Diffusion of Neodymium into Sputtered Films of Tantalum Pentoxide

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Abstract

In this communication the diffusion of neodymium into RF-sputtered films of tantalum pentoxide has been investigated using the SIMS technique. The diffusion characteristics were obtained for a temperature of 1100°C, and the results showed a time-dependent diffusion coefficient that reflects a transition of the sputtered films from the amorphous to the crystalline phase. The potential for doping films of Ta_2O_5 with Neodymium by diffusion, for the realization of novel active optical devices, is also discussed.

1. Introduction

Tantalum pentoxide is potentially an important material for photonic crystal waveguide applications, due to its high refractive index and excellent transparency in the visible and near infrared regions[1,2]. Many fabrication techniques have been employed in the deposition of tantalum pentoxide films, and it has been shown that good optical quality can be obtained by RF sputtering[3]. Waveguides in Ta_2O_5 have been employed, for example in fluorescence-based sensors, exhibiting losses of less than 1dB/cm at a wavelength of 650nm[4], and Ta_2O_5/SiO_2 waveguides have been used for low-loss wavelength filters at 1.5μm[5]. Doping of Ta_2O_5 thin films with rare earth ions is of particular interest for integrated lasers and amplifiers, and has been demonstrated by ion-implantation[6,7]. Localised diffusive doping of lithium niobate[8,9] from a photolithographically defined metal or metal oxide source has proved to be a powerful technique for combining active and passive waveguide components on a single substrate. In this paper, the doping of sputtered films of tantalum pentoxide with neodymium ions by thermal diffusion from a Nd metal film source is studied with the aim of enabling the fabrication of active optical devices. The diffusion coefficient of neodymium into sputtered films of tantalum pentoxide at a temperature of 1100^0C is reported. Diffusion depth profiling was performed using Secondary Ion Mass Spectrometry (SIMS) as it offers good resolution for the characterization of concentration profiles with penetration depth lower than 1μm.

2. Experimental procedure

A four inch diameter silicon wafer was thermally oxidized to produce a surface silicon oxide film of thickness 600±50nm. A thin film of Ta_2O_5 was deposited on the oxide film by RF sputtering in an atmosphere of 10% oxygen in argon at a total pressure of 10mbar and with RF power of 500W supplied to the 8-inch tantalum target. The wafer was then diced into pieces of 10x20mm^2 for subsequent processing and measurements. The thickness of the Ta_2O_5 film was measured to be 310±20nm in a scanning electron microscope. A neodymium metal film of thickness 5±1nm was deposited by thermal evaporation on eight of the prepared samples, using a low deposition rate of 0.1nm/s to achieve accurate control of the thickness. Seven of these samples were then annealed at 1100^{0}C in an oxygen atmosphere, each for a different time period of 1, 2, 4, 8, 16, 25 and 36 hrs.

SIMS analysis of the concentration profiles of Nd in the Ta_2O_5 films was carried out by Loughborough Surface Analysis Limited using a Cameca IMS 4f apparatus. A thin coating of silver was deposited on the samples in order to minimize sample-charging effects. The samples were sputter-etched to obtain depth profiles and were analyzed using O_2^+ primary ion bombardment, with 10keV energy, and positive secondary ion detection. During the sputter-etching process the Ta, Nd and Si counts were recorded, as shown in Figure 1. The depth scale of the concentration profiles was determined from the known depth of the Ta_2O_5 film and the step-like Ta concentration profile. The top surface of the tantalum pentoxide film was taken to be the depth at which the Ta signal reached a constant value, while the bottom of the Ta_2O_5 layer was defined where the Ta signal

began a rapid decay. Assuming a constant sputter-etching rate, the depths corresponding to the SIMS intensities were calculated from the thickness of the Ta_2O_5 layer and the sputtering time as indicated. The SIMS signals in this work could not be calibrated for absolute neodymium concentration, because a reference sample with a known quantity of Nd in Ta_2O_5 was not available.

3. Results and discussion

Diffusion profiles for Nd into the Ta_2O_5 layer are given for the samples diffused for 1, 16 and 36 hours in Figure 2, along with fitted complementary error functions. Conventional diffusion theory identifies two extreme cases during the diffusion of impurities from a thin film into a solid medium. When the solid solubility of the impurity is infinite, a thin film is characterized as an instantaneous source. In that case, the dopant is rapidly entirely dissolved in the medium from the outset of the diffusion, and the surface concentration immediately decays with time. In contrast, when the solid solubility is low, even a thin deposit can be incompletely dissolved during the diffusion. In this second case, referred to as constant source diffusion, the surface impurity concentration is constant during annealing and equal to the maximum solid solubility. Since the diffusion source is not exhausted at the end of the annealing process, an excess of impurity may be found at the surface. In this work constant source diffusion is assumed, as SIMS measurements showed a high Nd signal strength in a thin surface layer indicating a Nd residue on the surface of the samples after the diffusions; furthermore Nd is expected to have a low solid solubility because of its large ionic size. Consequently, according to the

solution of Fick's equation, the Nd depth profiles are fitted with complementary error functions, where the concentration as a function of depth is described by the relation:

$$C(x,t) = C_s erfc\left(\frac{x}{2\sqrt{Dt}}\right) \quad (1)$$

Where, C_s, is the constant surface concentration and also the maximum solid solubility of the impurity at the temperature of the diffusion, D is the bulk diffusion coefficient and t is the diffusion time. The factor $2\sqrt{Dt}$ gives the depth at which the concentration $C(x,t)$ has fallen to $0.157C_s$ and is called the effective diffusion depth. The effective diffusion depth and the diffusion coefficient deduced from fitting the complementary error function to the experimental diffusion profiles are given, against diffusion time, in Table 1.

The diffusion profiles in Figure 2 show that, while the data are fitted well by the complementary error function near the surface, the impurity concentrations deeper into the films are higher than expected. As all the samples were diffused at the same temperature it is expected that, if the thin film material does not change properties with time or with impurity concentration, the diffusion coefficient would be constant with diffusion time. Moreover, according to the simple diffusion model that results in Eqn. 1, the effective diffusion depth should follow a square root dependence upon time. However the results given in Table 1 show that the diffusion of Nd into the Ta_2O_5 slows down with annealing time, so that the apparent diffusion coefficient reduces and the effective diffusion depth does not show the expected time dependence. Figure 2 shows that the theoretical fit for the penetration profiles improves as the diffusion time increases, with

data for the sample diffused for 36 hours following the complementary error function throughout the thickness of theTa_2O_5 film.

The diffusion coefficient in Table 1 is plotted against diffusion duration in Figure 3. The experimental curve can be fitted with exponential decay functions, an arbitrary fit was selected and plotted in order to reveal this behavior using the following empirical function:

$$D(t) = D_0 \exp\left(\frac{b}{t+c}\right) \tag{2}$$

It can be seen that, as the diffusion duration increases, the diffusion coefficient falls towards a stable value. This stable value is given in equation 2 by the term D_0, which has units of diffusivity and is equal to 7.5×10^{-20} m^2s^{-1}.

As-deposited Ta_2O_5 films obtained by sputtering are expected to be amorphous due to the low temperature deposition[10]. However, annealing of Tantalum Pentoxide at temperatures above approximately 700^0C causes a transformation of the material from an amorphous to a crystalline state[10-12]. The Ta_2O_5 films become polycrystalline with annealing and the grain sizes are expected to become larger as the annealing temperature is raised further above 700^0C and as annealing time increases. The crystalline phase depends on film thickness and amorphous status and it may be the orthorhombic β-Ta_2O_5 phase or the hexagonal δ-Ta_2O_5 phase[10,13,14]. The steady reduction in diffusion coefficient with time shown in Figure 3 may be explained by the transformation of the Ta_2O_5 host from an

amorphous to a polycrystalline state during the diffusion, resulting in a time-dependent diffusion coefficient. This is expected to correspond to the neodymium mobility being lower for crystalline tantalum pentoxide than for the amorphous form. This effect may be further complicated by the diffusion coefficient and the phase transformation being Nd concentration dependent, and therefore depth dependent.

In this system two different diffusion systems coexist, those of Nd in amorphous Ta_2O_5 and in crystalline Ta_2O_5. In the cases of the diffusion profiles for the samples diffused for 1 and 16 hrs, the transition between the two different diffusion systems can be observed. In contrast, as the annealing duration increases, the crystalline system predominates and this can be seen in the good agreement with standard theory of the diffusion profile of the sample diffused for 36hrs.

4. Conclusions

In conclusion, the diffusion of neodymium into sputtered films of tantalum pentoxide has been investigated. Diffusion profiles were obtained at a temperature of 1100°C, and the results showed a transition between diffusion rates as the sputtered films changed from the amorphous to the crystalline phase. The diffusion coefficient in polycrystalline tantalum pentoxide tended to saturation at 7.5×10^{-20} m^2s^{-1}. A diffusion depth of approximately 200nm was achieved in a 300nm thick film of Ta_2O_5 on silicon dioxide, appropriate for a monomode neodymium-doped waveguide operating at a wavelength near 1μm. Diffusion studies at lower temperatures will be carried out to elucidate the diffusion coefficient of neodymium in amorphous tantalum pentoxide. Future work will

concentrate on investigating the optical properties of these films in order to establish the potential for the realization of novel active optical devices.

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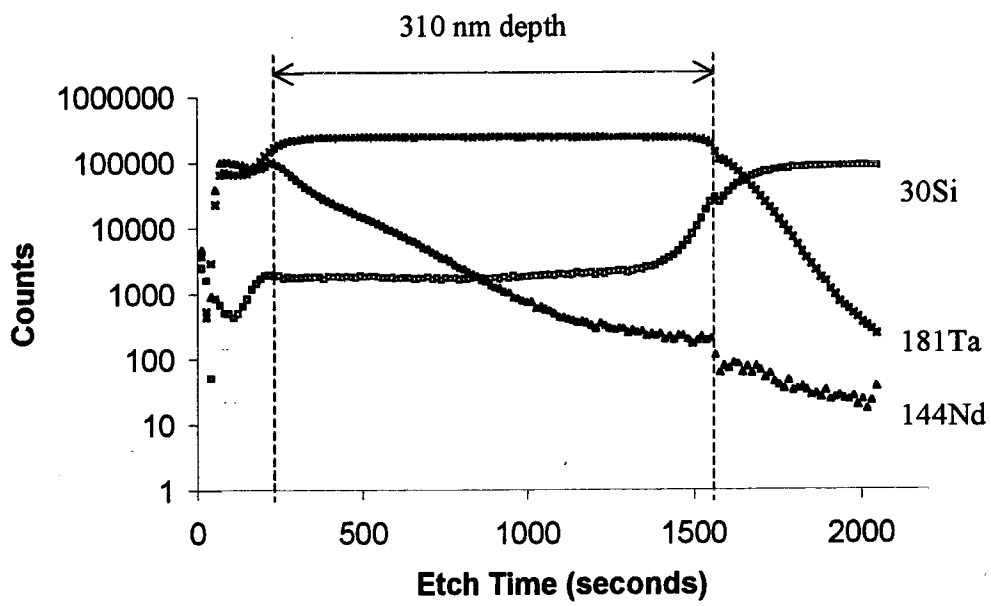
Figure captions

Figure 1. Depth profile of Ta, Si and Nd SIMS counts for the sample diffused for 1 hour.

Figure 2. Nd concentration profiles and erfc fits for samples diffused for 1, 16 and 36 hrs.

Figure 3. Effective diffusion coefficient against diffusion time, with exponential fitting function.



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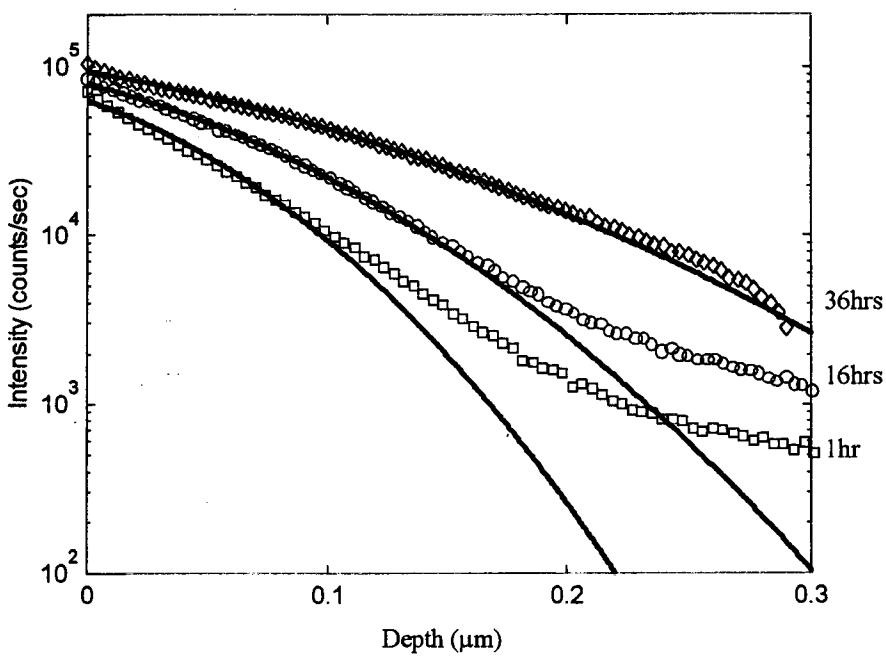

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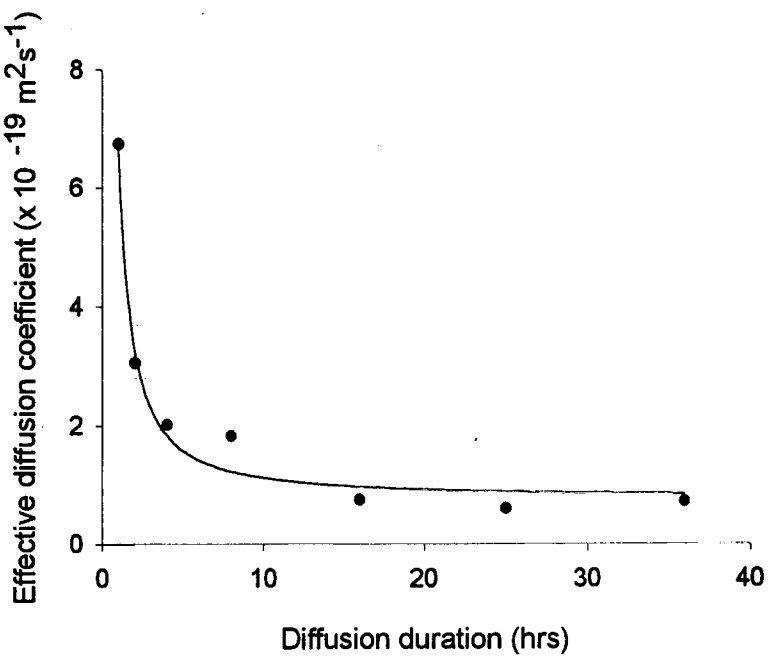

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Table 1. Diffusion parameters of the samples[†]

Diffusion time (hrs)	Effective diffusion Depth (nm)	Effective diffusion coefficient ($x10^{-19}$ m^2s^{-1})
1	99 ± 5	6.7 ± 0.5
2	94 ± 5	3.1± 0.4
4	108 ± 5	2.0 ± 0.2
8	145 ± 5	1.8 ± 0.2
16	132 ± 5	0.8 ± 0.2
25	148 ± 5	0.6 ± 0.1
36	194 ± 5	0.7 ± 0.1

[†]Diffusion time, effective diffusion depths and effective diffusion coefficients for Nd diffusion in Ta_2O_5 at 1100°C.