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Oxygen migration during epitaxial regrowth in Cs⁺-irradiated α -quartz investigated by means of nuclear reaction analysis

F. Roccaforte

II. Physikalisches Institut and SFB 345, Universität Göttingen, D-37073 Göttingen, Germany and Istituto Nazionale per la Fisica della Materia, corso Italia 57, I-95129 Catania, Italy

F. Harbsmeier, S. Dhar, and K. P. Lieb^{a)}

II. Physikalisches Institut and SFB 345, Universität Göttingen, D-37073 Göttingen, Germany

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The migration of oxygen in ion-beam-amorphized *c*-SiO₂ (α -quartz) was investigated by means of nuclear reaction analysis using the resonant reaction $^{18}\text{O}(p,\alpha)^{15}\text{N}$ for oxygen depth profiling. Only very small amounts of oxygen were observed to diffuse in crystalline or in Xe⁺-ion beam-amorphized α -quartz after high-temperature annealing. However, a dramatic migration of oxygen occurs in Cs⁺-implanted α -quartz in the same temperature range (600–900 °C), where Cs diffuses out of the amorphized layer and epitaxial recrystallization occurs. These results point out to a strong correlation of all these processes. A mechanism to explain the observed indiffusion of ^{18}O is proposed and is related to the Cs migration and the topological modification to achieve epitaxial regrowth of the SiO₂ matrix. © 2000 American Institute of Physics. [S0003-6951(00)02325-1]

The importance of amorphous SiO₂ (*a*-SiO₂) as well as α -quartz is essentially related to the fabrication of optoelectronic devices like light emitters, optical splitters, waveguides, etc.¹ The most fundamental step for making such devices consists in the modification of the optical properties by inducing controlled structural changes and local doping, for example by using ion implantation. Because of the possible applications of α -quartz, several studies were recently performed in order to understand the accumulation of ion-beam induced damage and its thermal recovery.^{2–4} The most important finding was probably the solid phase epitaxial growth (SPEG) of alkali-implanted α -quartz using thermal treatments in air at 700–900 °C.^{5–7} However, complete SPEG of Cs-implanted α -quartz did not occur after annealing in vacuum at 900 °C⁵ nor did Xe-implanted α -quartz recrystallize.^{5,6} More recently, epitaxial crystallization of *a*-SiO₂ thin films deposited on crystalline α -quartz substrate was also achieved.⁸ All these results suggest that both oxygen and alkali play a complementary role in the epitaxial regrowth process. Therefore, it is important to monitor simultaneously the behavior of the SiO₂ matrix, the implanted alkali, and the oxygen transport.

We report on the dramatic indiffusion of oxygen in Cs⁺-ion beam amorphized α -quartz during thermal treatments at 500–900 °C in ^{18}O atmosphere. A simple mechanism is proposed which not only explains the epitaxial growth, but also allows to estimate the amount of oxygen which diffuses in.

Single crystalline α -quartz samples, (0001) oriented, 10 × 10 × 1 mm³ in size, were implanted at 77 K with 250 keV Xe⁺ or Cs⁺ ions at a fluence of 2.5 × 10¹⁶ ions/cm². The irradiated samples were introduced inside quartz glass ampoules filled with 98% enriched ^{18}O gas and then annealed for 1 h in a conventional furnace at 500–900 °C. Some of

the nonirradiated samples were also annealed in ^{18}O atmosphere for comparison. Separate samples were used in each annealing step. After annealing, the ^{18}O -concentration profiles were determined by means of resonant nuclear reaction analysis using the $^{18}\text{O}(p,\alpha)^{15}\text{N}$ reaction at the 151 keV resonance.⁹ The α particles of the exothermic reaction $^{18}\text{O}(p,\alpha)^{15}\text{N}$ were detected with an annular silicon surface barrier detector, positioned at 180° around the beam axis. The Cs- and Xe-concentration profiles were measured with Rutherford backscattering spectrometry (RBS) with a 900 keV α beam. All ion-beam analyses and implantations were carried out at the Göttingen ion-implanter IONAS.¹⁰

Figure 1(a) shows the ^{18}O -concentration profile in single crystalline α -quartz after annealing at 900 °C. An indiffusion of ^{18}O can be observed, but is limited to a 20 nm wide near-surface region, the ^{18}O profile having a maximum concentration of 16 at. % at 10 nm depth. The diffusion takes place via $^{18}\text{O} \leftrightarrow ^{16}\text{O}$ exchange, as demonstrated by the simultaneous depth profiling of both oxygen isotopes with time of

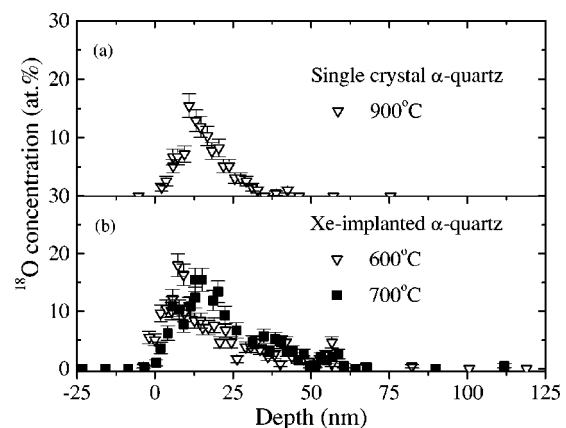


FIG. 1. ^{18}O concentration profiles for (a) single crystalline α -quartz after annealing at 900 °C and (b) Xe⁺-ion beam amorphized α -quartz at 600 and 700 °C.

^{a)}Electronic mail: lieb@physik2.uni-gottingen.de

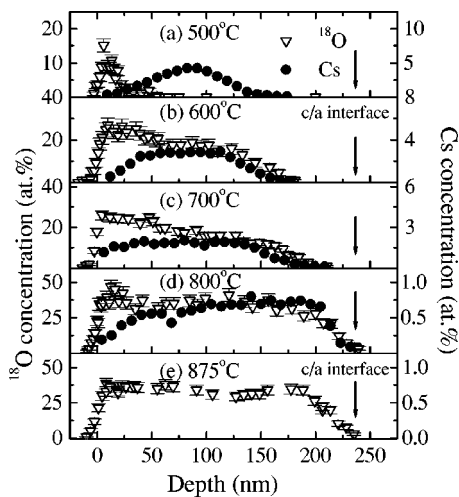


FIG. 2. ^{18}O - and Cs- concentration profiles for Cs^+ -ion beam amorphized α -quartz after annealing between 500 and 875 $^{\circ}\text{C}$. A strong correlation between the migration of the two species is evident at 600–800 $^{\circ}\text{C}$. The arrows report the position of the c/a interface after ion-beam amorphization.

flight-elastic recoil detection analysis in Li-doped α -quartz.¹¹ The concentration profiles of ^{18}O in the Xe^+ -irradiated samples, annealed at 600 and 700 $^{\circ}\text{C}$, are reported in Fig. 1(b). The thickness of the amorphous layer due to Xe^+ irradiation was about 230 nm, as measured by RBS in channeling geometry. Here, the $^{18}\text{O}\leftrightarrow^{16}\text{O}$ isotope exchange is limited to the top 50 nm. The slightly higher ^{18}O content with respect to the crystal suggests that the ion-beam induced damage resulting in the lower density of the amorphous material² may enhance the oxygen penetration. The amount of ^{18}O does not increase substantially after 700 $^{\circ}\text{C}$ annealing and no epitaxial recovery of the damage occurs.⁵

A completely different situation is observed in Cs^+ -implanted α -quartz which, in contrast to the Xe^+ -irradiated material, epitaxially recrystallizes at 800–900 $^{\circ}\text{C}$.⁵ The ^{18}O concentration profiles for the Cs^+ -implanted samples after annealing between 500 and 875 $^{\circ}\text{C}$ are shown in Figs. 2(a)–2(e). The Cs-concentration profiles, determined by means of RBS, are reported in the same plots after appropriately scaling to compare with the ^{18}O profiles. After annealing at 500 $^{\circ}\text{C}$, the ^{18}O depth distribution [Fig. 2(a)] is quite similar to that in crystalline or in Xe^+ -irradiated quartz (see Fig. 1). The Cs profile at 500 $^{\circ}\text{C}$, whose maximum is at about 90 nm depth in the 230-nm-thick damaged region, does not show appreciable changes with respect to the initial implantation shape. When increasing the annealing temperature to 600 $^{\circ}\text{C}$, a strong ^{18}O indiffusion takes place up to about 175 nm depth [Fig. 2(b)], towards the c/a interface. The ^{18}O concentration has a maximum of about 30 at. % at the surface and slowly decreases inside the damaged region. At the same time, the implanted Cs^+ ions are redistributed inside the amorphous layer by forming a *box-like* profile. At 700 $^{\circ}\text{C}$, ^{18}O diffuses further into a depth of 200 nm along with Cs^+ ions [Fig. 2(c)]. It is important to note that, apart from the oxygen surface peak, the profiles of Cs and ^{18}O are similar and their diffusion fronts move parallel inside the amorphized region towards the c/a interface. At the annealing temperature of 800 $^{\circ}\text{C}$, both the Cs and ^{18}O profiles reach the c/a interface [Fig. 2(d)]. The ^{18}O concentration is almost uniform inside the

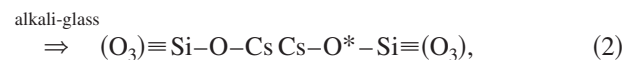
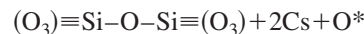
amorphous layer (30 at. %) and decreases abruptly in the proximity of the c/a interface, due to the extremely low oxygen diffusivity in the perfect crystal. The total amount of ^{18}O penetrated in the amorphous layer at this annealing temperature (i.e., the integral of the concentration profile) is $(618 \pm 42) \times 10^{15}$ at./ cm^2 . A further increase of the annealing temperature up to 875 $^{\circ}\text{C}$, where SPEG of the amorphous layer is completed⁵ and the Cs diffused completely out of the sample,⁵ does nearly not change the ^{18}O profile.

This dramatic oxygen migration in the Cs-implanted material, which manifests itself by means of the experimentally observed $^{18}\text{O}\leftrightarrow^{16}\text{O}$ exchange, and its strong correlation to the Cs diffusion are certainly related to the damage induced in the SiO_2 network by the chemically active alkali atoms. The results can be qualitatively explained by means of the topological changes in the SiO_2 network caused by alkali irradiation and annealing in oxygen. The network of SiO_2 is formed by elemental $[\text{SiO}_4]$ -tetrahedral units, both in the crystalline and in the amorphous phase. Recent extended x-ray absorption fine structure measurements¹² show that these $[\text{SiO}_4]$ units remain almost preserved even after high fluence irradiation. This means that the *network connectivity* C , i.e., the number of tetrahedra sharing each vertex of the $[\text{SiO}_4]$ tetrahedra, does not change after amorphization. Then, in the case of both crystalline and amorphous SiO_2 the network is said to be *fully connected* with $C=2$.¹³ The elemental intertetrahedral connection of SiO_2 can be represented by



where $(\text{O}_3)\equiv\text{Si}$ is generally used to indicate the continuation of the network.

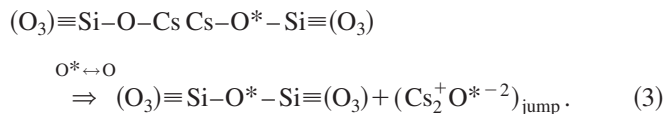
Introducing *network modifiers*¹⁴ like alkali-oxide breaks the continuity of the SiO_2 -network by creating oxygen atoms which do not bridge adjacent tetrahedra (*nonbridging oxygens*).¹⁴ In the case of Cs^+ -ion irradiated α -quartz, only a marginal fraction of nonbridging oxygens has formed after irradiation, which arises from the “scavenging” of oxygen atoms by the implanted Cs^+ -ions, located in weakly bond interstitial positions.¹⁵ When the oxygen diffuses into the alkali-implanted α -quartz, alkali oxide (i.e., $\text{Cs}_2^+\text{O}^{2-}$) is dissolved in the matrix by forming an alkali-glass silicate,^{5,6} in which the bridging oxygens of the fully connected network are replaced by nonbridging ones. The effect of Cs implantation and annealing in oxygen can thus be described as



where O^* indicates external ^{18}O .

The oxygen atoms (O or O^*) having a strong bond to silicon and a weak one to Cs can easily migrate through the opened glassy structure. Therefore, the pronounced migration of oxygen in Cs-implanted SiO_2 is thought to be due to preferential diffusion paths for oxygen which are opened at the broken intertetrahedral linkages. The correlation between the migration of Cs and ^{18}O suggests that each indiffusing oxygen (i.e., each isotope exchange) is accompanied by a “jump” of Cs from one linkage to another. During the pro-

cess, the conversion of nonconnected tetrahedra into integer linkages occurs with a migration process of the type



When at about 800 °C the Cs and oxygen reach the *c/a* interface, the high flexibility of the structure caused by the formation of nonbridging oxygen atoms (i.e., reduction of the network connectivity *C*), can favor epitaxial recrystallization.

On the basis of this scenario we estimated the amount of oxygen diffused in the amorphous layer. Considering as the average jump distance ν the lattice parameter of the crystalline material along the *c* axis (0.54 nm), the number of diffusion steps of each Cs can be estimated from the typical distance which the Cs needs to reach either the surface or the *c/a* interface. At 800 °C, where the oxygen exchange process has reached its saturation, the Cs diffusion front at half maximum has migrated 94 nm towards the *c/a* interface and 48 nm towards the surface, with respect to the initial gaussian implantation shape. Hence, one can calculate an average Cs migration path of $\bar{\lambda} = 71 \pm 5$ nm. The number of diffusion steps is then given by $N_{\text{step}} = \bar{\lambda}/\nu = 131 \pm 9$. Since according to our interpretation [see Eq. (3)], the isotope exchange of one oxygen atom is accompanied by the movement of two Cs ions (i.e., $Cs_2^+O^{*-2}$), the total number of oxygen atoms N_{O^*} is given by $N_{O^*} = \frac{1}{2} N_{Cs} N_{\text{step}}$, N_{Cs} being the number of Cs atoms in the network. Then, considering the experimental value of the Cs content calculated from RBS, $N_{Cs} = 11.4 \times 10^{15}$ at./cm², the total amount of exchanged oxygen is $(748 \pm 75) 10^{15}$ at./cm², which is close to the experimental integrated ¹⁸O content of $(618 \pm 42) 10^{15}$ at./cm² at 800 °C. It is quite satisfactory to see that at least the order of magnitude of the indiffused ¹⁸O is well reproduced by the proposed mechanism.

In conclusion, a dramatic oxygen migration via $^{18}O \leftrightarrow ^{16}O$ exchange has been observed in Cs⁺-implanted α -quartz, while in the Xe⁺-ion beam amorphized material the penetration of external oxygen is limited to the surface

region. The ¹⁸O migration is strongly correlated with the migration of Cs and epitaxial recrystallization of the SiO₂ matrix. A simple mechanism has been proposed, in which each oxygen exchange is correlated to a jump of the mobile Cs between intertetrahedral connections. This allows to estimate the amount of ¹⁸O penetrating inside the amorphous SiO₂ matrix and given hints on how the epitaxial growth process may be explained. The recovery of the damage occurs when both alkali ions and oxygen reach the *c/a* interface, where the presence of a high number of nonbridging oxygen atoms favours the epitaxial recrystallization of the amorphous layer.

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