Au implantation into various types of silicate glasses

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The implantation of gold ions into three types of silicate glass was studied. The energies of the implanted Au+ ions were 1701 keV, and the fluences of the ions were $1 \times 10^{14}$, $1 \times 10^{15}$, $3 \times 10^{15}$ and $1 \times 10^{16}$ cm$^{-2}$. The as-implanted samples were annealed in air at two temperatures (400 and 600°C). The Au concentration depth profiles were investigated using Rutherford Backscattering Spectrometry (RBS) and compared to simulated profiles from the SRIM. The structural changes were studied by UV–vis absorption spectroscopy. The obtained mono-mode waveguides were characterised using Dark Mode Spectroscopy at 671 nm to yield information on the refractive index changes. The results showed interesting differences depending on the type of glass and the post-implantation treatment. The obtained data were evaluated on the basis of the structure of the glass matrix, and the relations between the structural changes, waveguide properties and absorption, which are important for photonics applications, were formulated.

1. Introduction

Metal nanocluster composite glasses (MNCGs) are interesting for their potential application in non-linear optics due to the third-order optical non-linear responses of their metal nanoclusters [1]. Glasses containing metal colloids can be prepared using several techniques, such as melt doping, ion exchange or ion implantation [2]. As compared to the other techniques, ion implantation allows the synthesis of high-density metal nanoclusters in the glasses with well-defined dopant depth profiles [3]. Post-implantation annealing can control the size as well as non-linear properties of the nanoclusters [4,5]. In this paper, we have focused on the high-energy ion implantation of Au+ ions into three types of silicate glasses conducted under various conditions. Silicate glasses were selected as they are important materials for various nanotechnology applications because of their low cost, easy manufacturability, high chemical stability, transparency and flexibility in chemical composition [6]. The glasses used differed in their chemical compositions especially in terms of the concentration of the monovalent modifier (Na) and the network elements (Si and B). The glass containing gold nanoclusters exhibited enhanced third-order susceptibility $\chi^{(3)}$ at 532 nm [4], which, as a measure of optical non-linearity, can be considered as a figure of merit for its potential utilisation in photonics devices. Moreover, ions of gold have a low enough diffusivity (when compared to e.g. silver ions [7], which are too fast) to allow the study of the processes that occur during annealing. The main aim of this project was to study and subsequently formulate the relations between the chemical composition of the glass substrate and the formation of the Au nanoparticles.

2. Experiment

We have used three types of optical glasses with varying chemical compositions, namely specially designed Glasses A and B (made at the Glass Institute Hradec Kralove Ltd., Czech Republic) and a commercially available Glass C (BK7). The glasses varied especially in their concentrations of monovalent and divalent modifiers (Na$_2$O, K$_2$O, CaO, MgO) as well as their network formers (SiO$_2$, B$_2$O$_3$). The compositions of the glasses determined by X-ray Fluorescence (XRF) are provided in Table 1.

Au+ ions were implanted into the silicate glasses on a new Tandetron 4130 MC accelerator at the Nuclear Physics Institute in Prague, Czech Republic. The energy of the implanted Au+ ions was 1701 keV. The fluences of the Au+ ions into Glass A were $1 \times 10^{14}$, $1 \times 10^{15}$, $3 \times 10^{15}$ and $1 \times 10^{16}$ cm$^{-2}$, whereas the fluences used in the cases of Glasses B and C were $1 \times 10^{14}$, $1 \times 10^{15}$ and $1 \times 10^{16}$ cm$^{-2}$. The as-implanted glasses A were annealed at temperatures of 400°C for 5 and 25 h or 600°C for 5 h. The depth distribution and diffusion profiles of the implanted Au were

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investigated using Rutherford Backscattering Spectrometry (RBS) with 2.0 MeV He\(^+\) ions. The incoming angle was 0° while the scattering angle was 170°. The measurements were evaluated with the Gisa 3.99 [8] and compared with a simulation in the SRIM 2003 [9]. The UV–vis absorption spectra were collected using a Cary 50 dual-beam spectrometer in transmission modes ranging from 300 to 1000 nm. The implanted samples were also studied by Dark Mode Spectroscopy (DMS) at 671 nm for possible waveguiding properties. The method is based on coupling the light into the surface of the substrate through a prism. This results in the phenomenon of the so-called ‘dark modes’, which are in fact a consequence of the interference effect produced by the reflectivity of light at a single point on the coupling-prism interface. The waveguiding properties of the sample are then evaluated employing the well-known IWKB procedure. The accuracy of the method (refractive index value) is currently mentioned as 2 × 10\(^{-5}\) [10].

### 3. Results and discussion

#### 3.1. Implantation versus simulation

The typical depth profiles of the implanted Au ions in Glasses A and B as determined from the RBS spectra are shown in Fig. 1(a) and 1(b), respectively. Glass C contains a larger amount of Ba and hence RBS is not capable of determining the depth profile or the integral amount of Au with reasonable precision for this glass. The depth profiles of the glasses implanted at a fluence of \(1 \times 10^{16}\) cm\(^{-2}\) are not presented because of the extremely low concentration, making a comparison of the values over two orders of magnitude in one figure unconstructive. The profiles calculated with the SRIM 2003 code for the implanted glasses \((1 \times 10^{16}\) cm\(^{-2}\), 1701 keV) are shown in Fig. 1(a) and 1(b) for comparison. Fig. 1(a) and 1(b) indicate that the SRIM simulation results are in good agreement with the varying density of the glass. The projected range \(R_p\) and range straggling \(\Delta R_p\) calculated using the SRIM 2003 are \(R_p = 378.9\) nm and \(\Delta R_p = 68\) nm for Glass A and \(R_p = 402.5\) nm and \(\Delta R_p = 71.7\) nm for Glass B, with Glasses A and B differing in their composition and density. In Fig. 1(a) and 1(b), we observed two evident disagreements between the simulation and measured data. First, the measured depth profiles are broader than the simulated ones, which may be caused by higher straggling of the implanted ions. Second, the maximal concentration is shifted towards the surface as compared to the simulated values mainly for Glass A and at higher fluences. This disagreement is not surprising since the SRIM code does not take into account the structural changes of a glass matrix caused by ion irradiation. Consequently, Glass B, which is similar to silica glass (in terms of the network’s cross-linking), yielded better agreement of the simulation with the experimental data, unlike Glass A, which, being more basic (as compared to the rather covalent Glass B), provided much worse agreement. This may indicate that the structure of the treated thin layers had become more covalent (i.e. cross-linked to a higher extent) as a consequence of the depletion of oxygen from the glass surface. A different degree of cross-linking of the glass network was reported e.g. in [11].

#### 3.2. Post-implantation annealing

The annealing conditions, especially temperature, play the main role in creating gold nanoparticles in glass. Therefore, Glass A was annealed at temperatures below or near the glass transition temperature \(T_g = 615\) °C (as determined by Differential Thermal Analysis). The gold concentration profile changes caused by the different methods of annealing of Glass A are shown in Fig. 2(a) and 2(b). The Au depth profiles presented in Fig. 2(a) describe the Au distribution for the various annealing conditions for the samples implanted at \(1 \times 10^{16}\) cm\(^{-2}\). A change of Au depth profile was observed after the long-time annealing at 400 °C, namely for 25 h, when the Au was redistributed and formed an Au layer without a significant concentration maximum. The Au depth profiles in Glass A implanted at \(1 \times 10^{16}\) cm\(^{-2}\) are presented in Fig. 2(b). The concentration profiles of the non-annealed samples and samples annealed at 400 °C and 600 °C for 5 h were similar. The depth profile of the sample annealed at 400 °C for 25 h was narrower with a higher concentration maximum than the other samples. A substantial change of the Au depth profile occurred after the long-time annealing and could have been caused by the Ostwald ripening mechanism [12].

The RBS measurement of the Au integral amount is summarised in Table 2. The Au integral amount stayed the same for the as-implanted Glass A after a short-time annealing of 4 h at 400 °C.

### Table 1

<table>
<thead>
<tr>
<th>Substrate</th>
<th>SiO(_2)</th>
<th>Na(_2)O</th>
<th>Al(_2)O(_3)</th>
<th>CaO</th>
<th>MgO</th>
<th>K(_2)O</th>
<th>B(_2)O(_3)</th>
<th>BaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass A</td>
<td>63.2</td>
<td>24.4</td>
<td>1.1</td>
<td>5.6</td>
<td>5.3</td>
<td>0.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Glass B</td>
<td>88.0</td>
<td>8.7</td>
<td>3.3</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Glass C</td>
<td>68.3</td>
<td>8.8</td>
<td>–</td>
<td>0.1</td>
<td>–</td>
<td>8.1</td>
<td>12.1</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Fig. 1a. The depth profiles of the implanted Au in Glass A for the different fluences compared to the SRIM simulation.

Fig. 1b. The depth profiles of the implanted Au in Glass B for the different fluences compared to the SRIM simulation.
Increasing temperature and time caused a broadening of the depth profiles and a decrease of the Au maximum concentration in the samples implanted at the lowest fluence \(1 \times 10^{14} \text{ cm}^{-2}\). The decrease was so significant that the depth profiles could not be measured by RBS. Glass A implanted at a medium fluence \(1 \times 10^{15} \text{ cm}^{-2}\) exhibited a similar behaviour after annealing for 25 h, where the integral amount was decreased to 64% of the original value, see Table 2. The integral amount for the samples with the Au implanted at a fluence of \(1 \times 10^{16} \text{ cm}^{-2}\) is the same for all the samples with or without annealing.

We can hence conclude that the glass samples implanted at low and medium ion fluences show similar behaviour after the long-time annealing. The Au is redistributed in the glass substrate and creates a constant concentration profile with no significant maximum. Completely different Au depth profile changes were observed in Glass A when implanted at a high ion fluence (see Fig. 2b for where the sharp peak concentration occurred).

### 3.3. Optical properties

The glasses that were implanted at the highest fluence (i.e. \(1 \times 10^{16} \text{ cm}^{-2}\)) and subsequently annealed at the highest temperature (600 °C) changed from colourless to red. The colour red, which appeared in all three glass types and which was confirmed also by the appearance of the pertinent peak (at 532 nm) in the UV–vis absorption spectra (see e.g. the absorption spectrum for Glass A in Fig. 3) indicated the presence of colloid particles of gold. Glasses A and B had that peak with similar intensities and located at exactly 532 nm while Glass C differed in both, with a lower intensity of the ‘red’ peak shifted to a shorter wavelength (550 nm). Obviously, these findings are related to the structure of the glasses used and deserve further analysis.

The waveguiding properties as measured by DMS are shown in Table 3. The waveguiding effect was found only in Glasses A and B after applying higher fluences (\(3 \times 10^{15}\) and \(1 \times 10^{16} \text{ cm}^{-2}\)). The refractive index increments \(\Delta n\) in the waveguides ranged from 0.001 to 0.002, which is sufficient for the creation of single-mode waveguides.

### 4. Conclusion

Three silicate glasses were implanted with 1701 keV Au ions using fluences ranging from \(1 \times 10^{14}\) to \(1 \times 10^{16} \text{ cm}^{-2}\). A small disagreement between the predicted Au depth profiles calculated by the SRIM and the measured Au depth profiles was observed in correlation with the varying structures of the glasses. A dramatic change of the Au concentration depth profiles was observed after

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**Table 2**
The Au integral amount comparison before and after the annealing procedure for Glass A.

<table>
<thead>
<tr>
<th>Glass A</th>
<th>Au fluence (cm(^{-2}))</th>
<th>(n_{\text{substrate}})</th>
<th>Number of guided modes</th>
<th>(n)</th>
<th>(\Delta n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(1 \times 10^{14})</td>
<td>1.504</td>
<td>1</td>
<td>1.505</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>(1 \times 10^{15})</td>
<td>1</td>
<td>1</td>
<td>1.505</td>
<td>0.001</td>
</tr>
<tr>
<td>B</td>
<td>(1 \times 10^{14})</td>
<td>1.475</td>
<td>1</td>
<td>1.477</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>(1 \times 10^{15})</td>
<td>1.475</td>
<td>1</td>
<td>1.477</td>
<td>0.002</td>
</tr>
</tbody>
</table>

RBS was not able to measure the depth profile.
long-time annealing (25 h) at 400 °C. The presence of gold colloid particles was identified in the glass implanted at $1 \times 10^{16} \text{ cm}^{-2}$ and annealed at the highest temperature (600 °C), as proved by UV–vis spectroscopy. The results showed a certain similarity between Glasses A and B, both being silicate glasses. Glass C (BK7), on the other hand, revealed stronger resistance to the ion implantation as well as its consequences. A likely reason is that Glass C is a boron-silicate glass. Boron, with a much smaller size when compared to silicon, makes the structure of the glass network less open and denser than the mostly silicate network, which results in lower penetrability of the glass for the incoming particles (ions). Our experiments lead us to believe that rather than the concentration of monovalent (more mobile) modifiers in the glass (in our case sodium ions), it is the network-forming elements that are decisive for the behaviour of the glass in the ion implantation process applied here.

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