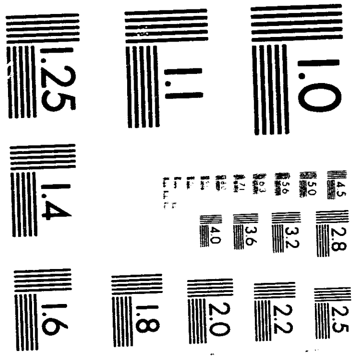
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Conf-931108--44

To be submitted to 1993 Fall MRS Meeting, Boston, Mass.

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Prepared by the
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

December 1993

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CHARACTERIZATION OF THERMALLY ANNEALED
Sb IMPLANTED FUSED SILICA

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ABSTRACT

The local environment of the polarizable ion in heavy metal oxide glasses is postulated to strongly influence the nonlinear response of these materials. We have previously observed that post-implantation thermal annealing changes the chemical properties of the implanted layer in a different fashion in Pb- and Bi- implanted SiO_2. In this paper we report the optical behavior of Sb-implanted SiO_2 as a function of annealing temperature and atmosphere. High purity fused silica substrates were implanted at room temperature to a dose of 6×10^{16} ions/cm^2, and subsequently annealed at temperatures from 500 to 1000 C in argon and oxygen atmospheres. RBS, optical absorption (1.8 to 6.2 eV), infrared reflectance (450 to 5000 cm^{-1}), and nonlinear index of refraction were measured before and after annealing. The results of these measurements indicate that annealing treatment significantly affects the local environment of the implanted Sb ions, and consequently the optical response.

INTRODUCTION

Glasses containing polarizable ions have been shown to be promising materials for all-optical waveguide switching applications.[1,2,3] In particular, an enhanced nonlinear optical response has been reported for oxide glasses containing heavy metals.[4,5] Ion implantation offers an established technique to create materials that cannot be obtained by conventional processes due to chemical and/or thermodynamical constraints. It offers concentration and depth control not possible with other techniques and is compatible with present waveguide and semiconductor processing technology. In this paper we report the effects of thermal annealing in argon and oxygen atmospheres on the linear and nonlinear optical properties of Sb implanted high purity SiO_2.

EXPERIMENTAL

Optical quality Spectrosil glasses were implanted on one side at room temperature with Sb^{++} for a nominal dose (integrated current density) of 6×10^{16} ions/cm^2 at an energy of 160 KeV and a current density of 5 $\mu A/cm^2$. After implantation the depth distributions and retained amounts of Sb in the samples were determined by Rutherford backscattering (RBS) using 2.3 MeV He^{++} ions at a scattering angle of 160°. Absolute amounts were determined by comparison with a random scattering spectrum from a Si standard. The total dose calculated from backscattering measurements was typically 90% of the nominal dose indicating minimal sample charging. The glasses were then sectioned and placed in argon and oxygen atmospheres for one hour at temperatures of 500 to 1000 C. RBS measurements were performed on each sample after annealing.

Optical measurements were made from 1.8 to 6.2 eV using a Cary 14 dual beam spectrometer with a dedicated PC. Three different positions on each sample were measured with the scatter always being less than ±10%. All measurements were made at room temperature using an unimplanted sample in the reference beam, and are therefore reported as differences between implanted and unimplanted glasses. Mid infrared measurements were made with a Bomem MB100 Fourier-transform spectrometer having a range of 450 to 5000 cm^{-1} at an angle of incidence of 15°. All reflectance spectra were referenced to a gold mirror to provide a consistent normalization.

The nonlinear index of refraction, n_2, was measured by the Z-scan technique[6] using a Lexel Model 480 mode-locked Ti:Sapphire laser. The laser operated at a wavelength of 760 nm with a pulse-width of 130 fs and a repetition rate of 100 MHz. Irradiance at the beam waist was typically 8×10^9 W/cm^2. Open aperture Z-scans were also measured in order to correct for nonlinear absorption, however this was found to be negligible.

RESULTS

The nominal dose for both sets of samples was 6.0×10^{16} $ions/cm^2$. Doses as determined by RBS measurements for the as-implanted samples were 5.43×10^{16} and 5.24×10^{16} $ions/cm^2$ for the argon and oxygen annealed samples respectively. The as-implanted profiles were Gaussian in shape with a peak approximately 100 nm below the surface and a width (FWHM) of approximately 85 nm.

Figure 1 shows the profiles for the samples which were annealed in oxygen atmosphere. For clarity, only the as-implanted, 700, 800 and 1000 C profiles are shown. As the annealing temperature increases from 500 to 700 C, the RBS profile remains symmetric, but the peak shifts from 100 nm to approximately 75 nm. There is little or no change in width and height. The sample annealed at 800 C shows a markedly assymmetric profile with a peak near 50 nm and a

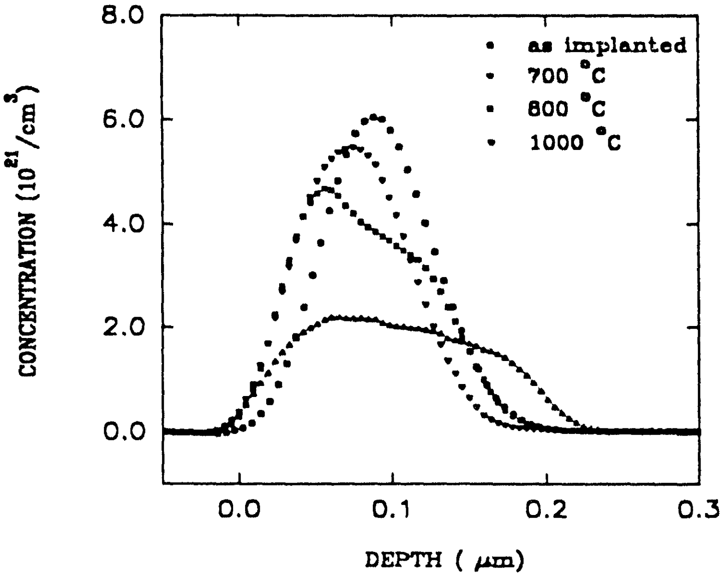

Figure 1: Rutherford backscattering profiles for Sb implanted SiO_2 glass as-implanted and annealed in oxygen at 700, 800 and 1000 C.

shoulder at about 100 nm. Samples treated at 900 C and 1000 C have RBS profiles which are no longer Gaussian in appearance and have broadened to 130 nm and 190 nm respectively. The retained dose decreases slightly (from 5.24×10^{16} to 5.02×10^{16} ions/cm^2) as the annealing temperature is increased to 900 C, but drops to 3.51×10^{16} ions/cm^2 after treatment at 1000 C. RBS profiles for all of the samples annealed in argon atmosphere are essentially identical to the profile for the as-implanted sample . The retained doses for the argon annealed samples are unchanged within experimental error.

The optical density as a function of photon energy for the samples annealed in argon is shown in Figure 2. The as-implanted sample exhibits an almost linearly increasing absorption from 1.8 to 6.2 eV. For samples annealed from 500 C to 800 C the absorption at energies above ~ 4 eV increases with annealing temperature over the as implanted sample. The samples annealed above 800 C show the formation of a broad peak at ~ 4.5 eV with a decrease in absorption for energies above 4.5 eV compared to the samples annealed at lower temperatures.

The optical density as a function of photon energy for the samples annealed in oxygen is shown in Figure 3. For annealing temperatures below 700 C there are virtually no changes. For 700 C and above the optical density throughout the spectra decreases with annealing temperature showing the largest percent change for the sample annealed at 800 C.

Changes in the mid infrared reflectance with annealing are independent of atmosphere. The most intense feature in the reflectance spectra is the peak near 1124 cm^{-1} which is assigned to the transverse optical (TO) mode of the Si-O stretch and the higher frequency component near 1220 cm^{-1} which is assigned to the longitudinal optical (LO) mode. The peak at 1025 cm^{-1} is attributed to the stretching vibration of Si-O dangling bonds. Upon implantation, the 1124 cm^{-1} peak decreases in intensity and red shifts by 6 cm^{-1} to 1118 cm^{-1}, while the 1025 cm^{-1} peak increases in intensity. For both argon and oxygen annealed samples, the intensity of the 1025 cm^{-1} peak decreases and the intensity of the 1124 cm^{-1} peak increases with annealing temperature. Annealing has little effect on the red shift of the Si-O stretching frequency, which remains near

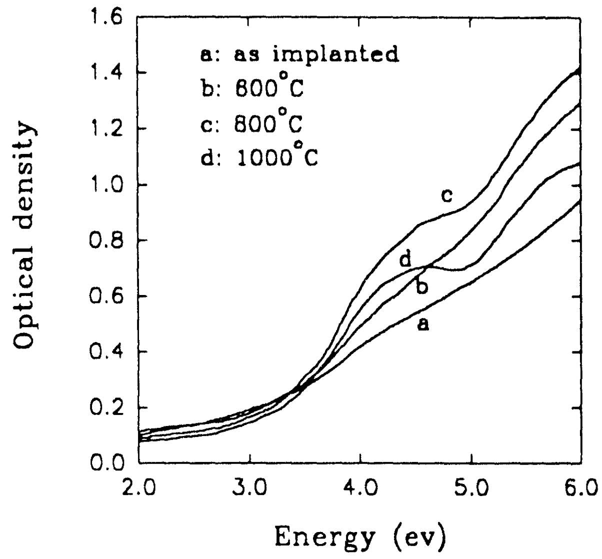

Figure 2: Optical absorption of Sb implanted SiO_2 glass annealed in argon at 600, 800 and 1000 C.

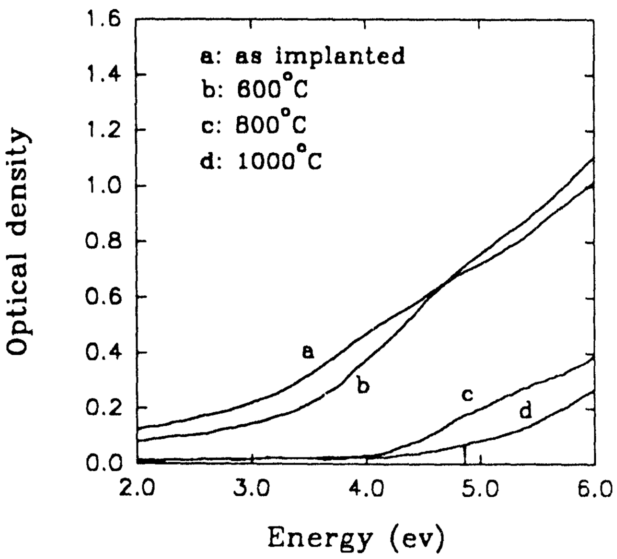

Figure 3: Optical absorption of Sb implanted SiO_2 glass annealed in oxygen at 600, 800 and 1000 C.

1118 cm^{-1} . The appearance of a weak peak near 950 cm^{-1} was observed in the spectra of the annealed glasses.

Figure 4 shows the nonlinear index of refraction versus annealing temperature for Sb implanted fused silica annealed in both argon and oxygen atmospheres. The nonlinear index of samples annealed in argon shows no change, within experimental error, from the value of 7.36 x 10^{-8} esu measured for the as-implanted glass. The sample annealed in oxygen at 500 and 600C also shows no change in n_2 from the as-implanted value. Above 600 C, however, n_2 decreases with annealing temperature. At 800 C, n_2 has decreased to 0.3 x 10^{-8} esu , and for the samples annealed at 900 C and 1000 C has dropped below the detection limits of our apparatus.

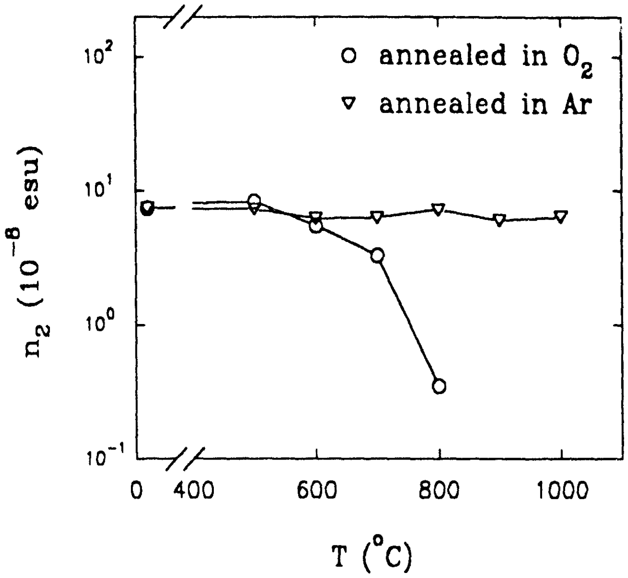

Figure 4: Nonlinear index of refraction as a function of annealing temperature and atmosphere.

DISCUSSION

Rutherford backscattering measurements on implanted glasses annealed in an argon atmosphere show no change in antimony distribution with annealing temperature up to 1000 C. For the samples annealed in oxygen at temperatures of 500 to 700 C, the width of the distribution remains essentially constant, but the shift of the peak from 100 to 75 nm indicates some migration of the Sb toward the surface. At temperatures of 800 C and above in oxygen, the Sb moves deeper into the sample as indicated by the broadening of the RBS profile.

There are two sources of optical absorption in ion implanted silica . The first source of absorption is defects created during ion implantation. The second is the presence of the implanted ions and their interaction with the host substrate. Ion implantation is known to introduce defects such as the B_2, E'', peroxy and homobond centers in silica which have broad absorption bands at 5, 5.8, 7.5 and 7.6 eV respectively.[8,9] Part of the absorption in the ultraviolet can be attributed to these defect centers.

The second source of absorption is the interaction of the implanted ions with the host substrate. We attribute most of the absorption in the as implanted sample to the formation of nanosize Sb metal particles. For particles with diameters less than $\lambda/20$, where λ is the wavelength of the incident radiation, the absorption is reasonably described by Mie scattering theory in the electric dipole approximation,[10,11,12] and is given by

$$\alpha = \frac{18\pi p n_d^3}{\lambda} \left(\frac{\varepsilon_2}{[\varepsilon_1 + 2n_d^2]^2 + \varepsilon_2^2} \right)$$

where α is the absorption coefficient, $\varepsilon(\lambda) = \varepsilon_1 + i\varepsilon_2$ is the dielectric constant of the metal, p is the volume fraction of the metal particles and n_d is the index of refraction of the dielectric host. The absorption is expected to exhibit a peak at the surface plasmon resonance frequency for which the condition $\varepsilon_1 + 2n_d^2 = 0$ is met. Because of the nature of the wavelength dependence of the dielectric function of Sb, Pb, Bi and Sn, nanosize metal particles of these ions are not expected to give rise to sharp surface plasmon resonance features as observed for the noble metals.[13] However nanosize metal particles of Sb formed in a dielectric are expected to exhibit a $1/\lambda$ dependence as observed in our samples. With annealing in argon we suggest these particles grow in size resulting in the increase in absorption observed. For the samples annealed at 900 and 1000 C we attribute the broad peak seen at ~ 4.5 eV to the formation of particles with diameter larger than $\lambda/20$ (~ 15 nm in radius) which requires additional terms beyond the dipole term in the Mie expansion to describe the absorption.[11,12]

With annealing in oxygen the absorption is unchanged within error for temperatures up to 700 C suggesting that under these annealing conditions, at most only small changes in the particle size occur. For 800 C and 900 C annealing treatments the absorption decreases dramatically without the appreciable loss of ions as seen from RBS measurements. We attribute the changes observed with annealing in oxygen at these higher annealing temperatures to formation of a Sb-O-silicate phase. This type of behavior has been reported for Pb implanted silica when annealed in air.[14] For annealing above 900 C the absorption decrease is probably due to the loss of Sb from the sample as observed from the RBS measurements.

The changes upon implantation in the Si-O stretching region in the infrared reflectance spectra are attributed to the rupture of Si-O-Si linkages and the concomitant formation of dangling bonds. With annealing in either oxygen or argon atmosphere, the 1025 cm^{-1} peak progressively decreases in intensity while the 1124 cm^{-1} peak increases. This trend is attributed to the reforming of Si-O linkages and therefore a loss of Si-O dangling bonds. Similar behavior has been observed in Pb and Bi implanted SiO_2 annealed at similar temperatures.[14,15,16] Healing of implantation damage by thermal annealing appears to be independent of annealing atmosphere.

We attribute the large n_2 response to the presence of nanosize metal particles in the as-implanted sample. For the oxygen annealed samples n_2 begins to decrease after the annealing treatment at 700 C, the same temperature at which significant changes occur in the optical absorption. If as suggested from the discussion of the optical measurements, the small Sb particles are dissolving and forming a Sb-O-silicate phase, a concurrent drop in the value of n_2 would be expected as the mechanism for the nonlinear response changes. Reports in the literature[1,17] suggest that the nonlinear response for nanosize metal particles should be larger than that for Sb in an antimony silicate phase. For the samples annealed in argon there are no apparent changes in the nonlinear index, which is consistent with the hypothesis that annealing in argon atmosphere results only in a change in size of the Sb particles.

CONCLUSION

The experimental results presented here demonstrate that the annealing treatment, in particular the annealing atmosphere, significantly affects the linear and nonlinear optical properties of Sb implanted SiO_2. These results suggest that upon inplantation, the Sb forms nanosize metal particles which change in size upon annealing in an argon atmosphere. Annealing in an oxygen atmosphere at temperatures above 700 C, on the other hand, results in the formation of an antimony silicate phase which reduces the nonlinear optical response.

ACKNOWLEDGEMENTS

The authors acknowledge the support of the U.S. Army Research Office under grant DAAH04-93-G-0123, NASA through Grant NAGW-2925, and of the Division of Materials Science, U.S. Department of Energy,under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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