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LASER INDUCED DIFFUSION OF ION-IMPLANTED BISMUTH IN FUSED SILICA

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ABSTRACT

The near surface regions of optical grade fused silica discs (Spectrosil A) were modified by implantation with bismuth ions at 160 and 320 keV and at room temperature. The glasses implanted with a nominal dose of $6x10^{16}$ Bi^{2+} ions/cm^2 at ~5 $\mu A/cm^2$ were subsequently annealed with a 5 eV KrF pulsed excimer laser and by a furnace in oxygen atmosphere. Rutherford backscattering and optical absorption were measured before and after the anneals. Backscattering profiles after laser anneal showed shifts of the profiles toward the surface with decrease in retained dose. We attribute the diffusion of bismuth to Soret effect. Profiles of furnace annealed samples showed that the diffusion was both toward and away from the surface.

INTRODUCTION

Silicon dioxide is one of the most abundant minerals on Earth. Low thermal expansion coefficient, high temperature stability, relative chemical inertness, and a simple chemical composition have been the bases for a variety of high purity silica glass products.[1] For applications such as optical switching and photonic devices, a large nonlinear index of refraction, n_2, and small two-photon absorption coefficients are needed.[2, 3] Both two-photon absorption and third order susceptibility, χ^3, of silica glass is small over a wide range of wavelengths.[4] By implanting polarizable ions and subsequently forming a composite in a thin layer in the near surface regions of a substrate material, the third order susceptibility, χ^3, in oxide glasses may be increased.[5, 6, 7] Bismuth silicate glasses and crystals are known to have interesting optical properties that may be useful for photonic devices.[8] Due to the high polarizability of the bismuth ion, it has been proposed that glasses containing bismuth ions may be candidate materials for nonlinear optical devices.[8, 9]

An adequate optical switching can be realized by producing small (≤20 nm) metal colloidal particles in the near surface regions of the fused silica. Recently, fused silica implanted with Cu[10], Au[11], Bi and Sb[12] have shown adequate third order susceptibility (~10^{-10} cm^2/W). The increase in the $\chi^{(3)}$ is due to classical and quantum confinement effects.[13]

Irradiation of material with laser photons whose energy is greater than the band-gap of the material results in absorption by surface layers and can cause melting. On the other hand, effects of laser radiation on wide band gap material whose band gap is larger than the energy of the laser light results in laser damage due to absorption of energy by impurities, defect sites, or multi-photon process.[14] Impurities introduced by implantation changes the optical properties of silica and silicate glasses.[15, 16, 17, 18, 19] These impurities in the form of colloidal particles will absorb photons whose energy is less than the band gap energy of silica. The purpose of this paper is to report the effects of laser and furnace annealing on the distribution of bismuth in bismuth implanted fused silica samples

EXPERIMENTAL PROCEDURE

Optical grade high purity type III[1] fused silica discs , 2 cm in diameter and 1 mm in thickness, were implanted with Bi^{2+} ions using an implantation accelerator (Varian-Extrion Model 200-1000) in a vacuum of $\sim 10^{-7}$ torr. Before mounting for implantation, samples were cleaned with isopropyl alcohol. A nominal dose of 6×10^{16} Bi^{2+} ions/cm^2 at 160 and 320 keV at 25 °C was implanted in several discs. The average beam current during implantation was ~ 5 μA/cm^2.

Samples implanted at 160 and 320 keV were irradiated with an unfocused 5 eV (248 nm) KrF pulsed excimer laser (Lambda-Physik EMG-160T-MSC) for 1, 100 and 200 pulses at a pulse power of 150 mJ/pulse/cm^2, at a repetition rate of 10 Hz, and with an average pulse duration of ~ 20 ns. The size of the unfocused beam was approximately 6×20 mm. The laser power density was monitored by a calorimeter before and after irradiation. The experiments were carried out in air at room temperature. Samples implanted at 320 keV were furnace annealed in oxygen for 60 minutes at 600, 800 and 1000 °C. Each sample was annealed only once at each annealing condition.

After implantation and subsequent anneals, depth distributions of the implanted ions and retained doses were measured by Rutherford backscattering (RBS) using 2.3 Mev He^{2+} ions as probe at a scattering angle of 160° using a silicon surface barrier detector. The sample was tilted by 3° in positive direction with respect to the beam line to improve depth resolution. By converting the number of backscattered particles into a concentration scale, concentration profiles were directly calculated from the RBS spectra.[20] The energy scale was converted into a depth scale using surface energy approximation. The average error in calculated retained dose from the concentration spectra was ±6 %.

RESULTS

The depth distribution of as implanted bismuth ions measured by backscattering technique had an approximate Gaussian distribution[21] with a projected range of ~60 nm and a full width at half maxima (FWHM) of ~80 nm for samples implanted at 160 keV. When the samples were implanted at 320 keV, the projected range was ~110 nm with FWHM of ~100 nm. Figures 1 and 2 show the distribution of bismuth before and after laser annealing in air in samples implanted at 160 and 320 keV, respectively. The concentration profiles show one-way diffusion of bismuth toward the surface after laser anneals. The retained dose after irradiation with 200 pulses decreased by >70 % for the sample implanted at 160 keV. For the sample implanted at 320 keV, there was no change in the retained dose after irradiation with ≤200 pulses. The maximum of the distribution shifted toward the surface, after 200 pulses, by ~35 nm, and the FWHM increased to ~130 nm. Figure 3 shows the distribution of bismuth before and after conventional isochronal annealing. There was no significant diffusion of bismuth after annealing at 600 °C for 60 minutes. For anneals at temperatures ≥800 °C, the concentration profiles show two-way diffusion of bismuth toward the surface and away from the surface. No change in retained dose, within errors of measurements, was observed for annealings at temperatures ≤800 °C. Following 1000 °C annealing, the retained dose of bismuth in the sample decreased by >70 %

DISCUSSION

The depth profiles of excimer laser annealed samples are significantly different from those of furnace annealed samples. The depth profiles after furnace annealing show two-way diffusion, toward the surface and away from the surface of the sample as shown in Figure 3. As a result of the two-way diffusion, the width of the distribution broadens after thermal annealing. On the other hand, the depth profiles after laser annealing consistently show one-way diffusion toward the surface, while the width of distribution decreases. Shimizu et al.[15] observed similar results from Si^+ implanted fused silica after XeCl excimer laser (308 nm) and dye laser (575 nm) anneals. They attributed the changes after laser anneals to the heating induced by optical absorption of the implanted silicon. In a previous report[19], we estimated the temperatures, which should be upper bounds because of the assumptions that were made, in the implanted regions at different laser power densities. At a power density of 150 mJ/pulse/cm^2, the estimated temperature was ~4700 K. Miotello and Kelly[22] estimated the temperatures in the silicon implanted fused silica during laser anneals to be between 2500 and 4000 K. Thus our temperature estimation is comparable with their results.

Diffusion occurs as a result of concentration gradient (ordinary diffusion) and temperature gradient (Soret effect[23]). During thermal annealing, the whole sample reaches a homogeneous and constant temperature in a relatively long time. High purity fused silica is transparent to the 5 eV light[1] and two-photon absorption coefficient of fused silica is small[2]. During pulsed laser annealing with nanosecond scale pulse duration time, only those regions of a sample which absorb 5 eV photons are heated in an extremely short time. The fast temperature rise in the implanted region of the sample during laser annealing will induce a large temperature gradient between the implanted layer and the surroundings.[14] This large temperature gradient will lead to thermodiffusion, Soret effect, of bismuth. Shimizu et al.[15] and Miotello and Kelly[22] attributed the diffusion of implanted silicon toward the surface after laser annealing to this effect. Figures 1 and 2 show diffusion of bismuth toward the surface with laser irradiation. Especially, Figure 2 shows of bismuth toward the surface with no change in the retained dose, which is a clear evidence of the Soret effect. Based on the results from our experiment and the reports[15, 22], we attribute the diffusion of bismuth toward the surface after laser annealing to the Soret effect as well as to ordinary diffusion.

Removal of surface layers by ablation during irradiation with high intensity laser photons can contribute to the removal of bismuth from the samples. The reported ablation threshold of a fused silica is about 10 J/pulse/cm^2 which is about three orders of magnitude higher than the maximum power density involved in this experiment.[24] Therefore, we assume that laser ablation of the surface is negligible at the power densities used in this experiment.

We have proposed that the irradiation of bismuth implanted glass with 5 eV KrF laser photons results in photo-thermal heating.[19] Assuming that the absorption of 5 eV photons is all converted to thermal energy, irradiation of the sample with 5 eV photons will result in heating the implanted region, and evaporation of bismuth from the surface of the sample as a result of diffusion may occur. Assuming one-dimensional diffusion, the flux J is defined as follows[25]:

$$J = -D\left[\frac{dC}{dx} + S_T C \frac{dT}{dx}\right] \quad (4\text{-}2)$$

where, D is diffusion coefficient of bismuth, C is concentration of implanted bismuth, S_T is Soret coefficient, x is direction normal to the surface, and T is temperature. The thermal gradient in equation 4-2 is proportional to optical absorption cross section (optical density divided by implanted dose).[15] For thermal annealing, the second term in equation 4-2 vanishes once the system reaches steady state. However, for laser annealing, the second term plays an important role since the thermal gradient is very high as shown by Miotello and Kelly.[22].

For thermal gradient induced diffusion, it is known that the direction of diffusion depends on the sign of the Sorret coefficient.[23, 26] Guy and Schott[26] reported that positive values of the coefficient induces diffusion of radioactive impurities in borosilicate glass toward the surface of the glass and negative values of the coefficient induces diffusion toward the bulk of the glass. Based on this report, we speculate that the Sorret coefficient of bismuth in the samples is positive. However, the value of the Soret coefficient of bismuth in fused silica is not known. Without knowing the value of the Soret coefficient, quantitative analysis of the flux is not feasible.

CONCLUSIONS

The difference in depth profiles between thermal and laser annealed samples is due to thermal gradients produced by laser annealing and subsequent diffusion. The thermal gradient is a result of the optical absorption of 5 eV excimer laser photons by bismuth particles. The diffusion of bismuth in the laser annealed samples is attributed to the Soret effect as well as to ordinary diffusion.

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FIGURE CAPTIONS

Figure 1. RBS spectra of fused silica samples implanted with 6×10^{16} Bi^{2+} ions/cm^2 at 160 keV and room temperature before and after irradiation with 5 eV KrF excimer laser for 1, 100 and 200 pulses in air. The power density of the laser was 150 mJ/p/cm^2 at 10 Hz.

Figure 2. RBS spectra of fused silica samples implanted with 6×10^{16} Bi^{2+} ions/cm^2 at 320 keV and room temperature before and after irradiation with 5 eV KrF excimer laser for 1, 100 and 200 pulses in air. The power density of the laser was 150 mJ/p/cm^2 at 10 Hz.

Figure 3. Bismuth depth profiles in fused silica implanted at 320 keV and room temperature before and after annealing at 600, 800 and 1000 °C in oxygen for 60 minutes.

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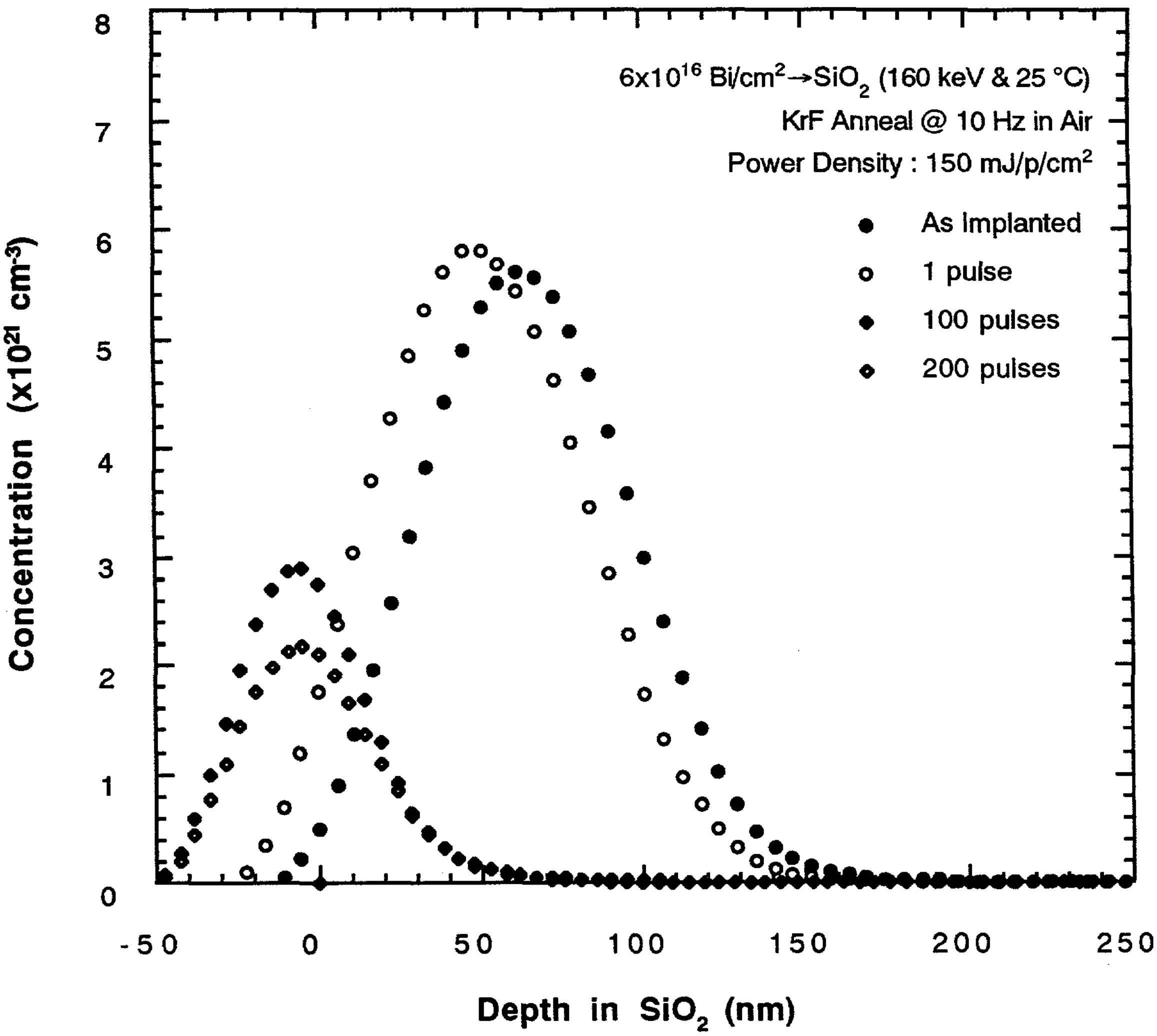

$6x10^{16}$ Bi/cm^2→SiO_2 (160 keV & 25 °C)
KrF Anneal @ 10 Hz in Air
Power Density : 150 mJ/p/cm^2
As Implanted
1 pulse
100 pulses
200 pulses
Concentration ($x10^{21}$ cm^{-3})
Depth in SiO_2 (nm)
0
1
2
3
4
5
6
7
8
-50
0
50
100
150
200
250

Figure 1

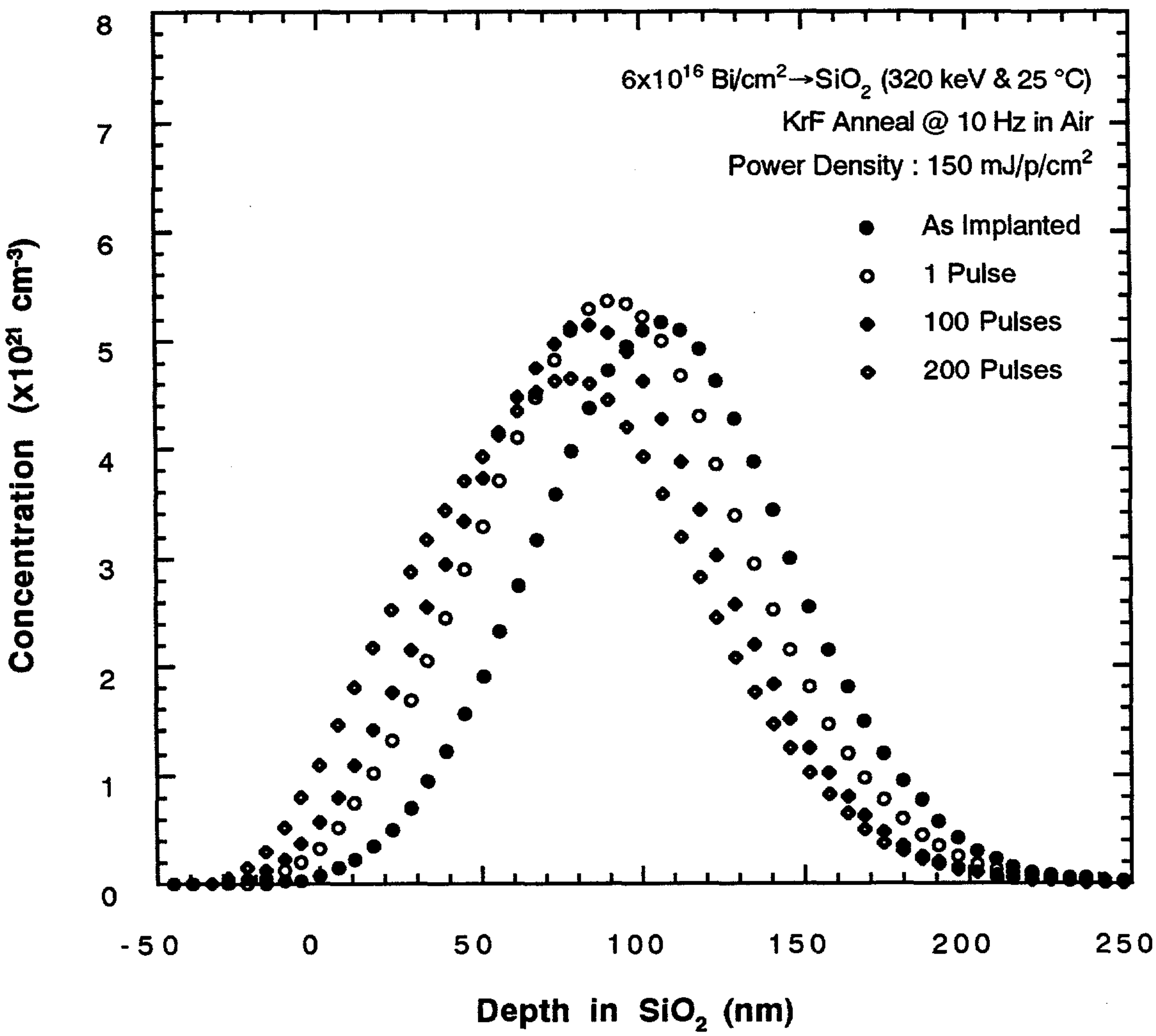
6x10^16 Bi/cm^2→SiO2 (320 keV & 25 °C)
KrF Anneal @ 10 Hz in Air
Power Density : 150 mJ/p/cm^2
As Implanted
1 Pulse
100 Pulses
200 Pulses
Concentration (x10^21 cm^-3)
Depth in SiO2 (nm)
0
1
2
3
4
5
6
7
8
-50
0
50
100
150
200
250

Figure 2

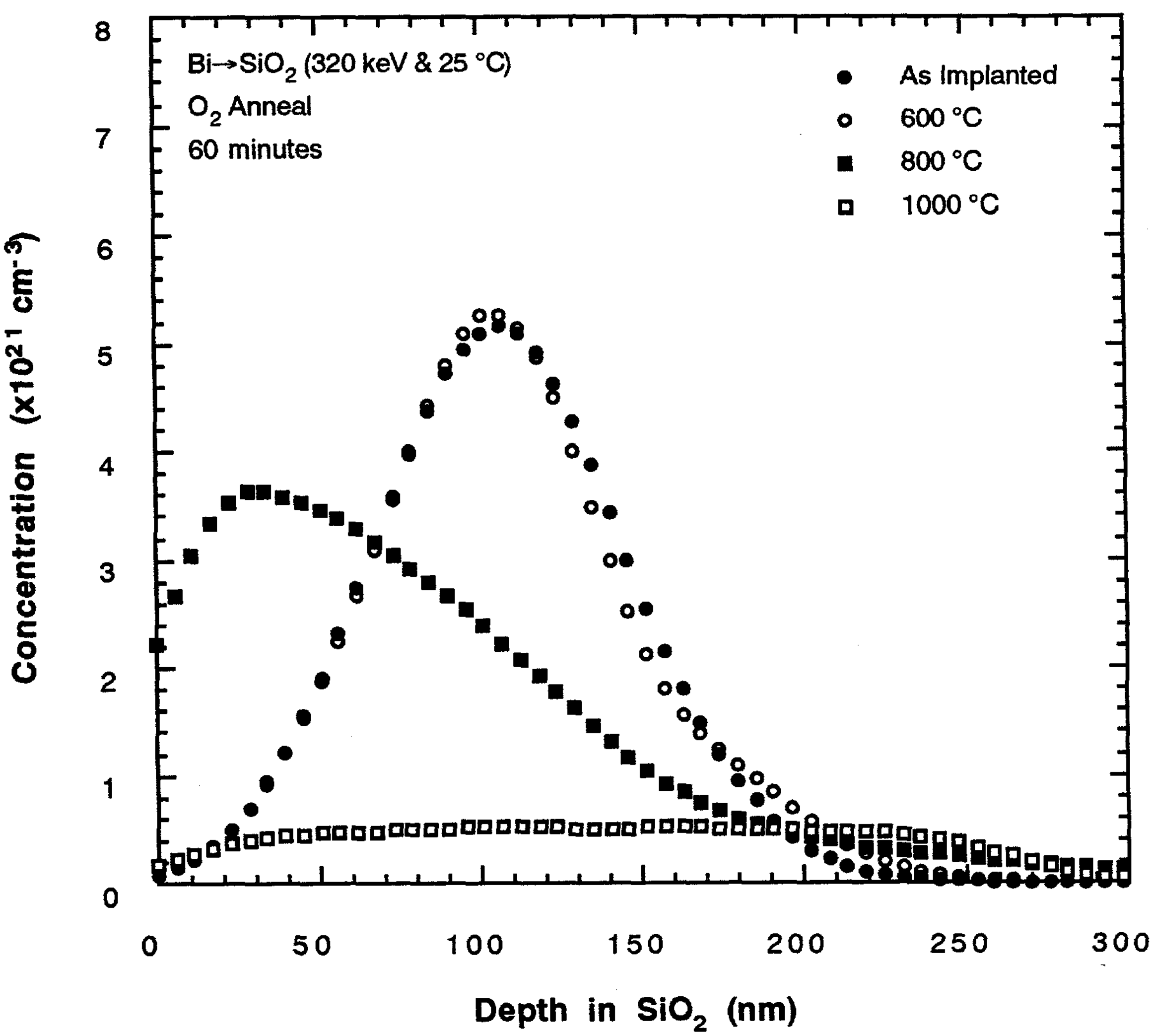
Bi→SiO2 (320 keV & 25 °C)
O2 Anneal
60 minutes
As Implanted
600 °C
800 °C
1000 °C
Concentration (x10^21 cm^-3)
Depth in SiO2 (nm)
0
1
2
3
4
5
6
7
8
0
50
100
150
200
250
300

Figure 3