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Nuclear Instruments and Methods in Physics Research B 166–167 (2000) 193–197

NIM B
Beam Interactions with Materials & Atoms

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Influence of tin ion implantation on the damage and annealing kinetics of sapphire

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Abstract

In order to study the amorphization of sapphire during room temperature ion implantation and the recrystallization of ion-implantation-induced amorphization, sapphire single crystals were implanted with tin (180 keV) at room temperature to fluences from 5×10^{15} to 1×10^{17} Sn/cm^2. The calculated damage energy at the amorphous/crystalline interface varied from 85 eV/atom (10^{16} Sn/cm^2) to 1.4 eV/atom (4×10^{16} Sn/cm^2). The concentration of Sn at the interface was less than 2 at%. Samples implanted with 4×10^{16} Sn/cm^2 were annealed for 1 hour in oxidizing or reducing atmospheres at a temperature of 700°C, 900°C, 960°C or 1100°C. Regrowth at temperatures below 960°C followed the sequence: amorphous $\rightarrow \gamma$-Al_2O_3; γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$. Essentially all (97%) implanted tin was lost during the 1100°C anneal in Ar–4% H_2, whereas all Sn was retained in the sample annealed in the oxidizing atmosphere. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 61.43.Er; 61.82.Ms
Keywords: Sapphire; Sn-implantation; Amorphization; Regrowth

1. Introduction

Ion implantation of solids presents a unique method for altering the near-surface structure of a wide range of materials in a manner that is independent of many of the constraint associated with conventional processing methods. Current activities in the area of integrated optics and the tailoring of oxides for specific applications have led to renewed interest in the use of ion implantation to alter the near-surface optical, electrical, magnetic or mechanical properties of amorphous and crystalline oxides.

Sapphire (single crystal α-$A1_2O_3$) can be crystalline with lattice disorder, e.g., damage in the form of dislocations and point defect clusters, or it can be amorphous after implantation [1]. The degree of disorder depends upon the implantation parameters of ion fluence, ion species, target temperature and orientation of the ion beam relative to crystallographic axes. The ion fluence required for amorphization at room temperature is significantly lower for some ion species than for others

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0168-583X/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S0168-583X(99)00654-0

[2]. This observation has led to the speculation of the existence of some "chemical" effect on amorphization.

For many potential applications, it will be necessary to anneal the material after implantation in order to remove the radiation damage, recrystallize the amorphous layer to the crystalline state, and/or redistribute the implanted species. The regrowth of sapphire has been extensively studied only for crystals amorphized by sequential implantation of Al + O in the ratio of 2:3 and the implantation of Fe, both at 77 K [3]. These studies found the amorphous Al_2O_3 first transformed to γ-Al_2O_3 and then the γ-Al_2O_3 transformed to α-Al_2O_3 by epitaxial growth from the α–γ interface in the temperature range of 700–1000°C. There was, however, a difference in the kinetics of the transformations between the (Al + O) and the Fe-implanted samples. The effect of annealing atmosphere (oxidizing or reducing) has received only limited attention.

The purpose of the present study is to study in greater detail amorphization due to implantation of Sn at room temperature and to study the effects of annealing atmosphere on the regrowth of the matrix and the distribution of the tin. An earlier study reported limited results for Conversion electron Mössbauer spectroscopy and transmission electron microscopy (TEM) examinations of a sample implanted with 4×10^{16} Sn/cm^2 [4].

2. Experimental details

High-purity Al_2O_3 single crystals having the *c*-axis normal to the surface were obtained with an optical polish from Crystal Systems, Inc. (Salem, MA). The disks were annealed for 120 h at 1450°C in flowing oxygen to remove any residual polishing damage or surface contamination. Minimum yields, χ_m, were ~2% in the Al sublattice and ~8% in the oxygen sublattice after annealing, indicating a high degree of perfection.

Crystals were implanted with ^{119}Sn (180 keV) at room temperature to fluences of 5×10^{15}, 1×10^{16}, 2×10^{16}, 4×10^{16} and 10^{17} Sn/cm^2 with the beam ~7° off-normal. Values of the projected range, R_p, and straggling, ΔR_p, calculated from the code EDEP-1(P.5) [5] were 53.3 and 7 nm, respectively.

Samples implanted with 4×10^{16} Sn/cm^2 were annealed for 1 h at 700, 900, 960 or 1100°C in an oxidizing (flowing oxygen) or reducing (Ar–4% H_2) atmosphere.

Specimens were analyzed by Rutherford backscattering ion channeling spectroscopy (RBS) using 2.0 MeV He^+ ions at a scattering angle of 160°. Specimens were prepared for TEM by mechanical polishing followed by ion milling.

3. Results and discussion

3.1. As-implanted

The RBS spectra of Fig. 1 shows the aligned spectrum to reach the random value at a fluence between 5×10^{15} and 1×10^{16} Sn/cm^2. The aligned scattering from the Al-sublattice for the 5×10^{15} Sn/cm^2 sample exhibits a strong broad surface peak and a second maximum at a distance approximately equal to $R_p + \Delta R_p$. The amorphous (random) layer extends to a depth of ~70 nm for a fluence of 1×10^{16} Sn/cm^2 and 80 nm at 2×10^{16} Sn/cm^2. This layer was about 95 nm thick at 4×10^{16} Sn/cm^2.

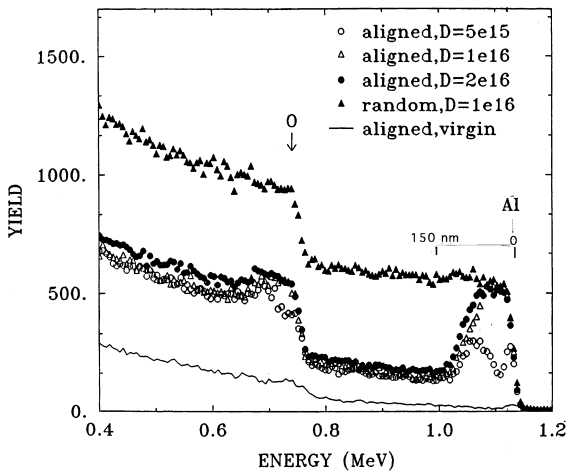

Fig. 1. RBS-ion channeling using 2 MeV He^+ for Al_2O_3 implanted with $^{119}Sn^+$/cm^2 at room temperature.

The value of deposited damage energy, $S(D)$, at the positions of the crystalline–amorphous interfaces, calculated using EDEP-1(P5), has values of 85, 28 and 1.4 eV/atom for fluences of 1, 2 and 4×10^{16} Sn/cm^2, respectively. The position of the interface does not correlate with $S(D)$. If a value of 18 eV is used for the displacement energy (E_d) for an Al ion from its lattice site, a calculation indicates that Al will not be displaced by incident Sn^+ at depths greater than about 60 nm. A similar calculation for oxygen, using $E_d = 72$ eV, suggests that oxygen ions will not be displaced at depths greater than about 40 nm. Ignoring any effect of differences in scattering cross-sections, these calculations suggest that an excess of Al-vacancies over O-vacancies will be created in a zone 40–60 nm from the surface. This corresponds to R_p for the implanted Sn.

The creation of an Al-deficient (or O-rich) zone could explain the TEM observations of the earlier study wherein two "amorphous" were observed after implantation to 4×10^{16} Sn/cm^2 [4]. The contrast in TEM images indicated one phase to be Sn-rich. The relative values of the free energies of formation, ΔG°, of α-Al_2O_3, SnO_2 and Al–Sn–O compounds indicate that Sn cannot reduce α-Al_2O_3. However, if the Al has been removed by energetic collisions, the Sn might react with the excess oxygen. The CEMS results for the same study indicated that amorphous SnO_2 or $SnAl_2O_5$ and $SnAl_2O_4$ were present in this sample.

The Sn/Al ratio at the position of the amorphous–crystalline interface was determined from the RBS-ion channeling measurements to have values of 1–2 at%.

3.2. Post-implantation annealing studies – oxidizing atmosphere

There were no significant changes in the RBS spectra for samples annealed 1 h at 700°C and 900°C in air. The previous CEMS study [4] showed tin to be present as Sn(II) and Sn(IV) in the as-implanted condition and in the same relative amounts after an 700°C anneal. Only the Sn(IV) state was present after anneals at 900°C and higher. In-diffusion of oxygen through the amorphous surface layer oxidized the Sn(II) state to the Sn(IV) state.

There was a slight (~5 nm) movement of the α–amorphous interface toward the surface during the 960°C anneal and movement of the Sn toward the surface. The peak Sn:Al ratio at the surface was 0.09 and 0.10 at R_p. There was no channeling of the Sn.

There were major changes in the RBS after the 1100°C anneal, Fig. 2. The strong peak from the

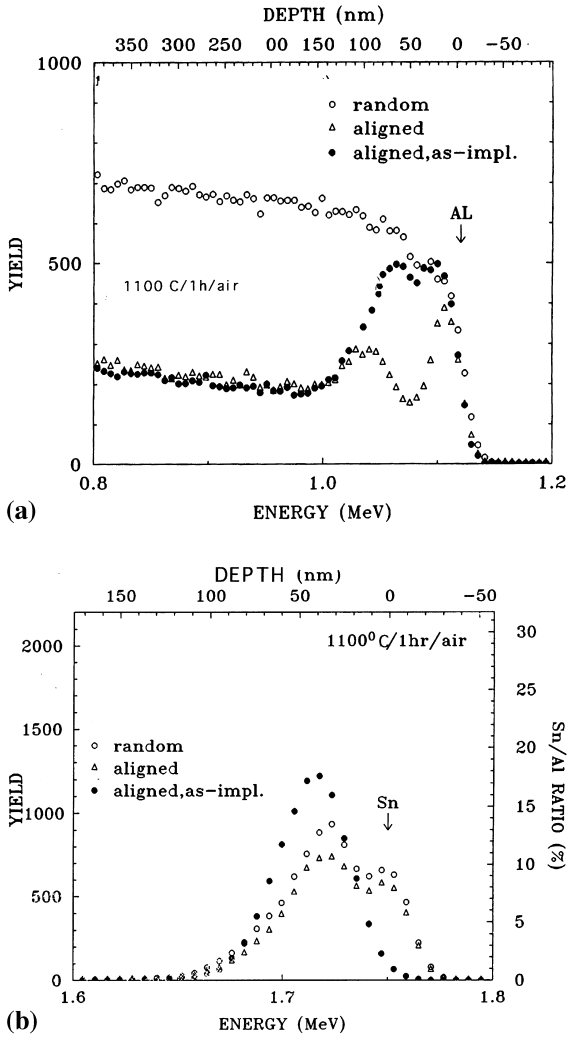

Fig. 2. RBS-ion channeling using 2 MeV He^+ for Al_2O_3 implanted with 4×10^{16} $^{119}Sn^+$/cm^2 at room temperature and annealed 1 h in air at 1100°C. (a) Al-sublattice; (b) Sn.

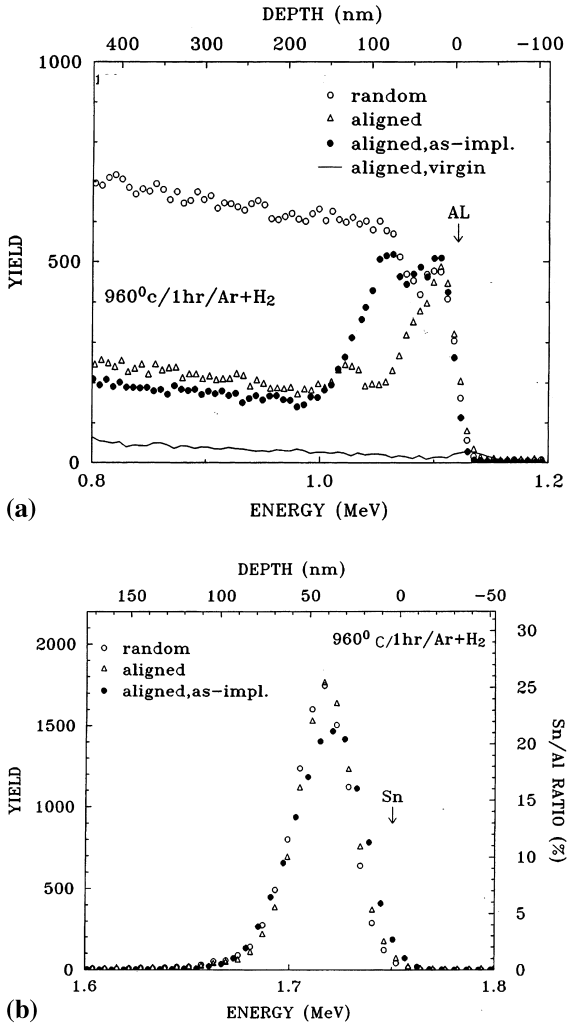

Fig. 3. RBS-ion channeling using 2 MeV He^+ for Al_2O_3 implanted with 4×10^{16} $^{119}Sn^+/cm^2$ at room temperature and annealed 1 h in Ar–4% H_2 at 960°C. (a) Al-sublattice; (b) Sn.

surface to ~30 nm suggests either a microcrystalline structure or, based on earlier studies [3], γ-Al_2O_3 with substructure. An examination by TEM showed that it is γ-Al_2O_3. The region from ~30 nm to the original amorphous/crystalline interface was α-Al_2O_3. A number of voids were detected in the region from ~30 to ~70 nm, corresponding to the region of higher channeling in Fig. 2(a). These voids may be due to condensation of Al-vacancies, as suggested above. Selected area diffraction patterns showed the Sn-rich precipitates to be SnO_2.

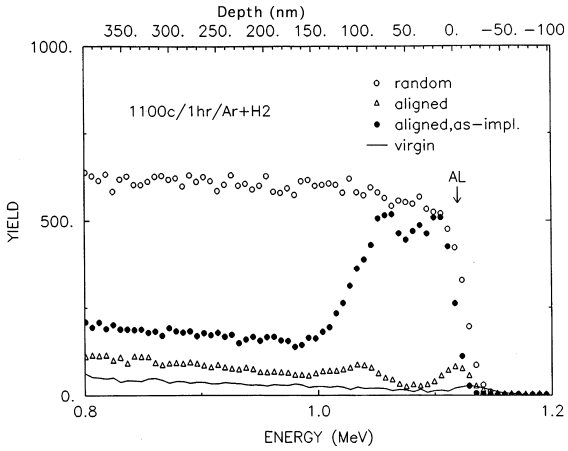

Fig. 4. RBS-ion channeling from Al using 2 MeV He^+ for Al_2O_3 implanted with 4×10^{16} $^{119}Sn^+/cm^2$ at room temperature and annealed 1 h in Ar–4% H_2 at 1100°C.

The precipitates and both Al_2O_3 phases exhibited a high degree of coherency with the following orientation relationships:

$$(2\,0\,0)_{SiO_2} || (0\,0\,0\,1)_{\alpha} || (1\,1\,1)_{\gamma},$$

$$[0\,0\,2]_{SiO_2} || [3\,0\,\bar{3}\,0]_{\alpha} || [4\,4\,0]_{\gamma}.$$

Fig. 2(b) shows a tendency for a surface peak in the Sn spectra as well as movement of the Sn from the position of R_p toward the surface. All of the implanted Sn was retained during this anneal. The melting point of SnO_2 is about 1730°C; thus, this oxide should be stable at this annealing temperature.

3.3. Post-implantation annealing studies – reducing atmosphere

Annealing at 700° did not change the RBS spectra for the Al or Sn. Annealing at 900°C caused the α-amorphous interface to migrate ~15 nm toward the surface. The Al-spectrum did not reach the random level, and the appearance indicates the formation of γ-Al_2O_3. There was no change in the Sn-spectra.

The spectra of Fig. 3(a) indicate that the α–γ interface is ~50 nm from the surface, indicating epitaxial regrowth of the α into the γ during the

960°C anneal. The Al spectrum suggests the regrown α is not as perfect as observed in the study of samples implanted with (Al + O) or Fe [3]. No changes were noted in the Sn spectra (Fig. 3(b)).

The spectra of Fig. 4 indicate complete regrowth to the α-phase occurred during the 1100°C anneal. The regrown phase contained more disorder than the virgin crystal, with values of $\chi \approx 0.26$ at the surface and ≈0.2 at 70 nm. Although 97% of the Sn was lost from the sample during this anneal, the spectra for both Al and Sn show a bimodal shape, suggesting that the disorder remaining in the Al sublattice is connected with the presence of this small amount of tin. Reduction of the Sn from Sn(II) and Sn(IV) to the metallic state is expected for the reducing anneals. Since Sn melts at 232°C, it is not surprising that most of the Sn was lost during this anneal. The retained tin appears to be tied up as $SnAl_2O_4$.

4. Summary

Sapphire crystals having the *c*-axis approximately parallel to the ion beam become amorphous at a fluence between 5×10^{15} and 1×10^{16} ions/cm^2 for implantation of Sn^+ at room temperature. The calculated damage energy and measured Sn concentration at the crystalline–amorphous interface are very low.

Only a slight amount of regrowth from the crystalline substrate into the amorphous zone occurs in 1 h for annealing in a oxidizing atmosphere at temperatures of 960°C and below. Annealing 1 h at 1100°C produces a surface layer of γ-Al_2O_3 from the surface to ~30 nm and regrown α-Al_2O_3 in the region ~30–95 nm. Examination by TEM reveals SnO_2 particles coherent with both phases. There is a tendency for Sn to migrate toward the free surface; however, very little Sn is lost during annealing. The presence of the Sn as SnO_2 precipitates may prevent the loss of Sn by evaporation.

Migration of the α-Al_2O_3 substrate into the amorphous layer is detected after 1 h at 900°C for anneals in a reducing atmosphere. A surface layer of γ-Al_2O_3 (0–50 nm) and epitaxially regrown α-Al_2O_3 (50–95 nm) was present after annealing 1 h at 960°C. Complete regrowth to α-Al_2O_3 was observed after the 1 h anneal at 1100°C; however, this α-Al_2O_3 contained significant disorder. The disorder may be due to the observed presence of $SnAl_2O_4$ precipitates. Approximately 97% of the Sn was lost during the 1100°C anneal.

These observations suggest that the interaction of Sn and/or Sn–Al–O compounds with irradiation-produced defects is very strong, effectively pinning them in place.

Acknowledgements

These studies were supported in part by the Department of Energy, Division of Materials Sciences, under contract DE-AC05-96OR with Lockheed Martin Energy Research Corporation. The implantations were performed in the Surface Modification and Characterization Facility of Oak Ridge National Laboratory. Special thanks go to Dr. P.S. Slad, Oak Ridge National Laboratory for assistance with the electron microscopy.

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