Silver Nanoparticles Formation By Redox Reaction In Laser Treated Sodalime Glass

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UJM-Saint-Etienne, CNRS, Institute of Optics Graduate School, Laboratoire Hubert Curien UMR CNRS 5516, F-42023 St-Etienne, France
18 rue Benoit Lauras 42100 Saint-Etienne

ABSTRACT

We report on the formation of silver nanoparticles by intense ultraviolet laser exposure of silver-exchanged sodalime glass. The laser exposure leads to the formation of a molten glass phase in which a redox reaction occursbetween diffused oxygen form the atmosphere and the silver ions. The mechanism responsible for their formation is rather counterintuitive as oxygen acts as a very efficient reducer of the silver ions.

PACS Keywords: glass, silver nanoparticles, redox reaction, oxygen diffusion.

INTRODUCTION

Glasses containing silver nanoparticles (Ag NPs) have been widely studied since roughly twenty years for their wide range of potential applications [1]. Together with the development of these applications, the fundamental mechanisms of the silver NPs formation during thermal/laser annealing at temperatures around the glass transition temperature (T_G) have been elucidated. Non Bridging Oxygen (NBO) act as strong reducers for the metallic ions allowing their further precipitation into NPs [2]. In this work, we show that when the glass melts thanks to an intense continuous wave (cw) laser exposure at 244 nm, O_2 diffused from the surrounding atmosphere acts as a strong reducer for the silver ions, through a redox process. This mechanism is responsible for the formation of very highly concentrated NPs at the surface of the glass, which can be used as an efficient substrate for the detection of low-concentrated species [3].

EXPERIMENTAL

Silver-sodium ion exchange has been performed using sodalime commercial glass slides to introduce large amounts of Ag^+ ions near the glass surface. The glass has then been submitted for 1s to cw laser exposure at 244 nm in various gaseous atmospheres (air pressures from few tens of mbar up to atmospheric pressure, atmospheric pressure of N_2 or O_2) to sort out their influence on the NPs growth process. The laser spots have been characterized by optical microscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and space-resolved absorption measurements.

RESULTS

The figure 1 shows optical microscopy pictures of the laser spots for the different atmospheres and several laser power densities. Each spot has been written two times to take into account possible local variations in the glass surface composition, which can affect the aspect of the spots.

It appears from figure 1 that when the laser exposure is performed either in pure N_2 atmosphere (fig. 1b) or for low air pressure (2 mbar in fig. 1d), the formation of the Ag NPs, mostly located in the outer bright ring [4], does not occur. The bright outer ring is systematically observed as soon as the laser exposure is performed for quite high air pressures (above 70 mbar) and in pure O_2 (fig. 1a, 1c, 1d). Oxygen in the surrounding atmosphere is therefore mandatory required to efficiently grow silver NPs. The formation of the bright outer ring appears progressively when increasing the air pressure and is strongly enhanced by a high laser power density. Since the glass temperature depends linearly on the laser power density, this shows that the efficiency of the process responsible for the Ag NPs growth increases with the temperature. Due to very large glass temperature rise, the laser exposure causes the formation of a molten glass phase, in which oxygen diffusion occurs [6]. Oxygen diffusion in silica-based glasses occurs usually as O_2 molecules but when the glass contain metal ions, oxygen gas can be chemically dissolved via a redox process. In our case, O^{2-}/O_2 and Ag^+/Ag redox couples are involved through reaction (1).

$$Ag_0 + 1/4O_2 \Leftrightarrow Ag^+ + 1/2O^{2-} \quad (1)$$

We demonstrate in this work that this reaction occurs mainly in the left direction during the short laser exposure and therefore favors the very efficient reduction of the Ag^+ ions. The Ag_0 atoms formed by this reaction are available in turn to precipitate into Ag NPs, which explain their very high concentration at the glass surface. The rate constant of reaction (1) in the left direction depends on the square root of the oxygen gas fugacity in the melt, which is approximated by the oxygen partial pressure P_{O_2} in the melt. Assuming that the efficiency of the Ag NPs formation depends on the number of Ag_0 atoms available to precipitate in to NPs, the concentration of the Ag NPs is expected to vary with $P_{O_2}^{1/2}$. This explains that the formation of the outer bright ring appears more and more marked for air pressures between 20 to 50 mbar before saturation

appears for higher air pressures, for a 70 kW/cm^2 laser power density (the vertical white arrow in fig. 1 underlines this behavior).

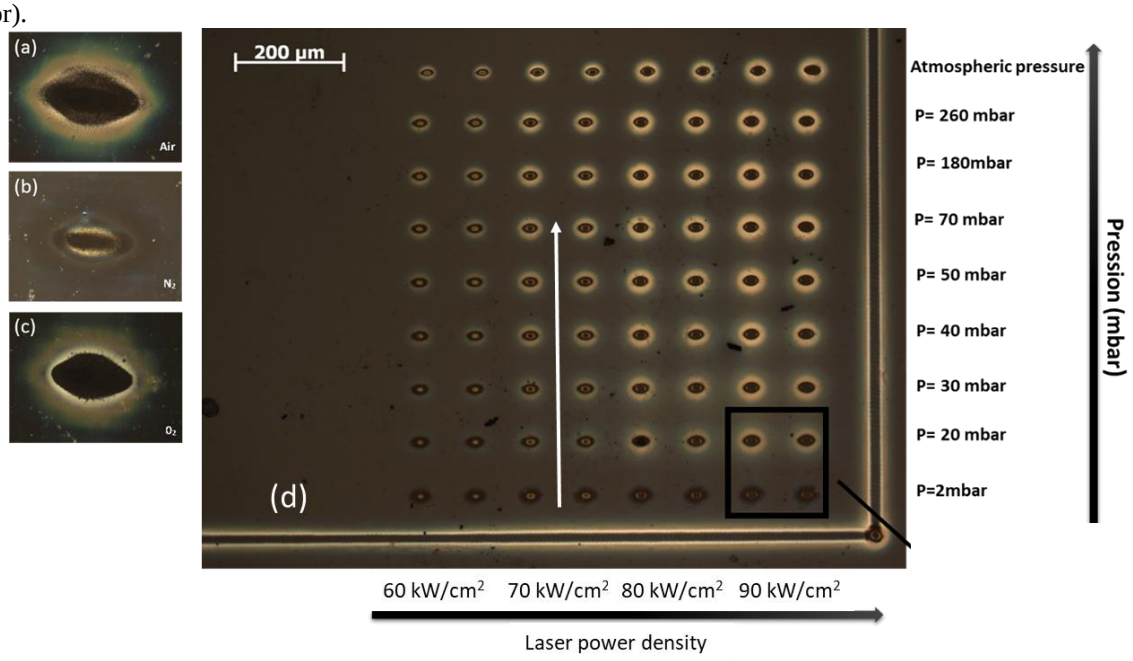

Figure 1 : pictures of laser spots written at 244 nm (τ = 1s): (a) Air (P_{atm}), (b) N_2 (P_{atm}), (c) O_2 (P_{atm}). (d) increasing air pressures and laser power densities.

Several relevant experimental observations further confirm the occurrence of this process. TEM experiments performed within the external bright ring around the laser spots reveal that the NPs consist in oxidized AgO/Ag_2O NPs, as expected considering the very oxidizing glass melt. Space-resolved absorption measurements performed in the same area of the spots show very intense absorption band centered at around 530 nm, ascribed to the Surface Plasmon Resonance (SPR) of the AgO/Ag_2O NPs. The intensity of the SPR band oxidized Ag NPs is usually quite low, due to very strong damping of the electrons oscillations within the oxide layer. This damping effect is considered as the main limiting process towards plasmonics applications based on AgO/Ag_2O NPs. In our case, the very efficiency of the Ag NPs growth largely overcomes the damping of the SPR band, rendering our composite glass suitable for Raman detection [3]. SEM analysis shows that the Ag NPs coalesce into much larger NPs by Oswald ripening mechanism. This way of coarsening of the Ag NPs is not observed for glass temperature around T_G [2] but, in our case, oxygen diffusion changes strongly the solubility of the AgO/Ag_2O, rendering much more likely the transfer of atoms from smaller NPs to larger NPs.

We have also investigated reaction (1) considering the redox potentials of the O^{2-}/O_2 and Ag^+/Ag couples. Their values have been calculated using the model developed by Braucke and Duffy [5], which requires to known the optical glass basicity. Its calculation gives a value of 0.575, which in turn leads to redox potential of -0.329V for Ag^+/Ag while the O^{2-}/O_2 redox potential is 0V. The very large difference between the redox potentials strongly favors reaction (1). Our model also explains the very shiny structures observed after intense nanosecond laser exposure of silver-exchanged sodalime glasses [7].

CONCLUSION

The mechanism responsible for the formation of highly-concentrated Ag NPs during intense cw laser exposure of silver-exchanged sodalime glass is investigated. A redox reaction between Ag^+ ions and oxygen diffused in the glass melt is responsible for their very efficient formation at the glass surface. Oxygen acts thus as a strong reducing agent of the Ag^+ ions. The reduction process is much more efficient than that involving NBO, usually called for lower temperatures.

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