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ION-IMPLANTATION-INDUCED PHASE SEPARATION
AND CRYSTALLIZATION IN LITHIA-SILICA GLASSES*

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Abstract

Crystallization of annealed $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glasses implanted with inert ions and fused SiO_2 glass implanted with Li ions was monitored using infrared reflection spectroscopy. Elastic recoil detection analysis was used to study changes in the Li and H concentration induced in these glasses by implantation and annealing. Implantation of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ with inert ions results in Li depletion, accompanied by H indiffusion, in the implanted region. For Li-implanted SiO_2 , crystallization of α -quartz is accompanied by appreciable Li diffusion to the surface and attendant H migration to the Li-depleted region. The crystallization mechanisms are discussed in terms of phase separation in the lithia-silica system.

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I. INTRODUCTION

It is well known that heating fused silica in the 1200 to 1700°C range results in coarse-grained cristobalite growth which nucleates at irregularities or surface impurities. We have previously shown¹ that crystallization of α-quartz in the near-surface region of high-purity fused silica can be produced by Li implantation followed by heat treatment at 700 to 800°C with a crystallite size typically on the order of one to five microns.

We have extended our investigation of ion-implantation-induced crystallization to lithium disilicate glass. The crystallization of lithia silicate glasses involves phase separation which occurs within a well-defined composition-temperature region.² Interstitial alkali ions can be removed from the near-surface region by the implantation of inert gas ions.³⁻⁵ The composition and thus the phase separation characteristics of the near-surface region of the glass can be altered in a controlled manner by proper choice of the implanted ion, ion energy, and fluence.

In the present paper we report results of crystallization studies in $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass implanted with Xe and He and in Li-implanted fused silica glasses. The depth distributions of the implanted Li were measured using elastic recoil detection (ERD) analysis.⁶ Structural changes in the implanted region ($\leq 1 \mu\text{m}$ in depth) were analyzed using infrared reflection spectroscopy (IRS). The ERD measurements also allow observation of the diffusion of hydrogen into the implanted region. Hydrogen distribution measurements are of interest because of changes in the corrosion resistance when hydrogen is incorporated into glass networks.^{7,8}

As discussed below, the results for fused silica and lithium disilicate glass lead us to speculate that these two glasses can be viewed as end members of the lithia-silica glass system. From this viewpoint, implantation of

Li into pure SiO_2 produces separation of a Li-rich phase on a microscale in the glass upon which displaced SiO_2 network ions can precipitate. On the other hand, implantation of inert gas ions into $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ causes sufficient loss of Li from the near-surface region to permit phase separation and subsequent crystallization.

II. EXPERIMENTAL DETAILS

The $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass was cast from a melt (Pt crucible) of SiO_2 and Li_2CO_3 powders held at 1350°C for 24 hours and annealed at 300°C for one hour. Fused silica samples were prepared from Corning fused silica (CFS 7940). Implantation fluences from 5×10^{15} to 1×10^{17} ions/cm² were used at implantation energies of 250 keV (Xe), 100 keV (He) and 50 to 200 keV (Li). Thermal annealing was done in a tube furnace under flowing N_2 , and the IRS measurements were made using a Beckman IR-12 spectrophotometer with a reflection attachment from N. J. Herrick, Inc.

The ERD analysis was performed using a 24 MeV ^{28}Si beam from Sandia's tandem Van de Graaff accelerator. The beam was incident at 75° to the sample normal and light ions recoiled at an angle 30° from the incident beam direction were detected. A $10 \mu\text{m}$ Al foil in front of the detector acted as a particle filter for the 24 MeV Si beams and also slowed the recoiled ions. Measurement of the recoil yield versus energy readily gives the light ion concentration versus depth. Detailed descriptions of the experimental arrangement and analysis have been given elsewhere.^{6,9}

III. EXPERIMENTAL RESULTS

A. $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ Glasses

The infrared reflection spectrum of SiO_2 and of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ is compared in Fig. 1. The major features in the SiO_2 spectrum are the Si-O-Si stretch

mode at 1115 cm^{-1} and the bending vibration at 800 cm^{-1} . Addition of Li_2O to form $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ produces bands near 1070 and 940 cm^{-1} which are characteristic of a homogeneous glass consisting of SiO_4 tetrahedra and Li_2O in which the presence of the Li_2O modifies the Si-O-Si stretching vibration and results in an Si-O dangling bond vibration near 940 cm^{-1} .

The IRS spectrum for $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass after implantation of 5×10^{15} and 1.1×10^{17} 250 keV Xe/cm^2 is shown in Fig. 2. The intensity of the Si-O-Si stretching vibration decreases as disorder is introduced and the Si-O-Si vibration shifts to higher energy while the Si-O vibration moves to lower energy. These energy shifts are associated with Li depletion as will be discussed below. Ferraro et al.¹⁰ have seen similar shifts for glasses with Li_2O concentrations between ~ 40 and 20 mole %. Spectral changes similar to those shown for Xe implantation in Fig. 2 are also observed for He implantation; however, the energy shifts are smaller indicating less Li depletion with He than with Xe.

A $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass sample implanted with 2×10^{16} 250 keV Xe/cm^2 was annealed at 500°C for various times. Indications of the tendency for phase separation are the appearance of the 1030 cm^{-1} absorption and the replacement of the 1070 cm^{-1} absorption with a relatively well-defined band at 1100 cm^{-1} after anneals of only 15 min.

Figure 3 shows that after an anneal of 20.5 hr. at 500°C , the spectrum contains sharp lines of crystalline $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ which have a one-to-one correspondence with the lines in the reference¹¹ spectrum of crystalline $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$. Comparison of the data for the implanted side shows that the energy of the Si-O-Si stretching vibration increases continuously and the intensity of the 1030 cm^{-1} band grows monotonically with anneal time until the implanted region crystallizes. For this relatively long annealing time

the 1030 cm^{-1} band is observable on the unimplanted side. The $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ composition is very near the immiscibility boundary, and we attribute this incipient phase separation to result from the Li depletion commonly observed in the near-surface region of these glasses (see Fig. 4). Results qualitatively similar to those for Xe implantation have been obtained with He implantation.

The data of Figs. 1-3 and observations¹² of a Li-colloid band imply movement of Li ions in the near-surface region of implanted and annealed glasses, and we have used elastic recoil detection measurements to quantitatively evaluate these changes. ERD spectra for $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ are presented in Figs. 4-6. The ERD spectra contain the depth distribution information for both Li and H in the near-surface region. In the raw data, the signal from H in the glass is superimposed on the Li signal from the bulk; however, this background ERD yield has been subtracted from the H yield and the data have been corrected for the energy dependence of the scattering cross section to permit quantitative presentations of concentration versus depth. The spectra in Fig. 4 give the Li depth distribution before implantation and after implantation of 5×10^{16} 250 keV Xe/cm² and after a 500°C anneal. Note that the Li distribution is not uniform very near the surface in the unimplanted glass. There is evidence for Li depletion in the first $\sim 3000\text{ \AA}$; in this region the Li has apparently been replaced by H (see Fig. 6). After implantation with Xe there is a pronounced dip in the Li concentration at a depth of $\sim 1500\text{ \AA}$ below the surface, which is near the Xe projected range. The He-implanted samples also show an increase in the Li concentration at the surface. After the 500°C anneal the enhanced Li concentration near the surface has disappeared; furthermore, there is a uniform reduction of Li in the bulk of $\sim 15\%$ throughout the $\sim 6000\text{ \AA}$ depth probed.

The H depth distribution in these same Xe-implanted samples is shown in Fig. 5. Before implantation, the H distribution extends $\sim 3000 \text{ \AA}$ into the sample with a peak concentration in the first $\sim 2000 \text{ \AA}$ of $\sim 17 \text{ at.\%}$. This H depth profile depends on the sample history and presumably results from H indiffusion as is well-known from studies of weathering in glasses.^{7,8} These particular samples were polished ~ 18 months before the ion implantation and ERD measurements were performed. After $5 \times 10^{16} 250 \text{ keV Xe/cm}^2$ implantation, the H redistributes in the implanted region. This H motion is presumably due to Li motion and the H partially compensates the Li loss. While the H compensation appears to be essentially complete for the "weathered" surface before implantation, the compensation during implantation is limited by a fixed supply of H, i.e., the H which was initially in the sample.

We have found¹² analogous results for He implantation in which most of the energy is deposited into electronic processes. As in the case with Xe implantation, He implantation produces an appreciable migration of Li toward the surface. In fact, the Li concentration approaches the stoichiometric value at the surface after implantation of $1 \times 10^{17} \text{ He/cm}^2$ in contrast to the Li depletion observed before the implant. A loss of Li from both the near-surface and bulk, completely analogous to the results for Xe implantation, is observed after annealing at 500°C . A further striking example of the depletion of near-surface alkali ions and their replacement by surface H, after inert-gas ion bombardment, is shown in Fig. 7. A sample of glass with composition 88% SiO_2 and 12% K_2O was prepared and implanted with $7 \times 10^{16} 250 \text{ keV Xe}^+$ ion/cm^2 . Before implantation the spectral features are the main Si-O-Si stretch near 1100 cm^{-1} and a weak band at $\sim 940 \text{ cm}^{-1}$. The latter is associated with non-bridging oxygen ions in an alkali-rich environment.¹³ After implantation the $\sim 940 \text{ cm}^{-1}$ band is replaced by a band at $\sim 980 \text{ cm}^{-1}$. This

is the Si-OH dangling bond¹³ and shows that as alkali is depleted by the bombardment, H from the surface replaces it to form the Si-OH species.

The combined results for the Li and H distributions in the $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glasses and the results of Fig. 7 conclusively demonstrate that Li outdiffusion is accompanied by H indiffusion after inert ion implantation. These observations support the suggestion that alkali diffusion is governed by chemical¹⁴ and electrostatic forces.¹⁵

B. Fused Silica

Measurements of Li motion associated with the crystallization of α -quartz induced by Li implantation and annealing were made for comparison with the observations in the $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ system. The 24 MeV ^{28}Si ERD spectra for CFS 7940 SiO_2 implanted with 1×10^{17} 50 keV Li/cm² for an as-implanted sample and after a 15 min. anneal at 600°C are shown in Fig. 8. The as-implanted Li distribution consists of two peaks, with the more shallow peak occurring near the predicted LSS range of 2000 Å and a broader distribution peaked near 4500 Å. There is no observable change in the Li depth distribution after a 600°C anneal. Similar double-peaked profiles were previously observed^{3,4} for Ag implantation into LAS glasses. Such distributions are attributed to the motion of high mobility ions induced by sample heating by the implant beam. It was found in the studies of Ag that this distribution could be altered by changing the beam current or by reducing the sample temperature. For Ag implants with the sample temperature at 77°K, the distribution approached a Gaussian distribution centered about the expected Ag ion range.

Although no change in the Li distribution is observed for 600°C anneals, which is below the temperature required for the onset of α -quartz crystallization, changes in the Li profile are observed for higher annealing temperatures. The effects of annealing at 700 and 800°C on the implanted Li profile

are shown in Fig. 9. After a 15 min. anneal at 700°C the Li distribution has changed markedly. The Li peak at ~ 2000 Å has essentially disappeared and the Li concentration in the 4500 Å peak is reduced while a significant accumulation of Li at the surface is observed. Annealing at 800°C further increases the Li concentration near the surface. Indeed, after an 800°C anneal, 30% of the Li migrated from the bulk to the surface; however, the bulk concentration of Li is still appreciable, and it is presumably this Li which forms Li_2O nuclei that permit the growth of crystalline α -quartz.

As Li migrates in SiO_2 during annealing, there is attendant H motion analogous to that observed for the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$. The H depth distribution in Li-implanted SiO_2 is shown before annealing and after the 700°C anneal in Fig. 10. Before annealing there is H very near the surface, and the H content of the bulk is much less for SiO_2 than that shown previously for the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass. The bulk H concentration is 1.4×10^{20} H/cm³, which is in good agreement with the value of 1.3×10^{20} H/cm³ found by Allred et al.¹⁵ for Suprasil fused SiO_2 glass. Surface hydrogen is always observed and it is probable that the H observed in the as-implanted sample was introduced during polishing and/or implantation. After the 700°C anneal, however, H migrates in the bulk of SiO_2 and peaks occur in the H distribution near the same depths that the peaks in the Li distribution were observed. Thus, as in the case for $\text{Li}_2\text{O}\cdot \text{SiO}_2$ glass, Li migration to the surface is accompanied by H indiffusion. It should also be noted that the total H content in the implanted region is greater after the 700°C anneal than for the as-implanted case, but that the H content in the 1000 to 5000 Å depth region is less than the Li depletion from this region.

IV. DISCUSSION

A. Crystallization of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ Glasses

The temperature-composition range in which phase separation occurs in the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ system is shown in Fig. 11. Since the Li_2O content of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ is above the Li_2O content of the immiscibility boundary, no phase separation is expected for $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$. However, if the Li_2O content were decreased by ≤ 2 mole %, phase separation could be expected for temperature $\leq 500^\circ\text{C}$. The present experiments clearly demonstrate that inert ion implantation depletes the Li concentration in the implanted region. These data further show that the Li depletion in the implanted region is sufficient to yield a composition well within the immiscibility boundary for the temperatures under consideration. A question remains as to the local O content in the implanted glass. We have no evidence that O is lost during implantation; however, the ERD measurements show that the Li depletion is compensated by H which presumably saturates dangling O bonds and the data of Fig. 7 clearly show the attachment of H to non-bonding oxygen. The net effect of implantation of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass with Xe and He is thus to reduce the Li_2O content so that the resulting composition is well within the immiscibility boundary. Upon annealing at 500°C , the implanted region crystallizes whereas the unimplanted region does not show evidence of crystallization.

It was noted in Section III A that, from the infrared reflection measurements there appeared to be tendency for phase separation in the unimplanted side of the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glasses after annealing at 500°C . This phase separation is also understandable within the framework of the above discussion of implantation-induced crystallization. As the data in Figs. 4 and 5 show, the Li has been depleted to a $\sim 3000 \text{ \AA}$ depth and replaced by H in the normal weathering process. Such Li depletion again moves the composition within the immiscibility boundary

where phase separation is expected. Indeed, it would not be surprising to find evidence for crystallization under annealing in this near-surface region, although no such evidence was found in the present measurements.

B. Crystallization of α -Quartz from SiO_2

The details of the Li-induced crystallization of SiO_2 glass to produce α -quartz are not as clear as those for the crystallization of $\text{Li}_2\text{O}\cdot\text{SiO}_2$. Implantation of Li into SiO_2 glass has at least two consequences: (1) Introduction of Li changes the chemical composition of the glass, and (2) The ion-implantation process introduces damage in the glass. In particular, near the end of range, the Li ions produce a region of intense displacement damage as much of their energy is expended in nuclear collision processes. The atomic displacement damage results in oxygen vacancies in fused SiO_2 as has been measured¹⁶ by UV absorption near 2450 Å of O vacancies with trapped electrons after implantation of Li, B, or Al. The O vacancies recombine with interstitials as the radiation damage anneals at temperatures near 700 to 800°C, which is the same temperature region for which α -quartz is observed¹ to crystallize.

In addition to the effects of implantation-induced disorder, the implanted Li concentration appears to be important to the crystallization process. No evidence for crystallization has been observed for implantation of the network ions Si and O or for implantation with the network-forming ions Al and B. Similarly, we have been unable to induce crystallization by implantation of the alkali ion Na. It is not clear why no crystallization was observed with Na, which is chemically similar to Li, but the fact that the mobility¹⁷ of Na is ~ 25 times that of Li at 350°C may allow the Na to migrate too readily during implantation and annealing to form nuclei.

For an implant of 1×10^{17} 50 keV Li/cm², the Li concentration at depths from ~ 1000 to 5000 Å was measured to be $\sim 0.3 \times 10^{22}$ Li/cm³. If all of this Li were to bond as Li₂O, the local Li₂O concentration could be as high as 7 mole %. For these compositions it is theoretically possible for there to be phase separation of small Li₂O·2SiO₂ particles within an SiO₂-rich host. If this were indeed the case, then the primary role of Li in the crystallization process is to form nuclei and to prevent the SiO₄ tetrahedra from recombining into the glass network before the crystallization temperature is reached. As the α -quartz crystallizes with the recombination of implantation-induced interstitial-vacancy complexes, much of the Li becomes superfluous and is swept to the surface. In this regard it is significant that no Li motion is observed for annealing temperatures below 700°C, where crystallization begins. At that temperature Li is lost primarily from the 2000 Å depth region, i.e., from end of range where the majority of the displacement damage was produced. If these suggestions are correct, then the implantation-induced crystallization of both Li₂O·2SiO₂ and SiO₂ glasses can be understood on the basis of phase separation in the lithia-silicate system.

V. CONCLUSIONS

We have shown that ion implantation can be used to selectively crystallize the near-surface regions of glasses and have discussed the crystallization in terms of the lithia-silica phase diagram. Ion implantation is used to alter the composition of the near-surface region, and crystallization is preferentially limited to the implanted areas of the glass. For the lithium disilicate glass system, implantation of inert ions depletes the near-surface region of Li until the composition within the implanted region falls within the immiscibility boundary. Crystallization then occurs when the glass is heated to

500°C. For pure fused SiO_2 glass, implantation of Li followed by heat treatment at 700 to 800°C results in the crystallization of α -quartz. Crystallization of this system was also discussed in terms of the lithia-silica phase diagram and it was suggested that crystallization in this system might also be governed by this diagram.

The motion of Li and H during the annealing process was measured by ERD spectroscopy. These measurements afford the first quantitative evaluation of the interrelation between Li and H during crystallization in these systems and show that Li depletion in both $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ and Li implanted SiO_2 is accompanied by H indiffusion. These measurements further show that crystallization of α -quartz from fused SiO_2 takes place with simultaneous motion of Li from the end-of-range depth to the surface. These results provide new insight into the crystallization processes and associated ion motion and may have important applications in the study of weathering and corrosion.

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FIGURE CAPTIONS

Fig. 1. Comparison of the IRS spectra of SiO_2 glass (CFS 7940) and lithium disilicate glass for the spectral region between 700 and 1300 cm^{-1} .

Fig. 2. Reflectance spectra for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass after implantation with 5×10^{15} and $1.1 \times 10^{17} 250 \text{ keV Xe/cm}^2$.

Fig. 3. Reflectance spectra for implanted ($2 \times 10^{16} 250 \text{ keV Xe/cm}^2$) and unimplanted (reverse side of sample) $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass after a 20.5 hr. anneal at 500°C .

Fig. 4. Li depth distribution of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ measured by ERD showing the effect of $5 \times 10^{16} 250 \text{ keV Xe/cm}^2$ implantation and a subsequent thermal anneal at 500°C .

Fig. 5. H depth distribution measured by ERD for the sample of Fig. 4.

Fig. 6. Comparison of the Li and H profiles in the near-surface region of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ implanted with $5 \times 10^{16} 250 \text{ keV Xe/cm}^2$.

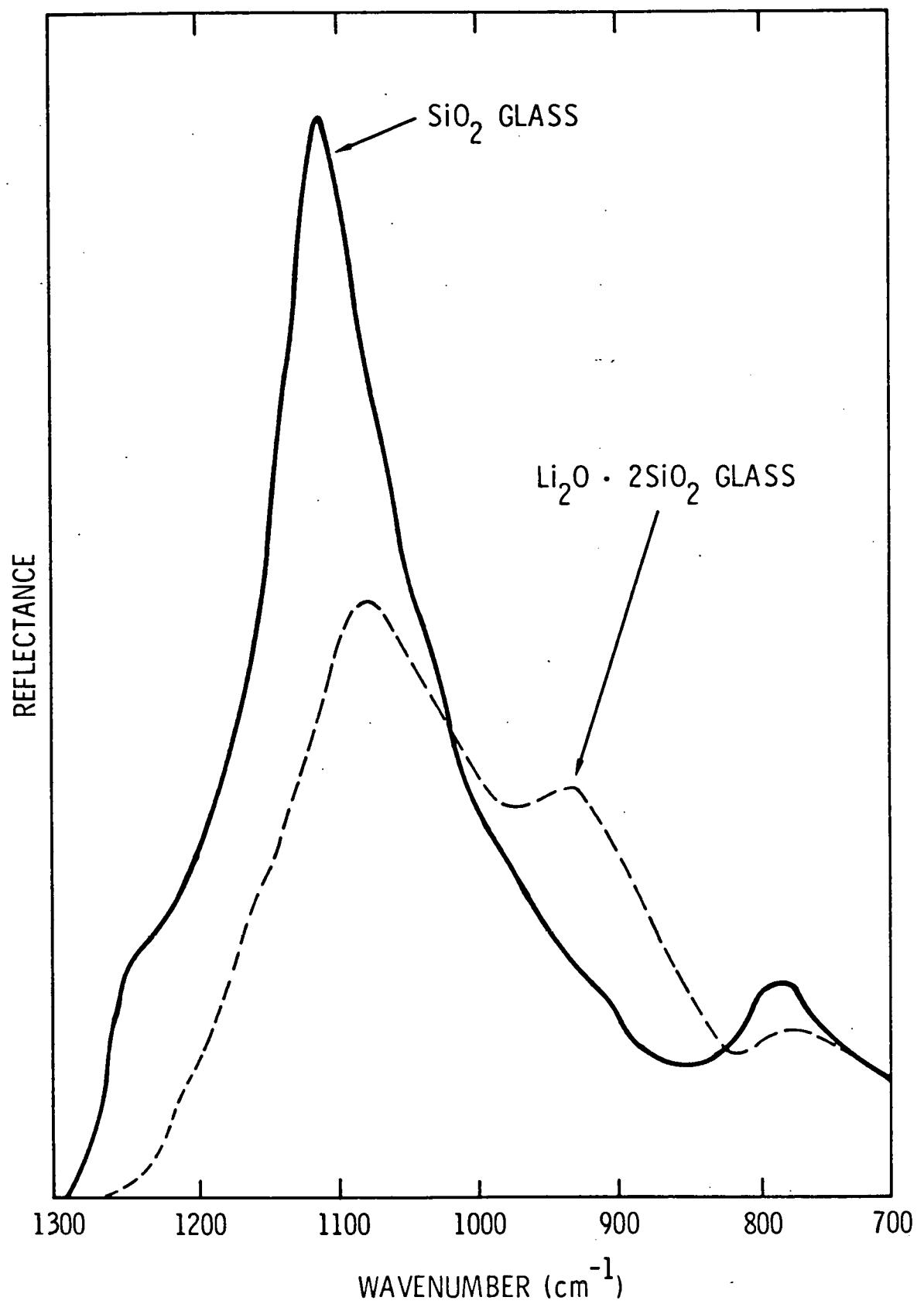
Fig. 7. Reflectance spectra for implanted ($7 \times 10^{16} 250 \text{ keV Xe}^+/\text{cm}^2$) and unimplanted 88% SiO_2 :12% K_2O glass.

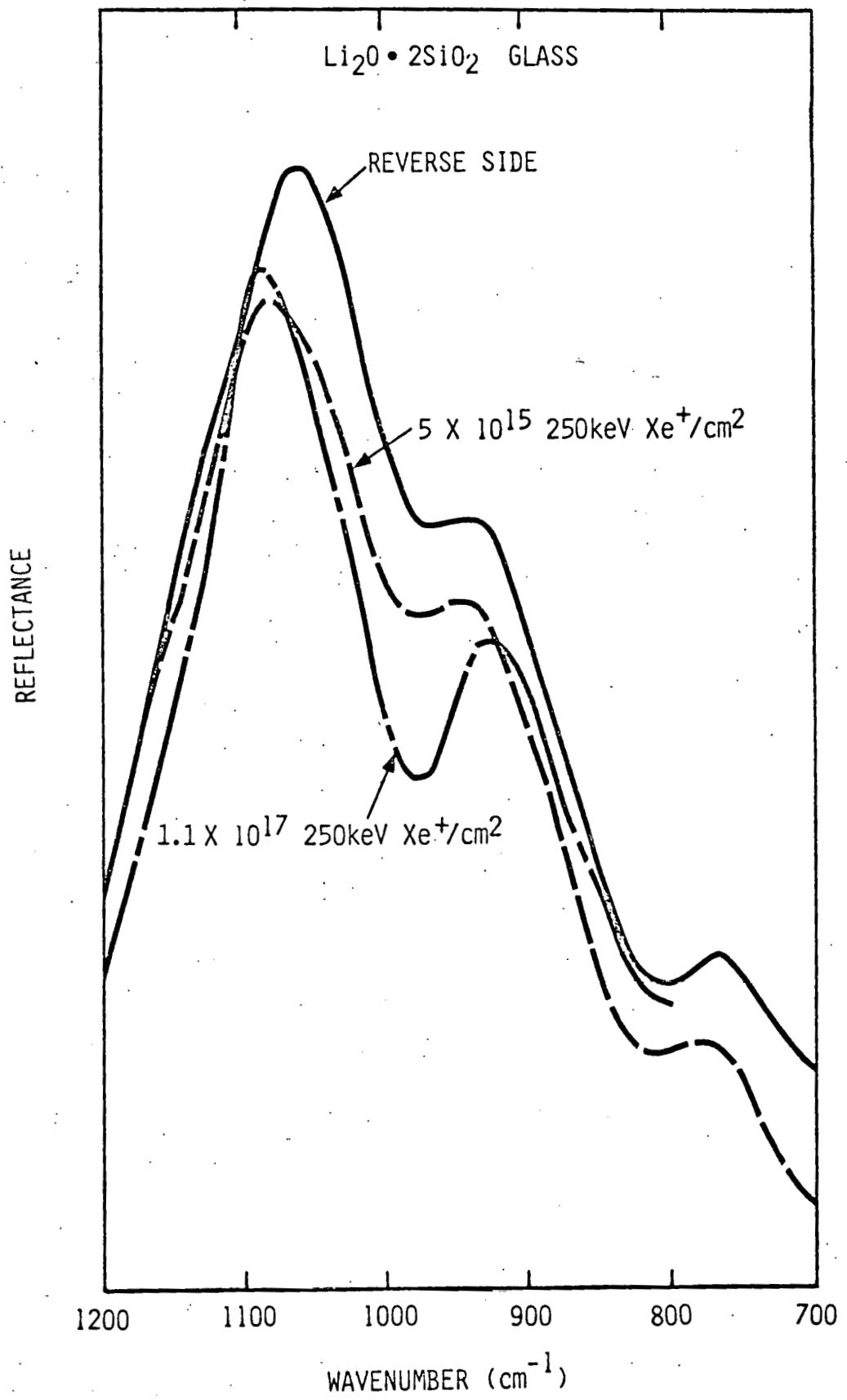
Fig. 8. Li depth distribution in CFS 7940 SiO_2 after implantation of $1 \times 10^{17} 50 \text{ keV Li/cm}^2$ at room temperature and after annealing at 600°C .

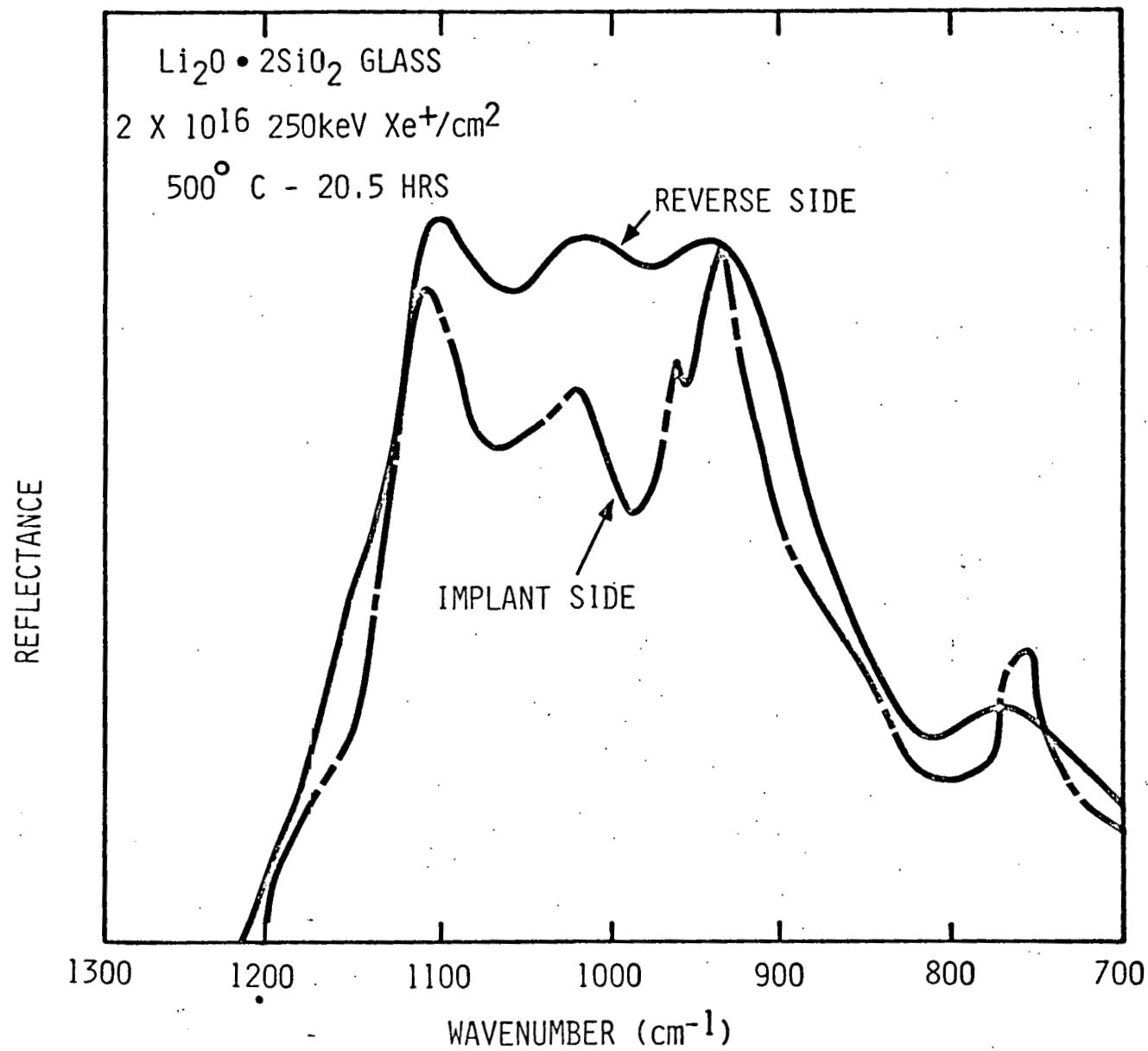
Fig. 9. Change in the Li profile in SiO_2 implanted with $1 \times 10^{17} 50 \text{ keV Li/cm}^2$ after anneals at 700 and 800°C .

Fig. 10. H distribution in SiO_2 implanted with $1 \times 10^{17} 50 \text{ keV Li/cm}^2$ and after annealing at 700°C .

Fig. 11. Phase diagram of the lithia-silica system showing the region of phase separation. After M. Tomazawa, Phys. Chem. Glasses 14 (1973) 112.







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