AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

TITLE: INCORPORATION OF IRON CATIONS INTO EPITAXIAL SAPPHIRE
THIN FILMS BY CO-EVAPORATION AND THERMAL ANNEALING

AUTHOR(S): Ning Yu, MST-4

Michael Nastasi, MST-4

SUBMITTED TO: The 1994 Spring Materials Research Society Meeting,
April 4-8, 1994, San Francisco, CA

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

MASTER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

INCORPORATION OF IRON CATIONS INTO EPITAXIAL SAPPHIRE THIN FILMS BY CO-EVAPORATION AND SUBSEQUENT THERMAL ANNEALING

Ning Yu, Harriet Kung, Michael Nastasi, DeQuan Li*
Materials Division, *Chemical Science and Technology Division,
Los Alamos National Laboratory, Los Alamos, NM 87545, USA

ABSTRACT

Iron-doped sapphire thin films have been successfully epitaxially grown onto sapphire single crystal substrates by electron beam deposition and subsequent thermal annealing. Amorphous Al_2O_3 thin films, about 280-390 nm thick, cation doped with iron have been deposited on [0001] oriented sapphire substrates. Iron doping with cation concentrations (a ratio of Fe content to total cation content) up to 5 at.% can be incorporated into the octahedral sites of Al-cation sublattice during the epitaxial regrowth process at 1000-1400 C, as determined by Rutherford Backscattering Spectrometry and ion channeling measurements. Cross-sectional Transmission Electron Microscopy shows the presence of two distinct regions in the annealed films. One exhibits the epitaxial relationship with the sapphire substrate and the second region has amorphous type of contrast. External optical transmittance measurements in the ultra violet and visible light range have exhibited the absorption associated with Fe^{3+} . This study has demonstrated a simple method of incorporating dopants into single crystal sapphire, which has potential in the fabrications of thin film planar optical waveguides.

Introduction

Alpha-alumina (sapphire) has important applications in the integrated electro-optical devices due to its high electrical insulation and refractive index. The doping of sapphire is a subject of practical and basic interests. The incorporation of a number of cation species such as Cr and Fe into Al-cation sublattice sites in sapphire single crystals with [0001] or [1210] orientation, has been studied by White *et al.* [1-6] using ion implantation in combination with post-implantation annealing process. The regrowth of sapphire has been found to follow the sequence of from amorphous to gamma (cubic) and then to alpha phase. The pre-existence of an amorphous layer through out the entire implanted layer has been demonstrated to be critical to the regrowth process during which the single crystallinity can be restored and the dopants can be activated into the Al sublattice sites [2,3,6]. For high quality epitaxial regrowth and dopant activation, it is desired to perform ion implantation at cryogenic temperature to produce a complete amorphous layer on the sapphire substrate. Recently, van den Hoven *et al.* [7] have demonstrated that Er cations, useful optical dopants, can be optically incorporated into Al_2O_3 thin films through thermal annealing process following Er ion implantation.

In this study, we have investigated the thermal annealing process of solid state epitaxial growth of sapphire thin films and the activation of Fe dopants for the Fe-doped amorphous Al_2O_3 thin films deposited by electron beam evaporation on the [0001] sapphire substrates. The results from Rutherford Backscattering Spectrometry (RBS) and ion channeling, and Cross-sectional Transmission Electron Microscopy (XTEM) studies show high quality epitaxy of regrown thin films containing Fe up to 5 at.% in the Al-cation sublattice sites. Optical measurements have also confirmed doped Fe taking the octahedral sites. This method could be expected to be operative in doping Er ions into sapphire for the fabrications of thin film planar optical waveguides.

Experimental Details

Single crystal sapphire substrates used in this study were from Union Carbide Corp., containing less than 100 ppm total impurities, with [0001] orientation and one-side polished to mirror finish. Electron beam evaporation was used to deposit amorphous Al_2O_3 thin films at room temperature onto the sapphire substrates from a high purity alumina target. The base pressure prior to the evaporation was about 2×10^{-8} torr. Fe dopants at cation concentrations ranging between 0 and 5 at.% were incorporated into the deposited films by co-evaporating high purity Fe from a second e-beam gun during the deposition process. The thickness of deposited films was 280-390 nm. The mass density of as-deposited films was found to be 2.55 g/cm^3 , about 64% of bulk density of sapphire (3.97 g/cm^3). The as-deposited samples were then annealed at temperatures of 900-1400 C for annealing cycle of from 15 minutes to 12 hours in oxidizing ambients either flowing O_2 or air.

The samples before and after thermal anneals were analyzed with RBS and ion channeling techniques with a 2 MeV He^+ ion beam generated from a 3 MV tandem accelerator. The scattered particles were detected at a scattering angle of 167° . The angular scans across two of the major crystallographic axes of sapphire, the [0001] and $[10\bar{1}5]$, were applied to determine lattice location of doped Fe cations in the annealed samples.

Two samples doped to 5 at.% Fe with and without annealing were selected and prepared for XTEM analysis. The samples were cut in half and the two halves were glued face-to-face. The samples were first sectioned by mechanically polishing down to 30 μm thick and then further thinned down by ion milling to final XTEM specimens. The specimens were examined on a Philips CM30ST microscope at 300 kV. Bright field images were taken on the as-deposited and the annealed samples, respectively, along with selected area diffraction (SAD) patterns taken from the film region and the substrate region.

The samples were optically characterized at room temperature in Perkin Elmer UV-VIS 330 system by using ultra violet and visible (UV-VIS) light spectroscopy in an external transmittance mode.

Results and Discussion

Figure 1 shows the RBS channeling spectra along the [0001] axis of the sapphire substrates, taken from the as-deposited and annealed (1400 C for 12 hours in air) samples, respectively, which contain 4 at.% Fe cations in the films. The channeling spectrum for the as-deposited sample reveals high backscattering yield for the signals of Al and O in the thin film region, the levels of which reach those in a random spectrum taken on the annealed sample. It indicates that the as-deposited Al oxide layers were amorphous. The amorphous structure of as-deposited films was further confirmed in the XTEM study by the SAD pattern taken in the thin film region which shows uniform amorphous halo (picture not shown here). The backscattering yield in the thin film region for the annealed sample is reduced significantly. The reduction in the scattering yield indicates the epitaxial growth of the deposited thin film, following the same crystal structure of the substrate. The minimum backscattering yield, as defined by the ratio of channeled to the random yield, is a measure of epitaxial quality of regrown layer. The minimum yield for the Al signal over the entire thin film region is found to be 10%. The higher minimum yield, in comparison to the value (2%) on a virgin sample (undeposited substrate), reflects the presence of residual disorder in the regrown layer.

Figure 1. 2 MeV He^+ ion aligned RBS spectra of a virgin sapphire, the as-deposited sample doped with 4 at.% Fe, and the annealed sample, along with a random spectrum of the annealed sample.

Although part of Fe dopants were lost during the 12 hours anneal, as seen from the reduction in the Fe yield near the original interface between the film and the substrate in the random spectrum in figure 1, the concentration of Fe near the surface remained the same as compared to the as-deposited case. A great reduction in the Fe yield from the random to aligned spectrum indicates that remained Fe has taken the lattice sites upon the anneal.

We have performed ion channeling angular scans along two directions to determine the lattice location of Fe cations. Figure 2 shows angular scan curves for Fe and Al signals near the surface across the $[0001]$ and $[10\bar{1}5]$ axes. The angular scan curve of Al taken across the $[0001]$ axis from a virgin sapphire is also included for comparison. Two features can be noted in figure 2. First, around both $[0001]$ and $[10\bar{1}5]$ directions, the angular width is consistent for Fe and Al signals. Second, the angular width for the thin film sample is identical to that of a virgin sapphire although the minimum scattering yield from the film is higher. The same angular width for Al in the film and in the virgin sapphire reveals that the regrown layer has restored the same crystallinity as in the substrate. Since the $[0001]$ and $[10\bar{1}5]$ axes are two independent channeling directions with an angle of 32.2° , the coincidence of angular width for Fe and Al along these two directions clearly demonstrates that the retained Fe has taken the octahedral sites of Al-cation sublattice.

Figure 3 shows the XTEM micrograph for the sample with 5 at.% Fe annealed at 1150 C for 15 minutes. The inserted SAD pattern taken in the regrown thin film region A is identical to that taken in the substrate region B. This verifies the epitaxial relationship of thin film with the sapphire substrate, as also revealed by RBS and channeling analysis. The XTEM micrograph shows the presence of two distinct regions in the annealed films. One exhibits the epitaxial relationship with the sapphire substrate and the second region has light contrast. Preliminary study

Figure 2. Ion channeling angular scan curves of Al-cation and doped Fe-cation across (a) the [0001] axis and (b) the $[10\bar{1}5]$ axis from the annealed sample doped with 4 at.% Fe, along with the angular scan curve of Al from a virgin sapphire.

of high resolution electron microscopy shows the amorphous type of contrast in the second phase region (data not shown). It has been noted in the previous studies that crystalline structure of Fe-rich phases such as Fe_3O_4 and $\text{Fe}(\text{Fe}_x\text{Al}_{1-x})_2\text{O}_4$ spinel with the size as large as 50 nm could be precipitated out in the doped region in the case where Fe ions were implanted at room temperature [5] or when the amount of Fe_2O_3 exceeded its solid solubility in $\alpha\text{-Al}_2\text{O}_3$ at annealing temperature [2,3]. The detail comparison of defect natures presented in our sample with those observed in the Fe-implanted sapphire following annealing is important to understand the resultant differences from these two processes.

The occupation of retained Fe in the octahedral sites of Al sublattice has also been revealed from the optical transmittance measurements. Figure 4 shows the UV-VIS spectra taken from a virgin sapphire, the as-deposited Fe-doped samples, and the samples annealed at 1400 C for 12 hours in air, respectively. The spectrum from the virgin sample reveals the featureless structure except the drop of transmission near 204 nm due to defect band. The spectrum of the as-deposited sample shows similar features as the virgin one. However, two additional absorption bands appear in the vicinity of 259 nm and 194 nm after the 1400 C anneal, which were ascribed to Fe^{3+} state in sapphire [8]. The same absorption bands were also found for the Fe-implanted sapphire following thermal anneal at 1500 C [8]. Since the Fe^{3+} state corresponds to coordination number of six, this indicates the substitution of Fe cations in the octahedral sites of sapphire.

Our present study has demonstrated that a significant fraction of Fe cations, up to 5 at.%, can be incorporated into the octahedral sites of sapphire through the procedure of co-evaporation of

Figure 3. XTEM micrograph of the sample doped with 5 at.% Fe after the 1150 C anneal for 15 min in air, along with the SAD patterns taken from the thin film area and the substrate area.

Figure 4. Transmittance optical spectra from a virgin sapphire, the as-deposited sample doped with 4 at.% Fe, and the annealed sample.

Fe and Al oxide followed by post annealing. The results from this study are consistent with those from previous studies of White *et al.* using Fe ion implantation to produce Fe-doped layers in sapphire. However, the cryogenic temperature was required for ion implantation process to

produce an entire amorphous layer on sapphire substrate to obtain high quality epitaxial regrowth. The quality of epitaxial regrowth achieved by using the simple method demonstrated here is comparable to the case of using ion implantation. Since the co-evaporation method is of great simplicity, it could be anticipated to apply to the fabrication of planar optical waveguides. The study of doping Er cations into sapphire thin films with sandwiched structure by using the same technique is under way.

Conclusions

We have successfully incorporated Fe-cation up to 5 at.% cation concentration into epitaxial sapphire thin films grown on undoped single crystal sapphire substrates with [0001] orientation. Fe cations can be incorporated into the thin films by co-evaporation of pure Fe and amorphous Al oxide followed by post-evaporation anneals at 1000-1400 C in oxidizing ambients. RBS and channeling analysis has clearly demonstrated the substitutionality of doped Fe cations in the octahedral sites as Fe^{3+} upon the epitaxial regrowth. It has been further supported by optical transmittance measurements where the Fe^{3+} state was identified. The epitaxy of the regrown sapphire thin films with respect to the sapphire substrates has been confirmed by both ion channeling and XTEM examinations. A fraction of second region with amorphous type of contrast has been revealed by XTEM, the details of which are required further studies. This study has demonstrated a simple method of incorporating dopants into single crystal sapphire, which has potential in the fabrications of thin film planar optical waveguides.

ACKNOWLEDGMENTS

The valuable discussions with Joe Wen and David Clarke at Materials Department, University of California at Santa Barbara, are gratefully acknowledged. All ion beam work was performed at Ion Beam Materials Laboratory at the Los Alamos National Laboratory. This research was sponsored by the U.S. Department of Energy, Office of Basic Energy Science, Division of Materials Science.

References

1. C.W. White, G.C. Farlow, C.J. McHargue, P.S. Sklad, M.P. Angelini, and B.R. Appleton, Nucl. Instru. and Meth. B7/8, 473 (1985).
2. C.W. White, L.A. Boatner, P.S. Sklad, C.J. McHargue, J. Rankin, G.C. Farlow, and M.J. Aziz, Nucl. Instru. and Meth. B32, 11 (1988).
3. P.S. Sklad, L. Romana, C.J. McHargue, C.W. White, and J.C. McCallum, Nucl. Instru. and Meth. B59/60, 1187 (1991).
4. C.J. McHargue, P.S. Sklad, C.W. White, J.C. McCallum, A. Perez, and G. Marest, J. Mater. Res. 6, 2160 (1991).
5. G.C. Farlow, C.W. White, C.J. McHargue, P.S. Sklad, and B.R. Appleton, Nucl. Instru. and Meth. B7/8, 541 (1985).
6. H. Naramoto, C.W. White, J.M. Williams, C.J. McHargue, O.W. Holland, M.M. Abraham, and B.R. Appleton, J. Appl. Phys. 54, 683 (1983).
7. G.N. van den Hoven, E. Snoeks, A. Polman, J.W. M. van Uffelen, Y.S. Oei, and M.K. Smit, Appl. Phys. Lett. 62, 3065 (1993).
8. C.J. McHargue, in Characterization of Optical Materials, edited by G.J. Exarhos (Butterworth-Heinemann, Boston, 1993), p. 150.

**DATE
FILMED**

6/22/94

END