STRUCTURAL CHARACTERIZATION OF EMBEDDED COPPER NANOCLUSTERS

- P. Manikandan[1, 2]*

- D. Manikandan[3]

- E. Manikandan[4]

Abstract

Copper nanoclusters have been embedded in the sodalime glass by binary ion exchange method. These ion-exchanged glasses are annealed in air 1h at different temperature. The optical absorption spectra show the presences of copper ions in the ion exchanged and different temperature annealed glasses corresponds to the characteristic surface plassmon resonance of copper nanocluster. Additional characterization of the samples was carried out by FESEM and GIXRD. FESEM studies prove that smaller size nanoclusters of copper (Cu) are embedded in randomly in the sodalime glasses. XRD patterns of ion exchanged and different temperature annealed also confirm the presence of copper and its crystalline spacing is varying for different annealing temperature. The FESE Mimages of ion exchanged and different temperature annealed glasses support the optical absorption spectroscopy results.

Keywords: Copper nanocluster, ion exchange, FESEM, XRD and Optical property.

INTRODUCTION

Formation of composite glasses containing metal colloids was done earlier by direct implantation of metals into the dielectric implantation of metals into the dielectric matrix or by sequential ion exchange and laser annealing of the metal-doped silicate glasses. The optical absorption spectroscopy is the most used tool for the investigation of such a system, 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. In this paper we examine the influence of different parameters (annealing temperature nanoclusters size, morphology and surface plasmon resonance (SPR) wavelength) on copper (Cu) ion exchanged glasses [1 - 8].

EXPERIMENTAL DETAILS

Copper nanoclusters were prepared by the pre cleaned soda-lime glasses slides were dipped in the molten salt bath of $CuSO_4:Na_2SO_4$ taken in equal moles for 1 min at the temperature of about 560-570°C. During immersion, in the molten state, copper ions of salt bath

[1]Research & Development Centre, Bharathiar University, Coimbatore 641046, India.
[2]Department of Physics, Krishnasamy College of Engineering & Technology, Cuddalore 607109, India.
[3]Department of Physics, Arignar Anna Govt Arts College, Villupuram 605602, India.
[4]Department of Physics TVUCAS Campus, Thennangur 604408, Thiruvalluvar University, Serkkadu, Vellore, India.
*Corresponding Author: E-Mail: p.manidotkandan@gmail.com, Tel: +91 9942011581 (P. Manikandan).

diffuse into the glass replacing the sodium ions coming out of the glass in to the bath. The diffused copper ions aggregate to form themselves clusters of nano-dimension inside the glass matrix. In this method, the Cu^+-Na^+ ion exchange is utilized as an essential first step to introduce Cu^+ ions into the glass matrix. Ion-exchange reaction involves equivalent substitution of one ion for another.

The ion-exchanged glasses are subjected to various post ion-exchanged treatments for cluster growth. It is of interest to observe the effect of post ion-exchange treatments on the size of the metal nanoclusters. The different treatments to which the copper and silver ion-exchanged glasses were subjected to are discussed below [8 - 11]. In this way, metal aggregation in nanometersized clusters can be promoted with several degrees of freedom for effectively defining the cluster structure and so the performances of the composite material [12, 13].

Thermal annealing is one suitable treatment for the ion-exchanged glasses for it causes effective reduction and aggregation of metallic dopants inside the superficial layers of the glass. A narrow size distribution of nanoclusters is achieved by this method, with the spatial distribution depending strongly on the treatment condition. The samples were annealed at different temperatures starting from 100°C to 400°C in steps of 100°C.

The optical absorption spectra of the ion exchanged and different temperature annealed samples were recorded at room temperature in the wavelength range from 200 to 1200 nm, using a Shimadzu ultraviolet visible–near infra-red (Shimadzu UV-VIS-NIR Model UV-3101 PC) dual beam spectrophotometer with the plain soda-lime glass as the reference.

The field emission scanning electron microscopes (FESEM) with energy dispersive X-ray (EDS) spectra were recorded by using SUPRA™ 55VP GEMINI® field emission scanning electron microscope (FESEM). Combining several instruments in one, the SUPRA™ 55VP with the improved GEMINI® column is a true nanoscience FESEM. SUPRA™ 55VP GEMINI® has been developed as an extremely versatile FESEM capable of delivering high quality imaging solutions for the many demanding applications in the field of nanotechnology.

Diffraction pattern gives information on translational symmetry - size and shape of the unit cell from peak positions and information on electron density inside the unit cell, namely where the atoms are located from peak intensities. The XRD pattern of copper ion exchanged and different temperature annealed soda-lime glasses were recorded using the X-Ray diffractometer (XRD-SMART Lab) - Rikagu, Japan.

## RESULT AND DISCUSSIONS

Optical Absorption Spectra

Copper nanoclusters of a few nanometers were formed into the soda-lime glass by ion exchange technique. The ion exchanged samples turned pale reddish brown due to presence of copper ions (Cu^+). Figure 3.7 shows the typical optical absorption spectra of copper ion (Cu^+) exchanged and different temperature annealed samples.

The average cluster radii R of the embedded copper (Cu) nanoclusters are calculated from the full width half maximum (FWHM, $\Delta\lambda$) of the SPR band of the optical absorption spectra. The inverse relation of the cluster radius R to the FWHM, ($\Delta\lambda$) is as given below:

$$R = \frac{V_F \lambda_P^2}{2\pi C \Delta\lambda} \quad ----------(1)$$

where V_F is the Fermi velocity of electron on bulk metal (Copper $= 1.57 \times 10^6$ m s^{-1}), $\Delta\lambda$ is the full-width half-maximum of the absorption peak band and λ_p is the characteristic wavelength that which (SPR) occurs. Both λ_p and $\Delta\lambda$ depend on the substrate and size of the metal nanoclusters forming the nanocomposite.

From the optical absorption spectra, it is found that absorption band edge ranges from 562 to 570 nm, and these absorption peaks correspond to the surface plasmon resonance (SPR) of copper clusters [14,15]. The spectra follow the trend of decreasing intensity with increasing wavelength. The average copper clusters sizes calculated using the equation (1) for various annealing temperatures. The copper cluster sizes vary from 4.41 nm to a maximum of 5.50 nm. But with increasing in annealing temperatures the size of cluster vary randomly without any trend.
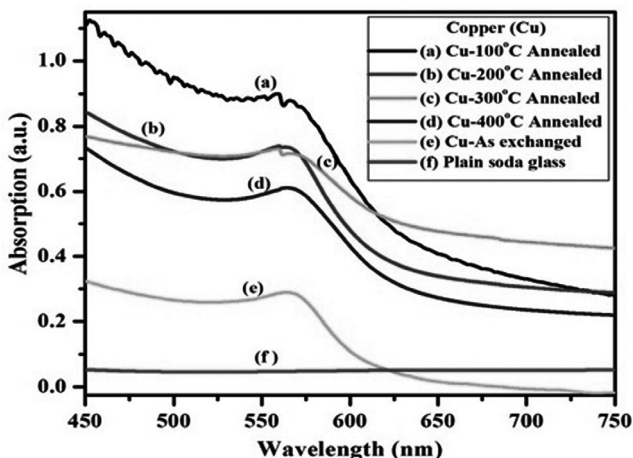
Fig. 19.1. Experimentally Recorded Optical Absorption Spectra for Plain, Copper Ion Exchanged and Different Temperature Annealed Soda-Lime Glasses

The clusters size increases and decreases at various annealing temperatures. This indicates that during the annealing process, aggregation and segregation of Cu ions into the Cu ion exchanged soda-lime glasses. A blue shift of SPR peak position is observed with increasing annealing temperatures. But in the case of 300 and 400°C annealed temperature, the red shift of SPR peak is observed. These shifting of SPR peaks are due to the change in clusters size during the annealing process, where a decrease of FWHM with increase in the SPR peak value is observed. The red shift of SPR peak is observed with increasing cluster size. Irrespectively, blue-shift SPR peak is also observed for increasing cluster size this is due to lower value (48.02 nm) of FWHM. The FWHM value decreases significantly with increases in cluster size. The FWHM decreases significantly with increases in cluster size. This kind of decrease in FWHM with increase in cluster size is due to the mean free path effect which comes into play for smaller ($R \leq 10$ nm) cluster [16].

FESEM Images of Copper Nanoclusters

FESEM image of copper ion exchanged and different temperature annealed soda-lime glasses are shown in Fig. 2. FESEM images showed that the copper ion exchanged and different temperatures annealed glass had a granular (island) structure. Annealing effect of copper ion (Cu^+) exchanged glass causes a surface mass transfer between the islands as well as bulk clusters due to inter-diffusion cluster at the annealing temperature.
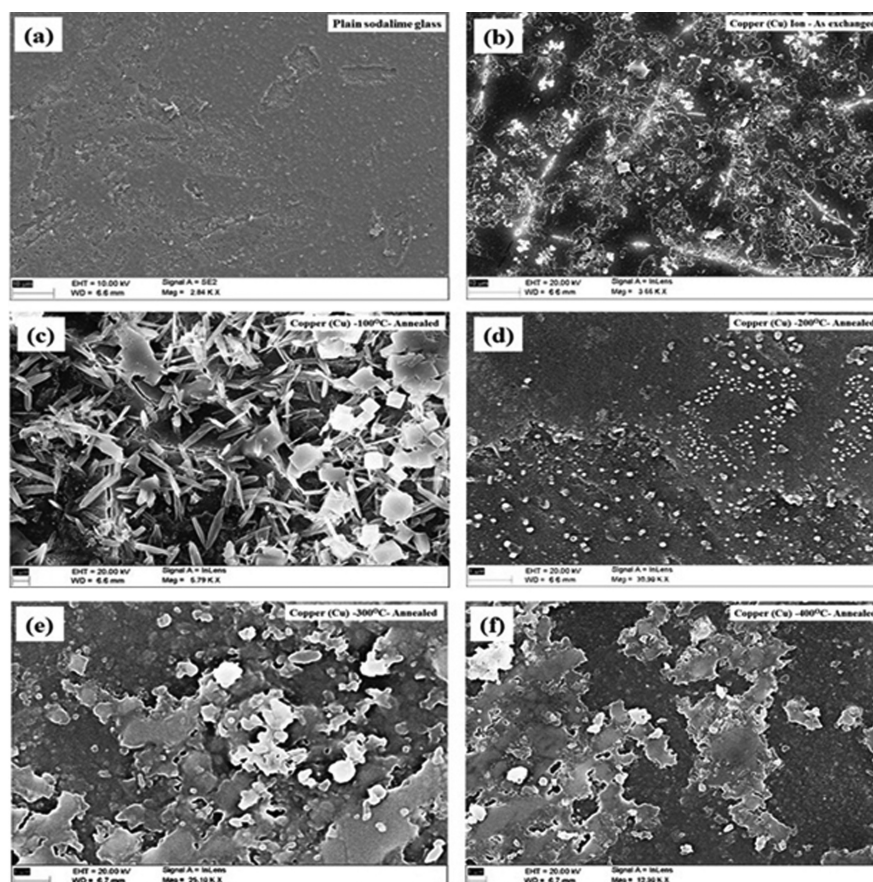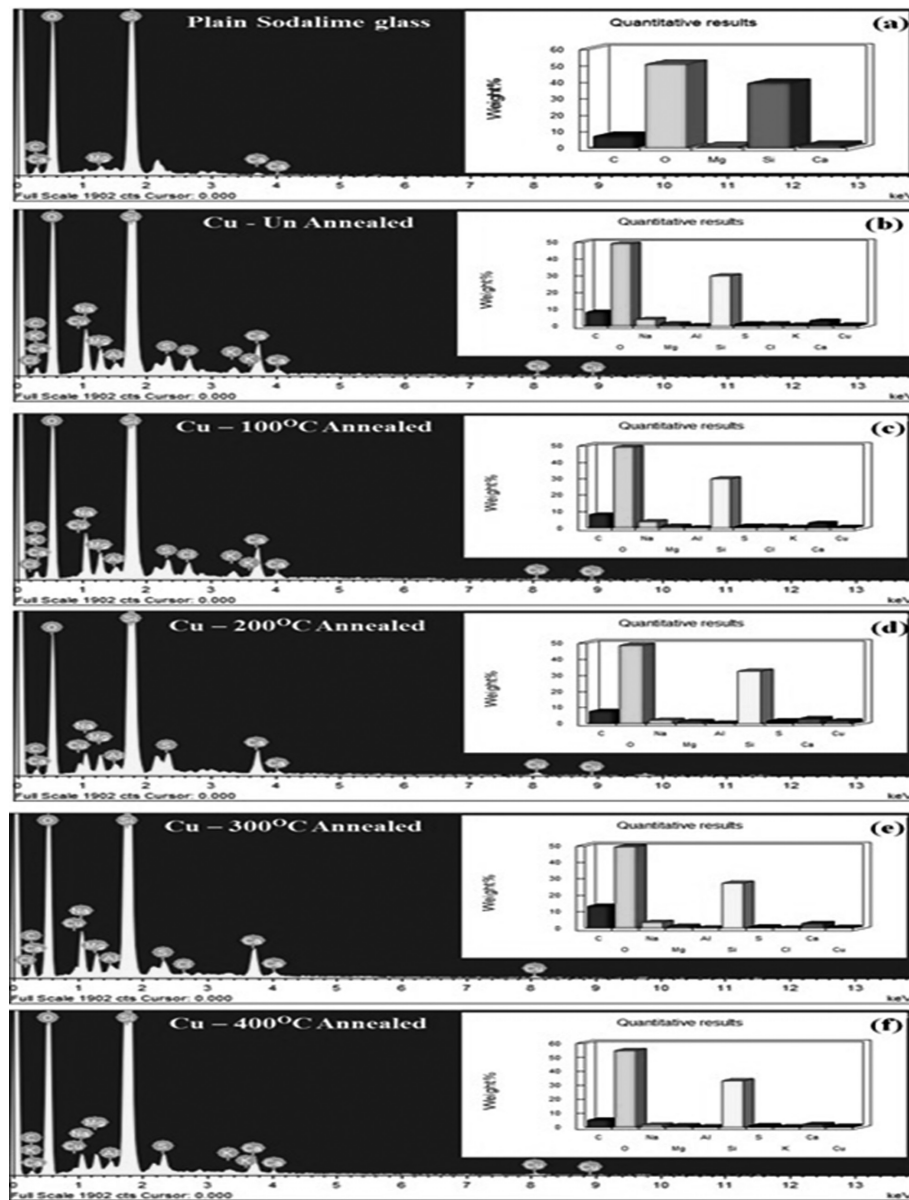

Fig.19.2: FE-SEM Images for (a). Plain (b). Copper ion Exchanged (c). 100°C annealed (d). 200°C Annealed (e). 300°C Annealed and (f). 400°C Annealed Soda-lime Glasses

Surface mass transfer between the islands was noticeable for copper ion exchanged different temperatures annealed glasses and resulted in the formation of equilibrium nanoparticles shape close to a spherical segment. We also observed sintering and agglomeration of nanoparticles located near one another and diffusion coalescence of nanoparticles resulting in an increase of the average particle size. FESEM image of Cu ion exchanged glass shows that very small size of clusters and 100°C annealed (Fig. 2.(c)) glasses has nanocluster are different shapes and close proximity between the clusters; the 200°C (Fig. 2(d)) annealed copper ion exchanged glass have nanocluster of shapes nearly spherical with almost same size and no close proximity.

But, the copper ion exchanged 300°C annealed glass (Fig. 2(e)) has nanocluster of shapes that is fractals and lower proximity between the clusters with decreasing average cluster size, and 400°C annealed copper ion exchanged (Fig. 2(f)) glasses have nanocluster of shapes also fractals and no close proximity between the clusters with increasing the average cluster size. This result supports that the variation of Cu cluster size with annealing temperature obtained by UV absorption spectra.

EDX Spectra of Copper Ion Exchanged Glasses

Fig.3. EDX Spectra for (a). Plain (b). Copper Ion Exchanged (c). 100°C Annealed (d). 200°C Annealed (e). 300°C Annealed and (f). 400°C Annealed Soda-lime Glasses

FESEM determinations of ion exchange and different temperature sample showed the formation of nanocluster, which were confirmed to be copper (Cu) by EDX [17, 18]. The EDX spectra of plain sodalime glass (Fig. 3(a)) shows the peaks only corresponds to C, O, Mg, Si and Ca for the elements present sodalime glass and there is no signature of copper cluster. Figure 3(b) to 3(f) shows the EDX analysis of copper ion exchange and different temperature annealed glasses showed a peak in the Copper (Cu) region, confirming the formation of copper nanoclusters.

The inset in the EDX spectra of the Copper (Ag) ion exchanged and different temperature annealed samples shows the percentage (quantitative result) of Copper and other elements present in the ion exchanged and annealed soda-lime glasses. EDX spectra and quantitative result

of Cu ion exchanged samples annealed at 300°C has higher percentage than the samples annealed at 100°C, 300°C & 400°C. This result also supports that variation of cluster sizes with annealing temperature of optical absorption spectra.

GIXRD Pattern of Copper Ion Exchanged and Different Temperature Annealed Soda-Lime Glass

The GIXRD pattern of copper ion exchanged and different temperature annealed soda-lime glasses shown in Fig.4. The XRD pattern shows four peaks in the whole spectrum of 2θ values ranging from 25 to 45. The peaks having the centered on at 2θ positions 29.6°, 36.11°, 36.6° and 42.20° corresponding to the formation of Cu (110), Cu_2O (111), Cu (111) and Cu (200) nanoclusters [19, 20].
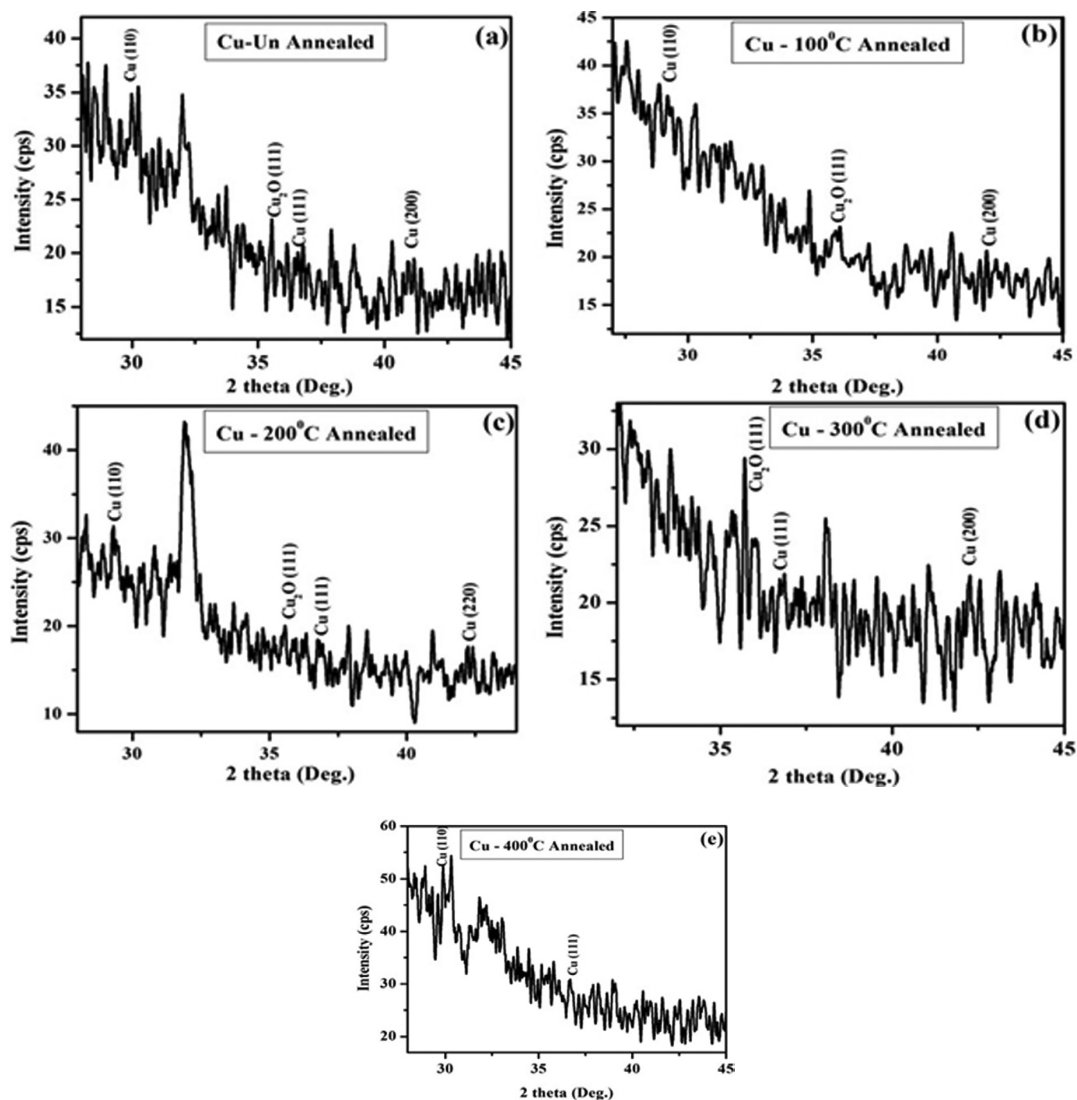

Fig.19.4 : XRD spectra for (a). Plain (b). Copper ion exchanged (c).100°C annealed (d). 200°C annealed (e). 300°C annealed and (f). 400°C annealed soda-lime glasses

The copper ions as exchanged and 200°C annealed soda-lime glass have the four characteristic peaks corresponding to copper and copper oxide formed inside in the ion exchanged soda-lime glass. The copper ion exchanged sample annealed at 100, 300, and 400°C shows that no sharp peaks corresponding to copper. This result clearly shows that the diffused copper ions in the soda-lime glass shows crystalline faces for certain annealing temperature and crystalline faces changes to some annealing temperatures and also the diffused copper (Cu) ions stay scattered inside the dielectric matrix as copper (Cu, Cu^+ and Cu^{2+}) particles and the cluster growth is induced by annealing processes.

This result also shows that the size and structure of copper nanocluster is varied during the annealing processes. It is also supported to the UV absorption spectra of copper ion exchanged and different temperature annealed soda-lime glass with different clusters size. The XRD patterns confirm the presence of copper in pure form of copper and copper oxide of copper ion exchanged and different temperature nanoclusters.

CONCLUSION

Copper (Cu) nanocomposite glasses were prepared by the binary ion exchanged method. The size of these nanoclusters varied small value and it can be adjusted by careful control of annealing temperature and different laser annealing time. The FESEM images of copper ion exchanged and different temperature annealed glasses clearly shows that morphology of embedded nanocluster varying due different annealing temperature. The XRD pattern of copper ion exchanged and different temperature annealed glasses shows that crystalline faces of copper are varying with increasing the annealing temperature. The experimental result shows advantages that binary ion exchanged method for preparing metal nanocluster and which might find an important future application in materials technologies like micro/nano-electronics and bio-medical chemical nanosensor devices.

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