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Interaction Between Implanted Ions and Intrinsic Defects in Silica

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Abstract

High purity silica (Spectrosil) samples were implanted with Ti, Cr, Mn, Fe and Cu at doses ranging from 1.0 to 5.0×10^{15} ions/cm^2 at 160 keV and 2.6 μA/cm^2. The optical absorption extinction coefficients per ion were measured from 1.8 to 6.0 eV. In all samples there was an increase in absorption over the unimplanted sample at energies ≥ 4.6 eV. The increase in absorption at 5.1 eV and 5.7 eV is attributed to B_2(E") centers and E' centers respectively. The relative values of the extinction coefficients of these bands are attributed to the relative oxygen activities of the TMI relative to the SiO_2 host substrate.

Introduction

Ion implantation in silica glass has been shown to change defect concentrations in the implanted material. Two of the commonly generated defects, the E' center (a positively charged oxygen vacancy)[1,2,3] and the E" or B_2 centers[1,2,3] (a neutral oxygen vacancy) are intrinsic defects in the silica created by ionization events and atomic displacements. Because the optical absorption, index of refraction and density of the implanted layer can depend on the concentration of these intrinsic defects, an understanding of the interaction between the implanted species and the defects is of fundamental importance.

Antonini and co-workers[4,5] have reported optical studies of the effects of MeV electron, proton and heavy ion radiation on vitreous silica. All particle radiations were observed to introduce defects, whose saturation level depended on the mass and energy of the incident particle. Arnold,[6] reported optical studies of the production of B_2 centers in silica implanted with H^+, He^+, B^+, O^+, A^+, Kr^+ and Xe^+ ions. He observed that the concentration of the B_2 defect increased with increasing mass of the implanted specie and dose rate.

A series of papers[3,7,8,9,10] have reported changes in optical and magnetic properties of silica with transition metal ion (TMI) implantation. The purpose of this research was to investigate the interaction of intrinsic defects with the TMI's.

Experimental

High purity silica (Spectrosil A) substrates 2.0 cm in diameter and 0.1 cm thick were implanted with singly charged transition metal ions at an energy of 160 keV and a flux of ~2.6μA/cm^2 as previously reported[3,8,9]. Table 1 shows nominal implantation dose for each ion implanted.

Table 1

Ion Specie	Nominal Dose
Ti	1.0×10^{15} ions/cm^2, 3.0×10^{15} ions/cm^2
Cr	5.0×10^{15} ions/cm^2
Mn	5.0×10^{15} ions/cm^2
Fe	5.0×10^{15} ions/cm^2
Cu	3×10^{15} ions/cm^2, 5×10^{15} ions/cm^2

Ion backscattering techniques[3,8,9] with 2 MeV He^+ ions were used to measure the depth profile for all ion species and doses. The implantations and backscattering measurements were carried out at Oak Ridge National Laboratory.

Optical measurements were made at room temperatures in the 1.8 to 6.2 eV range using a Cary 14 dual beam spectrometer. All samples were measured using an unimplanted Spectrosil A sample in the reference beam to compensate reflection and intrinsic bulk optical losses. Differences in thickness of the unimplanted samples and reference samples was ≤ 1%. All absorption measurements reported are differences between implanted and unimplanted silica samples at identical thickness. The spectra are shown as a function of absorption per implanted ion, i.e. extinction coefficient (EC) with the total number of implanted ions measured by the RBS technique.

The absorption spectra were measured at five different positions on each sample. The scatter in extinction coefficient for the five different positions was always greater than the uncertainty in intensity for one position. The scatter in extinction coefficient due to these five different positions is less than ± 10%.

Results

A Gaussian distribution of TMI as a function of distance from the surface was observed for all ion species from the Rutherford backscattering measurements (RBS). The dose as measured by RBS was always ≥ 90% of the nominal dose. All species demonstrated a ~0.14μm depth of maximum concentration with full width at half maximum of ~0.14μm.

As these absorptions were measured relative to an unimplanted sample the absorptions observed are due to the implanted region. Fig. 1 shows the extinction coefficient as a function of the energy of absorption for Cu, Mn, Fe and Cr implanted with a nominal dose of 5.0×10^{15} ion/cm^2. For the Cu and Mn implanta-tions, two bands centered at ~5.1 eV and ~5.7 eV are resolved. For the Fe and Cr implantations an absorption band is resolved at ~5.1 eV. For energies of absorption greater than this peak, the EC increases with the Cr implantation showing the largest increase.

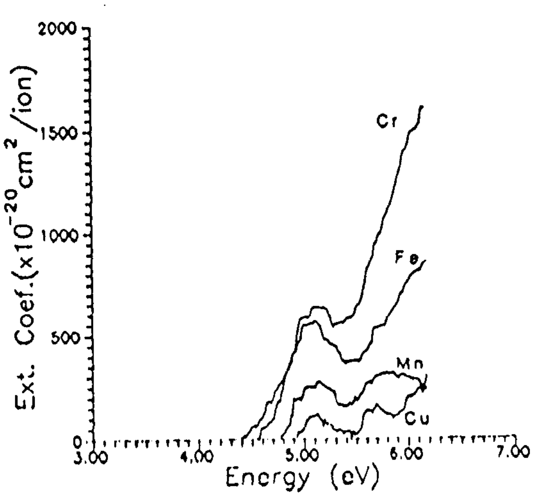

Fig.1. Optical absorption as a function of energy for Cr, Fe, Mn and Cu implanted samples with a nominal dose of 5.0×10^{15} ions/cm^2

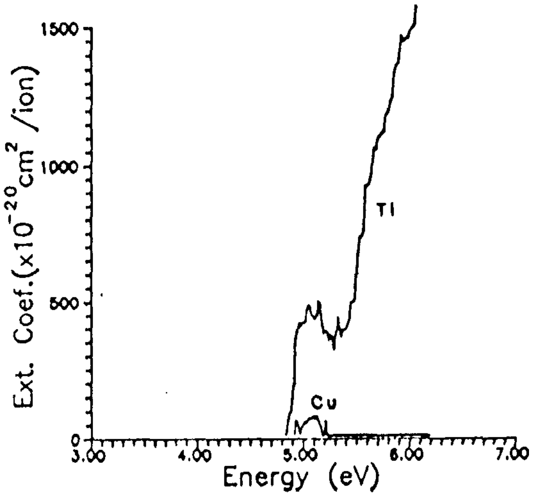

Fig.2. Optical absorption as a function of energy for Cu and Ti implanted samples with a dose of 3.0×10^{15} ions/cm^2

For the 5.1 and 5.8 eV absorption peaks, the EC displays the relative order of Cu<Mn<Fe<Cr. Between 5.7 and 6 eV the first derivative, dEC/dE, where E is the photon energy, shows a positive slope for the Cr and Fe implanted samples. This positive slope indicates absorption due to bands with peaks at energies above 6.0 eV.

Previous research has indicated that at a given dose rate and energy the B_2 center (~5.1 eV) concentration increases with increasing mass of implanted specie. We compared the lightest implanted ions, Ti, with the heaviest, Cu, at a dose of 3.0 x 10^{15} ions/cm^2 as shown in Figure 2. This dose was chosen because it was the lowest dose for Cu for which an absorption was observed. At this dose the Cu implanted sample shows only a very small absorption at 5.1 eV. There is no absorption detected at 5.7 eV for Cu implantation. The Ti implanted sample displays a resolved peak at ~5.1 eV but has an increasing absorption at energies greater than the 5.1 eV peak. These two ions differing in mass by a factor of 1.36 exhibit behavior contrary to earlier reports on mass dependence of absorption.

The absorption for a lower dose of Ti (1.0 x 10^{15} ions/cm^2)is shown in Fig. 3. At the lower dose level we resolved two absorption peaks at ~5.1 eV and ~5.7 eV. Fig. 4 shows the extinction coefficient as a function of energy for Cu doses of 3.0 x 10^{15} ion/cm^2 and 5.0 x 10^{15} ions/cm^2. By increasing the dose we were able to increase the 5.7 eV absorption to a detectable and resolvable peak. Figure 4 also shows that in the ~5.1 eV region the extinction coefficient increases with dose as has been reported.

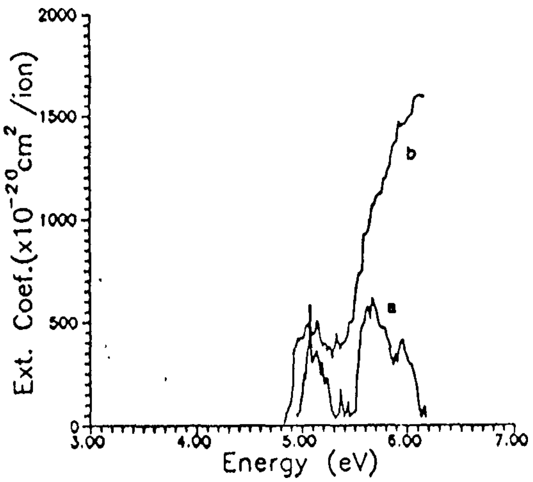

Fig.3. Optical absorption as a function of energy for Ti implanted samples with (a) 1.0x10^{15} ions/cm^2 and (b) 3.0x10^{15} ions/cm^2

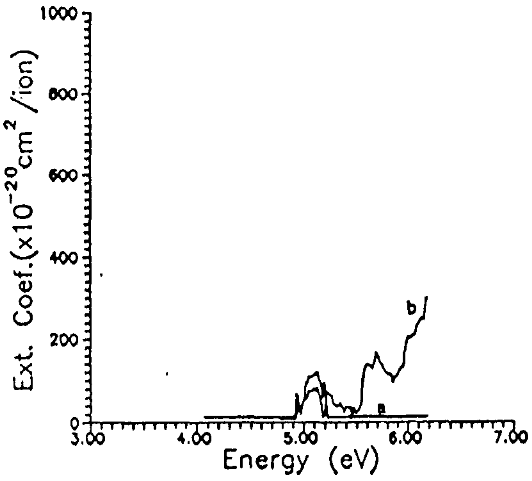

Fig.4. Optical absorption as a function of energy for Cu implanted samples with (a) 3.0x10^{15} ions/cm^2 and (b) 5.0x10^{15} ions/cm^2

Discussion

The formation of a E'' (B_2) centers with an absorption at ~ 5.1 eV due to ion implantation has been reported in the literature.[3,4,6] We attribute the ~5.1 eV absorption peak observed in our samples to the B_2 center. The peak intensity for Cu and Ti implantation increases with increasing dose.

We attribute the absorption peak at ~5.7 eV in the case of Cu and Mn with doses of 5.0x10^{15} ions/cm^2 and Ti with dose of 1.0x10^{15} ions/cm^2 to E'centers.[3,4,6] Based on the resolution of this band in the sample with Ti implantation with doses of 1.0 x 10^{15} ions/cm^2 as seen in Fig. 3, we speculate that part of the absorption in the 5.7 eV region for the Cr and Fe implanted samples with doses of 5.0 x 10^{15} ions/cm^2 and Ti with doses of 3.0 x 10^{15} ions/cm^2 is also due to E'centers. However as a peak is not resolved and dEC/dE is positive, for energies >6.0 eV, part of the absorption at this energy must also be due to centers whose absorption peak is at energies >6.0 eV. Candidates for these centers are peroxy radicals at 7.5 eV and homobonds at 7.6 eV[10,11] as discussed later.

Inspection of the results in Fig. 1 indicates that there is a significant difference in the absorption for constant dose that is dependent upon ion type. There are reports in the literature that B_2 center production increases with increasing mass for a given ion fluence.[4,5,6] We observe the opposite behavior. While ionic size of the TMI's will depend on their charge states, the free volume in silica glass, as shown by Haglund et al,[9] is greater than the volume occupied by the implanted ions at the highest dose examined. Hence we do not attribute the large differences in absorption to different ion sizes. We cannot attribute the differences observed in absorption to pure collision events as the dose rate and energy of the implanted ions are the same for all species.

We conclude that the formation of B_2 centers and E'centers is not a simple inertial radiation damage process as is the case for the lighter ions and for inert ions. These observations can be explained by differences in the thermodynamic affinity for oxygen between the implanted ions and the substrate silicon ions.

The B_2 and E'centers and homobond involve oxygen vacancies. The homobond may be considered to be a relaxed oxygen vacancy where as the B_2 center would be an unrelaxed oxygen vacancy.[11] The peroxy radical involves a local oxygen excess.[11] All of these defects are intrinsic to silica.

We next consider how these defects would arise in ion implantation processes. Two basic processes occur with implantation. The first is a series of elastic collisions that can create oxygen and silicon displacements and hence vacancies. The displaced oxygen may go to interstitial positions and form local areas of oxygen excess leaving behind vacancies, or may recombine with displaced silicons. There is sufficient kinetic energy in these collision events to result in slightly different environments in the glass. We envision relaxed and non-relaxed oxygen vacancies being formed giving rise to homobonds and B_2 centers. Coupled with these elastic collisions are ionization effects that can lead to electron and hole trapping. These ionization events give rise to charge trapping resulting in E' center formation from oxygen vacancies existing before implantation or charge trapping by oxygen vacancies created by atomic displacements. Since the momenta of the implanted ions do not differ by more than ~25%, we would anticipate that all these TMI's would produce similar concentrations of defect centers. Similar concentrations are not produced and as a result, we conclude that a second process, chemical reaction of ion specie with the glass host, plays a role in determining the defect concentration produced by implantation.

The competition of implanted ions with host silicon ions for oxygen is determined by thermodynamics after the kinetic processes are completed. We thus seek to rationalize the defect concentrations upon the basis of relative effectiveness of each implantated ion competing with host silicon ions for host oxygen ions. The related reactions for which data are available are:

$$\mathrm{TMI}^0 + O_2 = \text{TMI Oxide} \qquad (1)$$

$$Si + O_2 = SiO_2 \qquad (2)$$

The thermodynamic data for reactions 1 and 2 are tabulated in Table 2 for the formation of the most reduced and most oxidized form of the ion. These data indicate that in a competition between the implanted ion and the host silicon for oxygen the titanium ion will always prevail. The order of effectiveness in the competition is: Ti>Mn>Fe>Cr>Cu based upon the most oxidized form or: Ti>Mn>Cr>Fe>Cu based upon the more reduced oxide. In either case the order is similar to that observed for the concentration of the oxygen related defects discussed above. We thus conclude that the defect generation process involves kinetic processes followed by thermodynamic processes. Consideration of both processes permits prediction of the relative concentration of defects generated in ion implantation of the TMI's which we have examined.

Table 2

Gibbs Free Energy of Formation @ 298 K (Kcal/mole) (per mole oxygen)[12]

Reduced Oxide	G*	Oxidized Oxide	G*
a-SiO_2	-189.9		
TiO	-233.8	TiO_2	-212.4
MnO	-173.5	Fe_2O_3	-118.3
Cr_2O_3	-168.8	MnO_2	-111.3
FeO	-117.3	CrO_3	-80.6
Cu_2O	-35.5	CuO	-61.7

* Note these values are for the consumption of one mole of oxygen.

Additional evidence for this interpretation comes from results by Weeks and co-workers[4,10] in Cu, Cr, and Ti implanted glasses. They observed that Cu implanted glasses showed small homobond formation while the Cr implantations and the Ti implantations exhibit large homobond formation. Displaced oxygens which result in the creation of homobonds can also be attached to the Cr and Ti to form oxide precipitates in the glass host. In the case of Cu the homobond and oxygen vacancy defects have the lowest concentrations. One possible reason for this behavior is that the Cu forms metallic colloids as it does not compete well for the oxygen ions.[13]

Conclusions

1. The concentrations of E' and B_2 (E") and other oxygen related centers are a function of the oxygen activities of implanted transition metal ions.
2. The effect of mass of the implanted ions in producing B_2 (E") centers is not observed for TMI implantations.

Acknowledgements

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