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LASER IRRADIATION INDUCED NARROW SIZE DISTRIBUTION AND CORE SHELL CLUSTERISATION OF Cu AND Ag NaNO CLUSTERS

A.CHRISTY FERDINAND[1], D. MANIKANDAN[2], P. MANIKANDAN[3], S. ARAVAZHI[2]
[1]ST. Joseph's College of Arts and Science, Cuddalore-607 001, India.
[2]Arignar Anna Govt. Arts College, Villupuram-605 602, India.
[3]Krishnasamy College of Engineering and Technology, Cuddalore, India.
***Corresponding Author**: **E-mail:** a_dmani@yahoo.com, Ph**:** +91-9443445103

ABSTRACT

Dielectrics with nano size metal inclusions are engineered composite materials, receiving substantial attention in the last decade due to their high third order dielectric susceptibility. Such nanocomposite materials are prepared either by direct implantation of metal into the dielectric matrix or by any of the multi step methodologies like binary ion exchange technique followed by suitable treatments like low mass ion irradiation, thermal or laser annealing. Post ion exchange treatments result in metal clusterisation and a predestined size distribution which is desired of any metal nanocomposite glasses. Present endeavor is aimed at the effect of laser ablation on the Cu, Ag and CuAg ion exchanged soda lime glass and by UV-VIS optical absorption measurements.

KEY WORDS: Nanocomposite, plasmon resonance, ion-exchange, soda-lime glass, laser ablation, optical absorption.

1. INTRODUCTION

Embedded metal nanoclusters in glass matrix were formed either by direct ion implantation of the metal of interest into dielectric matrix or by binary ion-exchange followed by ion irradiation. These metal ion-exchanged glasses are of considerable interest due to their broad spectral potential applications such as production of stained glasses, formation of optical switches (Kondo, 1996; Asahara, 1997) and much more in the fabrication of opto-electronic and photonic devices (Haus,1989; Flytzanis, 1991; Mazzoldi,1994). The tool for the investigation of such metal nanocomposites is the optical absorption spectroscopy, where the surface plasmon resonance (SPR) exhibited by the embedded metal nanoclusters unveil the composition and cluster size. The present effort aims to study the effect of laser annealing on size distribution of the single and bimetallic ion-exchanged glasses by the optical absorption measurements.

2. EXPERIMENTAL

Binary ion-exchange is extensively used for doping silicate glasses with metal ions thus forming optical wave guides with increase in refractive index (Ramaswamy,1988; Arnold, 1996). 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 sulphate and sodium sulphate for Cu and silver nitrate and sodium nitrate bath for Ag ion-exchange for about one minute. In the bath Cu^+-Na^+ and Ag^+-Na^+ ion-exchange takes place in their respective molten salt baths. The copper ion-exchanged samples were cleaned and again dipped in silver bath for the formation of embedded bimetallic CuAg nanocluster glasses. Post ion-exchange the glasses were cleaned well to remove any surface impurities and then laser annealed for various exposure timings viz., 500 ms, 1000 ms, 1500 ms and 2000 ms using a 10 watt power Co_2 laser (SUDAR-300 ultra pulse) with output aperture lens of 0.3 mm diameter and wavelength λ=10.6μm. Optical absorption spectra of the ion-exchanged and laser annealed samples were recorded at room temperature in the 300-800 nm wavelength regions using a UV-VIS dual beam spectrophotometer with the plain soda-lime glass as the reference.

3. RESULTS AND DISCUSSION

The optical absorption spectra of copper and silver ion-exchanged and laser annealed glasses are show in the Figure 1 & 2. The average cluster radii R of the embedded nano particles are calculated from the full width half maximum $\Delta\lambda$ (FWHM) of the optical absorption peaks using the formula given below (Kreibig,1995).

$$R = \frac{V_f \lambda_p^{\ 2}}{2\pi C \Delta\lambda} \qquad (1)$$

V_f is the Fermi velocity of the electrons in bulk metal (Copper = $1.57X10^8$ cm/s and Silver = $1.39X10^8$ cm/s), $\Delta\lambda$ is the full width at half maximum of the absorption band and λ_p is the characteristic wavelength at which surface plasmon resonance occurs. Both λ_p and $\Delta\lambda$ depend on the substrate and size of the metal nanoclusters forming the composite. The calculated cluster sizes of copper and silver nanoclusters are shown in the Table. 1 & Table. 2. It is observed from the both the tables that the size of copper and silver clusters increase for the 500 ms exposure time. But for higher exposure timings the cluster radius decreases drastically for both copper and silver clusters which are well observed from the Figures. 1 and 2 also. This decrease in size of the clusters may be due to the sudden increase in sample temperature leading to the segregation of both Cu and Ag clusters inside the glass matrix.

3.1. Ag core and Cu shell: The optical absorption spectra of the sequential CuAg ion-exchanged and laser annealed sodalime glasses are shown in the Fig. 3. From the graph it is observed that for the 500 ms exposed CuAg sample the spectra exhibited two surface plasmon resonance (SPR) peaks one centered around at 416.19 nm corresponding to the silver and the another shoulder centered at 564.66 nm to that of copper in soda-lime glass. This kind of absorption spectra with a silver peak and a copper shoulder corresponds to the presence of copper coated silver nanoclusters. Similar core shell nanostructures were reported (Anderson,2000). Where Cu coated Ag nanocrystals were formed in silica by direct sequential implantation of Ag^+ and Cu^+ ions with TEM analysis depicting the diffracting rings of the core and shell metals embedded inside the matrix.

Thus, in our present case during the sequential Cu/Ag ion-exchange, copper clusters are formed in the glass matrix soon after the copper ion-exchange. When they are again dipped in the molten bath of silver nitrate for silver ion-exchange, an annealing effect takes place for the already diffused copper atoms. Hence, apart from the diffusion of silver atoms into the glass matrix, clustering and growth of copper clusters also takes place inside the host glass. Laser annealing of CuAg ion-exchanged glasses resulted in the migration of silver atoms to aggregate and form clusters. In the process of clusterisation, small clusters of silver are impregnated by the already formed copper clusters thus leading to the possible formation of a core shell arrangement inside the dielectric matrix. Such kind of phenomenon has already been reported in our earlier work (Manikandan, 2003). The size of the respective copper and silver clusters calculated using the equation 1 for various laser exposure timings are shown in the Table. 3. It is observed from the Table. 3 the sizes of both the copper and silver clusters increase with the increase in the exposure timings which is reflected well in the optical absorption spectra.

4.CONCLUSION

Embedded copper and silver nanoclusters were formed by commercial ion-exchange in soda lime glasses and were laser annealed at different exposure timings. The size of the embedded clusters reduced drastically for higher exposure timings, unveiling the fact that laser annealing can play a significant role in controlling the size of the embedded clusters.

As a novel route Copper coated silver nanoclusters were formed inside the soda-lime glass by sequential CuAg ion-exchange followed by laser annealing. The optical absorption spectra confirmed the formation of core shell structures between the embedded metals and it is found that the size of the respective metal nanoclusters increased with increase in laser exposure timings.

Table. 1: Calculated average cluster size (R), SPR peak (λ_p), FWHM ($\Delta\lambda$) of copper clusters

Exposure time (ms)	Radius (R) (nm)	FWHM ($\Delta\lambda$) (nm)	SPR peak (λ_p) (nm)
500	6.30	41.92	561.58
1000	4.50	56.26	562.16
1500	5.80	46.69	570.33
2000	5.42	48.58	562.50

Table. 2: Calculated average cluster size (R), SPR peak (λ_p), FWHM ($\Delta\lambda$) of silver clusters

Exposure time (ms)	Radius (R) (nm)	FWHM ($\Delta\lambda$) (nm)	SPR peak (λ_p) (nm)
500	0.84	156.4	422.0
1000	0.86	154.8	425.0
1500	0.53	242.54	418.6

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Table. 3:Calculated average cluster size (R), SPR peak (λ_p), FWHM ($\Delta\lambda$) of Cu and Ag clusters in CuAg ion-exchanged and Laser annealed glass

Exposure time (ms)	Copper			Silver		
	Radius (R) (nm)	FWHM ($\Delta\lambda$) (nm)	SPR peak (λ_p) (nm)	Radius (R) (nm)	FWHM ($\Delta\lambda$) (nm)	SPR peak (λ_p) (nm)
500	6.10	43.61	564.66	0.85	151.21	416.17
1000	8.80	30.20	564.67	2.02	61.30	409.62
1500	7.52	35.35	564.87	1.90	64.44	407.86
2000	7.50	35.18	562.56	1.44	86.51	410.71

Fig.1. Optical absorption spectra of Cu ion exchange & laser annealed glass

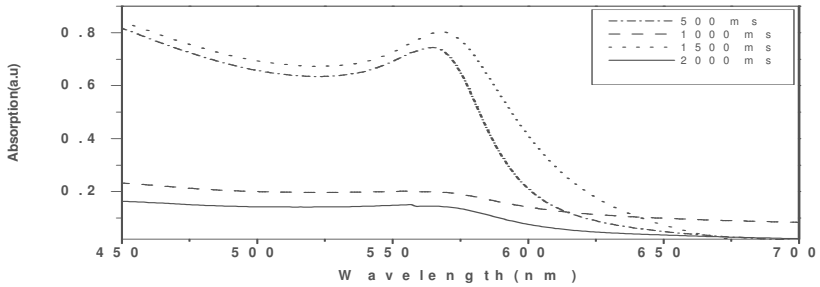


Fig.2. Optical absorption spectra of Ag ion exchange & laser annealed glass

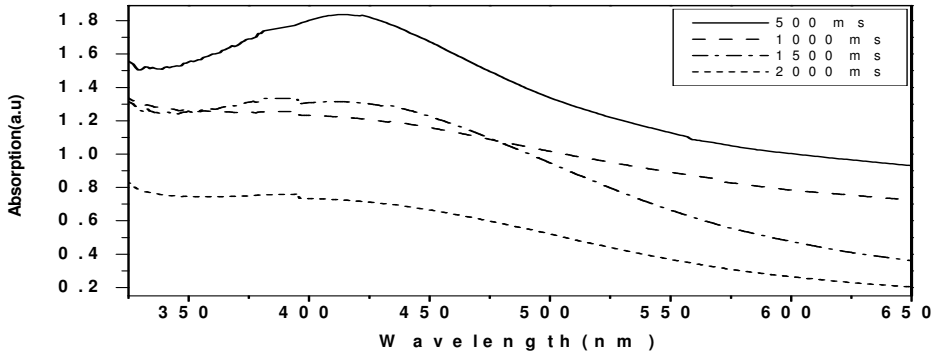
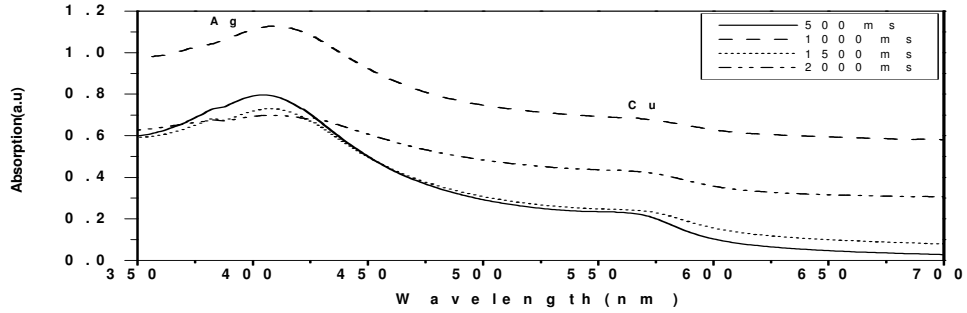


Fig.3. Optical absorption spectra of sequential CuAg ion exchange & laser annealed soda lime glass



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