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Photoluminescence and plasmon resonance in silver embedded glass matrices

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ABSTRACT

Nanoscale silver clusters were prepared in a soda-lime glass matrix through the ion-exchange ($Ag^+ \leftrightarrow Na^+$) method followed by thermal annealing in oxidizing atmosphere. The effects of annealing time and temperature on the plasmonic response and optical properties of silver nanocluster in glass matrices have been investigated by using UV-visible absorption spectroscopy and photoluminescence spectroscopy. The surface plasmon resonance of silver nanoparticles has been observed in annealed samples. The blue shift has been observed as a function of post annealing time at a constant temperature. Transmission electron micrographs show the presence of spherical nanoparticles with a maximum particle size of 4-5 nm after annealing, which is consistent with Mie theory based results. The nano-sized Ag nanocluster on glass matrix is suitable as future prospective for potential applications in optical data storage. Copyright © 2015 VBRI press.

Keywords: Glasses; metal nanocluster; optical materials; surface plasmon resonance.

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Introduction

Over the past few years, the plasmonic effects of metallic nanostructures has been established as an important field of physics due to their ability to manipulate light at the nanoscale by exploiting the interaction of light with metallic nanostructures for exhibiting the surface plasmon resonance (SPR) properties **[1, 2]**. Noble metal based metallic nanoparticles/ nanoclusters/ nanocomposites/ hybrid materials have numerous scientific and industrial applications **[3-12]**. The growing scientific interest in this area of research is due to their unique and unusual physicochemical properties and functionalities compared to their bulk counterparts which make them attractive in various applications such as plasmonics **[3, 4]**, nanoelectronics **[5, 6]** and biotechnology **[7, 8]**. Plasmonic materials with large third-order optical nonlinearities susceptibility near the surface plasmon resonance frequency with a picoseconds response time and fast nonlinear response time are usually considered promising candidates for potential applications in optoelectronics, photovoltaic and photonic devices including flat screen TVs, electronic book readers, optical computing, optical data storage, all-optical switching devices, organic thin film transistors, organic photovoltaic devices, biosensors, optical telecommunications, solid state lighting and photodynamic therapy **[4-17]**. Particularly, the noble metal nanoparticles dispersed in a transparent dielectric matrix exhibit interesting surface Plasmon resonance (SPR) absorption usually observed in the visible region due to their coherent oscillation of conduction band electrons when excited by electromagnetic radiations **[11-14]**. The wavelength of surface plasmon resonance (SPR) absorption can be tuned by the size, shape, inter-particle separation, volume fraction of the metal nanoparticles and the dielectric constant of the embedding matrix **[14-15]**. Generally high efficient non linear optical materials based devices are expected to become a key components for high-capacity communications networks in which the ultrafast switching signal regeneration and high capacity optical recording media is required **[16]**.

Noble metals based metallic nanoclusters can be synthesized in soda-lime glass matrix by various methods, such as direct ion implantation, sol-gel methods and ion exchange. Conventionally, the ion exchange has been considered one of the cheaper and important techniques to introduce metallic nanoclusters in glass surface because the techniques are simple and does not requires any sophisticated equipments. The ion exchange technique combines with thermal annealing has received an increase attention as it can be used to introduce metallic nanoclusters such as silver, gold and copper into sod -lime matrix **[18]**.

The main goal of the present work is the fabrication and characterization of Ag nanoclusters embedded in soda-lime glass which are based on thermal ion exchange process. The work provides an insight on nano scale pattering and plasmonic effects of Ag nanoclusters embedded in soda-lime glass.

Experimental

Materials and methods

Nanoscale silver clusters were prepared in a soda-lime glass matrix through the ion-exchange process of silver and sodium ions ($Ag^+ \leftrightarrow Na^+$). Commercial soda lime glass slides (Marienfeld glass) with composition (in weight %) of 72.0% SiO_2, 14.0% Na_2O, 0.6% K_2O, 7.1% CaO, 4.0% MgO, 1.9% Al_2O_3, 0.1% Fe_2O_3, 0.3% SO_3) of 0.5 mm thickness were first cleaned ultrasonically by using distilled water, trichloroethylene and acetone. Then the Ag doped soda lime glass samples were prepared after dipping the plane glass slides in a molten salt bath having the mixture of 20 mol% $AgNO_3$ and 80 mol% $NaNO_3$. This mixture was heated in a tubular furnace in air atmosphere at 370°C for 2 min in a Al_2O_3 crucible. Under these conditions, the silver ions in a molten salt bath diffuse inside the glass matrix and replace the Na^+ by Ag^+ ions in the glass as shown in **Fig. 1**. After inter-diffusion the ion exchange samples were removed from molten bath and cleaned with distilled water and acetone to remove any silver nitrate adhering from the surface. These samples are called pristine samples and were colourless or in faint yellow state after exchange.

Thus the whole mechanism for ion exchange process in pristine samples takes place as follows **[18]**.

$$\equiv Si - O - Na + Ag^+ NO_3^- \rightarrow \equiv Si - O^- - Ag^+ + Na^+ NO_3^- \qquad (1)$$

Thermal annealing in an electrical tubular furnace was employed to incorporate metallic nanoclusters in glass matrix in air at a temperature of 550 °C for different annealing time periods ranging from 10 minutes to 1h.

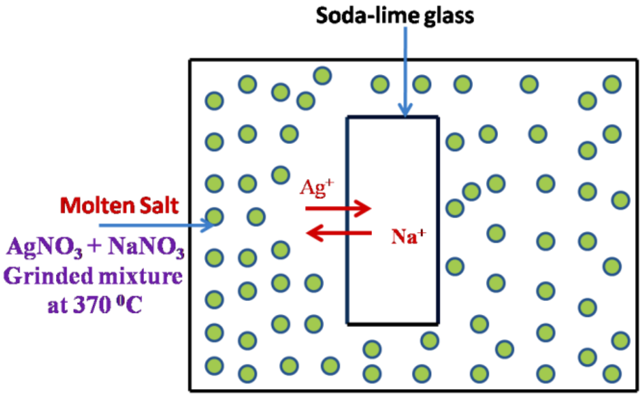

Fig. 1. Schematic diagram of Ag^+-Na^+ ion-exchange in the molten salt bath of $AgNO_3$ and $NaNO_3$.

Characterizations

The silver nanocluster formation in commercial soda-lime glasses have been studied by ultraviolet visible (UV-Vis) spectroscopy and photoluminescence (PL) measurements to understand the formation mechanism during thermal annealing in air, which is the key parameter to optimize the thermal processes of soda-lime glasses. A JEOL JEM 2100 ultra high resolution field emission gun transmission electron microscope (FEGTEM) operated at 200 kV was used to characterize the synthesized Ag ion exchange based annealed samples. Prior performing the FEGTEM measurements the glass–metal nanocomposites slides (metal in glass matrices) were crushed to form the powder samples by using the pestle mortar. The few milligrams of obtained powder samples were dispersed in acetone and then the solution was kept in an ultrasonic bath for 45 minutes. The resulted suspension was pipetted from top portion of the liquid and few drops of the liquid were placed on a carbon coated copper grid of 300-mesh. The dispersed solution was then evaporated; the images were recorded using FEGTEM..

Results and discussion

UV-visible absorption spectra

Fig. 2 show UV-visible absorption spectra of as-exchanged and thermally treated soda-lime glass samples in air at a temperature of 550 °C. The optical absorption spectra of as-exchanged Ag-doped glass samples does not show any SPR spectra indicating that the silver clusters formation did not occur, or the size of Ag nanoclusters were less than 1 nm in size during 2 min ion exchange at 370 °C. After annealing the silver-exchanged samples, an absorption band was observed at 435 nm at a temperature of 550°C for 10-min, which is apparently due to the surface plasmon resonance (SPR) band of the silver nanoparticles in the glass matrix. The intensity of the absorption peak increases with the increase of annealing time from 10 min to 1 h. This is because more Ag^+ ions were reduced into neutral Ag^0 atoms, which indicates an increase of volume fraction of silver nanoclusters in the glass matrix **[19]**.

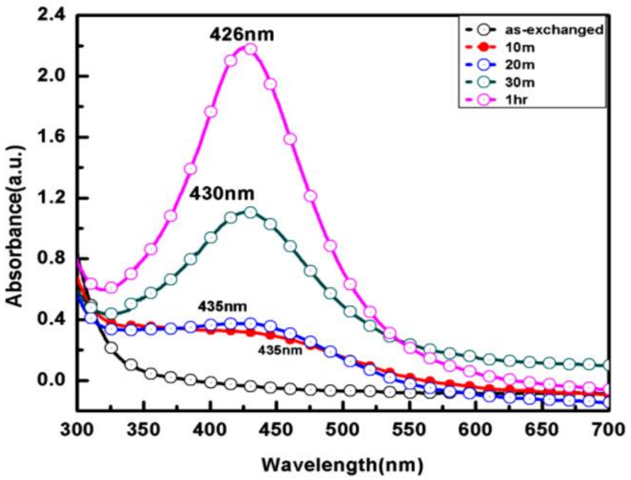

Fig. 2. Optical absorption spectra of silver ion exchanged soda lime glass before and after annealing in air 60 minutes at temperatures of 550 °C.

A blue shift of 9 nm of SPR peak was observed with increasing annealing time. The blue shift of SPR peak was observed with increasing clusters size due to the lower value of full width at half maxima (FWHM) for increasing clusters size. For a small clusters (R ≤ 10 nm), this kind of decrease in FWHM with increase in clusters size is due to the mean free path effect of electrons [20]. The average size of Ag nanoclusters was calculated by using formula given as follows in equation (1) **[21]**

$$d = \frac{2\,V_f}{\Delta E_{1/2}} \qquad (2)$$

where d is the average cluster size of the nanoparticles, $V_f = 1.39 \times 10^6$ m/s is the Fermi velocity of electrons in bulk silver and $\Delta E_{1/2}$ is the FWHM of the SPR band. Equation (2) is valid as long the size of silver clusters is much smaller than the mean free path of the electrons in the bulk metal. The mean free path of the electrons is about 27nm at room temperature for bulk silver **[9]**. Using equation (2), the average cluster size of the Ag nanoclusters based on Mie theory were found to be 2.5, 2.95, 3.89 and 4.2 nm for exchanged glasses annealed at 550 °C for the annealing time of 10, 20, 30 minutes and 1h respectively. This results show that the size of Ag nanoclusters increases with increasing annealing time due to the diffusion-limited aggregation of silver nanoclusters **[19]**. The change in optical properties occurs due to this inter diffusion in glasses because of different electrical polarisabilities of the exchanged ions, difference in their size (ionic radii) and mechanical stresses **[10,19-23]**. It is well known that the optical properties of Ag nanoclusters exchanged in transparent glass matrix depend on size-dependent permittivity $\varepsilon(\omega, R)$ of Ag nanoparticles and absorption extinction of Ag nanoparticles. The resonance occurs at the SPR condition ie. when $\varepsilon_1(\omega) = -2\,\varepsilon_m$, where ε_1 denote the real components of the metallic nanocluster dielectric constant of metal particles, ε_m is the dielectric constant of the surrounding medium which is assumed to be frequency independent. If this condition of SPR is fulfilled, the light field induces a resonant coherent oscillation of free electrons across the metal nanoparticles/nanoclusters **[10]**.

Photoluminescence spectra

Fig. 3 shows the room temperature photoluminescence spectra of Ag^+- Na^+ ion exchanged soda lime glass after annealing up to 1h at 550°C. At the excitation wavelength of 325 nm, the photoluminescence spectra of Ag exchanged soda lime glass show drastic changes in PL intensity after annealing at 550 °C for 10 minutes to 1h. It is evident from the figure that the PL intensity is highest for 10 minutes at 550 °C, but when annealing time is increased further from 20 minutes to 1h, the PL intensity decreases drastically and is lowest for 1h at 550 °C. M. A. Villegas et al. has already reported that Ag^+ ions are luminescent in nature in both crystalline and glassy matrices **[22]**. In contrast, till now no PL emission was observed for Ag^0 (neutral atoms) at any excitation wavelength. In addition to this the increase in PL intensity at an annealing temperature of 550 °C for 10 minutes could be due to the increase of volume fraction of Ag^+ ions in the bulk soda lime glass matrix. The decrease in PL intensity with further ion exchange at higher temperature and/or thermal annealing of ion exchanged glass results in reduction of Ag^+ ions leading to increased formation of Ag^0 atoms. Further increase in annealing temperature leads to the rapid growth of silver nanoparticles and that might have resulted in the quenching of PL intensity for the samples annealed at 550 °C for 30 minutes and 1hour **[8, 23-26]**. P. Gangopadhyay et al. has reported similar results for silver nanoclusters in ion exchanged soda lime glass followed by thermal annealing in vacuum **[24, 25]**.

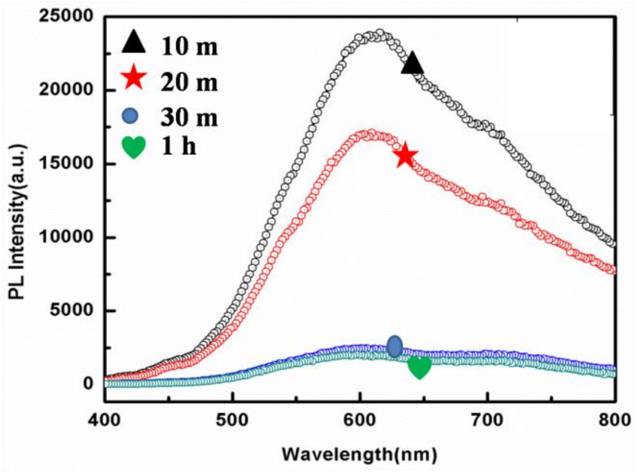

Fig. 3. PL spectra of silver ion exchanged glass after annealing at 550°C for 1h.

Transmission electron micrographs

FEGTEM measurement for Ag ion exchange sample annealed at 550 °C for 1h is shown in **Fig. 4**. The micrographs show the presence of spherical nanoparticles with a maximum radius of 4 to 5 nm which is in good agreement with the cluster size calculated by equation (2). The Ag (111) has been identified in the FEGTEM results which confirm the crystalline nature of metallic silver in amorphous glass matrices.

Therefore ion exchange at 370 °C leads to incorporation of Ag atoms into soda-lime glass matrix after substituting the Na atoms of glass matrix. These Ag atoms in ion exchanged glass exist mainly in the form of Ag^+ ions along with a small population of Ag^0 atoms **[8]**. The Ag-ion exchange process at higher temperature or as the annealing temperature / time increases results in further reduction of Ag^+ ions after capturing the electrons from the glass matrix or from the impurities on the surface leading to increased formation of silver neutral atom (Ag^0) as expressed follows **[25]**:

$$\equiv Si - O^- - Ag^+) \leftrightarrow Si - O - Si \equiv + O^{1-} + (Ag_2)^{1+} \qquad (3)$$

$$2O^{1-} + 2Ag^{1+} \leftrightarrow 2Ag^0 + O_2 \qquad (4)$$

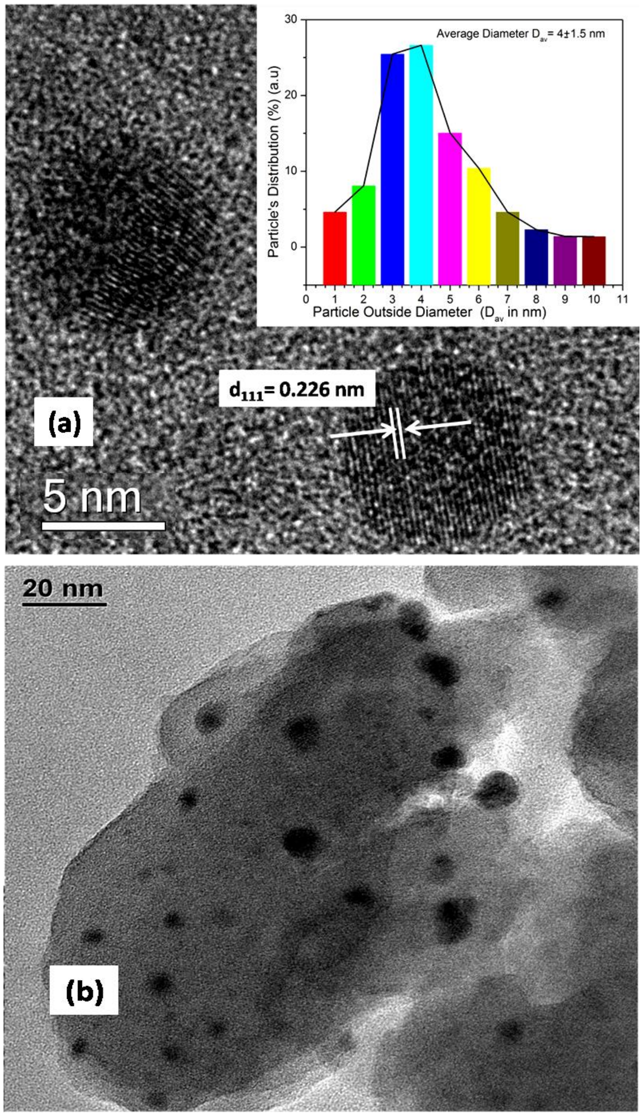

Fig. 4. FEGTEM image of silver ion exchanged glass after annealing at 550 °C for 1h; (**a**) at 5 nm scale: (**b**) at 20 nm scale. The inset in **Fig. 3** (**a**) shows the particle size distribution curve.

As annealing time and temperature increases further, the following reduction reaction may take place resulting in an increased amount of silver in the samples (or intense coloration and strong SPR band).

$$Ag^+ + Ag^+ \rightarrow Ag^{2+} + Ag^0 \qquad (5)$$

Therefore the coloration of annealed samples varies with annealing temperatures and times (light to dark yellow) as the size of Ag clusters increases. The increase in annealing time and temperatures further increases the formation of more silver (Ag^0) neutral atom. This clustering and precipitation of Ag atoms leads to the formation of Ag nanoclusters which is responsible for plasmon resonance. The silver atoms (Ag^0) are mainly bound to non-bridging oxygen (NBO) in glass matrix. During thermal annealing Ag atoms diffuse towards the glass surface for thermal relaxation of the surface which results into the tensile stress which was observed due to the size differences after cooling **[23]**.

Conclusion

The synthesis of Ag nanoclusters embedded in soda lime glass by Na^+-Ag^+ ion exchange process followed by thermal annealing in atmospheric conditions has been performed. The ion exchanged Ag nanoparticles diffuses inside the soda-lime glass matrix during annealing processes. After annealing these particles are reduced to neutral silver atom (Ag^0) and subsequently form silver nanoparticles in oxidizing atmosphere. The luminescence intensity of thermally exchanged samples decreases with increase in annealing time at a particular annealing temperature. FEGTEM image shows the presence of spherical nanoparticles with the average cluster size of 5 nm for the sample annealed at 550 °C for 1h, which agrees with the average cluster size calculated by Mie theory. Thus the nano-sized Ag nanocluster embedded on glass matrix is suitable for future prospective as it can significantly trap light of a particular wavelength by means of plasmonic resonance. These materials can have potential applications in optical data storage, plasmonics solar cell and optoelectronic devices as well as to increase the separation of photo-generated carriers for superior photovoltaic applications.

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