Self-assembled germanium islands grown on (0 0 1) silicon substrates by low-pressure chemical vapor deposition

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The time evolution of self-assembled Ge islands, during low-pressure chemical vapor deposition (LPCVD) of Ge on Si at 650 °C using high growth rates, has been investigated by atomic force microscopy, transmission electron microscopy, and Rutherford backscattering spectrometry. We have found three different island structures. The smallest islands are ''lens-shaped'' and characterized by a rather narrow size distribution, ≈ 4 nm high and ≈ 20 nm wide. Next to form are a distinct population of larger multifaceted ''dome-shaped'' islands, up to 25 nm high and 80–150 nm wide. Finally, the largest islands that form are square-based truncated pyramids with a very narrow size distribution, ≈ 50 nm high and ≈ 250 nm wide. The pyramidal islands normally seen in the intermediate size range (≈ 150 nm) are not observed. The small lens-shaped islands appear to be defect free, while some of the multifaceted islands as well as all the large truncated pyramids contain misfit dislocations. The existence of multifaceted islands, in the size range where pyramids have previously been reported and of truncated pyramids in the size range where multifaceted ''dome-shaped'' islands have previously been reported, is attributed to the high growth rate used. Furthermore, under the growth conditions used, the truncated-pyramid-shaped islands are characterized by a very narrow size distribution.

1. Introduction

In recent years, substantial research efforts have been devoted to the fabrication of quantum-dot structures, due to the interesting electronic and optical properties that can result from quantum confinement. Several novel applications for such structures have been envisaged, such as the single-electron transistor and intersubband quantum-dot infrared photodetectors. For such applications to be efficient, well-organized dots of near-identical size are required. Because of its compatibility with Si-based technology, the use of Ge quantum dots created by deposition on Si is of particular interest.

Qualitatively, Si and Ge are very similar in their structural and electronic properties. They both crystallize in the diamond structure and form a continuous series of solid solutions, of the type $Si_{1-x}Ge_x$, where the Ge composition, x, ranges between 0% and 100% and the lattice constant varies significantly with the composition [1, 2]. The lattice constant of Ge is $\approx 4.2\%$ larger than that of Si, resulting in a Stranski–Krastanow (SK) growth mode for Ge on Si. SK or layer-cluster mode starts as layer-by-layer or two-dimensional (2D) growth and proceeds as clustering or three-dimensional (3D) growth. Due to its larger lattice constant, the Ge lattice stores a high strain energy density as it grows on a Si substrate. After about three monolayers (ML) have been deposited, the growing surface becomes non-planar and islands form, thus relieving part of the misfit strain through expansion of the Ge lattice at the island peak [3].

The process of self-organization of Ge nanoscale dots is of great interest, both from a fundamental materials point of view, and from the practical viewpoint of fabrication of electronic and optical devices of dimensions smaller than those accessible by lithography. However, this process still has limitations that need to be overcome. In particular, the placement of individual islands cannot be defined at the beginning of growth and island sizes may be distributed over a wide range. It is hoped that a better understanding of the mechanisms involved in Ge island growth may lead to methods for narrowing the size distribution of these islands.

A significant number of studies have been performed with the aim of understanding the structural and compositional evolution of Ge islands grown on (0 0 1)

Si. The role played by different growth parameters, such as temperature, time, pressure, growth rate, and others, have been studied for different growth techniques.

In this paper we report results obtained on the structural evolution of Ge self-assembled islands grown under nominally identical conditions, for three different durations, in a low-pressure chemical vapor deposition (LPCVD) reactor designed and fabricated at the Southampton University Microelectronics center (SUMC). The SUMC–LPCVD reactor works at growth pressures up to 133 Pa, higher than those used in ultrahigh vacuum systems such as ultrahigh vacuum chemical vapor deposition (UHVCVD) and molecular beam epitaxy (MBE), and in other LPCVD equipments reported in the literature (16 Pa [4, 5] and 0.07–0.27 Pa [6, 7]), but lower than those used in atmospheric-pressure CVD (APCVD).

The growth rates used in this study (6–9 nm min^{-1}) are higher than have previously been reported. Under such growth conditions, multifaceted ''dome-shaped'' islands evolve into truncated pyramidal islands with a very narrow size distribution and no actual pyramids appear to form. This evolution is completely different from that described in the literature, where pyramidal structures are reported to form at intermediate sizes ($\approx$ 150 nm); they further evolve into multifaceted domes, and finally turn into larger stable pyramids [6–11].

2. Experimental procedure

The LPCVD reactor used for the growth of the samples studied is an experimental system designed and built at the Southampton University Microelectronics Centre with the aim of exploiting novel growth regimes between those operating in ultrahigh vacuum techniques (UHVCVD and MBE) and those in APCVD. The reactor can work at higher growth pressures and growth rates than is customary in conventional LPCVD machines.

In this study, we take advantage of the high growth rates available to investigate possible non-equilibrium effects in the evolution of Ge islands during growth. Three samples have been grown at high growth rates (6–9 nm min^{-1}) for three different durations.

The growth procedure was as follows: 100-mm $(0\,0\,1)$ oriented, n-type Si wafers were initially subjected to an *ex situ* standard RCA-clean. The ''RCA'' oxide was subsequently removed *in situ* through a hydrogen bake at 950 °C. The temperature was then lowered to 900 °C in a hydrogen flow and a 500-nm thick Si buffer was grown from silane (SiH_4) at 133 Pa, in order to further ensure an inhomogeneity-free growth surface. Finally, the temperature was lowered to 650 °C, in a hydrogen flow, the base pressure was reduced to 67 Pa and pure GeH_4 was flushed into the growth chamber.

The process was repeated on three different wafers for three different durations. The growth resulted in the formation of Ge islands ranging from a few tens of nanometers in width and less than 4 nm in height for the shortest growth time, up to 300 nm in width and 40–60 nm in height for the longest time. Samples were subsequently analyzed using Rutherford backscattering spectrometry (RBS), atomic force microscopy (AFM), and cross-sectional transmission electron microscopy (XTEM).

RBS measurements were carried out using a standard configuration (2-MeV He beam at near-normal incidence using both ''random'' and $\langle 1\,0\,0 \rangle$ channeling modes, and a solid-state detector with a resolution of 15 keV).

Information on the size and height distribution, and on the density of the Ge self-assembled islands was obtained using atomic force microscopy. A TopoMetrix Accurex II™ scanning probe microscope in contact mode was used for the topographical analysis of the three samples.

In addition to RBS and AFM analyses, samples from two of the wafers (those with Ge deposited for the medium and longest durations) have also been structurally analyzed in XTEM, in order to assess the state of misfit strain relaxation of the Ge islands through the presence or absence of misfit dislocations. A JEOL JEM 2000FX TEM was used at 200 kV, with a LaB_6 crystal source. The XTEM samples were prepared by mechanical grinding followed by milling at low angles ($\approx 6°$) in a Gatan precision ion polishing system (PIPS).

3. Results and discussion

The amount of Ge deposited on the three wafers was given by RBS measurements in the ''random'' orientation and is expressed here in terms of equivalent monolayers (ML) of Ge on the surface. For consistency with the literature, the lattice constant of bulk Ge is used, hence one equivalent monolayer is $\approx 6.3 \times 10^{14}$ Ge atom cm^{-2}. RBS results showed a Ge thickness (averaged over the beam-spot area of ≈ 1 mm^2 including a large sample of islands and the surface between them) of $\approx$ 3.6 ML in the shortest growth-duration wafer, $\approx$ 6.4 ML in the medium-duration wafer, and $\approx$ 10.7 ML in the longest duration wafer. The amount of Ge deposited increases linearly with the growth duration indicating good growth control. Upon analysis in the $\langle 1\,0\,0 \rangle$ channeling mode, all samples showed a low level of dechanneling, the level being lowest for the wafer with the smallest islands, indicating that these islands contain the lowest density of defects.

Two-dimensional (2D) AFM images of 1×1 μm^2 areas and three-dimensional (3D) AFM images of larger 5×5 μm^2 areas of each of the three wafers are shown in Fig. 1, while Fig. 2 shows height and size distributions, together with 2D AFM images of the larger areas $(5 \times 5\ \mu m^2)$ corresponding to the three growth conditions studied. In the case of 3.6 ML of Ge deposited, small ''lens-shaped'' islands with a density of 16 μm^{-2} (Fig. 1(a)) and a rather narrow size distribution, in the range 20–40 nm, can be observed (Fig. 2(a)). In the case of the 6.4 ML of Ge, in which 2.8 additional ML are deposited on the wafer, the system of islands has developed a bimodal size distribution consisting of small and intermediate-sized ''lens-shaped'' islands (Figs. 1(b) and 2(b)). The total density of islands $(19\ \mu m^{-2})$ does not change significantly from the previous case, suggesting that agglomeration and/or Ostwald ripening are not the dominant processes at this stage. Some small islands can still be observed, but most islands are of intermediate size ranging between 100–150 nm. These latter islands are multifaceted ''domes'', as seen in

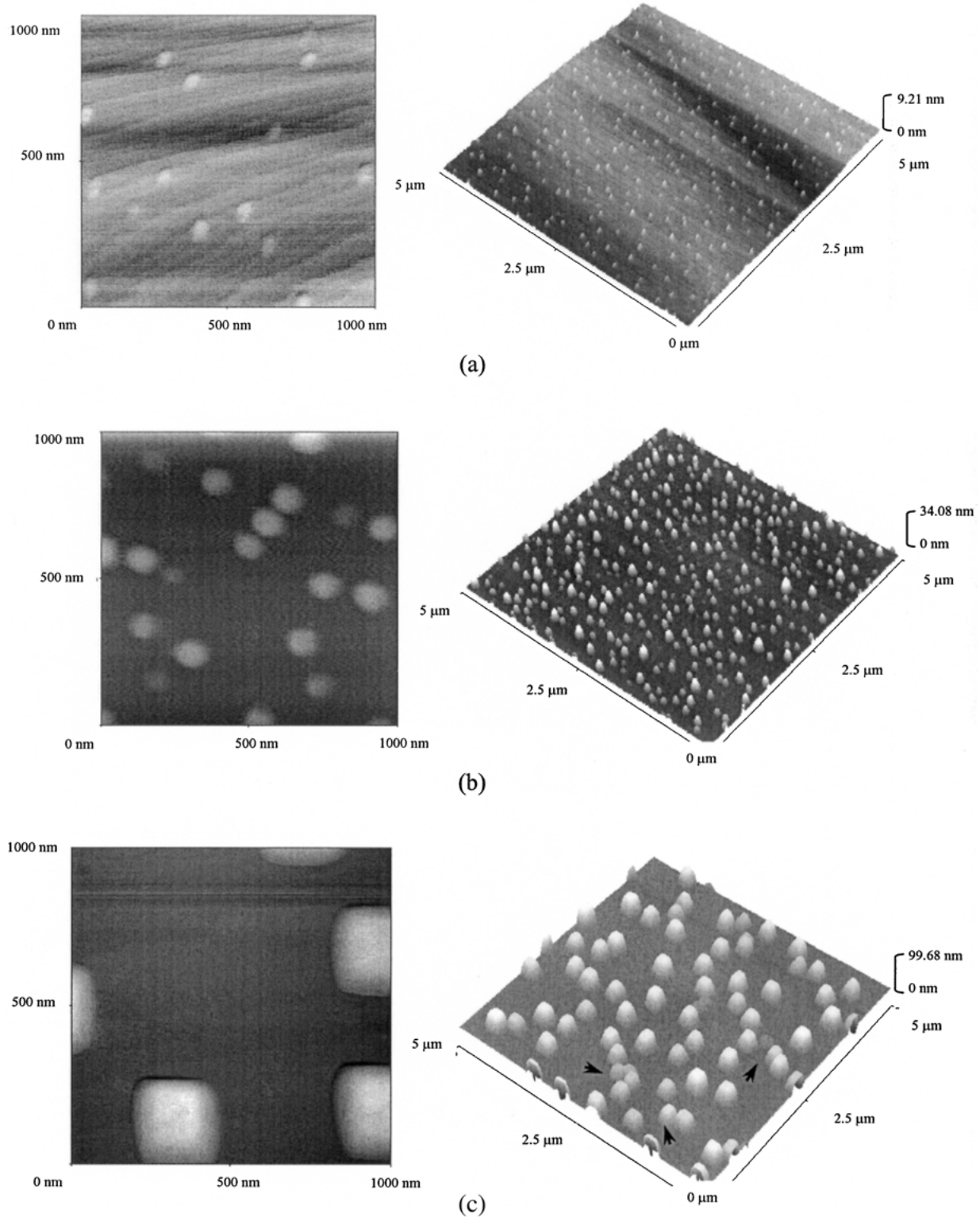

Figure 1 2D AFM images of $1 \times 1\,\mu m^2$ scanned areas and corresponding 3D AFM images of $5 \times 5\,\mu m^2$ scanned areas of: (a) the shortest growth-duration sample, showing a monomodal distribution of small ''lens-shaped'' islands; (b) the intermediate growth-duration sample, showing a bimodal distribution of ''lens-shaped'' islands of similar total density as in the previous sample; (c) the longest growth-duration sample, showing a monomodal distribution of square-based truncated pyramids of reduced density; a small number of smaller islands (of the intermediate size, but truncated-pyramid-shaped) can still be seen (indicated by the arrows), their growth being restricted by their proximity to other islands.

XTEM (Fig. 3) in contrast to previous observations reported in the literature, which have shown pyramidal-shaped islands in this size range. The facets of these islands are steeper near the interface with the substrate ($\approx 54°$, corresponding to the $(1\,1\,1)$ orientation) and become less steep toward the top ($\approx 22°$, which corresponds to the $(3\,1\,1)$ orientation). Some of these islands have a flat top (corresponding to the $(0\,0\,1)$ orientation) as seen in the XTEM micrograph shown in Fig. 3(a). Furthermore, very few of these islands show the presence of defects, as indicated by the white arrows in Fig. 3(a), suggesting that they are still elastically strained.

A dramatically different situation holds in the 10.7 ML of Ge case, in which a further 4.3 ML of Ge have been deposited. In this case, the density of islands has dropped by almost one order of magnitude ($3\,\mu m^{-2}$), the multifaceted ''dome-shaped'' islands have completely

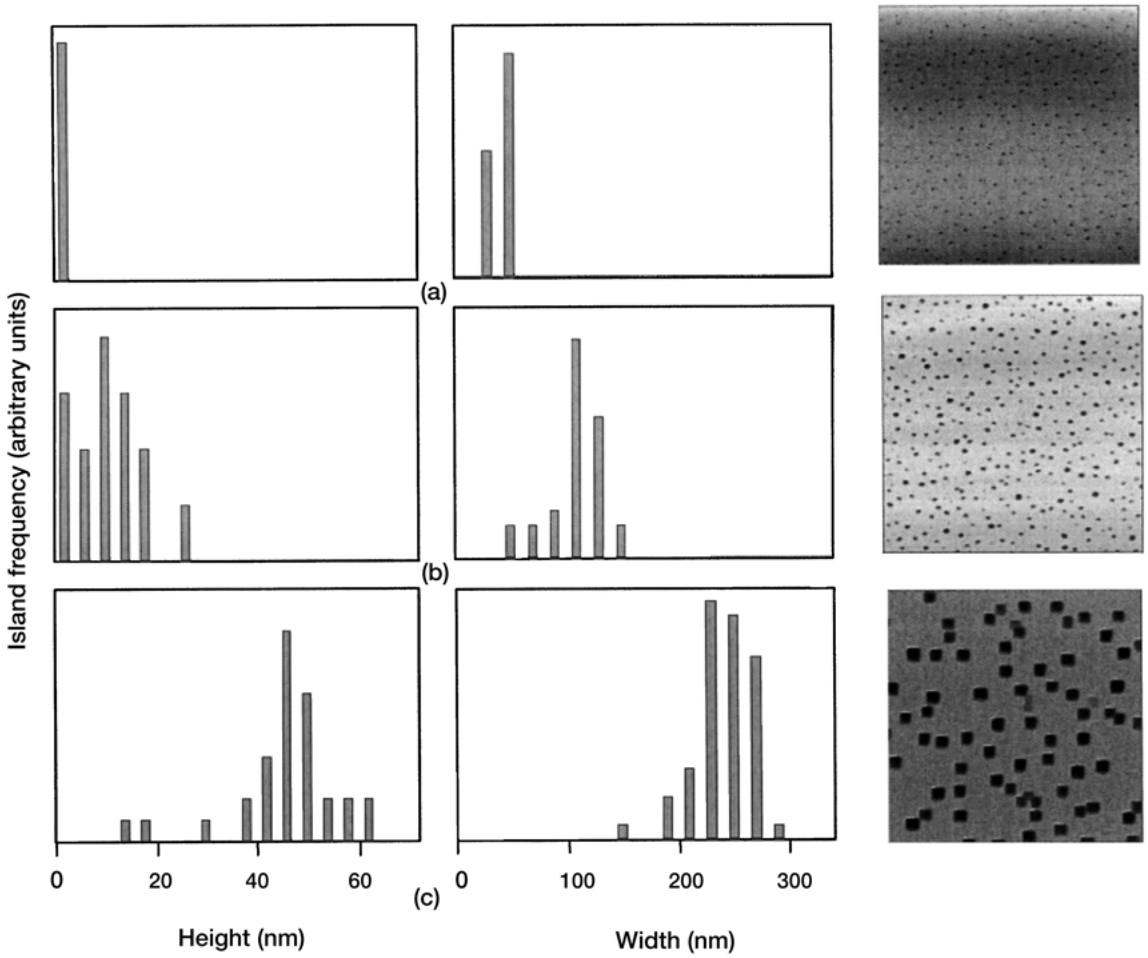

Figure 2 Height and width distribution together with 2D AFM images of $5 \times 5\,\mu m^2$ scanned areas of: (a) the shortest growth-duration sample, showing a narrow size distribution (20–30 nm width and 2–4 nm height); (b) the intermediate growth-duration sample, showing a bimodal size distribution; (c) the longest growth-duration sample, characterized by a very narrow size distribution (200–300 nm width and 40–60 nm height).

disappeared, and a population of large square-based truncated pyramids has appeared in their place (Fig. 1(c)). Such a rapid transition, whether by agglomeration or by Ostwald ripening, can only be expected to occur if the energy of the system decreases rapidly on conversion from dome-shaped to truncated-pyramidal islands, once a certain size is reached. In this case, only a very small number of islands are found in the size range corresponding to the intermediate-sized islands. The size distribution of the majority of islands is very narrow (≈ 250 nm wide) and the height of the islands has increased substantially (≈ 50 nm) (Fig. 2(c)). The few islands that remain within the intermediate size range have converted to truncated pyramids, but their growth

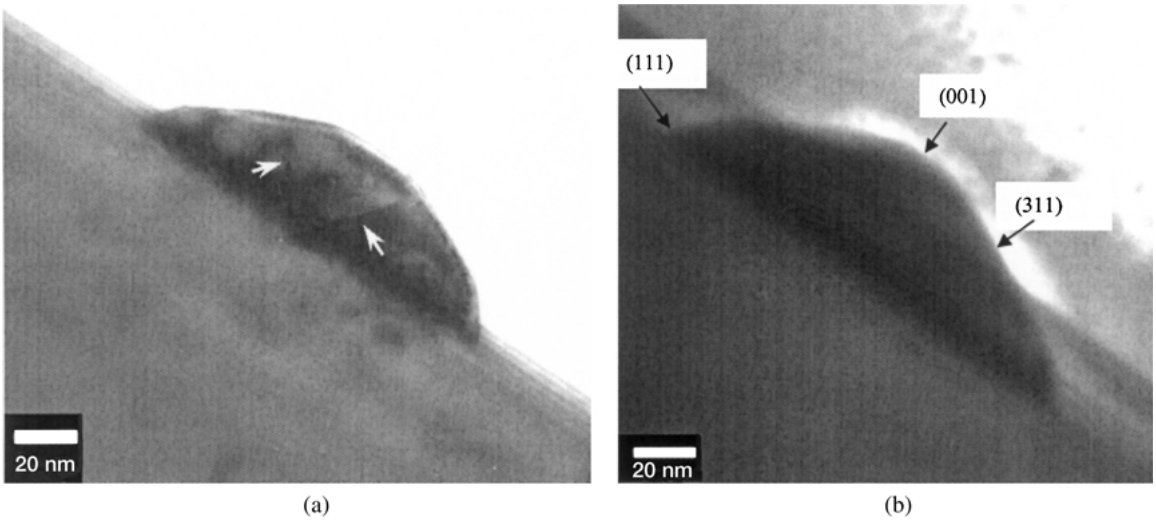

Figure 3 Bright-field XTEM micrographs of the intermediate growth-duration sample: (a) multifaceted dome with misfit dislocations gliding along {1 1 1} planes indicated by the white arrows; the facet orientation is steeper near the interface [1 1 1], becomes less steep toward the tip, turning into a [3 1 1] orientation and finishing with a flat [0 0 1] top; (b) a multifaceted dome without misfit dislocations.

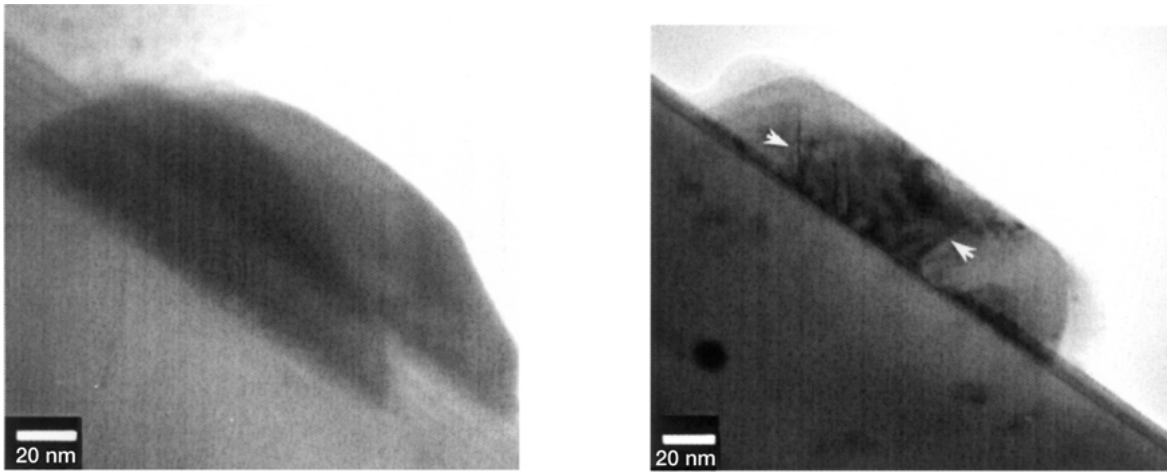

Figure 4 Bright-field XTEM micrographs of the longest growth-duration sample: (a) asymmetrical medium-sized islands prevented from becoming truncated pyramids by their proximity; they are characterized by one multifaceted side and one truncated-pyramid [1 1 1] faceted side; (b) large truncated-pyramidal island with misfit dislocations running along {1 1 1} planes, indicated with the white arrows.

has been restricted by their proximity to another island (arrows in Fig. 1(c)). It is an interesting possibility that these islands may mark the size at which the multifaceted ''dome-shaped'' islands begin to transform into truncated pyramids. XTEM analysis of such vicinal islands shows an asymmetric configuration, in which one side of the islands remains multifaceted, while the other turns into a (1 1 1) facet, which characterizes the truncated-pyramidal islands (Fig. 4(a)).

In most of the large truncated-pyramidal islands, a significant density of typical misfit dislocations gliding on {1 1 1} planes can be seen (as indicated by the white arrows in Fig. 4(b)). It is interesting to speculate that the transition to the truncated-pyramidal structure may arise from the onset of misfit dislocations as the multifaceted islands reach a critical size for the formation of misfit dislocations. Once this occurs, the energy density in the islands is able to decrease with size, leading to Ostwald ripening (or agglomeration) and a consequent decrease in island density and increase in island size.

4. Summary and conclusions

The LPCVD growth of Ge islands on (0 0 1) silicon substrates has been studied using a higher deposition rate than has previously been reported in the literature. We observe a novel island structure in the size range from 100–150 nm, consisting of a multifaceted ''dome-shaped'' structure, rather than the pyramidal structure that is typically reported. A tentative conclusion is that the ''dome-shaped'' structure has a higher energy than the pyramidal one, and is thus a nonequilibrium structure driven by the kinetics of the growth process.

Under the growth conditions used, the ''dome-shaped'' structure appears to undergo an abrupt transition to a truncated pyramidal structure once a critical size is reached. The energy of the truncated pyramidal structure evidently decreases with island size, as the system rapidly evolves to a smaller density of larger islands, once the truncated-pyramidal islands have been formed.

Our studies indicate that the use of high growth rates for the formation of nonequilibrium structures on silicon offers the potential for a novel route to the fabrication of Ge islands with a more controled structure and size distribution.

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