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FORMATION OF NANOMETALLIC CLUSTERS IN SILICA BY ION IMPLANTATION.

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Abstract

We have changed both linear and nonlinear optical properties of suprasil-1 by implanting 2.0 MeV copper, 350 keV tin, 1.5 MeV silver and 3.0 MeV gold. These changes were induced both by over implantation above the threshold fluence for spontaneous cluster formation and by subsequent thermal annealing, and are due to an increase in resonance optical absorption as well as an enhancement of the nonlinear optical properties. Using optical absorption spectrophotometry and Rutherford Backscattering spectrometry, we have measured the cluster size for each heat treatment temperature. Using Z-scan technique we have determined the third order electric susceptibility for each implanted species to be $1.5 \times 10^{-6}$ esu for Sn nanoclusters, $2.7 \times 10^{-6}$ esu for Cu nanoclusters, $5 \times 10^{-7}$ esu for Ag nanoclusters, to $6.5 \times 10^{-7}$ esu for Au nanoclusters in suprasil-1.

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INTRODUCTION

In recent years, ion implantation has been used to introduce foreign ions into pure silica to change its linear and nonlinear optical properties in layers near the surface [1-8]. To form nanoclusters after ion implantation the material must be treated either by thermal annealing, by laser annealing or by inert ion bombardment [3]. An attractive feature of ion implantation to form these nanoclusters, compare to the classical technique of mixing selected metal powder with molten glass, is that the linear and nonlinear properties occur in a well defined space in an optical device, and by using focused ion beams, point quantum confinement may be accomplished.

In this paper, we have used both keV and MeV ion implantation to introduce metals, such as tin, copper, silver and gold into a chemically ultra-pure silica glass known as suprasil-1. Then we studied the optical properties of the ion implanted suprasil-1 before and after thermal annealing at each heat treatment temperature.

EXPERIMENTAL PROCEDURES

The pure silica glass used in this work is Suprasil-1 provided by Heraeus Amersil, Inc. It contains 150 ppm OH, 0.05 ppm of Ti, Na, Ca and Al and less than 0.01 ppm other metals. The Suprasil-1 samples, 10 x 10 x 0.5 mm, were implanted with 2.0 MeV copper, 350 keV tin, 1.5 MeV silver, or 3.0 MeV gold ions at a current density less than 2 μA/cm² to avoid the premature formation of metal clusters due to the ion beam heating, and meanwhile we kept the target holder cooled to room temperature. Ion fluences were chosen to give a guest atom to silicon ratio between 1:100 to 1:10. This allowed us to determine the threshold fluence for spontaneous cluster formation for each implanted ion species.
The heat treatments were done in air at temperatures between 500°C and 1000°C for intervals between 0.5 hr to several hours at each heat treatment temperature. After each heat treatment, an optical absorption spectrum at room temperature was measured. Using these spectra, the RBS results, as well as TRIM simulations [9], we calculate the size of the metallic clusters which are responsible for the optical absorption band.

The average radius of metal spheres small compared with the wavelength of light is determined [10] from the resonance optical absorption spectrum according to the equation

\[ R = \frac{v_f}{\Delta \omega} \]

where \( v_f \) is the Fermi velocity of metal and \( \Delta \omega \) is the full width at half maximum of the absorption band due to the plasmon resonance in small metal particles.

A frequency doubled mode locked Nd:YAG laser (532 nm) with 4.5 ps width at a 76 MHz repetition rate with a peak power density of 2.57 GW/cm² was employed for Z-scan measurements of the third order susceptibility [11]. Prism coupling of light into the implanted surface was used to investigate the waveguide that is formed as a consequence of the layered structure.

RESULTS and DISCUSSIONS

The higher the atomic number and fluence of the bombarding ion, the more the damage and modification of the optical properties [12,13] of the silica glass. This was observed by absorption spectrometry during all of our bombardments. Except for the effects attributable to the metal clusters, these other effects were reduced with heat treatments above 500-700°C.

We used ion fluences from \( 2 \times 10^{16} \) ion/cm² to \( 2 \times 10^{17} \) ion/cm² for each implanted species to find the threshold fluence for spontaneous cluster formation. The threshold fluence for spontaneous formation of nanoclusters in suprasil-1 is below \( 4 \times 10^{16} \) ion/cm² for 1.5 MeV silver,
below $2 \times 10^{17}$ ion/cm$^2$ for 2.0 MeV copper, below $2 \times 10^{17}$ ion/cm$^2$ for 3.0 MeV gold and below $9.4 \times 10^{16}$ ion/cm$^2$ for 350 keV tin. We used low current densities such that no significant temperature increase occurred during implantation, while, we also cooled the target holder to keep the target temperature at room temperature.

Heat treating the implanted sample reduces the strains and charge imbalances caused by implantation of these metal species. Moreover, heating increases the diffusion coefficient and the implanted atoms move to the lower energy metallic state of the clusters increasing the localized volume fraction. With an initial mean separation of implanted atoms only a few nanometers virtually all will diffuse to a cluster and not reach the surface of the suprasil-1 or diffuse deep into it. Moreover other experiments have shown that the damaged region in the host may itself offer lower energy states to individual guest atoms and inhibit diffusion loss from, and enhance diffusion into, that region. With heat treatment the near neighbor clusters coalesce and the host accommodates to the volume reduction. RBS measurements confirm that the depth profile of the metal clusters formed after heat treatment is almost identical to, or slightly narrower than, that of the atoms initially implanted by ion bombardment [3].

Figures 1 and 2 show the optical density for 1.5 MeV silver implanted in suprasil-1 at $2 \times 10^{16}$ Ag/cm$^2$, below the threshold fluence, and at $4 \times 10^{16}$ Ag/cm$^2$ at various heat treatment temperatures. The prominent resonance optical absorption at 405 nm at room temperature implantation appears only for $4 \times 10^{16}$/cm$^2$, which is just above the threshold fluence. This absorption band also appears for the fluences below the threshold fluence only after heat treatment, as shown in figure 1. The other common effects which were observed for all implanted species are; A) increase in the in the optical density of the absorption band as the HTT is increased for the fluences above the threshold fluence, B) reduction in the optical density of the absorption band at
a given high HTT. The illustrated behavior is typical of the other implanted species with the exception of tin. The optical absorption photospectrometry of tin implanted suprasil-1 showed no absorption band before or after heat treatment, which is in agreement with Mie's theory [14].

Figure 3 compares the optical absorption spectra for four suprasil-1 samples implanted with either with gold, silver, copper, or tin after subsequent heat treated at a temperature near that of the respective bulk material melting point. For a heat treatment temperature beyond a critical temperature the resonance optical absorption disappears as metal atoms evaporate from the clusters as shown in Fig. 1 for silver implanted suprasil-1. The critical temperature correlates only roughly with the bulk metal melting temperature.

Using the Doyle theory [10] and the resonance optical absorption bandwidths, average cluster radii in the three metal implanted samples are calculated for each heat treatment temperature. Figure 4 shows the dependence of the cluster radius of silver as a function of the reciprocal of the HTT for various implantation fluences. Table 1 shows ion species and their implantation energies, the calculated average cluster size, the threshold fluence for spontaneous cluster formation, and $\text{Chi}(3)$ for selected fluences and heat treatment temperatures. The average cluster size was calculated using the FWHM of the absorption band and the results obtained from RBS.

CONCLUSION

We have induced large third order electric susceptibility in suprasil-1 by implanting elements such as Cu, Sn, Ag, and Au at various fluences below and above the threshold fluence and by careful heat treatment at temperatures between 500 to 1000°C for various heat treatment times. We have also shown that the threshold fluence can be as low as $1.5 \times 10^{16}/\text{cm}^2$ for Sn and as
high as $2 \times 10^{17}$ cm for Au and Cu after which the nanoclusters are spontaneously formed, even at room temperature. The dependence of the cluster radius as a function of the reciprocal of the HTT shows a sudden change of slope near the bulk melting temperature of the implanted metal.

ACKNOWLEDGMENTS

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REFERENCES


Table 1 showing ion species and their implantation energies, the calculated average cluster size, the threshold fluence for spontaneous cluster formation, and Chi(3) for each fluence and heat treatment temperature.

<table>
<thead>
<tr>
<th>Ion Species</th>
<th>Fluence (ions/cm²)</th>
<th>Energy (MeV)</th>
<th>Temperature (°C)</th>
<th>Peak (nm)</th>
<th>Chi(3) (esu)</th>
<th>Threshold Fluence (x 10¹⁷/cm²)</th>
<th>Ave. Radius (nm)</th>
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<tr>
<td>Cu</td>
<td>4 x 10¹⁷</td>
<td>2</td>
<td>1000</td>
<td>570</td>
<td>2.7 x 10⁻⁶</td>
<td>&lt; 2</td>
<td>4.4</td>
</tr>
<tr>
<td>Cu</td>
<td>1 x 10¹⁷</td>
<td>2</td>
<td>1000</td>
<td>569</td>
<td>4.7 x 10⁻⁷</td>
<td>&lt; 2</td>
<td>4.2</td>
</tr>
<tr>
<td>Ag</td>
<td>4 x 10¹⁶</td>
<td>1.5</td>
<td>900</td>
<td>405</td>
<td>5.0 x 10⁻⁷</td>
<td>&lt; 0.4</td>
<td>4.7</td>
</tr>
<tr>
<td>Sn</td>
<td>8 x 10¹⁷</td>
<td>0.35</td>
<td>200</td>
<td>none</td>
<td>1.5 x 10⁻⁶</td>
<td>&lt; 0.94</td>
<td>------</td>
</tr>
<tr>
<td>Au</td>
<td>1.2 x 10¹⁷</td>
<td>3</td>
<td>1200</td>
<td>410</td>
<td>6.5 x 10⁻⁷</td>
<td>&lt; 2</td>
<td>3.3</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Figures 1, the optical density for 1.5 MeV silver implanted suprasil-1 at 2 \times 10^{16}/cm^2 at various heat treatment temperatures.

Figure 2, the optical density for 1.5 MeV silver implanted suprasil-1 at 4 \times 10^{16}/cm^2 at various heat treatment temperatures.

Figure 3, the optical absorption spectra for four suprasil-1 samples implanted with either with 3.0 MeV gold, 1.5 MeV silver, 2.0 MeV copper, or 350 keV tin after subsequent heat treatment.

Figure 4, the dependence of the cluster radius of silver as a function of the reciprocal of the HTT for various implantation fluences.
Figure 1
Figure 2