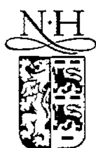
ELSEVIER

Nuclear Instruments and Methods in Physics Research B 120 (1996) 248–251

NIM B
Beam Interactions
with Materials & Atoms

Low temperature epitaxial regrowth of mercury implanted sapphire

E. Alves [a,*], M.F. da Silva [a], J.G. Marques [b], J.G. Correia [b,c], J.C. Soares [b], K. Freitag [d]

[a] *Instituto Tecnológico e Nuclear, Estrada Nac. 10, P-2685 Sacavém, Portugal*
[b] *CFN, University of Lisboa, Av. Prof. Gama Pinto, 2, P-1699 Lisboa Codex, Portugal*
[c] *ISOLDE Collaboration, CERN, CH-1211 Geneva, Switzerland*
[d] *ISKP, University of Bonn, 14–16 Nussallee, D-53115 Bonn, Germany*

Abstract

Hg ions were implanted into sapphire at room temperature and 80 keV energy to a fluence of 1×10^{15} Hg^+/cm^2. This fluence was enough to produce an amorphous surface layer. The annealing behaviour was studied combining RBS/channeling and hyperfine interaction techniques. Surprisingly, the RBS/channeling results show there is an epitaxial regrowth of the damaged layer after annealing at 800°C for 20 min. Although some of the implanted Hg segregates to the surface during the epitaxial regrowth, a significant fraction is incorporated into regular sites along the *c*-axis. The hyperfine interactions results, obtained after implantation of a dose of 5×10^{12} Hg^+/cm^2, show that a small fraction of Hg is probably bound to oxygen. This result is in agreement with the RBS/channeling measurements which also show that the system formed after annealing is stable even at high temperatures.

1. Introduction

The effects of ion implantation and post-annealing treatments in sapphire have been widely investigated for several species, leading to a global understanding of the ion induced amorphisation and defect recovery [1,2]. However, the interplay between ballistic and chemical effects is not yet clear. Sapphire is usually amorphized implanting doses in the range of 10^{16} to 10^{17} at/cm^2, at room temperature, or of the order of 10^{14} at/cm^2 at liquid nitrogen temperature [1,3]. The amorphous layers created by the implantation recrystallize via a solid-phase epitaxial process with two distinct phase transitions [4]. First occurs a fast phase transition in the temperature range of 700–900°C, leading to the formation of γ-Al_2O_3. This phase transforms into α-Al_2O_3 at higher temperatures (> 1000°C) or for longer annealing times (~ 100 h) through a layer by layer growth starting at the original amorphous/crystalline interface [4,5].

In the present work we show that α-Al_2O_3 is amorphized at room temperature by the implantation of a dose of 1×10^{15} Hg^+/cm^2 and that the annealing for 20 min at a temperature as low as 800°C is enough to recrystallize the amorphous phase into the crystalline α-Al_2O_3 phase.

2. Experimental details

High purity α-Al_2O_3 single crystals with optically polished surfaces cut perpendicularly to the $\langle 02\bar{2}1 \rangle$ direction were implanted at room temperature with Hg^+ ions of 80 keV to a fluence of 1×10^{15} at/cm^2, using the isotope separator of the University of Bonn. Thermal annealings were carried out for one hour at temperatures in the range of 800 to 1400°C in vacuum. After implantation and after each stage of thermal annealing, RBS/channeling studies were performed with a 1.6 MeV He^+ beam to characterize the structural changes induced by the annealing. The backscattered particles were detected at 140° and 180° using silicon surface barrier detectors located in the standard IBM geometry, with resolutions of 13 and 18 keV, respectively. A Ni mask with a 4 mm hole was used in front of the sample in order to minimize the effect of charge accumulation on the Al_2O_3 surface during the analysis. Computer simulations were performed using a Monte Carlo code previously described [6] which was modified to accommodate the α-Al_2O_3 crystal lattice.

For the hyperfine interaction measurements, using the Perturbed Angular Correlation (PAC) technique, radioactive ^{199m}Hg was implanted at 60 keV using the ISOLDE/CERN isotope separator, to a dose of 5×10^{12} at/cm^2. The expected projected range of the Hg^+ ions is 180 Å with a peak concentration of 5×10^{18} Hg/cm^3. After implantation the samples were annealed under 0.9

* Corresponding author. Fax: +351-1-955-0117.

0168-583X/96/$15.00 Copyright © 1996 Elsevier Science B.V. All rights reserved.
PII S0168-583X(96)00519-8

atm Ar, at temperatures between 500 and 800°C, for 30 min. The e^-–γ PAC experiments were performed at room temperature using the 374–158 keV cascade from the decay of ^{199m}Hg with anisotropy $b_2 A_{22} = +0.235$. The 158 keV state has spin $I = 5/2$, half-life $T_{1/2} = 2.4$ ns and quadrupole moment $Q = 0.674(77)b$ [7]. The experimental set-up consists of two β spectrometers for the detection of conversion electrons and two BaF_2 scintillators for γ detection [8]. From the coincidence spectra $N(\theta, t)$, where θ is the angle between detectors and t is the time delay between events, the time differential anisotropy $R(t) = 2.[N(180°, t) - N(90°, t)]/[N(180°, t) + 2.N(90°, t)] \sim b_2 A_{22} G_{22}(t)$ was calculated. $G_{22}(t)$ is the perturbation function which describes the modulation of the angular correlation. For a cascade with $I = 5/2$ three frequencies $\omega_n = C_n(\eta)\nu_Q$ are observed, giving

$$G_{22}(t) = \sum_{n=0}^{3} S_{2n} \cos\left[C_n(\eta)\nu_Q t\right] \exp\left[-\delta C_n(\eta)\nu_Q t\right].$$

The quadrupole coupling constant $\nu_Q = eQV_{zz}/h$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, which can be deduced from the frequency factors $C_n(\eta)$, contain information about the magnitude of the principal component V_{zz} and the asymmetry of the electric field gradient (EFG). The exponential factor allows for a Lorentzian distribution of EFGs around a mean value. Such a distribution can be caused e.g. by different lattice defects in the vicinity of the probe atoms. The S_{2n} coefficients, which give the amplitudes for each frequency, can be calculated for polycrystalline as well as for single crystalline samples.

3. Results and discussion

Fig. 1 shows the random and aligned RBS spectra obtained after implantation and after annealing. The random and aligned spectra obtained after implantation overlap for a region of 350 Å from the surface, showing the complete amorphization of this layer. The range of the implanted ions is 200 Å, in good agreement with TRIM predictions (220 Å). The amorphization was obtained with a maximum nuclear energy deposition of 4.75×10^{22} keV/cm^3. According to the modified Kinchin–Pease model [9] and assuming a displacement energy for Al of 72 eV we obtain about 9 dpa which is much lower than the values reported previously [10] for the amorphization of sapphire. Recrystallization of the amorphous layer occurs during the annealing at 800°C as we can see in the aligned spectrum of Fig. 1b. The small peak observed at a depth of 350 Å shows the presence of some residual damage in a region where the amorphous-crystalline interface was located. Considering the thickness of the amorphous layer and the annealing time we were able to obtain a lower limit for the epitaxial regrowth velocity of 2.4 Å/s, i.e, 3 orders of magnitude higher than the value measured by other authors [4]. The residual damage disappears completely after annealing at 1400°C (Fig. 1d).

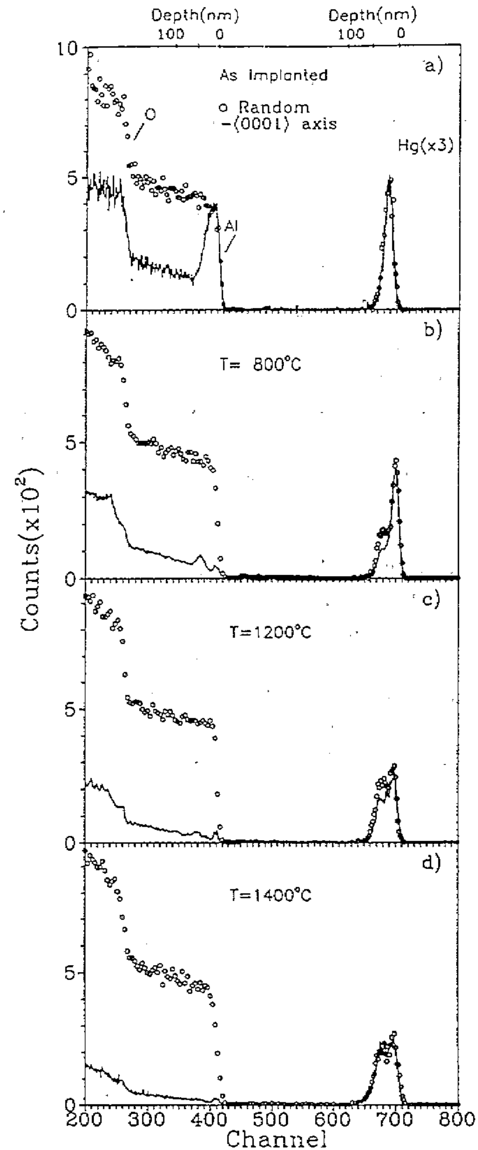

Fig. 1. Random and aligned RBS spectra, obtained (a) after implantation at room temperature of Hg at 80 keV with a dose of 1×10^{15} at/cm^2; (b) after annealing at 800°C for 20 min; (c) after annealing at 1200°C for 1 h; (d) after annealing at 1400°C for 1 h.

The Hg profile changes simultaneously with the epitaxial regrowth of the amorphous layer and some of the Hg segregates towards the surface. The flat region of the Hg profile obtained after the annealing at 800°C corresponds to Hg ions trapped in the recrystallized layer(1.7×10^{20} at/cm^3). The differences observed between the random and aligned profiles also show that a part of the Hg trapped is in regular lattice positions. The Hg at the surface starts to diffuse into the bulk when the annealing temperature is increased, as shown in Fig. 1c and d. After annealing at 1400°C a nearly flat profile is observed, correspond-

ing to a Hg concentration of 2.3×10^{20} at/cm^3. The complete overlap of the random and aligned spectra shows that all the ions are now in random positions. The total amount of Hg in the sample remained constant through all the thermal treatments.

Fig. 2 shows the angular scans for the ⟨0001⟩, ⟨11$\bar{2}$0⟩ and ⟨01$\bar{1}$0⟩ axes after annealing at 800°C. The narrow dip of Hg in the ⟨01$\bar{1}$0⟩ axis excludes the presence of Hg in substitutional sites. Monte Carlo simulations of these results show that 35% of the Hg atoms are located in displaced octahedral (~ 0.7 Å along the c-axis) sites and the rest is randomly distributed. The result of the simulations indicated by the continuous and dashed curves shown in the figure reproduce quite well the experimental data.

Fig. 3 shows the PAC spectra for the sapphire single crystal measured after implantation and after annealing at 800°C. In all spectra the anisotropy of the cascade is only observed at time $t = 0$ and approaches the hardcore in a few nanoseconds. After implantation most of the implanted Hg ions are associated with uncorrelated defects. In this way the quadrupole interaction does not result in a sharp frequency, but in a frequency distribution, with $\langle \nu_{Q1} \rangle =$ 788 MHz and $\delta_1 = 0.43(1)$. The remaining probes, with relative fraction $f_2 = 0.23(5)$, are characterized by the parameters $\nu_{Q2} = 1291(13)$ MHz, with $\eta_2 = 0.48(3)$. The value of ν_{Q2} is close to the frequency of ^{199m}Hg in HgO, $\nu_Q = 1162$ MHz, with $\eta = 0.185(13)$ [11], suggesting that part of the implanted Hg ions are in a configuration close to the one assumed in HgO. From previous work [12] the frequency for Hg in substitutional Al sites can be estimated to be ~ 190 MHz excluding this lattice site for the Hg implanted ions, in agreement with the channeling results. The fraction f_2 decreases with the annealing temperature and even after annealing at 800°C the other Hg probes are still in damaged environments, and only a decrease of the mean value of the frequency distribution to $\langle \nu_{Q1} \rangle = 520$ MHz was observed.

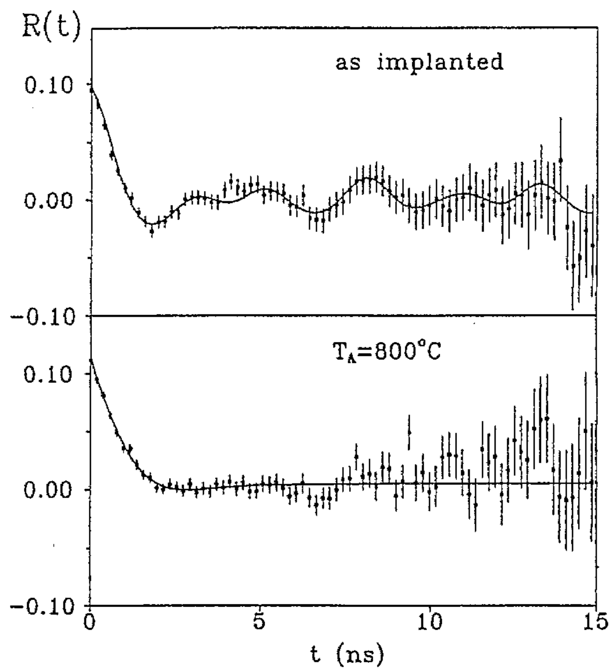

Fig. 3. PAC spectra obtained after implantation and after annealing at 800°C. The c-axis of the single crystal was on the detectors plane at 45° with two of the detectors.

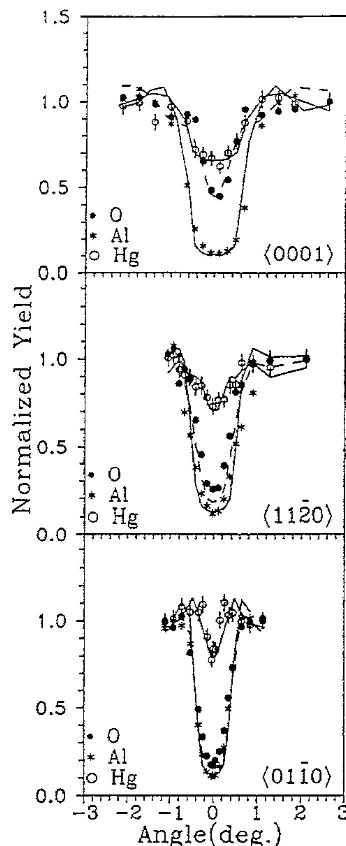

Fig. 2. Angular scans for the ⟨0001⟩, ⟨11$\bar{2}$0⟩ and ⟨1$\bar{1}$10⟩ axes after annealing at 800°C. The continuous and dashed curves are the results of the Monte Carlo simulation.

4. Conclusions

A fluence of 1×10^{15} Hg$^+$/cm^2 at room temperature was enough to amorphize sapphire. The epitaxial regrowth of the damaged layer was observed directly after annealing at 800°C for 20 min, whereas only the formation of the intermediate γ-phase was expected. The epitaxial regrowth velocity is about 3 orders of magnitude higher than the previously reported for sapphire stoichiometric amorphized. A fraction of the Hg ions is incorporated into displaced free octahedral sites along the c-axis. The RBS/channeling measurements also show that the Hg redistributes in the implanted region forming a flat profile after annealing at high temperatures. The hyperfine interaction results show that a part of the implanted Hg ions are

probably bound to oxygen forming an HgO complex in the implanted region. These results prove that the final state of the implanted region and its behaviour are strongly influenced by the chemical nature of the implanted ions.

Acknowledgements

This work has been partially funded by JNICT, Portugal, through projects CERN/CA/137/94 and two post-doc grants (J.G.M. and J.G.C.).

References

[1] See, for example: G.C. Farlow, P.S. Sklad, C.W. White and C.J. McHargue, J. Mater. Res. 5 (1990) 1502, and references therein.

[2] L. Romana, P. Thevenard, B. Canut, G. Massouras and R. Brenier and M. Brunel, Nucl. Instr. and Meth. B 46 (1990) 94.

[3] E.Alves, M.F. da Silva, G.N. van den Hoven, A. Polman, A.A. Melo and J.C. Soares, Nucl. Instr. and Meth. B 106 (1995) 429.

[4] C.W. White, L.A. Boatner, P.S. Sklad, C.J. McHargue, J. Rankin, G.C. Farlow and M.Z. Aziz, Nucl. Instr. and Meth. B 32 (1988) 11.

[5] P.S. Sklad, J.C. McCallum, C.J. McHargue and C.W. White, Nucl. Instr. and Meth. B 46 (1990) 102.

[6] L. Rebouta, P.J.M. Smulders, D.O. Boerma, F. Agulló-López, M.F. da Silva and J.C. Soares, Phys. Rev. B 48 (1993) 3600.

[7] W. Tröger, T. Butz, P. Blaha and K. Schwarz, Hyp. Int. 80 (1993) 1109.

[8] J.G. Marques, J.G. Correia, A.A. Melo, M.F. da Silva, J.C. Soares and ISOLDE Collaboration, Nucl. Instr. and Meth. B 99 (1995) 645.

[9] A.P. Mouritz, D.K. Sood, D.H. John, M.V. Swain, J.S. Williams, Nucl. Instr. and Meth. B 106 (1995) 602.

[10] P. Sigmund, Radiat. Eff. 1 (1969) 15.

[11] T. Butz, Th. Volkel and O. Nuyken, Chem. Phys. 149 (1991) 437.

[12] J.G. Marques, A.A. Melo, J.C. Soares, E. Alves, M.F. da Silva and K. Freitag, Nucl. Instr. and Meth. B 106 (1995) 602.