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Efficient and Controllable Silver Nanoparticles Generation in Ion-exchanged Soda-lime Glasses by Simultaneous Heat Treatment and UV Exposure

F. Goutaland, E. Marin, H. Gagnaire, J.Y. Michalon and A. Boukenter

Laboratoire Hubert Curien, UMR CNRS 5516
18F rue Benoît Lauras 42000 Saint Etienne, France
francois.goutaland@univ-st-etienne.fr

ABSTRACT

In this paper, we report on the space-selective precipitation of silver nanoparticles in ion-exchanged silica-based glasses, by simultaneous continuous wave UV exposure and heat treatment. Changes in the absorption spectrum of the glass are explained by the growth of the silver nanoparticles when increasing the UV power density and the annealing temperature. Nanoparticles of average diameter 40 nm have been observed, whereas silver nanoparticles formed under laser exposure at room temperature are usually limited to few nanometers in diameters.

Keywords: glass, continuous wave exposure, annealing, silver nanoparticles, coalescence.

1 INTRODUCTION

Pulsed laser exposure of ion-exchanged soda-lime commercial glasses is commonly used to space-selectively grow silver nanoparticles [1-3]. This technique leads to nanoparticles of only few nanometers in diameter [2, 3], therefore limiting their applications to those requiring small particles, like ultrafast optical switching.

In this paper, we show that simultaneous continuous wave (cw) UV laser irradiation and thermal annealing of Ag-exchanged glasses leads to the precipitation of silver nanoparticles, whose diameter and concentration depend both on UV power density and annealing temperature. Particles from 2 nm up to 50 nm can be obtained, showing the high flexibility of this combined technique.

2 EXPERIMENTS

Silver-exchanged soda-lime glasses have been obtained by immersing 1 mm-thick commercial soda-lime glass slides for 20 minutes at 320°C, into a molten salt bath of molar concentration 0.1% $AgNO_3$ in $NaNO_3$. This treatment leads to an exchanged zone whose refractive index (measured using the M-lines technique) varies from 1.61 to 1.52 across the 8 µm depth. A 244 nm cw laser, whose power was adjusted between 80 and 245 mW, was focused on the glass surface by means of a 200 mm focal lens, giving a spot size of about 20 µm. UV-exposed lines have been written by scanning the laser beam at a speed of 2mm/s. Scanning Electron Microscope (SEM) was used to measure the nanoparticles size. Absorption spectra of the irradiated area were recorded by use of a confocal spectrometer with a spatial resolution of about 10 µm.

3 RESULTS

The figure 1 displays the evolution of the absorption spectrum of the Ag-doped glass with the annealing temperature. The broad band centered between 380 and 450 nm is attributed to the Surface Plasmon Resonance (SPR) of the silver nanoparticles [2]. Increasing the annealing temperature leads to much higher absorption as well as a redshift of this band. Notice that the corresponding irradiated lines move simultaneously from very pale to a dark orange color.

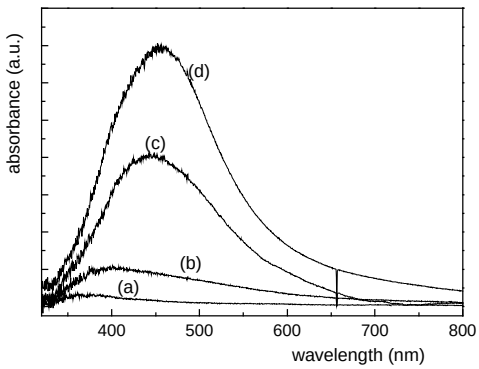

Fig. 1 : absorption spectrum of the ion-exchanged glass after UV exposure (25 kW/cm^2) and simultaneous heating : (a) room temperature, (b) 260°C, (c) 350°C and (d) 450°C

The silver nanoparticles responsible for the low intensity absorption band centered at around 380 nm after room temperature eposure, are too small to be correctly mesured by use of SEM. Simulation of this band based on the Maxwell-Garnett theory [4] reveals an average size of 2 nm. The redshift of this band and its intensity enhancement, when annealing temperature reaches 260°C, are most likely due to an enhancement of the filling factor of the nanoparticles together with a slight diameter increase up to 5 nm. The absorption band characteristic of SPR becomes more intense for 350 and 450°C annealing temperature and

SEM measurements show an average diameter between 10 and 15 nm. Consequently, increasing the annealing temperature enhances the nanoparticles diameter as well as their concentration. This is most likely due to the higher mobility of the silver ions in the glass at high temperature, which favors the coalescence of the small nanoclusters into bigger ones.

Increasing the UV laser power density shifts the maximum position of the nanoparticles absorption band towards the red part of the spectrum in case of high temperature exposure (fig. 2). No significant change except the band intensity have been observed for temperature below 260°C. The asymetric shape of the band for 350 and 450°C annealing temperature is ascribed to a large distribution in the nanoparticles diameters. More precisely, SEM measurements indicate that the irradiated area contains nanoparticles of 10-15 nm in diameter. Assuming the existence of smaller particles (few nm) in the same region leads to bimodal distribution of nanoparticles diameters and explains the asymetric shape of the band for 350 and 450°C annealing temperature.

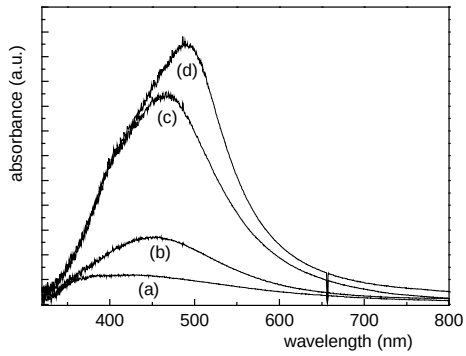

Fig. 2 : absorption spectrum of the ion-exchanged glass after UV exposure (40 kW/cm^2) and simultaneous heating : (a) room temperature, (b) 260°C, (c) 350°C and (d) 450°C

Similar experiments have been performed with a 248 nm KrF-pulsed laser emitting 5 ns pulses. No significant influence of the annealing temperature has been observed , whatever the annealing temperature. The temperature increase due to absorption of the pulsed laser was estimated at around 1500 K by Miotello et al. [2] and makes the influence of the annealing temperature negligible. Increasing the number of pulses result in nanoparticles dissolution rather than in diameter increase [5], so that pulsed lasers are not suitable to grow large nanoparticles

Increasing the UV power density up to 80 kW/cm^2 reinforces the asymetric shape of the band. The bandwidth decrease observed for the highest temperature is attributed to the growth of much larger particles. This is confirmed by SEM picture (fig. 3) which shows both 40 nm and smaller (few nm) nanoparticles in the UV-exposed area. Coalescence phenomenom, which is not observed in case of room temperature exposure, is most likely responsible for the formation of the largest nanoparticles.

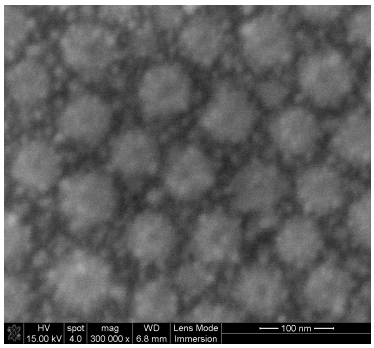

Fig. 3 : SEM picture of the UV-exposed area, simultaneously annealed at 450°C (UV power density 80 kW/cm^2).

4 CONCLUSION

We have demonstrated that cw UV laser irradiation of Ag-exchanged glasses performed at high temperature, leads to the formation of silver nanoparticles. The diameter of these particles varies between few nanometers and 40 nm and can be adjusted by careful control of the power density and the annealing temperature. This wide range of diameter allows several applications to be considered, like optoelectronic devices for the glass embedded with small particles, and surface-enhanced Raman scattering for the glass containing the largest nanoclusters.

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