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Linear and nonlinear optical properties of silver nanoparticles synthesized in dielectrics by ion implantation and laser annealing

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Kazan Physical-Technical Institute, Russian Academy of Sciences
Russian Federation
Laser Zentrum Hannover
Germany

1. Introduction

Composite metamaterials containing metallic nanoparticles (MNPs) are now considered a basis for designing new photonic media for optoelectronics and nonlinear optics (Sarychev & Shalaev, 2007). Simultaneously with the search for and development of modern technologies intended for nanoparticle synthesis, substantial practical attention has been devoted to designing techniques for controlling the MNP size. This is caused by the fact that the properties of MNPs, such as the quantum size effect, single-electron conduction, etc., which are required for various applications, take place up to a certain MNP size. An example of their application in optoelectronics is a prototype of integrated electronic circuit - chip that combines metallic wires as conductors of electric signals with fibers as guides of optical signals. In practice, light guides are frequently made of synthetic sapphire or silicon oxide, which are deposited on or buried in semiconductor substrates. In this case, electrooptic emitters and that accomplish electric-to-optic signal conversion are fabricated inside the dielectric layer. This light signal from a microlaser is focused in a light guide and then transmitted through the optoelectronic chip to a high-speed photodetector, which converts the photon flux to the flux of electrons. It is expected that light guides used instead of metallic conductors will improve the data rate by at least two orders of magnitude. Moreover, there is good reason to believe that optical guide elements will reduce the energy consumption and heat dissipation, since metallic or semiconductor components of the circuits may be replaced by dielectric ones in this case. Prototype optoelectronic chips currently available are capable of handling data streams with a rate of 1 Gbit/s, with improvement until 10 Gbit/s in future.

Key elements of dielectric waveguides used for light propagation are nonlinear optical switches, which must provide conversion of laser signal for pulse duration as short as pico- or femtoseconds. The nonlinear optical properties of MNP-containing dielectrics stem from the dependence of their refractive index and nonlinear absorption on incident light intensity...
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(Flytzanis et al., 1991). This effect is associated with MNPs, which exhibit an enhancement of local electromagnetic field in a composite and, as consequence, a high value of the third order nonlinear susceptibility when exposed to ultrashort laser pulses. Therefore, such MNP-containing dielectric materials may be used to advantage in integrated optoelectronic devices, for example, as shown in Fig. 1.

It is well known (Kreibig & Vollmer, 1995) that a local field enhancement in MNPs stimulates a strong linear optical absorption called as surface plasmon resonance (SPR). The electron transitions responsible for plasmon absorption in MNPs cause also a generation of an optical nonlinearity of a composite in the same spectral range. As a result, the manifestation of nonlinear optical properties is most efficient for wavelengths near the position of a SPR maximum. In practice, to reach the strong linear absorption of a composite in the SPR spectral region, attempts are made to increase the concentration (filling factor) of MNPs. Systems with a higher filling factor offer a higher nonlinear susceptibility, when all other parameters of composites being the same. Usually noble metals and copper are used to fabricate nonlinear optical materials with high values of third order susceptibility. There are variety ways to synthesis MNPs in dielectrics, such as magnetron sputtering, the convective method, ion exchange, sol–gel deposition, etc. One of the most promising enhanced fabrication methods is ion implantation (Townsend et al., 1994, Stepanov, 2005a) because it allows reaching a high metal filling factor in an irradiated matrix beyond the equilibrium limit of metal solubility and provides controllable synthesis of MNPs at various

![Fig. 1. Prototypes of optoelectronic chip with a dielectric waveguide combined with silicone substrate. Ion implantation can be applied to fabricate selective area doped by rear metal ions (marked by stars) to work as microlaser and to illuminate in waveguide, created by rear-gas ion radiation with MNPs to form an optical switcher.](www.intechopen.com)
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2. Ion synthesis of metal nanoparticles

Ion implantation is an effective technological tool for introducing single impurities into the surface layer of the substrate to a depth of several micrometers. The degree of surface modification of the materials depends on their individual chemical and structural properties, as well as on variations of implantation parameters, such as the type and energy of an implant, current density in ion beam, substrate temperature, etc. A most critical parameter is ion dose $F_0$, which determines the implant amount. Depending on the modification of dielectrics by irradiation, ion implantation can be conventionally divided into low-dose and high-dose processes.

In the case of low-dose irradiation ($\sim F_0 \leq 5.0 \times 10^{14} \text{ion/cm}^2$), the Ag ions implanted, after stopping and thermalization, are dispersed throughout the volume of the dielectrics and are well separated from each other. The energy of the implant is transferred to the matrix via electron shell excitation (ionization) and nuclear collisions. This causes radiation-induced defects, which, in turn, may reversibly or irreversibly modify the material structure (Townsend et al., 1994). Various types of crystal structure damage have been observed in practice: extended and point defects, amorphization and local crystallization, precipitation of a new phase made up of host atoms or implanted ions, etc.
<table>
<thead>
<tr>
<th>Matrix type</th>
<th>Ion energy, keV</th>
<th>Ion dose, ion/cm²</th>
<th>Current density, μA/cm²</th>
<th>Post-implantation heat treatment</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ crystal &lt;1010&gt;</td>
<td>50</td>
<td>4.0×10¹⁶</td>
<td>1-5</td>
<td>Annealing in air at 650°C, 30 min</td>
<td>Rahmani et al., 1988, Rahmani &amp; Townsend 1989</td>
</tr>
<tr>
<td>Al₂O₃ crystal &lt;0001&gt;</td>
<td>360</td>
<td>5.0×10¹⁶, 8.0×10¹⁶</td>
<td>2-3</td>
<td>Annealing in air at 1100°C, 2 h or in Ar+4%H₂ at 500°C, 2 h</td>
<td>White et al., 1993</td>
</tr>
<tr>
<td>Al₂O₃ crystal</td>
<td>1.5×10³</td>
<td>(0.2-2.0)×10¹⁷</td>
<td>2-3</td>
<td>Annealing in air at 550 and 1100°C</td>
<td>Steiner et al., 1998</td>
</tr>
<tr>
<td>MgO crystal (100)</td>
<td>1.2×10¹⁷</td>
<td>2-3</td>
<td></td>
<td>Annealing in air at 550 and 1100°C</td>
<td>Ganeev et al., 2005, 2006</td>
</tr>
<tr>
<td>LiNbO₃ crystal</td>
<td>1.0×10²⁶</td>
<td>1.0×10¹⁶</td>
<td>2</td>
<td>Annealing in air at 1200°C, 22 h</td>
<td>Marques et al., 2006</td>
</tr>
<tr>
<td>MgO crystal (100)</td>
<td>2.0×10¹⁷</td>
<td>2</td>
<td></td>
<td>Annelling in air at 200°C, 600°C, 2h</td>
<td>Mazzoldi et al., 1993</td>
</tr>
<tr>
<td>MgO crystal (100)</td>
<td>2.0×10¹⁷</td>
<td>2</td>
<td></td>
<td>Some samples annealed in air, Ar, O₂ or 70%N₂ + 30%H₂ at 300-900°C, 1h</td>
<td>Qian et al., 1997, Zimmerman et al., 1997, van Huis et al., 2002</td>
</tr>
<tr>
<td>MgO crystal (100)</td>
<td>200</td>
<td>2.0×10¹⁷</td>
<td>2</td>
<td></td>
<td>Xiao et al., 2008</td>
</tr>
<tr>
<td>MgO crystal</td>
<td>600</td>
<td>1.0×10¹⁶</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgOP₂O₅ glass</td>
<td>150</td>
<td>(0.1-1.0)×10¹⁷</td>
<td>0.5-3</td>
<td></td>
<td>Matsunami &amp; Hosono, 1993a</td>
</tr>
<tr>
<td>Lithia-alumina-silica glass</td>
<td>275-285</td>
<td>1.0×10¹⁶</td>
<td>1-2</td>
<td></td>
<td>Arnold &amp; Borders, 1977</td>
</tr>
<tr>
<td>LiNbO₃ crystal</td>
<td>50</td>
<td>(4.0-0.8)×10¹⁶</td>
<td>1-4</td>
<td>Annealing in air at 650°C, 30 min</td>
<td>Rahmani et al., 1988, 1989</td>
</tr>
<tr>
<td>LiNbO₃ crystal</td>
<td>360</td>
<td>8.0×10¹⁶</td>
<td>1-4</td>
<td></td>
<td>Deying et al., 1994</td>
</tr>
<tr>
<td>LiNbO₃ crystal</td>
<td>20, 25</td>
<td>(0.5-8.0)×10¹⁶</td>
<td>1-4</td>
<td></td>
<td>Shang et al., 1996</td>
</tr>
<tr>
<td>LiNbO₃ crystal</td>
<td>3×10⁻³</td>
<td>1.8×10¹⁶</td>
<td>1-4</td>
<td></td>
<td>Saito &amp; Kitahara, 2000</td>
</tr>
</tbody>
</table>
### Linear and nonlinear optical properties of silver nanoparticles synthesized in dielectrics by ion implantation and laser annealing

<table>
<thead>
<tr>
<th>Material</th>
<th>As implanted and annealing in air at 500-800°C, 1 h</th>
<th>As implanted and annealing in Ar at 100-1100°C, 30 min</th>
<th>Annealing in Ar at 500-1000°C, 1 h</th>
<th>Annealing in air at 300-500°C, 30 min</th>
<th>Ion dose, ion/cm²</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>200 (2.3-9.0)·10⁶</td>
<td>1-5</td>
<td>150 (0.1-6.0)·10⁶</td>
<td>150 (0.1-6.0)·10⁶</td>
<td>2-3</td>
<td>Rahmani &amp; Townsend, 1989</td>
</tr>
<tr>
<td>SiO₂</td>
<td>65 (1.5-5.0)·10⁶</td>
<td>1-5</td>
<td>65 (1.5-5.0)·10⁶</td>
<td>65 (1.5-5.0)·10⁶</td>
<td>2-3</td>
<td>Rahmani &amp; Townsend, 1989</td>
</tr>
<tr>
<td>SiO₂</td>
<td>20-58, 130, 200 (2.3-9.0)·10⁶</td>
<td>0.6</td>
<td>20-58, 130, 200 (2.3-9.0)·10⁶</td>
<td>20-58, 130, 200 (2.3-9.0)·10⁶</td>
<td>2-3</td>
<td>Rahmani &amp; Townsend, 1989</td>
</tr>
<tr>
<td>SiO₂</td>
<td>65 (1.5-5.0)·10⁶</td>
<td>1-5</td>
<td>65 (1.5-5.0)·10⁶</td>
<td>65 (1.5-5.0)·10⁶</td>
<td>2-3</td>
<td>Rahmani &amp; Townsend, 1989</td>
</tr>
</tbody>
</table>

**Notes:**
- As implanted and annealed in Ar gas at 500-1000°C, 1 h
- Annealing in air at 300-500°C, 30 min
- Some samples annealed in air or 4%H₂
- Other annealing conditions and references are also listed in the table.
### Table 1. Types of dielectric inorganic matrix with silver nanoparticles fabricated by ion implantation combined with post-implantation heat treatment.

<table>
<thead>
<tr>
<th>Matrix Type</th>
<th>SiO$_2$ sol-gel films</th>
<th>SiO$_2$ on Si</th>
<th>SiO$_2$ on Si</th>
<th>SiO$_2$</th>
<th>SiO$_2$</th>
<th>SiO$_2$</th>
<th>SiO$_2$</th>
<th>SiO$_2$</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5-100</td>
<td>10</td>
<td>30</td>
<td>40</td>
<td>60</td>
<td>32-40</td>
<td>0.7, 1.5, 3</td>
<td>200</td>
<td>305</td>
</tr>
<tr>
<td></td>
<td>(5.0-6.0)·10$^{16}$</td>
<td>(1.0-5.0)·10$^{15}$</td>
<td>(1.0-5.0)·10$^{16}$</td>
<td>0.3·10$^{15}$</td>
<td>(0.3-1.0)·10$^{17}$</td>
<td>(0.1-1.0)·10$^{17}$</td>
<td>(1.2-4.7)·10$^{15}$</td>
<td>(0.1-2.0)·10$^{17}$</td>
<td>6.0·10$^{16}$</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>2</td>
<td>3</td>
<td>3-5</td>
<td>3</td>
<td>1.7·10$^{3}$</td>
<td>2.4·10$^{3}$</td>
<td>&lt; 2.5</td>
<td>4.0·10$^{16}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Annealed in air, Ar, O$_2$ or 70%N$_2$+30%H$_2$ at 300-800°C, 1 h</td>
<td>Annealing in Ar at 500-900°C, 1 h</td>
<td>Some samples annealed in 50%N$_2$+50%H$_2$ or in air at 230-800°C, 1 h</td>
<td>Some samples annealed in air at 500°C, 1 h</td>
<td>Annealing in vacuum at 550°C, 20 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1. Types of dielectric inorganic matrix with silver nanoparticles fabricated by ion implantation combined with post-implantation heat treatment. (Abbreviations - ANZT glass, 2Ag₂O·3Na₂O·25ZnO·70TeO₂; ABSG, alkali-borosilicate glass, 0.2K₂O·0.8B₂O₃·3SiO₂; BPYR – borosilicate Pyrex glass; SLSG, soda-lime silicate glass).

<table>
<thead>
<tr>
<th>Material</th>
<th>Range</th>
<th>Concentration</th>
<th>Dose Range</th>
<th>Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta₂O₅ crystal</td>
<td>80-130</td>
<td>6.0·10⁻¹⁶</td>
<td>0.6–6.4</td>
<td>Annealing in Ar at 400°C, 1h</td>
</tr>
<tr>
<td>TiO₂ sol-gel</td>
<td>50</td>
<td>(0.3-1.0)·10⁻¹⁷</td>
<td>2</td>
<td>Annealing in Ar at 300-600°C, 1h</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>(0.1-0.5)·10⁻¹⁷</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Basic physical processes (from left to right) involved in the formation of nanoparticle from an implant vs. the ion dose with regard to surface sputtering under irradiation.

The range of high-dose implantation may be divided into two characteristic dose sub-ranges. In the range $10^{15} \leq F_0 \leq 10^{17}$ ion/cm², the concentration of Ag ions exceeds the solubility limit of metal atoms in matrices and the system relaxes by nucleation and growth of MNPs (Fig. 2), as illustrated in plane (Carles, et al. 2009) and cross-section (Ren, et al., 2007) transmission electron microscopy (TEM) views of SiO₂ glass with ion-synthesized Ag particles (Fig. 3 and 4). The threshold dose value (at which MNPs nucleate) depends on the
type of the dielectric matrix and implant. For example, for 25-keV Ag$^+$-ion implantation into LiNbO$_3$, the threshold dose was found to be $F_0 \approx 5.0 \times 10^{15}$ ion/cm$^2$ (Deying, et al. 1994), for 30-keV silver ions embedded in epoxy glass, $F_0 \approx 10^{16}$ ion/cm$^2$ (Stepanov et al., 1995). The next subrange of high-dose implantation,

Fig. 3. Plan-view TEM image of SiO$_2$ with Ag nanoparticles fabricated at a dose of $6.0 \times 10^{16}$ ion/cm$^2$ and an energy of 3 keV. Fragment from (Carles, et al. 2009).

Fig. 4. Cross-section TEM image of SiO$_2$ with Ag nanoparticles fabricated at a dose of $5.0 \times 10^{16}$ ion/cm$^2$ and an energy of 90 keV. Fragment from (Ren, et al., 2007).

Fig. 5. Plan-view TEM image of silicone polymer-glass with Ag nanoparticles fabricated at a dose of $3.0 \times 10^{16}$ ion/cm$^2$ and an energy of 30 keV. Fragment from (Khaibullin, et al. 1999).

$\sim F_0 \geq 10^{17}$ ion/cm$^2$, leads to the coalescence of already existing MNPs with the formation of either MNP aggregates or thin quasi-continuous films at the dielectric surface. For instance, the irradiation of silicone polymer-glass by 30-keV Ag ions at higher-than threshold-nucleation doses favors the formation of aggregate structures (Fig. 5) (Khaibullin, et al. 1999).
The MNP distribution established in the dielectrics after coalescence or Ostwald ripening may be dramatically disturbed by postimplantation thermal or laser annealing.

3. Laser annealing of glasses with silver nanoparticles

Despite advantages the use of ion implantation for nanoparticle synthesis there have not yet emerged clear mechanisms which allow precisely controlled particles sizes and depth distributions. Latter has a certain drawback, which is the statistically nonuniform depth of penetration of implanted ions into a material (Stepanov et al., 2000d). This leads to a wide size distribution of synthesized nanoparticles not only in the plane parallel to the irradiated surface but to a great extent also over the depth of the sample (Nistor et al., 1993). Dispersion of nanoparticles with respect to sizes leads to a broadening of the SPR optical absorption band accompanied by a decrease in the intensity (Kreibig & Vollmer, 1995). This is also attributable to the dependence of the SPR spectral position on the particle size, i.e. the absorption spectrum in real sample is a superposition of several overlapping less intense bands that corresponding to particles of various sizes. The concern of the modern task is to increase the uniformity of the size distribution of MNPs synthesized by ion implantation using an approach of high-power pulse laser annealing with sequential furnace one. Experience gained from using the laser annealing techniques for various purposes allowed MNPs to be modified in various dielectrics. The main feature most of all the experiments with laser annealing of composites with MNPs is that the laser light was applied directly into the spectral region of the transparency of the dielectric matrix, and consequently, the intense laser pulses were primarily absorbed by the metal particles. Contrary to that, a new approach for annealing was demonstrated, when SLSG with Ag particles was irradiated by a laser light at wavelengths of glass absorption in the ultraviolet region (Wood et al., 1993). When applying high-power excimer ArF (193 nm) laser pulses, a decrease of the reflectance intensity of composite samples was observed. It was suggested that the implanted silver particles in glass can be dissolved and the glass matrix can be modified to be a silver rich metastable new glass phase. If this is correct then the new phase will be the potential to be destabilized to precipitate out the new silver particles in a controlled fashion by furnace.

As seen in Fig. 6 at low energy implantation the silver depth concentration in the SLSG derived from experimental Rutherford backscattering spectrometry (RBS) spattering shows a maximum near the implanted surface of the sample with some penetration to about 60-65 nm (Stepanov et al., 1999a).
An excess of metal atoms in the glass, above the solubility limit, causes nucleation of the nanoparticles. As usually the size distribution of MNPs appears. Additional to this distribution in the implanted sample there is distribution particles in the depth. Since the increase of metal concentration in the depth profile and the sputtering yield depend on implantation time, then the metal particle nucleation and growth will also vary with time and depth. It is obvious that during the implantation the size of the growing particles with depth is “proportional” to the metal filling factor, because they are both determined by the ion concentration profile. Consequently, according to the Fig. 6 the large silver nanoparticles (or/and the higher filling factor) in the glass are close to the implanted surface with small ones in the interior of the implant zone. These features can be recognized in optical spectra of dielectrics with implanted nanoparticles. As example, transmittance and reflectance data of the non-implanted and implanted glass are presented in Fig. 7 (Stepanov et al., 1999a).

Fig. 7. Optical transmittance and reflectance of the silver implanted and original SLSG with a dose of $7 \times 10^{16} \text{ion/cm}^2$ and an energy of 60 keV. Reflectance was measured from both the implanted and rear faces of the sample.
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The transmission spectrum of implanted glass is maximized near 430 nm and the shape of the spectral curve is almost symmetrical. The reflectance spectra of same sample are more complex and, although the transmission must be the same whether the glass is viewed from the implanted or the reverse face, the shapes of the reflectivity curves differ. Overlapping peaks of reflectance spectra measured from the implant face of the samples exhibit a shoulder at about 430 nm, on the side of a clearly determined maximum at 490 nm, whereas reflectivity from the rear face appears to have a simpler peak at longer wavelengths near 500 nm. The contrast between the spectrum available from transmittance and reflectance of the implanted glass is recognized as coming from the non-uniform silver profile and size distribution of the nanoparticles in the implanted glass (Fig. 6). Since the distribution pattern is not symmetric, the reflectivity determined from the ion implanted and rear faces of the sample differ (Fig. 7), and the reflected intensity from a particular layer depends on their local absorption in the depth. The atomic force microscope (AFM) images implanted surfaces of the same samples shown in Fig. 8 (Stepanov et al., 1998). As seen from the figure the implanted surface is smoother (roughness) and there are many hemispherical hills on this surface with an average diameter of approximately 100-150 nm. There are no such protrusions on the unimplanted sample. The reason for the existence of surface hills is assumed to be from a sputtering of irradiated glass during implantation, which leads to unequal ejection of ions of different elements from the surface, exposing the synthesized nanoparticles in the sub-surface glass. The sputtered glass thickness is typically of the order of tens of nanometers for the present ion dose (Hole et al., 1998), and hence, the synthesized buried MNPs appear near to the glass surface in the implanted sample. Consequences of the excimer laser pulse with nanosecond pulse width and high beam intensity are heating, melting and/or vaporisation (ablation) of material on a time scale of nanoseconds to microseconds. The excimer laser treatment has been applied to many glasses, but there is less information on high-power pulse laser interaction with dielectrics containing metal nanoparticles. In the present case the energy density is lower than the value of the ablation threshold for the SLSG, which was determined to be about 5 J/cm².
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(Buerhop et al., 1990). Also, the excimer laser is characterised by a UV-wavelength, which is much longer than the typical sizes of the nanoparticles formed by ion implantation. Hence, present metal/glass composites may be considered similar to be a homogeneous material for light propagation (Kreibig & Vollmer, 1995). This is a simplification, which is true generally for low intensity light, but it gives an estimate of the optical penetration depth as \( \alpha^{-1} \) of the laser pulses into the composite material, where \( \alpha \) is the linear absorption coefficient. An intense laser pulse is absorbed and relaxed into heat into the surface SLSG layer of a thickness of \( \alpha^{-1} \), which is several microns (Townsend & Olivares, 1997), i.e., deeper than the thickness of the implanted layer (Fig. 6).

The optical spectral result of pulse laser treatment by 5 pulses of a KrF excimer laser with pulse length of 25 ns full-width at half-maximum at a wavelength of 248 nm with the total released energy of 0.2 J/cm² on the optical spectra of the Ag-implanted glass is presented in Fig. 9 (Stepanov et al., 2001). Applied laser pulses did not change the reflectance and transmittance spectra of the non-implanted SLSG, but for implanted sample the location of the transmittance minimum shifts slightly towards shorter wavelengths, and the transmittance in peak position increases from 16 to 23% (Fig. 9a). Remarkable change was found in the reflectance spectra, where in the case of the implanted surface, the peak of the overlapping bands shifts continuously from 490 to 450 nm with modifications in the

![Optical spectra of SLSG after silver implantation](image)

Fig. 9. Optical spectra of the SLSG after silver implantation as in Fig. 7 and the implantation followed with laser treatment (0.2 J/cm²): (a) transmittance; (b) reflectance measured from the implanted face; (c) reflectance measured from rear faces of the sample.

shape of the envelope of the bands, which become narrower (Fig. 9b). The reflectance intensity falls from 38 to 27%. However, for reflectance from the rear face of the same
sample (Fig. 9c) there is only a decrease of the intensity to a 13 % maximum, which is at the same initial wavelength as in the implanted sample.

For composite materials with MNPs effective-medium theories (Maxwell-Garnett, Bruggeman, etc) can be considered (Kreibig & Vollmer, 1995). According to this approach, the measured optical intensities corresponding to the implanted glass (Figs. 7 and 9) are determined mainly by the near-surface layer, where there is the largest metal filling factor, and also the largest nanoparticles. The smaller filling factors (and smaller nanoparticles) that exist at the other depths effectively only influence a smearing of the optical spectra. Moreover, consistent with effective-medium considerations, a decrease of the filling factor is accompanied by movement of the optical peak position to shorter wavelengths, as is observed in Fig. 9. Thus, a decrease of the filling factor in the composite resulting from laser treatment suggests there is a size reduction of all the silver nanoparticles, and again the biggest nanoparticles are localized near the SLG surface. The difference between reflectance spectra from implanted and rear faces of laser treated sample (Fig. 9 b, c) emphasizes the existence of a non-symmetrical depth distribution of the Ag nanoparticles as being similar to the distribution in the implanted sample.

As presented in Fig. 10, (note an increased magnification of ten times in the direction perpendicular to plane of the figure), it is seen that there are a lot of clearly defined hills

![Fig. 10. An AFM image as a top view under lateral illumination of the surface of SLSG Ag-implanted with a dose of 7·10^{16} ion/cm^2 and an energy of 60 keV followed with irradiation with an excimer laser (0.2 J/cm^2). The step along the X and Y axes id 100 nm, and the step along the Z axis is 40 nm.](www.intechopen.com)

(believed to be silver particles) on the glass surface whose size is one order smaller in contrast to large hills on the implanted glass surface in Fig. 8 (Stepanov et al., 1998). The Ag MNPs accumulate effect on the laser irradiated surface of glass is result of melting implanted composite layer and some desorption of glass material under the laser pulses, which exposes the melted metal particles after their solidification. Hence, the first of the conclusions from the present data on excimer laser treatment of implanted glass is the reduction of the size of the silver nanoparticles, and second is the existence of some asymmetry in their depth distribution (Fig 9b, c). To recognize the mechanisms by which the changes occur for strongly absorbed excimer laser pulses the thermal propagation after the laser-irradiation must be considered. The laser heating is traditionally characterized by the heat diffusion length, \( l(t) = (D \cdot t)^{1/2} \), where \( D \) is the heat diffusivity, and \( t \) is the laser pulse duration. In the present experiment with laser pulses of 25 ns, the heat propagation is
approximately \( l(t) = 115 \) nm, that is shorter than the \( \alpha^{-1} \), i.e., the temperature rise is no longer controlled by the diffusion of the heat. However, the \( l(t) \) surpasses the depth of the implanted Ag nanoparticles. As was estimated earlier (Townsend & Olivares, 1997), the temperature at the surface of laser treated SLSG reaches values exceeding \( \sim 700^\circ \text{C} \), which is equivalent to the SLSG melting temperature. Under these temperature conditions there is also a possibility for melting small silver particles, because their melting temperature is drastically decreased, for example, to \( \sim 400^\circ \text{C} \) for sizes < 30 nm, compared with the bulk metal melting temperature of \( 960^\circ \text{C} \) (Castro et al., 1990). The time scale of electronic relaxation and energy transfer to the lattice vibrations in the metal particles is several orders faster than in the surrounding glass medium. Therefore, during the interaction of the excimer laser pulse with the metal/glass composite, the Ag nanoparticles are heated and melted more quickly than solidification of the melted glass can occur. Atomically dispersed Ag released from nanoparticles enters into the glass melt, and immediately diffuse throughout all the heated thickness of the laser treated substrate. In principle in this could lead to a uniform metal distribution, where the silver atom concentration exceeds the solubility value in the solid glass. However, following glass solidification spreading from the depth to the surface, as heat from the laser pulse penetrates into the depth of the sample, the cooling part of the annealing cycle will stimulate new nucleation and regrowth of metal particles. In this case, the possibility of regrowth of metal particles will depend on competition between regrowth and the cooling speed of the moving solidification front, resulting in a new non-uniform size distribution of new MNPs over a depth scale similar to that after ion implantation. Obviously, under some conditions the metal particles may be dispersed into separate metal ions and/or into such small units that they cannot display nanoparticle type optical properties. As shown here, subsequent high power excimer laser pulse treatments of the ion implanted layer may be used to melt, and/or regrow, the MNPs within the insulator medium. Overall this results in a tighter distribution of small particles. The laser treatments have slightly reduced, but not completely removed evidence for a non-symmetric depth distribution of the silver particles. The Ag-insulator composite material is complex, and so a much wider range of laser pulse conditions, and more data on the cooling rates are required to fully model the changes in the size distributions, which can occur.

4. Nonlinear optical properties of ion-synthesized silver nanoparticles

The Ag nanoparticles doped in different dielectrics demonstrate variable nonlinear optical properties (Palpant, 2006). The interest on such structures is based on the prospects of the elaboration of optical switches with ultrafast response, optical limiters, and intracavity elements for mode locking. Ag nanoparticles have an advantage over another metal nanoparticles (i.e., gold and copper) from the point of view that the surface plasmon resonance energy of Ag is far from the interband transition energy. So, in the silver nanoparticle system it is possible to investigate the nonlinear optical processes caused solely by SPP contribution. It should be noted that previous studies of nonlinear optical parameters of silver nanoparticles-doped glasses were mostly focused on determination of third-order nonlinear susceptibility \( \chi^{(3)} \). The saturated absorption in silicate glasses doped with Ag nanoparticles at wavelength of 532 nm and their dependence on laser radiation intensity are considered at present review.
The Ag nanoparticles ion-synthesized in SLSG (Ag:SLSG) and (Ag:SiO$_2$) demonstrate the SPP band with minimum transmission in the range of 410–440 nm (Fig. 11).

![Fig. 11. Optical transmittance of the Ag nanoparticles formed in SLSG and SiO$_2$ by implantation with a dose of 4 $10^{16}$ ion/cm$^2$ and an energy of 60 keV.](image)

It was previously predicted that silver-doped glasses possess by saturated absorption. The spectral dispersion of the imaginary part of third-order susceptibility $\chi^{(3)}$ of silver-doped glass matrices was analyzed and it was shown that $\chi^{(3)}$ was negative in the spectral range of 385 - 436 nm (Hamanaka et al., 2000). The nonlinear absorption coefficient $\beta$ is also negative in the case of saturated absorption.

![Fig. 12. Normalised transmittance Ag:SLSG (1) and Ag:SiO$_2$ (2) samples at laser radiation intensity of $I_0 = 2.5 \times 10^9$ W/cm$^2$. Solis lines show theoretical fittings.](image)

The normalized transmittance dependences of Ag:SLSG and Ag:SiO$_2$ samples measured using open aperture Z-scan scheme (Sheik-Bahae et al., 1990) at laser radiation intensity of...
$I_0 = 2.5 \times 10^9 \text{ W/cm}^2$ and pulse duration of 55 ps is presented in Fig. 12. The transmission of samples was increased due to saturated absorption as they approached close to the focal plane. The theoretical fitting was done by the method described early (Ganeev et al., 2004b). After fitting of experimental data the $\beta$ are $-6.7 \times 10^{-5}$ cm/W in Ag:SLSG and $-3.6 \times 10^{-5}$ cm/W in Ag:SiO$_2$. Coefficient $\beta$ can be presented as $\beta = \alpha/\text{s}$, where $\alpha$ is the saturated intensity. The values of $I_s$ are $1.1 \times 10^{10}$ and $1.4 \times 10^{10}$ W/cm$^2$, also the $\text{Im}\chi^{(3)}$ are $-2.4 \times 10^{-8}$ and $-1.3 \times 10^{-8}$ esu in Ag:SLSG and Ag:SiO$_2$, respectively.

In Figs. 13 and 14 values of $\beta$ in dependence of laser intensity varied from $10^9$ to $2 \times 10^{10}$ W/cm$^2$ are presented. As seen from the figures there is a decrease of $\beta$ with higher intensities. In particularly, a 21- and 12-fold decrease of $\beta$ was measured at $I_0 = 1.15 \times 10^{10}$ W/cm$^2$ for Ag:SLSG and Ag:SG, respectively, compared to $\beta$ detected at $I_0 = 1 \times 10^9$ W/cm$^2$.

![Graph](image)

Fig. 13. Coefficient $\beta$ of Ag:SLSG in dependence of laser intensity.

The variations of transmission in similar MNP structures were attributed in some cases to the fragmentation (Kurata et al., 1998; Link et al. 1999; Mafune et al., 2002), or fusion (Chandrasekharan et al., 2000) of nanoparticles following the photothermal melting. It was reported about the alteration of the sign of nonlinear refractive index of small Ag clusters embedded in SLSG (Osborne et al., 1998). They noted that thermal effects could change the properties of nanoclusters. The transparency in these samples was associated with oxidation of Ag nanoparticles. However, no irreversible changes of transmittance were observed in present experiments.

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The reverse saturated absorption can be responsible for the decrease of negative nonlinear absorption of Ag nanoparticles and it could be assumed that in the case of picosecond pulses the reverse saturated absorption starting to play an important role in the overall dynamics of nonlinear optical transmittance of metal nanoparticles contained compounds, taking into account the saturation of intermediate transitions responsible for saturated absorption. Thus, saturated absorption in Ag:SLSG and Ag:SiO$_2$ was dominated at small intensities and decreased with the growth of intensity due to influence of competing effects, whereas the selfdefocusing at low intensities was changed to self-focusing at high intensities. The possible mechanism of the decrease of Im$\chi^{(3)}$ is the influence of nonlinear optical processes with opposite dependences on laser intensity, also such as two-photon absorption (Sheik-Bahae et al., 1990). The wavelength range corresponded to the interband transitions in Ag is located below 320 nm, so the two-photon absorption connected with interband transitions can be involved in the case of 532 nm radiation. The possibility of two-photon absorption due to interband transition of photoexcited electrons was previously demonstrated for Ag particles (Magruder et al., 1994). The three-photon absorption connected with interband transition for Ag nanoparticles was analysed in (Kyoung et al., 1999). Thus, saturated absorption in Ag:SLSG and Ag:SiO$_2$ was dominated at small intensities and decreased with the growth of intensity due to influence of competing effects, whereas the selfdefocusing at low intensities was changed to self-focusing at high intensities.

5. Acknowledgements

6. References


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Nanotechnology will be soon required in most engineering and science curricula. It cannot be questioned that cutting-edge applications based on nanoscience are having a considerable impact in nearly all fields of research, from basic to more problem-solving scientific enterprises. In this sense, books like “Silver Nanoparticles” aim at filling the gaps for comprehensive information to help both newcomers and experts, in a particular fast-growing area of research. Besides, one of the key features of this book is that it could serve both academia and industry. “Silver nanoparticles” is a collection of eighteen chapters written by experts in their respective fields. These reviews are representative of the current research areas within silver nanoparticle nanoscience and nanotechnology.

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