

# Optical properties of small silver particles embedded in soda-lime silica glasses

MARIA SUSZYŃSKA\*, TERESA MORAWSKA-KOWAL, LUDWINA KRAJCZYK

Institute of Low Temperature and Structure Research, Polish Academy of Sciences,  
ul. Okólna 2, 50-950 Wrocław, Poland

\*Corresponding author: [Maria.Suszynska@int.pan.wroc.pl](mailto:Maria.Suszynska@int.pan.wroc.pl)

The optical characteristics of silver nanoparticles embedded in a surface layer of commercial soda lime silica glass have been analysed. Additional results were obtained by the transmission electron microscopy observations and the selective area electron diffraction patterns. In this report, we have shown the effect of deviation from the spherical shape and non-homogeneous distribution on the optical characteristics of the Ag nanocrystals embedded in the dielectric matrix under study.

Keywords: soda-lime silica glass, ion exchange, silver nanoparticles, optical absorption, transmission electron microscopy.

## 1. Introduction

Embedding silver-clusters of nanometer dimensions in a dielectric matrix, *e.g.*, the oxide glasses, provides a simple way to study the linear and nonlinear optical properties of the systems thus composed [1]. The main feature of the linear optical response of these new materials is the collective excitation of the free conduction band electrons, known as the surface plasmon resonance (SPR), and observed in the visible region of the optical spectra [1]. In addition to the basic interest, the presence of a quantum-size behaviour has attracted much attention in view of the potential photonic applications of the systems mentioned [2, 3].

In the present communication, we report on the optical response of Ag-clusters embedded in a soda-lime silica (SLS) glass. This study extends our previous works reporting on the optical, mechanical and dielectric characteristics of the same system [4–6]. Because of the results obtained recently for the copper-doped SLS glass [7], special attention was paid to changes of the shape of matrix droplets as well as to the shape and size of the metal nanoparticles during the thermal treatment which follows the Ag/Na ion exchange process.

## 2. Experimental part

The main constituents of the SLS glass were (mole percent): SiO<sub>2</sub> (73.5), Na<sub>2</sub>O (13.8), CaO (6.5), MgO (4.5), and Fe<sub>2</sub>O<sub>3</sub> (0.15) that contains about 50% of divalent iron; this composition corresponds to the miscibility gap in the SiO<sub>2</sub>–Na<sub>2</sub>O system [8].

For ion exchange, the sample (about two millimetres thick) was kept at a temperature  $T_{\text{ex}}$  for a time  $t_{\text{ex}}$  in a molten mixture of NaNO<sub>3</sub> and AgNO<sub>3</sub>. After exchange, the samples were annealed at 873 K either for 0.5 or 4 h in the ambient air. The Table gives the concentration  $c$  of AgNO<sub>3</sub>, the parameters  $T_{\text{ex}}$  and  $t_{\text{ex}}$  as well as values of the penetration depths (pd) of metallic silver obtained after the thermal treatment. Values of  $\text{pd}_{0.5}$  and  $\text{pd}_4$  were determined by microspectrophotometric measurements, *cf.* [5, 9].

Table. Parameters of the ion exchange process and the silver penetration depths for specimens annealed at 873 K for 0.5 and 4 h.

Sample	$c$ [%]	$T_{\text{ex}}$ [K]	$t_{\text{ex}}$ [h]	$\text{pd}_{0.5}$ [ $\mu\text{m}$ ]	$\text{pd}_4$ [ $\mu\text{m}$ ]
FAG1	0.5	673	2	130	250
FAG2	2	673	2	180	380
FAG3	0.5	603	310	250	490
FAG4	2	603	310	330	595

The optical absorption (OA) spectra were recorded in the range between 250 and 600 nm using a Varian (Cary 5) spectrophotometer; all measurements were performed at 294 K.

Microstructural data were obtained by means of a transmission electron microscope (TEM; PHILIPS-CM20) operating at 200 kV and providing a 24 nm point-to-point resolution. Two types of replica (extraction and carbon-shadowed) were prepared from surfaces normal to the exchanged one. The selected area electron diffraction pattern (SAEDP) evidenced the presence of crystalline species.

## 3. Results and discussion

### 3.1. TEM observations and SAED performances

A typical TEM image of the doped SLS glass is shown in Fig. 1 for the sample FAG2. The crystalline nature of nanoparticles is revealed by the SAED, *cf.* the inset of Figs. 1a and 1b (left-hand side). The detected diffraction rings with reflections from the {111} and {200} type planes correspond to the *fcc* structure of metallic silver. Figures 1a and 1b (right-hand side) shows the matrix morphology for the same specimens.

It is evident that after a short annealing time, the silver nanoparticles are mostly spherical in shape, their size ranging between 2 and 10 nm. With increasing annealing time, coalescence of adjacent nanocrystals is facilitated and a marked

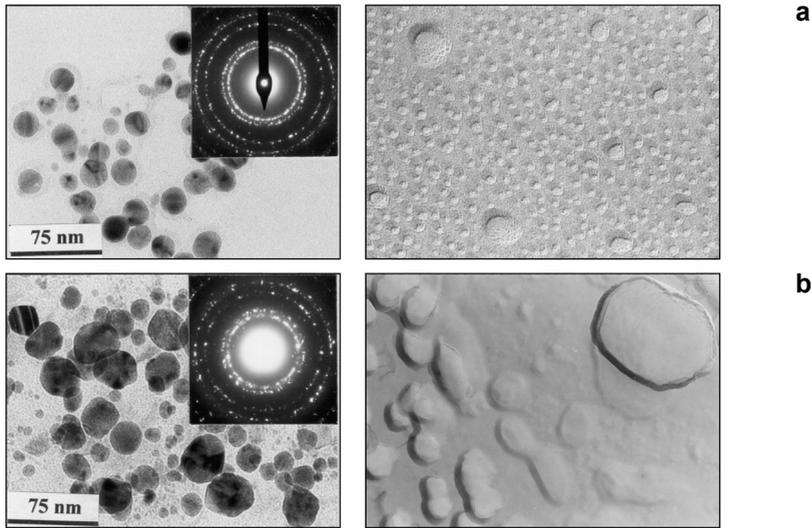


Fig. 1. TEM-micrographs of the ion exchange sample FAG2 after annealing at 873 K for 0.5 h (a) and 4 h (b).

deviation from the spherical shape of the Ag-particles is observed. The phase separated droplets, present yet in the glass-matrix, behave qualitatively in the same way, *i.e.*, they change their size and shape along with the thermal treatment.

It should be stressed that the variation of the shape of metal nanocrystallites with size is often overlooked and a simplistic description of the optical behaviour based on spherical particles is assumed [10–13]. On the other hand, the altered matrix morphology, not considered up to now, has been tentatively related with the formation of mixed sodium-silver silicates, similar to the case of copper-doped SLS glass [7].

### 3.2. Optical absorption data

Figures 2a–2c shows the OA-characteristics of spectra obtained for annealed specimens, and the last picture gives values of the Ag-particle diameters versus their penetration depth.

It was detected that the spectra exhibited a shift of the absorption-edge in the near-UV-region (not shown here) towards lower energies, and the spectral features of the UV-Ag-absorption were affected by the UV-absorption of the glass-matrix.

The occurrence of the SPR absorbance is attributed to the interband transitions which dominate UV-vis region. The blue and red shift (for different depths of each sample) of the band position  $\lambda$  is accompanied by changes of the absorbance  $A$  and of the full-width half-maximum of the absorption peak  $\delta_{1/2}$ . These changes are strongly dependent upon the annealing time, *cf.* Figs. 2a–2c.

The behaviour of the SPR absorption peak corresponds well with the size of the Ag-particles which are changing not only with the exchange parameters but also with the penetration depth characteristic of the thermal treatment.

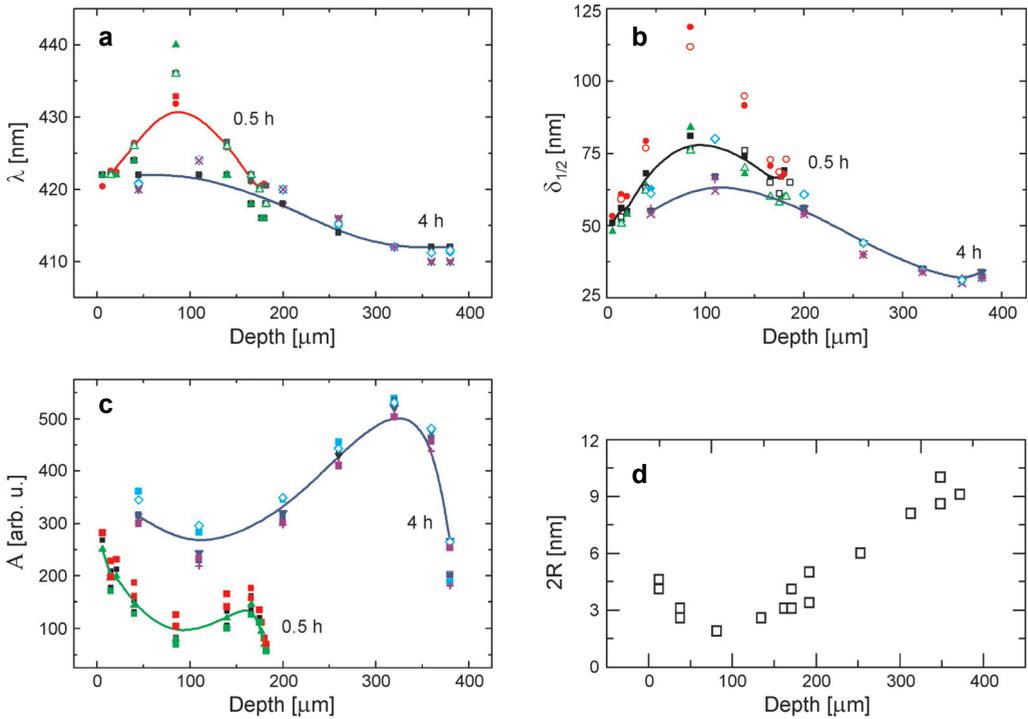


Fig. 2. OA-characteristics of the FAg2 specimen annealed for 4 h at 873 K (a–c), and the size of the created silver particles (d). All data are shown as a function of the silver penetration depth.

The formation of mixed silver-alkali ion silicates at a given stage of the production is probably responsible for the complex character of the depth-dependences of  $2R$ ,  $A$ ,  $\lambda$  and  $\delta_{1/2}$  shown in the present communication.

Several attempts have been made to model the OA spectra of dielectrics doped with metal nanoparticles by taking into account the effect of their size [1]. The effect of shape, which also modifies the optical properties and the effective dielectric constant, has drawn lesser attention; for instance, the effective medium theory introduced by MAXWELL-GARNETT [12] and BRUGGEMAN [13] considered the spherical and ellipsoidal shapes only. Unfortunately, the complex character of our results cannot at present be explained on the basis of the aforementioned models. It seems that more experimental work is necessary, especially with respect to the nucleation and growth of the matrix occlusions and the metal nanoparticles, as well.

## 4. Conclusions

We have reported changes of the half-width, intensity, and shift of the position of the plasmon resonance absorption peak with increasing size of the Ag-particles embedded in the SLS glass matrix.

The following conclusions have been drawn:

1. The substitution of Na by Ag-ions cannot be described by a simple replacement reaction; one has to take into account some structural rearrangements during the ion exchange well below the glass-transformation temperature;
2. The effect of size, shape and distribution of the silver nanoparticles upon the optical absorption of a composite material is more complicated than anticipated theoretically on the basis of the free metal nanoparticles;
3. A combination of the ion exchange process with thermal treatments is a proper technique for obtaining waveguiding structures with Ag-metallic-aggregates.

*Acknowledgements* – The authors wish to thank Dr. K.-J. Berg from the MLU in Halle/Saale (Germany) for making the microspectrophotometric measurements possible.

## References

- [1] KREIBIG U., VOLLMER M., *Optical Properties of Metal Clusters*, Springer, Berlin, 1995.
- [2] HACHE F., RICARD D., FLYTZANIS C., KREIBIG U., *The optical Kerr effect in small metal particles and metal colloids: The case of gold*, Applied Physics A **47**(4), 1988, pp. 347–357.
- [3] RAMASWAMY R.V., SRIVASTAVA R., *Ion-exchanged glass waveguides: A review*, Journal of Lightwave Technology **6**(6), 1988, pp. 984–1000.
- [4] CAPELLETTI R., COISSON R., VAN HOI P., MORA C., SUSZYNSKA M., VEDDA A., *Thermally stimulated depolarisation currents of quartz and mixed alkali silicate glasses*, 8th International Symposium on Electrets (ISE 8), 1994, pp. 511–516.
- [5] BERG K., CAPELLETTI R., KRAJCZYK L., SUSZYNSKA M., *Optical and electrical characterization of silver nanoparticles in soda lime silicate glasses*, 9th International Symposium on Electrets (ISE 9), 1996, pp. 378–383.
- [6] SUSZYNSKA M., SZMIDA M., GRAU P., *Mechanical characteristics of mixed soda-lime silicate glasses*, Materials Science and Engineering A **319–321**, 2001, pp. 702–705.
- [7] SUSZYNSKA M., SZMIDA M., CIZMAN A., *Structure and hardness of the copper-doped soda-lime silica glass*, 2009, accepted for publication in J. Phys. (c).
- [8] PORAI-KOSHITS E.A., AVERJANOV V.I., *Primary and secondary phase separation of sodium silicate glasses*, Journal of Non-Crystalline Solids **1**(1), 1968, pp. 29–38.
- [9] BERG K.-J., BERGER A., HOFMEISTER H., *Small silver particles in glass surface layers produced by sodium-silver ion exchange – their concentration and size depth profile*, Zeitschrift für Physik D: Atoms, Molecules and Clusters **20**(1–4), 1991, pp. 309–311.
- [10] STEUBING W., *Über die optischen Eigenschaften kolloidaler Goldlösungen*, Annalen der Physik **331**(7), 1908, pp. 329–371.
- [11] KREIBIG U., *Electronic properties of small silver particles: the optical constants and their temperature dependence*, Journal of Physics F: Metal Physics **4**(7), 1974, pp. 999–1014.
- [12] MAXWELL-GARNETT J.C., *Colours in metal glasses and in metallic films*, Philosophical Transactions of the Royal Society A **203**, 1904, pp. 385–420.
- [13] BRUGGEMAN D.A.G., *Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen*, Annalen der Physik, Leipzig **416**(7), 1935, pp. 636–664.

Received November 12, 2009  
in revised form January 6, 2010