

Vacuum 64 (2001) 169-177



www.elsevier.com/locate/vacuum

Interaction of high-power excimer-laser pulses with soda-lime silicate glass containing ion-implanted metal nanoparticles

A.L. Stepanov^{a,b,*}, D.E. Hole^c, A.A. Bukharaev^b

^a Physikalisches Institut A der RWTH, Aachen Technical University, Sommerfeldstrasse 14, Turm 28, 52056 Aachen, Germany ^b Kazan Physical-Technical Institute RAS, 420029 Kazan, Russian Federation ^c School of Engineering, Pevensey Building, University of Sussex, Brighton, BN1 9QH, UK

Abstract

Silver nanoparticles have been synthesised by ion implantation in soda-lime silicate glass at 60 keV at a dose of 7.0×10^{16} ion/cm² with a current density of $10 \,\mu$ A/cm² at a temperature of 50°C. The size distribution of the metal particles was monitored by optical transmittance and reflectance registered from both the implant and rear face of the samples, together with atomic force microscopy measurements and Rutherford backscattering spectroscopy. The differences between the data indicate the asymmetry in the size distribution with depth. Annealing of the glasses was made by pulses from a high-power KrF excimer laser. Pulsed laser treatment has been used at a wavelength of 248 nm and a pulse length of 25 ns. The laser was partially focused on the sample area to yield a pulse fluence, of 200 mJ/cm². Several pulses of the equal energy density were accumulated in the same area of the sample. Changes induced by pulsed laser exposure suggest that there are both reductions in average size of the silver nanoparticles, and some longer range dissolution of silver into the glass. The treatments have reduced, but not removed evidence for a non-symmetric depth distribution of the silver particles. The present work discusses the possibilities of metal regrowth changes for control and modification of metal nanoparticle sizes. © 2001 Elsevier Science Ltd. All rights reserved.

PACS: 78.66.V; 78.66.J; 61.80.B

Keywords: Silver; Soda-lime silicate glass; Ion implantation; Nanoparticles; Transmittance; Reflectance; Laser treatment

1. Introduction

The interaction of high-power laser pulses with dielectrics containing metal nanoparticles for modification of their optical properties has been the subject of intense investigation for the last few years. This interest was conditioned by both a development of microelectronics based on composites with nanoparticles and also on a need for a fundamental understanding of the influence of high-power light on the properties of non-uniform composite media. In particular, such research is directed to the changes in the shape, the size, the size distribution, and the structure of the nanoparticles. As an example, it is possible to mention experiments with the Nd:YAG (355, 532 or 1064 nm) laser treatment of an aqueous solution with silver particles produced by a chemical reduction method [1] or photochromic aluminosilicate glass containing metal nanoparticles [2]

^{*}Corresponding author. Tel.: +49-241-80-7208; fax: +49-541-8888-331.

E-mail address: anstep@dionis.kfti.knc.ru (A.L. Stepanov).

and a study of silver clusters embedded into the soda-lime glass formed by helium-ion irradiation of ion-exchange waveguides [3,4]. Also there is information about annealing of plasma metal/ polymer layers by a Nd: YAG laser (1064 nm) [5]. The work relates to many composite materials that are of interest in studies of laser treatments of insulators containing metal nanoparticles, for example, as produced by ion implantation for different optical devices [6,7]. Depending on the laser wavelength, the power density or the pulse length, composite materials made by ion implantation can be successfully modified. It was shown that Nd: YAG laser irradiation in the visible and near-IR region converts implanted spherical titanium silicide particles into ellipsoidal ones in silica and soda-lime glass [8], or that there are changes of the internal crystallographic structure of implanted iron particles after ruby laser (690 nm) treatment [9].

The main feature of all the experiments described above is that the laser light was applied directly into the spectral region of transparency of the dielectric matrix, and consequently, the intense laser pulses were primarily absorbed by the metal particles. Contrary to that, some years ago [10], a new approach for annealing was demonstrated, when float glass with silver particles was irradiated by a laser light at wavelengths of glass absorption in the ultraviolet region. When applying highpower excimer ArF (193 nm) laser pulses, a decrease of the reflectance intensity of composite samples was observed. Potentially, this new technique gives a variety of possibilities for controlled change of optical properties of implanted dielectrics, as suggested for the case of the combined laser annealing of float glass implanted with metal ions [11,12]. However, a number of questions regarding mechanisms of such modifications and interactions of high-power light with non-uniform composite materials are now just beginning to be understood.

2. Experimental

The implantation of soda-lime silicate glasses (SLSG) has been performed with Ag^+ ions at

60 keV, to a dose of 7.0×10^{16} ion/cm² at a beam current density of $10 \,\mu\text{A/cm}^2$ using a Whickham ion implanter. The bulk temperature of the samples $(3 \times 3 \,\text{cm}^2)$ was maintained at about 50°C during the implantation. The implantation was carried out in a controlled vacuum of 10^{-5} Torr. The approximate chemical composition of the glass (from Societa Italiana Vetro) is 70% SiO₂, 20% Na₂O, and 10% CaO.

Pulsed laser treatment has been made by a KrF excimer laser (ATLEX 210) with a wavelength of 248 nm and pulse length of 25 ns full-width at halfmaximum, which was partially focused on the sample area of $10 \times 10 \text{ mm}^2$. Three pulses of equal energy density of 200 mJ/cm^2 were accumulated in the same area of the sample at a repetition rate of 1 Hz. Pulse-to-pulse energy variation was typically within $\pm 2\%$, and the energy density was determined with a laser power meter DGX FL150A-EX-RP (OPHIR). Reproducibility of the laser effect was checked with five equivalent samples, which were implanted and treated by laser pulses at same conditions. Data corresponding to one sample are presented later in the article.

Depth analyses were made by Rutherford backscattering spectrometry (RBS) with an analysing beam of ⁴He⁺ with an energy of 1.89 MeV, at a total dose of 50 μ C using a Van de Graaff accelerator. The backscattering collection angle and detector acceptance angles were $\theta = 150^{\circ}$ and $\Omega = 0.33$ msr. The energy resolution was 21 keV, ~10 channels, and beam currents were limited to about 10 nA. Some spectra were converted to depth scale from the channel numbers using RBS 'Data Furnace' computer programme from the University of Surrey [13].

Optical reflectance and transmittance spectra at normal incidence of the light, with an analysing beam of 4 mm diameter, were recorded with a Monolight fibre-optical system in the range from 350 to 800 nm at room temperature. The repeatability of the optical spectra for the analysed samples was about 2%.

Topographic profiling of the as-implanted and laser treatment surface was performed with an atomic force microscope (AFM) P4-SPM-MDT, working in tapping mode. Vertical displacement of the sensitive cantilever in the microscope was registered by deflection of the lower power laser beam reflected from the probe tip. The samples were clamped on a tube piezoscanner providing a scanning area of $3.7 \times 3.7 \,\mu\text{m}^2$ and they were measured in an air environment. The constant force-operating mode was employed and a conventional feedback loop circuit was used to maintain the constant force at less than 100 nN.

3. Results and discussion

3.1. Non-uniformity in structure of the glass with ion-implanted metal nanoparticles

Low energy implantation of metal ions, as in our case, leads to a non-uniform distribution in the glass, which is different from the Gaussian profile traditionally predicted by statistical theory, primarily because of the effective sputtering from the substrate surface during the irradiation [14,15]. As seen in Fig. 1, the silver depth concentration in the SLSG derived from experimental RBS spectra shows a maximum near the implanted surface of the sample with some penetration to about 65 nm. This characterises the implanted sample as a depth non-uniform metal/insulator object [16].

An excess of metal atoms in the glass, above the solubility limit, causes nucleation of the nanoparticles. As usual, a size distribution of metal nanoparticles is present. Added to this distribution

12 10 Atomic fraction (at. %) 8 6 4 2 40 50 0 10 20 30 60 70 Depth (nm)

Fig. 1. The depth distribution of silver derived from the RBS spectrum for ion implantation with a dose of 7×10^{16} ion/cm² into the soda-lime silicate glass.

in the implanted sample, there is a distribution of particles in the depth. Since the increase of metal concentration in the depth profile and the sputtering yield depend on implantation time, 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 Fig. 1 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 are also confirmed by an electron microscopy study for similar implantations of metal ions into glass [17].

Noble metal nanoparticles in a dielectric medium show optical absorptance and reflectance determined by collective electron oscillations called the surface–plasma resonance [18]. Transmittance and reflectance data of the non-implanted and implanted glass are presented in Fig. 2. The transmission spectrum of implanted glass is maximised 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 recognised as coming from the non-uniform silver profile and size distribution of the nanoparticles in the implanted glass (Fig. 1). Since the distribution pattern is not symmetric, the reflectivity determined from the ion implanted and rear faces of the sample differ (Fig. 2), and the reflected intensity from a particular layer depends on the their local absorption in the depth [6].

The AFM images of the non-implanted and implanted samples are shown in Figs. 3a-c. As seen from these figures, compared with the initial glass, the implanted surface is smoother (roughness), which is typical for irradiated glasses [19]. However, 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 synthesised nanoparticles in the sub-surface glass. The sputtered glass thickness is typically of the order of tens of nanometers for the present ion dose [15], and hence, the synthesised buried metal nanoparticles appear near the glass surface in the implanted sample (Fig. 1).

3.2. Excimer-laser treatment of the glass with ion-implanted metal nanoparticles

In general, the mechanisms of laser processing depend on the parameters of the laser beam and the physical-chemical properties of the material. The primary interactions between light and matter are non-thermal and lead to an electronic or vibrational photoexcitation. A prediction of how the laser processing will develop through thermal (photothermal) or non-thermal (photochemical) processes depends particularly on the values of the relaxation times involved. In laser processing for the present composite materials, the relevant excitations and conversions can be classified into those of the glass-substrate and the metal nanosize inclusions. Irradiation with a high-power excimer laser at the wavelength of 248 nm (5 eV) couples directly through the spectral absorption of the SLSG, as the glass has a smaller energy bandgap $(\sim 3.5 \text{ eV})$. This creates electron-hole pairs by exciting an electron from the valence into the conduction band. In metals, both conduction and valence-band electrons may participate in laser excitations. The number and energy of absorbed photons immediately establishes the temperature rise in a laser-irradiated metal, whereas the number of valence to conduction-band excitations establishes the initial density of electron-hole pairs in an insulator [20]. In a metal, the time between electron-electron collisions is of the order of 10^{-14} - 10^{-13} s and electron-phonon relaxations are typically one to two orders of magnitude slower [21]. In non-metals, interband electronic excitations range from 10^{-12} to 10^{-6} s [20]. Overall, most of these times are short in comparison to the pulse duration (25 ns) of the laser used here, and so the laser energy can be viewed as relaxing directly into a heating of the metal/glass composite. Thus, our following consideration of the laser modifications will be based on the effects of thermalisation processes.

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 [22,23], but there is less information on high-power pulse laser interaction with insulators containing metal nanoparticles. In the present study, the energy density was lower than the value of the ablation threshold for the SLSG, which was determined to be about 5 J/ cm^{2} [23]. 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 that of a homogeneous material for light propagation [18]. This is a simplification, which is true generally for



Fig. 3. An atomic force microscope image of the surface of soda-lime silicate glass: (a) the glass before treatment; (b) the glass after Ag-ion implantation; (c) the glass after ion implantation followed with laser pulses. In (c), magnification is increased ten times in the direction perpendicular to plane of the figure according to (a) and (b) ones.

low intensity light, but it gives an estimate of the optical penetration depth (α^{-1}) of the laser pulses into the composite material, where α is the linear absorption coefficient. An intense laser pulse is absorbed and relaxed into heat in the surface

SLSG layer of a thickness of α^{-1} , which is several microns [11], i.e., deeper than the thickness of the implanted layer (Fig. 1).

Applied laser pulses did not change the reflectance and transmittance spectra of the nonimplanted SLSG. The result of pulse laser treatment on the optical spectra of the implanted glass is presented in Fig. 4. The location of the transmittance minimum shifts slightly towards shorter wavelengths, and the transmittance in peak position increases from 16% to 23% (Fig. 4a). 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 shape of the envelope of the bands, which become narrower (Fig. 4b). The reflectance intensity falls from 38% to 27%. However, for reflectance from the rear face of the same sample (Fig. 4c), there is only a decrease of the intensity to a 13% maximum, which is at the same initial wavelength as in the implanted sample.



Fig. 4. Optical spectra of the soda-lime glass after silver implantation and the implantation followed with laser treatment: (a) transmittance; (b) reflectance measured from the implanted face; (c) reflectance measured from rear faces of the sample.

In practice, for the size evaluation of the metal nanoparticles, Mie theory is often employed, which is used also to describe qualitatively the laser modification of the metal-nanoparticle sizes in the implanted glass. However, Mie theory is really only properly applicable for highly separated and non-interacting particles, i.e., if the metal filling factor is extremely small (from 10^{-3} to 10^{-5}) [18]. As seen from Fig. 1, this value is much smaller than in real implanted samples. For composite materials with large filling factors, and when electrodynamic particle-particle interactions are dominant, alternative effective-medium theories (Maxwell-Garnett, Bruggeman, etc.) should be considered [18]. According to these models, the measured optical intensities corresponding to the implanted glass (Figs. 2 and 4) are determined mainly by the near-surface layer, where there is the largest metal filling factor, and also the largest nanoparticles (Fig. 1). 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. 4. Thus, a decrease of the filling factor in the composite resulting from laser treatment suggests that there is a size reduction of all the silver nanoparticles, and again the biggest nanoparticles are localised near the SLSG surface. The difference between reflectance spectra from implanted and rear faces of laser-treated sample (Figs. 4b and c) emphasises the existence of a non-symmetrical depth distribution of the silver nanoparticles as being similar to the distribution in the implanted sample [24].

RBS measurements (Fig. 5) show that the laser treatment causes a loss of 30% of the entire silver content in the samples, because of some evaporation of silver from the sample. Reduction of total silver concentration (filling factor) in the glass leads to decrease in the reflectance intensities measured both from implanted and rear side of sample (Fig. 4). These data are consistent with an earlier observation of the thermal metal dissolution from the heated surface of the float glass with implanted silver nanoparticles after excimer-laser



Fig. 5. The RBS spectrum for the silver-implanted glass before and after laser treatment.

irradiation [10], and with a later study of silica glass with implanted bismuth particles [25]. At the same time, as seen in Fig. 5, the concentration peak position was not shifted, but the distribution of silver atoms is broadened compared with that of the as-implanted sample and is explained by diffusion into the depth of the SLSG. All these processes decrease the filling factor.

The assumption about the size-reduction is in agreement with AFM measurements of lasertreated samples. As presented in Fig 3c (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 (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. 3b. The silver accumulate effect on the laser-irradiated surface of glass is a result of melting implanted composite layer, 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 (Figs. 4b and c).

To recognise the mechanisms by which the changes occur for strongly absorbed excimer-laser pulses, the thermal propagation after the laserirradiation must be considered. The laser heating is

traditionally characterised by the heat diffusion length, $l(t) = (Dt)^{1/2}$, 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 α^{-1} , i.e., the temperature rise is no longer controlled by the diffusion of the heat. However, l(t) surpasses the depth of the implanted silver nanoparticles. As was estimated earlier [11], the temperature at the surface of laser-treated soda-lime glass reaches values exceeding 700°C which is equivalent to the SLSG melting temperature. Under these temperature conditions, there is also a possibility of melting small silver particles, because their melting temperature is drastically decreased, for example, to $\sim 400^{\circ}$ C for sizes < 30 nm, compared with the bulk metal melting temperature of 960°C [26]. As was noticed above, 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 silver nanoparticles are heated and melted more quickly than solidification of the melted glass can occur. Atomically dispersed silver released from nanoparticles enters into the glass melt, and immediately diffuses throughout all the heated thickness of the laser treated substrate. In principle, in time, 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 metal nanoparticles 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. The present

consideration of the melting of the metal nanoparticles is also suitable for a description of the reflectance modification discussed in the previous article [10]. In alternative interpretations of the data in that article, the authors of [27] preferred to see the data as evidence for en evaporation of metal atoms from the surface of nanoparticles, which resulted in shrinkage of the average size. Similarly, in [25], for the case of the implanted bismuth nanoparticles in silica-glass, treated with a KrF excimer laser, the melting of the particles was completely ignored, though the melting point of the bismuth nanoparticles is very low ($\sim 140^{\circ}$ C for the size of 20 nm [28], and primarily the feature was thought to be the thermal evaporation atoms from the particles. Evaporation is of course one of the thermal consequences from high-power laser processing and leads to some ablation of the metal and film surface, and dissolution of metal inclusions on non-metal substrates, for example in [27]. However, in the case of implanted composite material, the metal nanoparticles are not only localised immediately at the glass surface, but also extend into the depth of heated solid media. Hence, processes of atom evaporation from the nanoparticles will be very different from those limited to particles on the outer surface. Therefore, the description of the size modification of the implanted metal nanoparticles based on a particlemelting approach seems reasonable.

4. Conclusions

Metal ion implantation in glass invariably results in a very wide distribution of nanoparticle sizes that vary with the depth. As firstly shown here, subsequent high power excimer-laser pulse treatments of the ion-implanted layer may be used to melt, and/or regrow, the metal nanoparticles 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 silver-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.

Acknowledgements

We are grateful to the Royal Society Ex-Quota Postdoctoral Visit Programme for financial support of Dr. A. Stepanov at University of Sussex (UK), also the EPSRC, to the Brite Euram contract BE 4427 (AMENIDAD) and the RFBR 99-02-17767 and 00-15-96615. We wish to thank Mr. N.I. Nurgazizov for help with AFM measurements and Prof. P.D. Townsend for helpful discussion and comments on the present results.

References

- Takami A, Yamada H, Nakano K, Koda S. Jpn J Appl Phys 1996;35:L781.
- [2] Akella A, Honda T, Liu AY, Hesselink L. Opt Lett 1997;22:967–70.
- [3] Gonella F, Mattei G, Mazzoldi P, Cattaruzza E, Arnold GW, Bertoncello G, Haglund Jr. RF. Appl Phys Lett 1996;69:3101–4.
- [4] Osborne Jr. DH, Haglund Jr. RH, Gonella F, Garrido F. Appl Phys B 1998;66:517–22.
- [5] Werner J, Heilmann A, Stenzel O. Int J Elect 1994;77:945– 51.
- [6] Townsend PD, Chandler PJ, Zhang L. Optical effects of ion implantation. Cambridge: University Press, 1994.
- [7] Haglund Jr. RF. Mater Sci Eng A 1998;253:275-83.
- [8] Battaglin G, Borsella E, Cattaruzza E, Gonella F, Haglund Jr. RF, Mattei G, Mazzoldi P, Osborne DH, Polloni Jr. R. Nucl Instrum Methods B 1998;141:274–81.
- [9] Bukharaev AA, Kazakov AV, Manapov RA, Khaibullin IB. Sov. Phys. Solid State 1991;33:578–88.
- [10] Wood RA, Townsend PD, Skelland ND, Hole DE, Barton J, Afonso CN. J Appl Phys 1993;74:5754–7.
- [11] Townsend PD, Olivares J. Appl Surf Sci 1997;109:275-84.
- [12] Can N, Townsend PD, Hole DE, Snelling HV, Ballestors JM, Afonso CN. J Appl Phys 1995;78:6737–45.
- [13] Barradas NP, Jeynes C, Webb RP. Appl Phys Lett 1997;71:291–4.
- [14] Townsend PD, Kelly JC, Hartley NEW. Ion implantation, sputtering, and their applications. London: Academic Press, 1976.
- [15] Hole DE, Stepanov AL, Townsend PD. Nucl Instrum Methods B 1999;148:1054–8.
- [16] Stepanov AL, Zhikharev VA, Hole DE, Townsend PD, Khaibullin IB. Nucl Instrum Methods B 2000;166:26–31.

- [17] Nistor LC, van Landuyt J, Barton JB, Hole DE, Skelland ND, Townsend PD. J Non-Cryst Solids 1993;162:217–24.
- [18] Kreibig U, Vollmer M. Optical properties of metal clusters. Berlin: Springer, 1995.
- [19] Bukharaev AA, Janduganov VM, Samarsky EA, Berdunov NV. Appl Surf Sci 1996;103:1198–205.
- [20] Baüerle D. Laser processing and chemistry. Berlin: Springer, 1996.
- [21] Bigot JY, Merle JC, Cregut O, Daunois A. Phys Rev Lett 1995;75:4702–6.
- [22] Arai K, Imai H, Hosono H, Abe Y, Imagawa H. Appl Phys Lett 1988;53:1891–4.

- [23] Buerhop C, Blumenthal B, Weissmann R, Lutz N, Biermann S. Appl Surf Sci 1990;46:430–6.
- [24] Stepanov AL, Hole DE, Townsend PD. J Non-Cryst Solids 1999;244:275–9.
- [25] Park SY, Isobe T, Senna M, Weeks RA, Zuhr RA. Appl Phys Lett 1998;73:2687–90.
- [26] Castro T, Reifenberger R, Choi E, Andres RP. Phys Rev B 1990;42:8548–57.
- [27] Bosbach J, Martin D, Stietz F, Wenzel T, Träger F. Appl Phys Lett 1999;74:2605–8.
- [28] Itoigawa H, Kamiyama T, Nakamura Y. J Non-Cryst Solids 1997;210:95–101.