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**ORIENTED Si AND Ge NANOCRYSTALS FORMED IN Al_2O_3
BY ION IMPLANTATION AND ANNEALING**

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ORIENTED Si AND Ge NANOCRYSTALS FORMED IN Al_2O_3 BY ION IMPLANTATION AND ANNEALING

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ABSTRACT

Ion implantation followed by thermal annealing in a reducing atmosphere has been used to create a high density of oriented Si and Ge nanocrystals in (0001) Al_2O_3 . Both types of nanocrystals are three-dimensionally aligned with respect to the Al_2O_3 matrix, but the orientational relationships are different, and the two types of nanocrystals have different shapes in Al_2O_3 . Implantation of Si and Ge in fused silica also produces nanocrystals, but in this case, the nanocrystals are randomly oriented relative to each other.

INTRODUCTION

Room temperature (RT) visible light emission from nanometer size structures of Si and Ge has created considerable interest in the fabrication and properties of such structures.¹ Included in this is the light emission observed from structures such as porous Si,^{2,3} as well as microcrystallites of Si⁴ and Ge.⁵ Nanometer size crystallites of Si and/or Ge have been produced by a number of methods including cosputtering,⁵ plasma decomposition⁴ of SiH_4 , spark ablation,⁶ hydrothermal oxidation of $\text{Si}_{0.6}\text{Ge}_{0.4}$ alloys,⁷ etc. We are investigating the use of ion implantation and annealing as a method to create nanocrystals of Si and Ge in materials such as $\alpha\text{-Al}_2\text{O}_3$ and fused silica. In both materials, we find that high-dose implantation can be used to form Si or Ge nanocrystals. Furthermore, in the case of $\alpha\text{-Al}_2\text{O}_3$, our results show that the Si and Ge nanocrystals are oriented with respect to the lattice; in fused silica, the nanocrystals are oriented at random. In this paper, we will discuss the formation of Si and Ge nanocrystals in Al_2O_3 and fused silica by ion implantation and show measurements of the orientation of these nanocrystals relative to the Al_2O_3 matrix.

EXPERIMENTAL DETAILS

The implantation of Si and Ge into (0001) Al_2O_3 samples was carried out at energies of 400 keV for Si and 500 keV for Ge. This results in projected ranges of ~ 4000 Å for Si and ~ 2000 Å for Ge. Doses in the range of $6 \times 10^{16}/\text{cm}^2$ to $6 \times 10^{17}/\text{cm}^2$ were used. Similar energies and doses were used for fused silica. Substrate temperatures during implantation ranged from RT to 650°C . Following implantation, annealing was carried out in a reducing atmosphere at temperatures of 800°C – 1100°C for time periods of 30 min. to 2 h. Sample characterization was carried out by RBS-ion channeling (2.3 MeV He ions), x-ray diffraction ($\text{CuK}\alpha_1$ radiation), cross-section transmission electron microscopy (TEM), and Raman spectroscopy (4880 Å wavelength).

RESULTS AND DISCUSSION

Figure 1 shows Raman scattering spectra taken from (0001) Al_2O_3 implanted by Si in the as-implanted state and after subsequent annealing. The sharp line at 526 cm^{-1} corresponds to the crystalline Si-Si excitation mode. The spectral feature at $\sim 415\text{ cm}^{-1}$ arises from Al_2O_3 . The

results show that Si crystallites form in Al_2O_3 during implantation at elevated temperature and that the crystallites coarsen and grow during subsequent thermal annealing. The shift of the Raman line relative to pure Si (at $\sim 520\text{ cm}^{-1}$) may indicate these nanoclusters are under compressive stress. The Si Raman line narrows from a width of $\sim 17\text{ cm}^{-1}$ to $\sim 8\text{ cm}^{-1}$ during annealing.

Figure 2 shows x-ray diffraction scans revealing how the Si nanocrystals in (0001) Al_2O_3 are oriented with respect to the matrix. The $\theta - 2\theta$ scan along the c axis of Al_2O_3 (Fig. 2, top) shows the expected diffraction from the (0001) planes of Al_2O_3 . In addition, however, there is a strong diffraction peak from (111) silicon planes, as well as (weaker) diffraction from (220) silicon planes. Both domains exhibit in-plane alignment, and both exhibit six-fold rotational symmetry about the surface normal. A ϕ scan through the {220} reflections for the (111) oriented domains is shown in Fig. 2, bottom. Analysis of the x-ray diffraction results shows that the Si nanocrystals are three-dimensionally aligned predominantly in the orientation $\text{Si}(111) \parallel \text{Al}_2\text{O}_3(0001)$; $\text{Si}[1\bar{1}0] \parallel \text{Al}_2\text{O}_3[1\bar{1}20]$. To a much lesser extent, the orientation $\text{Si}(110) \parallel \text{Al}_2\text{O}_3(0001)$; $\text{Si}[001] \parallel \text{Al}_2\text{O}_3[10\bar{1}0]$ is also observed. The width of the Si(111) diffraction peak corresponds to a correlation length (size of coherently diffracting domains) of $\sim 140\text{ \AA}$ in the direction of the surface normal. Preliminary measurements show that nanocrystal size increases with implantation dose and subsequent annealing (time and temperature). Previous studies⁸⁻¹³ have shown that a number of other impurities including Fe, Au, Cr, Ni, and Mn will form oriented precipitates as a result of ion implantation into Al_2O_3 followed by annealing. In addition, the formation of oriented silicon crystallites in α -quartz by ion implantation and annealing has been reported.¹⁴

Figure 3 is a cross-section TEM micrograph showing the near-surface region of Si implanted (0001) Al_2O_3 after annealing. (The first 2000 $\text{\AA}$ of the surface were inadvertently removed in the ion milling process to produce a thin sample.) In this micrograph, the Si crystallites are observed to be "pancake" shaped. The "pancake" crystallites are aligned parallel to the (0001) planes of Al_2O_3 . Si crystallite dimensions up to $\sim 100\text{ \AA}$ perpendicular to the (0001) planes and $\sim 1000\text{ \AA}$ parallel to the planes have been observed. The diffraction pattern shows spots characteristic of crystalline Si in addition to those characteristic of Al_2O_3 . The size of the Si crystallites increases with dose and with increasing temperature and time during annealing.

Ge implantation of Al_2O_3 followed by annealing also results in the formation of oriented Ge nanocrystals. Figure 4 shows x-ray diffraction results from (0001) Al_2O_3 implanted by Ge (400 keV, $6 \times 10^{17}/\text{cm}^2$, RT) and annealed ($1100^\circ\text{C}/1\text{ h}$). In this case, Ge nanocrystals oriented with (111) planes parallel to the (0001) planes of Al_2O_3 are again observed. In addition, crystallites oriented with (110) Ge planes parallel to (0001) Al_2O_3 are observed with nearly equal intensity. Both types of domains exhibit in-plane alignment. In contrast to the Si case, however, both types of Ge domains exhibit three-fold rotational symmetry about the surface normal. (The ϕ scan through the {220} reflections for the (111) oriented domains is shown in Fig. 4, bottom.) Sizes of Ge nanocrystals inferred from the width of the diffraction lines is in the range of 50–100 $\text{\AA}$. TEM results show the shape of Ge crystallites to be faceted and nearly spherical. Crystallite dimensions in the range of 20–150 $\text{\AA}$ are observed. The crystallite size increases with increasing dose and with temperature during annealing.

Si and Ge nanocrystals have also been formed by the implantation of Si and Ge into fused silica, followed by annealing. Figure 5 shows Raman spectra taken from fused silica samples implanted by Ge (left) and Si (right) after thermal annealing. Strong Raman lines characteristic of Ge and Si are observed in these spectra. The Ge line occurs at 297 cm^{-1} with a width of $\sim 10\text{ cm}^{-1}$. The Si line occurs at 519 cm^{-1} with a width of $\sim 7\text{ cm}^{-1}$. X-ray diffraction shows that both Si and Ge crystallites have a polycrystalline diffraction pattern demonstrating that the crystallites are randomly oriented relative to each other.

The nanocrystals that we have produced in Al_2O_3 and SiO_2 are of a size such that visible luminescence might be observed as a result of quantum confinement. Preliminary attempts have been to excite luminescence in both Al_2O_3 and SiO_2 implanted with Si using uv radiation from a He Cd laser. No intense visible luminescence has been observed in the samples that have been

examined to date, but these measurements are still in progress and will be reported at a future date.

CONCLUSIONS

Oriented nanocrystals of Si and Ge have been produced in (0001) Al_2O_3 by ion implantation followed by thermal annealing in a reducing environment. For the Si in Al_2O_3 , the predominant orientation is (111) Si $\parallel$ (0001) Al_2O_3 and to a much lesser extent (110) Si $\parallel$ (0001) Al_2O_3 . Both domains exhibit six-fold rotational symmetry about the surface normal. For Ge in (0001) Al_2O_3 , the orientations (111) Ge $\parallel$ (0001) Al_2O_3 and (110) Ge $\parallel$ (0001) Al_2O_3 are observed with nearly equal intensity. Both Ge domains exhibit three-fold rotational symmetry about the surface normal. Nanocrystals of Si and Ge are also produced by the implantation into fused silica followed by annealing. In that case, the nanocrystals are randomly oriented relative to each other. Visible luminescence has not been observed from Si implanted Al_2O_3 or fused silica to date.

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REFERENCES

1. S. S. Iyer and Y. H. Xie, *Science* **260**, 40 (1993).
2. L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
3. V. Letmann and U. Gösel, *Appl. Phys. Lett.* **58**, 856 (1991).
4. H. Takagi, H. Ogawa, Y. Yamazaki, A. Ishizaki, and T. Nakagiri, *Appl. Phys. Lett.* **56**, 2379 (1990).
5. Y. Maeda, N. Tsukamoto, Y. Yazawa, Y. Kanemitsu, and Y. Masumoto, *Appl. Phys. Lett.* **59**, 3168 (1991).
6. W. A. Saunders et al., *Appl. Phys. Lett.* **63**, 1549 (1993).
7. D. C. Paine, C. Caragianis, and Y. Shigesato, *Appl. Phys. Lett.* **60**, 2886 (1992).
8. P. S. Sklad, C. J. McHargue, C. W. White, and G. C. Farlow, *J. Mat. Sci.* **27**, 5895 (1992).
9. G. C. Farlow, P. S. Sklad, C. W. White, and C. J. McHargue, *J. Mat. Res.* **5**, 1502 (1990).
10. C. W. White, C. J. McHargue, P. S. Sklad, L. A. Boatner, and G. C. Farlow, *Mat. Sci. Reports* **4**, 43 (1989).
11. M. Ohkubo and N. Suzuki, *Phil. Mag. Lett.* **57**, 261 (1988).
12. M. Ohkubo, T. Hioki, and J. Kawamoto, *J. Appl. Phys.* **60**, 1325 (1986).

13. M. Ohkubo, T. Hioki, N. Suzuki, T. Ishiguro, and J. Kawamoto, Nucl. Inst. & Methods B **39**, 675 (1989).
14. U. B. Ramabadran, H. E. Jackson, and G. C. Farlow, Appl. Phys. Lett. **55**, 1199 (1989).

FIGURE CAPTIONS

Fig. 1. Raman spectra from Si (400 keV, $6 \times 10^{17}/\text{cm}^2$) implanted (0001) Al_2O_3 at 650°C. Spectra are shown in the as-implanted state and after annealing (1100°C/2 h).

Fig. 2. X-ray diffraction results for Si (400 keV, $6 \times 10^{17}/\text{cm}^2$, 650°C) implanted (0001) Al_2O_3 after annealing 1100°C/2h.

Fig. 3. Cross-section TEM micrograph for Si (400 keV, $6 \times 10^{17}/\text{cm}^2$, 650°C) implanted (0001) Al_2O_3 after annealing 1100°C/2h.

Fig. 4. X-ray diffraction results Ge (500 keV, $6 \times 10^{16}/\text{cm}^2$, RT) implanted (0001) Al_2O_3 after annealing (1000°C/1h).

Fig. 5. Raman spectra for Si and Ge implanted into fused silica after annealing. The implantation and annealing conditions are indicated.

Si Nanocrystals Formed in (0001)Al₂O₃

Si (400 keV, $6 \times 10^{17}/\text{cm}^2$, 650°C)

Fig 1

Si Nanocrystals in (0001)Al₂O₃

Si (400keV, $6 \times 10^{17}/\text{cm}^2$, 650°C)
Annealed 1100°C / 2h

Fig 3

Ge Nanocrystals in (0001)Al₂O₃

Ge (500keV, $6 \times 10^{16}/\text{cm}^2$, RT)
Annealed 1100°C / 1h

Germanium and Silicon Implanted Fused Silica

Fig 5

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