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Blue shift of plasmon resonance in Cu and Ag ion-exchanged and annealed soda-lime glass: an optical absorption study

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Abstract

Metal nanocluster composite glasses are formed by the ion-exchange technique of dipping the host matrix in the respective metal salt bath of interest. These ion-exchanged glasses are then annealed in air for 1 h at different temperatures. The optical absorption spectra of the ion-exchanged and annealed samples confirmed the presence of nano sized metal clusters embedded inside the glass matrix. With increase of the annealing temperature, the absorption peak of the Cu and Ag nanoparticles showed a blue shift which can be attributed to the change in particle size and volume fraction. Annealing of the sequential Cu and Ag ion-exchanged soda-lime glass resulted in the formation of complex metal nanocluster composite glass, with the optical spectra exhibiting two peaks corresponding to the surface plasmon resonance of both metals.

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Keywords: Blue shift; Plasmon resonance; Ion exchange; Annealing; Soda-lime glass; Optical absorption

1. Introduction

Composite glasses containing dilute nanoclusters of transition meals are most promising materials due to their nonlinear optical property and high potential figure of merit for switching devices. An enormous interest has grown in the development of new preparation and characterization methods of these metal nanocluster composite glasses as they serve as key materials for the fabrication of photonic devices [1–3]. Formation of composite glasses containing metal colloids was done earlier by direct implantation of metals into the dielectric matrix or by sequential ion exchange and ion irradiation of the metal-doped silicate glasses. The most used tool for the investigation of such colloidal systems is the optical absorption spectroscopy, where the surface plasmon resonance (SPR) exhibited by the embedded metal nanoclusters give information on the composition and particle size, since the position and shape of the SPR band depends on the structure and distribution of the clusters as well as on the dielectric functions of metal and matrix forming the composite.

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In this paper, we report the effect of annealing on the optical absorption of the metal nanocluster composite glasses formed by ion exchange and subjected to heat treatment at various temperatures in air for 1 h. Also, we have formed by a novel route a heterosystem composite glass which contains both copper and silver nanoclusters in the same soda-lime glass matrix by sequential Cu/Ag ion exchange and annealing technique.

2. Experimental

Introduction of metal particles into dielectric matrix is done in many ways by ion implantation, sequential ion exchange and ion irradiation, thermal ionic diffusion and electric field assisted mechanism, etc., Binary ion exchange is extensively used for doping silicate glasses with metal ions, thus forming optical wave guides with increase in refractive index [4–5]. Copper and silver ion-exchanged glasses were prepared by dipping commercial soda-lime glasses (composition, wt%, 72.90 SiO_2, 14.50 Na_2O, 6.72 CaO, 4.10 MgO, 1.40 Al_2O_3, 0.03 SO_3, and 0.08 Fe_2O_3) in the molten salt bath mixtures of copper sulfate and sodium sulfate for Cu and silver nitrate and sodium nitrate bath for Ag ion exchange for about 1 min. In the bath, Cu^+–Na^+ and Ag^+–Na^+ ion exchange takes place in their respective molten salt baths. The ion-exchanged samples are then annealed in air for 1 h at four different temperatures ranging from 250°C to 650°C. Optical absorption spectra of the ion-exchanged and annealed samples were recorded at room temperature using a double beam UV-VIS spectrophotometer with the plain soda-lime glass as the reference.

Sequential CuAg and AgCu ion exchange was also done by first dipping the glass in copper bath for Cu ion exchange and then in silver bath for Ag ion exchange and vice versa, for the formation of the heterosystem. The CuAg and AgCu samples were also subjected to heat treatment at different temperatures for 1 h and their optical spectra were also recorded.

3. Results and discussion

3.1. Optical absorption analysis

Fig. 1(a) and (b) shows the theoretically calculated (Mie's theory) and experimentally recorded optical absorption spectra of copper and silver nanoclusters in soda-lime glass, respectively. The theoretical spectra was calculated using Mie's formula [6] in which the absorption coefficient α of a material of refractive index n occupied with metal spheres of volume fraction V, where the radii of the spheres are small when compared to

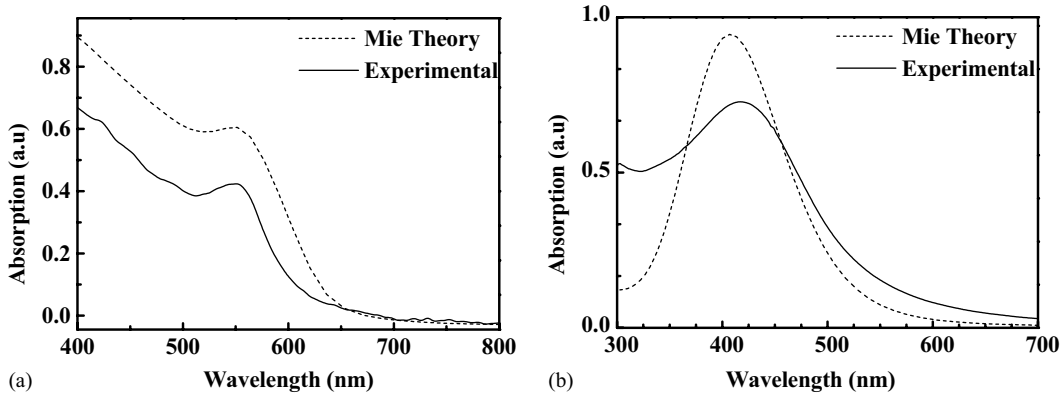

Fig. 1. Experimental and theoretically (Mie's theory) calculated optical absorption spectra of embedded (a) copper and (b) silver nanoclusters in soda-lime glass.

the wavelength λ of the incident light

$$\alpha = \frac{18\pi V n^3}{\lambda} \frac{\varepsilon_2}{(\varepsilon_1 + 2n^2)^2 + \varepsilon_2^2} \text{cm}^{-1}, \quad (1)$$

where ε_1 and ε_2 are the real and imaginary components of the metal sphere, calculated from their optical constants of the bulk metal. The average cluster radii R of the embedded nanoparticles are calculated from the full-width half-maximum $\Delta\lambda$ (FWHM) of the optical absorption peaks using the formula given below

$$R = \frac{V_f \lambda_p^2}{2\pi C \Delta\lambda}, \quad (2)$$

where V_f is the Fermi velocity of the electrons in bulk metal (copper $= 1.57 \times 10^8$ cm/s and silver $= 1.39 \times 10^8$ cm/s), $\Delta\lambda$ is the full-width at half-maximum of the absorption band and λ_p is the characteristic wavelength at which SPR occurs. Both λ_p and $\Delta\lambda$ depend on the substrate and size of the metal nanoclusters forming the composite. Fig. 1(a) shows theoretical and experimental absorption peaks for copper clusters, centered around 552 nm and Fig. 1(b) that of the silver nanocluster centered around 425 nm as reported earlier for the above two metal nanoclusters [5]. It is found that for copper, the ion-exchanged sample itself shows SPR peak confirming the presence of embedded copper clusters formed during ion exchange. But in the case of silver the SPR peak appears only after annealing or after He^+ implantation of the ion-exchanged sample, this is because the diffused silver ions stay scattered inside the dielectric matrix as silver particles and cluster growth is induced either by coagulation during annealing or by defect-induced electronic energy deposition during He^+ implantation. A good match between the theory and experiment was observed from the graphs for both the systems.

Figs. 2 and 3 show the optical absorption vs. wavelength for the ion exchanged and different temperature-annealed copper and silver samples. The spectra follow the same trend of decreasing intensity with increasing wavelength for both copper and silver systems. A blue shift of the SPR peak was observed with increase in annealing temperatures for both copper and silver samples.

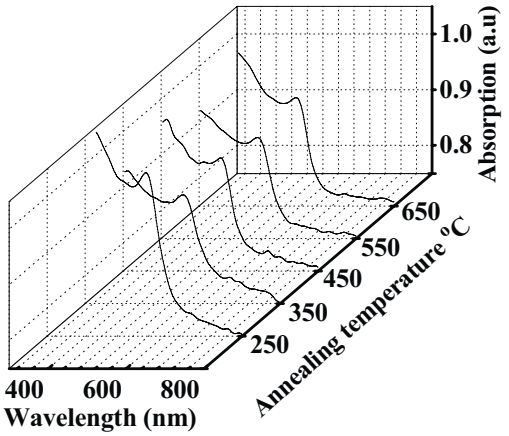

Fig. 2. Optical absorption vs. wavelength of copper ion-exchanged and annealed soda-lime glass.

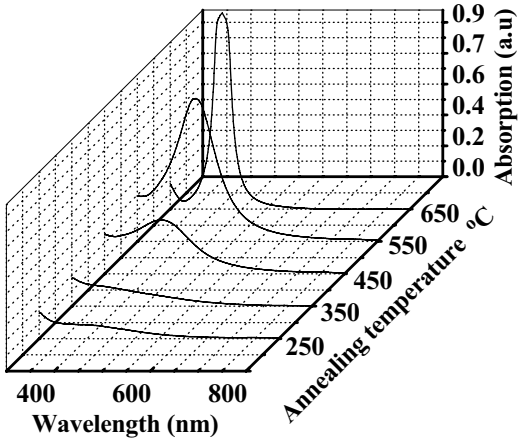

Fig. 3. Optical absorption vs. wavelength of silver ion-exchanged and annealed soda-lime glass.

This can very well be observed from Figs 4(a) and (b) for both the systems. The magnitude of the shift was more in the case of silver than copper. These shifting of the SPR peaks were due to the change in the cluster sizes during annealing. A plot of the SPR peak position vs. the cluster size is shown in Fig. 5(a) and (b) for the copper and silver systems. A red shift of SPR peak is observed with increasing cluster size in the case of copper, while the same is shifted towards the blue for silver clusters. For larger cluster sizes these shiftings are caused by the phase shifts, due to the retardation

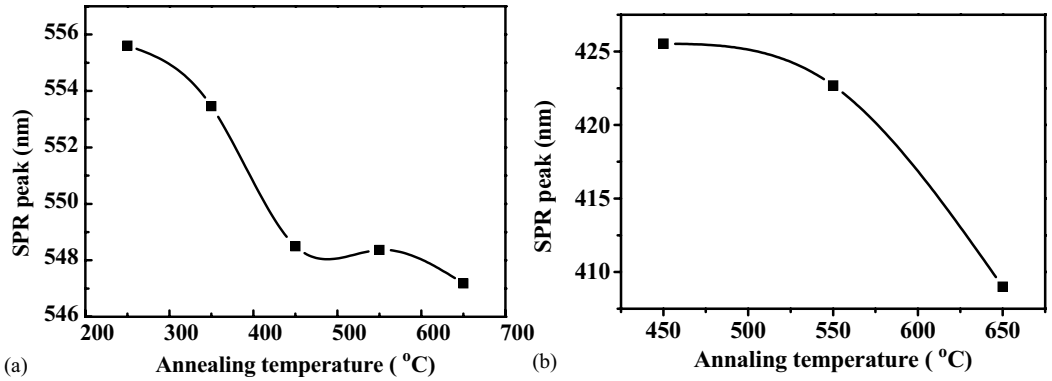

Fig. 4. SPR peak position vs. annealing temperatures for (a) copper and (b) silver nanoclusters embedded in soda-lime glass.

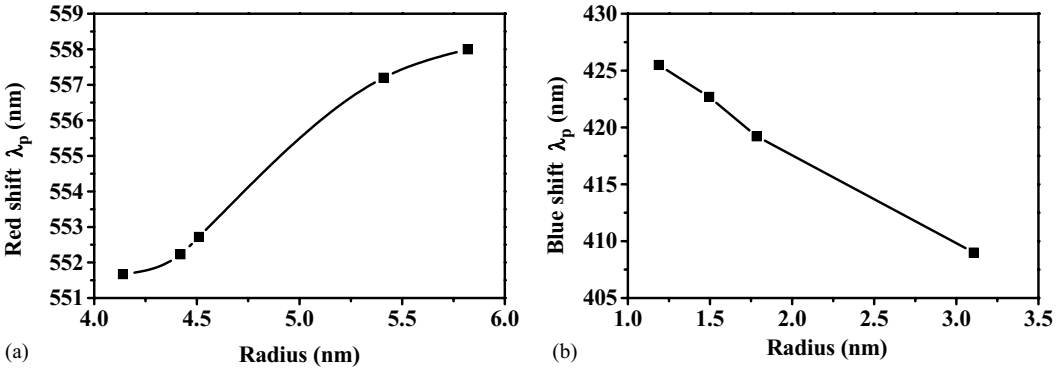

Fig. 5. SPR peak position vs. average cluster radius R of embedded (a) copper and (b) silver nanoclusters in soda-lime glass.

Table 1
Calculated average cluster size (R), SPR peak (λ_p), FWHM ($\Delta\lambda$) and absorption (α) for the various (I) copper and (II) Silver nanoclusters

System	Radius (R) (nm)	SPR peak (λ_p) (nm)	FWHM ($\Delta\lambda$) (nm)	Absorption (α) (a.u.)
(I) Copper	4.14	551.67	61.20	0.10
	4.41	552.23	57.52	0.10
	4.51	552.72	56.41	0.08
	5.41	557.20	47.76	0.05
	5.82	558	44.53	0.09
(II) Silver	1.19	425.53	112.35	0.50
	1.50	422.69	88.14	1.73
	1.78	419.23	72.65	0.02
	3.10	409	39.71	3.15

of the electromagnetic waves along with the influence of the higher-order multipoles. While for the smaller metal clusters, the shift is due to the spill out of the conduction electrons, resulting in the electron density drop thus effecting the change in SPR position [7]. The calculated average cluster

radii R, and observed values of SPR peak position, FWHM and absorption for both copper and silver systems are given in Table 1. The size dependency of the FWHM is also very well shown in Table 1 where, a decrease of FWHM with increase in the cluster size is observed. This decreasing trend of the FWHM, which is due to the limited mean free path effect for the small metal clusters in the above range, has also been reported elsewhere [7].

3.2. Cu/Ag heterosystem composite

Dielectrics containing complex metal clusters synthesized by direct sequential implantation of the metals have been reported earlier [8–10]. But in this present work, we report the formation of Cu/Ag nanoclusters in the same soda-lime glass matrix formed by sequential copper and silver ion exchange. The spectra showed only one peak at 560 nm corresponding to the SPR band of copper alone, but post-annealing of the CuAg ion-exchanged sample resulted in the growth of the silver clusters also with spectra exhibiting two peaks one centered around 410 nm corresponding to that of silver clusters and other at 565 nm to that of the copper as shown in Fig. 6. Increase in annealing temperatures of the CuAg ion-exchanged samples resulted in the vanishing of the copper peaks with the spectra exhibiting SPR band of the silver clusters alone. This is due to the dissolution of the already formed copper cluster during the silver clusterization. But the annealing of the AgCu ion-exchanged samples resulted in the growth of the silver clusters alone with no signatures of copper clusters in them.

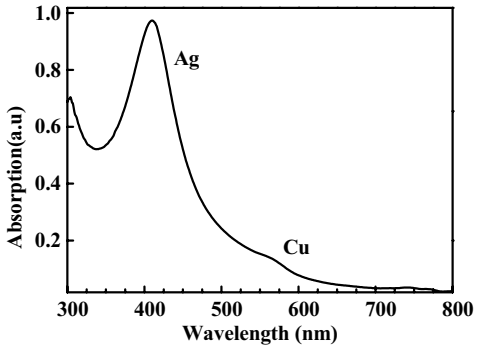

Fig. 6. Optical absorption vs. wavelength of Cu/Ag ion-exchanged and annealed soda-lime glass showing copper and silver nanoclusters in the same soda-lime glass matrix.

4. Conclusion

Copper and silver nanocluster composite glasses are formed by ion exchange and annealing. The optical absorption spectroscopic analysis of the annealed samples showed a blue shift of the SPR bands due the change in clusters sizes. The size dependency of the SPR peak position and FWHM of these embedded metal clusters were analyzed and they behaved as predicted by the theories before. CuAg composite glass was prepared by a novel route, whose optical absorption spectra showed two SPR resonance bands, that are due to both copper and silver nanoparticles embedded in the same matrix.

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