AIP Applied Physics Letters

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Citation: Applied Physics Letters **75**, 2903 (1999); doi: 10.1063/1.125185
View online: http://dx.doi.org/10.1063/1.125185
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Epitaxial crystallization of amorphous SiO_2 films deposited on single-crystalline α-quartz

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(Received 19 July 1999; accepted for publication 8 September 1999)

The epitaxial α-quartz thin film could be a promising material for fabricating optical devices because of its unique optical and mechanical properties and processing advantages compared to bulk materials. This letter reports on the solid-phase epitaxial growth of thin amorphous SiO_2 films deposited by electron gun evaporation on single-crystalline α-quartz substrates. This was achieved by high-dose Cs^+-ion implantation and subsequent thermal annealing in air. Also, a thin amorphous layer produced by Si^+-ion implantation on α-quartz was epitaxially regrown, thus indicating that the epitaxy is independent of the preparation history of the amorphous layer. The results are explained on the basis of network modifications induced by alkali and oxygen in the SiO_2 structure. © *1999 American Institute of Physics.* [S0003-6951(99)02845-4]

Passive integrated optical devices can be produced by selective modifications of the refractive index of SiO_2-based materials. Such devices, for example, can be useful for splitting optical signals into two or more parts and for distributing them into the desired channel waveguides.[1] The selective modification of the refractive index can be achieved using ion implantation technology, as proposed by Chandler *et al.*[2] for the construction of α-quartz waveguides. However, the implantation process induces (generally unwanted) radiation damage which severely restricts the use of this technology. Efforts have been made to understand the mechanisms of radiation damage[3] and its dynamic annealing behavior[4] in single-crystalline α-quartz. Recently, an elegant solution for removing the radiation damage has been realized after the discovery of complete epitaxial regrowth in ion-beam amorphized α-quartz.[5–7]

This finding also raises the possibility of epitaxial regrowth of thin amorphous SiO_2 films deposited on single-crystalline substrates. Thin α-quartz films would be more advantageous compared to the bulk crystals in terms of optical patterning, selective processing, and interconnecting optical devices.[1] Moreover, epitaxial α-quartz films may also be useful in making sensors[8,9] and light-emitting optical devices either by suitable coatings[10] or appropriate impurities doping[11] or in the imaging technology.[1]

In this letter, we present results on the solid-phase epitaxial regrowth (SPEG) of a thin amorphous SiO_2 layer, deposited on single-crystalline α-quartz. The epitaxial crystallization of the films was achieved by thermal treatment in air after high-fluence Cs^+-ion doping. The epitaxial regrowth process is independent of the preparation method of the a-SiO_2 layers. This is demonstrated by epitaxially growing a thin amorphous SiO_2 layer created by Si^+-ion implantation on α-quartz substrates.

Thin amorphous SiO_2 films were deposited on single-crystalline (0001) α-quartz substrates by means of an e-beam gun evaporation system, equipped with a thickness monitor. The deposition was performed under a high vacuum of 6×10^{-8} mbar and the samples were water cooled to avoid heating. After deposition, the samples were irradiated with 250 keV Cs^+ ions at a fluence of 2.5×10^{16} ions/cm^2. Another set of α-quartz samples was postirradiated with 250 keV Cs^+ ions at the same fluence of 2.5×10^{16} ions/cm^2 after having irradiated them with 70 keV Si^+ ions at a fluence of 2.5×10^{16} ions/cm^2. All ion irradiations were performed at liquid-nitrogen temperature. Homogeneous implantations over an area of 10×10 mm^2 were achieved using an electrostatic $x-y$ beam sweeping system. During irradiations, the beam current was maintained below 1 μA to avoid beam heating of the samples. During thin-film depositions and irradiations, a portion of each sample was covered with an Al foil in order to preserve a virgin crystalline part for the purpose of analysis at different experimental steps. Isochronal thermal annealing of all these irradiated samples were carried out in air up to 875 °C. All the samples before and after irradiations were analyzed by means of Rutherford backscattering spectrometry in channeling geometry (RBS-C) using a 0.9 MeV He^{2+} beam provided by the Göttingen ion implanter IONAS.[12] Mechanical surface profiling of the sample surface was used to monitor the variation in the step height between the nonirradiated base material and the regions on which SiO_2 films were deposited and irradiated.

Figure 1 illustrates random and channeling RBS spectra of such an as-deposited sample. For comparison, a virgin spectrum of single-crystalline quartz is also shown. The analysis proved that the film is stoichiometric and homogeneous in nature with an areal density of 5.3×10^{17} atoms/cm^2. The thickness of the film in nm was determined from the surface profile scanned across the border of the base crystal and the deposited film (see Fig. 2). The thickness of the film obtained from the difference in step height is about 90 nm. Using the experimental areal density and film thickness, the atomic density of the deposited film was determined to be 5.9×10^{22} atoms/cm^3. This atomic film density is 6% lower than the density of thermally grown SiO_2 film and 25% lower than the single-crystal quartz.

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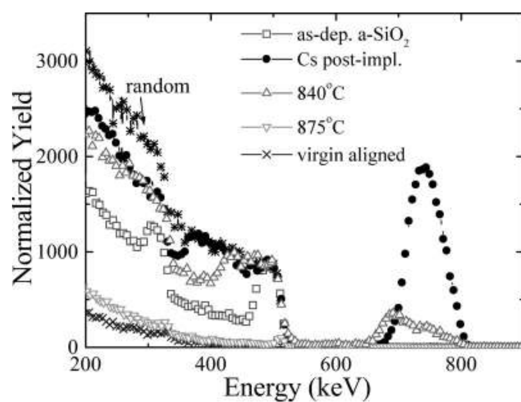

FIG. 1. RBS-C spectra of a thin a-SiO_2 film after deposition on α-quartz (□), post-implantation with Cs^+ (●), and annealing in air at 840 °C (△) and 875 °C (▽), which indicate complete epitaxial crystallization of the film. For comparison, the channeling spectrum of the crystalline SiO_2 virgin aligned (×) and the random spectrum (⋆) are given.

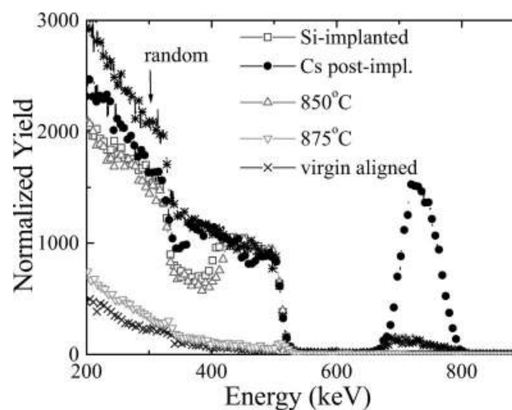

FIG. 3. RBS-C spectra of the sample pre-amorphized with Si^+ ions (□) and then postimplanted with Cs^+ (●) and annealed at 850 °C (△) and 875 °C (▽). Full epitaxial recrystallization of the amorphous layer occurs at 875 °C, as can be seen from the comparison with the virgin aligned spectrum (×).

Thereafter, the thin films were post-irradiated with 250 keV Cs^+ ions and the resulting RBS-C and surface profile curves are reported in Figs. 1 and 2, respectively. It is clear from the comparison between the as-prepared and the irradiated RBS-C spectra that the near-surface region of the crystalline quartz substrate has become amorphous at this fluence and then the original interface of the film and substrate cannot be seen any more. Due to the surface sputtering, the thickness of the deposited film has reduced to approximately 60 nm. Thus, after irradiation the total thickness of the amorphous (film+amorphized substrate) layer became about 230 nm. However, no noticeable change in the step height was observed after Cs^+ ions irradiation (see Fig. 2). This is because the reduction in the step height due to sputtering is approximately compensated by the increase in the step height due to the swelling of the underlying amorphized quartz substrate. The implanted Cs profile is almost Gaussian with a maximum at about 90 nm depth.

The irradiated samples were then annealed in air for 1 h up to 875 °C. The RBS-C spectra taken after two annealing steps are compared in Fig. 1. The 840 °C annealing produced a planar epitaxial regrowth of the substrate amorphous layers and the c/a interface shifted from 360 to 410 keV, which is close to the original interface of the film and crystalline substrate. It is interesting to note that the implanted Cs completely redistributed during annealing and was swept towards the surface as the c/a interface advanced. With increasing temperature, the epitaxial regrowth proceeded across the SiO_2 film/bulk interface. In fact, annealing carried out at 875 °C resulted in the complete epitaxial recrystallization of the full sample including the deposited SiO_2 film: the channeling spectrum is almost identical to the virgin one. At this stage there was no detectable amount of Cs in the sample, indicating that most of the Cs had migrated to the surface and was evaporated from the sample. After achieving full epitaxy, the surface profile of the recrystallized sample (see Fig. 2) showed a step height of about 42 nm which now corresponds to the recrystallized SiO_2 film. The reduction of the step height is expected, as the density of the deposited amorphous film should reach the density of quartz after epitaxial crystallization.

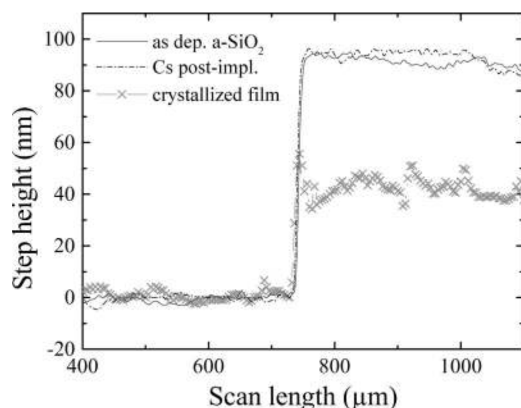

FIG. 2. Surface profile of the thin-film SiO_2 deposited on the quartz substrate showing the step height after deposition (-), Cs^+ post-implantation (-·-), and after complete recrystallization at 875 °C (×).

Finally, Fig. 3 shows the RBS-C spectra of an α-quartz sample irradiated first with 70 keV Si^+ ions and then with 250 keV Cs^+ ions. In this case, the initial amorphous SiO_2 layer of 13.8×10^{17} atoms/cm^2 thickness was created due to Si^+-ion irradiation. After Cs *post-implantation*, the amorphous layer extended up to a depth of about 18.6×10^{17} atoms/cm^2. Air annealing performed at 850 °C induced a partial epitaxial regrowth and the c/a interface moved to 12×10^{17} atoms/cm^2 (see Fig. 3). This depth is slightly beyond the depth of the originally amorphous film produced by Si^+ ions. After annealing at 875 °C, complete SPEG of the amorphized layer was obtained (see Fig. 3). This means that again complete epitaxial recrystallization of the amorphous layer created by Si^+ ions was achieved.

Consequently, epitaxial recrystallization of thin a-SiO_2 layers on quartz substrates produced either by thin-film deposition or by ion irradiation can be achieved by air annealing after Cs^+-ion implantation. It should be noted that annealing in vacuum hardly produced epitaxial regrowth of the amorphous layer, thus indicating the importance of oxygen in the regrowth process.[5] It is also important to mention that amorphous SiO_2 films after deposition did not show any transition to the crystalline phase even after annealing at 1000 °C.[13]

In the following, the experimental results are discussed by considering the network topology of SiO_2. The crystalline

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as well as the amorphous form of silicon dioxide can be described as a *fully connected* [SiO_4]-tetrahedral network, in which each tetrahedron has four oxygen atoms at the vertices and a Si atom at its center. Each pair of Si atoms corresponding to two adjacent tetrahedrons is bridged by an oxygen atom.[14] Because of its low degree of topological freedom, atomic rearrangements of this structure are very much restricted and the kinetics for these rearrangements is too slow to be observed experimentally. Indeed, SiO_2 is a typical example of a glass-forming system.[14] On the other hand, it was realized that the introduction of catalyst impurities, acting as *network modifiers*, improves the degree of topological freedom which in turn increases the mobility of the tetrahedral structure.[14–16] Actually, the alkali are cation modifiers which open up the fully connected network by forming nonconnected tetrahedral corners (nonbridging oxygen).[15] They can be incorporated into the network by forming a weak ionic bond with the nonbridging oxygen corners, thus weakening the strong Si–O bond.[17] The incorporation of network modifiers reduces the viscosity and the melting temperature, and that can facilitate the atomic or structural rearrangements (crystallization).[18] Using similar arguments, Fratello *et al.*[19] were able to justify the formation of quartz crystals into fused silica in which the high topological freedom of the network was provided by the presence of the hydroxyl group OH attached to the nonbridging oxygen. On the other hand, several attempts failed to recrystallize epitaxially α-quartz amorphized using rather than alkali-ion species,[20–22] except the result of Devaud *et al.*,[23] which showed SPEG of Brazilian natural quartz crystals after irradiation with silicon and oxygen ions and annealing in air above 1050 °C.

In the present case, instead, complete epitaxial recrystallization of the amorphous SiO_2 layers was achieved. During annealing, homogeneous redistribution of the implanted Cs in the amorphous region starts at approximately 600 °C. At about 800 °C the profile reaches the c/a interface and SPEG of the amorphous layer sets in. The RBS-C spectrum of the sample annealed at 840 °C indeed shows a considerable amount of epitaxial regrowth of the amorphous layer (see Fig. 1). The role of oxygen is equally important in the recrystallization process. Our recent experimental works[24,25] on alkali-irradiated samples annealed in O^{18} atmosphere showed that a dramatic in-diffusion of oxygen occurs between 600 and 800 °C. The diffusion of oxygen strongly correlates with the migration of alkali ions inside the amorphous layer: in the case of Cs, their concentration profiles move together and they simultaneously reach the c/a interface at 800 °C.[25] The dramatic exchange of oxygen in the presence of alkali network modifiers can be explained by assuming that the incorporation of each oxygen is correlated to a single jump of Cs between the tetrahedra during its diffusion process. In this way, at each diffusion step a tetrahedral interconnection can be repaired.[7] When the Cs reaches the c/a interface, epitaxial regrowth of the substrate together with the deposited film takes place and the Cs is driven out of the sample.

In conclusion, epitaxial crystallization of a-SiO_2 thin films on single-crystalline α-quartz substrates has been achieved. It has been shown that the regrowth of α-quartz layers is independent of the method of production of the amorphous layer (evaporation, ion implantation). The observed correlation between the migration of Cs and oxygen is used to explain the rearrangement process of the SiO_2 network.

This work was supported by the Deutsche Forschungemeinschaft. The authors thank D. Purschke for running the IONAS and W. Bolse for his precious suggestions. Two of the authors (F.R. and S.D.) are grateful to C. A. Carosella of the Naval Research Laboratory, U.S., for the stimulating discussions during the IBMM-1998 (Amsterdam).

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