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# OPTICAL BLEACHING OF BISMUTH IMPLANTED SILICA GLASS: A THRESHOLD EFFECT



S.Y. Park*, R.H. Magruder, III*, R.A. Weeks*, and R.A. Zuhr**
*Materials Science and Engineering, Vanderbilt University, Nashville, TN
**Solid State Division, ORNL, Oak Ridge, TN

## ABSTRACT

The near surface regions of high purity silica glass discs, Spectrosil A, were modified by implantation with bismuth ions at 160 keV and room temperature. The glasses implanted with a nominal dose of $6x10^{16}$ Bi/cm$^2$ at ~5 $\mu$A/cm$^2$ were subsequently bleached with a 5.0 eV KrF pulsed excimer laser. The laser had an average pulse duration of ~20 ns and repetition rate of 10 Hz. It was found that the bleaching was dependent upon the power density of the laser for a constant total integrated energy. Ion backscattering and optical absorption measurements were made before and after laser irradiation. Large changes in optical density and depth distribution of the implanted ions were observed at power densities of ≥45 mJ/cm$^2$-pulse. On the basis of our experimental results, the onset of the threshold for bleaching of silica glass implanted with $6x10^{16}$ Bi/cm$^2$ at 160 keV and at room temperature is between 30 and 45 mJ/cm$^2$-pulse.

## INTRODUCTION

High purity silica glass has useful optical properties for various purposes due to its broad transmission range that extends from infra-red to near vacuum ultra-violet. For applications such as optical switching and second harmonic generation, a large nonlinear coefficient, $n_2$, and small two photon absorption coefficients are needed.[1] Two photon absorption of silica glass is small over a wide range of wavelengths, but the index of refraction has a small second order term. By implanting polarizable ions, we may increase the nonlinear coefficient, $n_2$, in silica glass.[2] Ion implantation provides a convenient method for changing the optical properties of the outermost regions of a material such as transparent glass without altering the material below the implanted layer.[3]

Bismuth silicate crystals have high photosensitivities and fast response times that may be useful for photonic devices.[4,5,6,7] Bismuth silicate crystals have been used for optical phase conjugation, real-time holography, interferometry, and optical information storage.[4,5,6,7] Lines[6] and Lapp[7] have suggested that bismuth silicate glasses would be suitable for optical switching applications due to the high polarizability of bismuth ions. We have proposed that some of these interesting properties may be realized by implanting bismuth ions into high purity silica glass.[8] A series of measurements of bismuth implanted high purity silica glasses showed a bleaching phenomenon following 5.0 eV excimer laser irradiation.[8] "Optical bleaching" is defined to mean change in color and optical density during irradiation. This bleaching effect may be a means of producing read only memory materials with a spot size whose dimensions are limited only by the wavelength of the bleaching light. Therefore, knowledge about the threshold effects of the bleaching will be useful. In this paper, we report a threshold effect in optical bleaching of bismuth implanted high purity silica glass with 5.0 eV (248 nm) KrF pulsed excimer laser photons. It was found that the bleaching was dependent upon the power density (energy density per pulse) of the laser at a constant total integrated energy.

## EXPERIMENT

High purity type III[9] fused silica discs (Spectrosil A, manufactured by Thermal American Fused Quartz Corporation), 2 cm in diameter and 1 mm in thickness, were implanted with $Bi^{++}$ ions at room temperature using a Varian-Extrion Model 200-1000 implantation accelerator. The implantation was carried out for a nominal dose of $6x10^{16}$ Bi/cm$^2$ at 160 keV and at room temperature. The average beam current density during implantation was ~5.0 μA/cm$^2$. After implantation and backscattering measurements, the specimen was cut into eight samples for laser treatment. Samples were bleached with radiation from a 5.0 eV KrF pulsed excimer laser in air at various densities ranging from 30 mJ/cm$^2$-pulse to 150 mJ/cm$^2$-pulse. Each sample was irradiated with a constant total integrated energy of 15 J/cm$^2$ at 10 Hz. The laser had an average pulse duration of ~20 ns.

The depth profiles of the as implanted samples and the subsequently laser irradiated samples were obtained by backscattering measurements using 2.3 MeV $He^{++}$ ions at a scattering angle of 160°. Optical absorption measurements were carried out from ~1.9 eV (650 nm) to ~6.2 eV (200 nm) at room temperature using a Perkin-Elmer Lambda 9 dual-beam spectrometer. An unimplanted sample was placed in the reference beam, therefore all optical data reported here will be differences in optical density between the unimplanted glass and the implanted glass.

## RESULTS

The projected range for the as-implanted sample with a nominal dose of $6x10^{16}$ Bi/cm$^2$ was 70 ± 5 nm below the surface, with a full width at half maximum (FWHM) of 80 ± 5 nm. Retained dose of the as-implanted sample was calculated to be $4.9x10^{16}$ ± 0.5 Bi/cm$^2$. Figure 1 shows the backscattering profiles of the bismuth ions after irradiation with 5.0 eV KrF pulsed excimer laser photons. The distribution of the as implanted bismuth ions was reasonably fitted by a Gaussian function. After irradiation with 5.0 eV photons at a power density of 30 mJ/cm$^2$-pulse, the position of the maximum concentration was at 40 ± 5 nm, while the FWHM remained unchanged at 80 ± 5 nm. However, with irradiation at a power density of 45 mJ/cm$^2$-pulse, the position of the maximum concentration moved to the surface and the number of ions decreased by more than 70 %.

Optical densities of the samples after bleaching as a function of energy (or wavelength) are shown in Figure 2. After irradiation with 5.0 eV photons at 30 mJ/cm$^2$-pulse, the optical density of the samples at 5.0 eV decreased by less than 10 %. However, with power densities ≥45 mJ/cm$^2$-pulse, changes in optical density were observed in the range from ~1.9 eV to ~6.2 eV. The optical density in this range decreased by more than 90 %.

Figure 3-(a) shows retained dose, determined from backscattering measurements, as a function of power density of the laser. Figure 3-(b) shows optical density at 5.0 eV as a function of power density of the laser. Since the sample has been irradiated with 5.0 eV laser photons, we have chosen the absorption at 5.0 eV to compare the effects of exposure to laser radiation with differing intensities. (Note that each sample was irradiated with the same integrated photon dose.) Figure 3-(a) and 3-(b) show that there is a large change in retained dose and optical density for laser power densities between 30 mJ/cm$^2$-pulse and 45 mJ/cm$^2$-pulse. For laser power densities >45 mJ/cm$^2$-pulse, both retained doses and optical densities remain the same as those at 45 mJ/cm$^2$-pulse within error.

DISCUSSION

In Figure 2, we show optical density as a function of photon energy. We attribute the absorption from ~1.9 to ~6.2 eV, with the exception of the absorption centered at approximately 5 eV, to both scattering and electronic excitations of bismuth colloidal particles in the glass.[10,11] In the figure, a broad absorption shoulder near 5 eV is resolved in the as-implanted sample. We suggest that the origins of this broad absorption shoulder are two fold. The first source is defects introduced by the energetic ions[12,13], while the second source is the bismuth ions themselves.[8] Laser irradiation reduces absorption in the implanted glass from ~1.9 to ~6.2 eV as shown in Figure 2. Backscattering depth profiles show that the retained dose as shown in Figure 3 decreases with laser irradiation. We, therefore, attribute the decrease in optical absorption from ~1.9 to ~6.2 eV to this decrease in the number of bismuth ions in the glass.

We propose that the irradiation of bismuth implanted glass with 5.0 eV KrF laser photons results in photothermal heating. The absorption band at 5 eV has been attributed to $Bi^{3+}$ ions.[8] Assuming that the absorption of 5.0 eV photons is converted to thermal energy, irradiation of the sample with 5.0 eV photons will result in heating of the glass. It is the temperature rise in the glass due to absorption that produces the decrease in the number of bismuth ions either by ablation or the surface of the sample or by diffusion of bismuth ions to the surface and subsequent evaporation, or, by both ablation and diffusion. To calculate the temperature rise due to absorption of 5.0 eV (248 nm) KrF laser photons, we have made following assumptions;

1. The heat transfer is one-dimensional and all the energy of the 5.0 eV photons is converted to thermal energy.
2. The thermal properties of the absorbing materials are not dependent on temperature.
3. Reradiation from the absorbing materials is neglected.
4. Bismuth ions are the primary absorbing material since the absorption coefficient of the silica glass (~$10^{-2}$ cm$^{-1}$) and of the bismuth implanted regions

(~$10^4$ $cm^{-1}$) at 248 nm differ by six orders of magnitude in reciprocal centimeters.

On the basis of these assumptions and using specific heat of Spectrosil silica glass ($C_p$ = 0.7457 J/g-°K)[14] at 305 °K, we have estimated the temperatures in the implanted regions at different laser power densities. These estimated temperatures, which should be upper bounds because of the assumptions that were made, are tabulated in Table 1.

TABLE 1. Estimated temperatures in the implanted regions of silica glasses implanted with a nominal dose of $6.0x10^{16}$ Bi/$cm^2$ at 160 keV and at room temperature at various 5.0 eV laser power densities.

| 5.0 eV KrF LASER POWER DENSITY ($mJ/cm^2$-pulse) | ESTIMATED TEMPERATURE (°K) |
|---|---|
| 30 | 900 |
| 45 | 1400 |
| 60 | 1900‡ |
| 90 | 2800* |
| 120 | 3800 |
| 150 | 4700 |

‡Boiling Temperature of Bi = 1833 °K
*Boiling Temperature of $SiO_2$ = 2503 °K

From Figure 3, it is clear that there is a threshold power density between 30 $mJ/cm^2$-pulse and 45 $mJ/cm^2$-pulse for bleaching of bismuth implanted silica glass by 5.0 eV KrF laser photons. The small change in retained dose and optical density above the threshold laser power density as shown in Figure 3 can be explained by a small temperature increase. As the concentrations of absorbing materials are reduced, the temperature increase in the sample will become smaller. Assuming large temperature gradients and rapid time rates of change of temperature, the photothermal heating of the sample will be minimum. Therefore, irradiation at higher laser power densities above a threshold does not result in lower retained doses or smaller optical densities.

Comparing Figure 3-(a) and 3-(b), there is a strong correlation between the retained dose of bismuth ions and the optical density of the bismuth implanted glass. On the basis of these experimental results, the onset of bleaching is estimated to be between 30 and 45 $mJ/cm^2$-pulse. This bleaching phenomenon in bismuth implanted silica glass at power densities of between 30 and 45 $mJ/cm^2$-pulse for KrF laser may be a means of producing read only memory materials with a spot size whose dimensions are limited only by the wavelength of the bleaching light.

## CONCLUSIONS

On the basis of our experimental results, the following conclusions can be drawn:

1. There is a strong correlation between retained dose and optical density of bismuth implanted glass and the decrease in optical density after irradiation with 5.0 eV photons is due to the decreasing number of bismuth ions in the implanted glass.

2. There is a threshold effect in the power density of 5.0 eV (248 nm) KrF laser photons needed to bleach bismuth implanted silica glass. For $6.0\times10^{16}$ $Bi/cm^2$ room temperature implants at 160 keV in Spectrosil A silica glass, that threshold is between 30 and 45 $mJ/cm^2$-pulse.

3. The loss of bismuth ions is attributed to thermal effects produced by conversion of photon energy to thermal energy.

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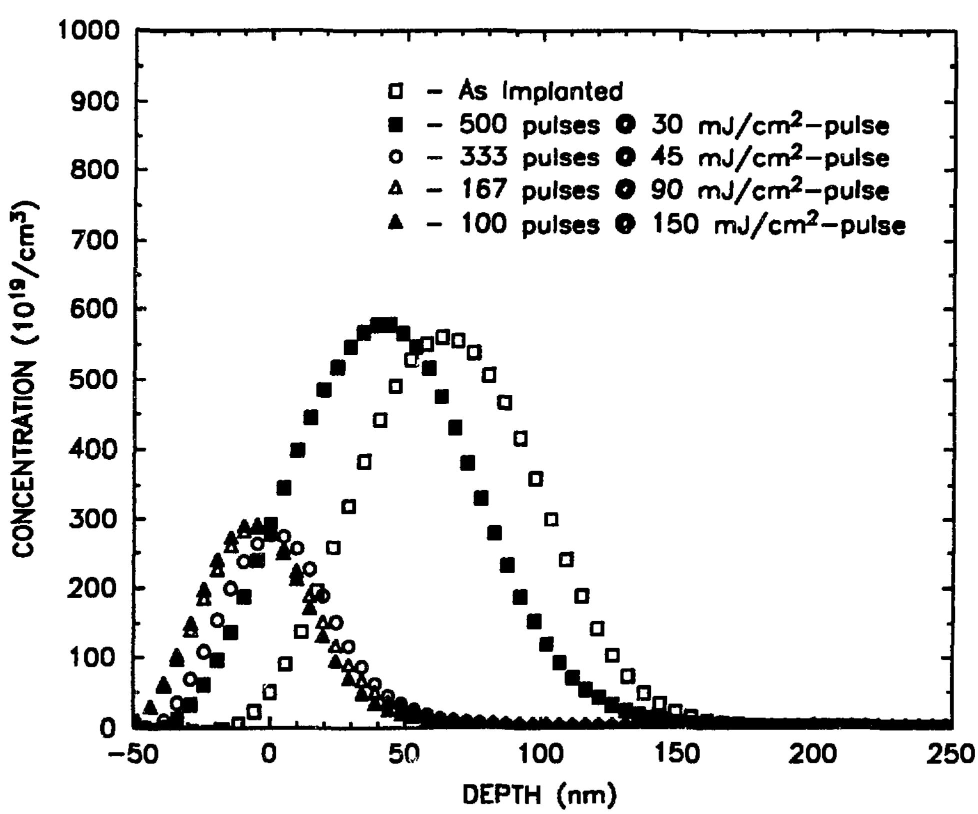


FIGURE 1. Backscattered depth profiles of bismuth implanted high purity silica glass after irradiation with 5.0 eV KrF pulsed excimer laser at various power densities.

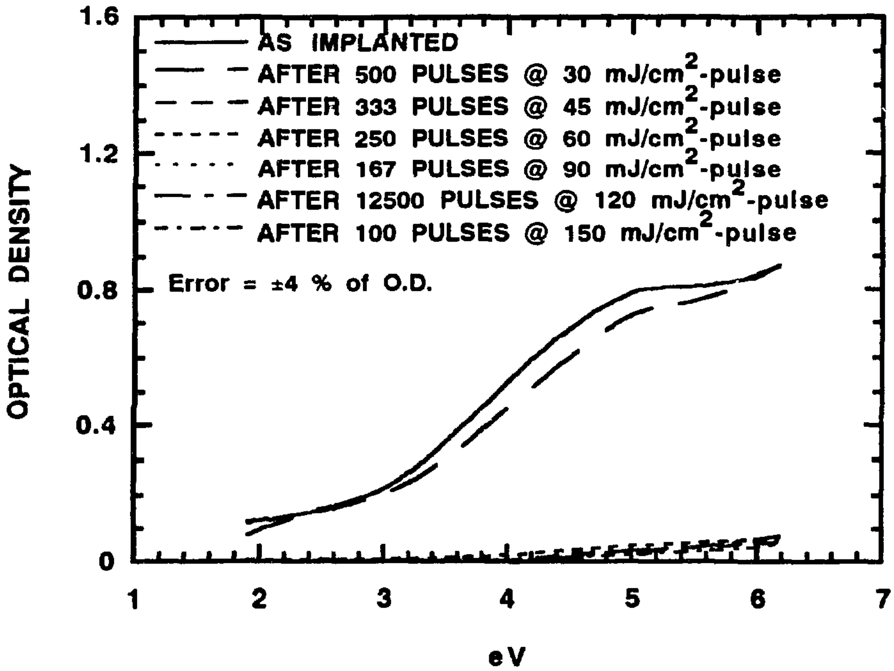


FIGURE 2. Optical densities of silica glass implanted with a nominal dose of $6.0 \times 10^{16}$ $Bi/cm^2$ at 160 keV and at room temperature as a function of photon energy.

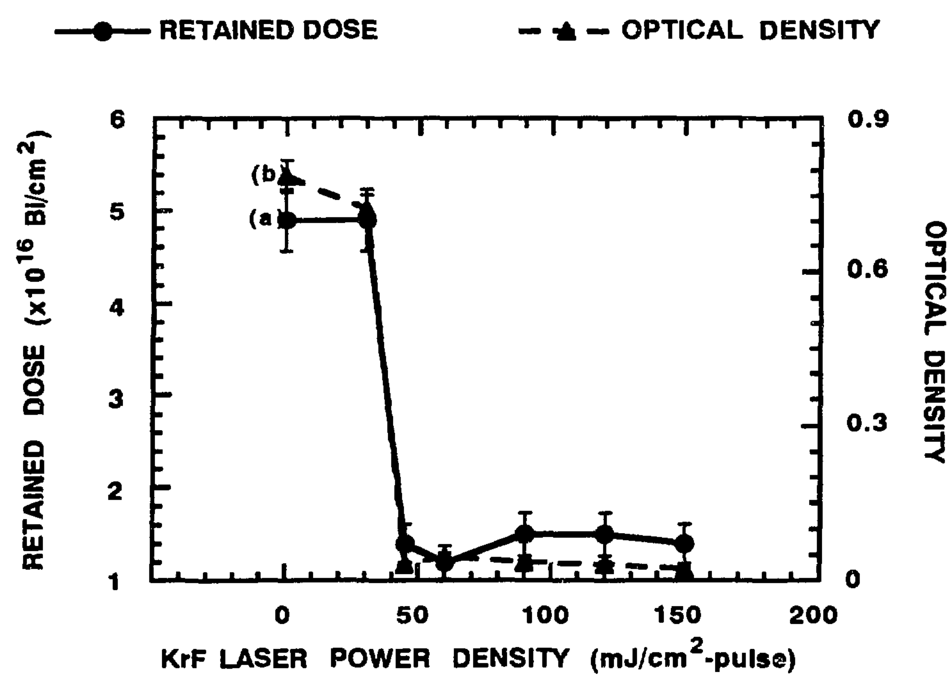


FIGURE 3. Retained dose by RBS before and after 5.0 eV laser irradiation at various power densities.