

ESTIMATION OF SILVER NANOPARTICLES SIZE IN SiO₂ SOL-GEL LAYERS BY USE OF UV-VIS SPECTROSCOPY

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Silica glass layers containing silver nanoparticles were prepared by the sol-gel method. The layers were deposited on a glass substrate by the dip-coating method, dried and heat treated at various temperatures. The average silver particle size was determined from absorption spectra according to Mie's theory. A good correlation was found between the calculated values and analysis of HRTEM images. A very narrow size distribution was obtained by this procedure. The average particle size of silver particles fell between 1 and 2 nm for dried samples; in case of glasses treated at 500 and 550°C the size ranged between 2 and 4 nm.

INTRODUCTION

Silver doped silica glass sol-gel layers find application possibilities in many areas, e.g. catalysis, sensors, batteries or by the preparation of photosensitive or antibacterial glasses [1-11]. These applications require high material quality and process reliability. Deep analysis, its description and understanding of formation and constitution of the layers are indispensable for their preparation and final properties.

Some important properties of glasses containing silver depend on the presence of silver nanoparticles, namely on their concentration, size and shape. These parameters were investigated preferably in bulk glasses. Silver was often incorporated in a glass by ion exchange, which occurred in contact of a glass with a melt containing silver salt. Berg at al. [12] investigated formation of small spherical silver particles in a surface layer of commercial glass. The surface layer was produced by means of a sodium-silver ion exchange. It was found that the mean diameter of particles increases with the penetration depth and can vary from 4.5 nm at the glass surface up to more than 50 nm at the end of the layer enriched by silver. Berger [13] prepared spherical silver particles in a soda - lime glass by an Ag/Na ion exchange and a subsequent annealing of ion-exchanged glasses. Diameters of the particles ranged from 10 to 100 nm. The dependence of the diameter on the ion-exchange process was described by a model. Hofmeister at al. [14] detected silver particles

of a ~ 4 nm diameter in a glass matrix doped by silver by ion-exchange in an electric field. By this procedure a high concentration of silver particles was achieved. The particles were homogeneously distributed in the glass surface layer and exhibited narrow size distribution. The shape, the internal structure, and structural parameters of silver nanoparticles embedded in glass were described by Dubiel at al. [15] and Hofmeister at al. [16]. Mechanism of the Ag/Na ion-exchange and the formation of very small silver nanoparticles (1-2 nm) were described by Dubiel at al. [17].

In addition to silver nanoparticles formed in glass by ion-exchange, silver nanoparticles created by the sol-gel process were also studied. Wenyan Li at al. [18] deposited nano-doped silica films on glass slides by the sol-gel process using TEOS and AgNO₃ as primary precursors. Optical and chemical properties were investigated and also structure characterization of the films was studied. The dried films thickness was determined to be 150-200 nm. A reduction up to 20% of the thickness was observed in the case of heat-treated films. The size of the silver particles in dried silica films detected by HRTEM was about 5-7 nm. The Ag particles size and shape depends on silver concentration and heat-treatment temperature. The experimental and calculated data of Hyung Jinn Jeon at al. [11] confirmed the role of annealing temperature on silver particles formation in a thin SiO₂ layer doped by Ag. The size of silver particles in the thin layers was estimated by analyzing the

X-ray diffraction peak. The silver particle mean diameter ranged from 15-23 nm with the maximum value at 500 °C. Also the soda-lime glass substrate had an important influence on the Ag particles formation through sodium diffusion from the substrate into the coatings. Popok et al. [19] synthesized silver nanoparticles in thin surface layers of silica glass by 30 keV implantation of Ag⁺ ions with various fluencies. AFM study showed formation of hemispherical nanosized bumps on the glass surface which represent a near surface fraction of partly towered nanoparticles. The size of silver nanoparticles was not determined.

It is the aim of this paper to extend the existing published data on the size of silver nanoparticles present in thin silica glass layers which are prepared by the sol-gel method. The experimental data will be verified by the data calculated using a theoretical model.

EXPERIMENTAL

Layers Preparation

The silica glass layers doped with silver were prepared via sol-gel method. For the sol preparation, tetraethoxysilane (TEOS), glycidoxypropyltrimethoxysilane (GPTS) and aminopropyltriethoxysilane (ATEOS) were used as the precursors, ethanol (EtOH) and water as solvents and nitric acid as a catalyst. The basic scheme of the preparation procedure is shown in Figure 1.

Detailed preparation conditions can be found in the previous article [20]. ATEOS ensured uniform distribution of silver particles in the sol by forming of stable amino-complexes with silver. The glycidic group, present in GPTS, is easily oxidizable and allowed the silver ions reduction at a lower temperature.

The layers were deposited on a glass substrate by a dip-coating method. As the glass substrate commercially produced microscopic slide was used, it was composed of 72 % SiO₂, 13.3% of Na₂O, 8.8 % CaO, and 4.2 % MgO (wt.%).

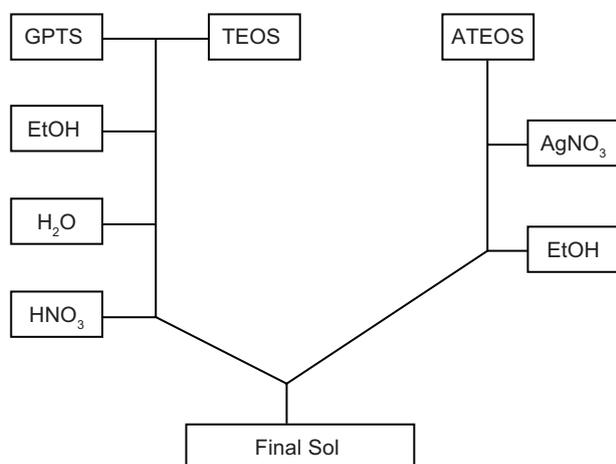


Figure 1. Sol preparation.

Drying at 60 °C took place for 30 minutes, and consequent heat-treatment at 500 or 550°C in the air atmosphere followed afterwards. Yellow coloured layers were obtained after the heat-treatment of the samples.

The final layer thickness measured by Profilometer Tencor P-1 ranged from 390 to 630 nm and decreased with the increasing time and temperature. Burn-out of the organic residuum and solvents together with the layer thickening occurs during the heat-treatment [33].

RESULTS AND DISCUSSION

UV-VIS Spectrophotometry

The spectrophotometer Shimadzu UV-1201 was used for absorbance measurements of samples treated under various conditions. Measurements were performed in the wavelength range of 350-500 nm; not coated clear original substrate fired at 550°C was used as a reference. (Figures 2-4). These curves were used for the average particle size determination (see below).

Absorbance curves for the layers dried at 60°C have their maximum at the wavelength of 420 nm which is more pronounced with the rising time. A similar absorption peak was detected at 400 nm in the case of layers treated at 500°C. The most pronounced absorption peak was found for layers prepared at the

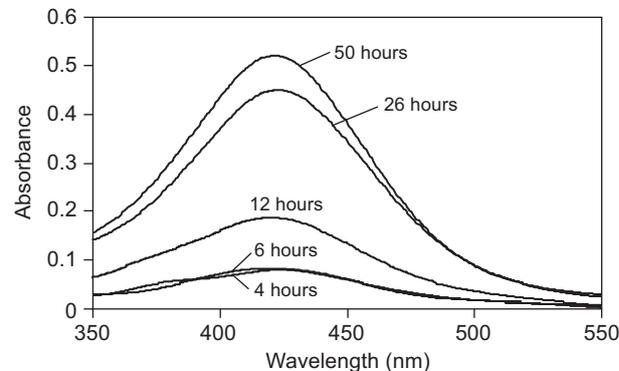


Figure 2. Influence of treatment time on layers absorbance dried at 60°C.

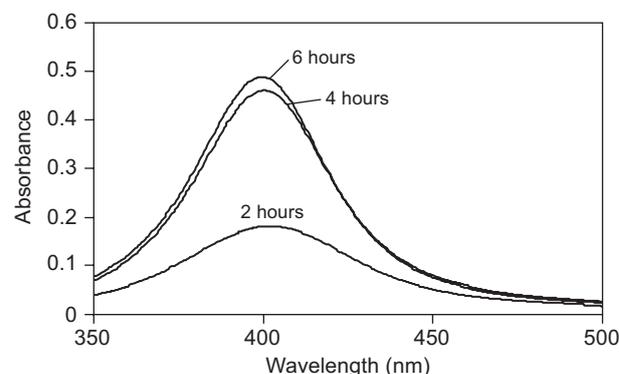


Figure 3. Influence of time on layers absorbance treated at 500°C.

temperature of 550°C close to the wavelength of 415 nm and again rising with the time of heat treatment. All samples had yellow colour. The intensity of the colour was rising with the temperature and the time of the heat treatment according to the absorption curves presented above.

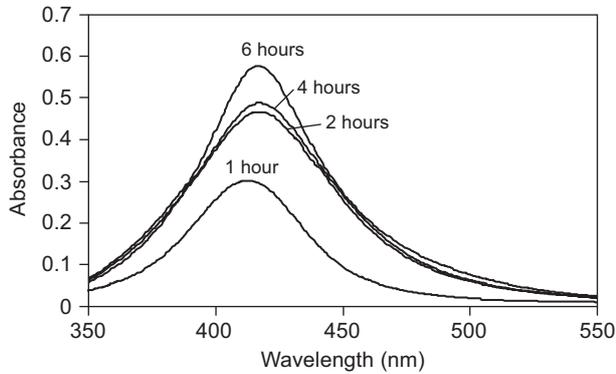


Figure 4. Influence of time on layers absorbance treated at 550°C.

Average silver particles size

The average particle size of silver distributed in the glass matrix was determined according to Mie's theory [21]. The wavelength of the highest absorbance value (λ_{max}) and the width of the absorption peak in the half of its height ($d_{1/2}$, see Figure 5) had to be measured in the first step.

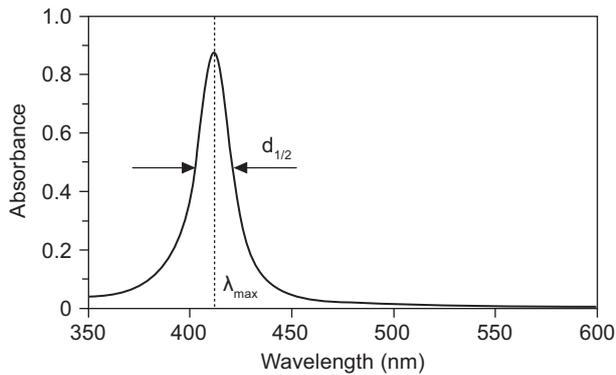


Figure 5. Parameters needed for average silver particle size determination [22].

The silver average particle radius can be deduced afterwards based on these values. For the particle size evaluation, substitution of the λ_{max} and $d_{1/2}$ parameters into the Figure 6 was needed. This curve was specially calculated for silver particles according to Mie's theory by Rainer [22].

The λ_{max} and $d_{1/2}$ values were determined from the absorption curves presented on Figures 2-4. The values of these parameters and the resulted particle radius data are summarized in the Table 1.

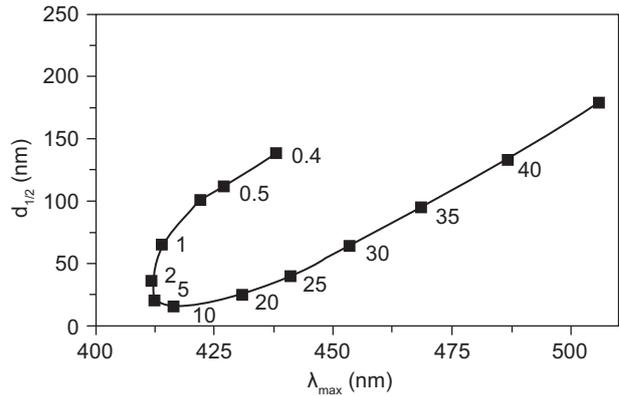


Figure 6. Determination of silver particle radius from λ_{max} and $d_{1/2}$ [22].

Table 1. Average silver particle radius at different treatment conditions.

Treatment temp. (°C)	Treatment time (h)	λ_{max} (nm)	$d_{1/2}$ (nm)	Particle radius (nm)
60	4	425	97	0,5-1
60	6	423	99	0,5-1
60	12	420	102	0,5-1
60	26	423	94	0,5-1
60	50	421	92	0,5-1
500	2	412	63	~1
500	4	411	49	~1
500	6	411	48	~1
550	1	413	54	1-2
550	2	416	70	1-2
550	4	416	71	1-2
550	6	416	60	1-2

Obviously, the average particle size is growing with the increasing temperature. Dried samples contain mainly particles of the diameter 1-2 nm; the samples treated at 500 and 550 °C contained mainly particles of the 2-4 nm diameter. These results correspond with the data published by other authors (see following table).

The particle radius values found by means of UV.VIS spectra were verified for samples treated at 500 and 550°C by the help of the High Resolution Transmission Electron Microscopy (HRTEM, JEOL JEM2200FS, operating at 200 kV). Particle size distribution was obtained by counting a total of 300 particles in each case.

As seen in the figures, the particle distribution is very narrow with the majority of size below 6 nm and with an average value between 2 and 3 nm. The average size is increasing a little with the treatment temperature. These observations fully confirm the calculation method used in the previous chapter. The particle size calculation could be therefore used for a quicker approximate particle size determination.

Table 2. Comparison of literature data on silver particles diameter in silica glass sol-gel layers.

Author	Silver particle diameter (nm)	Treatment temp. (°C)	Treatment time (min)	Atmosphere
Goutam [1]	1-5	300	200	Air
Mitrikas [8]	3-5	500	60	4 % H ₂ - 96 % Ar
Goutam [24]	2-5	550	200	5 % H ₂ - 95 % N ₂
Mennig [34]	7	500	60	10 % H ₂ - 90 % N ₂
Ma [35]	6-10	400	30	H ₂
Villegas [26]	8-30	500	60	10 % H ₂ - 90 % N ₂
Villegas [26]	5-20	500	60	10 % H ₂ - 90 % N ₂ + As ₂ O ₅ incl. in glass

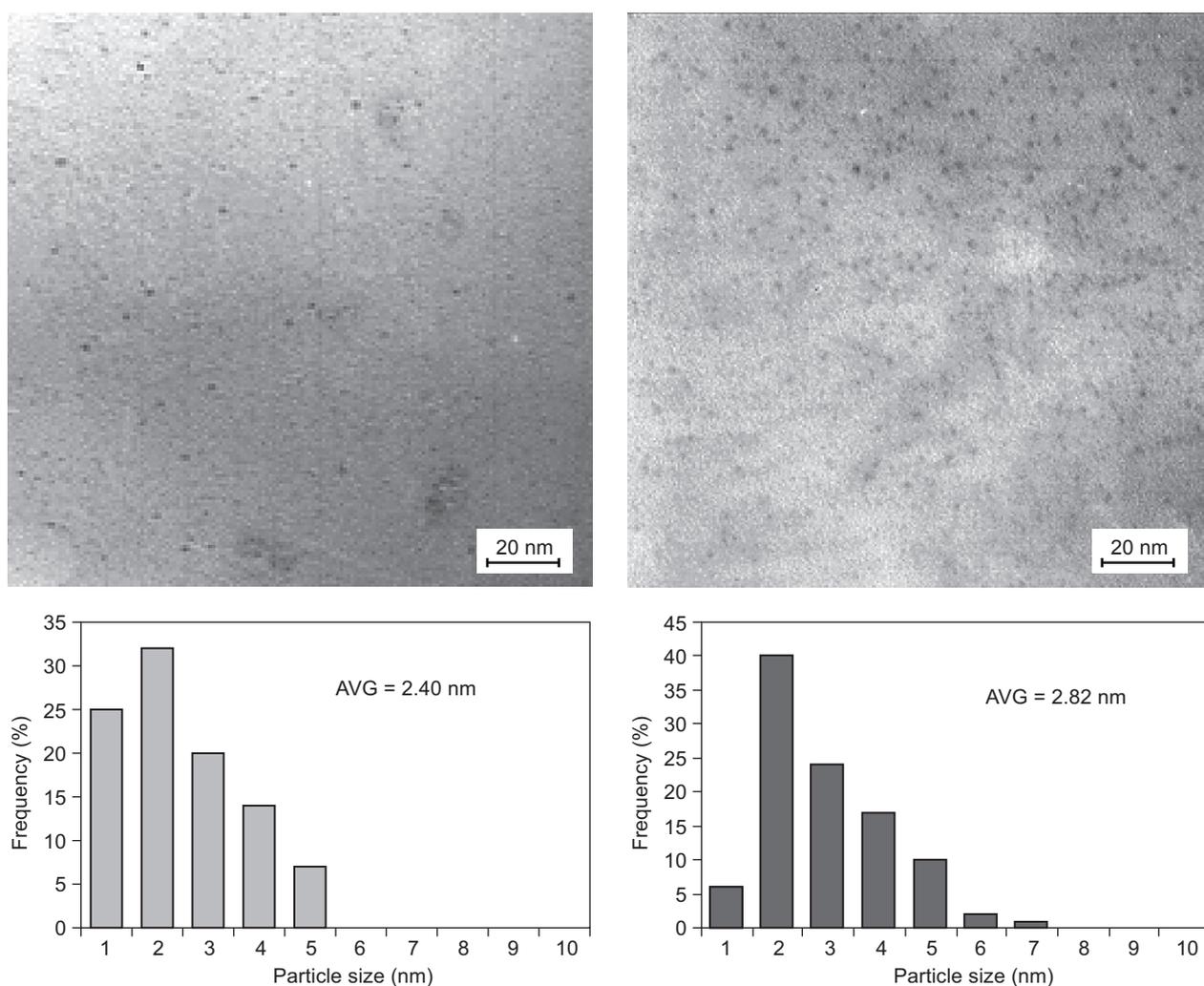


Figure 7. TEM Image and the particle diameter distribution of silver nanoparticles distributed in silica matrix after the heat-treatment at 500°C (left) and 550°C (right).

CONCLUSION

Silver doped silicate layers were prepared via the sol-gel method at various conditions. Tetraethoxysilane (TEOS), glycidoxypropyltrimethoxysilane (GPTS) and aminopropyltriethoxysilane (ATEOS) were used as the precursors, silver nitrate as a source of silver.

The average silver particle size was calculated according to Mie's theory and by the help of UV-VIS Spectrophotometry. The diameter of silver particles in the dried layers ranged between 1 and 2 nm, the layers treated at 500 and 550 °C included bigger silver particles: 2-4 nm. These results were confirmed by HRTEM; average silver particle size can thus be easily calculated from UV-VIS spectra.

Acknowledgement

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