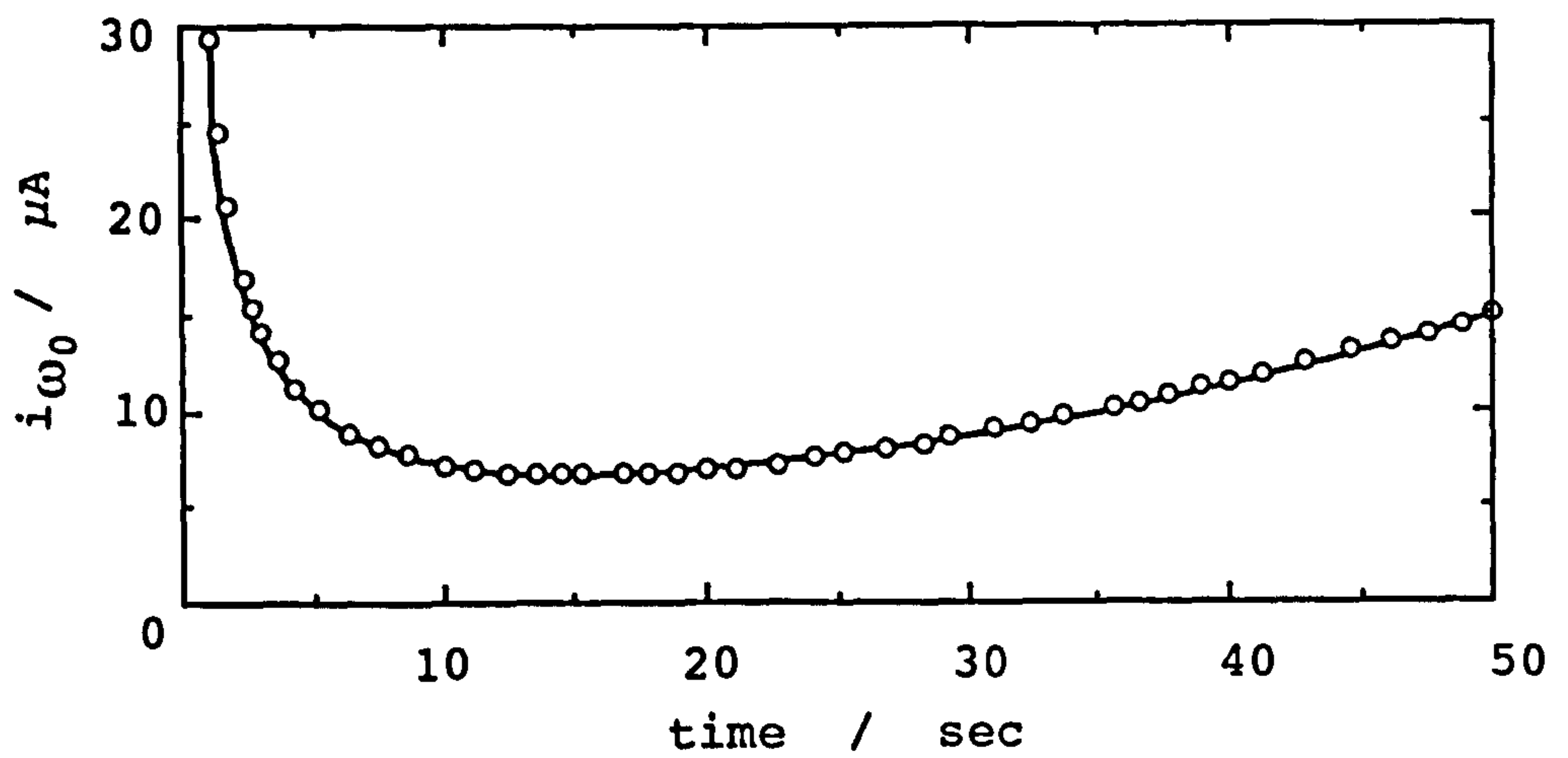
The experimental conditions employed are shown in figure 4.7.

The HMRDE and the RDE current transients are shown in figure 4.8. The deposition potential for this experiment was -220mV. Figure 4.8(b) shows that large current flows in the initial transient, probably indicating monolayer deposition of Te as described in section 4.3.1. Since a large HMRDE current is obtained at the same time when a large RDE current is observed, it suggests that the current is controlled by diffusion. i.e. diffusion of HTeO_2^+ . The diffusion controlled Te deposition is discussed in Appendix 4.I. As shown in figure 4.8 (b), after the large current spike, the HMRDE current was zero for the initial 27sec, and then it increased gradually. This suggests that the nucleation current shows no influence of linear diffusion in the 27sec and that, therefore, electrocrystallization theories can be applied for the period. The analysis of $(i\omega_0)-t$ shown in figure 4.8(b) was carried out with special emphasis on the data obtained up to 27sec. Figure 4.9 shows the analytical result of the relationship between the RDE current and the deposition time. Here, the induction time (t_0) was 16 sec. The $i - (t-t_0)^{1.5}$ plot showed excellent linearity in $(t-t_0)^{1.5} < 42$, i.e., $t < \sim 27\text{sec}$.

Consequently, the result of HMRDE experiments suggests that electrocrystallization theories can be applied and that the nucleation and the growth follows the progressive nucleation / 3-D growth model under hemispherical diffusion control.



(a) HMRDE current transient ($\Delta i - t$ curve).



(b) RDE current transient ($i_{\omega_0} - t$ curve).

Figure 4.8 RDE and HMRDE current transient curves for the deposition of tellurium. The experimental conditions were shown in Figure 4.7. Deposition potential = -220mV vs. SCE.

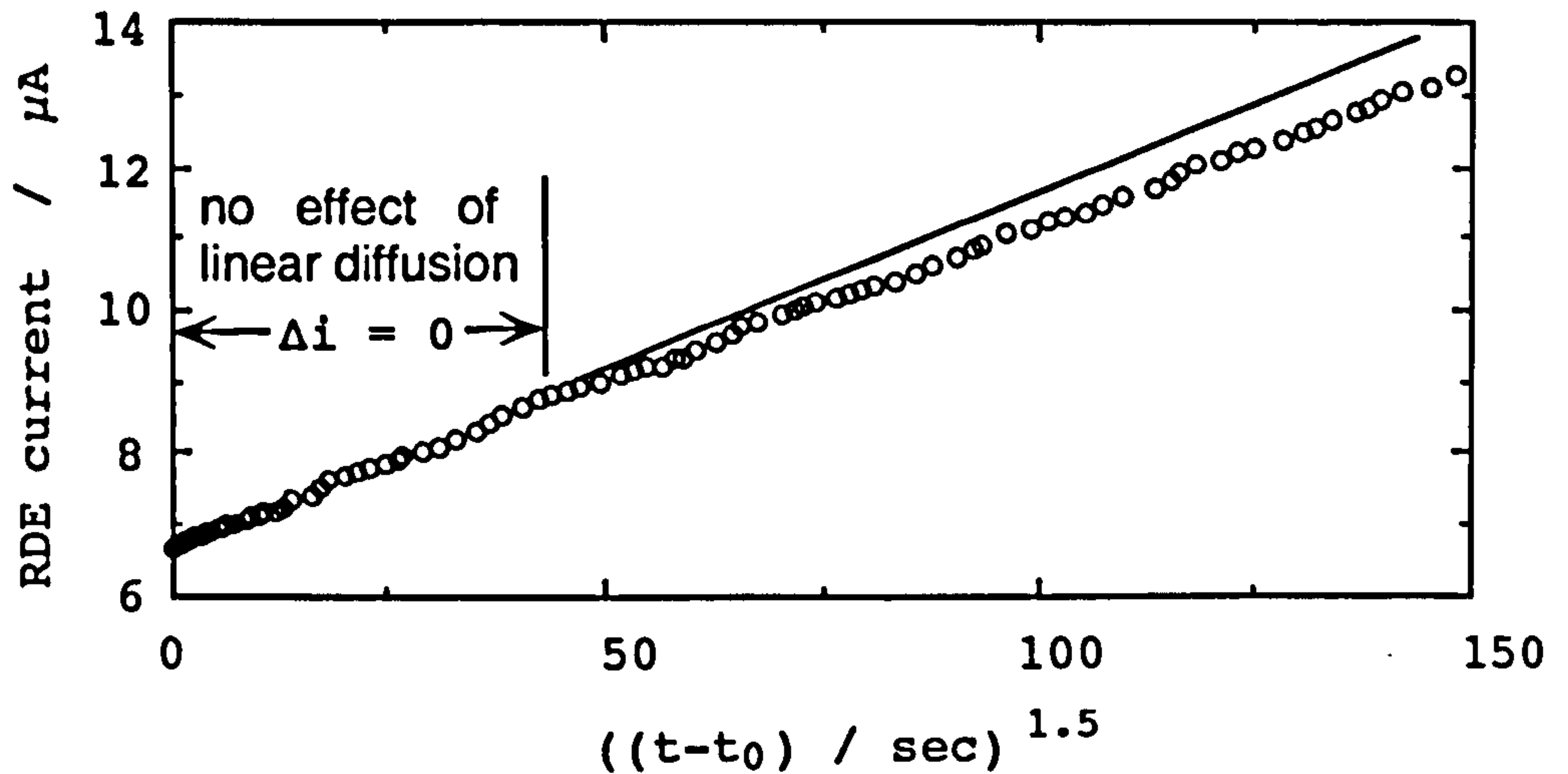


Figure 4.9 $i-(t-t_0)^{1.5}$ plot for the transient shown in Figure 4.8(b). The effect of linear diffusion on the nucleation current was investigated by HMRDE. The region where there was no effect of linear diffusion is shown in this figure. Deposition potential = -220mV vs. SCE.

4.3.3 Nucleation rates.

As described in chapter 2, the initial relationship between deposition current density and deposition time for progressive nucleation and hemispherical growth under diffusion control is given by

$$j(t) = \frac{2nF\pi AN_0(2DC_b)^{3/2}M^{1/2}}{3\rho^{1/2}} \cdot t^{3/2} \quad (4.13)$$

AN_0 has the units of $\text{cm}^{-2} \cdot \text{sec}^{-1}$ and corresponds to the number of nuclei formed per second and is referred to as the nucleation rate. The nucleation rate can be obtained from

equation (4.13). For Te deposition, n , ρ , M and C_b are 4, 6.24g/cm³, 127.6 and 2x10⁻⁷mol/cm³, respectively. The diffusion coefficient for HTeO₂⁺ was obtained from a Levich plot. Since the diffusion plateau for HTeO₂⁺ was narrow (see figure 4.2) and the plateau potential shifted with the rotation rate, currents at the second plateau were measured. The currents correspond to deposition current of Te rich CdTe controlled by diffusion of HTeO₂⁺. The limiting deposition currents were measured at various rotation rates, while the potential was kept at -500mV. The Levich plot is shown in figure 4.10.

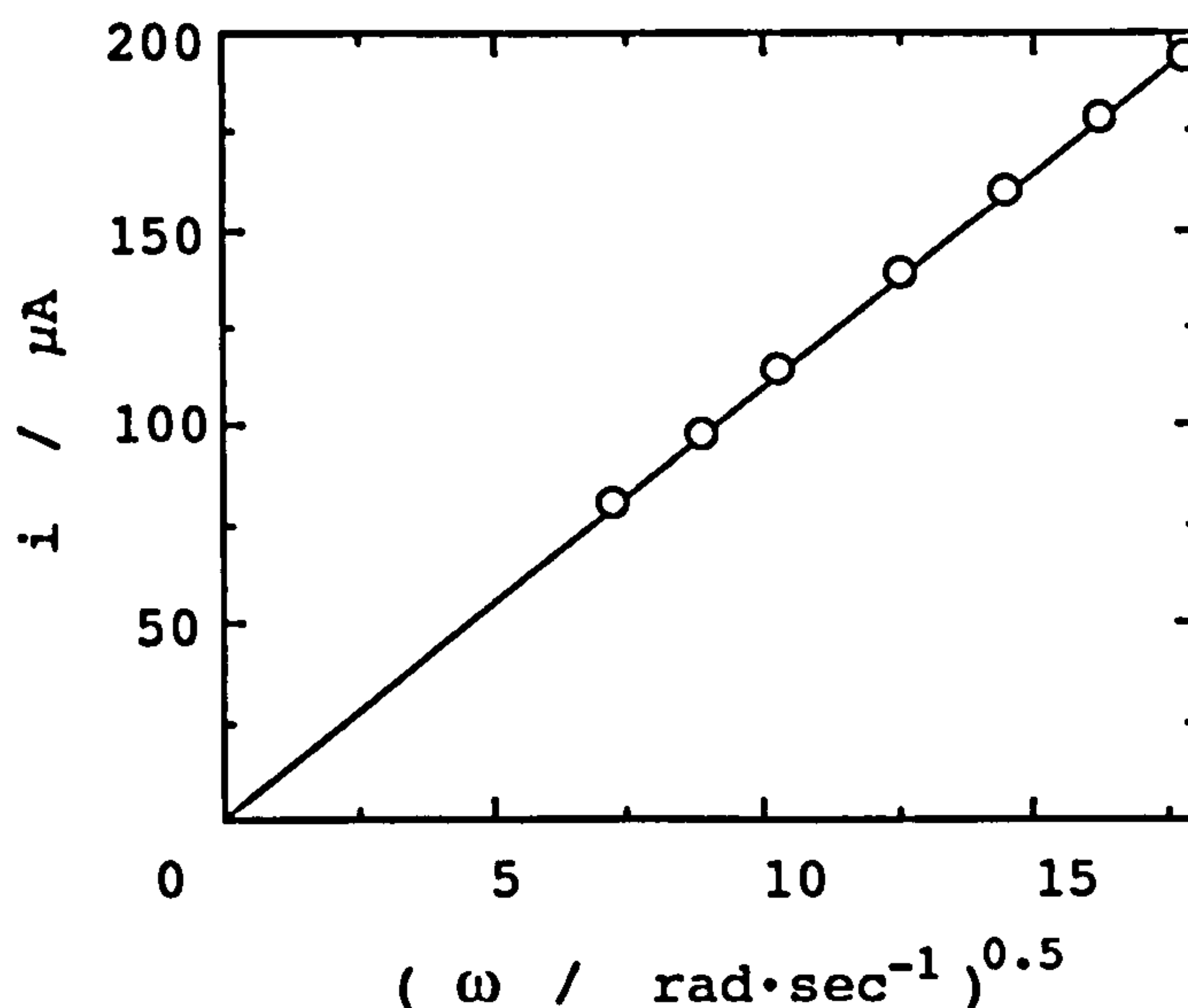


Figure 4.10 Levich plot for CdTe deposition at -500mV vs. SCE. The deposition rates were determined by diffusion of HTeO₂⁺ ions.

The relationship between current and time shows a good linearity, indicating that the current is controlled by diffusion. From the Levich plot of CdTe (Cd:Te = 0.4:0.6) deposition, the diffusion coefficient for HTeO_2^+ was found to be $5.6 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$. We have also obtained the diffusion coefficient for HTeO_2^+ from the Cottrell plots and the value was $5.3 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ (see chapter 5). Some values of diffusion coefficient for HTeO_2^+ have been reported. Dennison et al.[6] and Mishra et al.[19] have obtained 5.1×10^{-6} , $7.2 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ respectively from the Levich equation. Although Mori et al.[3] have derived $1.14 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ from the Cottrell equation, the diffusion coefficient obtained here can be regarded as a reasonable value. (Sella et al.[14] have reported $2 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ as the diffusion coefficient. However, when the authors obtained the diffusion coefficient, they left out dividing the value by $(2\pi)^{1/2}$. Therefore the corrected value obtained from their experiment is $8.0 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$.)

With the slopes of $i-(t-t_0)^{1.5}$ plots, the nucleation rates were calculated from equation (4.13). As the result of the calculation, for instance, the nucleation rates at -220mV and -250mV are 1.6×10^4 and $6.9 \times 10^4 \text{ cm}^{-2} \cdot \text{s}^{-1}$, respectively. The variation of these rates (AN_0) as a function of the deposition potential is shown in figure 4.11. It can be shown that there is an excellent linear relationship between the logarithm of nucleation rate and the deposition potential with a slope of 30mV/decade. Two nucleation theories are presented in chapter 2. These theories are referred to as the classical nucleation theory and the atomistic theory. In the classical theory, macroscopic physical quantities are used to characterize the critical nuclei. On the other hand, the atomistic theory characterizes the critical nuclei through the energy of

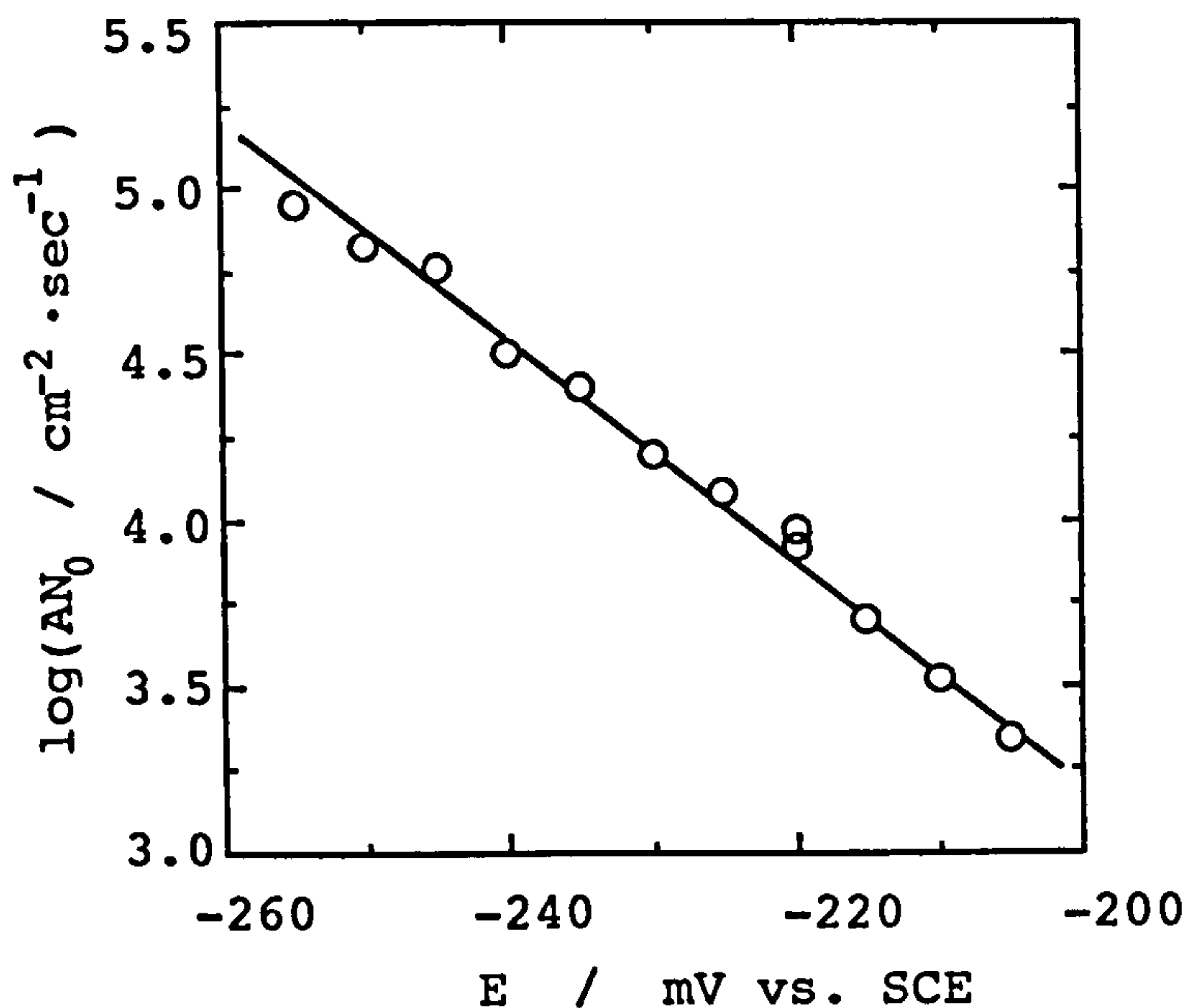


Figure 4.11 Nucleation rates for Te deposition on a glassy carbon electrode as a function of deposition potential.
Rotation rate = 2000 rpm.

interaction between their building elements. In the case of electrocrystallization, the classical and the atomistic theories predict that τ is proportional to $\exp(-1/\eta^2)$ and to $\exp(\eta)$ respectively, where τ is the steady-state nucleation rate and η is the overpotential (see equations 2.25 and 2.38). Milchev et al.[20] reported that, in general the behaviour of $\ln(\tau) - \eta$ will be similar to that shown in figure 2.6. Thus, the interval corresponding to the smooth part of the curve (low overpotential region) gives the range of validity of the classical theory and the interval corresponding to the straight lines (high overpotential

region) represents the range of validity of the atomistic theory.

As shown in figure 4.11, an excellent linear relationship between the logarithm of nucleation rates and deposition potential was obtained. If the nucleation rates obtained are regarded as steady state nucleation rates, the result suggests that the atomistic theory is valid in the potential region employed for the experiments. If the equilibrium potential of Te deposition is given by the foot of the steady-state polarization curve shown in figure 4.2, its value is approximately -80mV vs. SCE. However, this value is different from the equilibrium potential (+196mV vs. SCE) predicted by thermodynamic data. This big difference could be explained by existence of a single step which requires high activation energy. Since the overpotential employed for the experiments must be larger than 100mV, it can be inferred that the overpotential range is beyond the range of validity of the classical theory and, hence the atomistic theory is valid for this case.

According to the atomistic theory, the number of atoms in a critical nucleus, n_k is given by

$$n_k = \frac{kT}{ze} \cdot \frac{\ln(\tau_{st})}{\eta} - (1-\alpha) \quad (4.14)$$

where k is the Boltzmann constant, z is the electron number of rate determining step, e is the elementary electric charge and α is the transition (or transfer) coefficient. From equation (4.14), a value of n_k can be obtained. The value of z was assumed to be 1 (associated with a 1 electron rate determining step). By substituting the slope obtained from figure 4.11 into $\ln(\tau_{st})/\eta$, 0.5 for α and 1 for z , it was found that the number of atoms in the critical nuclei is approximately 2. The result, $n_k = 2$, means that 3 atoms

adsorbed on an active site of the substrate can be considered as a stable "cluster" which could grow spontaneously at the supersaturation region. Such a small value of n_k is consistent with the application of the atomistic theory.

Effect of rotation rate on nucleation rate.

The current transients for Te deposition were measured at various rotation rates. For the purpose of maintaining the same electrode surface conditions, the electrode was immersed into the electrolyte with rotation at 2000 rpm for 2min. The rotation rate was then adjusted to a value for the measurements (0~3000rpm). The deposition potential was -230mV in all the measurements. The current transients are shown in figure 4.12. Although nucleation currents were obtained at 500rpm(b) and 2000rpm(c), in the case of a stationary electrode (0rpm), no nucleation current was observed during the measurement. The $i-(t-t_0)^{1.5}$ plots obtained from figure 4.12 exhibit a linear relationship. From the slopes of these straight lines, the nucleation rates at various rotation rates were calculated. Figure 4.13 shows the nucleation rates as a function of the rotation rates.

Since there was no effect of linear diffusion on current transients in the short time, the nucleation rates should not be influenced by the rotation rates. However, figure 4.13 shows that the nucleation rate depends on the rotation rate, especially in the region of slow rotation. Two possible hypotheses can be considered as the reason for the effect of rotation on nucleation rates.

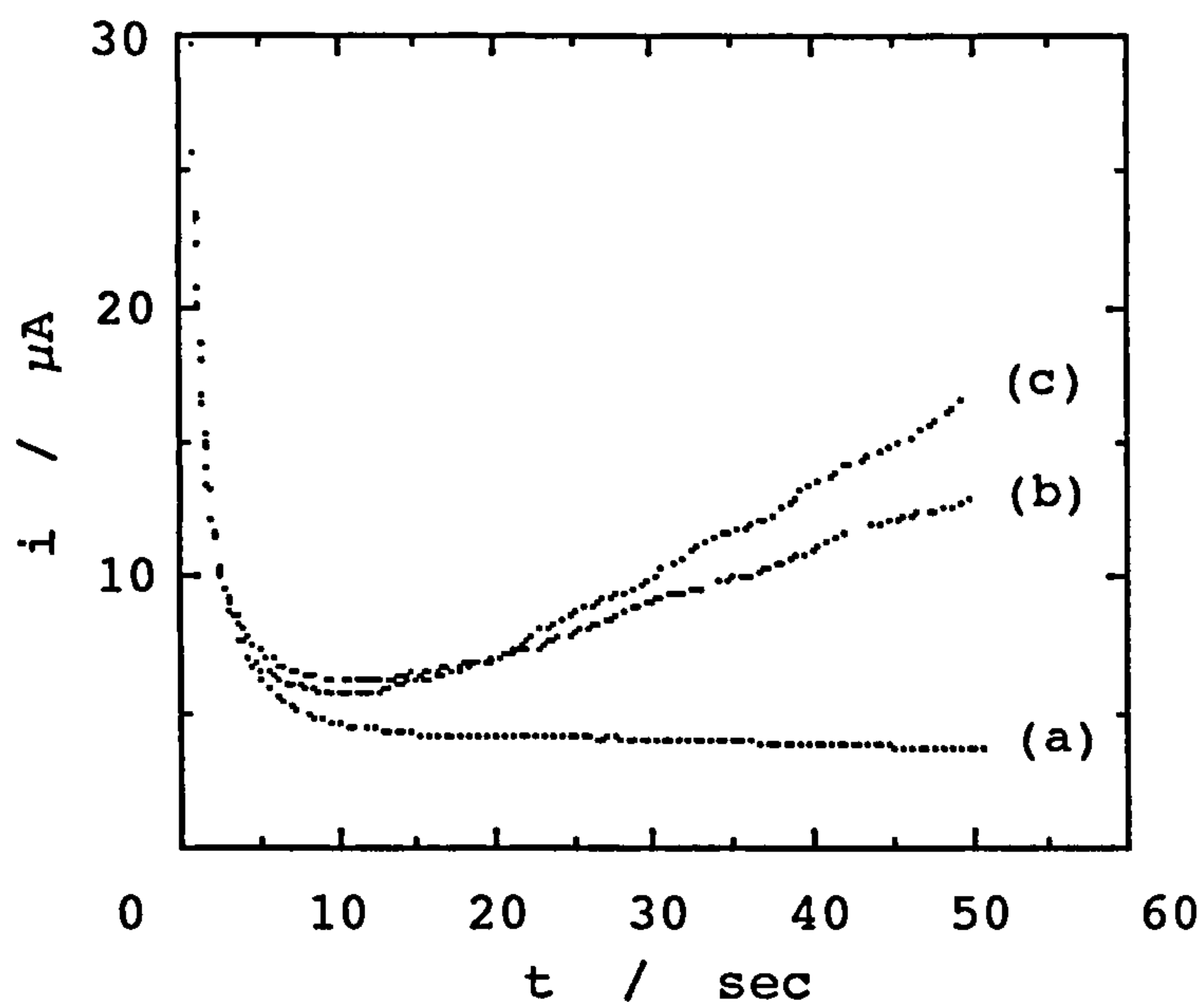


Figure 4.12 Current transient curves for Te deposition on a glassy carbon disk electrode.
(a) at 0rpm, (b) at 500rpm and (c) at 2000rpm
Deposition potential = -230mV vs.SCE.

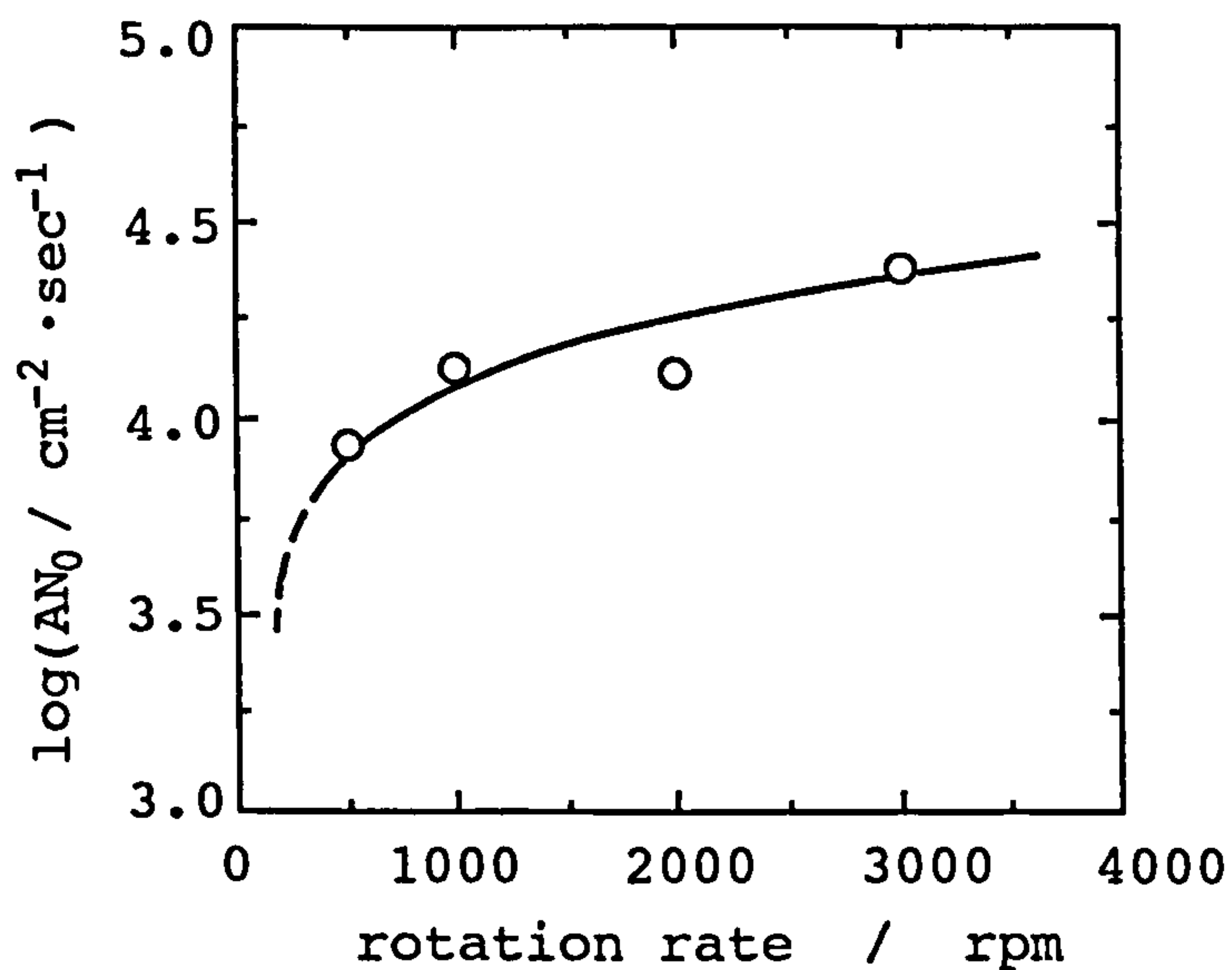


Figure 4.13 Nucleation rates for Te deposition on a glassy carbon electrode as a function of rotation rate.
Deposition potential = -230mV vs.SCE.

(1) As described in section 4.3.1, the current spike observed just after the potential step may correspond to the deposition of a tellurium monolayer. During and after the charging, the electrode surface is depleted in HTeO_2^+ . The thickness of the diffusion layer depends on the rotation rate. If the nucleation rate depends on the concentration of HTeO_2^+ on the electrode surface, the rotation rate affects the nucleation rate.

(2) The second possibility is the formation of a high pH layer on the electrode surface. The back ground current observed on the current transient curves may be associated with proton reduction. By the decrease in proton concentration, the solubility of HTeO_2^+ decreases (see equations 1.1 and 1.2). It can be expected that the decrease in HTeO_2^+ concentration decreases the nucleation rates as described above. Furthermore, since the reduction of HTeO_2^+ is a reaction involving H^+ (see equation 4.1), the decrease in H^+ concentration may inhibit the reduction of HTeO_2^+ .

4.4 Conclusions.

Electrocrystallization studies of Te deposition from acid solution containing HTeO_2^+ and Cd^{2+} were carried out with a glassy carbon rotating disk electrode. From the results obtained, the following conclusions can be drawn.

(I) From voltammetric and EDAX studies, it has been shown that pure Te could be obtained at more positive potentials than -280mV vs. SCE. The morphology of electrodeposited Te depends whether Cd^{2+} exists in the electrolyte. This indicates that Cd^{2+} may work as a so-called levelling agent by adsorption on electrode surface.

(II) From current transients, it was concluded that Te nucleation and growth involves the progressive nucleation and 3-D hemispherical growth under diffusion control.

(III) By use of a hydrodynamically modulated rotating electrode, it was confirmed that there is no influence of rotation on the nucleation currents in the short deposition time. This suggests that the electrocrystallization theory can be applied to the rotating disk currents.

(VI) The nucleation rates were obtained from the electrocrystallization theories. The values at -230 and -250 mV vs. SCE are 1.6×10^4 and $6.9 \times 10^4 \text{ cm}^{-2} \cdot \text{sec}^{-1}$, respectively. The logarithm of the nucleation rates showed a linear relationship with the deposition potentials. This suggests that the atomistic theory of nucleation can be valid in the overpotential region employed for the experiments. From the atomistic theory, it has been shown that the number of atoms in the critical nuclei is approximately 2 for the experiments.

(V) The influence of rotation rate on nucleation rate was observed. This may be due to the depletion of HTeO_2^+ on the surface during formation of a monolayer of Te or due to increase in pH.

Appendix 4.I Discussion of the initial 'charging' current.

As shown in figures 4.5 and 4.8, large currents flowed just after the potential step. The HMRDE study suggests that these currents are controlled by diffusion of HTeO_2^+ . If the currents are purely controlled by diffusion, the Cottrell equation should be applicable. However, if the currents lead to formation of a Te monolayer, the Cottrell relation must be modified to take into account the surface coverage of deposited Te. The following equation shows the modified Cottrell equation which applies for diffusion controlled monolayer deposition.

$$j = \frac{nFD^{1/2}C_b}{(\pi t)^{1/2}} \cdot (1-\theta) \quad (4I.1)$$

θ is surface coverage by deposited Te and is expressed as

$$\theta = \frac{N_A}{nF} \cdot \int_0^t j(t) dt \cdot \left(\frac{M}{N_A \rho}\right)^{2/3} \quad (4I.2)$$

where N_A , ρ and M are the Avogadro constant, the density of the deposit and the molecular mass, respectively.

The transients obtained from equation (4I.1), from the Cottrell equation and obtained experimentally are shown in figure 4I.1. As shown clearly in this figure, the Cottrell equation gives larger currents than the experimental data, whereas the modified Cottrell equation (4I.1) fits the experimental result very well. Thus, the currents observed at initial transients can be attributed to diffusion limited deposition of Te monolayer.

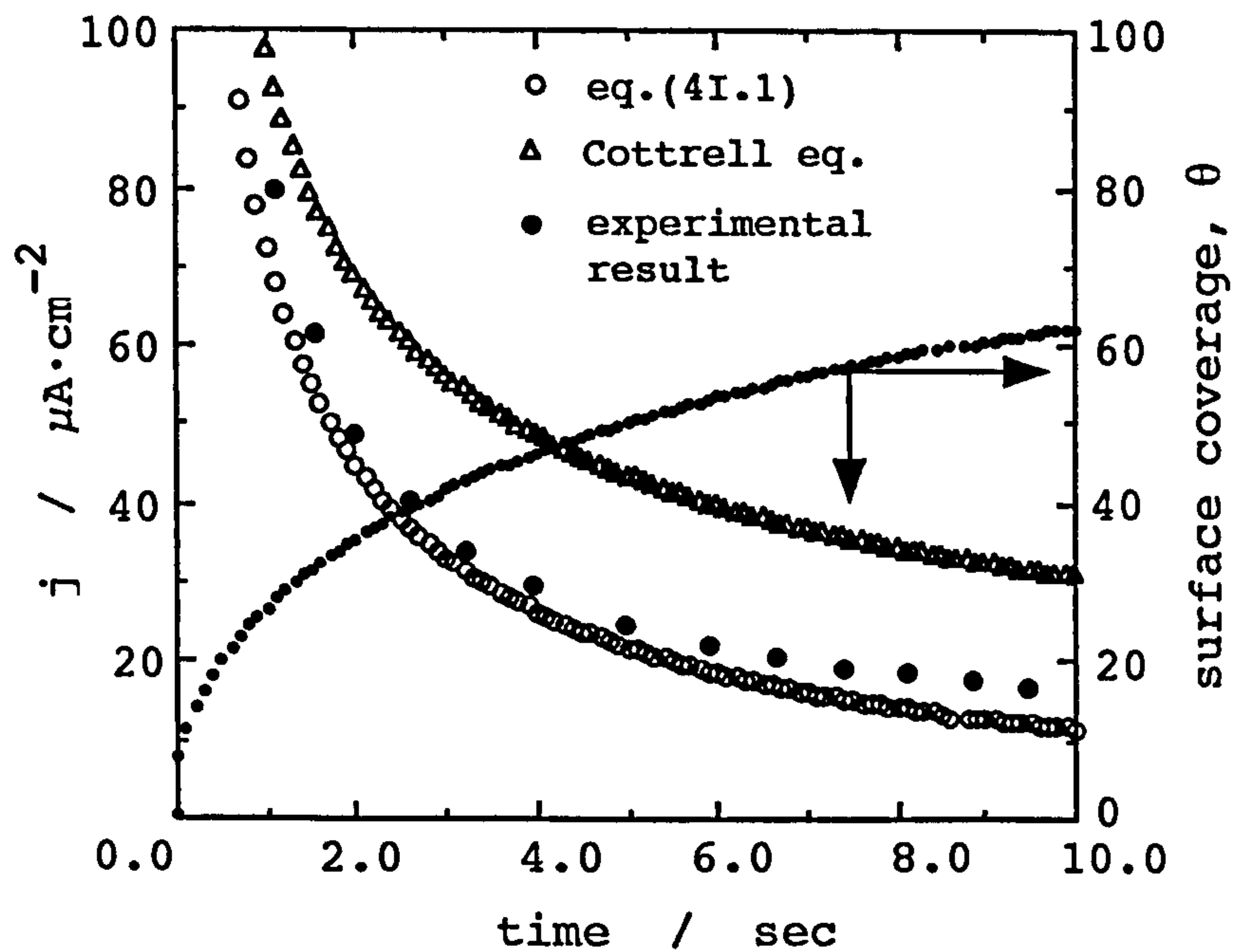


Figure 4I.1 Current spike observed during the initial current transients. The experimental result is taken from figure 4.5(a). The surface coverage is calculated from equation (4I.2).

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CHAPTER 5.

ELECTRODEPOSITION OF CdTe ON
TIN OXIDE COATED GLASS.

- 5.1 Introduction.
- 5.2 Voltammetric studies.
- 5.3 Nucleation studies.
 - 5.3.1 Nucleation and growth model.
 - 5.3.2 Effect of potential on nucleation rates.
 - 5.3.3 Effect of temperature on nucleation rates.
- 5.4 Quantitative discussion of the effect of temperature on nuclear number density.
- 5.5 A new approach to derive the j - t relation for progressive nucleation / hemispherical growth under diffusion control.
- 5.6 Conclusions.
- Appendix 5.I
 - (a) How to deal with the assumptions employed.
 - (b) Effect of β on nucleation number density.
 - (c) Effect of β on current density.
- Appendix 5.II FORTRAN program used in this chapter.
- References.

5.1 Introduction.

In chapter 4, the electrodeposition of Te on glassy carbon was reported. From the studies, it was found that large background currents flow and decay with the deposition time especially at relatively high overpotential. In the case of Te deposition (low overpotential), since long induction times were required, the decaying part of background current did not overlap with the deposition current. However, as CdTe is obtained at more negative potentials than pure Te, the induction time for CdTe deposition becomes shorter and the deposition current overlaps with the decaying part of the background current. This situation is shown schematically in figure 5.1. In the case of glassy carbon electrodes, the deposition current could not be obtained exactly from the current transient curves, because of the overlap between the decaying part and the deposition current.

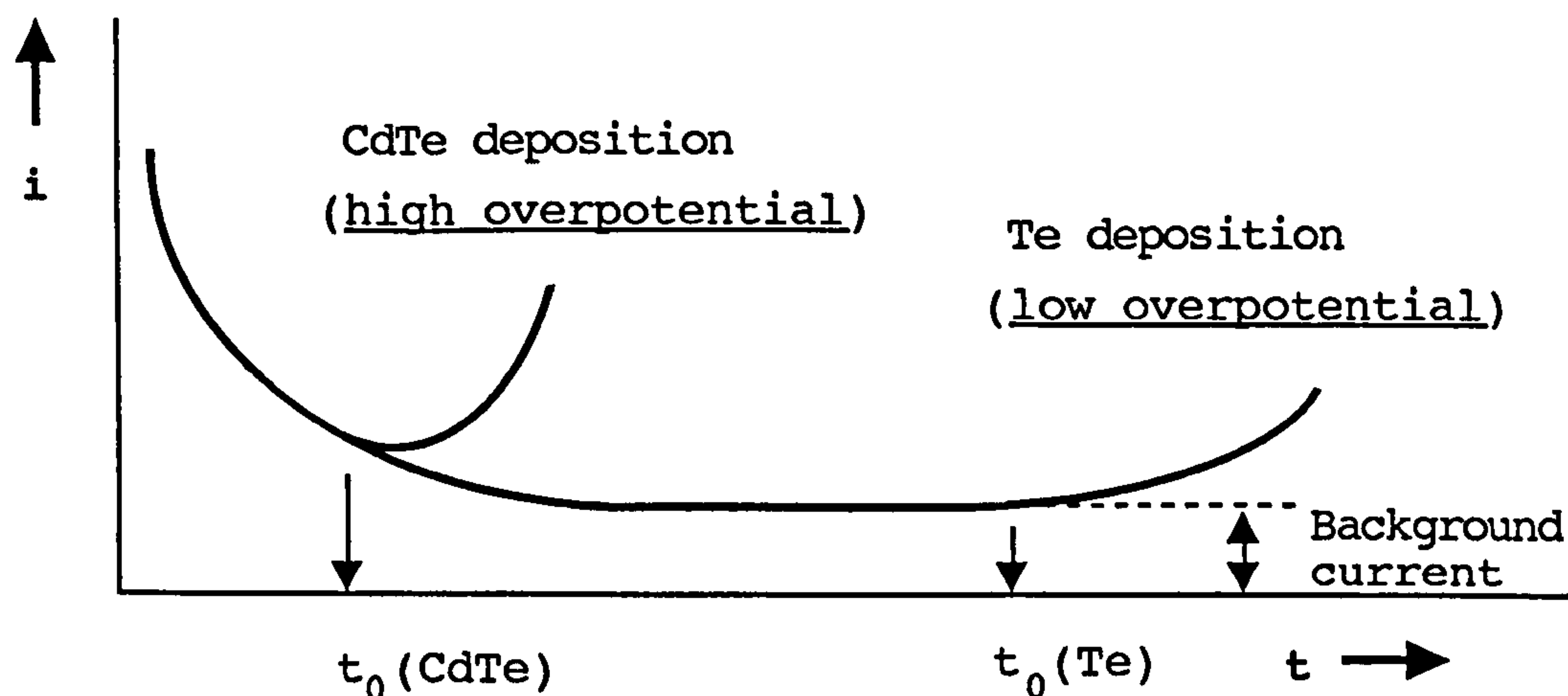


Figure 5.1 Schematic current transients on glassy carbon for Te and CdTe deposition.

Therefore, as an alternative material, the tin oxide coated glass electrode (TO) was tried for the studies of CdTe electrodeposition and it was found that the electrode is more suitable than glassy carbon.

For the studies of CdTe deposition on TO, the solution shown in table 3.1 (b) was employed. The TeO_2 concentration was ten times higher than that in the solution employed for the Te deposition studies. The use of the more concentrated solution improved reproducibility of the experimental results. With the increase in TeO_2 concentration, the pH of the solution was lowered, because the solubility of TeO_2 is given as a function of pH as shown in equations (1.1) and (1.2). Stationary TO electrodes were used for the experiments discussed in this chapter.

5.2 Voltammetric studies.

Cyclic voltammetric studies were carried out to investigate macroscopic CdTe electrodeposition behaviour on TO electrodes. Figure 5.2 shows the cyclic voltammogram measured at a scan rate of 5mV s^{-1} .

A deposition current wave was observed at -370mV on the cathodic scan. At -400mV , the deposition current reached a maximum value (peak I) and then decreased. The increase in the deposition current corresponds to a spread of active area on the electrode (i.e., growth of nuclei and increase in nuclear number). The decrease in the current after the peak is due to overlap of diffusion zones. Since the concentration of HTeO_2^+ is 250 times smaller than that of Cd^{2+} , it is considered that the diffusion of HTeO_2^+ controls the deposition current.

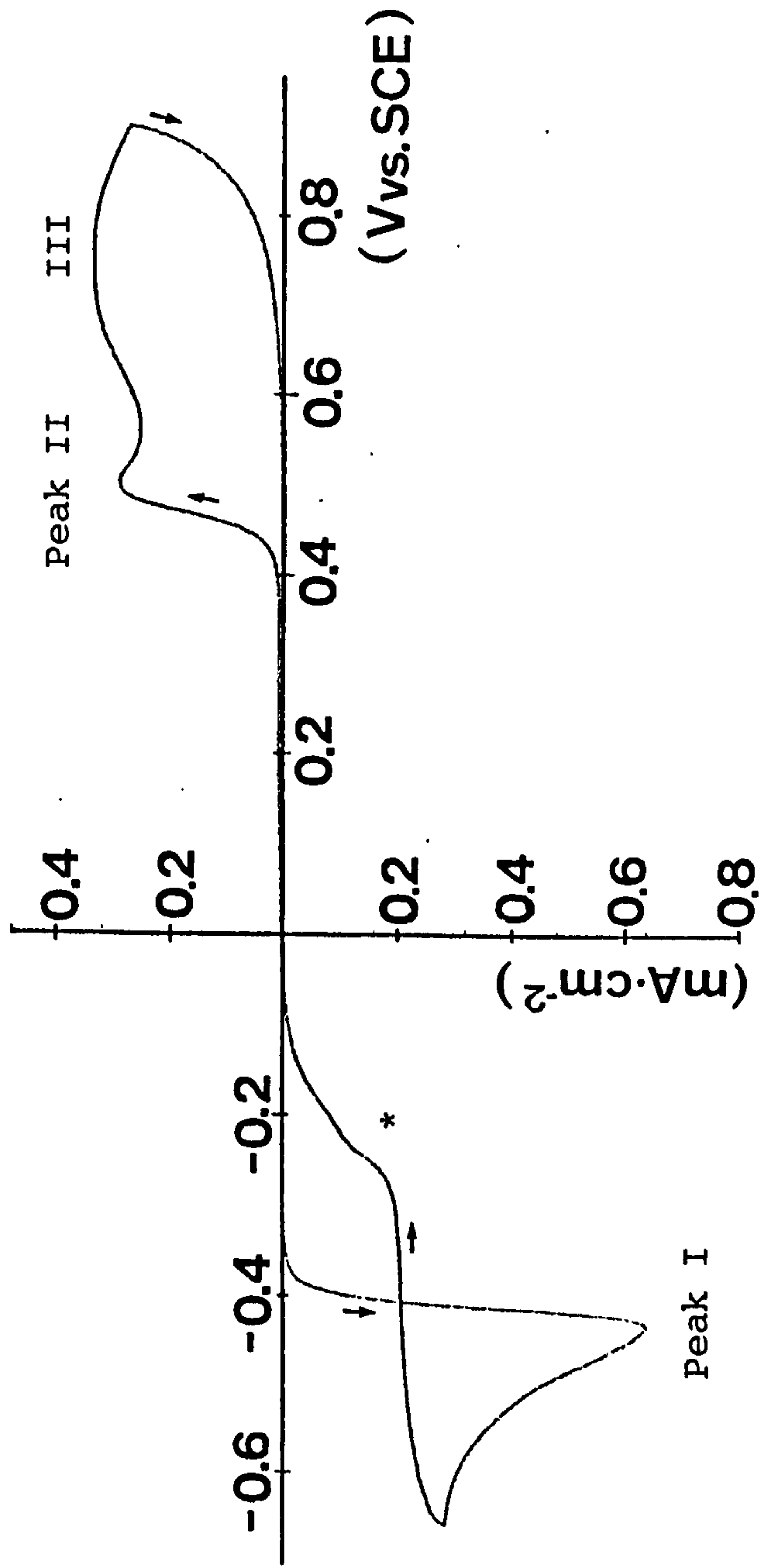


Figure 5.2 Cyclic voltammogram of a TO electrode in $\text{TeO}_2 + \text{CdSO}_4 + \text{H}_2\text{SO}_4$ solution shown in Table 3.1(b).

scan rate = $5\text{mV}\cdot\text{s}^{-1}$
temperature = 25°C

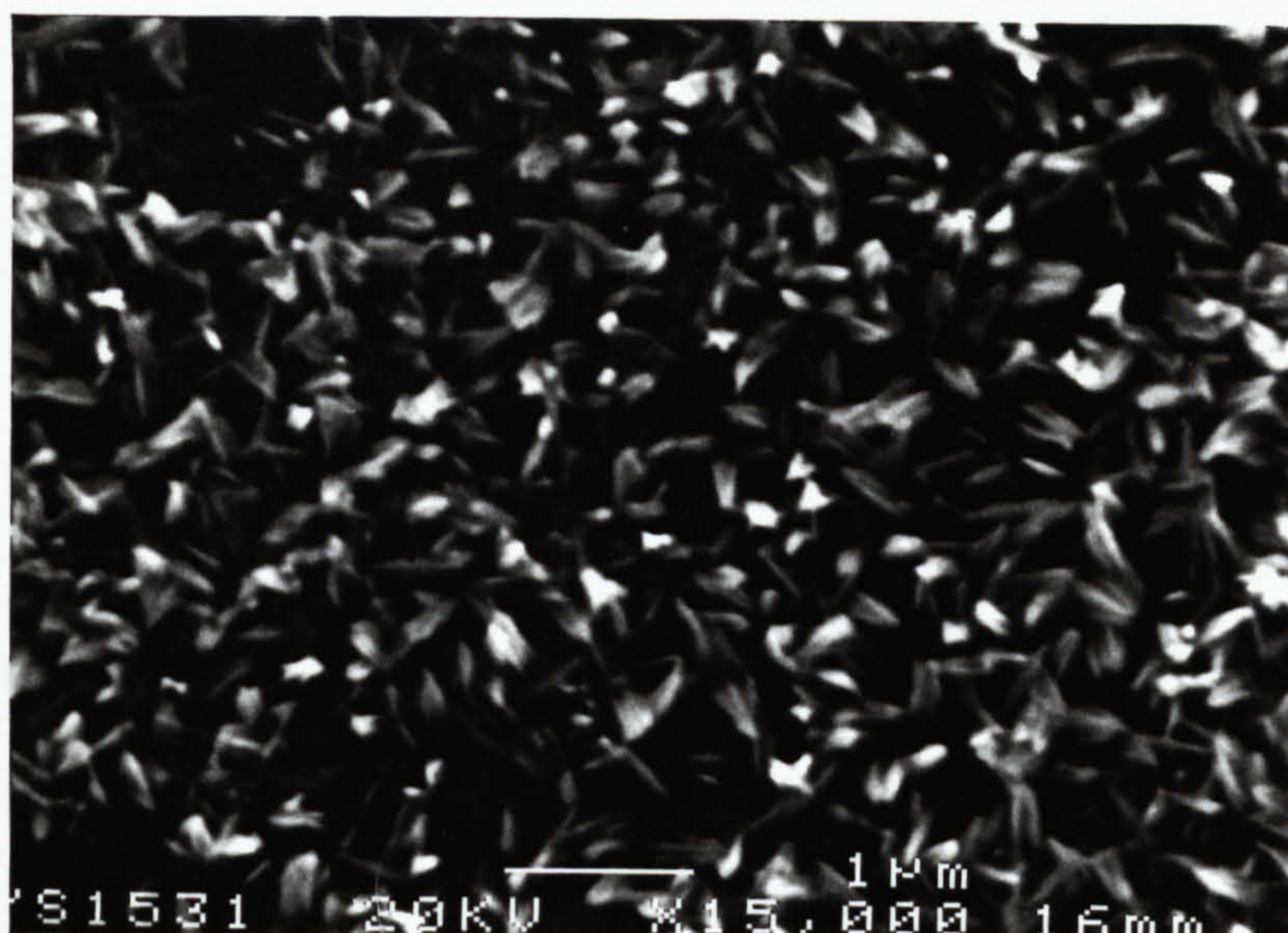
On the anodic scan, the current changed little between -500 and -300mV. After -300mV, the current decreased and finally, the deposition ceased at 0mV. During the decrease in current, a characteristic phenomenon was observed. The current decreased rapidly between -300mV and -250mV and then decreased slowly at more positive potentials than -250mV (* in figure 5.2). When the steady-state polarization curve was measured on the rotating glassy carbon disk electrode (figure 4.2), a similar phenomenon was also observed. This phenomenon on TO as well as that on glassy carbon can be interpreted as evidence that pure Te deposition occurs at more positive potentials than -250mV whereas CdTe can be obtained at more negative potentials. The maximum current of pure Te deposition (i.e., the current at -250mV) was $0.13\text{mA}\cdot\text{cm}^{-2}$ and the current of CdTe deposition was $0.2\text{mA}\cdot\text{cm}^{-2}$ (= current at -500mV). The ratio of the pure Te deposition current to the CdTe deposition current is approximately equivalent to the ratio of the electron number of Te deposition to that of CdTe deposition (=4/6).

The stripping current of the deposits was observed at potentials more positive than +400mV. In this potential region, two current peaks appeared (peaks II and III). Cowache et al.[1] have suggested that a Sn-Te monolayer can be formed. The charge of peak(II) is about $2\text{mC}\cdot\text{cm}^{-2}$ and the theoretical charge of the Te monolayer is $1.06\text{mC}\cdot\text{cm}^{-2}$. Although these two values are relatively close, the charging current for Te monolayer did not appear in the current transient curves shown in figure 5.4. Therefore, the peaks(II) and (III) do not correspond to the current for Te monolayer, but they may correspond to the stripping of CdTe and pure Te respectively. Before the potential arrives at the stripping potential (+400mV), the deposit is covered with pure Te layer. Thermodynamically, the stripping of CdTe should occur at more negative potential than that of

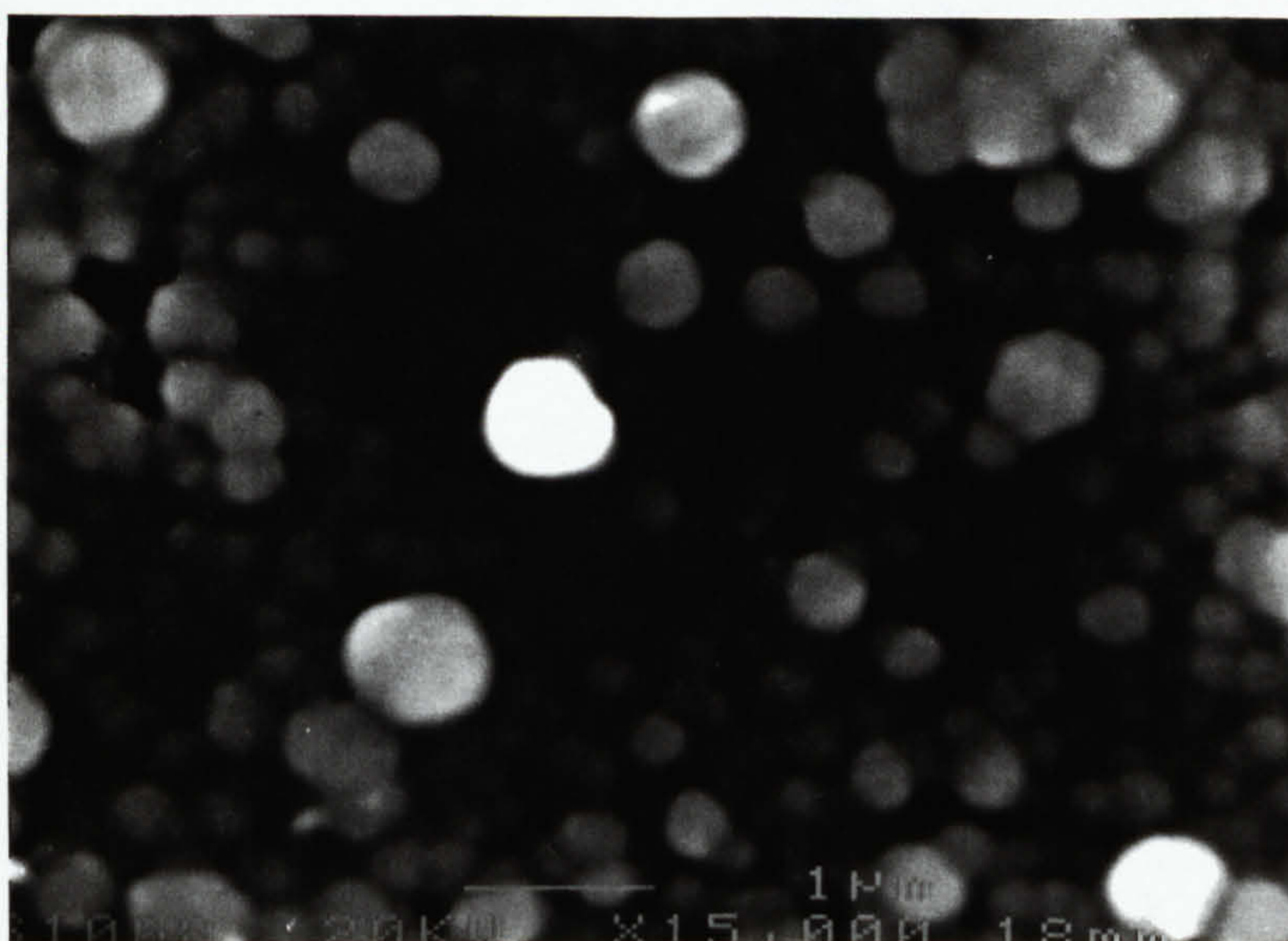
pure Te. However, the structure of the deposits does not allow the precedence of the stripping of CdTe and, therefore, the two peaks overlap. (It should be noticed that the charges of peak(II) and (III) do not correspond to the amount of CdTe and pure Te, respectively.)

Scanning electron micrographs were taken to show the morphologies of CdTe and pure Te. Although the cyclic voltammogram showed that the nucleation on TO does not occur at potentials more positive than -350mV , the deposition of pure Te should be carried out at a more positive potential than the thermodynamic deposition potential of CdTe (-176mV). Therefore, the following double potential step method was employed to get a pure Te deposit. First, tiny nuclei were formed at -560mV for 0.4sec and then the bulk deposit was formed at -170mV for 10min . A SEM image of the pure Te deposit is shown in figure 5.3(a). The pure Te showed a dendritic morphology as reported by Dennison et al.[2]. They have shown that two morphologies of Te are observed. When Te deposition occurs by the reduction of $\text{Te}(+4)$ to $\text{Te}(0)$, the morphology of Te film is dendritic and when Te is obtained by the chemical reaction between $\text{Te}(+4)$ and $\text{Te}(-2)$, a compact smooth Te is observed. As the potential of formation of $\text{Te}(-2)$ is approximately -950mV , it is obvious that the chemical reaction between $\text{Te}(+4)$ and (-2) does not occur and that compact Te can not be obtained at the potential employed.

Figure 5.3(b) shows the SEM image of the CdTe film obtained at -560mV . The CdTe deposit consists of spherical grains and it was found that the morphologies of the deposits changed drastically from dendrite to sphere by co-deposition of Cd. The quantitative analysis of CdTe obtained at -560mV was carried out by EDAX.



(a) Pure Te deposit obtained at -170mV vs. SCE



(b) CdTe deposit obtained at -560mV vs. SCE

Figure 5.3 SEM images of Te deposit (a) and CdTe deposit (b) obtained from the solution shown in Table 3.1 (b).

As the Sn (l line) overlaps with the Te (k line), a reliable result could not be obtained. However, the ratio of Cd/Te was estimated as 0.4/0.6 to 0.45/0.55.

5.3 Nucleation studies.

Mori et al.[3] have reported the nucleation and growth of CdTe as well as those of pure Te. They interpreted their results as evidence that CdTe electrodeposition takes place by instantaneous nucleation and 2-D growth under kinetic control. However, as described in section 4.3.1, their conclusion leads to the contradiction that the rate determining step changes from kinetic control to diffusion control with the deposition time. In this section, the studies of the nucleation and growth of CdTe on TO are reported.

5.3.1 Nucleation and growth model.

Current transient curves for CdTe deposition were measured by a double potential step method. As a large charging current was not observed at the beginning of transients, it was not necessary to choose the first step potential close to the second step potential. Therefore, the potential of the first step was +500mV at which thermodynamically HTeO_2^+ is more stable than $\text{Te}(0)$. After the first step, the electrode potential was shifted to potentials for the measurements of current transients. The current transient curves were measured in a potential range of -500 to -600mV. All the measurements were carried out at 25 °C. Figure 5.4 shows the current transients of CdTe deposition measured at several potentials.

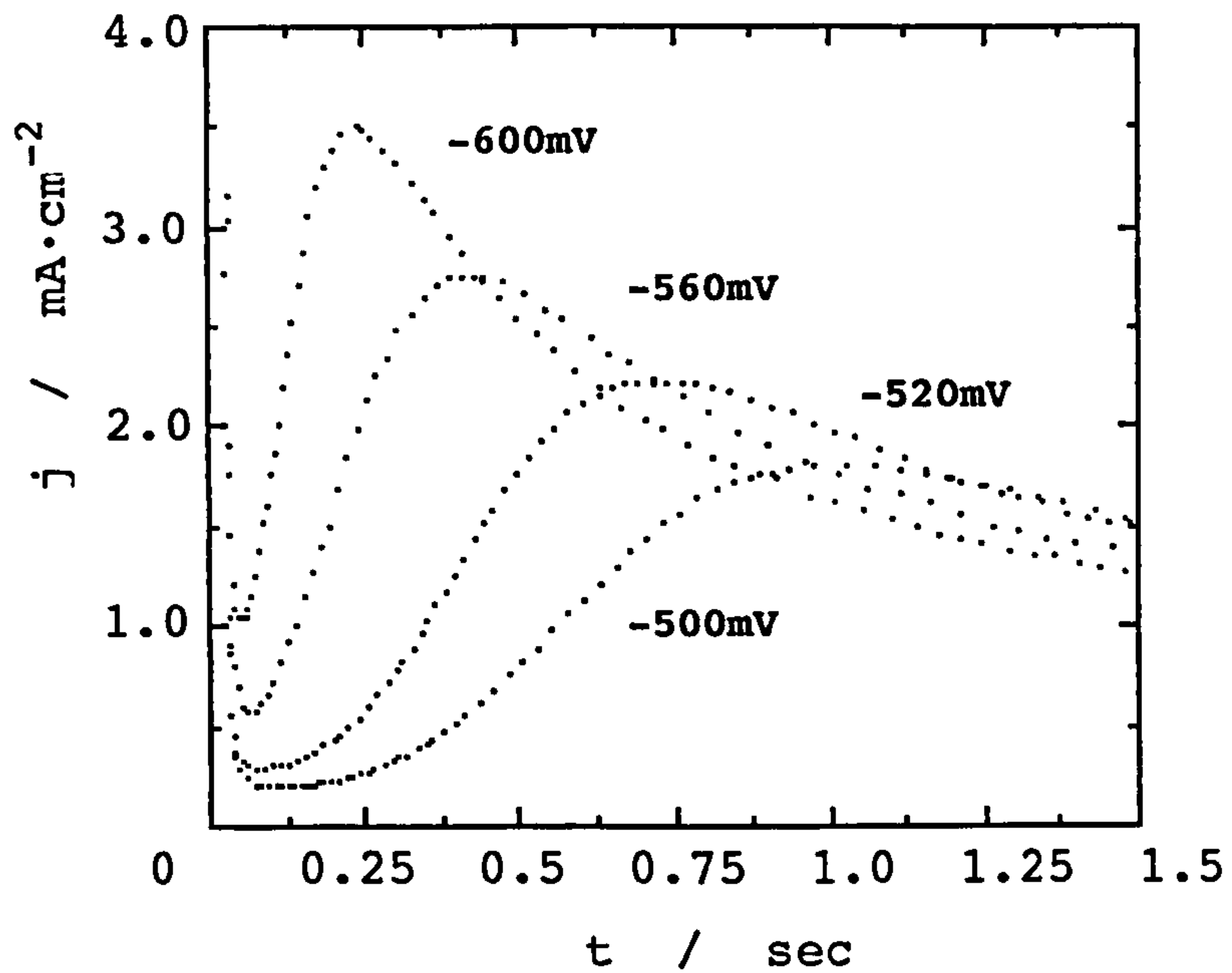


Figure 5.4 Current transient curves for CdTe deposition measured on TO. Temperature : 25°C

The curves shows typical current transients of electrodeposition on a foreign surface (i.e., the current increases with increase in surface area of deposits and decreases with the overlap of deposits or diffusion zone.). Before significant overlap of deposits or diffusion zones occurs, the current transients can be expressed in the general form

$$j = k \cdot (t - t_0)^n \quad (5.1)$$

where k is a constant and n is given a particular value (0.5, 1, 1.5, 2 or 3) for each nucleation and growth process. These values of k and n for each nucleation system are shown in Table 2.1. In equation (5.1), t_0 is the induction time. The current transients were re-plotted as function of $(t - t_0)^n$ to find the best number of n . As the results of these tests, it was found that $j - (t - t_0)^{1.5}$ plots gave the best straight lines. Figure 5.5 shows the $j - (t - t_0)^{1.5}$ plots obtained at -520, -560 and -600mV.

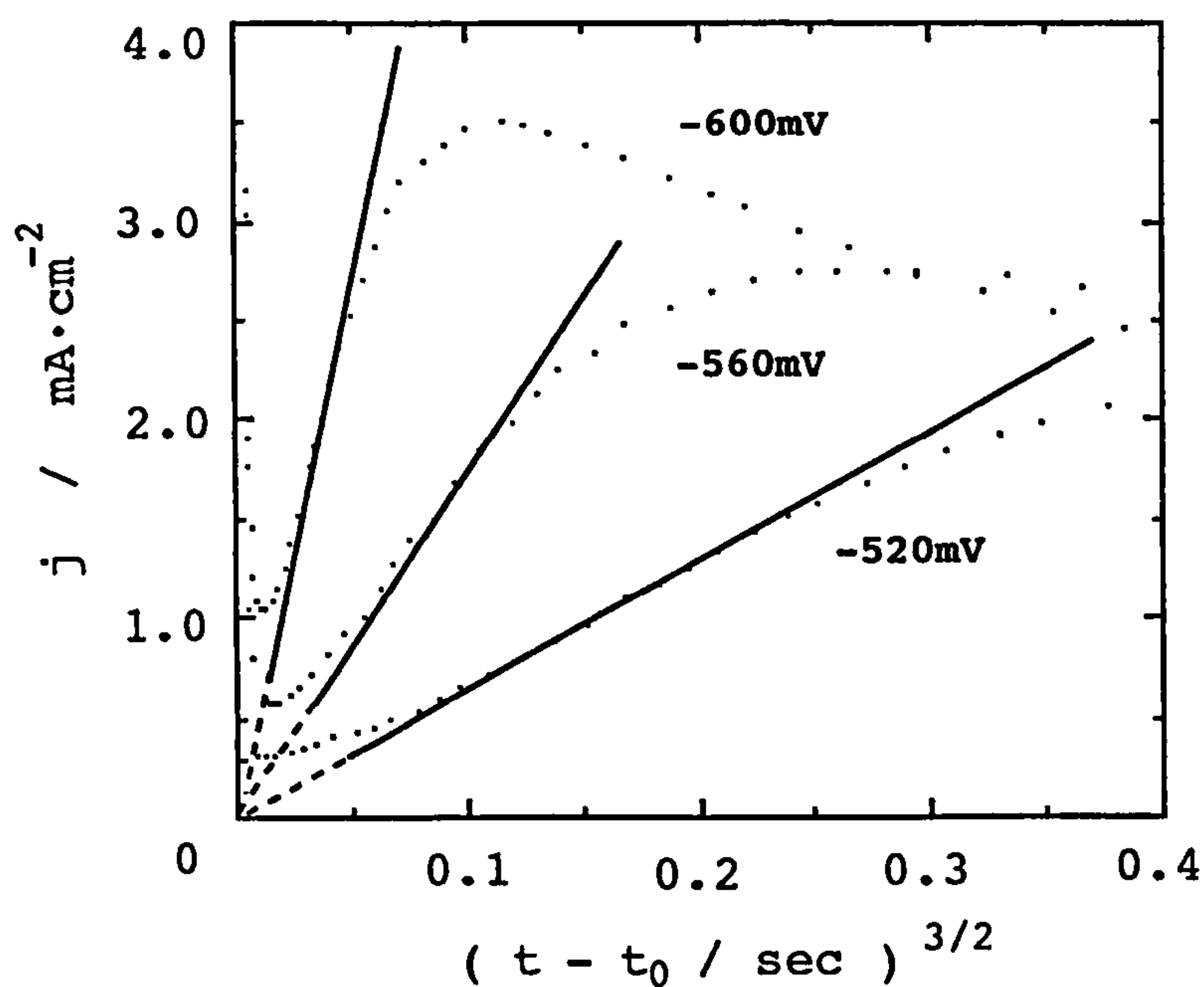


Figure 5.5 $j - (t-t_0)^{3/2}$ plot of transients shown in figure 5.4.

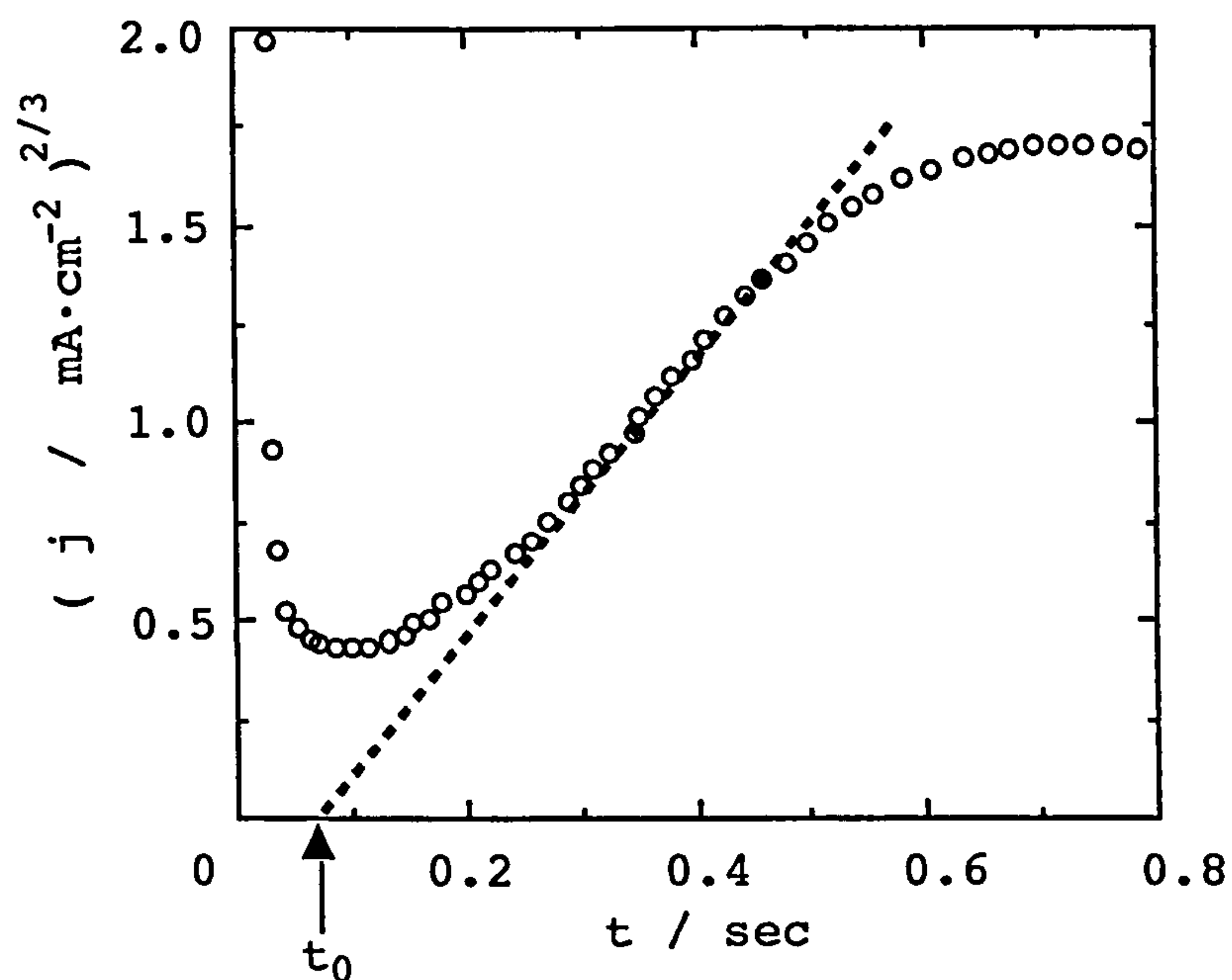


Figure 5.6 $j^{2/3} - t$ plot to obtain the induction time. t_0 is found to be 0.07sec.

potential : -520mV vs. SCE
temperature : 25°C

The values of t_0 were obtained from $j^{2/3} - t$ plots. Figure 5.6 shows the $j^{2/3} - t$ plot of the transient measured at -520mV. In many cases, it is difficult to obtain exact induction times from transient curves, unless the background currents are completely constant. The time giving the minimum current in current transients is often used as t_0 . However, the t_0 obtained from the minimum current must be longer than the real induction time, because the deposition current observed is given by the sum of background current and deposition current and, therefore, the nucleation begins during the decay of the total current (see the transient for CdTe deposition in figure 5.1. The deposition current begins flowing at t_0 . However the minimum current is observed after t_0). The difference is most marked in the case of short induction times. For the current transients measured at -520 and -560mV, t_0 obtained from $j^{2/3} - t$ plots are 0.07sec and 0sec. On the other hand, t_0 obtained from the minimum currents are 0.1sec and 0.06sec. At -520mV, both of the methods gave close values. However, at -560mV, the difference is not small. The reason for this difference can be explained as described above (i.e., t_0 obtained from the minimum current is too long, because the period from the beginning of nucleation to the minimum current is ignored).

NOTE : The method employed does not always give better values than the method using the minimum current. For example, when large background currents are observed, the method employed may give too small value for t_0 . Therefore, the method to obtain t_0 should be chosen case by case.

As shown in figure 5.5, the relationships of $j - (t-t_0)^{1.5}$ show good linearity. The linearity indicates that the nucleation and growth of CdTe occur by progressive nucleation and three dimensional growth under diffusion

control. In the case of diffusion controlled growth, the Cottrell relation should be observed at longer times as shown in figures 2.12 and 2.13. The Cottrell relation expresses the decrease in current with the growth of planar diffusion layer. The equation is given by

$$j = \frac{nFD^{1/2}C_b}{\pi^{1/2} \cdot t^{1/2}} \quad (5.2)$$

However, as shown clearly in figure 2.12, the planar diffusion layer does not form at $t=0$. Before formation of planar diffusion layer, a certain time is required for formation of nuclei (t_0) and growth of diffusion zones from isolated diffusion to planar diffusion. By introducing the period required for formation of planar diffusion, t_d , the Cottrell equation is rewritten as

$$j = \frac{nFD^{1/2}C_b}{\pi^{1/2} \cdot (t-t_d)^{1/2}} \quad (5.3)$$

In order to obtain t_d , the relationship of $j^{-2} - t$ was plotted as shown in figure 5.7. From this figure, it was found that t_d at -560mV is 0.31 sec . Figure 5.8 shows the plot of equation (5.3). The good linearity proved that at longer time, the rate of deposition is controlled by planar diffusion. From the slope of the straight line shown in figure 5.8, the diffusion coefficient of HTeO_2^+ can be obtained. By substituting $n = 6$, $C_b = 2 \times 10^{-6} \text{ mol} \cdot \text{cm}^{-3}$, $t_d = 0.31\text{sec}$ and the slope, $j/(t-t_d)^{-1/2} = 1.5$ into equation (5.3), $5.3 \times 10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}$ was obtained as the diffusion coefficient of HTeO_2^+ .

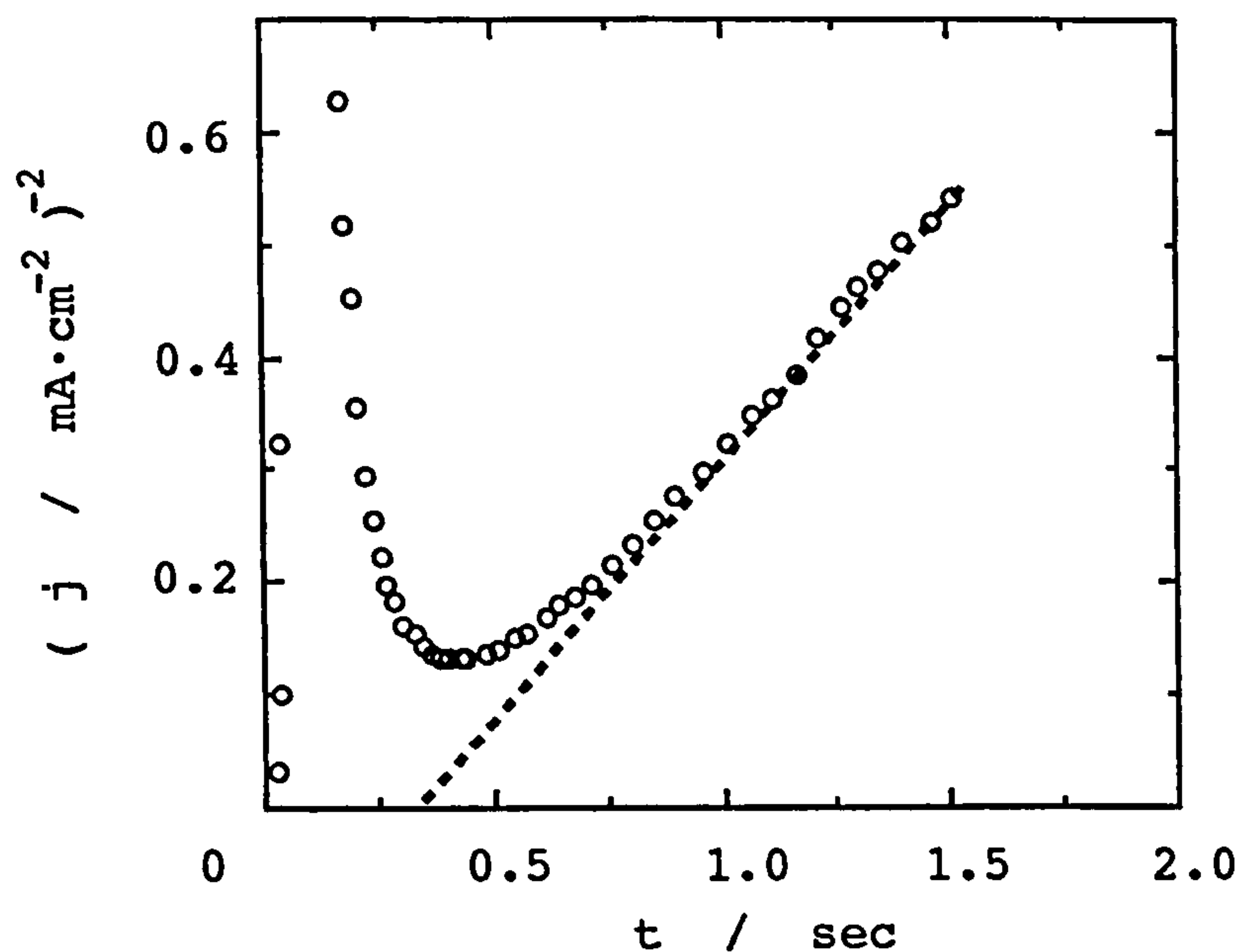


Figure 5.7 $j^{-2} - t$ plot for CdTe deposition measured at -560mV. From this figure, it was found that t_d at -560mV (25°C) is 0.3sec.

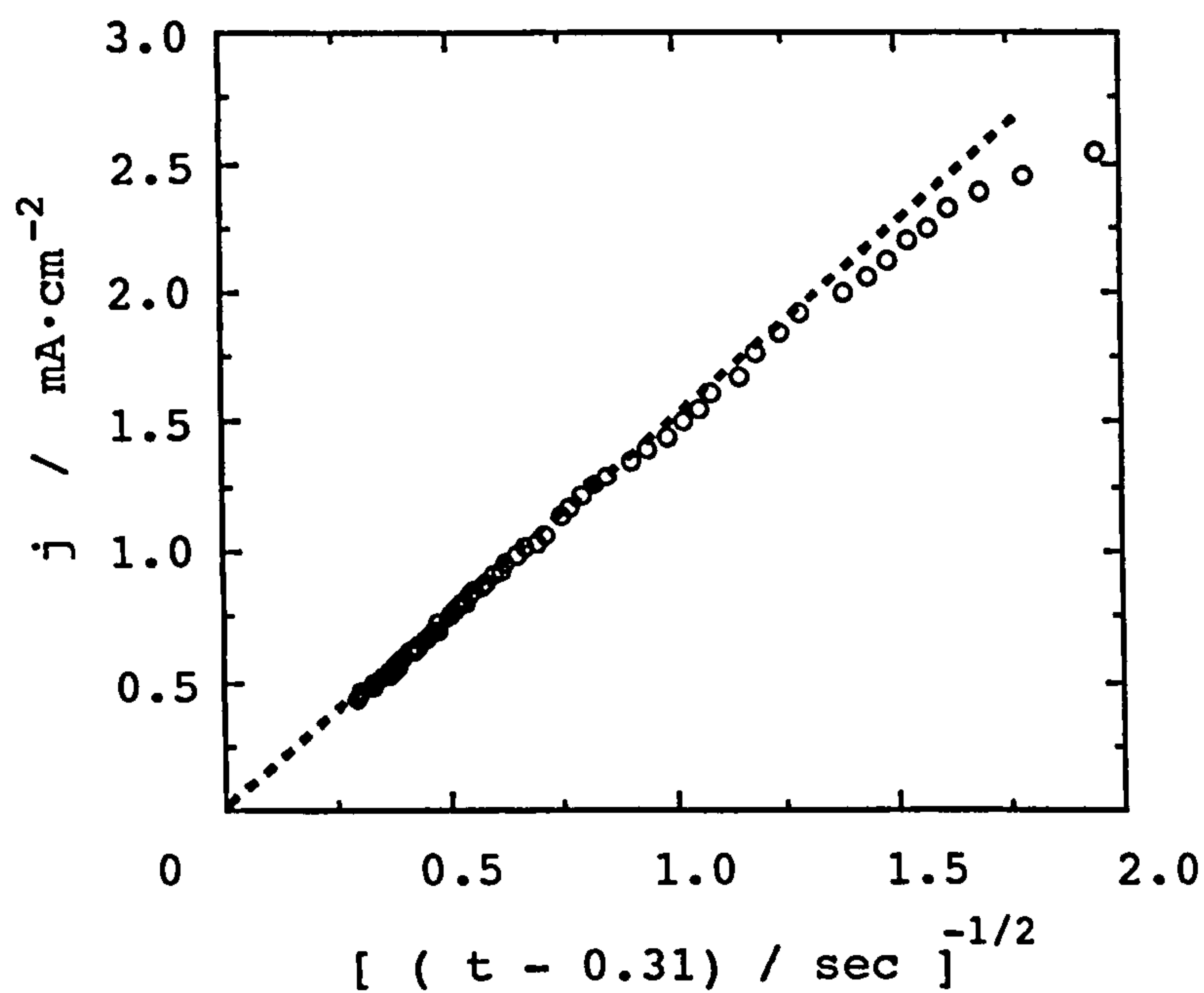


Figure 5.8 Cottrell plot for CdTe deposition at -560mV. t_d was obtained from figure 5.7.

As described in chapter 4, the diffusion coefficient was found to be $5.6 \times 10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}$ from the Levich plot. Compared with the value obtained by the Levich plot and other values reported in published papers [2~4], the diffusion coefficient of HTeO_2^+ obtained by the Cottrell plot can be regarded as a reasonable value.

From the Cottrell plot, it is obvious that the deposition of CdTe is controlled by the diffusion of HTeO_2^+ . In order to make sure that the deposition takes place by progressive nucleation and three dimensional growth, the deposit was observed by SEM. Figure 5.9 shows the image of the deposit obtained at -560mV. The micrograph was taken at an angle of 45° . This SEM image shows that the deposits are hemispherical and that the deposits are not of uniform size. This means that the nucleation is progressive and the deposition is three dimensional hemispherical growth.

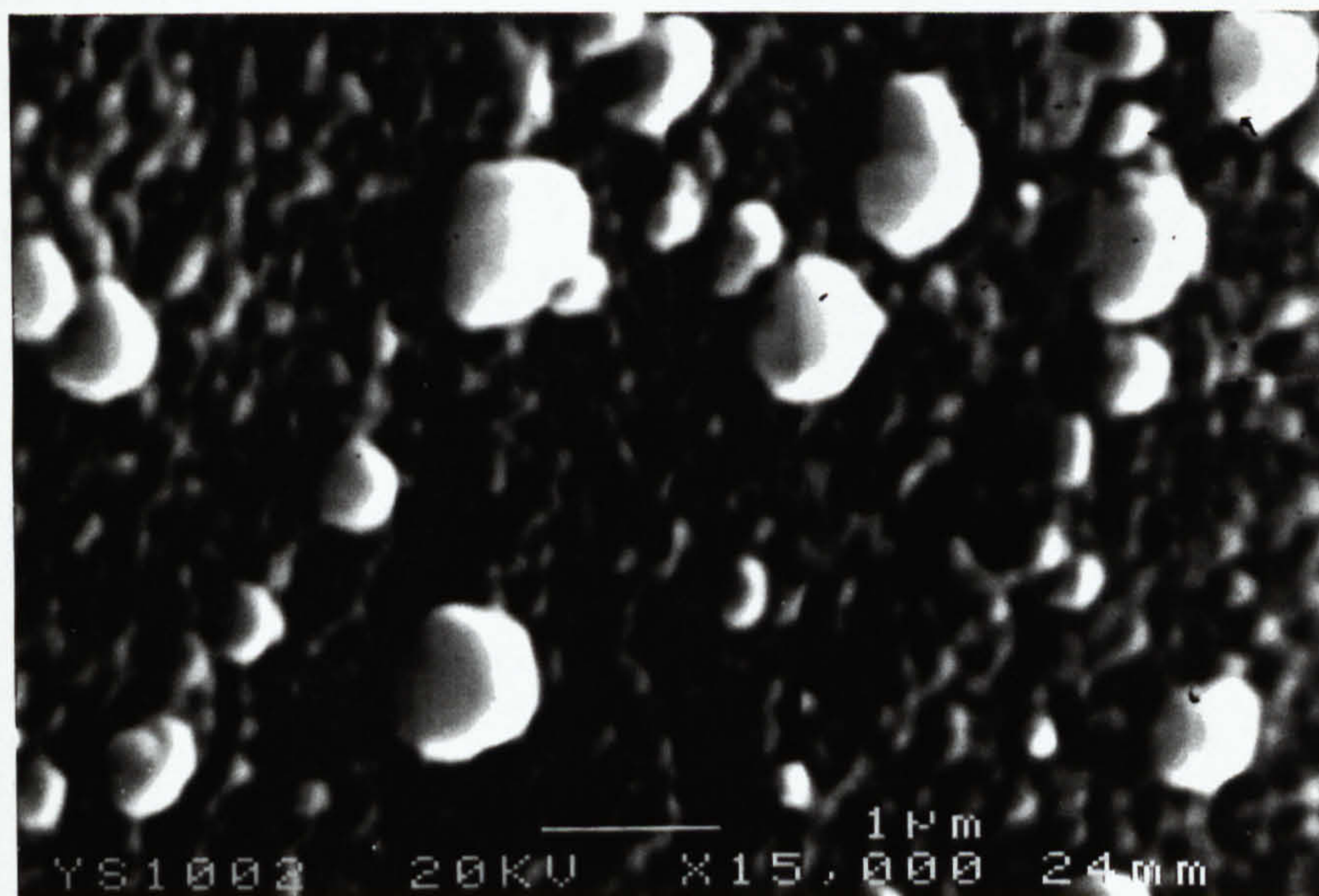


Figure 5.9 A scanning electron micrograph of CdTe deposition obtained at -560mV. The image was taken at an angle of 45° .

In this section, the nucleation and growth of CdTe electrodeposition were described. The early part of current transients showed that CdTe deposition takes place by progressive nucleation and three dimensional growth under diffusion control. In order to make sure of the nucleation and growth system, the analysis of the transient at longer time and the observation of the deposit were carried out. The analysis of transients shows that the Cottrell relation is established at longer time. Therefore, it was found that the deposition is controlled by diffusion. The observation of the deposit by SEM shows that the deposits are hemispherical and the nucleation occurs progressively. Thus, all of the investigations made (i.e. the analysis of both the transients observed at short time and at long time and the observation of the deposit) prove that the nucleation and growth of CdTe electrodeposition is *progressive nucleation / three dimensional growth under diffusion control*.

5.3.2 Effect of potential on nucleation rates.

The initial transient for progressive nucleation / hemispherical growth under diffusion control is expressed as

$$j(t) = \frac{2nF\pi AN_0(2DC_b)^{3/2}M^{1/2}}{3\rho^{1/2}} \cdot t^{3/2} \quad (5.4)$$

The nucleation rate, AN_0 , can be obtained from this equation. As the rate determining step of CdTe deposition is the diffusion of HTeO_2^+ , the deposition of a Cd atom occurs rapidly after the deposition of a Te atom. This phenomenon means that a couple of a Cd atom and a Te atom acts as one atom. In order to obtain the nucleation rates, $n = 6$ (4 electrons from $\text{Te}(+4)$ to $\text{Te}(0)$ and 2 electrons from $\text{Cd}(+2)$ to $\text{Cd}(0)$), $M = 240$ ($M_{\text{Te}} = 127.6$, $M_{\text{Cd}} = 112.4$), $D = 5.3 \times$

$10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}$, $C_b = 2 \times 10^{-6} \text{ M} \cdot \text{cm}^{-3}$ and $\rho = 6.2 \text{ g} \cdot \text{cm}^{-3}$ [5] were substituted into equation (5.4). From the slopes of the straight lines shown in figure 5.5, the nucleation rates at different potentials were obtained. The nucleation rates at -520mV and -560mV are 1.0×10^7 and $2.9 \times 10^7 \text{ cm}^{-2} \cdot \text{sec}^{-1}$ respectively. Figure 5.10 shows the nucleation rates as a function of deposition potential. The logarithm of the nucleation rates exhibits a good linear relation with the deposition potential. The linearity is predicted by the atomistic theory (see chapter 2). According to the atomistic theory, the number of atoms in a critical nucleus, n_k , is expressed as

$$n_k = \frac{kT}{ze} \cdot \frac{\ln(\tau_{st})}{\eta} - (1-\alpha) \quad (5.5)$$

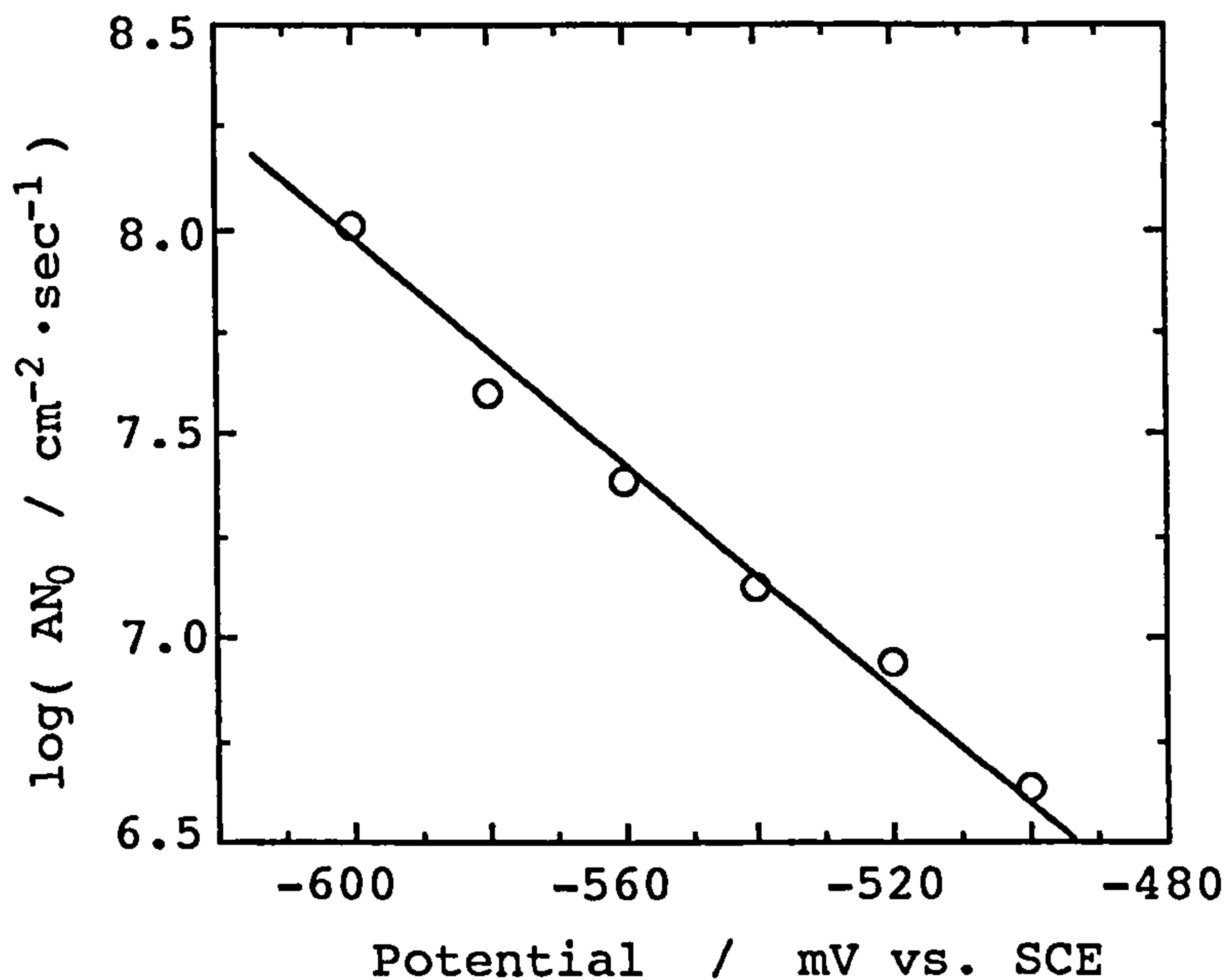


Figure 5.10 Effect of potential on nucleation rate for CdTe deposition.
temperature = 25°C

where k is the Boltzmann constant, α is the transition coefficient, z is the electron number of the rate determining step and τ_{st} is the steady state nucleation rate. The slowest reaction of CdTe deposition is reduction of HTeO_2^+ (reaction 4.4). As described in section 4.3.3, it is assumed that the number of electrons in the rate determining single step is 1. By substitution of $z = 1$, $\alpha = 0.5$ and the slope shown in figure 5.10, it was found that the number of atoms in a critical nucleus was zero. According to the atomistic model, the result ($n_k = 0$) means that a single atom adsorbed on an active site can be considered as a stable "cluster" which could grow spontaneously in the supersaturation region. Therefore, the active centre itself will play the role of a critical nucleus.

5.3.3 Effect of temperature on nucleation rates.

The current transient curves of CdTe deposition were measured at several temperatures (-6 to 50°C). The measurements were carried out at -520mV and -560mV. Figure 5.11 shows the current transients measured at -560mV. The current transients were influenced greatly by temperature. As the temperature increased, the peak current increased and the time giving the peak current shortened. The change in the current transients is mainly due to the temperature dependence of nucleation rate and diffusion coefficient. Figure 5.12 shows the $j-(t-t_0)^{1.5}$ plots of the transients shown in figure 5.11. In the range of temperature employed, linear relationships between j and $(t-t_0)^{1.5}$ were observed at the short times.

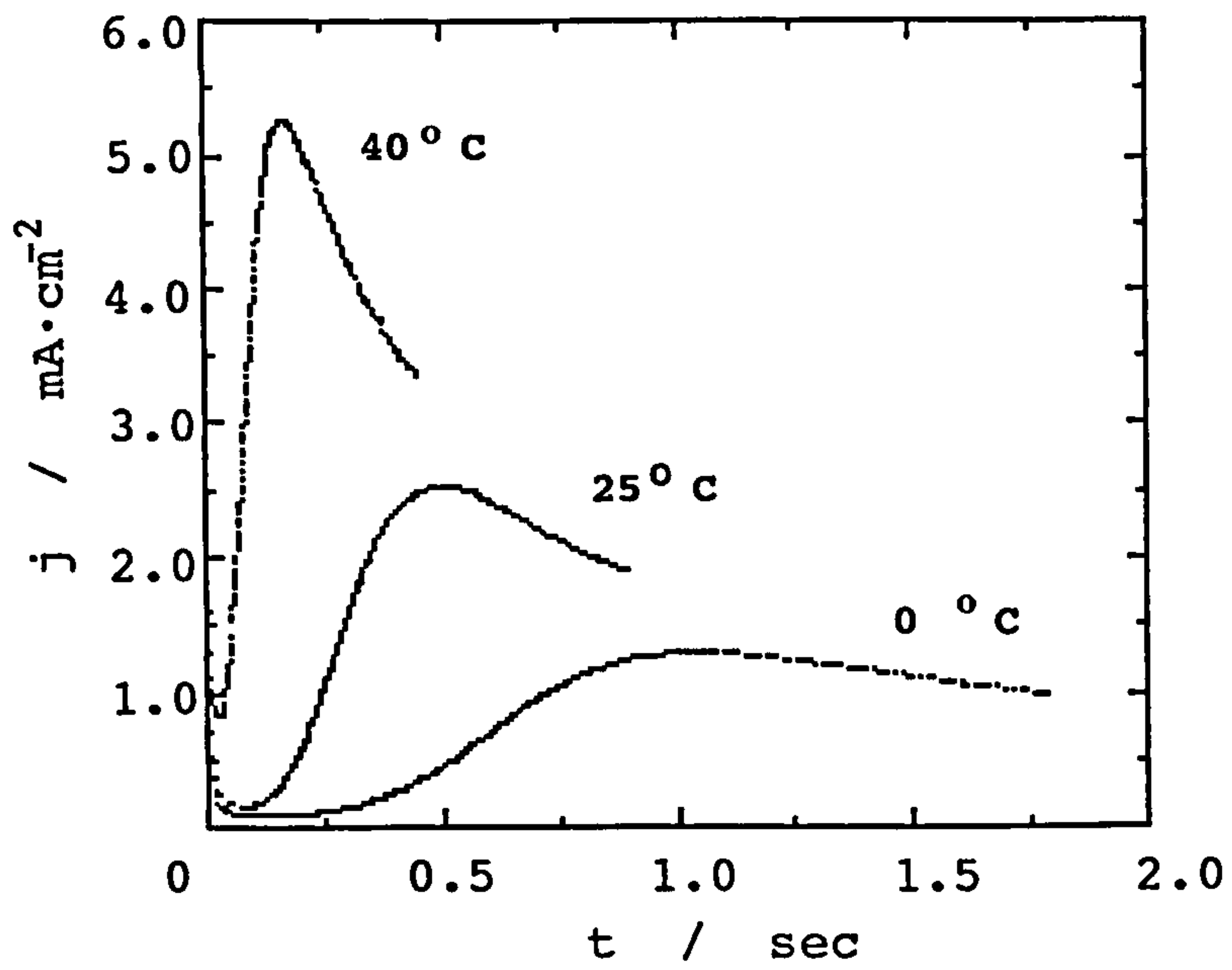


Figure 5.11 Current transients for CdTe deposition obtained at different temperatures. (potential = -560 mV)

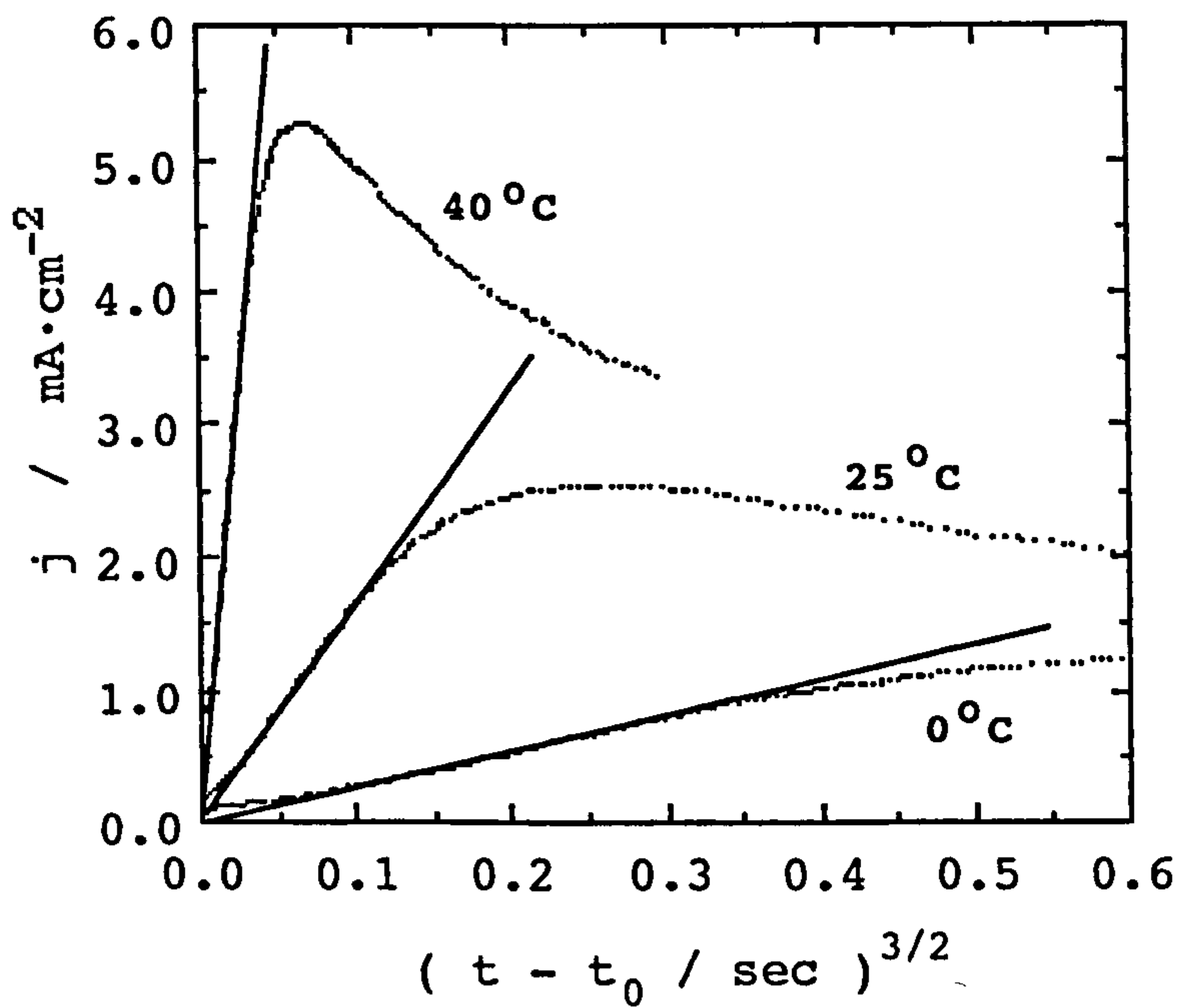


Figure 5.12 $j - (t - t_0)^{3/2}$ plots of the transients shown in figure 5.11. potential = -560 mV

The results show that, in the whole temperature region, the nucleation and growth system does not change and therefore the electrodeposition of CdTe takes place by progressive nucleation / three dimensional growth under diffusion control.

In order to obtain the nucleation rates from equation (5.3), the diffusion coefficients at different temperatures are required. The diffusion coefficients were obtained from the Cottrell plots as shown in section 5.3.1. Figure 5.13 shows the Cottrell plots at 0, 25 and 40°C. Substituting the slopes of the straight lines into equation (5.3) gives the diffusion coefficients of HTeO_2^+ . The temperature dependence of diffusion coefficient is shown in figure 5.14 as the Arrhenius plot. The Arrhenius equation is given by

$$k = A \cdot \exp\left(\frac{-E_A}{RT}\right) \quad (5.6)$$

where k is a rate constant, E_A is the activation energy and A is the frequency factor. When experiments are carried out over wide range of temperature, it is sometimes observed that the Arrhenius plot consists of several straight lines. The changes in the slopes indicate changes in activation energy indicating transition of the rate determining step. However, as a straight line was shown in figure 5.14, it was found that the rate determining single step did not change in the range of temperature. The activation energy was calculated from equation (5.6) and the value is 0.24 eV (23kJ/mol).

As described in section 5.3.2, the nucleation rates were obtained from equation (5.4). The diffusion coefficients obtained above were used for the calculation. Figure 5.15 shows the Arrhenius plot of the nucleation

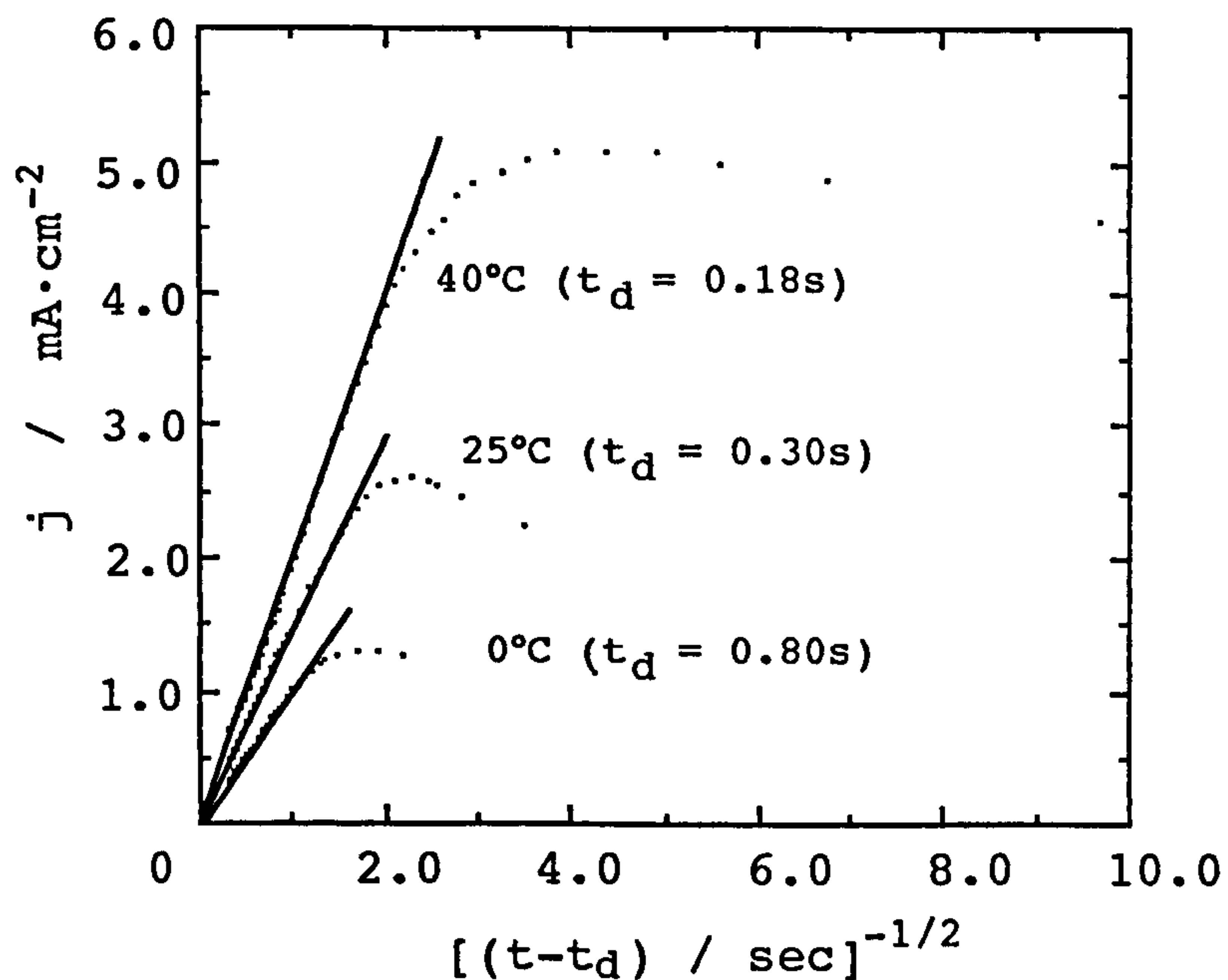


Figure 5.13 Cottrell plots for CdTe deposition measured at 0, 25 and 40°C . The induction time at each temperature is shown in this figure.
potential = -560mV

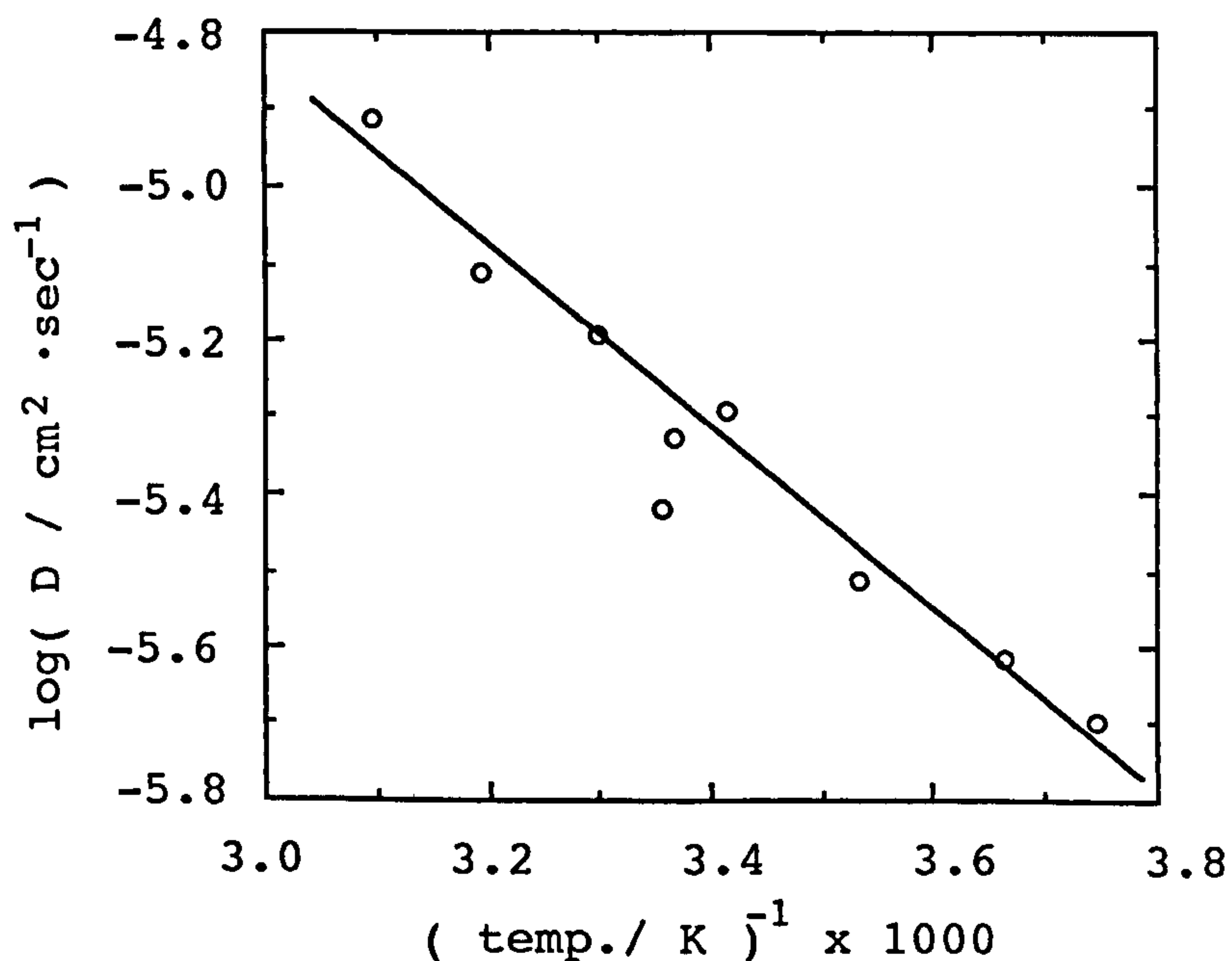


Figure 5.14 Arrhenius plot for diffusion of HTeO_2^+ . The diffusion coefficients were obtained from the Cottrell plots shown in figure 5.13.

rates. The Arrhenius plots of the nucleation rates obtained at -520 and -560mV show linear relations and the straight lines have the same slope. From the slope of these straight lines, the activation energy of formation of a nucleus can be obtained and it was found to be approximately 0.39eV (37kJ/mol).

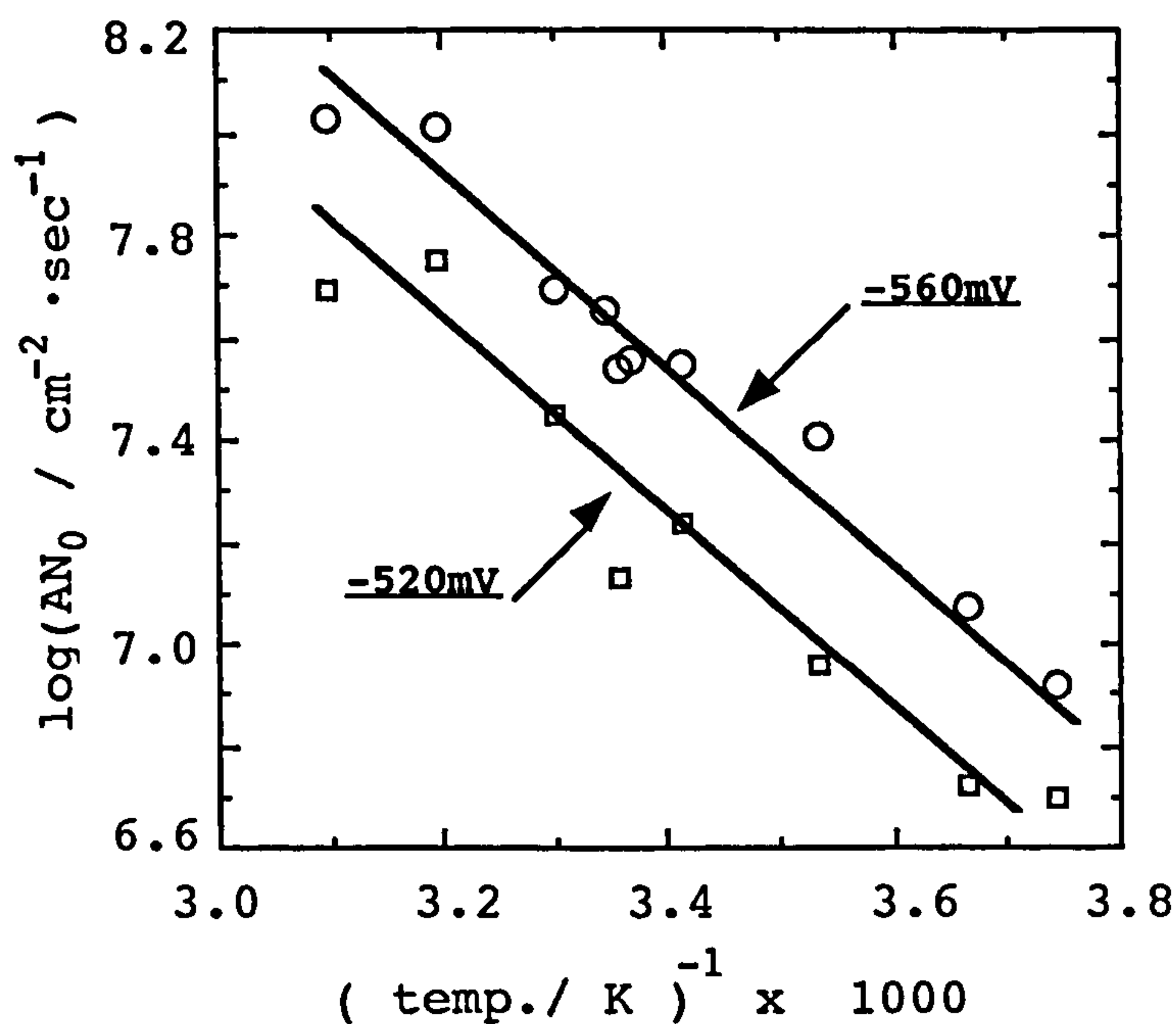


Figure 5.15 Arrhenius plots for nucleation rates obtained at -520mV and -560mV.

5.4 Quantitative discussion of the effect of temperature on nuclear number density.

The nucleation rates at different temperatures were obtained from the initial current transient curves. Although depletion of the active sites on the electrode

surface causes the decrease in the nucleation rate, particularly in the case of diffusion controlled deposition, the formation of diffusion zones also reduces the nucleation rates, because the depletion of depositing species in diffusion zones decreases the probability of nucleation. This means that the nuclear number density depends on both the nucleation rate derived at short time, AN_0 , and the growth rate of diffusion zones. From equation (2.72), the growth rate of diffusion zone is expressed as

$$S/t = \pi\lambda D \quad (5.7)$$

where $\lambda = (8\pi C_b M / \rho)^{1/2}$ and S is the base area of a diffusion zone. As the growth rate is a function of diffusion coefficient, the nuclear number density at long times depends on the nucleation rate, AN_0 , and diffusion coefficient, D . In section 5.3.3, it was shown that the nucleation rate and the diffusion coefficient become increase with temperature. The increase in nucleation rate leads a larger nuclear number density but, on the other hand, the increase in diffusion coefficient promotes the rapid growth of diffusion zones and makes the nuclear density smaller. Therefore, the overall effect of temperature on nuclear number density is not clear. A quantitative discussion is carried out in this section to make the effect clear.

The change in nucleation rates due to growth of the diffusion zones around nuclei has been reported by Markov et al.[6], Markov [7] and Scharifker et al.[8]. They have assumed that new nuclei can develop only on the electrode surface uncovered by diffusion zones (i.e. no probability of formation of new nuclei in diffusion zones). However, their assumption is too extreme, because the decrease in the probability of nucleus formation is due to a decrease in the concentration of depositing species in diffusion zones.

Therefore, as an more reasonable assumption, it is proposed that the probability of nucleus formation changes linearly with the concentration. This assumption is illustrated in figure 5.16, as well as the assumption of Scharifker et al.. In this figure, the cylindrical diffusion zones are drawn instead of hemispherical diffusion zone. As shown in equation (2.71), the conversion of hemispherical diffusion into cylindrical diffusion is also done to obtain the j-t relations. By consideration of the average probability of nucleation based on the linear model, it was found that the assumption is equivalent to one in which no nucleation occurs in area of 1/3 of the diffusion zone. The calculation to get the equivalent area is described in Appendix 5.I (a).

The extended diffusion area and the radius are given by equations (2.75) and (2.72) respectively. Substituting equation (2.72) into (2.75) yields

$$S_{\text{ext}}(t) = \pi \lambda D \int_0^t \frac{dN}{du} \cdot (t-u) \cdot du \quad (5.8)$$

where λ is $(8\pi C_b M / \rho)^{1/2}$. Gunawardena et al. [9] have given $4/3 \cdot (8\pi C_b M / \rho)^{1/2}$ for the value of λ for progressive nucleation and $(8\pi C_b M / \rho)^{1/2}$ for instantaneous nucleation. In a new equation of j-t proposed in this section, it was found that $(8\pi C_b M / \rho)^{1/2}$ can be used as the value of λ . The discussion about the value of λ is described later. Under the assumption employed, the nucleation rate at time, t, can be expressed by the product of nucleation rate observed in

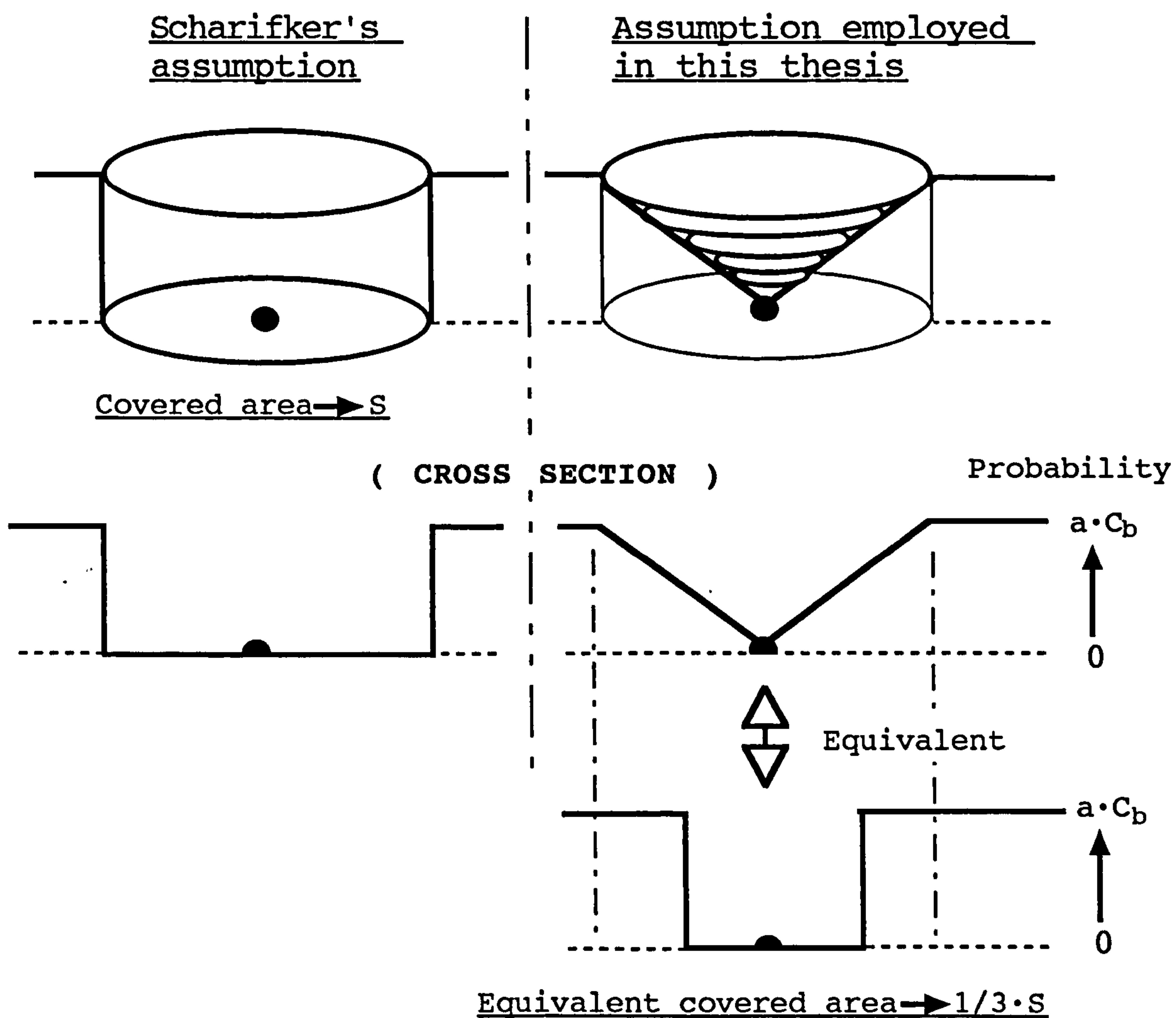


Figure 5.16 Comparison of probability profiles proposed by Scharifker et al. [8] and employed here.

Bulk probability = $a \cdot C_b$

Probability at nucleus = 0

the initial transient, AN_0 , multiplied by the normalized area uncovered with diffusion zones.

$$\frac{dN}{dt} = AN_0 \cdot \exp(-\beta \cdot S_{ext}) = AN_0 \cdot \exp(-\beta \cdot \pi \lambda D \int_0^t \frac{dN}{du} \cdot (t-u) \cdot du) \dots (5.9)$$

In this equation, β is 1/3 for the linear assumption and as derived in Appendix 5.I (a) (1 for Scharifker's assumption). The effect of β on nuclear number density is shown in Appendix 5.I (b). Integrating equation (5.9) with respect to time gives the nuclear number density at t .

$$N(t) = AN_0 \int_0^t \exp(-\beta \cdot \pi \lambda D \int_0^{\omega} \frac{dN}{du} \cdot (t-u) \cdot du) \cdot d\omega \quad (5.10)$$

Although the nucleation rate is given by equation (5.9), for the purpose of expressing nuclear number density (5.10) more plainly, Scharifker et al. assumed again that the nucleation rate is given by AN_0 (i.e. ideal progressive nucleation). Substituting AN_0 into dN/dt of equation (5.10) gives

$$N(t) = AN_0 \int_0^t \exp(-\frac{\beta \cdot AN_0 \pi \lambda D}{2} \cdot u^2) du \quad (5.11)$$

From equations (5.10) and (5.11), the nuclear number densities were calculated with a personal computer. The calculation was carried out at every 0.001 sec. As values of AN_0 and D , the experimental values obtained at 25°C were used ($AN_0 = 2.88 \times 10^7 \text{ s}^{-1} \cdot \text{cm}^{-2}$, $D = 5.3 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$). Figure 5.17 shows the nuclear number density as a function of time.

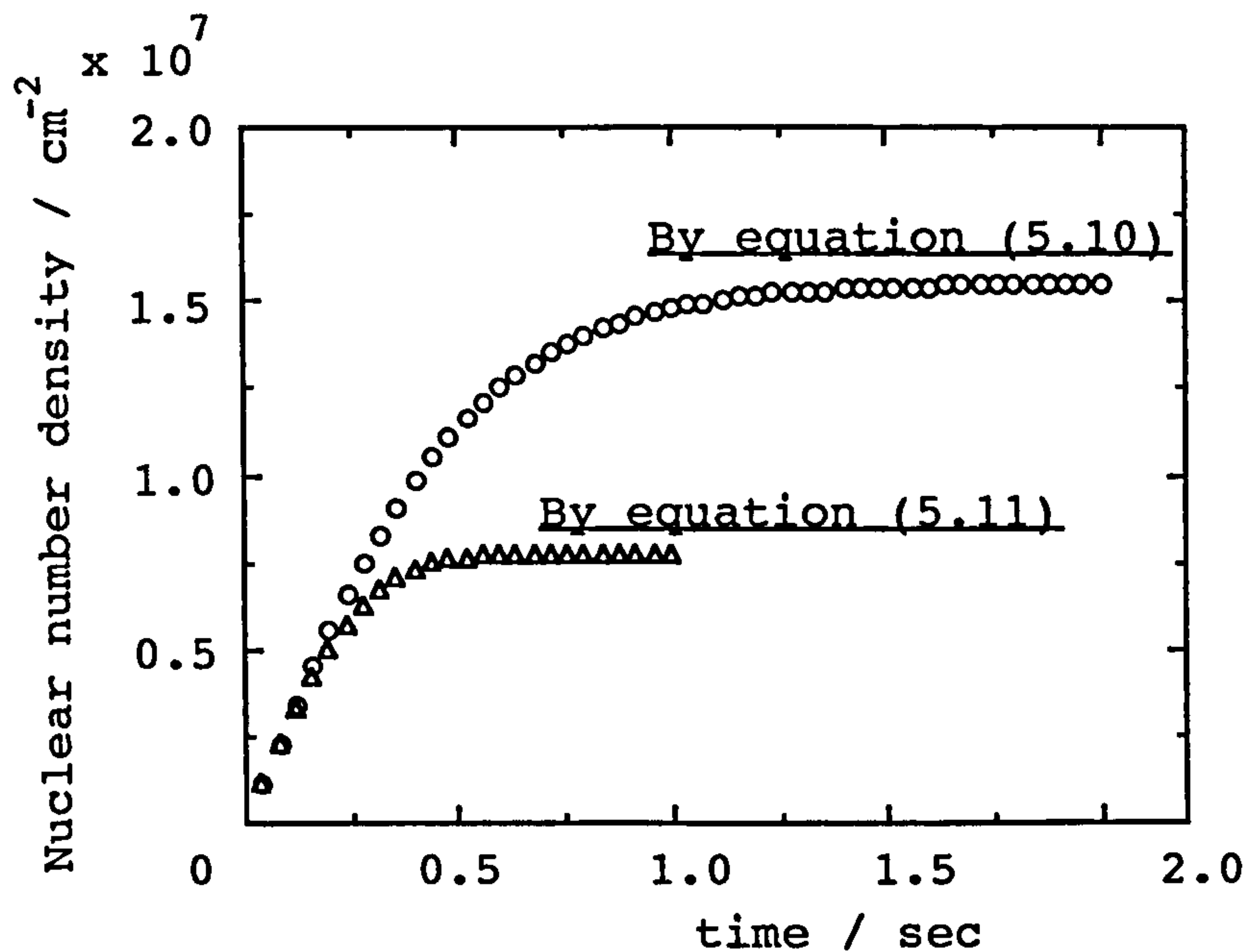


Figure 5.17 Nuclear number density calculated from Scharifker's equation (5.11) and new proposed equation (5.10).
 $AN_0 = 2.88 \times 10^7 \text{ s}^{-1} \cdot \text{cm}^{-2}$
 $D = 5.3 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$

NOTE: By setting $t \rightarrow \infty$, the saturation nuclear number density, N_s , is obtained from equation (5.11). According to the Gamma function, the integration of $\exp(-a^2t^2)$ from 0 to ∞ is given by $(1/2a)\pi^{1/2}$. Therefore, N_s obtained from equation (5.11) is expressed as

$$N_s = (AN_0 / 2\beta\lambda D)^{1/2} \quad (5.12)$$

From this equation, it is found that the saturation nuclear number density is $7.8 \times 10^6 \text{ cm}^{-2}$. Of course, the saturation nuclear number density is also obtained by calculation with the computer as shown in figure 5.17.

At short times, equations (5.10) and (5.11) give the same nuclear number density, though at longer times the nuclear number density obtained from equation (5.10) becomes two times larger than that obtained from equation (5.11). This difference is due to the approximation made by Scharifker et al. to obtain equation (5.11) from (5.10). They have regarded the nucleation rate as a constant value, AN_0 , though the nucleation rate is given by equation (5.9). The approximation yielded too large an extended diffusion area and, as the result, the smaller nuclear number density was obtained from equation (5.11).

Figure 5.18 shows the nuclear number densities at 0 °C, 25°C and 40 °C. They were calculated with equation (5.10) using experimental values of AN_0 and $D_{HTeO_2^+}$. This figure shows that the nuclear number density increases linearly with slopes of AN_0 and then with the significant overlap of diffusion zones, the rates decrease and finally the saturation nuclear number densities are obtained. From this figure, it can be seen that the calculated nuclear number density decreases and then increases with increase in temperature. However, since the nucleation rate and diffusion coefficient measured at each temperature are scattered as shown in figures 5.14 and 5.15, it is difficult to determine the effect of temperature on the saturation nuclear number density. Therefore, in order to determine the effect of temperature, the Arrhenius equations for nucleation rate and for diffusion coefficient were used as follows. As result of the calculation of equation (5.10),

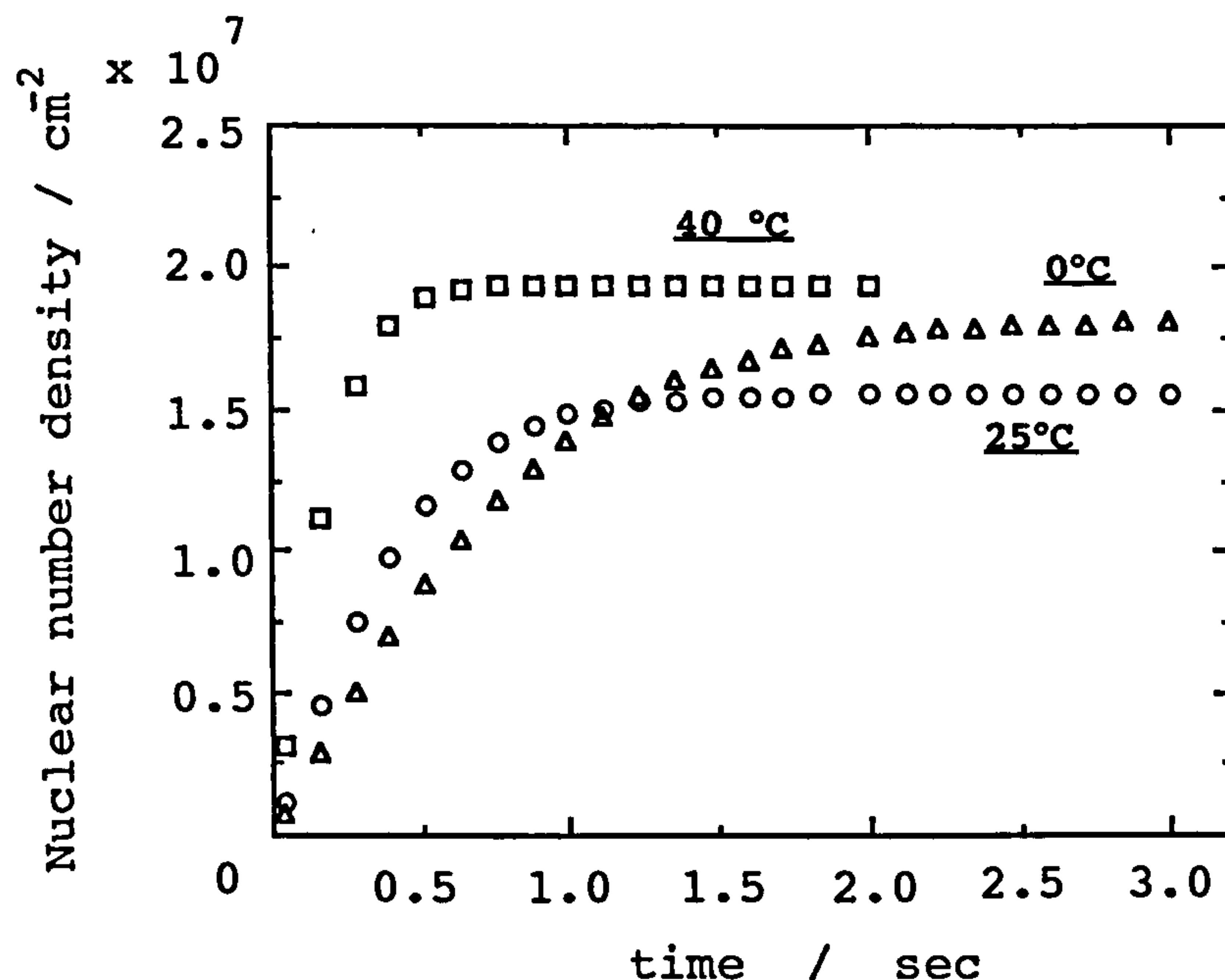


Figure 5.18 Nuclear number densities calculated from equation (5.10).

$$\begin{aligned}
 AN_0, D \text{ at } 0^\circ\text{C} &= 1.8 \times 10^7 \text{ s}^{-1} \cdot \text{cm}^{-2}, 2.4 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1} \\
 AN_0, D \text{ at } 25^\circ\text{C} &= 2.9 \times 10^7 \text{ s}^{-1} \cdot \text{cm}^{-2}, 5.2 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1} \\
 AN_0, D \text{ at } 40^\circ\text{C} &= 7.9 \times 10^7 \text{ s}^{-1} \cdot \text{cm}^{-2}, 9.2 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}
 \end{aligned}$$

it was found that the saturation nuclear number density is given by

$$N_s = 2 \cdot (AN_0 / 2\beta\lambda D)^{1/2} \quad (5.13)$$

The Arrhenius equation for the nucleation is given by

$$AN_0 = A_n \cdot \exp(-E_n/RT) \quad (5.14)$$

and for the diffusion coefficient,

$$D = A_d \cdot \exp(-E_d/RT) \quad (5.15)$$

where A_n and E_n are the frequency factor and the activation energy of nucleation and A_d and E_d are those of diffusion. Substituting equations (5.14) and (5.15) into (5.13) yields

$$N_s = (2 A_n / (A_d \beta \lambda))^{1/2} \cdot \exp((E_d - E_n) / RT) \quad (5.16)$$

The activation energies of nucleation and diffusion are 0.39eV (37.1kJ/mol) and 0.23eV (22.9kJ/mol) respectively as shown in section 5.3.3. Substituting these values into equation (5.16) gives

$$\begin{aligned} N_s &= (2 \cdot 1.35 \times 10^{14} / 0.33 \cdot 0.138 \cdot 5.89 \times 10^{-2})^{0.5} \\ &\quad \times \exp((22.9 - 37.1) \times 10^3 / 8.314 \cdot T) \\ &= 3.17 \times 10^8 \times \exp(-854/T) \end{aligned} \quad (5.17)$$

The saturation nuclear number densities obtained from equation (5.17) are shown in figure 5.19 as a function of temperature. The saturation nuclear number density increases with increase in temperature. This tendency arises from the negative value in the exponential term of equation (5.17). If the activation energy of nucleation was smaller than that of diffusion, the value in the exponential term would become positive and N_s would decrease with increase in temperature.

Thus, under the assumption that the probability of nucleation is linearly proportional to the concentration of depositing species, the effect of temperature on saturation nuclear number density is expressed by equation (5.16). The saturation nuclear number density is predicted to increase with increase in temperature and the values at 0°C, 25°C and 40°C are 1.4×10^7 , 1.8×10^7 and $2.1 \times 10^7 \text{ cm}^{-2}$, respectively.

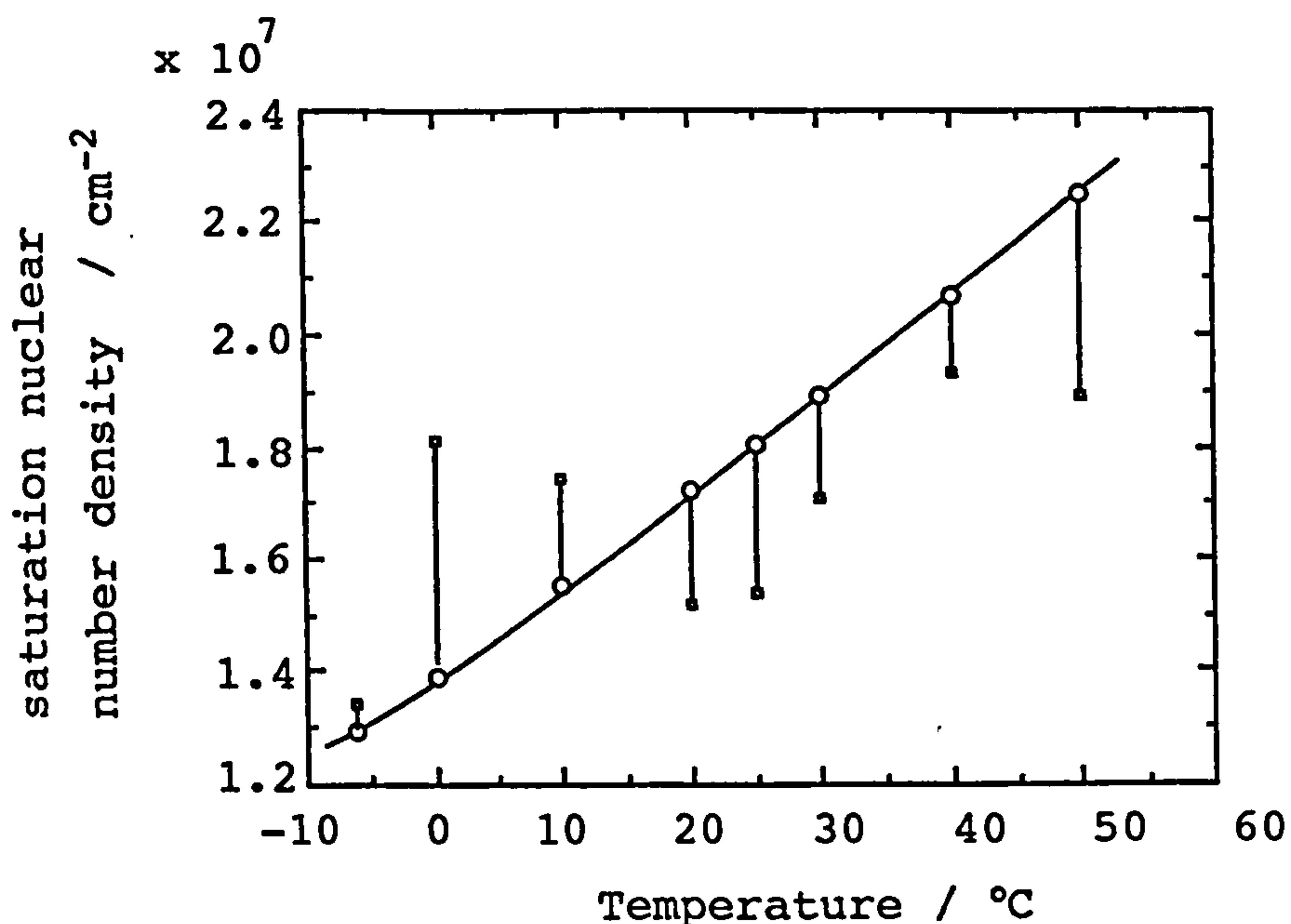


Figure 5.19 Saturation nuclear number densities obtained from equation 5.17 (o) and from equation 5.10 (▪). The results obtained from eq.(5.10) are scattered because of experimental errors in the determination of D and AN₀.

5.5 A new approach to derive the j - t relation for progressive nucleation /hemispherical growth under diffusion control.

The deposition current for instantaneous and progressive nucleation / hemispherical growth under diffusion control has been proposed by Gunawardena et al.[9] (equations 2.74 and 2.77), Scharifker et al.[10] (equation 2.81) and Sluyters et al.[11] (equation 2.87). As described in section 2.3.3, for the limiting cases of nucleation (i.e. progressive nucleation and progressive nucleation), the

equations proposed by the three groups are the same. In this section, a new equation to explain the current transient for progressive nucleation / hemispherical growth under diffusion control is proposed. Then the new equation is compared with the experimental results and the equations proposed already.

The equations proposed by the three groups have been derived by the product of the Cottrell current and active area given by Avrami's theorem. To obtain a new equation, it is considered that the deposition current can be derived by the sum of the currents flowing into each nucleus. From the Cottrell equation, the current flowing into a nucleus is given by

$$i(t) = S(t-u) \cdot \frac{nFD^{1/2}C_b}{\pi^{1/2} (t-u)^{1/2}} \quad (5.18)$$

where u is the moment of the birth of a nucleus and $S(t)$ is the surface area covered by the diffusion zone around the nucleus. From equation (2.72), $S(t-u)$ is expressed as

$$S(t-u) = \pi \cdot D \cdot \lambda \cdot (t-u) \quad (5.19)$$

where λ is $(8\pi C_b M / \rho)^{1/2}$. Equations (5.18) and (5.19) yield

$$i(t) = nF \lambda \pi^{1/2} D^{3/2} C_b (t-u)^{1/2} \quad (5.20)$$

The sum of deposition current flowing at each nucleus, $j_{\text{sum}}(t)$, is given by the following integration.

$$j_{\text{sum}}(t) = nF \lambda \pi^{1/2} D^{3/2} C_b \int_0^t \frac{dN}{du} \cdot (t-u)^{1/2} \cdot du \quad (5.21)$$

where dN/du is the nucleation rate ($\text{cm}^{-2} \cdot \text{s}^{-1}$) at time, u , given by equation (5.9). In other words, $j_{\text{sum}}(t)$ represents the current flowing into the extended surface area, $S_{\text{ext}}(t)$.

Divided by the extended surface area (equation 5.8) and multiplied by Avrami's theorem (2.54), equation (5.21) yields a new equation to express the current density, $j(t)$.

$$j(t) = \frac{j_{\text{sum}}(t)}{S_{\text{ext}}(t)} \cdot [1 - \exp(-S_{\text{ext}}(t))] \quad (5.22)$$

$$= f(t) \cdot \frac{nFD^{1/2}C_b}{\pi^{1/2}t^{1/2}} \cdot [1 - \exp(-S_{\text{ext}}(t))] \quad (5.23)$$

Here,

$$f(t) = \frac{t^{1/2} \int_0^t \frac{dN}{du} \cdot (t-u)^{1/2} \cdot du}{\int_0^t \frac{dN}{du} \cdot (t-u) \cdot du} \quad (5.24)$$

It should be noticed that equation (5.22) is given by the product of Gunawardena equation (2.74) multiplied by $f(t)$ (Gunawardena has expressed the extended area as equation (2.76), although equation (5.8) is used in the new equation proposed.).

In the case of progressive nucleation / hemispherical growth under diffusion control, the initial transient is expressed by equation (5.4) and at long times, the Cottrell equation (5.2) is established. At short time, $(1 - \exp(-S_{\text{ext}}))$ and dN/dt can be regarded as S_{ext} and AN_0 , respectively. From these approximations, equation (5.22) can be rewritten as

$$j(t) = j_{\text{sum}}(t) = nF\lambda\pi^{1/2}D^{3/2}C_b \int_0^t AN_0 \cdot (t-u)^{1/2} \cdot du$$

$$= \frac{2nFAN_0(2DC_b)^{3/2}M^{1/2}}{3\rho^{1/2}} \cdot t^{3/2} \quad (5.25)$$

Thus, it was shown that equation (5.4) can be obtained from equation (5.22). Now, consider the current at long time. At long time, $(1-\exp(-S_{ext}))$ is regarded as 1. If $f(t)$ shown in equation (5.24) becomes 1 at long times, equation (5.23) can be converted into the Cottrell equation. The values of $f(t)$ were calculated with a personal computer. The calculation was done every 0.001sec until 15sec. The result is shown in figure 5.20. As shown in this figure, $f(t)$ decreases with time and approaches to 1 (of course, $f(t \rightarrow \infty) = 1$ can be also shown analytically). Therefore, it was found that equation (5.23) tends towards the Cottrell equation at long times.

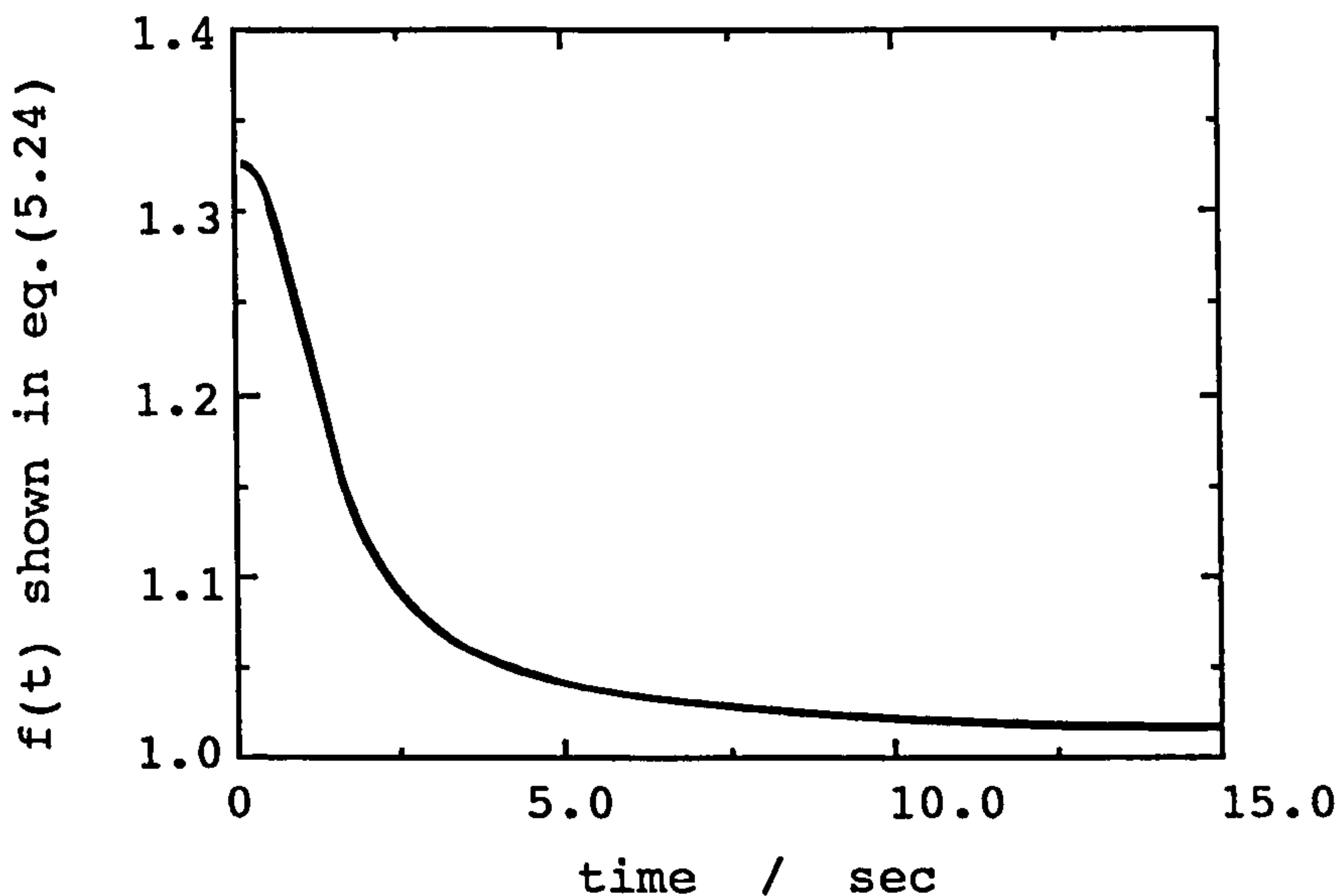


Figure 5.20 Time dependence of function, $f(t)$ shown in equation (5.24). $f(t)$ is independent of AN_0 , D , β and λ .

Figure 5.20 illustrates another interesting point namely that $f(t)$ tends towards 1.33 ($= 4/3$) at short times. As described in section 2.3.3, Gunawardena et al. [9] have proposed the following equation for progressive nucleation (Equations (5.26), (5.27) have already described in chapter 2 as equation 2.77 and 2.78, but for convenience, they are described here again).

$$j(t) = \frac{nFC_b D^{1/2}}{(\pi t)^{1/2}} \cdot [1 - \exp(-\frac{1}{2} \cdot AN_0 \pi \lambda D \cdot t^2)] \quad (5.26)$$

At short times, the equation can be rewritten as

$$\begin{aligned} j(t) &= \frac{nFC_b D^{1/2}}{(\pi t)^{1/2}} \cdot (\frac{1}{2} \cdot AN_0 \pi \lambda D \cdot t^2) \\ &= \frac{nF \pi AN_0 (2DC_b)^{3/2} M^{1/2}}{2\rho^{1/2}} \cdot t^{3/2} \end{aligned} \quad (5.27)$$

where λ is $(8\pi C_b M/\rho)^{1/2}$. The equation is different from equation (2.69) and it is obvious that the current obtained from (5.4) is 4/3 larger than that obtained from equation (5.27). To compensate the difference, there were two choices. The choices are

$$j(t) = \frac{4}{3} \cdot \frac{nFC_b D^{1/2}}{(\pi t)^{1/2}} \cdot [1 - \exp(-\frac{1}{2} \cdot AN_0 \pi \lambda D \cdot t^2)] \quad (5.28)$$

or

$$j(t) = \frac{nFC_b D^{1/2}}{(\pi t)^{1/2}} \cdot [1 - \exp(-\frac{4}{3} \cdot \frac{1}{2} \cdot AN_0 \pi \lambda D \cdot t^2)] \quad (5.29)$$

However, equation (5.28) becomes $\frac{4}{3} \cdot nFC_b D^{1/2} \cdot (\pi t)^{-1/2}$ at long times and 4/3 times larger current is given by equation (5.28) than the current expected by the Cottrell equation. Therefore, Gunawardena et al. employed equation (5.29). For the compensation, Gunawardena et al. have given $\frac{4}{3} \cdot (8\pi C_b M/\rho)^{1/2}$ to λ for progressive nucleation. By giving

λ the value $4/3 \cdot (8\pi C_b M / \rho)^{1/2}$, equation (5.26) can be converted into equation (5.4) at short time and into the Cottrell equation at long time. However, by the compensation, the spread of diffusion zones becomes 4/3 times faster than the theoretical rate (see equation 5.19). Therefore, the compensation is an undesirable method. In the case of the new equation (5.23), since $f(t)$ in equation (5.24) gives 4/3 at short time and 1 at long time, the compensation of λ is not needed and $(8\pi C_b M / \rho)^{1/2}$ can be used as a value of λ . Therefore, equation (5.23) can express the whole range of transients without any undesirable compensation.

Thus, equation (5.23) can be expected to fit well with experimental results. Let us compare the experimental current transients to the equations proposed by Gunawardena et al. (5.26) and proposed here (5.23). For progressive nucleation, the equations proposed by Gunawardena et al., Scharifker et al. and Sluyters et al. become the same equation. Therefore, Gunawardena equation is used for the following comparison. Figure 5.21 shows the transients obtained by Gunawardena equation (5.26), the modified Gunawardena equation (5.30), the equation proposed here (5.23) and the experimental transient. As the Gunawardena equation is proposed for ideal progressive nucleation, the extended diffusion area is given by equation (2.76). However, it is more likely that the extended diffusion is given by equation (5.8). Therefore, the Gunawardena equation was modified by using equation (5.8) instead of equation (2.76). Namely,

$$j(t) = \frac{nFC_b D^{1/2}}{(\pi t)^{1/2}} \cdot [1 - \exp(-\pi \lambda D \int_0^t \frac{dN}{du} \cdot (t-u) \cdot du)] \quad (5.30)$$

where λ is $4/3 \cdot (8\pi C_b M)^{1/2}$. In figure 5.21, the experimental transient measured at 25°C, -560mV was used for the comparison. The diffusion coefficient and nucleation rate obtained experimentally were used for the calculation of the equations. The values are $5.27 \times 10^{-6} \text{ cm}^2 \cdot \text{sec}^{-1}$ and $2.88 \times 10^7 \text{ cm}^{-2} \cdot \text{sec}^{-1}$, respectively. Figure 5.21(a) shows the comparison between the experimental result, Gunawardena equation (5.26) and the modified equation (5.30). In Gunawardena equation, it has been assumed that the nucleation rate is constant. However, since the nucleation rates should decrease with time, the constant nucleation rate leads too high nuclear number indicating too large extended diffusion area, S_{ext} . Because of the too large S_{ext} , Gunawardena equation (5.26) shows that the current increases rapidly at short times and then also decreases rapidly at longer times. For the modified Gunawardena equation (5.30), the time giving the peak current shows good agreement with the experimental result. The good agreement is probably attributable to the reasonable S_{ext} . However, the peak current given by equation (5.30) is obviously too small. As shown in figure 5.21(b), equation (5.23) shows the best fit with the experimental transient. Especially, in the initial part and the longer part of the transient, the equation shows a perfect fit. However, this equation gives approximately 10% smaller peak current than the experimental transient. The reason for the smaller peak current is not clear, but it may be due to assuming that the diffusion zones are not hemispherical but cylindrical. Figure 5.22 shows the comparison with the experimental transients obtained at different temperatures. In this figure, the two equations proposed by Gunawardena and the equation proposed here are used. As the transient measured at 0°C has an induction time of 0.095sec, $(t-t_0)$ is used instead of t . The induction time of transients obtained at 25 and 40°C was zero. From these figures, it is obvious

that equation proposed here shows much better agreement with the experimental results. Especially, in the case of a slow nucleation process, equation (5.23) shows excellent fit (see the transient measured at 0°C). From the good fit to the transients measured at different temperatures, it can be expected that equation (5.23) is applied not only to a particular case, but also to more general cases.

In Appendix 5.I (c), the effect of β on the transient obtained from equation (5.23) is described. Appendix 5.II shows the program to calculate equations (5.23), (5.24) and (5.30).

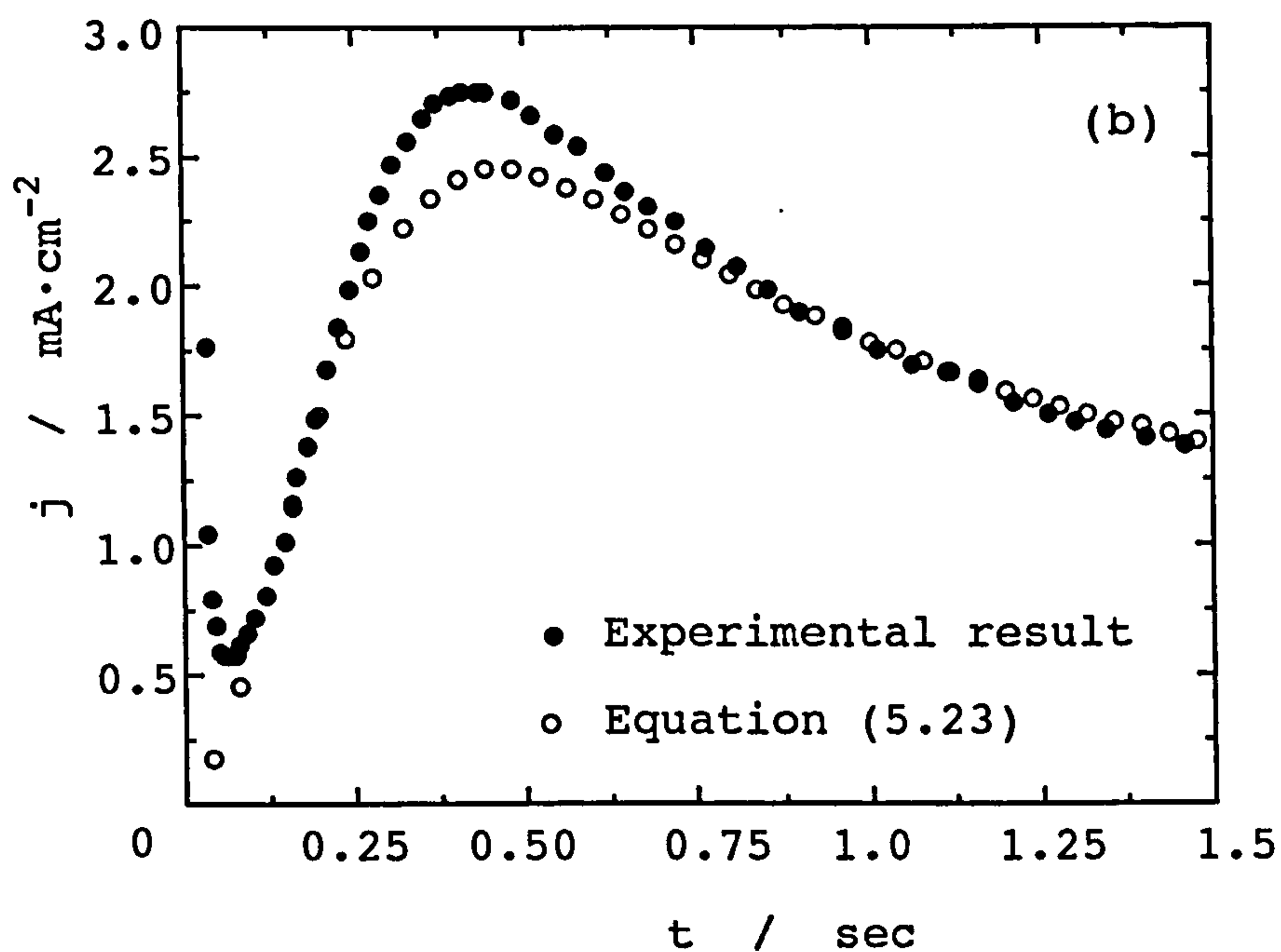
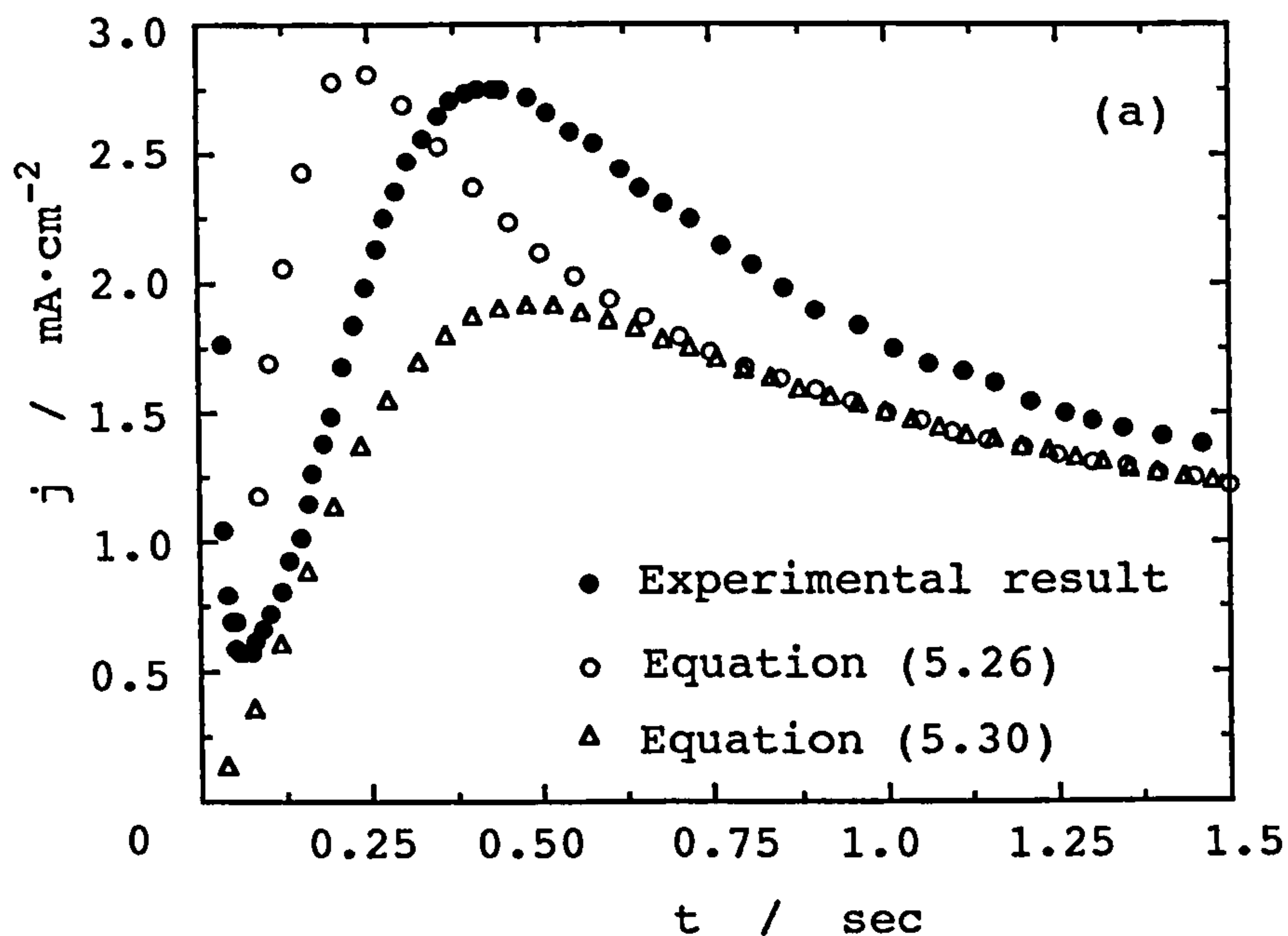


Figure 5.21 Comparison of transients obtained experimentally and theoretically.

Experimental condition : 25°C, -560mV vs.SCE

Equation (5.26) : Gunawardena equation

Equation (5.30) : Modified Gunawardena equation

Equation (5.23) : New equation proposed here

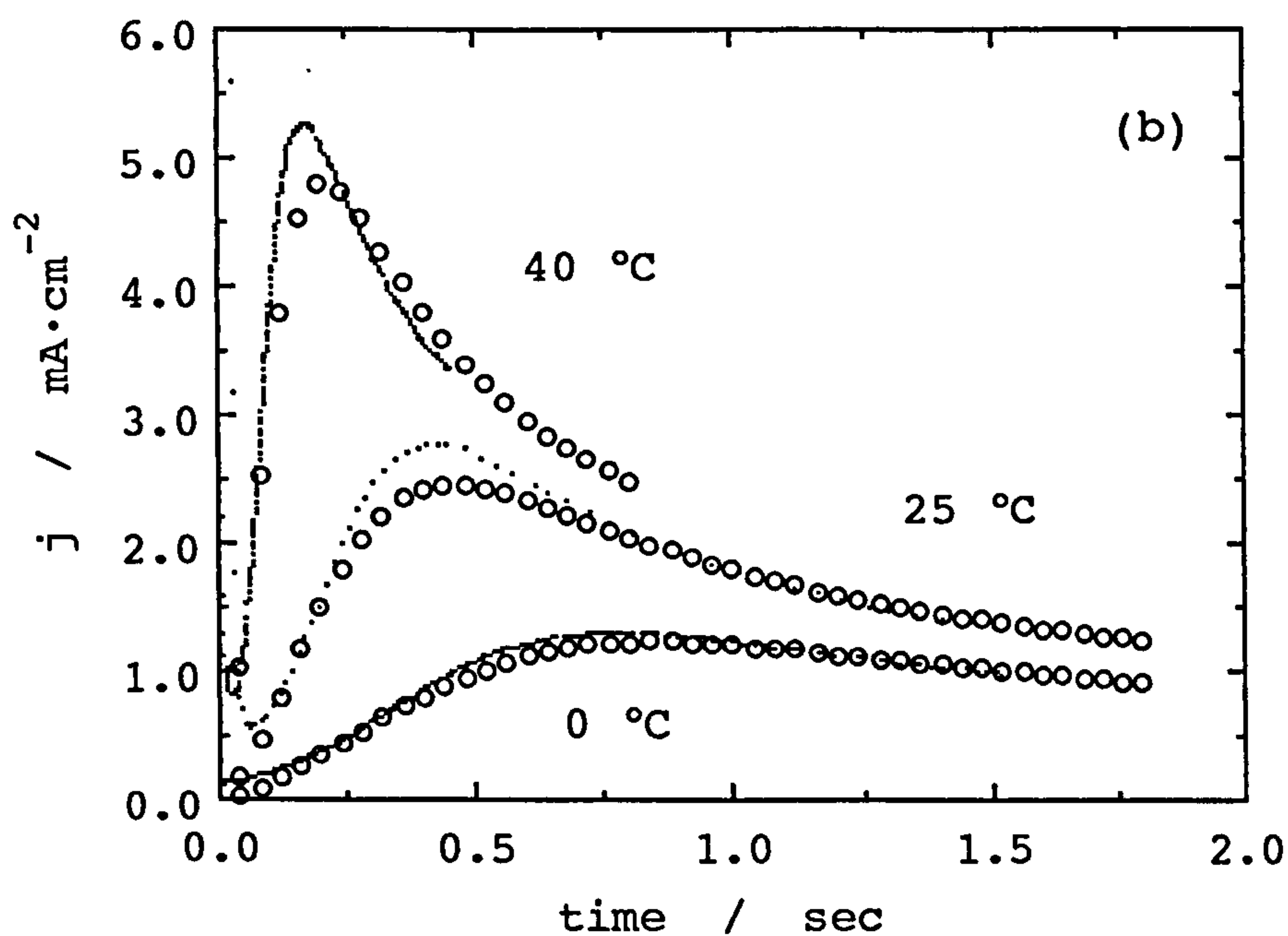
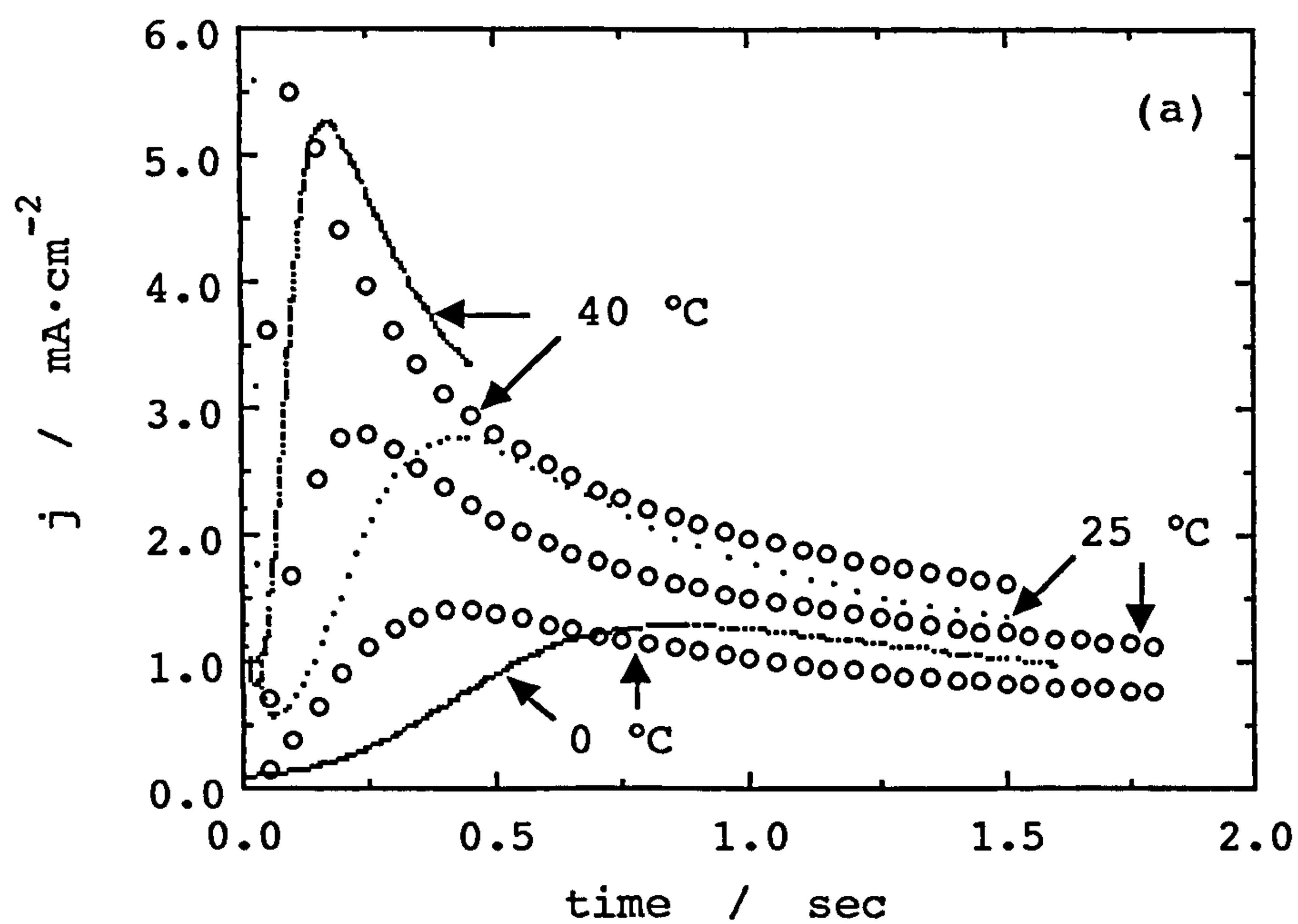


Figure 5.22 Comparison of transients obtained experimentally and theoretically.
 (a) : Gunawardena equation (5.26),
 (b) : new equation proposed here.

ooo : Calculation results : Experimental results
 Experimental conditions : 0, 25 and 40°C
 at -560mV vs. SCE

5.6 Conclusions

Electrocrystallization studies of CdTe were carried out with a tin oxide coated glass electrode. Then, theoretical considerations led to the development of a new equation for the deposition current of progressive nucleation / hemispherical growth under diffusion control. From the results obtained, the following conclusions can be drawn.

- (I) From voltammetric studies, it has been shown that large overpotentials are required for formation of the nuclei. By SEM, it was observed that the pure Te deposits are dendritic and CdTe deposits are hemispherical. The results of EDAX indicated that the CdTe film included some amount of pure Te.
- (II) From the analysis of the current transients for CdTe deposition, it was shown that CdTe deposition takes place by progressive nucleation / hemispherical growth under diffusion control. The conclusion is supported by the establishment of the Cottrell relation at longer times and, in addition, observation of the deposit.
- (III) The nucleation rates were obtained from the transient curves. The dependence of nucleation rate on overpotential could be explained by the atomistic nucleation theory. From the atomistic theory, it has been shown that the number of atoms in the critical nuclei is zero. This means that an active site of the substrate will play the role of a critical nucleus.
- (VI) Under the assumption that nucleation rate is linearly proportional to the concentration of depositing species, the effect of temperature on saturation nuclear number density has been considered. Since the experimental errors in the

determination of D and AN_0 were rather large, the investigation of the effect has been done by equation (5.16) proposed from consideration of the Arrhenius equation (the activation energies of nucleation and diffusion were obtained from the Arrhenius plots). Equation (5.16) suggests that the saturation nuclear number densities showed increase with increase in temperature.

(V) From theoretical considerations of the current transient for progressive nucleation / hemispherical growth under diffusion control, a new equation (equation 5.23) has been proposed. This equation showed better agreement with the experimental results than equations proposed previously in the literature.

Appendix 5.I (a) How to deal with the assumptions employed.

Consider the average probability of nucleation in the diffusion zone. The assumption proposed by Scharifker and proposed here are illustrated in figure 5.16. In the case of Scharifker's assumption, the probability of nucleation in the diffusion zone is zero. According to the assumption employed here, as the nucleation probability is a function of the concentration, the probability is given by

$$P(c) = a \cdot c \quad (5I.1)$$

where a is a constant and c is the concentration ($a \cdot c_b$ is the probability outside the diffusion zone). If the concentration can be regarded to be proportional linearly to distance from the nucleus,

$$C(x) = (c_b / r) \cdot x \quad (5I.2)$$

where x is the distance from the nucleus and r is the radius of the diffusion zone. Substituting equation (5I.1) in (5I.2) yields

$$P(x) = a \cdot (c_b / r) \cdot x \quad (5I.3)$$

where $P(x)$ is the nucleation probability at a distance, x . The whole probability of nucleation in the diffusion zone is given by the integration of equation (5I.3).

$$\begin{aligned} P &= \int_0^r 2\pi x \cdot a(c_b/r) \cdot x \, dx \\ &= (2/3) \cdot \pi a c_b r^2 \end{aligned} \quad (5I.4)$$

Since the probability in an area of πr^2 is given by $\pi r^2 \cdot a c_b$, it can be considered that $1/3 \cdot \pi r^2 \cdot a c_b$ of probability decreases by the formation of a nucleus. From these calculations, it is found that the probability in the

diffusion zone is 1/3 lower than outside the diffusion zone on average. The decrease by a factor of 1/3 of probability is equivalent to zero probability in an area of 1/3 of the diffusion zone. Therefore, although Scharifker assumed no nucleation in the diffusion zone, according to the assumption employed here, it can be considered that no nucleation occurs in an area of 1/3 of the diffusion zone.

Appendix 5.I (b) Effect of β on nuclear number density.

Figure 5I.1 shows the nuclear number densities obtained by equation (5.10). The nuclear number densities were calculated with two values of β , 0.33 and 1. 0.33 is a value for the assumption employed here and 1 is one for Scharifker's assumption. $\beta = 1$ gives larger extended diffusion area, compared with that $\beta = 0.33$. Therefore, in the case of $\beta = 1$, the nuclear number density saturates earlier and gives a lower saturation nuclear density.

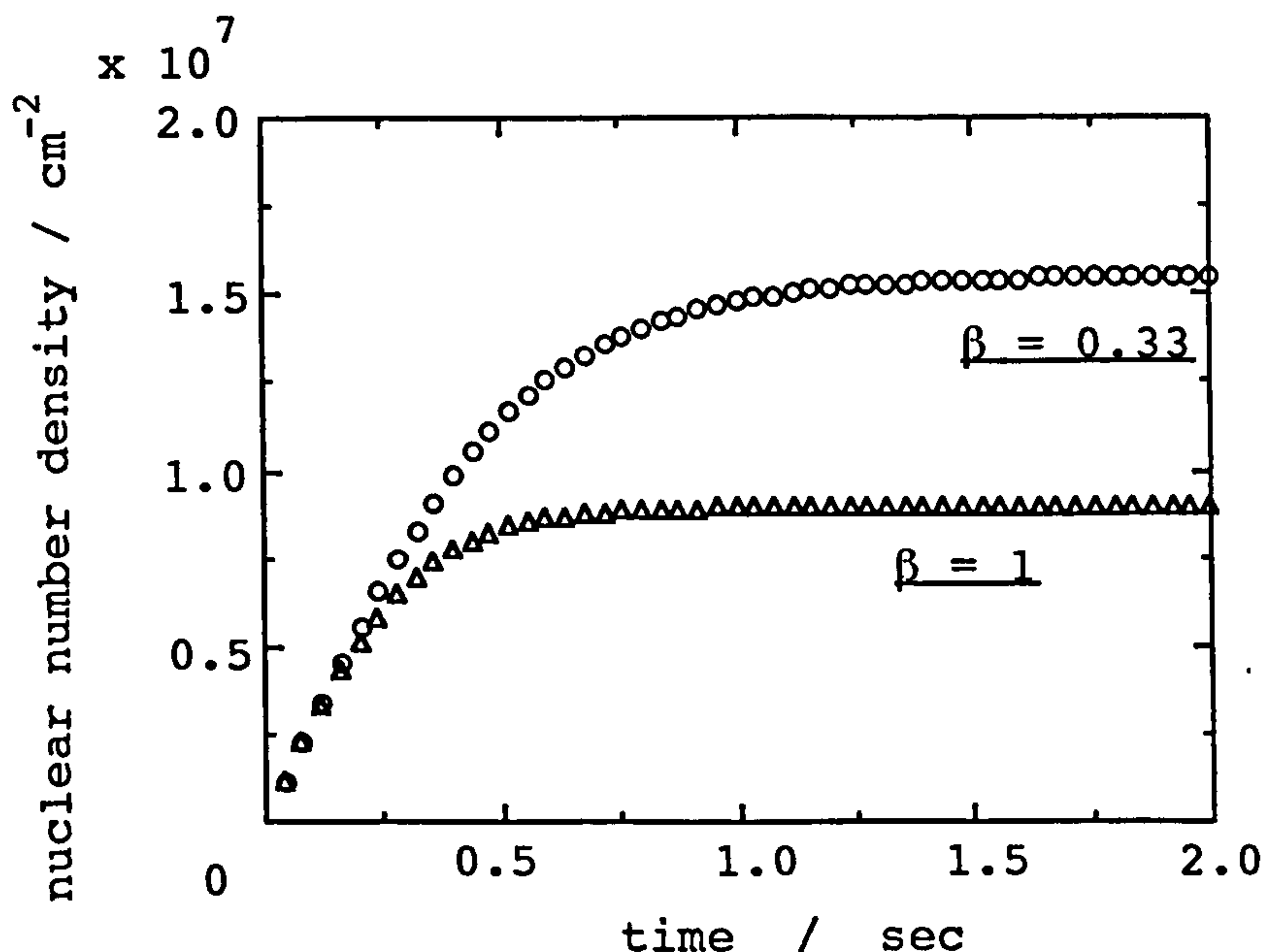


Figure 5I.1 Effect of β on nuclear number density.

$\beta = 0.33$ from the assumption proposed here.

$\beta = 1$ from the assumption proposed by Scharifker.

Appendix 5.I (c) Effect of β on current density.

Figure 5I.2 shows the current densities obtained from equation (5.23). The calculation results are shown with the experimental result. The experimental result was obtained at 25°C, -560mV. A large difference is observed between the saturation nuclear number densities obtained from the two values of β . However, in terms of current density, as shown in figure 5I.2, relatively similar current densities are obtained from the two values of β . When the peak currents are compared, it is found that $\beta = 0.33$ gives closer current to the experimental result than $\beta = 1$. The result suggests that Scharifker's assumption ($\beta = 1$) overestimates the influence of depletion of the depositing species. However, for the assumption employed here, it is possible that the influence of the depletion is still overestimated. If a smaller value of β than 0.33 is substituted into equation (5.23), it is expected that the peak current obtained from equation (5.23) will approach closer to the peak current by the experiment.

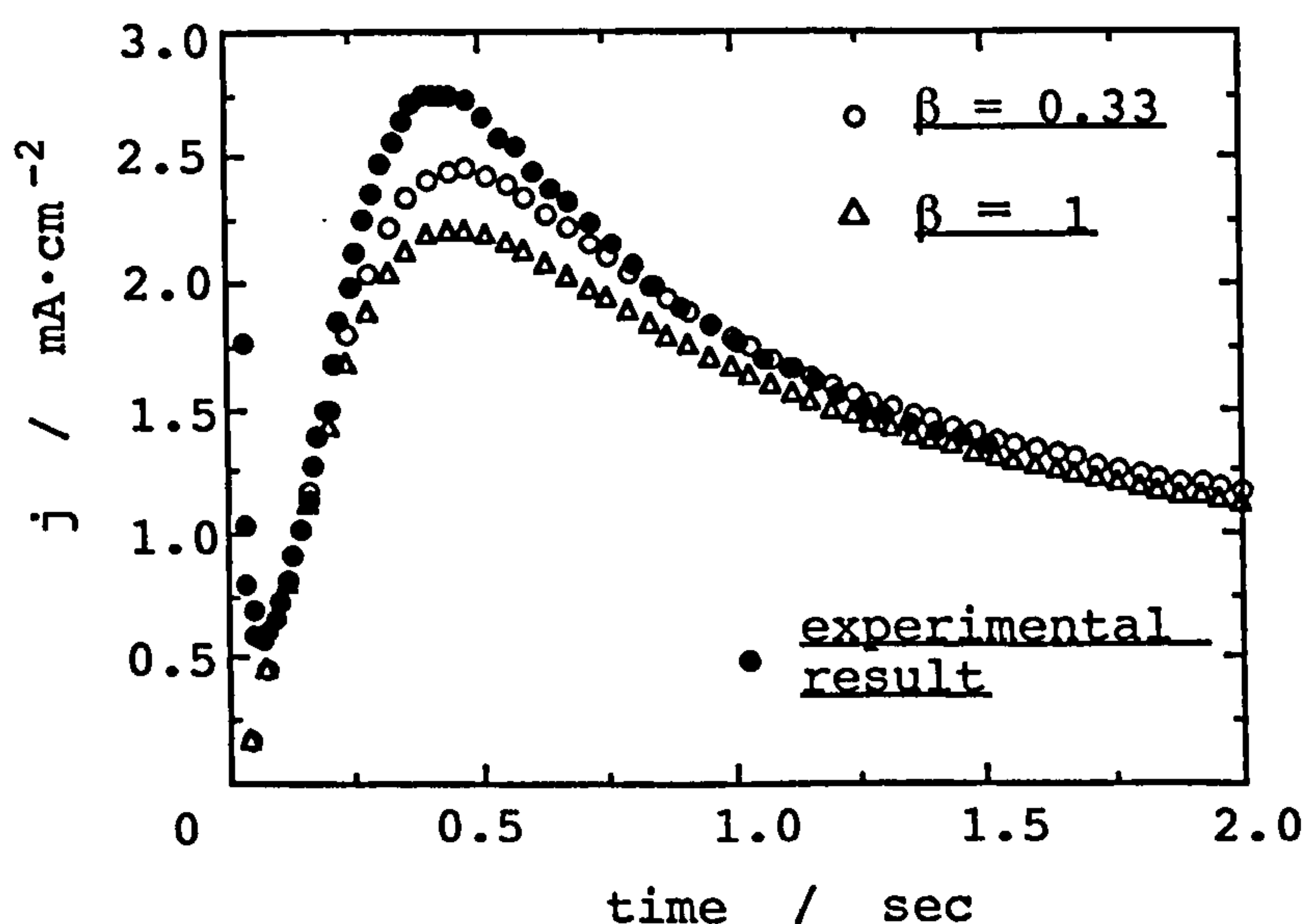


Figure 5I.2 Effect of β on current density calculated from equation (5.23). The experimental data were obtained at -560mV (25°C).

Appendix 5.II FORTRAN program used in this chapter.

Equations(5.23), (5.24) and (5.30) are calculated by this program. Equation (5.23) is an equation proposed in this chapter. Equation (5.24) is a function used in equation(5.23) and is referred to as $f(t)$ in the text. Gunawardena equation was modified and the modified equation (5.30) can be calculated by this program.

```

C      PROGRAM  3D GROWTH
* ***  3-D NUCLEATION CURRENT BY YOSHI'S IDEA ***
*
*      We can get current transients for progressive
*      nucleation/hemispherical growth under diffusion
*      control. The program can calculate the modified
*      Gunawardena equation (5.30) and the new equation
*      proposed in the text. The current is calculated at
*      every 0.001sec.
*
*      j2 :      current by equation (5.23)
*      j1 :      current by modified Gunawardena equation
*                (5.30) (select 1.8419 for SELECT)
*      A  :       $f(t)$  shown in equation (5.24)
*      NUM :      nucleation number density
*      CON :       $\beta$  in the text. 0.33 (under my assumption)
*                1 (under Gunawardena's)
*      SELECT :  $\lambda$  in the text.  $(8\pi C_b M/\rho)^{1/2} = 0.13814$ 
*                 $4/3 \cdot (8\pi C_b M/\rho)^{1/2} = 0.18491$ 
*
*      INTEGER M,E,MAX
*
*      REAL DELTANUM,NUM,TIME,DELTA,RATE,CON,j1,j2,A,SELECT,
+      DIF,DELTATHETA1,DELTATHETA2,DELTATHETA3,DELTATHETA4
      REAL AREA(0:20000)
*
*      CHARACTER*18 fileloc
*      CHARACTER*8 name
*      CHARACTER*32 place
*      CHARACTER*4 dat
*
*      *****
*
*      fileloc ='c:\PROFOR\F77DATA\'

```

```
dat='.dat'
*
print*, 'enter filename for data.(max 8 characters).. '
read*,name
place = fileloc//name//dat
print*, place
OPEN(10,FILE=PLACE)
*
PRINT*, ' '
PRINT*, 'DIFFUSION COEFFICIENT ?'
READ*, DIF
PRINT*, 'NUCLEATION RATE ?'
READ*, RATE
PRINT*, 'MAXIMUM CALCULATION STEPS ?(LESS THAN 20000)'
READ*, MAX
PRINT*, 'CONSTANT TO COMPENSATE DIFFUSION AREA?...'
READ*, CON
PRINT*, 'WHICH VALUE OF K 0.13814 OR 0.18419...'
READ*, SELECT
*
NUM = 0
DELTATHETA2 = 0
DELTATHETA4 = 0
DELTA = 0.001
*
DATA AREA/ 20001*0/
*
DO 100 M =1,MAX
  DELTATHETA2 = 0
  DELTATHETA4 = 0
  TIME = DELTA * M
  DELTANUM = RATE * DELTA * EXP(-1 * AREA(M-1))
  NUM = NUM + DELTANUM
*
  DO 200 E = 1,M
    DELTATHETA1 = (M-E+1) * EXP(-1*AREA(E-1))
    DELTATHETA2 = DELTATHETA2 +DELTATHETA1
    DELTATHETA3 = (M-E+1)**0.5 * EXP(-1*AREA(E-1))
    DELTATHETA4 = DELTATHETA4 + DELTATHETA3
*
200  CONTINUE
  AREA(M) =DELTA*DELTA*RATE*CON*SELECT*DIF*DELTATHETA2
  PRINT*,AREA(M),M
*
  IF( MOD( M, 40 ) .EQ. 0 ) THEN
    j1 =6*96485*0.000002*(DIF**0.5)/(3.1415*TIME)**0.5*
+    (1-EXP(-1*AREA(M)/CON))*1000
    A = DELTATHETA4/DELTATHETA2*M**0.5
    j2 = A*j1
    PRINT 6000 , TIME, NUM, j1,j2,A
    WRITE(10,6000) TIME,NUM,j1,j2,A
6000  FORMAT(1H , 5X, F7.4, 5X, E10.5, 5X,
```

```
      +          F10.4,5X,F10.4,5X,F6.4)
      END IF
100  CONTINUE
      CLOSE(10)
      STOP
      END
```

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CHAPTER 6.

ELECTRODEPOSITION OF CdTe ON n-TYPE
MONOCRYSTALLINE SILICON.

- 6.1 Introduction.
- 6.2 Nucleation and growth.
 - 6.2.1 Electrochemical approach.
 - 6.2.2 Characterization of electrodeposited films.
- 6.3 Photoeffects during electrodeposition.
- 6.4 Conclusions.
- Appendix 6.I Dependence of photocurrent on
light intensity.
References.

6.1 Introduction.

The electrodeposition of CdTe on monocrystalline n-type silicon has been studied. Although several papers for cathodic deposition of metals and semiconductors on p-type semiconductors have been published [1,2], no report of CdTe electrodeposition on n-type silicon substrates has appeared yet. In section 6.2, the studies of electrocrystallization and growth of CdTe on n-type silicon in the dark are discussed. In section 6.3, photoeffects observed during electrodeposition are described. Cathodic photocurrents under illumination during the deposition of CdTe were reported by Mishra et al.[3]. They interpreted the currents as evidence that the film behaves as a p-type semiconductor. However, it is shown that the mechanism of photocurrent generation is more complicated than suggested by Mishra et al..

6.2 Nucleation and growth.

As silicon substrates, monocrystalline n-type silicon with (100), (110) and (111) orientations was used for the studies of CdTe electrodeposition in the dark. The removal of surface oxide is the key technique to get reproducible results. The method for the removal of surface oxide is described in section 3.3. In order to prevent formation of oxide on the silicon surface during deposition, ammonium fluoride was added into the electrolyte. The composition of the solution is shown in Table 3.1(c).

6.2.1 Electrochemical approach.

As the first study on silicon electrodes, cyclic voltammograms were recorded. The first cycles of the

voltammograms on (100), (110) and (111) faces are shown in figure 6.1. These figures shows the similarity among these three voltammograms. At -250mV, a cathodic current wave was observed. The cathodic currents reached maximum values in a potential range of -430 to -500mV. The increase in current in this potential region is influenced by nucleation and growth processes. After the peaks, the currents decreased indicating overlap of deposits or overlap of isolated diffusion zones. Then, pure Cd deposition was observed at about -680mV. On the anodic scan, the cathodic current density at -600mV was roughly $-200\text{mA}\cdot\text{cm}^{-2}$. As shown in figure 5.2, the diffusion limiting current obtained on TO is $-200\text{mA}\cdot\text{cm}^{-2}$. The comparison with figure 5.2 suggests that the deposition rate in this potential region is controlled by diffusion of HTeO_2^+ . Finally, the deposition current disappeared at -100mV. Since n-type silicon was used, the anodic dissolution of the deposits could not occur in the dark.

The largest differences between the voltammograms were observed in the early deposition region. The origin of the differences may be associated with nucleation. In order to study nucleation of CdTe on n-type silicon, current transient curves were measured by the following potential step method. The electrode potential was kept at -200mV by using a substitute electrode (Pt), prior to immersion of silicon electrodes into the electrolyte. Then the silicon electrode was immersed into the electrolyte and the electrode potential was shifted immediately from -200mV to -660mV (potential for measurements). The transient curves observed on the three different crystal faces are shown in figure 6.2. The initial currents increased linearly with the deposition time.

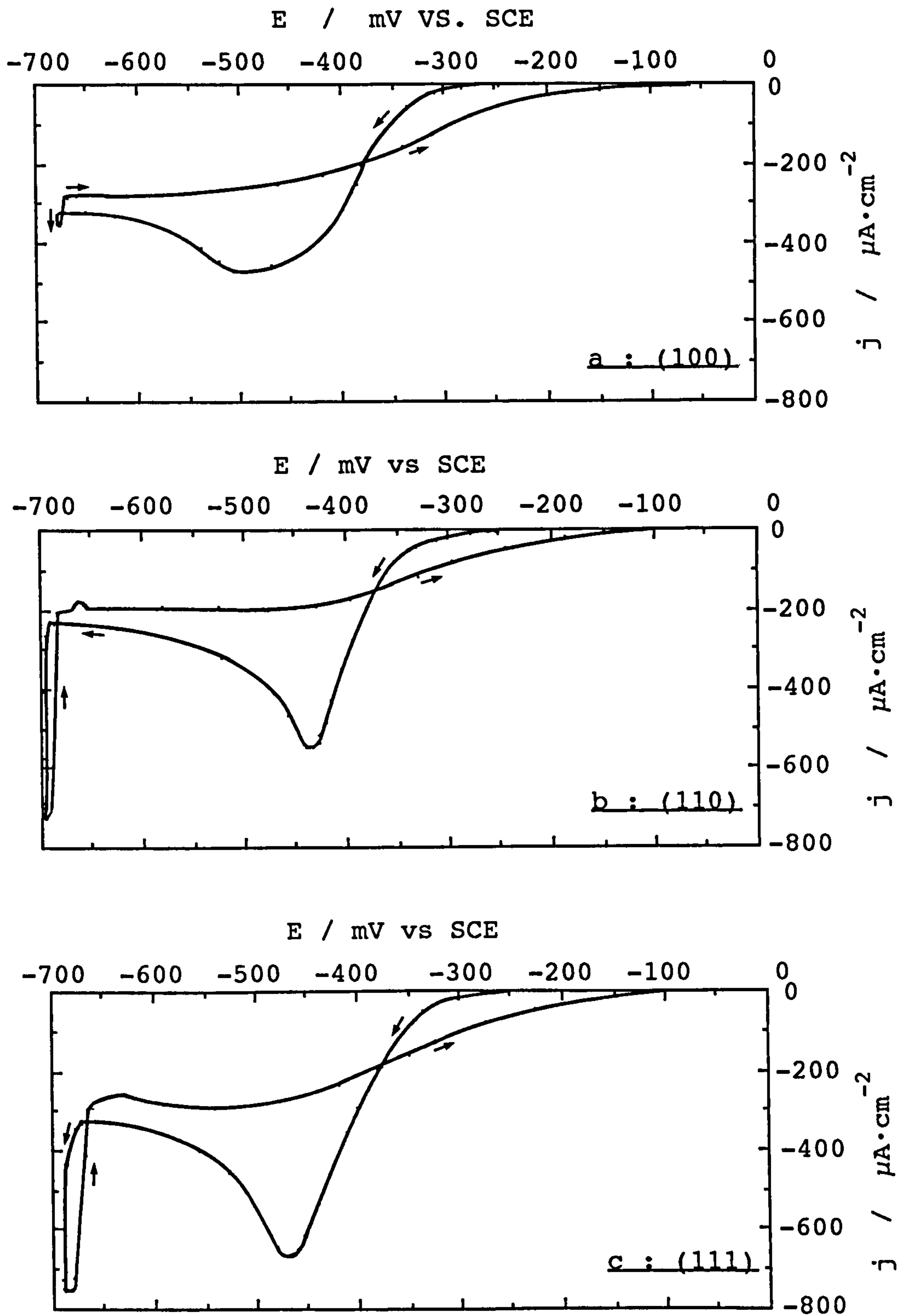


Figure 6.1 Cathodic cyclic voltammograms
(first cycle) obtained on a:(100),
b:(110) and c:(111) silicon surfaces.
scan rate : $5\text{mV}\cdot\text{sec}^{-1}$

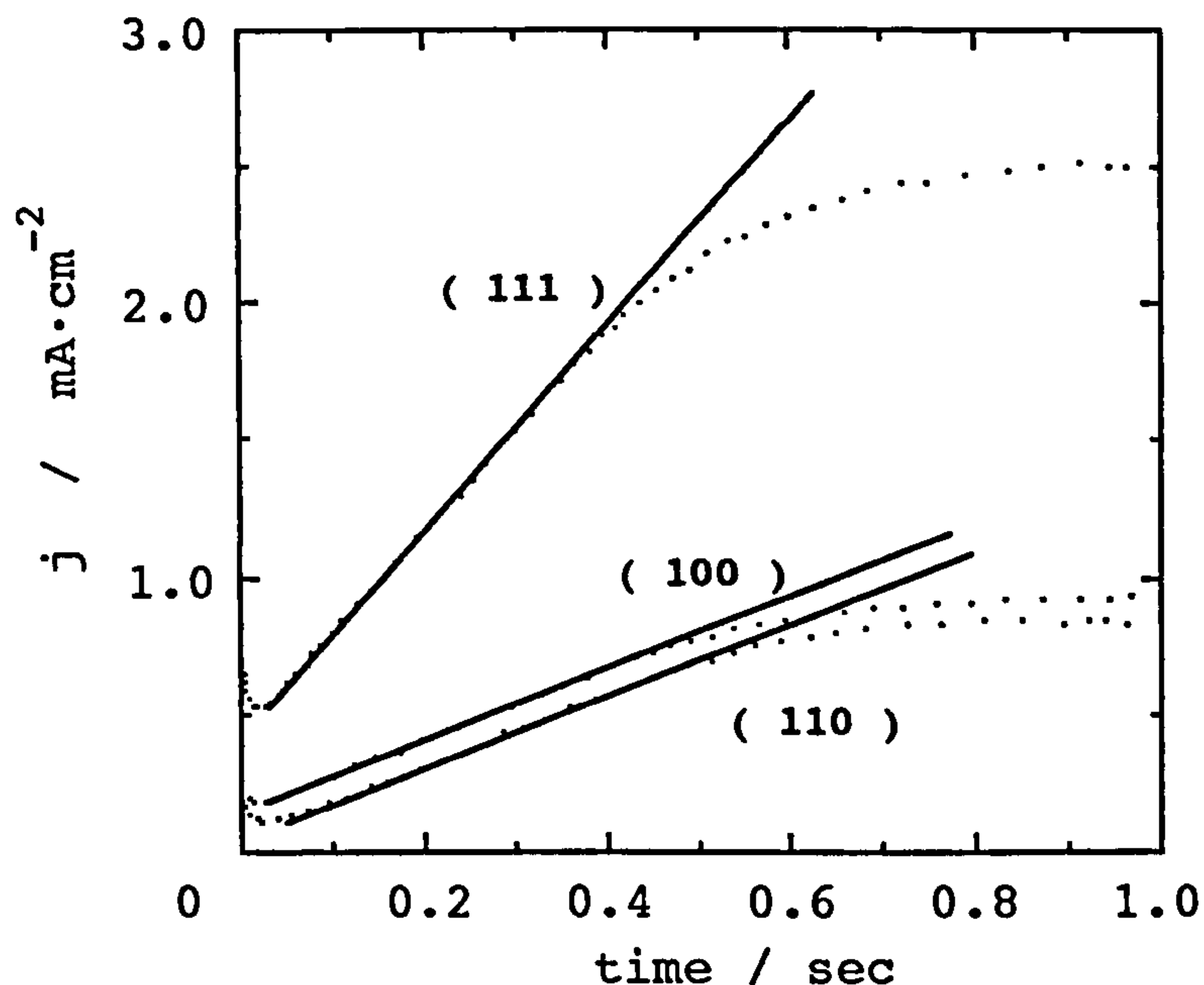


Figure 6.2 Current transients for CdTe deposition on monocrystalline n-Si substrates of different orientation.

This current-time dependence suggests that the nucleation and growth takes place by instantaneous nucleation / two dimensional growth under kinetic control. As described in table 2.1, the transient can be expressed as

$$j(t) = (2\pi F k^2 h M N_0 / \rho) \cdot t \quad (6.1)$$

where k is a constant, h is the height of growing cylindrical centres, M is the molecular mass, ρ is the density of deposit and N_0 is the nuclear number density. This equation indicates that the slope of j - t depends on the nuclear number density. Figure 6.2 shows that the slope of the straight line obtained on (111) face is two times larger than those on (110) and (100) faces, and therefore it may be expected that two times as many nuclei are formed on the (111) face than on the (100) and (110) faces. Although the j - t relations show good linearity at short times, it should be noticed that large background currents are observed

especially on the (111) face. If the background current is constant, it can be considered that the deposition current is given by a linear function with the deposition time as described above. However, since the time dependence of background currents cannot be estimated from the transients, it is difficult to be convinced of the linear relation between deposition current and time. Therefore, for the purpose of making nucleation and growth process clear, further investigation was undertaken.

Figure 6.3 shows the current transient curves measured for longer times. At longer times the transients were less reproducible than those at initial times. In this figure, a typical transient measured on (110) face is shown. The deposition current increased at the beginning of the deposition and then two current peaks appeared. The charge passed by the second increase in current (* in the figure) is approximately $0.7 \text{ mC}\cdot\text{cm}^{-2}$ and is equivalent to less than a monolayer of CdTe ($1.1 \text{ mC}\cdot\text{cm}^{-2}$).

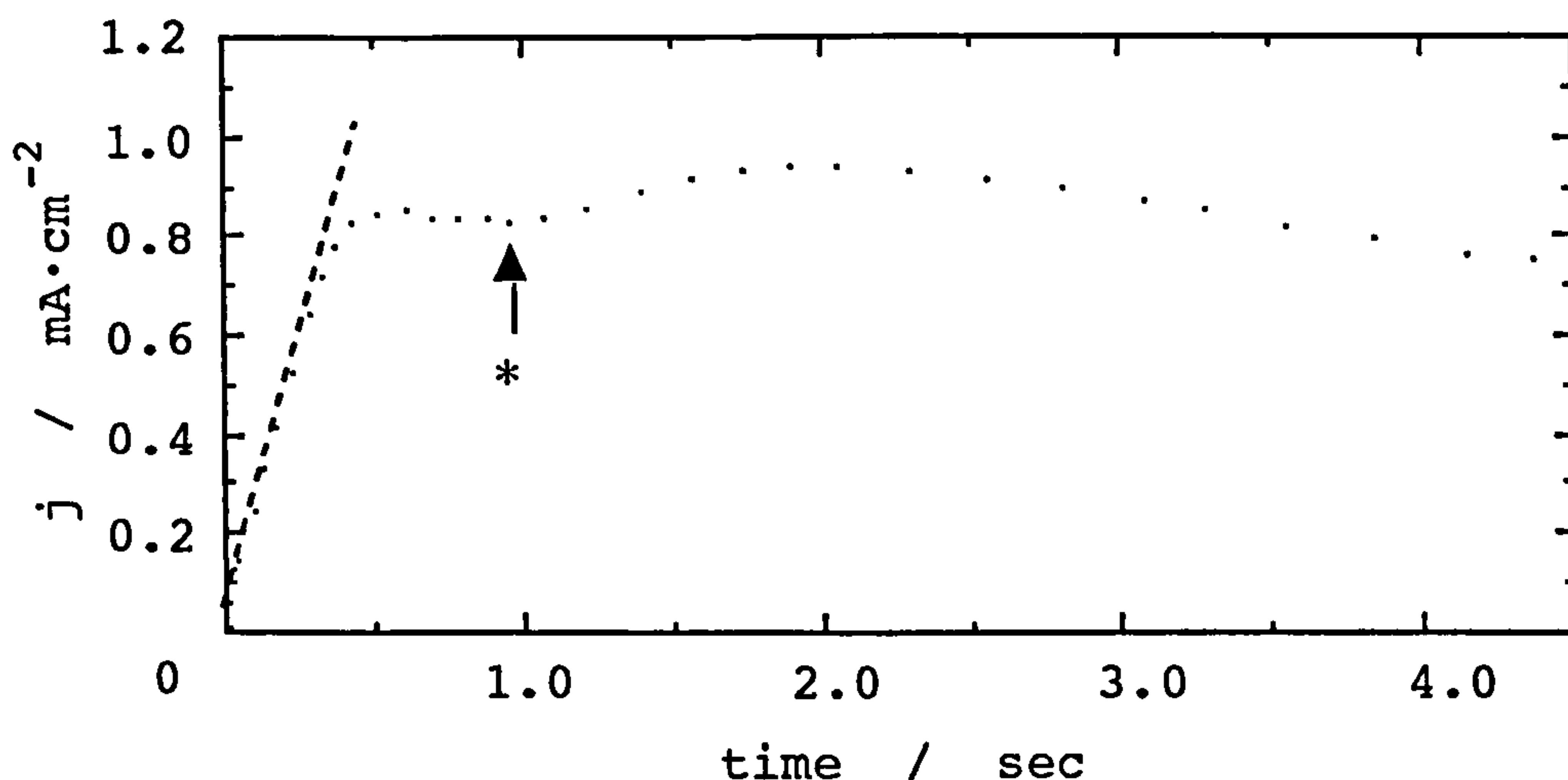


Figure 6.3 Current transient for CdTe deposition on n-Si(110). The charge passed before * is about $0.7 \text{ mC}\cdot\text{cm}^{-2}$ (less than the charge for monolayer).
potential : -660mV vs. SCE.

This transient curve seems to be typical of two dimensional layer-by-layer growth as shown in figure 2.10. After the second peak, the deposition current decreased slowly. Attempts to fit the j - t relation to the Cottrell equation were not successful. Since the deposition current was increased by stirring the solution, these results suggest that the rate determining step at longer times is not kinetics or mass transfer but mixed control. However at much longer times, the comparison with diffusion limiting currents measured on TO suggests that the deposition on silicon is also controlled by diffusion. Since kinetic control is expected from the initial transients, it may be concluded that the rate determining step changes from kinetic control to mixed control and finally to diffusion control. The origin of the transition of the rate determining steps was deduced by observation of the deposits (section 6.2.2).

6.2.2 Characterization of electrodeposited films.

The morphology of the electrodeposited CdTe films was characterised by SEM and profilometry (three-dimensionally surface). The structure of electrodeposited CdTe was investigated by x-ray diffraction. The films were deposited at -660mV from the solution shown in table 3.1 (c). During the deposition, the solution was stirred by a magnetic stirrer. The thickness of the films was approximately $1.5\mu\text{m}$.

Observation of morphology.

Since the deposited films appeared very uniform when viewed at normal incidence, they were mainly characterised in cross section. Figure 6.4 shows the cross sectional image of a CdTe deposit. The image illustrates the uniformity of the deposit. The orientation of silicon substrates did not influence the morphology of deposits.

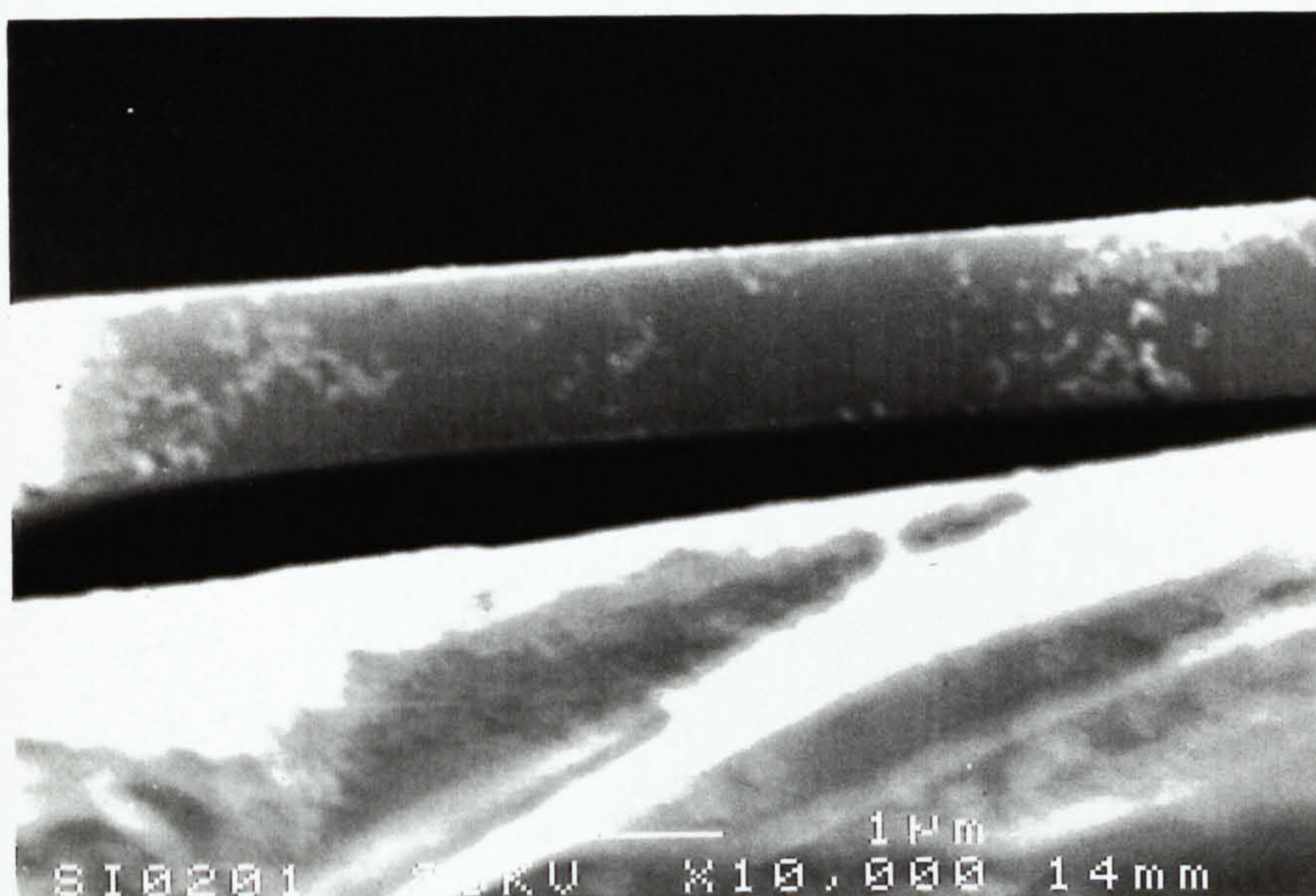
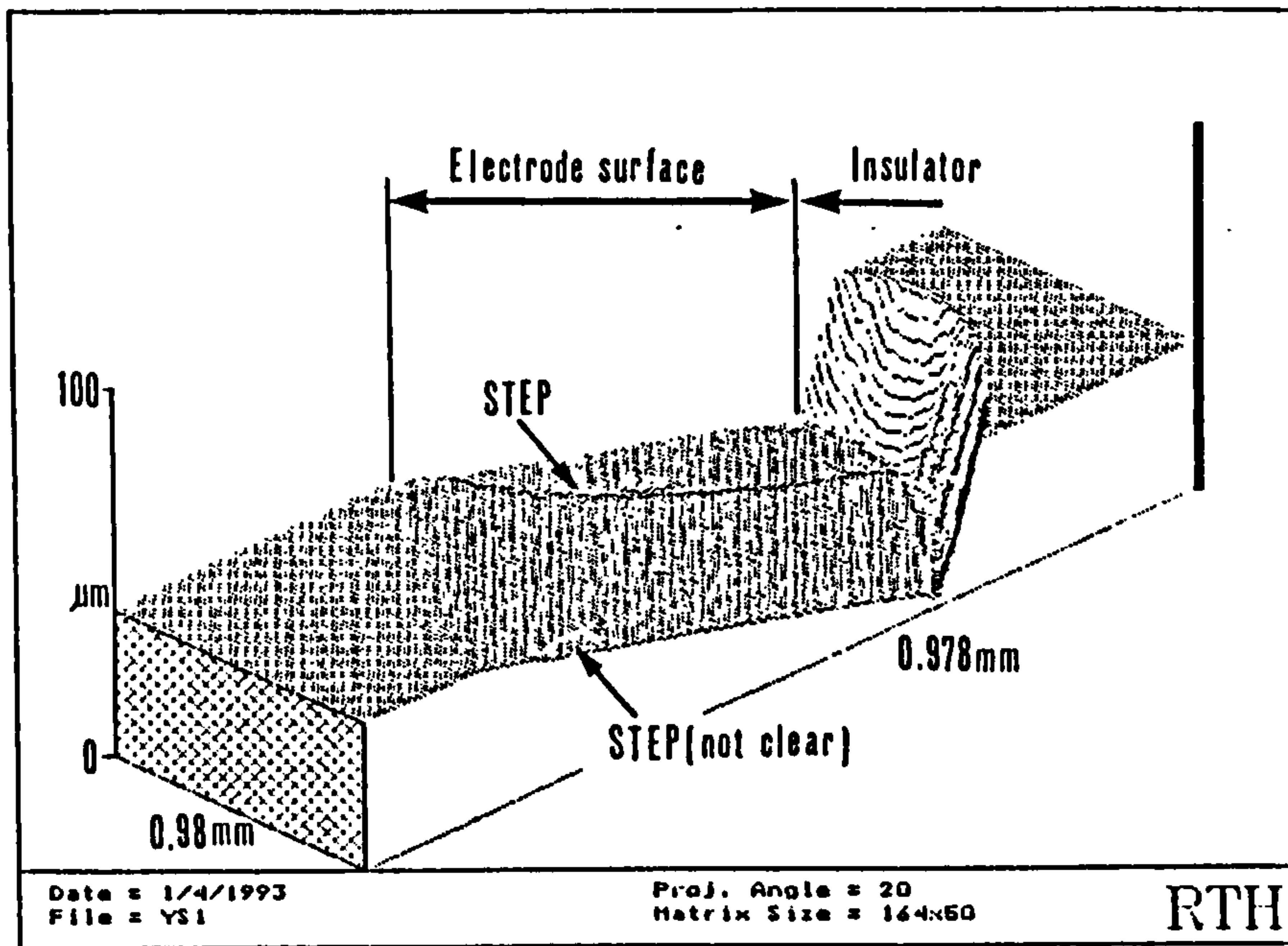
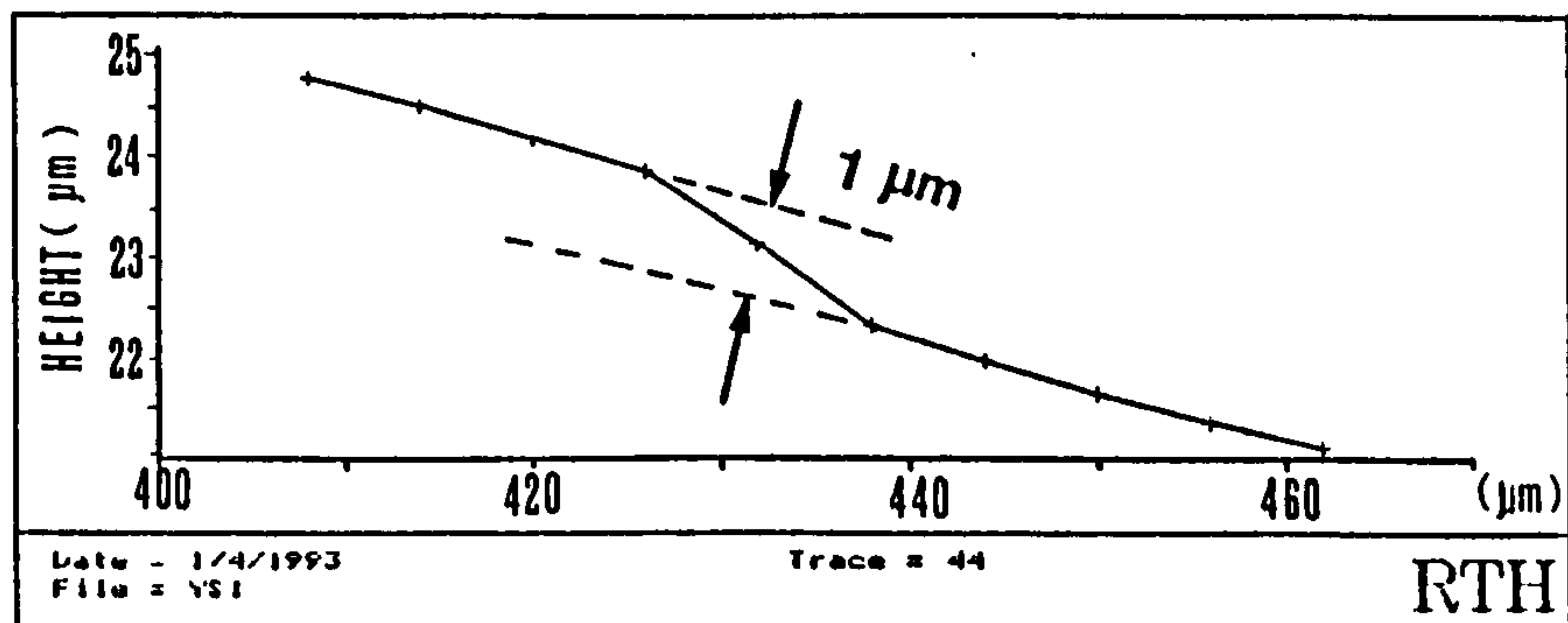


Figure 6.4 Cross sectional SEM of CdTe deposit
on n-Si (111).
deposition potential : -660mV vs SCE

In many cases, well defined steps in the film could be seen by eye. In order to visualise the steps, the surface was characterised by profilometry. Figure 6.5 (a) shows the 3-D surface image.



(a) Surface image.



(b) Cross sectional image of the larger step shown in (a).

Figure 6.5 Profilometric surface image (a) and cross sectional image (b) of the deposit shown in figure 6.4.

In figure 6.5 (a), one large step and one small step are illustrated. These steps correspond to the edge of growing layers. Figure 6.5 (b) shows the cross section of the larger step shown in (a). This figure shows that the height of the step is approximately $1\mu\text{m}$. The height of the smaller step is less than $0.5\mu\text{m}$.

Although it is obvious that the deposition takes place predominantly by layer-by-layer growth, three dimensional growth centres were also observed on two dimensional growth films. A typical SEM image is shown in figure 6.6. This growth of spherical centres on the two dimensional film may be explained by taking account of the interaction between deposit and substrate. In the initial stages of deposition, the substrate influences greatly the morphology of deposits.

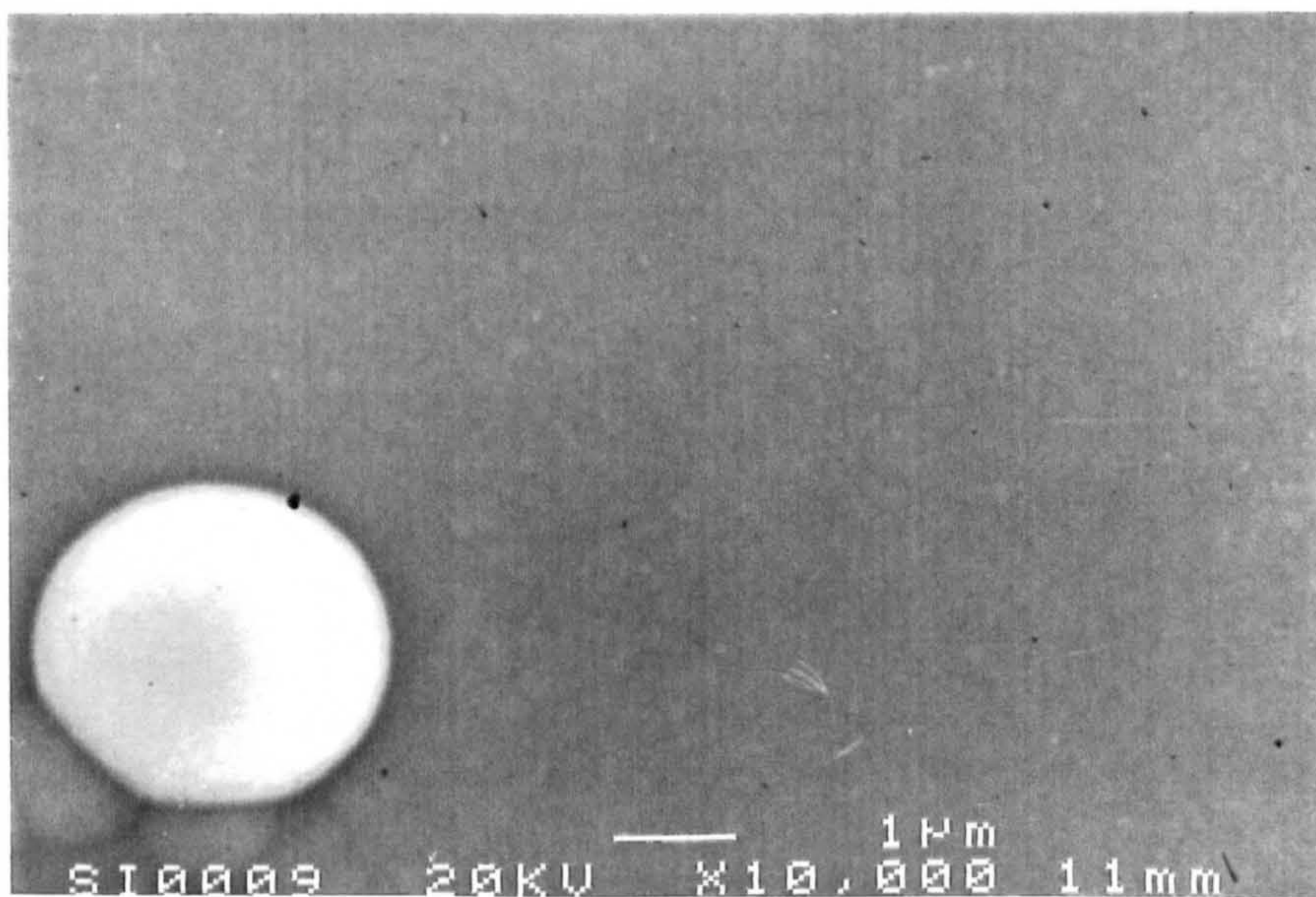
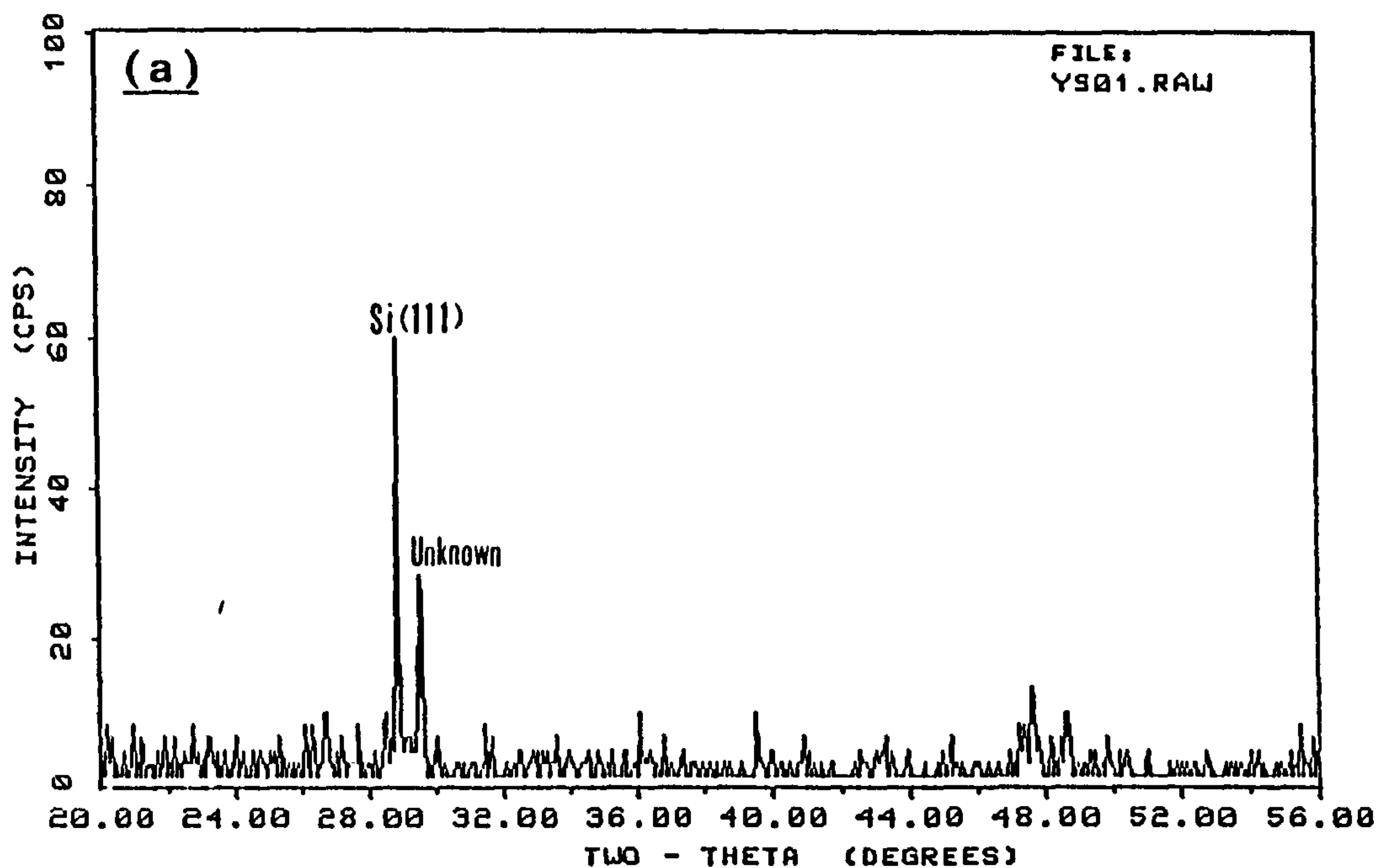


Figure 6.6 SEM image of CdTe deposit showing the existence of spherical growth centres.

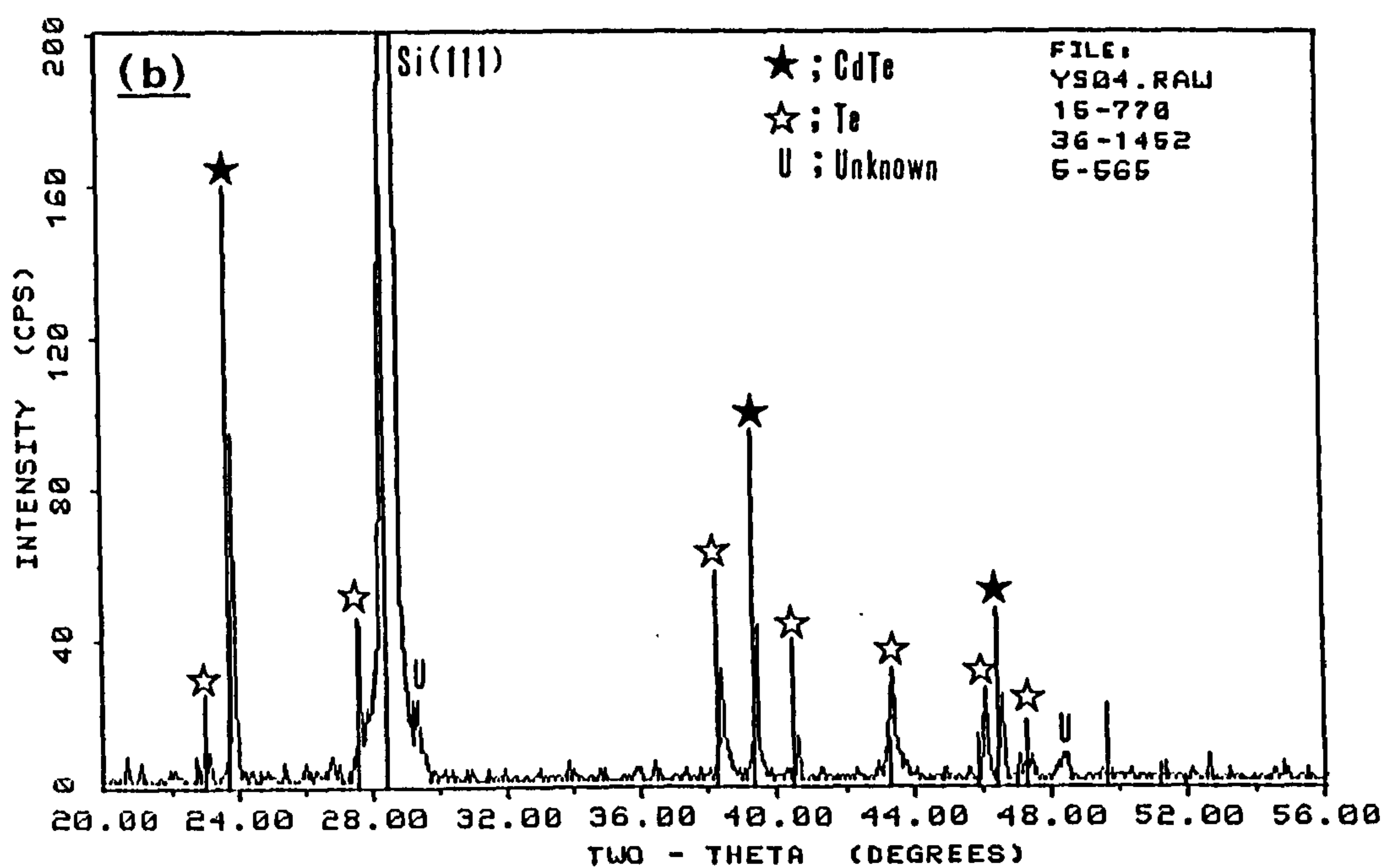
In the case of CdTe deposition on silicon, it may be considered that the strong interaction between silicon and CdTe makes the deposition take place by two dimensional layer-by-layer growth. Then, as the influence of silicon substrate on the morphology decreases with the growth of deposits, different morphology (i.e. spherical deposits) appears on the 2-D growth film. When the deposition is carried out in unstirred solution, the spherical growth tends to take place at an earlier stage of deposition. Since hemispherical CdTe growth on TO is controlled by diffusion (see chapter 5), it is possible that the spherical growth on silicon is also controlled by diffusion. Under two dimensional growth conditions, the deposition is controlled by kinetics and then, with the birth of spherical centres, the rate determining step changes from kinetics to mixed control. Finally the diffusion control regime is established by an increase in the number of spherical deposits and by significant overlap of diffusion zones. The changes in morphology of deposits are therefore probably related to changes in rate determining step of CdTe deposition.

Investigation of crystal structure.

In order to investigate the structure of the electrodeposited CdTe films, x-ray diffraction patterns were measured. The XRD pattern of the film obtained on the (111) Si face is shown in figure 6.7 (a). The peak corresponds to the (111) face of monocrystalline silicon, and peaks corresponding to CdTe are not observed. This suggests that the electrodeposited CdTe film is amorphous [4,5]. By further measurements, it was found that the films obtained on (100) and (110) faces are also amorphous. The uniformity of the cross section exposed by breaking the film also suggests an amorphous structure (figure 6.4).



(a) As deposited CdTe on (111) face.



(b) CdTe annealed at 400°C

Figure 6.7 X-ray diffraction patterns of as deposited CdTe (a) and annealed CdTe (b).
Substrate : n-Si(111), Target : Cu
Film thickness : 1.5 μm .

Touskova et al.[4] have reported that the amorphous phase is found in deposits prepared at high overpotential or at low bath temperature ($< 60^{\circ}\text{C}$) or in solutions with high concentration of TeO_2 . The conditions employed here satisfy the conditions which Touskova et al. have shown to give amorphous films. The amorphous film was converted into polycrystalline CdTe by thermally annealing at 400°C . The annealing temperature was increased at $5^{\circ}\text{C}\cdot\text{min}^{-1}$ up to 400°C followed by holding at 400°C for 15 minutes, then slow cooling to room temperature. Figure 6.7 (b) shows the XRD pattern after the annealing. The pattern shows that the film consists of CdTe and pure Te. From quantitative analysis by EDAX, the Cd/Te atomic ratio in the film obtained was approximately 35/65 suggesting the mixed structure of CdTe and Te. Figure 6.8 shows the cross sectional SEM of the annealed deposit.

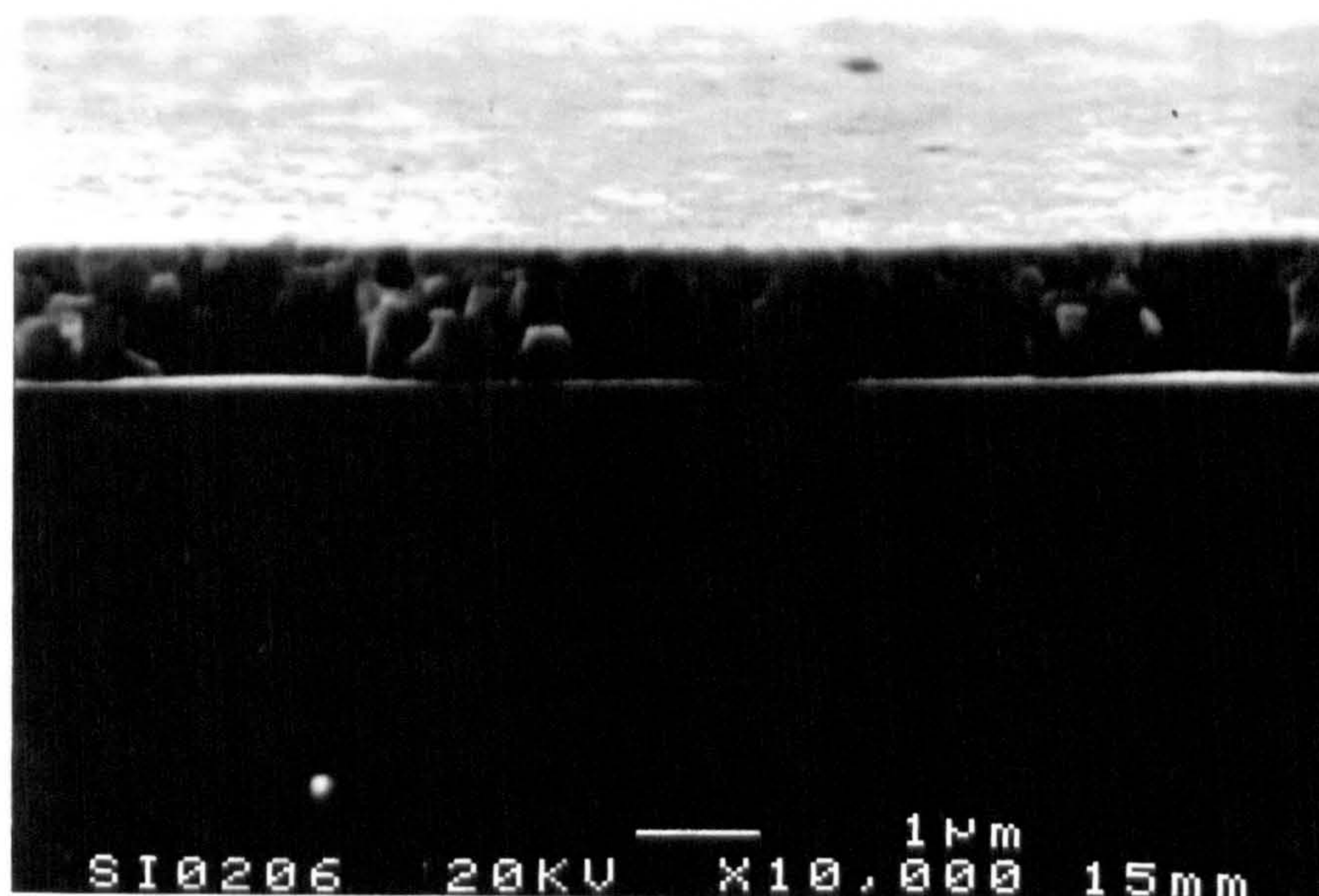


Figure 6.8 Cross sectional SEM of annealed CdTe film showing the polycrystalline structure.
substrate : n-Si (111)

The formation of grains by the annealing was observed (compare to figure 6.4). As the annealed films on (100) and (110) faces give the similar diffraction pattern to figure 6.7 (b), it was found that the orientation of the substrate does not influence the orientation of the annealed films.

6.3 Photoeffects during electrodeposition.

Photoeffects during electrodeposition of CdTe have been reported by Mishra et al.[3]. They observed cathodic photocurrents under chopped illumination during the deposition and have interpreted the photocurrents as evidence that the film behaves as a p-type semiconductor. The mechanism of photocurrent generation has been reinvestigated and the results are described in this section.

For measurements of photocurrent, CdTe films grown from the solution shown in table 3.1 (c) were used (in this section, this solution is referred to as solution (MT) which stands for more TeO₂). Films were deposited in stirred solution for 20 minutes at -650mV. The thickness of the films was approximately 1.5 μ m. As the substrate, monocrystalline silicon with a (110) orientation was used. The measurements of photocurrent were carried out in solution (MT) and in a solution which contained 0.2mM TeO₂, 0.5M CdSO₄ and 16mM H₂SO₄ (this solution is referred to as solution (LT) which stands for less TeO₂).

Figure 6.9 shows the transient increase in cathodic current caused by illumination. For the illumination, the full power laser beam (5mW) was used.

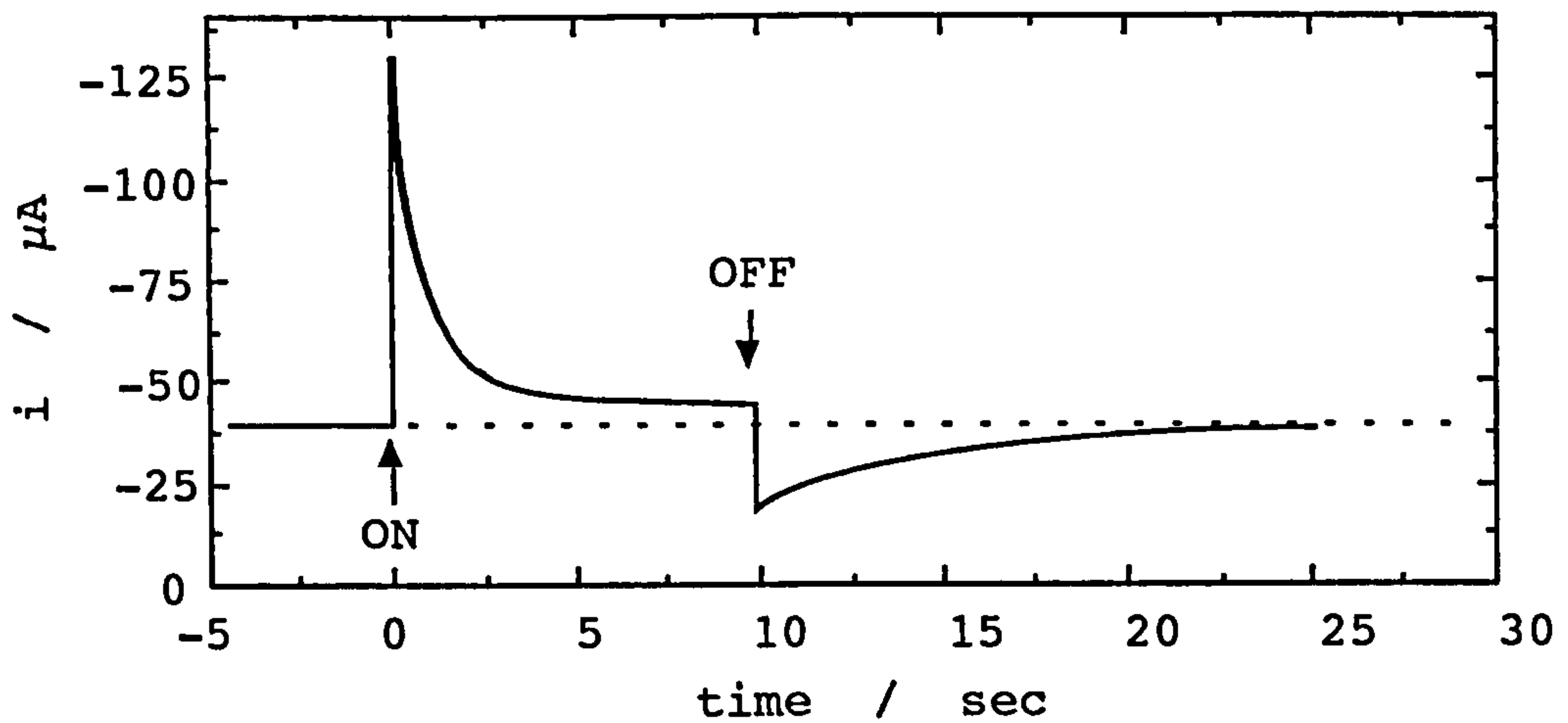


Figure 6.9 Transient currents observed during deposition of CdTe on n-Si(110).
 solution : (MT), thickness : $1.5\mu\text{m}$.
 potential : -650mV vs. SCE.
 illumination : 5mW laser (633nm).

The laser was not focused and the spot size was approximately 5mm in diameter. The film was illuminated for 10sec in unstirred solution (MT). When the light was switched on, an instantaneous increase in the cathodic current was observed and then the photocurrent decayed rapidly. When soon as the light was switched off, an overshoot in the opposite direction was observed and the overshoot recovered slowly. The decay and overshoot are not symmetrical, so that it is unlikely that they are associated with surface recombination [6]. Figure 6.10 shows the instantaneous photocurrents obtained at different potentials. Since the deposition rate was controlled by diffusion in the potential region employed, the deposition current changed little with potential.

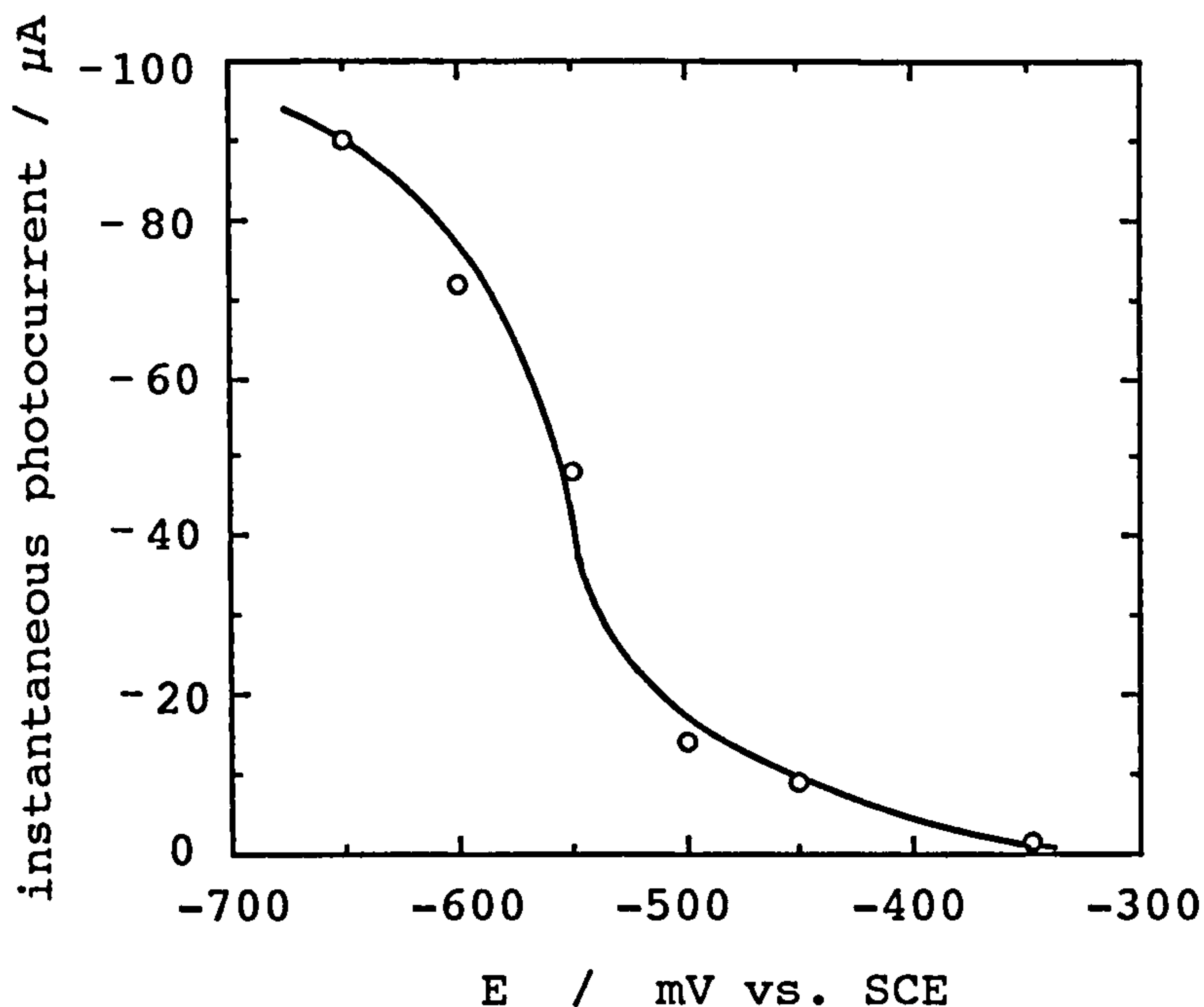


Figure 6.10 Potential dependence of instantaneous photocurrent.
(conditions as in figure 6.9)

However, as shown in this figure, the cathodic photocurrent depends greatly on potential.

The influence of repetitive pulsed illumination on photocurrent response is shown in figure 6.11. This figure shows the results observed in unstirred and stirred solution (LT). In the absence of stirring, successive photocurrent pulses become progressively smaller until the effect almost disappears. By contrast, the response to pulsed illumination in stirred solution does not decay to a significant extent. Figure 6.12 shows the photocurrent response measured in unstirred solution (MT). The photocurrent response is similar to the result obtained in stirred solution (LT) (see figure 6.11). These results suggest that the photocurrent response depends on the concentration of HTeO_2^+ on electrode surface.

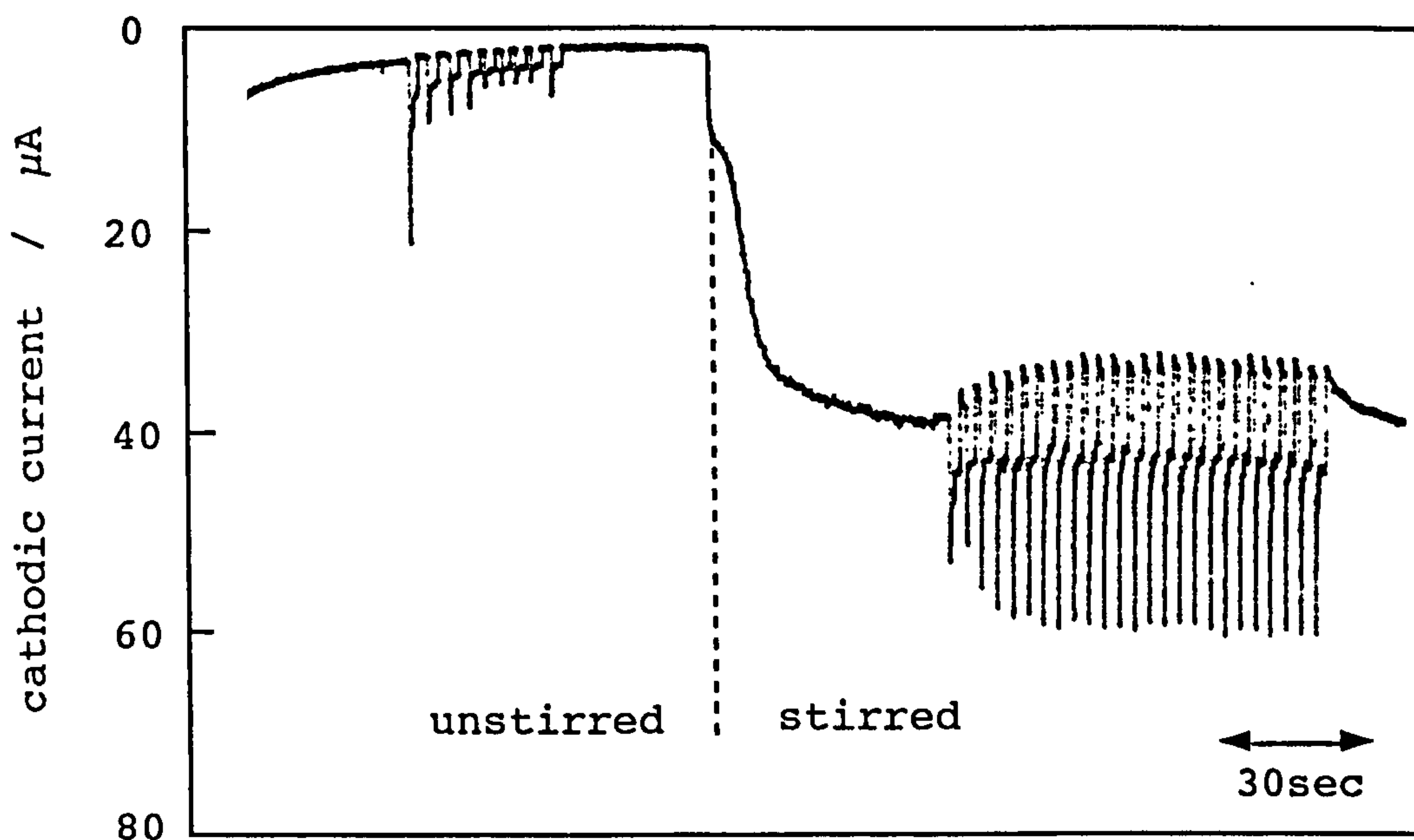


Figure 6.11 Influence of stirring on transient photocurrent response.
solution : (LT), film thickness : $1.5\mu\text{m}$.
potential : -650mV vs. SCE.
laser intensity : 5mW .

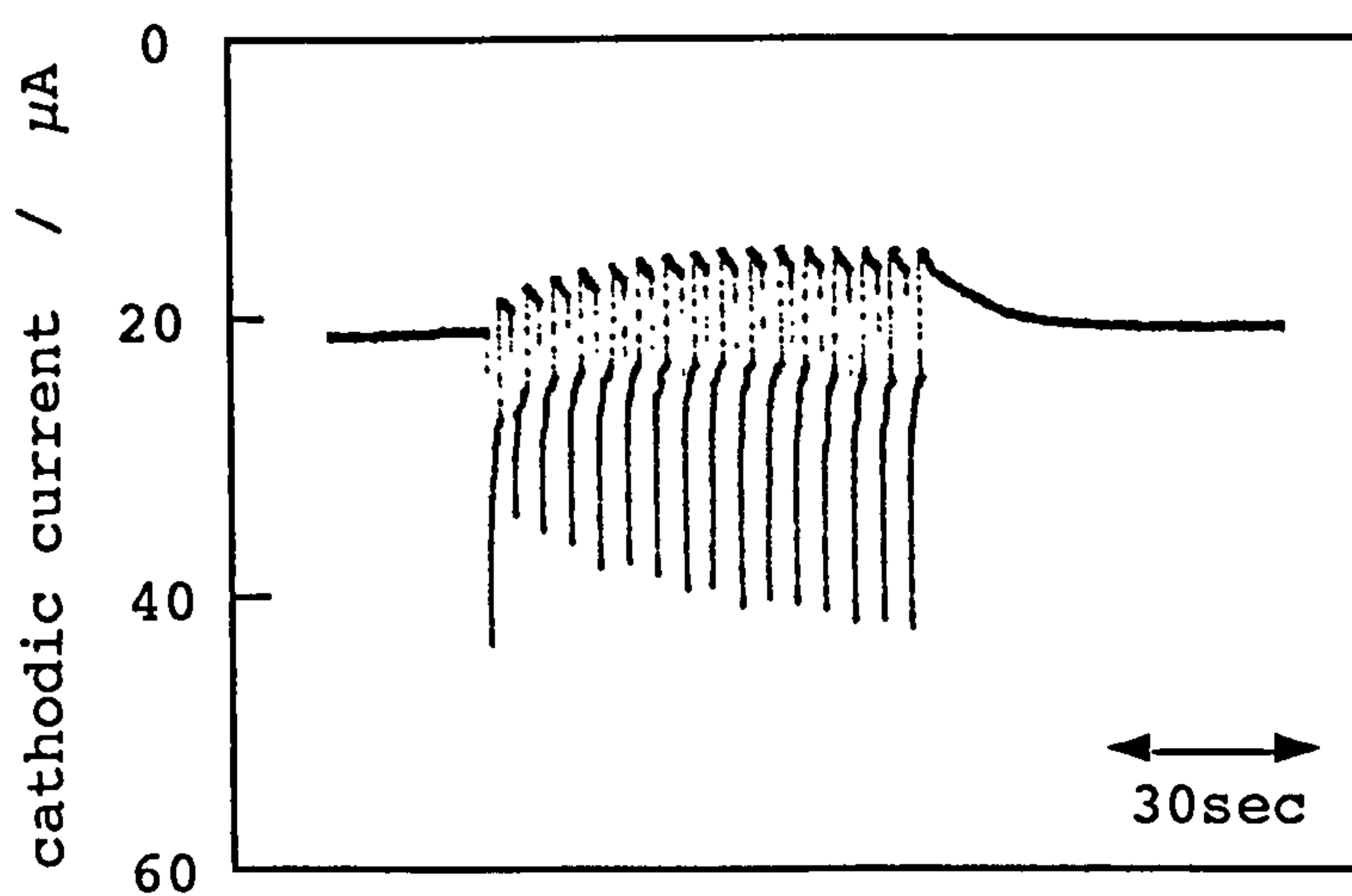


Figure 6.12 Photocurrent response measured in unstirred solution (MT).
(conditions shown in figure 6.11.)

It is also seen in figures 6.11 and 6.12 that the first photocurrent pulses obtained in unstirred solution (LT), in stirred solution (LT) and in unstirred solution (MT) are almost the same. The lack of influence of the conditions in solution on the first photocurrent pulse suggests that the photocurrent is determined by properties of the CdTe films themselves.

Illumination during deposition resulted in substantial changes in morphology and composition of the deposits. Figure 6.13 shows the SEM of deposit formed in stirred solution (MT) under illumination. This figure shows that the uniform film shown in figure 6.4 was changed greatly by illumination and that flower like deposits formed. The flower like deposits were analysed by EDAX and figure 6.14 shows the result. This figure shows that the flower like growth produced in solution (MT) was pure tellurium, whereas the stoichiometry of the underlying material corresponded to CdTe with excess Te.

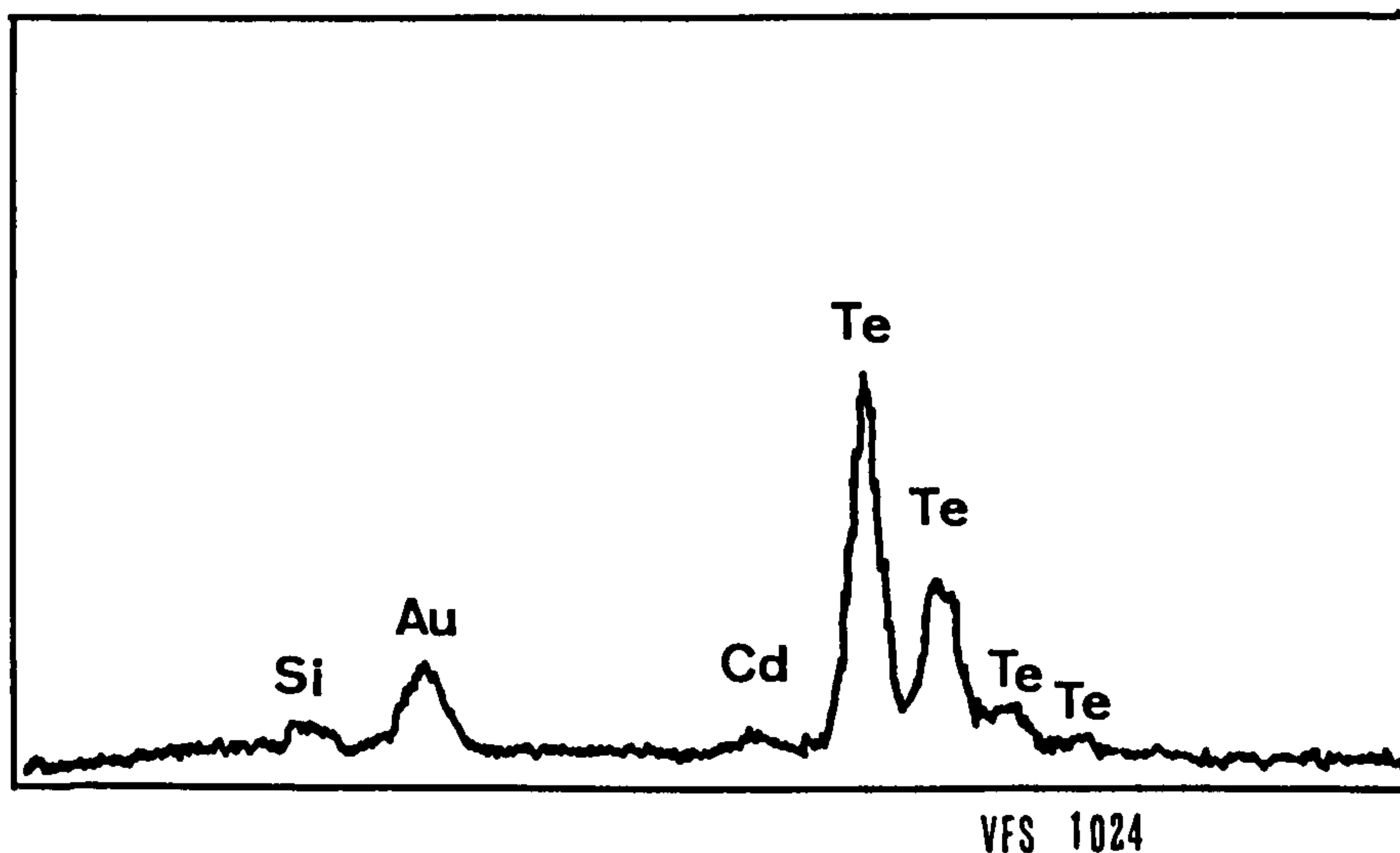
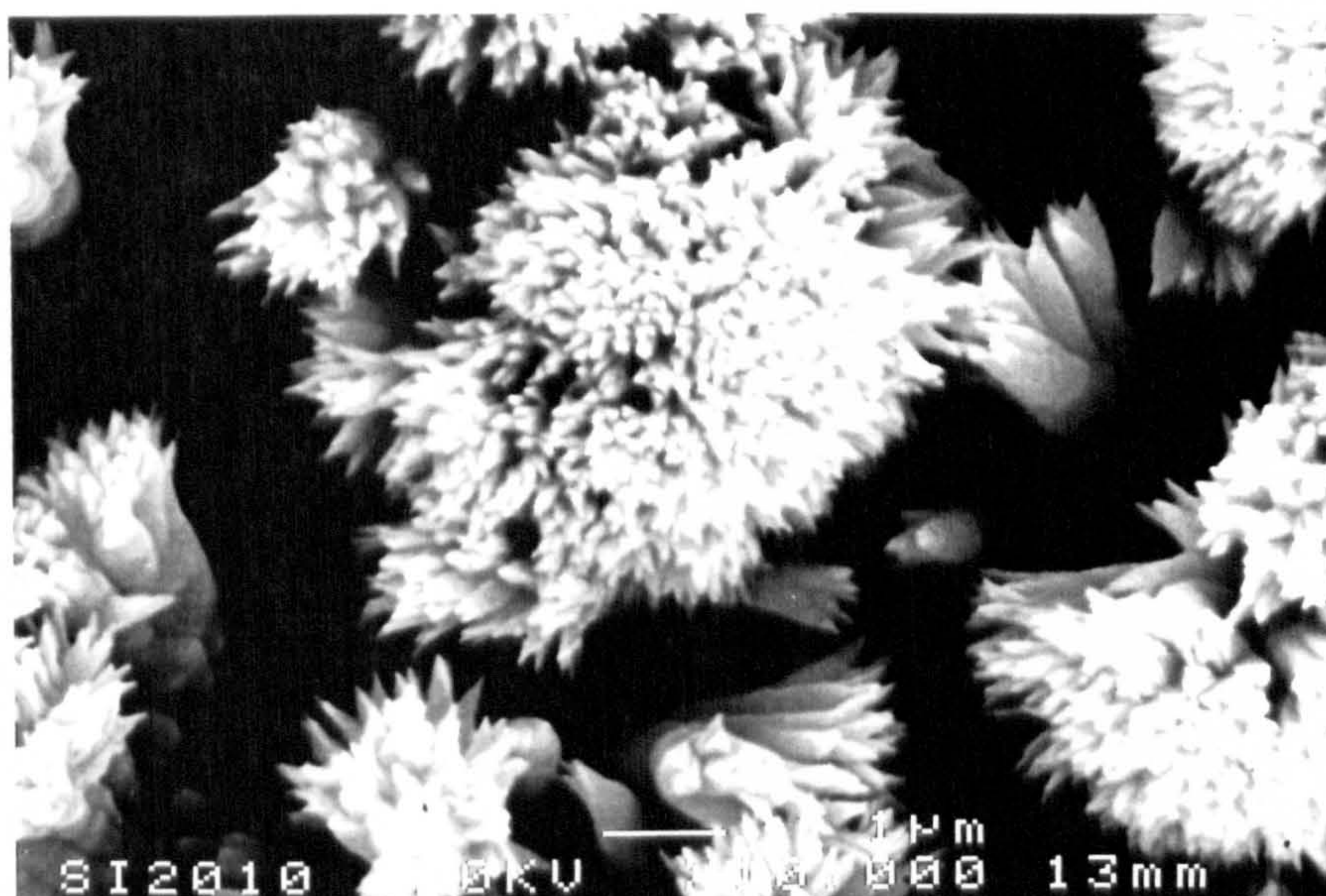


Figure 6.14 EDAX analytical result of the flower-like deposits shown in figure 6.13.
(figure 6.13 is shown at next page.)



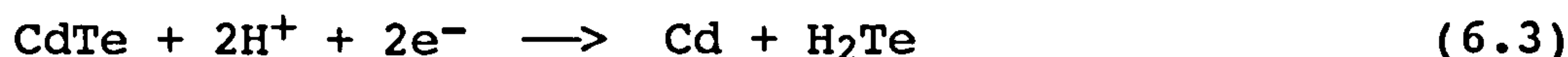
(a) Surface image.



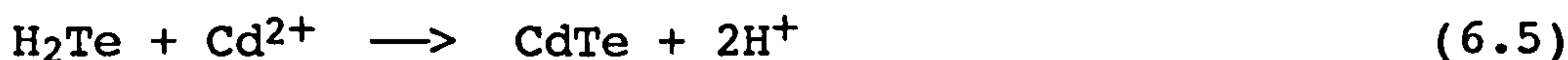
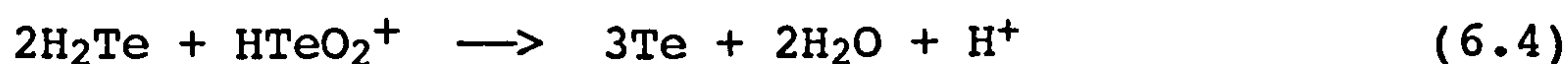
(b) Cross sectional image.

Figure 6.13 SEM of deposit formed in stirred solution (MT) during growth under illumination with 5mW laser (633nm) for 20 minutes
deposition potential : -650mV vs. SCE.

On the other hand, figure 6.15 shows the SEM image of the deposit obtained in solution (LT) under the same conditions as figure 6.13. The spherical particles seen in this micrograph are only present in the illuminated area. The EDAX result of the spherical particles is shown in figure 6.16. This result indicated that the stoichiometry of the particles corresponds to CdTe with some excess Cd. The changes in morphology and composition suggest that illumination causes photodecomposition of the CdTe deposit. CdTe is unstable with respect to cathodic photodecomposition, and therefore the first step of the decomposition can be proposed as



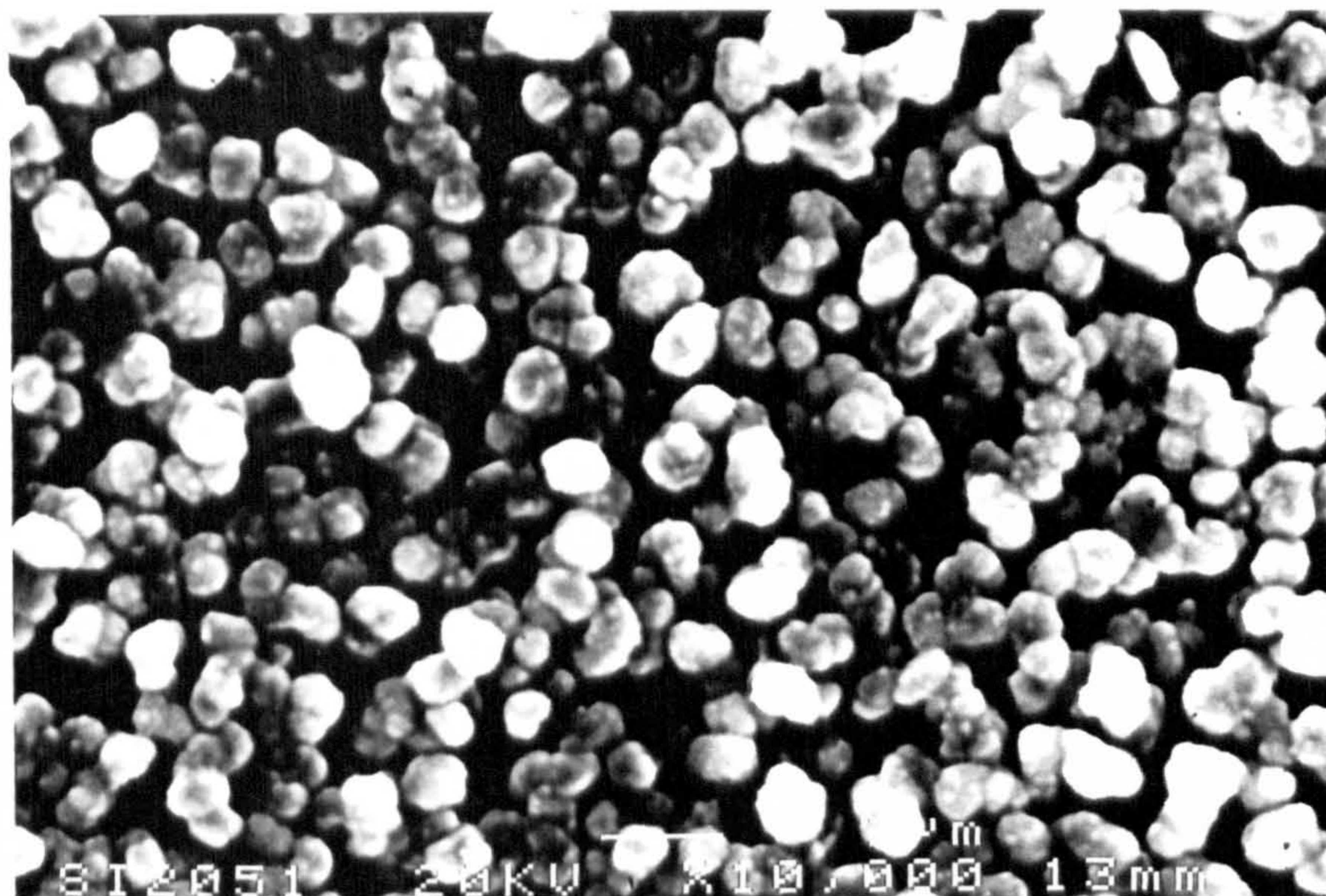
The products of the photoreaction (i.e. Cd and H₂Te) are both thermodynamically unstable in the deposition solution containing Cd²⁺ and HTeO₂⁺. Therefore, possible following chemical and electrochemical reactions are



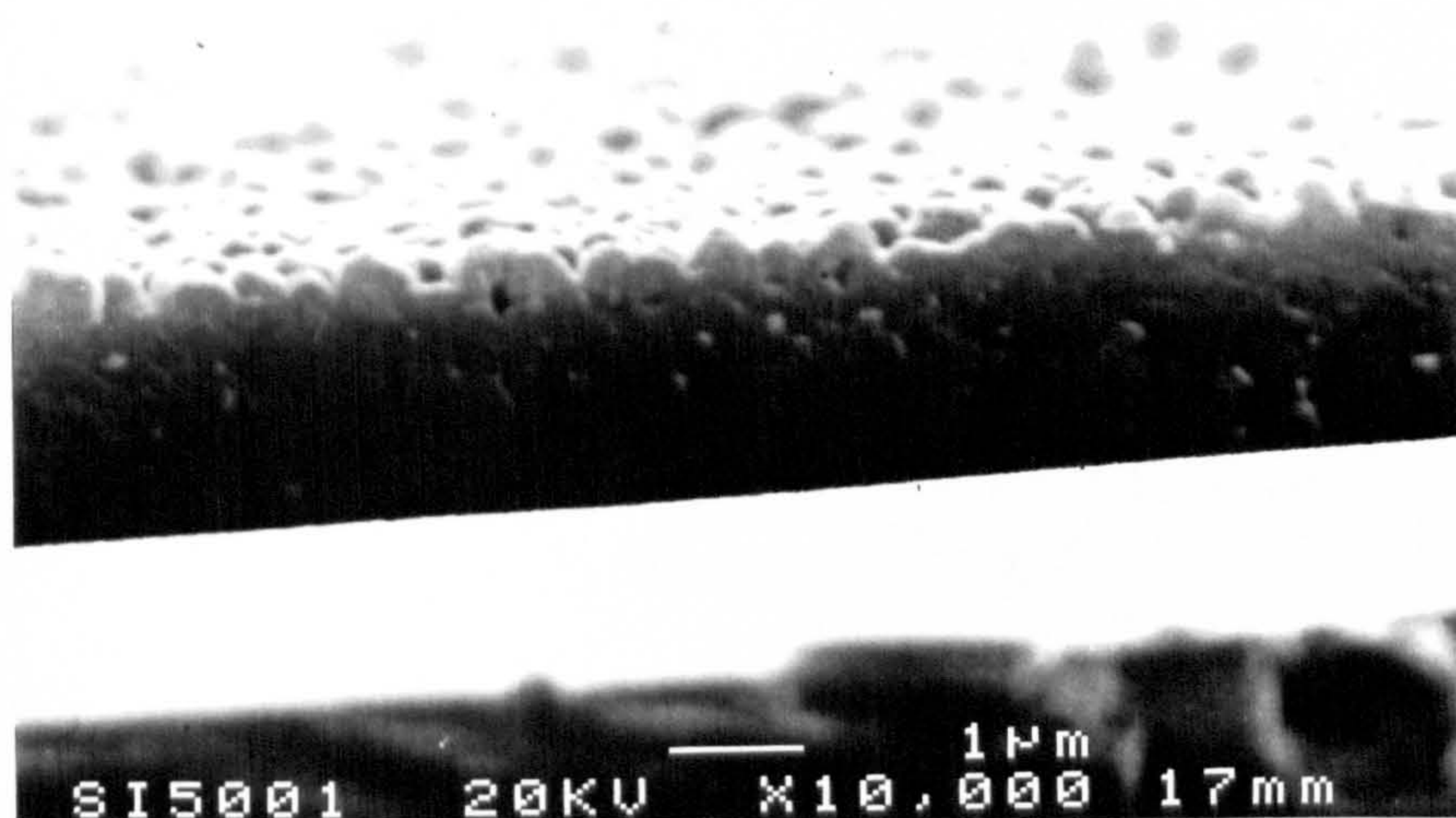
for H₂Te (chemical reactions) and



for Cd (electrochemical reactions). The Gibbs energy changes of reactions (6.4) and (6.5) are -251kJ·mol⁻¹ and -157kJ·mol⁻¹, respectively (thermodynamic data are taken from reference [7]). These data suggest that reaction (6.4) is thermodynamically more favoured than reaction (6.5). From these considerations, the following mechanism for decomposition of CdTe under illumination is proposed.



(a) Surface image.



(b) Cross sectional image.

Figure 6.15 SEM of deposit formed in stirred solution (LT) during growth under illumination with 5mW laser (633nm) for 20 minutes
This film was obtained from stirred solution (MT) in the dark (20min) and then it was illuminated in solution (LT).
deposition potential : -650mV vs. SCE.

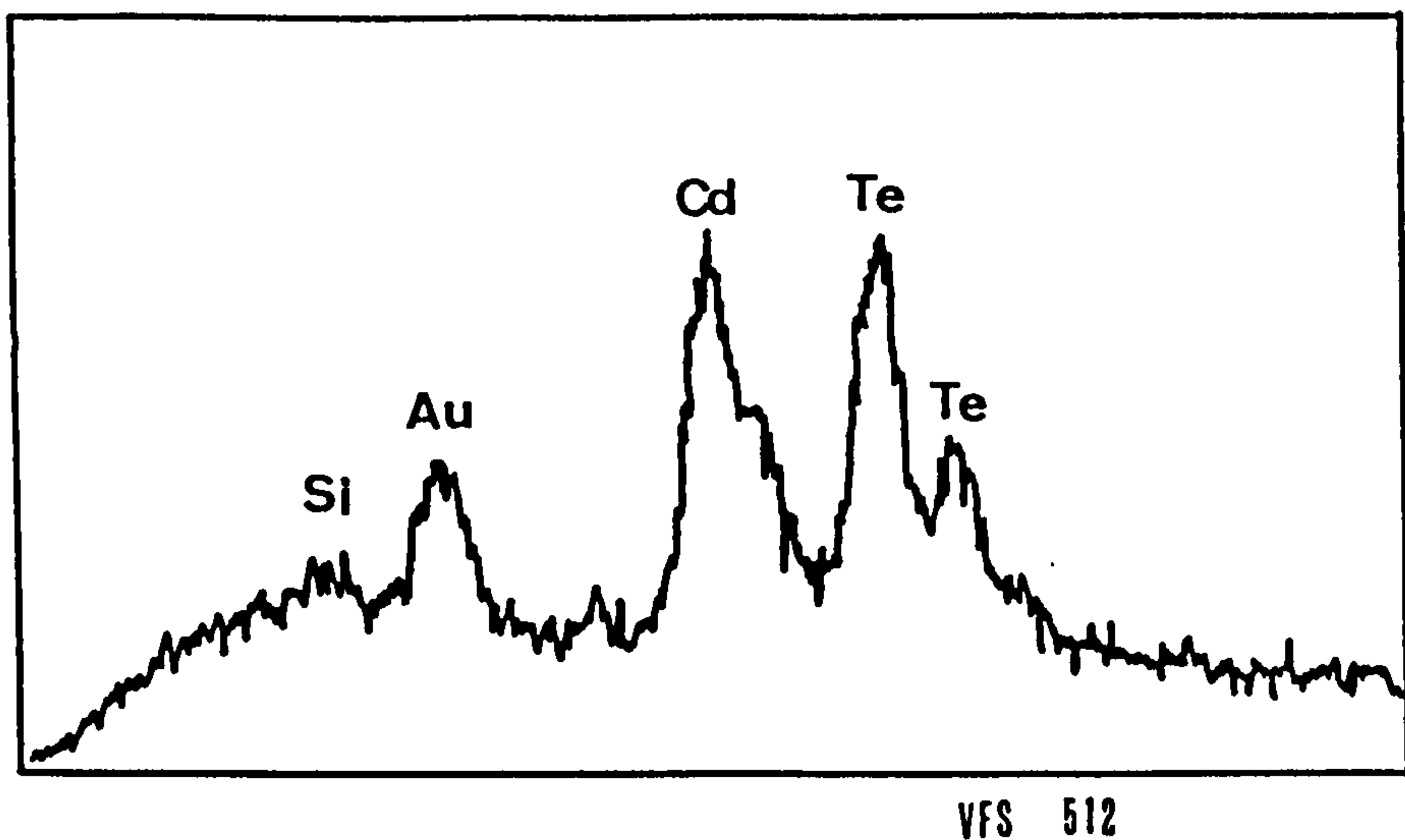


Figure 6.16 EDAX analytical result of the spherical deposits shown in figure 6.15.

(1) In solution (MT), reaction (6.4) which is more favoured thermodynamically than reaction (6.5) can occur mainly. Although reaction (6.5) can also occur simultaneously, the CdTe formed by (6.5) is consumed by reaction (6.3) again. Furthermore, since the Cd formed by reaction (6.3) may be consumed by reactions (6.6) and (6.7), only pure Te is left on electrode. During deposition, HTeO_2^+ depletes at the electrode surface. Due to the depletion of HTeO_2^+ , the deposit grows toward regions with higher concentration of HTeO_2^+ . This may be a reason for the flower like growth morphology.

(2) In the case of deposition in solution (LT), it may be considered that reaction (6.4) cannot occur, because of the low concentration of HTeO_2^+ and the thick depletion layer of HTeO_2^+ formed during deposition. Therefore, H_2Te is consumed only by reaction (6.5) and CdTe forms. The CdTe is

decomposed by illumination, and reactions (6.3) and (6.5) are repeated. Since this repetition occurs in the depletion layer of HTeO_2^+ , compact deposits can be obtained as shown in figure 6.15.

The Cd formed by reaction (6.3) may be consumed by reactions (6.6) and (6.7). When illumination was interrupted, an anodic overshoot was observed as shown in figure 6.9. The overshoot may be due to reactions (6.6) and (6.7). As shown in figure 6.11, the transient photocurrent response to repetitive pulsed illumination is sensitive to stirring. Since reaction (6.6) is controlled by diffusion of HTeO_2^+ , if the supply of HTeO_2^+ is not fast enough, conversion of Cd into CdTe cannot be completed. The accumulation of Cd is expected to cause the photocurrent to become smaller. This phenomenon was observed in unstirred solution (LT). Since the supply of HTeO_2^+ is increased by stirring and by the use of high concentrated solution, it is possible that Cd can be converted into CdTe under these conditions. Complete conversion would explain the fact that the photocurrent does not decay as shown in figures 6.11 (stirred) and 6.12.

Figure 6.17 shows the relationship between laser intensity and photocurrent. As this figure shows, the intensity dependence of the photocurrent is not linear but follows instead a square root relationship. The square root relationship is expected for second order electron-hole recombination in the bulk (see appendix 6.I). This is typical of the behaviour observed in many quasi-intrinsic photoconducting materials [8].

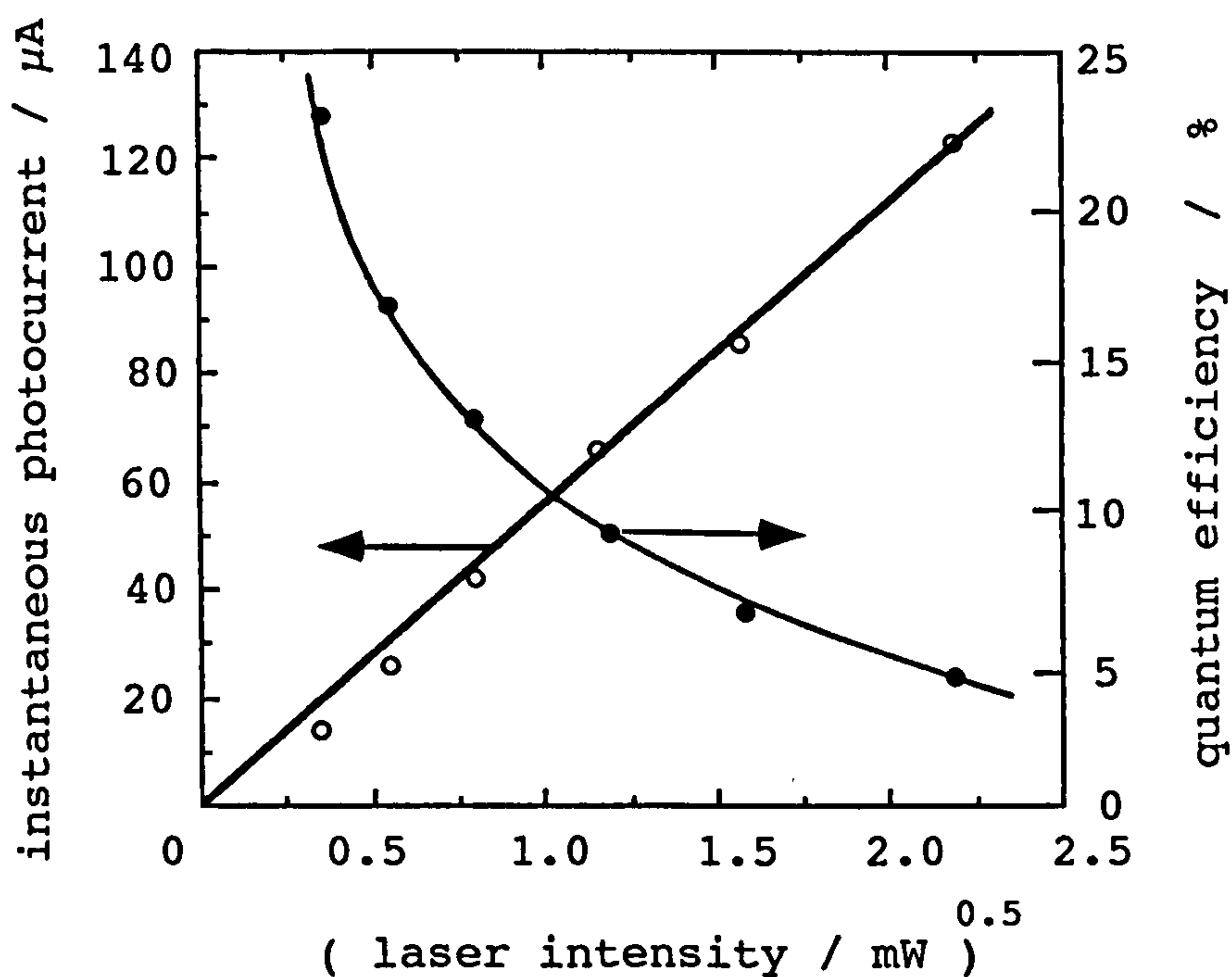


Figure 6.17 Intensity dependence of the instantaneous photocurrent.
solution : (MT), potential : -650mV

As shown in figure 6.7 (a), as deposited CdTe films are essentially amorphous, and this could explain the observation of second order recombination. It may therefore not be appropriate to consider the films as doped (i.e. p-type) semiconductors. Instead they may be insulating with low mobilities for carrier transport. The main influence of illumination in such system is to change the ratio of free to trapped carriers and hence the conductivity. The sign of the photocurrent simply reflects the direction of the electric field vector rather than the minority carrier type [9,10].

6.4 Conclusions.

The electrocrystallization and growth of CdTe on monocrystalline n-type silicon and photoeffects during CdTe electrodeposition were studied. As the result, the following conclusions can be drawn.

(I) From current transient measurements, it appears that the electrocrystallization and growth take place by the instantaneous nucleation and two dimensional layer-by-layer growth. From SEM and profilometry, layer-by-layer growth was confirmed. The initial transients depended on the exposed face of monocrystalline silicon. This may be due to difference in the nuclear number density on each exposed face.

(II) By x-ray diffraction, it was shown that as deposited CdTe films are amorphous. Amorphous films are converted into polycrystalline by annealing. From XRD patterns of as deposited and annealed film, it was found that the orientation of substrate does not influence the orientation of deposit. This suggests that the films do not grow epitaxially during electrodeposition and during annealing.

(III) The rate determining step of CdTe electrodeposition changes from kinetic to mixed control and finally to diffusion control. This change is related by changes in morphology of deposit (layer growth to spherical growth).

(IV) Cathodic photocurrents observed during electrodeposition are associated with changes in film composition and morphology. This points to the occurrence of photodecomposition reactions. The reactions are expressed by reactions (6.3) to (6.7). The overall mechanism is complicated by the presence of solution species

which can react with the primary products of the photodecomposition reaction (6.3).

(V) The relatively low quantum efficiency and more importantly the square root intensity dependence of the photocurrent suggest that the CdTe deposit behaves as an amorphous insulator with a high density of bandgap states which act as carrier traps and recombination centres.

Appendix 6.I Dependence of photocurrent on light intensity.

In the case of n-type semiconductors, the number of electrons in the dark, n_{dark} (majority carriers) is much larger than that of holes, p_{dark} (minority carriers). Further electrons (Δn) and holes (Δp) are produced by illumination and the quantitative relationships between n_{dark} , Δn , p_{dark} and Δp are expressed as

$$\begin{aligned} n_{\text{dark}} &\gg \Delta n \quad (n_{\text{dark}} \approx n_{\text{light}}), \quad p_{\text{dark}} \ll n_{\text{dark}}, \\ \text{and } \Delta p &\geq p_{\text{dark}} \end{aligned}$$

Since the recombination of electrons and holes can be written as



the following equation is obtained under steady state illumination conditions (*)

$$I_{\text{abs}} = k_{\text{rec}}[p][n] \quad (6I.2)$$

$$\approx k'_{\text{rec}}[p] \quad (6I.3)$$

where I_{abs} is the number of photon absorbed, and k_{rec} is the recombination rate constant. Thus, the recombination can be considered as a pseudo first order reaction and $k'_{\text{rec}} = k_{\text{rec}}[n]$ is the pseudo first order recombination rate constant.

On the other hand, in the case of insulators, the relationships between n_{dark} , Δn , p_{dark} and Δp are expressed as

$$\Delta n \text{ and } \Delta p \geq n_{\text{dark}} \text{ and } p_{\text{dark}} \quad (6I.4)$$

(*) Since k_{rec} is generally high for defective materials, we expect steady state conditions to be established on a short timescale (typically $< 10^{-3}\text{s}$).

Therefore, equation (6I.2) can be rewritten as

$$\begin{aligned} I_{\text{abs}} &= k_{\text{rec}}[p][n] \\ &= k_{\text{rec}}[p]^2 = k_{\text{rec}}[n]^2 \end{aligned} \quad (6I.5)$$

where the number of electrons can be considered to be approximately equal to that of holes ($[p] \approx [n]$). Equation (6I.5) yields

$$[p] = [n] = (I_{\text{abs}} / k_{\text{rec}})^{1/2} \quad (6I.6)$$

If we assume that photocurrent is proportional to the hole or electron density, a square root intensity dependence of the photocurrent can be expected if recombination is a second order reaction.

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CHAPTER 7.

COMPUTER SIMULATION OF GROWTH OF
HEMISPHERICAL CENTRES UNDER DIFFUSION
CONTROL.

7.1	Introduction.
7.2	Simulation procedure.
7.3	Results and discussion.
7.3.1	Qualitative discussion.
7.3.2	Quantitative discussion.
7.3.3	Current transients obtained by the simulation.
7.3.4	Transformation to dimensional results.
7.4	Conclusions.
Appendix 7.I	FORTTRAN program used for the simulation of instantaneous nucleation / hemi- spherical growth under diffusion control. References.

7.1 Introduction.

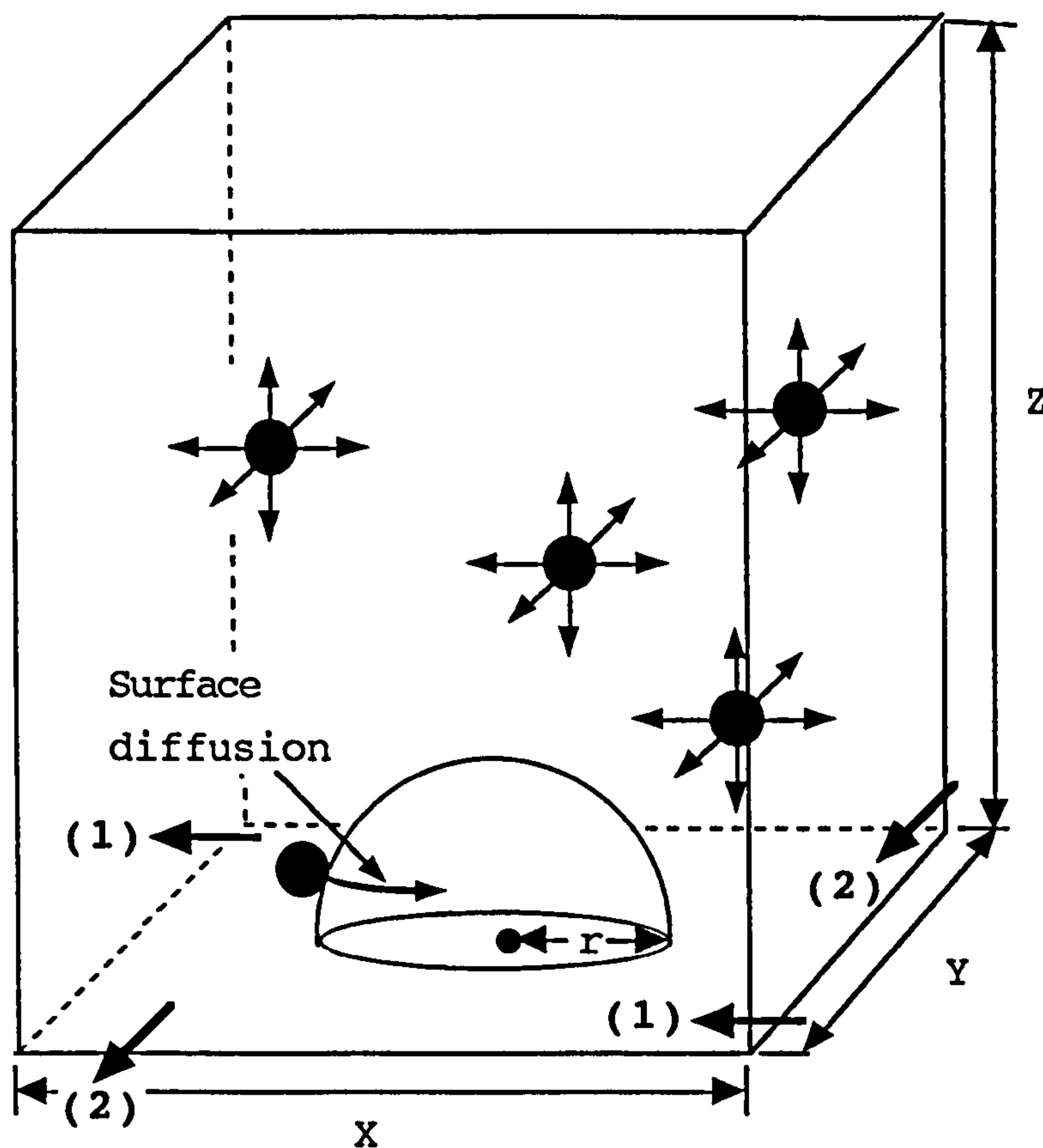
With the improvement of computing speed, computer simulation has been carried out more often in many fields of science. Of course, many articles have also been published in the field of electrodeposition [e.g. 1~7]. In terms of electrodeposition controlled by mass-transfer, dendritic (or fractal) growth [2,4,5] and two dimensional growth (single and multi-layer growth) [3,6] have been dealt with. The basic idea for the simulation of diffusion controlled deposition is summarized as follows : (1) mobile particles are randomly generated in a simulation space, (2) they then move randomly (brownian motion [8]) in the space, (3) if a particle arrives on a site where deposition is allowed, it is given a possibility of deposition and it may deposit. If the probability of deposition is decided by considering total energy changes of the system after and before deposition, this method of simulation can be regarded as "Monte-Carlo (MC) simulation" [9]. If deposition always occurs on active sites (probability = 100%) , the simulation should be referred to as "diffusion limited aggregation (DLA)".

In this chapter, instantaneous nucleation / hemispherical growth under diffusion control is considered using a three dimensional diffusion limited aggregation model. According to the theoretical equations described in section 2.3.3 (see table 2.1), j is first proportional to $t^{1/2}$ (initial transients) and the Cottrell relation can be obtained at longer times. These limiting relations have been shown by many researchers [10]. The current transients obtained by the computer simulation are compared with the theoretical equations. Finally, the dimensionless simulation results are converted into dimensional values.

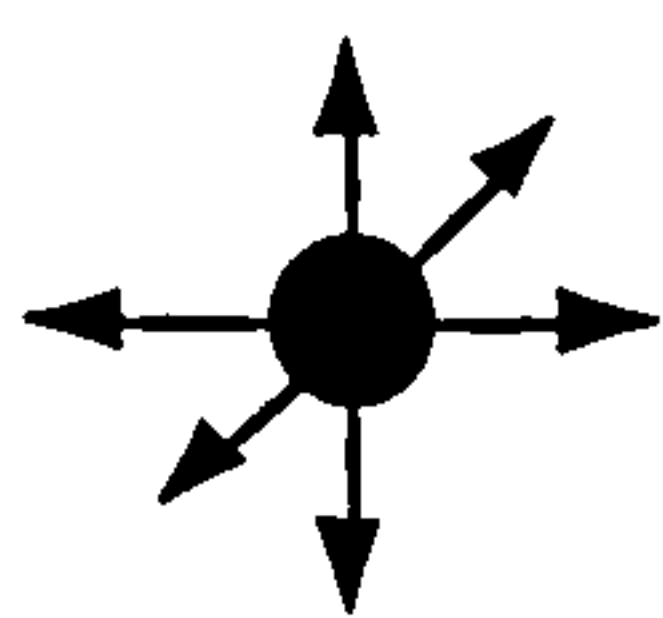
7.2 Simulation procedure.

In many papers [2,4~7,11,12], the simulations have been conducted in a two dimensional slice of a three dimensional space because this simplification yields shorter simulation times. Few simulation results obtained in a three dimensional space have appeared [3]. Since difficulty in simulating overlap of diffusion zones in two dimensional slices is expected, the simulation in a three dimensional space was carried out. The reason for the difficulty is described later. Figure 7.1 illustrates the procedure of the simulation conducted here. The X-Y plane ($z=0$) and the space (typically $50 \times 50 \times 1500$) correspond to the electrode surface and to the solution containing depositing ions, respectively. The procedure of the simulation conducted here is as follows.

- (1) Mobile particles are put in the simulation space randomly. The mobile particles are only allowed to stay on sites defined by a cubic lattice. The ratio of the number of mobile particles to the total number of cubes within the 3-D lattice, r , is typically 0.1%. For instance, in the case of $r = 0.1\%$, 3750 ($=0.001 \times 50 \times 50 \times 1500$) of the mobile particles exist in a domain containing $50 \times 50 \times 1500$ solution sites. The ratio, r , corresponds to the concentration of depositing ions.
- (2) An active site is generated on the centre of the electrode. (In fact, the location of the active site does not influence the simulation results because of periodical boundary conditions.)



(1), (2) Boundary conditions



Mobile particles (ions)

they move in one direction out of the six arrows during a time step.



Deposited particle

When a mobile particle arrives on the growth centre, the particle moves to the deposition site(*) immediately and is fixed permanently.



Hemispherical growth centre

Figure 7.1 Schematic diagram of the simulation employed here.
Typically, $x = 50$, $y = 50$, $z = 1500$

(*) : deposition site = a vacant site giving the shortest distance from the active site (● in the figure)

(3) During a time step, each of the mobile particles is randomly moved once. One direction of movement is chosen out of six by a random number generator. A particle can only move to a neighbouring site, in other words, during one time step a particle can only travel over a distance equal to the distance between two lattice sites. This rule is thus analogous to a diffusion coefficient. In this simulation, several particles are allowed to occupy the same site at the same time.

(4) ~ Boundary conditions ~

If a particle existing on the electrode surface attempts to move downward, the particle is not allowed to move but stays at the same site. A particle existing on the ceiling ($z = \max$) is also not allowed to move but stays at the same site, if it chooses to move upward. Periodic boundary conditions are used in the horizontal directions (see e.g. [8]).

Simply speaking, a particle which leaves to the right re-enters the domain from the left and vice-versa. From the boundary conditions, it is apparent that the right and the left sides of the simulation space are connected (in the case of two dimensional simulation, the simulation field can be regarded as a cylinder, although it is more complicated in the case of three dimensional simulation).

(5) If one of the six nearest sites surrounding a particle is occupied by a deposited particle (or an active site), the particle becomes part of the deposit (i.e. the particle deposits). A site giving the shortest distance from the active site is chosen as a deposition site and the particle moves immediately to the deposition site (the movement is considered as a rapid surface diffusion : the diffusion coefficient for surface diffusion is much greater than that for solution diffusion). By this surface diffusion, the quasi-hemispherical shape of deposits can always be maintained. After the deposition, the particle is prohibited permanently from moving.

(6) The simulation is repeated to a maximum of 200,000 time steps.

(7) As the simulation proceeds, the relationship between total number of deposited particles and simulation time steps is saved onto hard disc.

(8) IBM RS6000 (Model : 350, 45MHz) and IBM compatible personal computer 486 (33MHz) were used in the simulation. The program was written using standard F77 FORTRAN. The typical FORTRAN program used for this simulation is shown in Appendix 7.I.

How can we compare simulation results obtained from 2-D slices with experimental results?

Simulations have been conducted in a two dimensional slice of a three dimensional space in many published papers. When the simulation results are compared with experimental results and theories, they must be converted into results for a 3-D space. However, in the published papers dealing with 2-D simulation, the conversion is not done at all. This means that the results obtained in 2-D slices are dealt as results obtained from 3-D spaces. For instance, if hemispherical growth is simulated in a 2-D slice, the deposition currents can be regarded as currents obtained to form the tunnel-type (not hemispherical) deposit shown in figure 7.2 (a). (Furthermore, in the case of studies of dendritic growth by 2-D simulation, it can be considered that the image of dendrite is like figure 7.2 (a').) Thus in order to simulate hemispherical growth, a proper method of conversion from 2-D to 3-D is required. As the method, rotation of the semicircular centre was proposed.

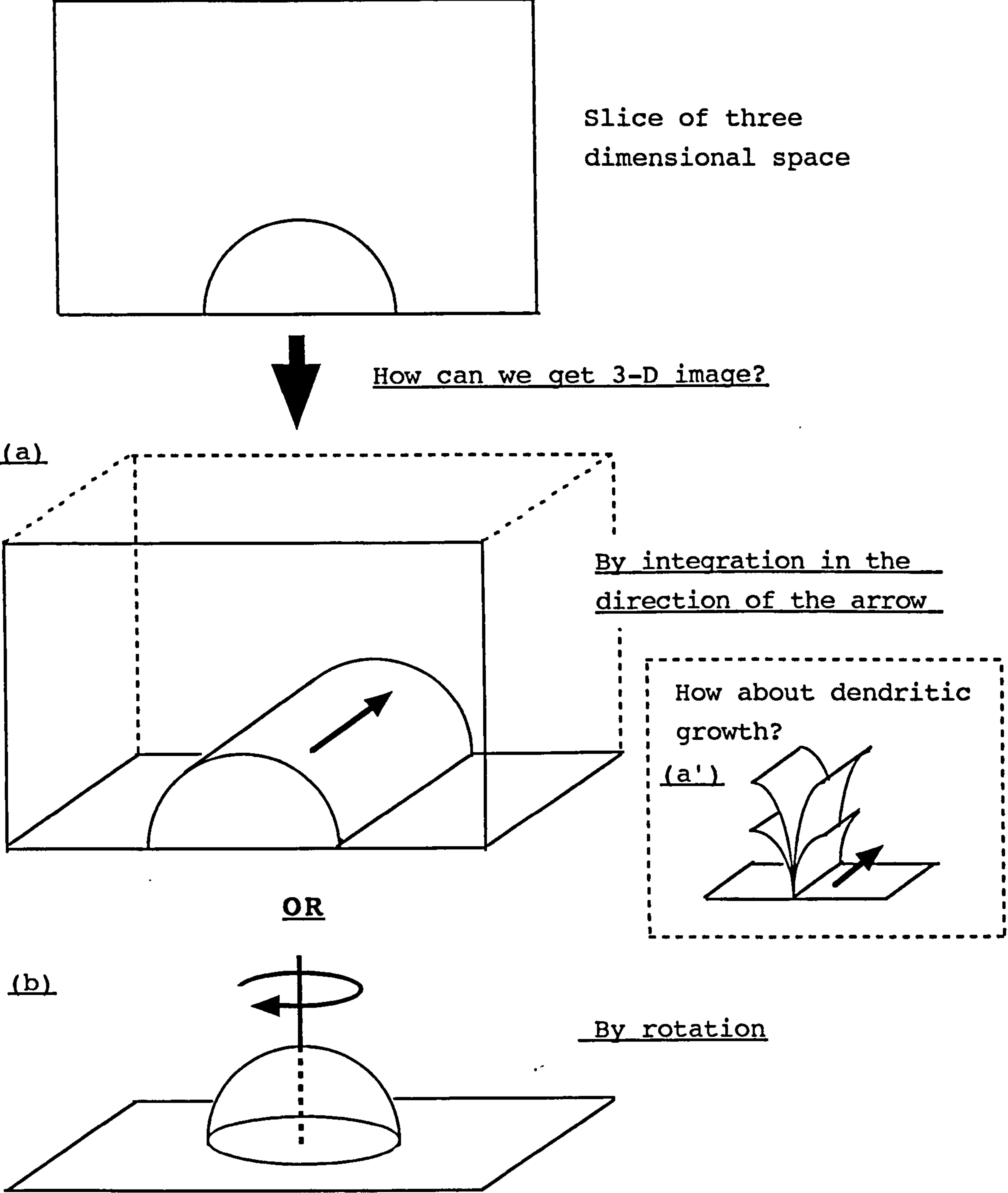


Figure 7.2 Conversion from two dimensional simulation into three dimensional simulation.

Since the hemispherical centre can be obtained by the rotation of semicircle, it was expected that the proper current of hemispherical growth could be obtained. However, the following problem shown in figure 7.3 is found. By the rotation of one growth centre, the neighbour centre forms a doughnut-type deposit.

(NOTE : in the simulation used here, just one active site is put on an electrode. However, since periodical boundary conditions are applied, it is considered that the hemispherical centre on the active site is surrounded by many imaginary hemispherical centres as shown in figure 7.7.)

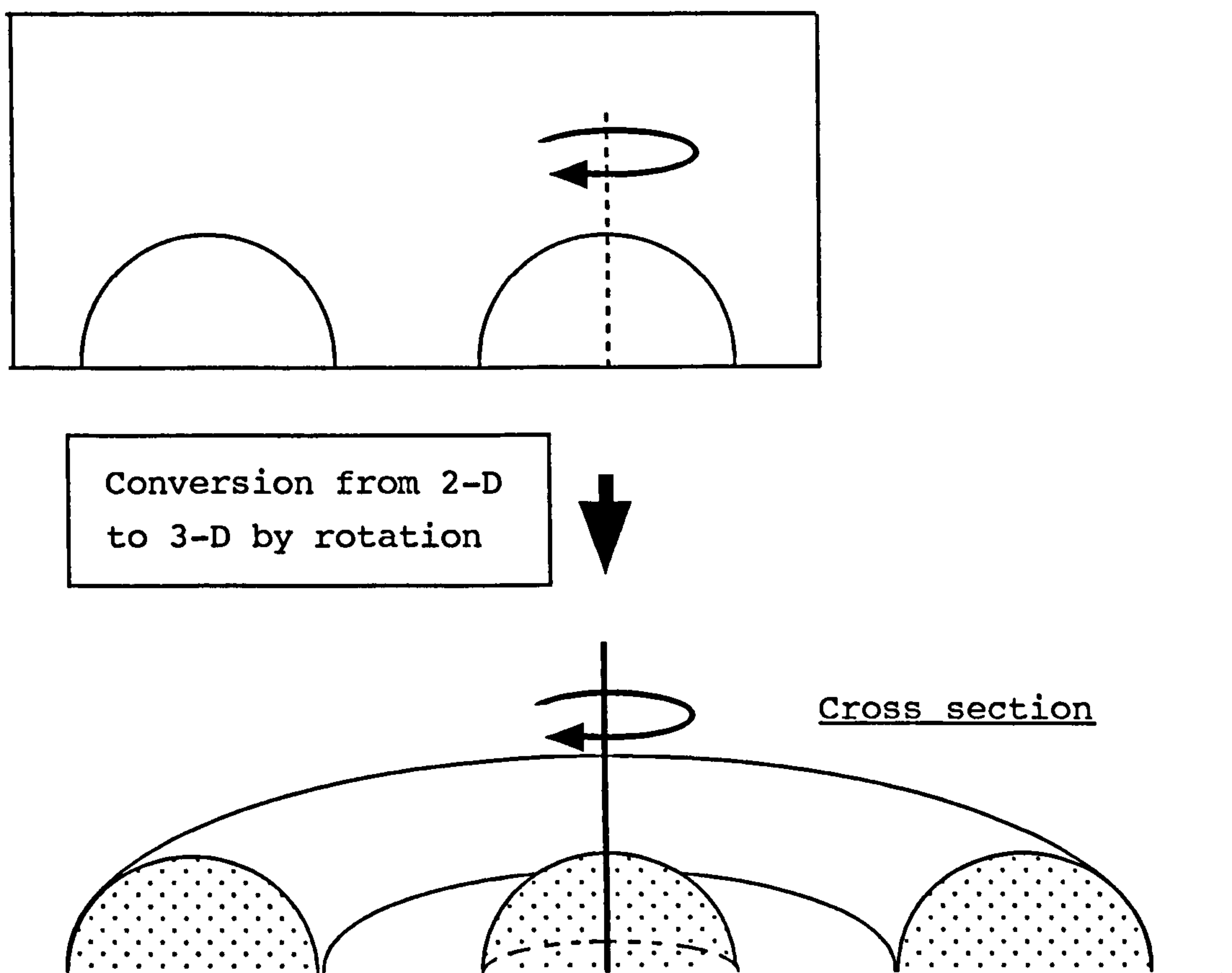


Figure 7.3 Growth of hemispherical centre surrounded by doughnut-type deposit ?

Since the growth of the hemispherical centre is influenced by the overlap of diffusion zones around the hemispherical centre and around the doughnut-type deposit, it is obvious that the simulation of the overlap of hemispherical diffusion zones is very important. From these points, it can be concluded that overlap of diffusion zones cannot be modelled properly by the simulation using a 2-D slice and that the simulation using a 3-D space should be carried out.

7.3 Results and discussion.

7.3.1 Qualitative discussion.

Figure 7.4 shows the deposit obtained by the simulation programmed here. The size of the domain is $50 \times 50 \times 80$ and the ratio of number of mobile particles to lattice sites, r is 10%. The snapshot was obtained after 4000 time steps. During the 4000 time steps, 7,500 deposition events occurred, i.e. the deposit consists of 7,500 particles. Thus, the hemispherical centre can be obtained by diffusion limited aggregation with the unique sticking condition (before sticking, a depositing particle moves to the closest vacant site to the active site by surface diffusion and sticks permanently at the site). Figure 7.5 shows the relationship between the number of deposited particles and the number of time steps. The simulation conditions are the same as those in figure 7.4. The simulations were repeated 20 times and the average is shown in this figure. This relationship is equivalent to the relationship between charge and time. Since current-time responses are more familiar than charge-time responses, the current-time relation is obtained from figure 7.5 by numerical differentiation and shown in figure 7.6. The current is derived by dividing the number of particles deposited in

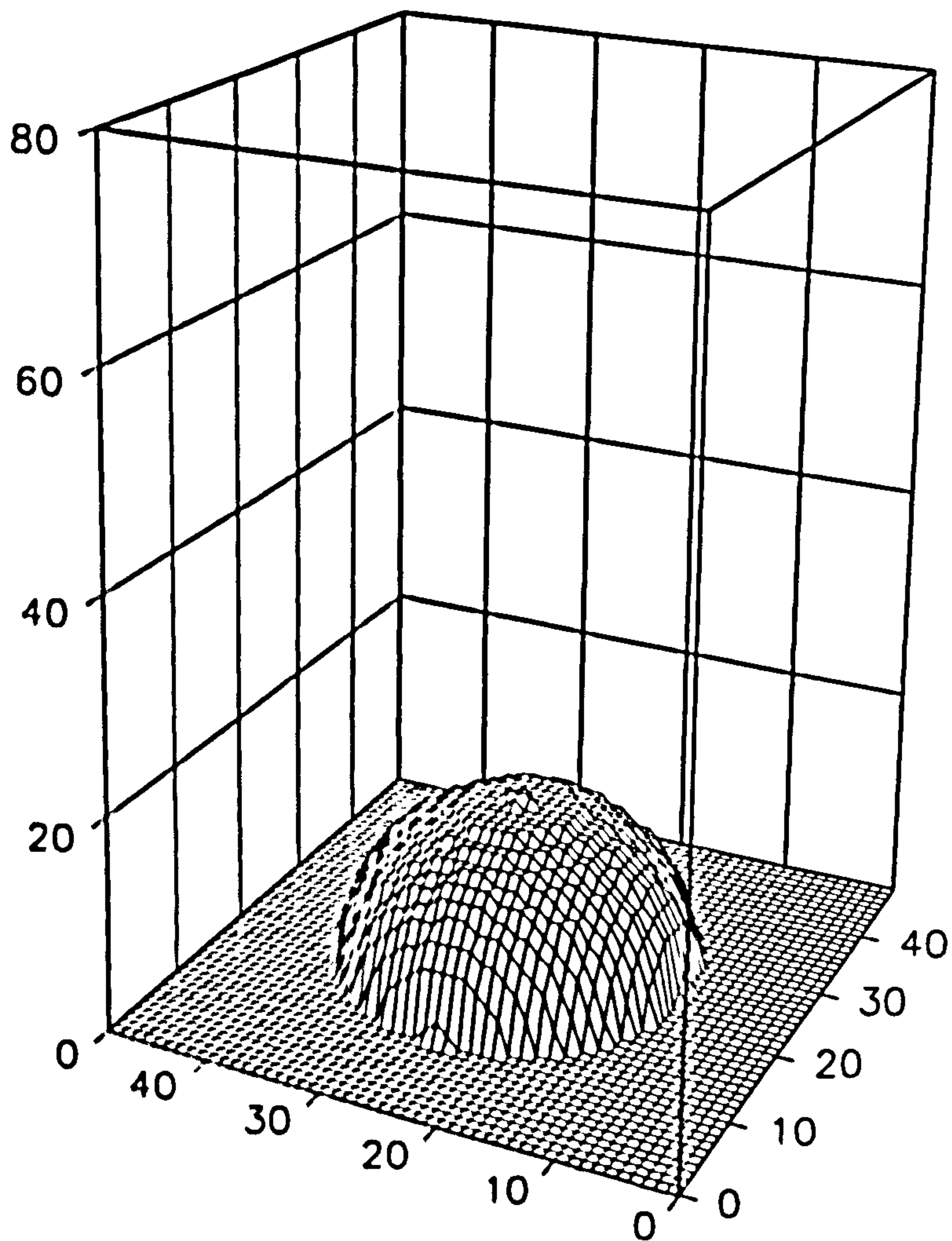


Figure 7.4 Snapshot of simulated hemispherical growth centre taken at 4000 time steps.
(number of deposited particles = 7500)
concentration, $r = 10\%$
domain size = $50 \times 50 \times 80$

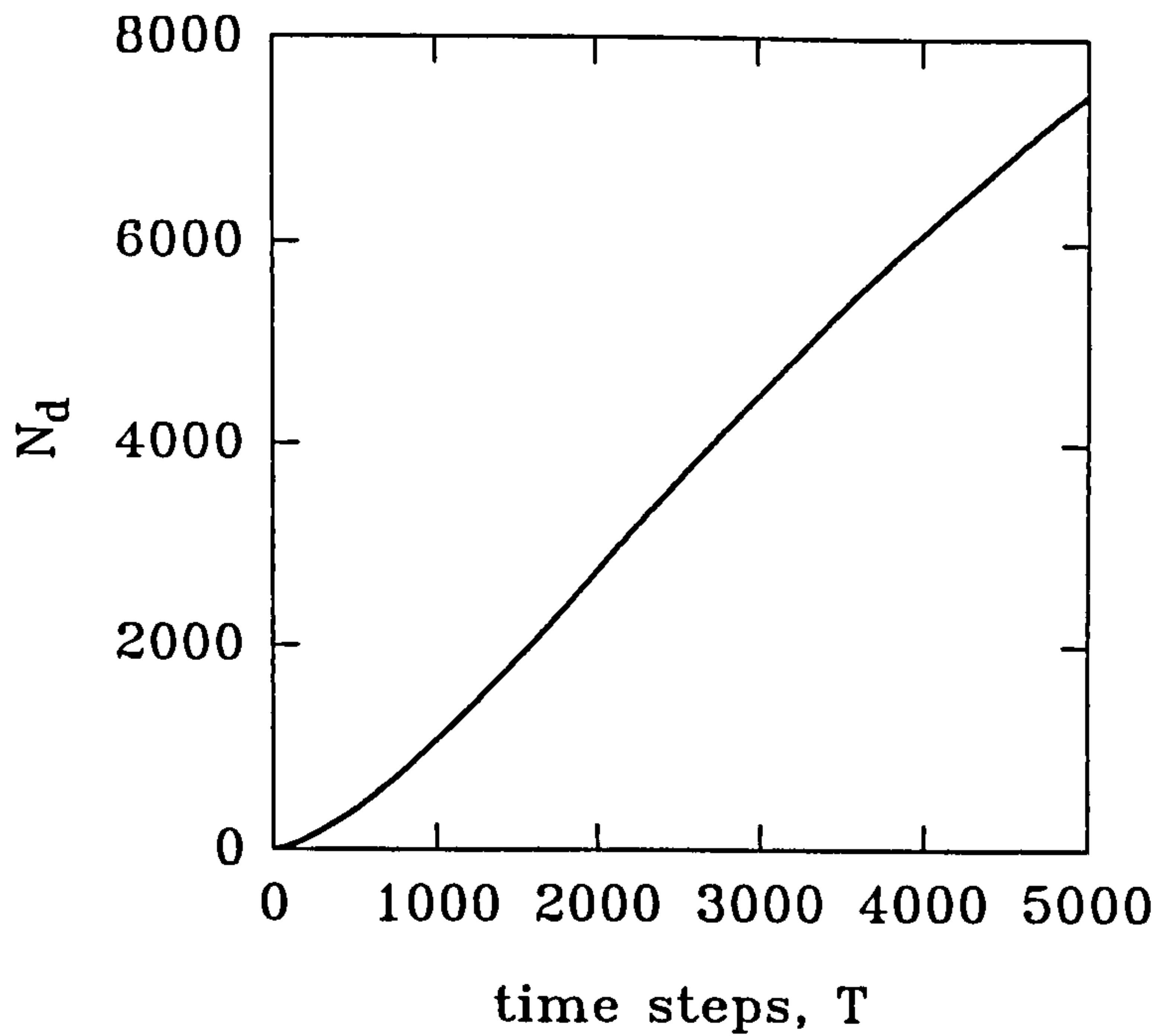


Figure 7.5 Simulated charge-time curve obtained by averaging 20 simulations.
(simulation condition as in figure 7.4)

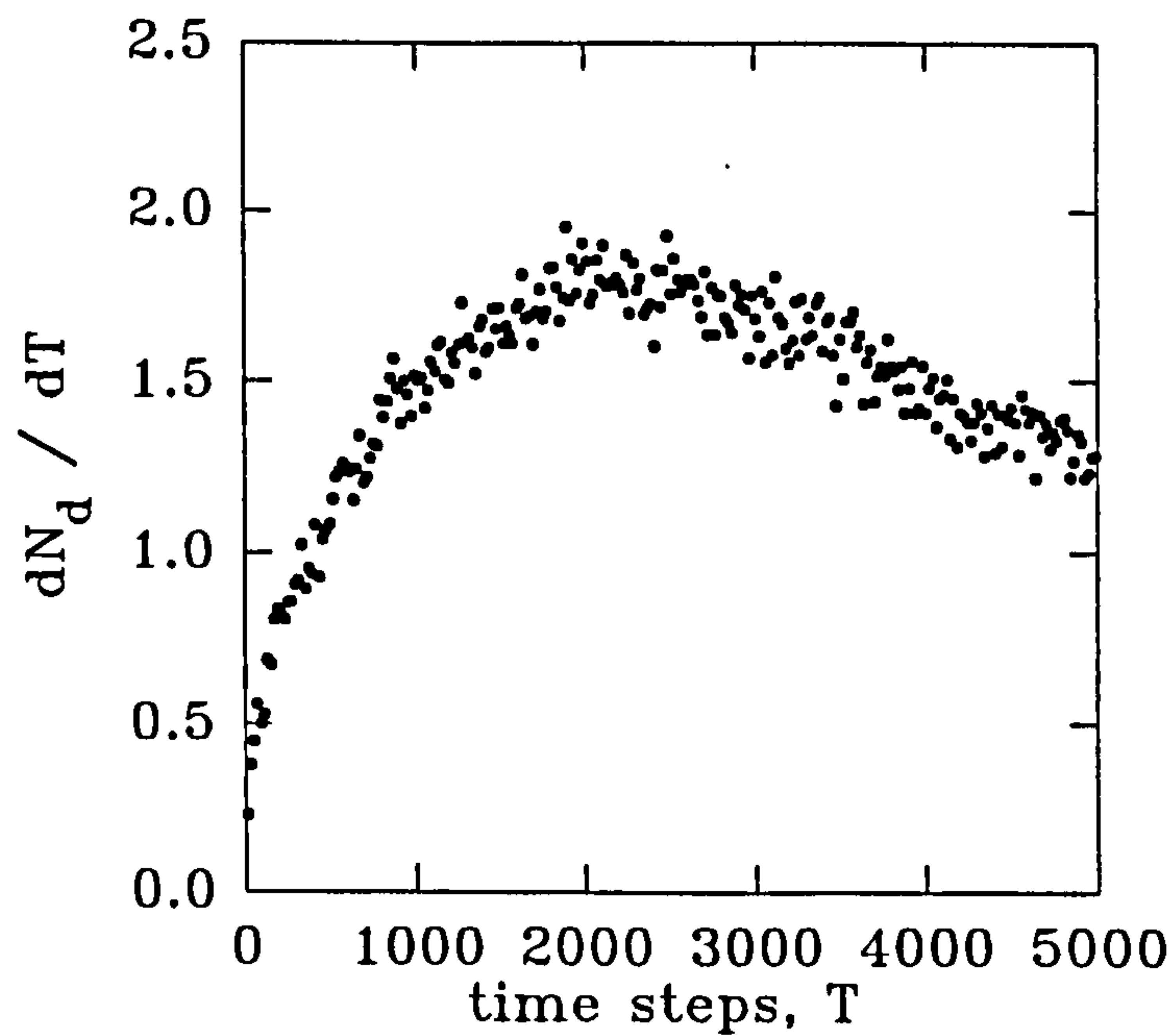


Figure 7.6 Simulated current transient obtained by averaging 20 simulations.
Simulation conditions as in figure 7.4.

$$dN_d / dT = (\text{number of deposited particles during } 20 \text{ time steps} / 20)$$

twenty time steps by twenty. Although the relation is noisier than the Q - t relation, it shows that the current increases initially and then decreases. As explained in section 2.3.3, the increase in current at early times is due to the growth of isolated hemispherical centres and the decrease at longer times is due to the overlap of diffusion zones. Although the growth of only one hemispherical centre is simulated, it can be regarded as a good model since the simulation space is surrounded by an infinite array of *ghost* simulation spaces arising from the periodical boundary conditions. The imaginary electrode surface is shown in figure 7.7.

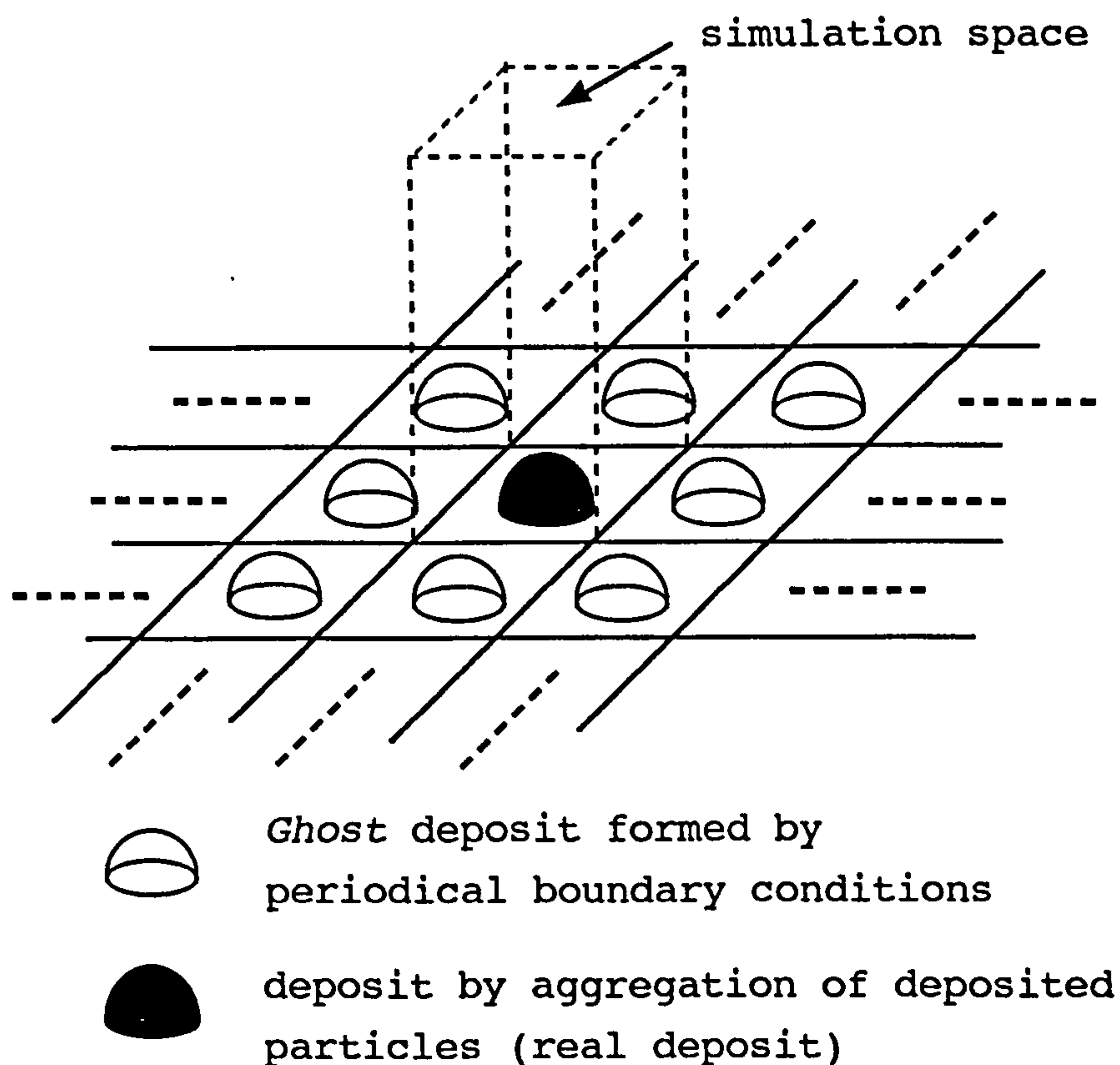


Figure 7.7 Imaginary electrode surface expected by periodical boundary conditions. This suggests that one active site is enough to discuss overlap of diffusion zones.

Thus, the existence of many *ghost* centres allows us to simulate the overlap of diffusion zones and overlap of growth centres. As already described in chapter 2, the current-time of a hemispherical growth under diffusion control is given by

$$i = \frac{nF\pi(2DC_b)^{3/2}M^{1/2}}{\rho^{1/2}} \cdot t^{1/2} \quad (7.1)$$

This relation can be observed before significant overlap of diffusion zones. Figure 7.8 shows $i^2 - t$ plots of figure 7.6. This figure shows an initial linear relation suggesting no significant overlap of diffusion zones up to 1000 steps. Although the Cottrell relation can be expected to be obtained at longer times, it could not be seen because

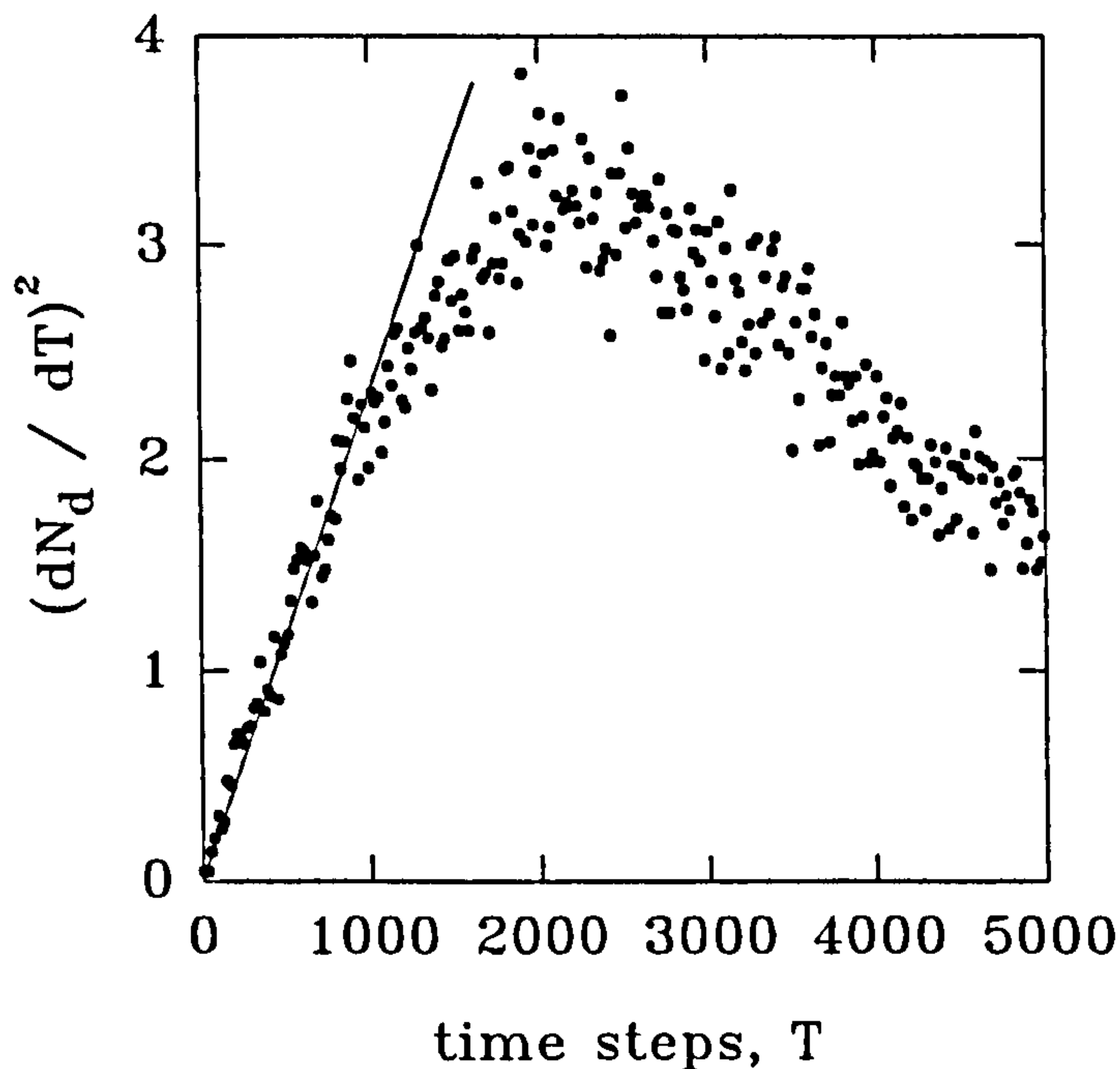


Figure 7.8 $(dN_d / dT)^2 - T$ plot obtained from figure 7.6.

5000 step times was not enough to reach the limiting behaviour. In order to investigate the overlap of diffusion zones, the distribution of mobile particles in the simulation space was observed at 1000, 2000, 3000 and 5000 time steps. Figure 7.9 shows cross sectional snapshots of the simulation space. A growth centre is observed on the centre of the electrode surface, and many mobile particles are shown in the simulation space. After 1000 time steps, the formation of a diffusion zone around the centre is visible. This diffusion zone has not grown to the edges of the simulation space and therefore it can be considered that the diffusion zones are isolated. After about 2000 time steps, the current reaches the maximum value. The distribution of mobile particles at 2000 time steps does not show clearly that the depletion zone of mobile particles has arrived at the boundaries. The arrival of the depletion zone at the boundary is, however, observed clearly in the image taken after 3000 time steps. The image taken after 5000 time steps shows that the modification of the diffusion zone from hemispherical to planar is almost complete, and it can be expected that the Cottrell relation will soon be obeyed.

7.3.2 Quantitative discussion.

Transformation of dimensional to dimensionless equations.

It was shown that the diffusion controlled growth of hemispherical centres could be simulated qualitatively. However, figure 7.9 also shows that the growth of the centre is rapid compared with the growth of the diffusion zone (i.e. although the thickness of the diffusion zone should be much larger than the radius of the centre, they appear to be the same).

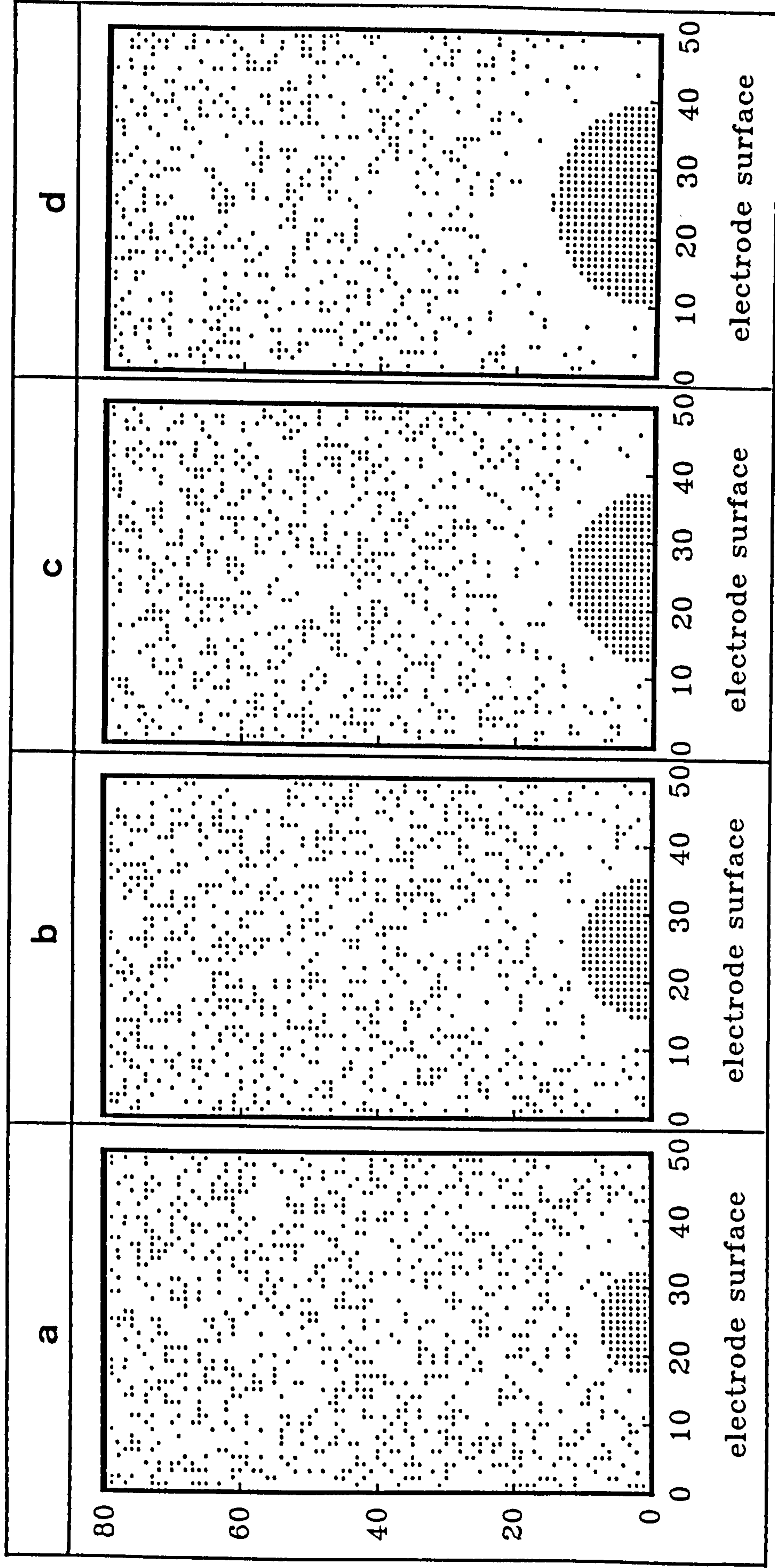


Figure 7.9 Snapshots showing distribution of mobile particles.
Images (a), (b), (c) and (d) are taken at 1000, 2000, 3000 and 5000 time steps.
Simulation conditions are shown in figure 7.4.

This is due to the high concentration of mobile particles, i.e. $r=10\%$. It is, therefore, necessary to establish the relationship between experimental conditions and simulation conditions.

Since the number of deposited particles is equivalent to the charge passed during the electrodeposition, the dimensionless form of the Q - t relationship is discussed (on the other hand, figures 7.4 and 7.5 show that the Q - t relation is much smoother than the i - t one). At short time, the i - t relation is given by equation 7.1. Integrating the current with respect to time yields

$$Q = \frac{2nF\pi(2DC_b)^{3/2}M^{1/2}}{3\rho^{1/2}} \cdot t^{3/2} \quad (7.2)$$

where Q (C) is the charge passed for electrodeposition during time, t / sec. For transformation, the following parameters are used.

- T : dimensionless time ($T = t/\Delta t$).
- Δt (sec) : diffusion time for distance, Δl .
- Δl (cm) : unit length, i.e. distance between two lattice sites.
- S^* (cm²) : dimensionless electrode area.
- N^* : total number of atoms in the simulation space.
- N_d : number of deposited particles.
- N_p : number of atoms in a mobile particle.
(it is assumed that mobile particles consist of N_p atoms.)

as simulation conditions,

- X, Y, Z : number of lattice sites along x , y and z axes of the simulation domain.
(volume of simulation space is $X\Delta l \cdot Y\Delta l \cdot Z\Delta l$ (cm³))

and the total number of lattice sites is XYZ).
 r : ratio of number of mobile particles to total number of lattice sites.

The bulk concentration, C_b ($\text{mol}\cdot\text{cm}^{-3}$) is expressed as

$$\begin{aligned} C_b &= \frac{\text{total number of atoms in simulation space}}{\text{Avogadro constant} \times \text{volume of the space}} \\ &= \frac{N^*}{N_A \times XYZ \cdot \Delta l^3} \end{aligned} \quad (7.3)$$

where N_A is the Avogadro constant and N^* is given by

$$N^* = r \cdot N_p \cdot XYZ \quad (7.4)$$

From equations (7.3) and (7.4),

$$C_b = \frac{r \cdot N_p}{N_A \times \Delta l^3} \quad (7.5)$$

(NOTE : The concentration, C_b , is only influenced by 'r' in the simulation conditions. This is clearly expressed in equation 7.26.)

The density of the deposit, ρ ($\text{g}\cdot\text{cm}^{-3}$) is given by

$$\begin{aligned} \rho &= \frac{\text{mass of } N_p \text{ atoms}}{\text{volume of unit space}} \\ &= \frac{N_p \cdot (M/N_A)}{\Delta l^3} \end{aligned} \quad (7.6)$$

The diffusion coefficient ($\text{cm}^2\cdot\text{sec}^{-1}$) is given by the Einstein-Smoluchowski relation and is expressed as

$$D = \frac{\Delta l^2}{6\Delta t} \quad (7.7)$$

Since dimensional time, t , is expressed as $t = \Delta t \cdot T$, substituting equations (7.5), (7.6) and (7.7) into (7.2) yields

$$Q = \frac{2nF\pi \cdot N_p}{N_A} \cdot \left(\frac{r}{3}\right)^{3/2} \cdot T^{3/2} \quad (7.8)$$

Q is also expressed as

$$Q = \frac{nF \cdot N_d \cdot N_p}{N_A} \quad (7.9)$$

where $(N_d \cdot N_p / N_A)$ is the number of moles in the deposit. From equations (7.8) and (7.9), the number of deposited particles, N_d , is given as a function of simulation step times.

$$N_d = \frac{2\pi}{3} \cdot \left(\frac{r}{3}\right)^{3/2} \cdot T^{3/2} \quad (7.10)$$

This dimensionless equation shows the relationship between the number of deposited particles and the simulation time steps in the early stages of the transients.

Then, since the Cottrell relation should be obtained at longer times, the dimensionless form of the Cottrell equation is discussed. The charge-time relation of the Cottrell equation is given by

$$q = \frac{2nFD^{1/2}C_b}{\pi^{1/2}} \cdot t^{1/2} \quad (7.11)$$

where q has a unit of $C \cdot cm^{-2}$ (i.e. q is the charge density and Q is the charge). Dividing equation (7.9) by the electrode area, q is also given by

$$q = \frac{nF \cdot N_d \cdot N_p}{N_A} \cdot \frac{1}{S^*} = \frac{nF \cdot N_d \cdot N_p}{N_A} \cdot \frac{1}{X\Delta l \cdot Y\Delta l} \quad (7.12)$$

From equation (7.5), (7.7), (7.11) and (7.12), the dimensionless form of the N_d - T relation derived from the Cottrell equation can be expressed as

$$N_d = \frac{2}{(6\pi)^{1/2}} \cdot r \cdot XY \cdot T^{1/2} \quad (7.13)$$

Comparison between simulated and theoretical Q-T curves.

The theoretical slope of the N_d - T relation at short times is obtained by substituting the simulation condition, r into equation (7.10). By the substitution, the value of $N_d / T^{3/2}$ was found to be 0.0127. Figure 7.10 shows the relation of $N_d^{2/3}$ - T obtained from figure 7.5. In this figure, a broken straight line is drawn at the theoretical

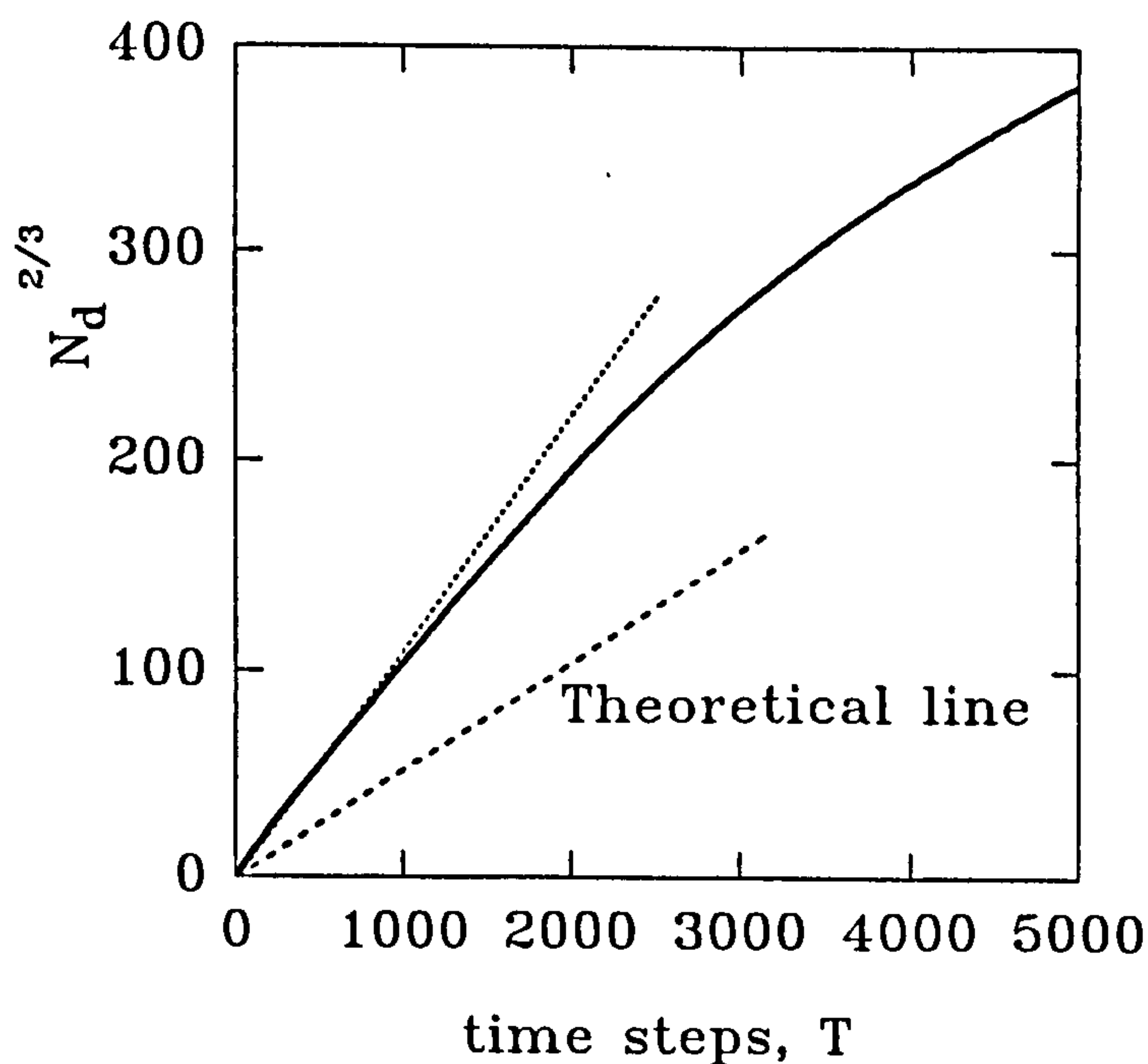


Figure 7.10 Comparison between slopes obtained by the simulation ($r=10\%$ is equivalent to 6.2M) and obtained from equation (7.10). The simulation conditions are shown in figure 7.4.

slope of 0.054 ($0.0127^{2/3}$). As shown in this figure, the simulation result is two times steeper than the theoretical one, and therefore it was found that results expected theoretically cannot be simulated quantitatively. The big difference is due to the high concentration of mobile particles as indicated in the observation of growth rates of deposit and diffusion zone (figure 7.9). The concentration, C_b can be derived by equation (7.5). Now, it is assumed that atoms are cubic in shape and the size is $3\text{\AA} \times 3\text{\AA} \times 3\text{\AA}$. Since N_p is the number of atoms in unit volume, Δl^3 , N_p is expressed as a function of Δl .

$$N_p = \Delta l^3 / (3\text{\AA})^3 \quad (7.14)$$

Substituting equation (7.14) into (7.5) yields

$$C_b = \frac{r}{N_A \cdot (3 \times 10^{-9})^3} \quad (7.15)$$

For $r = 0.1$, the concentration is found to be 6.15M. This concentration is obviously much too high, particularly for diffusion limited deposition. Equation (7.1) is obtained under the assumption that the growth rate of deposits is negligibly small compared with the growth of diffusion zones, and it is clear that this assumption is not valid for such a concentrated solution.

Effect of concentration on simulation results.

By the use of dilute solutions, it can be expected that proper N_d -T relations are obtained. In order to investigate the effect of concentration on the slope of N_d -T relations, simulations at different values of r (10%, 1%, 0.1% and 0.02%) were carried out. The four concentrations 10%, 1%, 0.1% and 0.02% correspond to 6.2M, 0.62M, 62mM and 12mM

respectively, as given by equation (7.15). Figure 7.11 shows $N_d^{2/3}$ -T relation obtained from 0.1% solution.

Comparison between figures 7.11 and 7.10 suggests that with decreasing concentrations, the difference of simulated and theoretical slopes becomes smaller. Figure 7.12 shows the ratio of simulated / theoretical slope as a function of concentration. Although the ratio decreases rapidly when the concentration changes from 10% to 1%, the ratio tends toward 1.2 at lower concentrations. The reason why the simulation results are 1.2 times larger than theoretical ones is not clear. Gunawardena et al.[13] have obtained current-time relations for hemispherical centre growth under diffusion control by the finite difference technique (overlap of diffusion zones was not simulated). They simulated two moving boundaries (i.e. boundaries of growing centre and of diffusion zone) which influence each other. As the result, they described that the current is proportional to square root of the time and that the slope of i - $t^{1/2}$ is 1.04 times larger than that expected by equation (7.1). The difference was explained by the fact that growth of deposit is neglected to get the theoretical equation ('moving boundary' effect). They regarded the value as a constant attached to this particular type of 'Stefan flux' problem and modified equation (7.1) by multiplying the equation by the constant, 1.04. However, as they proposed 1.04 as a compensation obtained by finite difference, we also propose 1.3 ($1.2^{3/2} = 1.3$) as a new value of the constant obtained by diffusion limited aggregation. (NOTE : Although this value depends on concentration above 0.6M, it cannot be expected that, in practice, we encounter hemispherical growth under complete diffusion control in concentrations higher than 0.6M. This constant does not depend on the other conditions.)

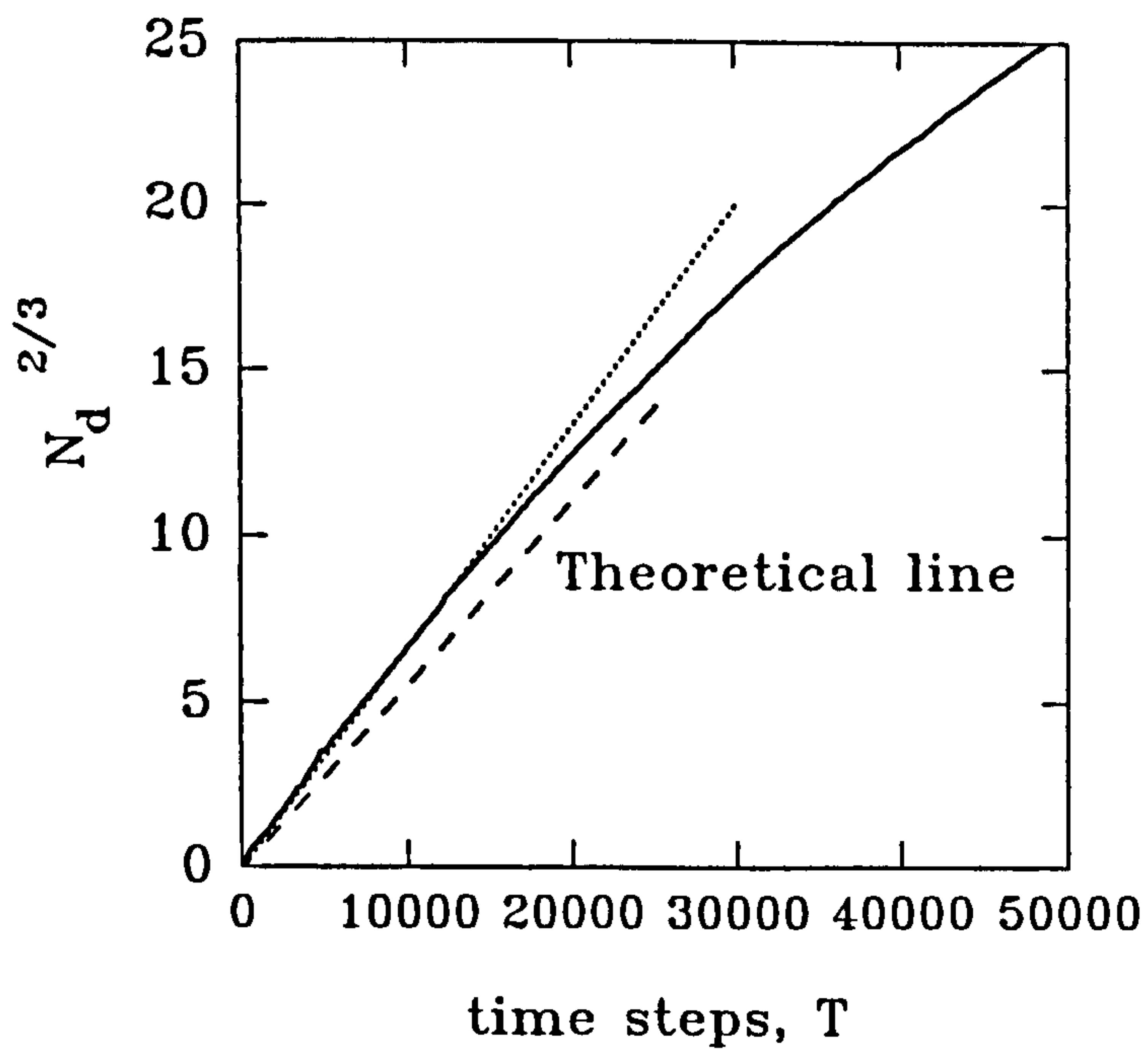


Figure 7.11 Comparison between slopes obtained by the simulation ($r=0.1\%$ is equivalent to 62mM) and obtained from equation (7.10).

CONDITIONS : domain size = 50 x 50 x 80, $r=0..1\%$
average of 100 simulations

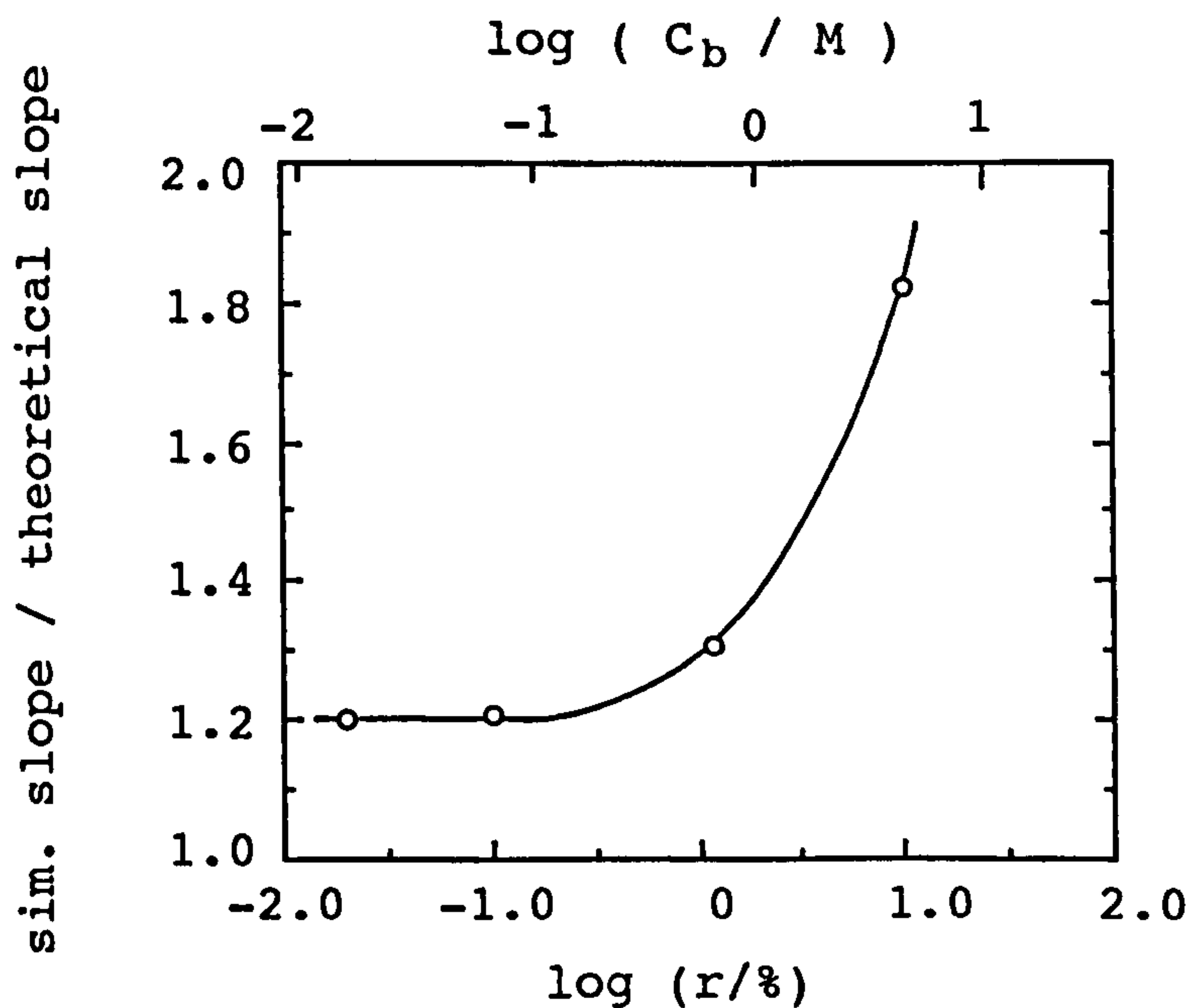


Figure 7.12 Effect of concentration on slopes obtained from $N_d^{2/3} - T$ plots.

Effect of height of simulation spaces on the Cottrell region.

The Cottrell relation can be observed in the current transients of hemispherical growth under diffusion control at longer times. However, as the diffusion zones grow with time, the ceiling of the simulation domain may influence the prolonged transients. Figure 7.13 shows the simulated result obtained from a simulation space of $50 \times 50 \times 80$. The concentration, r is 0.1%. In order to verify if the Cottrell relation is obeyed, the results are plotted as N_d^2 vs. T . In the region of 40000 to 60000 time steps, a linear relationship is observed indicating establishment of the Cottrell relation. However, after 60000 time steps, the simulated result showed a smaller number of deposited particles than the number expected from the straight line.

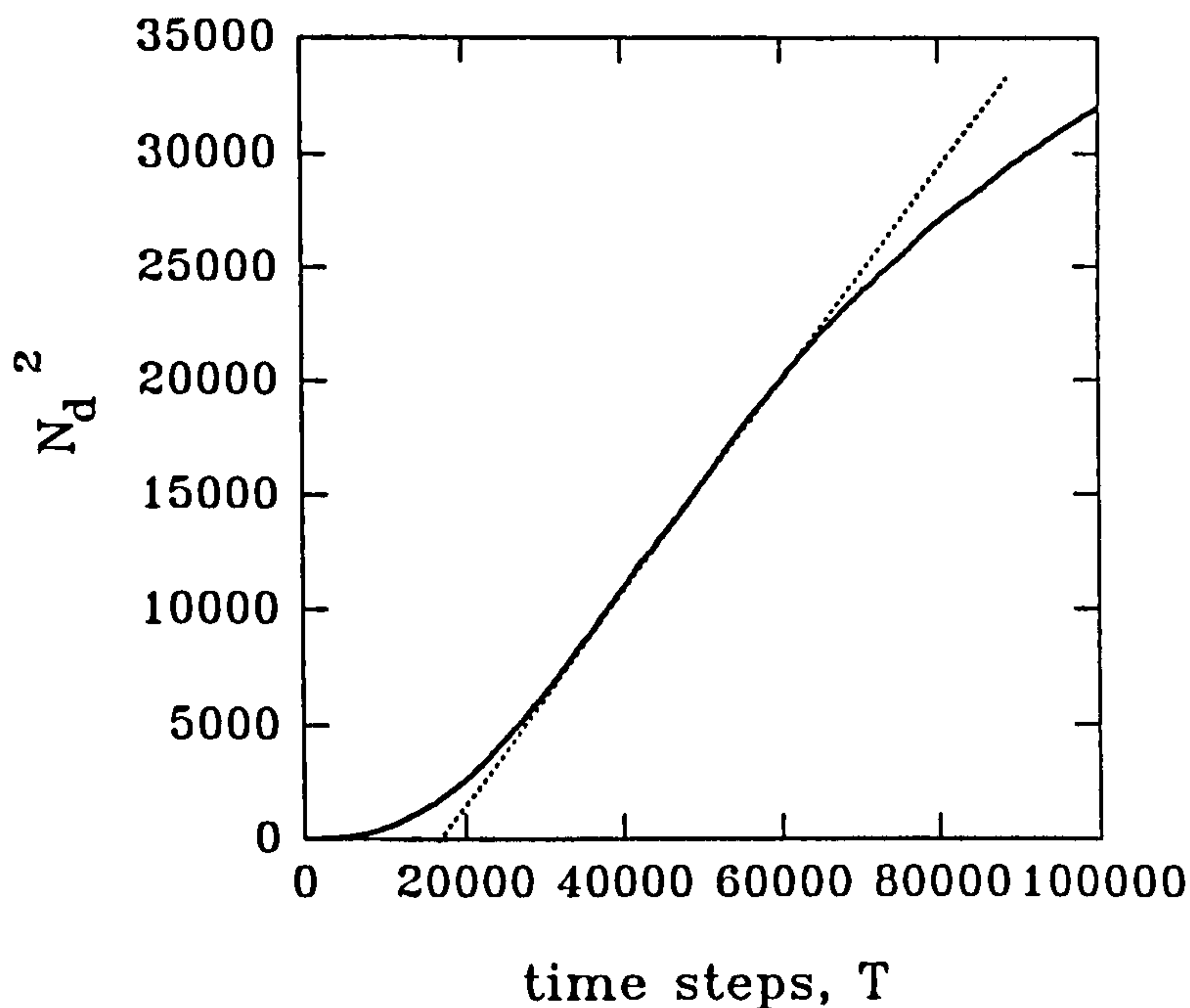


Figure 7.13 The Cottrell plot showing influence of ceiling. The simulation conditions are shown in figure 7.11.

This is obviously due to the influence of the ceiling of the simulation domain and suggests that the diffusion zone has reached the ceiling.

The theoretical slope of $Nd^2 - T$ (not $Nd-T^{1/2}$) can be obtained from equation (7.13) and the value is 1.3 ($X=Y=50$, $r=0.001$). Since the slope obtained by the simulation is 0.5, it was found that the straight line does not suggest the Cottrell relation. This straight line may be due to the combined effects of hemispherical growth (the growth rate is greater under hemispherical diffusion than planar diffusion) and of solution depletion (the arrival of the diffusion zone near the ceiling causes the depletion of mobile particles in the domain and thus the decay of the deposition rate).

Since the influence of the ceiling on transients was observed, the height required to obtain proper transients was investigated. The root-mean-square displacement (i.e. the thickness of the diffusion layer) at time t is derived roughly by considering a random walk process and is expressed as [14]

$$\begin{aligned}\delta &= (t/\Delta t)^{1/2} \Delta l \\ &= T^{1/2} \cdot \Delta l\end{aligned}\tag{7.16}$$

By substitution of 200,000 into T , the height of diffusion zone at 200,000 time steps is found to be $450\Delta l$. We considered 3 as the safety factor and regarded 1500 as an adequate height. The result simulated in a space of $50 \times 50 \times 1500$ is shown in figure 7.14. The slope obtained from the simulation is 1.2. The slope is slightly smaller than theoretical value ($=1.3$). Since it is known experimentally [13] that quite long deposition times are required to obtain the theoretical slope, it may be expected that the simulated

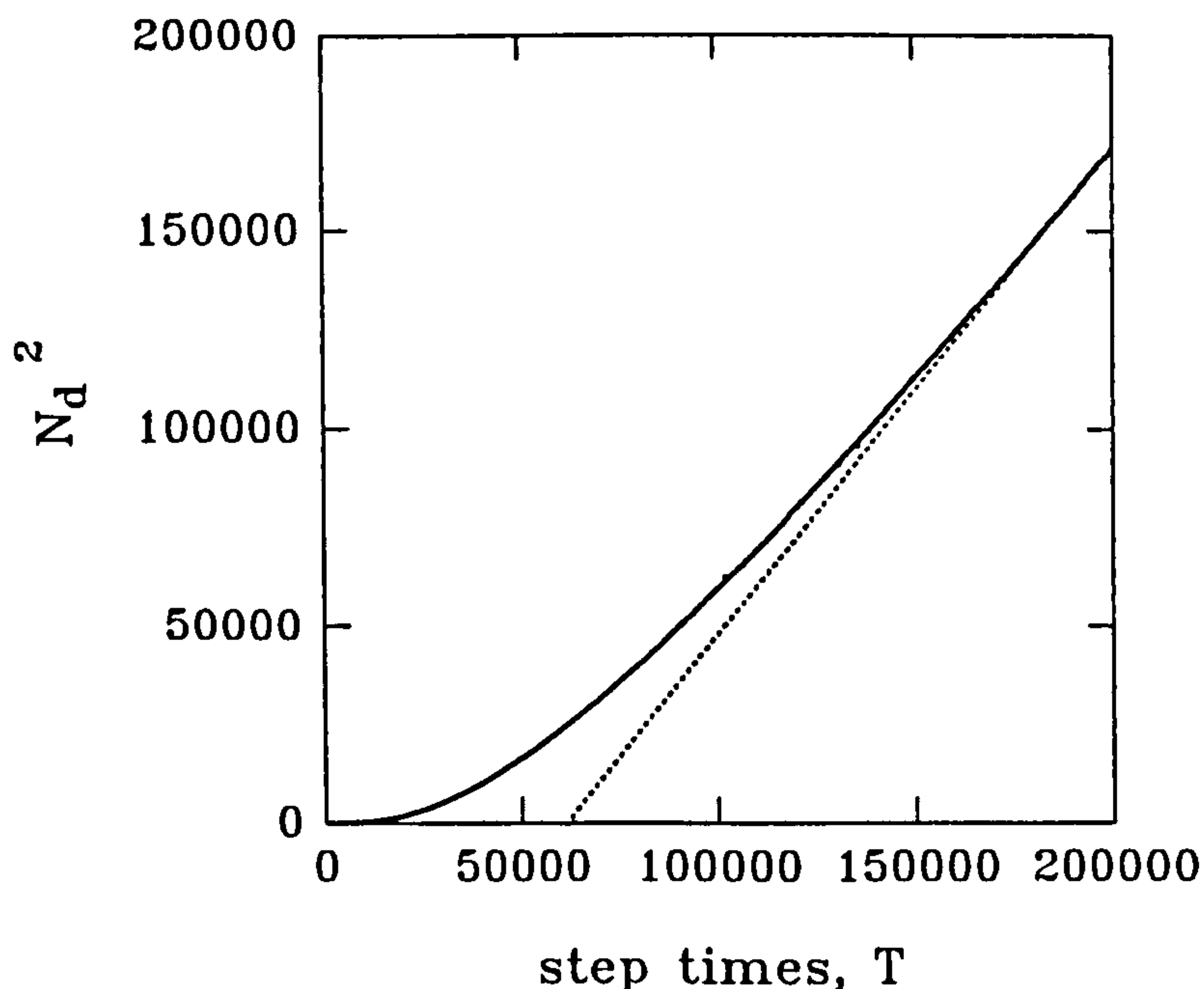


Figure 7.14 The Cottrell plot obtained in a large simulation space, 50 x 50 x 1500.
 $r = 0.1\%$ (equivalent to 62mM)

slope converges towards the theoretical value, when the simulation is prolonged. (it should be noticed that the height must be made larger when the simulation is extended.) From these points, it was decided that a height of 1500 was sufficient to observe the transition from isolated hemispherical diffusion to planar diffusion provided the simulation was stopped after 200,000 time steps.

7.3.3 Current transients obtained by the simulation.

As shown above, it was found that the simulation works well qualitatively and quantitatively for $r \leq 0.001$ and $\text{height} \geq 1500$. Figure 7.15 shows the current transients obtained by the simulation under the conditions $r=0.001$,

height=1500. The electrode sizes, $X \times Y$ in figure (a), (b) and (c) are 50×50 , 40×40 and 30×30 respectively (an electrode bigger than 50×50 requires a larger height, because the planar diffusion regime is not fully established even after 200,000 steps). The currents were the average of 100 simulations and were obtained by dividing the number of particles deposited during each 200 time steps by 200. In these figures, the current obtained with the 30×30 and 40×40 electrode surfaces have been rescaled to have an area equivalent to the 50×50 electrode surface (the electrode size, 50×50 is referred to as standard area in the figures). The series of dots show the current density-time relations. Although these data are obtained by average of 100 simulations, they still scatter. For the purpose of decreasing the scattering, a smoothing filter with Fast Fourier Transform [15] was used and the data after the smoothing (averaging of approximately 30 neighbour points) are shown with circles. Since one growth centre is located in the electrode surface, the difference in electrode area corresponds to a difference of nuclear number density (i.e. the nuclear number density of the simulation on an electrode of 30×30 is $25/9$ times larger than that on an electrode of 50×50). From these figures, it was found that the peak currents in the transients become larger and that the peaks occur earlier with increasing nuclear number density. This tendency was obtained experimentally and reported by e.g. Gunawardena et al.[13] and in this thesis (see chapter 5).

The simulated results are now compared with an analytical solution proposed by Gunawardena et al.[16] which describes the whole current transient obtained under instantaneous nucleation / diffusion controlled hemispherical growth.

$$j = \frac{nFC_b D^{1/2}}{\pi^{1/2} \cdot t^{1/2}} \cdot [1 - \exp(2\pi^{3/2} N_0 D \frac{(2C_b M)^{1/2} k}{\rho^{1/2}} \cdot t)] \quad (7.17)$$

Scharifker et al.[17], Sluyters et al.[18] and we (see chapter 5) have proposed equations for progressive nucleation / hemispherical growth under diffusion control. These equations can be rewritten for instantaneous nucleation, and as a result of the conversion, all the equations reduce to equation 7.17 (see chapter 2 for Scharifker's and Sluyters's equations). In order to compare the simulated results with equation 7.17, the equation was rewritten in dimensionless form. The current density can be expressed as

$$j = \frac{nF \cdot N_p}{(X\Delta l \cdot Y\Delta l) \cdot N_A \cdot \Delta t} \cdot \frac{dN}{dT} \quad (7.18)$$

Substituting equations (7.5), (7.7) and (7.18) into (7.17) yields the dimensionless form of equation (7.17).

$$\frac{dN_d}{dT} = \frac{XY \cdot r}{(6\pi T)^{1/2}} \cdot [1 - \exp(- \frac{(2\pi)^{3/2} r^{1/2} k \cdot T}{6XY})] \quad (7.19)$$

In this equation as well as in equation (7.17), a new constant, k is introduced. This constant compensates for the difference of slope of $N_d^{2/3}$ - T obtained by the simulation and equation(7.1), and the value is 1.3 as described above. The transients obtained from equation (7.17) are also plotted in figure 7.15. It was found that the equation shows a better fit with the simulated results at initial and longer times than at intermediate ones. The smaller current at the intermediate region may be due to an overestimate of the influence of planar diffusion. To improve the equation, the following point can be considered.

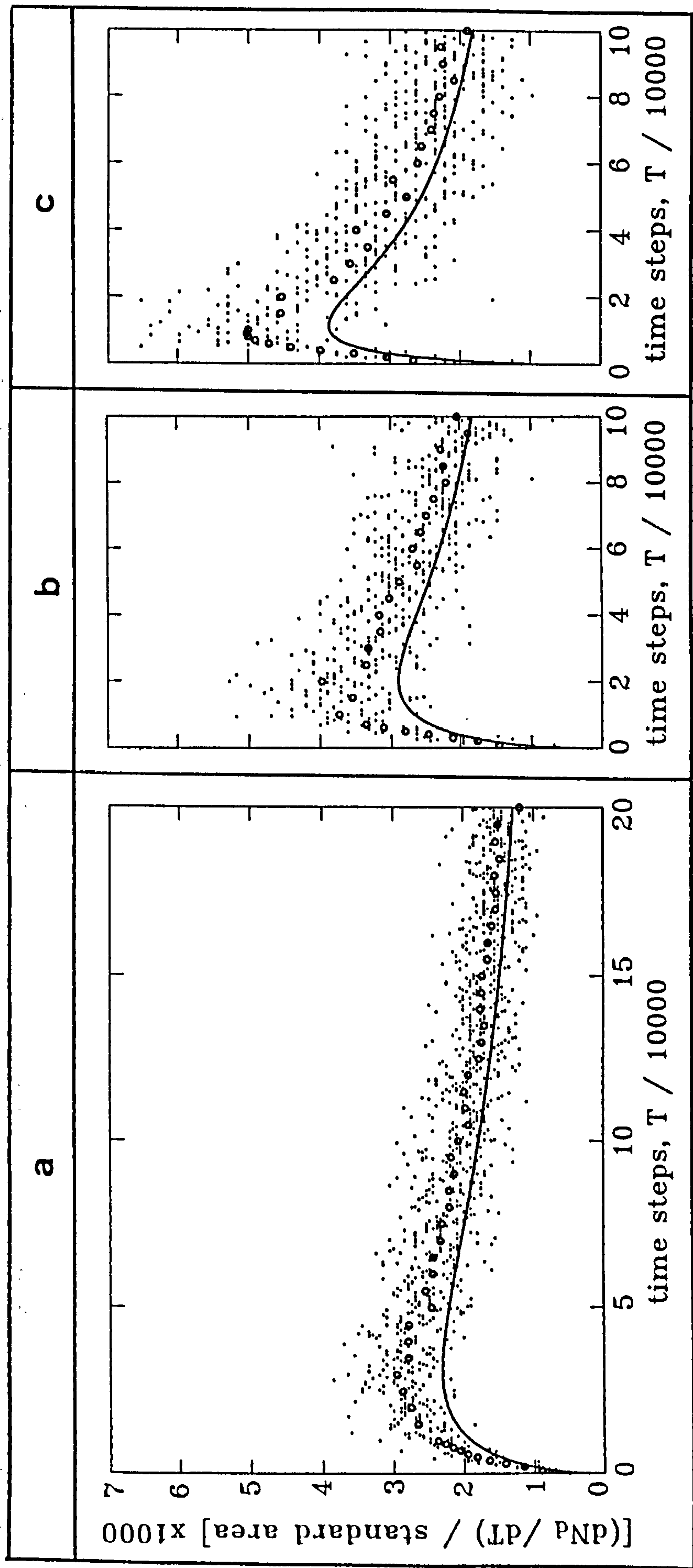


Figure 7.15 Simulated current transient curves obtained on electrodes of (a) 50 x 50, (b) 40 x 40 and (c) 30 x 30. Dots and circles show the raw data and the smoothed data, respectively. The lines show the current transient obtained from equation (7.19). Currents in b and c have been rescaled by multiplying with 25/16 and 25/9 respectively. (Height = 1500, $r = 0.18$)

As shown in figure 7.14 (as the experimental results, figure 5.7), the Cottrell plot does not pass through the origin of the ordinates. In figure 7.14, the intersect between the dashed line and the time axis defines the time at which planar diffusion starts, it is clearly remote from $T=0$. This suggests that a period is required for establishment of planar diffusion regime. However, equation (7.17) does not take this delay into account, and therefore the Cottrell term in this equation gives too large an effect on the current.

7.3.4 Transformation to dimensional results.

Results obtained by computer simulation are always dimensionless. In order to compare with experimental results, the results must be transformed to dimensional values. In this section, the transformation of the simulation results to dimensional form is described and the dimensional current transients are obtained from figure 7.15.

First, the time scale is discussed. The distance between active sites, l_{A-A} is given by

$$l_{A-A} = A^{-1/2} \quad (7.20)$$

where A is the nuclear number density. From equation (7.20), Δl is given by

$$\Delta l = \frac{l_{A-A}}{X} = \frac{1}{A^{1/2} \cdot X} \quad (7.21)$$

where the electrode is a square ($X=Y$). Substituting equation (7.21) into (7.7) yields

$$\Delta t = \frac{1}{6D \cdot A \cdot X^2} \quad (7.22)$$

By this equation, the dimensionless time can be given a unit. Then, dN_d/dT (i.e. number of deposited particles per time step) is converted to current density ($A \cdot cm^{-2}$). N_p can be rewritten from equation (7.6) as

$$N_p = \frac{N_A \cdot \rho \cdot \Delta l^3}{M} \quad (7.23)$$

where M is the molecular mass and ρ is the density of the deposit. Current density can be described as

$$j = \frac{nF \cdot N_p}{l_{A-A}^2 \cdot N_A \cdot \Delta t} \cdot \frac{dN}{dT} \quad (7.24)$$

Substituting equations (7.20), (7.21), (7.22) and (7.23) yields

$$j = \frac{\frac{nF \cdot \frac{N_A \cdot \rho \cdot \left(\frac{1}{A^{1/2} \cdot X}\right)^3}{M}}{\frac{1}{A} \cdot N_A \cdot \frac{1}{6D \cdot A \cdot X^2}}}{\frac{1}{A} \cdot N_A \cdot \frac{1}{6D \cdot A \cdot X^2}} \cdot \frac{dN}{dT} = \frac{6nF\rho D A^{1/2}}{MX} \cdot \frac{dN}{dT} \quad (7.25)$$

Thus, the equations to convert the dimensionless time and dimensionless current into dimensional values are obtained (equations 7.22 and 7.25). Next, the conversion of dimensionless concentration into dimensional value is described. Although C_b is given by equation (7.15), it can be expressed in a more general form. Substituting equation (7.23) into equation (7.5) yields

$$C_b = \frac{\rho}{M} \cdot r \quad (7.26)$$

This equation suggests that the dimensional concentration is determined only by the simulation condition, r .

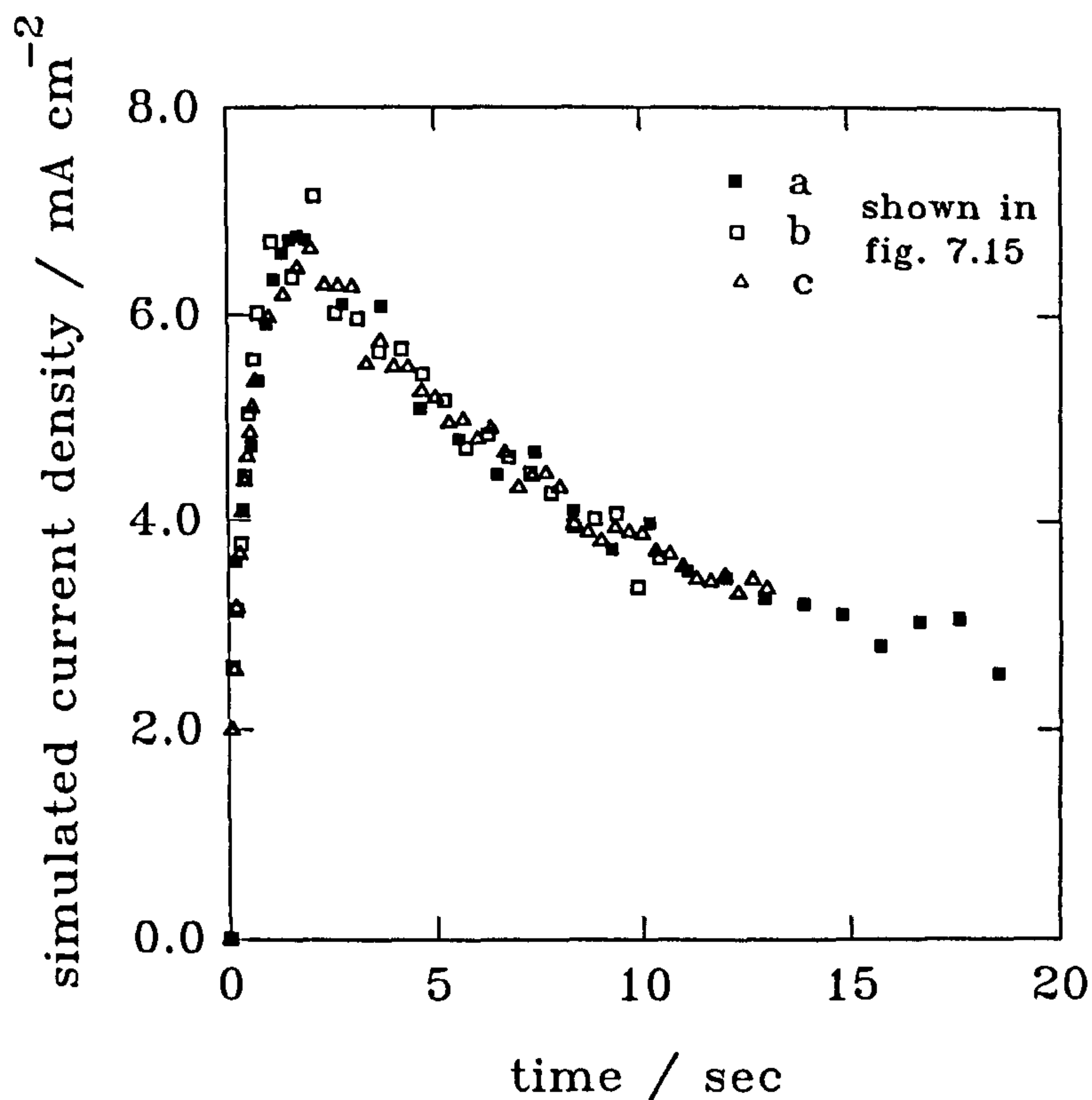


Figure 7.16 Dimensional current transients obtained from the simulation results shown in figure 7.15. Simulation conditions are shown in figure 7.15. Conversion conditions (mercury deposition)

$$1 \text{ mole of } \text{Hg}_2^{2+} = 401.2 \text{ g},$$

$$\rho = 13.53 \text{ g} \cdot \text{cm}^{-3}, n = 2$$

$$D = 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}, A = 10^5 \text{ cm}^2.$$

With equations (7.22) and (7.25), the simulated results shown in figure 7.15 are converted to dimensional values. The conversion is made for mercury deposition (7.27) as an example.



The following data are used for the conversion.

$$1 \text{ mole of } \text{Hg}_2^{2+} = 401.2\text{g} \text{ (1 mole of Hg} = 200.6\text{g)},$$

$$\rho = 13.53 \text{ g} \cdot \text{cm}^{-3}, n = 2, D = 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$$

Furthermore, as a value of nuclear number density, 10^5 is used. The converted result is shown in figure 7.16 (the smoothed data shown in figure 7.15 are used in this figure). Since the value of r used for the simulations is 0.001, the concentration of Hg_2^{2+} is found to be 34mM from equation (7.26). The simulation results obtained on electrodes of 50 x 50, 40 x 40 and 30 x 30 gave the same transient curves after transformation. Since the three transients were converted under the same conditions (same nuclear number density, same concentration and so on), the three transients ought to be the same. The identity of the three simulations may be considered as evidence to show that the simulation works properly. The difference of electrode sizes simply corresponds to different simulation resolutions. This is , for instance, suggested by equation (7.22), i.e. with increase in x , Δt becomes shorter. Table 7.1 shows the differences in the resolution.

Table 7.1 Influence of electrode size on dimensional values showing that simulation resolution increases with increase in electrode size.

Electrode size	C_b (Hg_2^{2+}) / mM	Δt / μsec	Δl / μm	$N_p^* \times 10^{-10}$
30 x 30	34	185	1.05	4.8
40 x 40	34	104	0.79	2.0
50 x 50	34	67	0.63	1.0

N_p^* : number of atoms consisting one particle

The data for conversion are described in the text.

Finally, with the conversion conditions used to obtain figure 7.16, the effect of nuclear number density on converted transient curves is shown. Figure 7.17 shows the transient curves calculated using $A = 1 \times 10^5$, 2.5×10^5 , 5×10^5 and $7.5 \times 10^5 \text{ cm}^{-2}$ (see table 7.2). The curves are converted from the simulation result obtained on an electrode of 50×50 . Similar series of transients to figure 7.17 may be observed when current transients are measured at different potentials. For example, similar experimental results has been reported by Gunawardena et al. [13]. Since the nuclear number density changes with deposition potentials (see chapter 2), it can be considered that change in potentials (experiments) and change in nuclear number densities (simulation) are equivalent. The similarity is also considered to be an evidence to justify the simulation.

Table 7.2 Variation of dimensional values with change in nuclear number density, A.

$A \times 10^{-5}$ / cm^{-2}	$C_b (\text{Hg}_2^{2+})$ / mM	Δt / μsec	Δl / μm	$N_p^* \times 10^{-10}$
1.0	34	67	0.63	1.0
2.5	34	27	0.40	0.26
5.0	34	13	0.28	0.092
7.5	34	8.9	0.23	0.050

Electrode size used for conversion : 50×50 .

(NOTE : Gunawardena et al.[13] obtained the current transients of mercury deposition at various potentials. Their concentration was 10mM which is lower than the one

used here, and quantitative comparison cannot be carried out. However, as an example, in the case of $A = 10^5$, Gunawardena measured about $1.5\text{mA}\cdot\text{cm}^{-2}$ for the peak current and we obtain $7\text{mA}\cdot\text{cm}^{-2}$.)

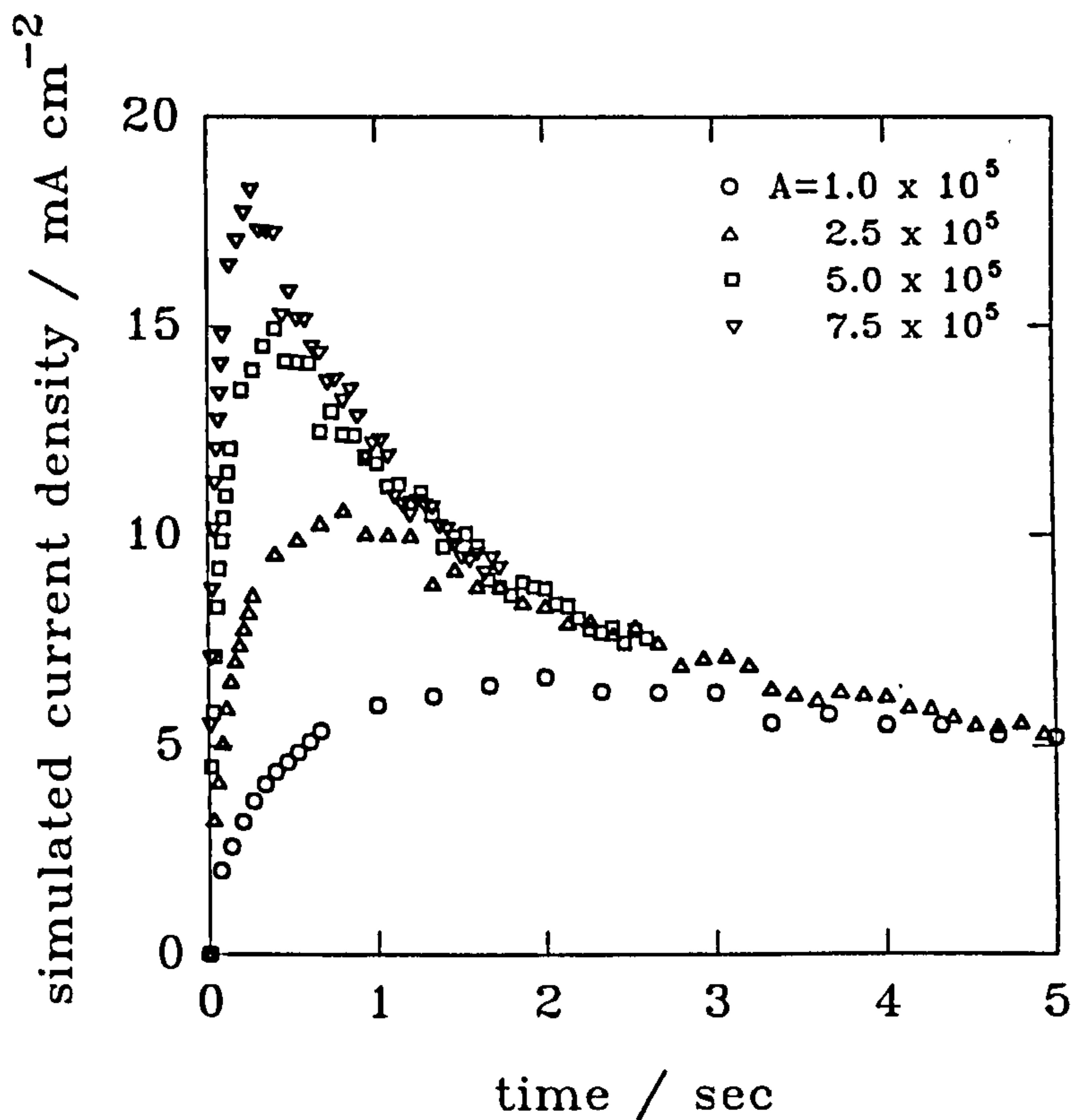


Figure 7.17 Dimensional current transients obtained from the simulation results shown in figure 7.15 (a). Simulation conditions are shown in figure 7.15. Conversion conditions are shown in figure 7.16. Four different values of A (nuclear number density, cm^{-2}) are used as shown in this figure.

7.4 Conclusions.

Computer simulations of instantaneous nucleation / hemispherical growth under diffusion control were carried out by three dimensional diffusion limited aggregation including a rapid surface diffusion step prior to the deposition, and the following conclusions have been reached.

(I) The influence of the model parameters has been studied. It was shown that a low concentration of mobile particles was required for an accurate modelling . It was also shown that the domain ceiling had to be larger in order to simulate planar diffusion. Simulations performed under various resolution conditions (i.e. electrode sizes used for simulations) have yielded identical results.

(II) The model has been used to image the growth of the deposit as well as that of its associated diffusion layer. It was possible to image the overlap of diffusion zones, and furthermore to visualize the transition from hemispherical to planar diffusion control.

(III) Simulated current transients have been compared to analytical expressions at short and long times. At short times, it was found that the slope of $Q^{2/3}$ -T relationship is 1.2 times larger than the theoretical value. This may be due to the fact that the growth of the deposit is always neglected when derived the analytical expressions. At longer times, the simulation yielded results in agreement with the Cottrell equation. An analytical equation valid at all times was found to deviate from the simulated transients.

(IV) Simulated transients obtained here have been successfully converted to dimensional values. A simulated

transient was obtained which can be used to model the influence of varying nuclear number density equivalent to varying the electrode potential.

(V) The simulation can be expected to be used for further theoretical predictions where analytical treatments fail due to the mathematical complexity of the situation.

(VI) Future work includes comparison with further experimental results, an in depth study of the 1.3 factor found for the growth of hemispherical centres and the development of this program for progressive nucleation.

Appendix 7.I. FORTRAN program used for the simulation of
instantaneous nucleation / hemispherical
growth under diffusion control.

The random number generator is taken from [19].

```
PROGRAM XYZSIM
*****
*   Instantaneous nucleation / hemispherical growth under *
*   diffusion control can be simulated.                    *
*   Number of active site :1                               *
*   Location of active site : (25,25)                      *
*   NOTE : Since periodical boundary conditions are       *
*           applied, location of the active site          *
*           does not influence simulation results.         *
*   Number of mobile particles : equal or less than 5000  *
*           (check parameters)                             *
*   MAXIMUM ARRAY SIZE : it is decided by the number of  *
*           mobile particles.                              *
*   Recommended XYZ : 50 x 50 x 1500 or bigger            *
*   Recommended PPS (r in the text) : 0.1% or less        *
*   This program will save data after 10 simulations.     *
*                                                         *
*           BY YOSHI                                       *
*   modified on 26 May 1993                               *
*                                                         *
*****
      INTEGER*4 XA, YA, h, XP, YP, SKI, AU, ST, XMINA, XMAXA,
+             YMINA, YMAXA
      INTEGER*4 XX, YX, ZX, X, Y, Z, OX, OY, OZ, BESTX,
+             BESTY, BESTZ, sd, SEA, SDP, a, b, c, d, k, i,
+             m, n, o, p, ES, NST, TNPS
      INTEGER*4 NSS,j,th,ths,tht,e,TE
      REAL      PPS,ran1,RMIN,R,s

*
      PARAMETER (max1=10,max2=10,max3=1,max4=5000,max5=10,
+             max6=2000)
      integer*4  TD(17:33,17:33,-1:15)
      integer*4  ID(max4)
      integer*4  XAS(max3),YAS(max3)
      integer*4  XPS(max4),YPS(max4),ZPS(max4)
      integer*4  DP(max5,max6)

*
      character*12 place
*****
      RINT*, 'Enter filename for data.(max 12 characters). '
      READ*,PLACE
      PRINT*, ' '
      PRINT*, PLACE
      OPEN(15,FILE=PLACE)

*
      INPUT SIMULATION CONDITIONS
*
```

```

PRINT*, 'Input length of X ..... '
READ*, XX
PRINT*, 'Input length of Y ..... '
READ*, YX
PRINT*, 'Input length of Z ..... '
READ*, ZX
PRINT*, 'Percents of sites occupied <=0.1% ...'
READ*, PPS
PRINT*, 'Number of simulation steps <=400000 ..... '
READ*, NSS
PRINT*, ' '
PRINT*, 'Number of simulation times=10(10times = 1set)'
NST = 10
PRINT*, ' '
PRINT*, 'Data are stored each ... times'
READ*, ES
PRINT*, ' '
PRINT*, 'How many times do you want to repeat?.....'
READ*, SEA
PRINT*, ''
PRINT*, 'Give a seed from your watch....'
READ*, sd

*
*   DECIDE A SEED
*
*   s = -1*sd
*
*   INITIAL VALUES
*
DO 4 SKI = 1,SEA
  DO 3 AU=1,NST
    DO 3 ST=1,NSS/ES
      DP(AU,ST)=0
3  CONTINUE
  DO 5 a= 1,NST
    SDP = 0

*
*   TNPS = NINT((XX+1)*(YX+1)*(ZX+1)*PPS*0.01)
*
*   SET OF AN ACTIVE SITE ON ELECTRODE
*
  Z = -1
  XAS(1) = 25
  YAS(1) = 25
  X = 25
  Y = 25
  PRINT*, 'POSITION OF ACTIVE SITE IS (25,25)'
  XMINA = X-8
  YMINA = Y-8
  XMAXA = X+8
  YMAXA = Y+8
  DO 14 b = -1,+15,1
    DO 14 c = X-8,X+8,1
      DO 14 d = Y-8,Y+8,1
        TD(c,d,b) = 0
14  CONTINUE
    TD(X,Y,Z) = 1

```

*
*
*

DISTRIBUTION OF PARTICLES(IONS) INTO SOLUTION

```
DO 40 i = 1, TNPS
  X = INT((XX+1)*RAN1(s))
  Y = INT((YX+1)*RAN1(s))
  Z = INT((ZX+1)*RAN1(s))
  XPS(i) = X
  YPS(i) = Y
  ZPS(i) = Z
  ID(i) = 2
40 CONTINUE
```

*
*
*

RANDOM WALK OF PARTICLES IN SOLUTION

```
DO 55 j = 1, NSS
  DO 60 k = 1, TNPS
    IF (ID(k) .NE. 2) GO TO 60
    OX = XPS(k)
    OY = YPS(k)
    OZ = ZPS(k)
    P = INT(RAN1(s) * 6 + 1)
    GO TO (61,62,63,64,65,66), P
61  X = MOD(OX+XX+2, XX+1)
    Y = OY
    Z = OZ
    GO TO 70
62  X = MOD(OX+XX, XX+1)
    Y = OY
    Z = OZ
    GO TO 70
63  Y = MOD(OY+YX+2, YX+1)
    X = OX
    Z = OZ
    GO TO 70
64  Y = MOD(OY+YX, YX+1)
    X = OX
    Z = OZ
    GO TO 70
65  Z = OZ + 1
    IF(Z .GT. ZX) Z = OZ
    X = OX
    Y = OY
    GO TO 70
66  Z = OZ - 1
    IF(Z .LT. ZN) Z = OZ
    X = OX
    Y = OY
    GO TO 70
70  IF (X.GE.XMINA .AND. X.LE.XMAXA .AND. Y.GE.YMINA
+    .AND. Y.LE.YMAXA .AND. Z .LE.15) THEN
    TD(X,Y,Z)=2
    ELSE
    GO TO 125
  END IF
```

*

IF (TD(X+1,Y,Z).NE.1.AND.TD(X-1,Y,Z).NE.1.AND.

```
+   TD(X,Y+1,Z).NE.1.AND.TD(X,Y-1,Z).NE.1.AND.
+   TD(X,Y,Z-1).NE.1) THEN
      TD(X,Y,Z) = 0
      GO TO 125
END IF
TD(X,Y,Z) = 0
SDP = SDP+1
DMIN = 1000
MIN = 1000
*
*   SELECT BEST SITE FOR DEPOSITION
*
      h = 0
      XA = XAS(1)
      YA = YAS(1)
1200  IF (TD(XA,YA,h).EQ.1) THEN
      h = h + 1
      GO TO 1200
END IF
*
IF( MOD (SDP,2) .EQ.1) THEN
  DO 1300 m = 0, h
    DO 1300 n = XA-h,XA+h
      XP = MOD(n+XX+1,XX+1)
      DO 1300 o = YA-h,YA+h
        YP = MOD(o+YX+1,YX+1)
        IF (TD(XP,YP,m).NE.1) THEN
          R = (YA-o)*(YA-o)+(XA-n)*(XA-n)+m*m
          IF (R.LT.RMIN) THEN
            BESTX = XP
            BESTY = YP
            BESTZ = m
            RMIN = R
          END IF
        END IF
      END IF
    END IF
  END IF
1300  CONTINUE
ELSE
  DO 1400 m = 0, h
    DO 1400 n = XA+h,XA-h,-1
      XP = MOD(n+XX+1,XX+1)
      DO 1400 o = YA+h,YA-h,-1
        YP = MOD(o+YX+1,YX+1)
        IF (TD(XP,YP,m).NE.1) THEN
          R = (YA-o)*(YA-o)+(XA-n)*(XA-n)+m*m
          IF (R.LT.RMIN) THEN
            BESTX = XP
            BESTY = YP
            BESTZ = m
            RMIN = R
          END IF
        END IF
      END IF
    END IF
  END IF
1400  CONTINUE
END IF
X = BESTX
Y = BESTY
Z = BESTZ
TD(X,Y,Z) = 1
```

```

        ID(k) = 1
125    XPS(k) = X
        YPS(k) = Y
        ZPS(k) = Z
        60    CONTINUE
            If(mod(j,ES).eq.0 ) THEN
                th = j/ES
                DP(a,th) = SDP
                PRINT*,SKI,a,j,DP(a,th)
            END IF
55    CONTINUE
        5    CONTINUE
            ths = NSS/ES
            DO 7,e=1,ths
                tht = e*ES
                PRINT*,tht,DP(1,e)
                IF(MOD(e,50).EQ.0 ) THEN
                    WRITE(15,2100) tht,DP(1,e),DP(2,e),DP(3,e),DP(4,e),
+                DP(5,e),DP(6,e),DP(7,e),DP(8,e),DP(9,e),DP(10,e)
                END IF
2100    FORMAT(1I8,10I5)
        7    CONTINUE
        4    CONTINUE
            PRINT*, '*****'
*
*    If you want to take an image of your deposit,
*    use the following program.
*
*        DO 500 t = 0,XX
*            DO 500 u = 0,YX
*                v = 0
*    510    IF (TD(t,u,v).EQ.1) THEN
*                v = v+1
*                GO TO 510
*            END IF
*            PRINT*,t,u,v
*            WRITE (15,2200) t,u,v
*    2200    FORMAT(3I4)
*    500    CONTINUE
            PRINT*, '*****'
            CLOSE(15)
15    END

        FUNCTION ran1(idum)
            INTEGER idum,IA,IM,IQ,IR,NTAB,NDIV
            REAL ran1,AM,EPS,RNMX
            PARAMETER (IA=16807,IM=2147483647,AM=1./IM,IQ=127773,IR=2836,
*            NTAB=32,NDIV=1+(IM-1)/NTAB,EPS=1.2e-7,RNMX=1.-EPS)
            INTEGER j,k,iv(NTAB),iy
            SAVE iv,iy
            DATA iv /NTAB*0/, iy /0/
            if (idum.le.0.or.iy.eq.0) then
                idum=max(-idum,1)
                do 11 j=NTAB+8,1,-1
                    k=idum/IQ
                    idum=IA*(idum-k*IQ)-IR*k
                    if (idum.lt.0) idum=idum+IM

```

```
11          if (j.le.NTAB) iv(j)=idum
            continue
            iy=iv(1)
        endif
        k=idum/IQ
        idum=IA*(idum-k*IQ)-IR*k
        if (idum.lt.0) idum=idum+IM
        j=1+iy/NDIV
        iy=iv(j)
        iv(j)=idum
        ranl=min(AM*iy,RNMX)
        return
    END
```

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