Chapter 5

6 MeV Electron Assisted and Ion exchanged Diffusion of Silver and copper metal in Soda Lime Glass

In this chapter, the results on 6MeV electron assisted and ion exchanged diffusion of silver and copper metal in soda lime glass was presented. 1N AgNO₃ solution was prepared and poured into the plastic cylinder of appropriate size. The sample was mounted vertically in each cylinder and irradiated with 6Mev race track Microtron accelerator with the fluences ranging from 10 × 10¹⁴ to 40 × 10¹⁴ electrons/cm² with subsequent annealing at 450°C. These irradiated samples were characterized by UV Visible spectrometer, X-ray diffraction, EDS and scanning electron microscopy. Moreover, the diffusion of silver into soda lime glass by ion exchanged method is also explained. Similarly, copper was diffused in soda lime glass by ion exchange and 6 MeV electron irradiation. These samples were then irradiated with 6 MeV energy electrons in the fluences ranging from 10 × 10¹⁴ to 40 × 10¹⁴ electrons/cm² and annealed for the temperature of 400°C. The optical properties and the corresponding induced effects were characterized by the techniques such as UV-Visible, FTIR, SEM and XRD. The UV-Vis absorption spectra show a peak at 432nm which corresponds to the absorption band of metal silver nanocluster. The XRD peaks show 2θ position at 38.08°, 44.28°, 64.57° and 77.26° respectively which corresponds to (111), (200), (220), (311) planes of nanocrystalline silver. SEM image of diffused silver nanoparticles observed an average size of 40nm and the rate of agglomeration of the silver nanoparticles increases with increase in the electron fluence. The UV-Vis absorption spectra of copper samples show two peaks, one at 754 nm and other at around 533nm. The XRD peak at 2θ position at 43.19° which corresponds to (111) plane of nanocrystalline copper having FCC structure. SEM image of diffused copper nanoparticles show an average size around 15nm for the electron fluence of 40 X10¹⁴ ele/cm² and the EDS confirms the diffusion and existence of copper into the soda lime glass.
5.1: Introduction

Soda lime glass shows several advantages such as low cost, the ease of processing, the high durability, high resistance and the high transparency with the possibility of tailoring the behaviour of the glass-based structures [1]. Composite materials were prepared by metal clusters embedded in silicate glass matrices exhibited promising optical properties for photonic application, and magnetic properties such as superparamagnetism, enhanced coercivity and shift of the hysteresis loop [2]. The properties of composites also have importance in catalysis, sensor and telecommunication technology [3]. These properties of composites are dependent on their size, shape, density and spatial distribution [4].

Many researchers having interest in nano-sized metal particles embedded in glass due to their specific linear and non-linear optical properties [5]. Silver nanoparticles have been studied extensively and synthesised by using different methods. Silver nanoparticles possess several unique electrical, optical and biological properties. Due to their crucial properties, silver nanoparticles have several applications in catalysis, biosensing, imaging, drug delivery, nanodevice fabrication and in medicine [6]. In the past few years, antimicrobial activity of silver nanoparticles have been studied very well [7]. Due to the antimicrobial property, silver nanoparticles are considered as future generation antimicrobial agents [8]. Thus, the diffusion of silver into glass and synthesis of silver nanoparticles becomes an important area of research and development.

Diffusion of silver using 6MeV electron irradiation and Ion exchange method are useful to alter the surface properties of an existing glass. Recently, an exchange of sodium or other alkali form a glass with silver from AgNO₃ or other silver salts, or from oxidized metallic silver films has been used to produce localized variations in refractive index[9]. Exchange of alkali ions is useful to strengthen glasses by producing a compressive layer in the near surface region. If ion exchange process is carried out at temperatures well below Tₜ, very little stress relaxation occurs[10]. Furthermore, if the ion in the glass is replaced by a larger ion from the external source, the difference in volumes of the two ions may results into a large compressive stress in the exchanged
region. This process is known as ion exchange strengthening. The sodium-potassium pair typically has a very favourable inter diffusion coefficient. Therefore, a special silicate glasses with high sodium diffusivities for ion exchange strengthening has been developed [11]. Conventional methods for synthesis of metal nanocluster composite glasses are ion exchange and consequent thermal processing show limited flexibility to control concentration, size and configuration of particles. Therefore, the combination of different methods is preferred with special emphasis given to those based on ion exchange and irradiation [12]. Ionising radiation like X-ray or electron beams causes oxidation of the metal atoms and reduction of metal ions contained in glass [13]. The irradiation of ion-exchanged glasses has a less internal reductive content to generate charged defects within the matrix due to electronic excitations [14]. The addition of silver into the glass is to make bioactive materials by considering the antimicrobial activity of the Ag\(^+\) ions. Therefore, the fabrication of novel bioglass materials containing silver has importance in the research field of biomaterials and devices [15]. Several reports are available on antimicrobial activity of silver-based materials [16]. There is no report available on size control of silver nanoparticles in soda lime glasses irradiated by 6 MeV electrons. Hence this chapter deals with 6MeV electron assisted and ion exchange diffusion of silver metal and synthesized silver nanoparticles.

### 5.2 : 6 MeV Radiation Assisted Diffusion of Silver in Soda Lime Glass

#### 5.2.1 : Experimental details

Optically polished sodalime glass samples of size 1cm x 1cm x 1mm were taken for the irradiation. These sample were washed with acetone, then with distilled water and finally with methyl alcohol and dried with absorbent paper. These glass samples were wrapped in aluminum paper and then stored in a dust free dark paper to avoid light effects.
AgNO₃ solid was then dissolved in the distilled water and 1N solution was prepared. The solutions were then poured into the plastic cylinder of appropriate size. The sample holder was placed at the bottom of the cylinder and then the sample was mounted vertically in each cylinder. The typical arrangement is shown in Figure 5.1. The samples were then irradiated with 6MeV electrons with the fluences ranging from 10×10¹⁴ to 40×10¹⁴ electron/cm² and subsequent annealing at 450°C. After the irradiation, the samples were taken out of the cylinder and washed thoroughly with the distilled water, and then wrapped in the black papers. These irradiated samples were characterized by UV Visible spectrometer, X-ray diffraction and scanning electron microscopy.

5.2.2: Results and Discussion

The diffusion of Ag in the sodalime glass sample is carried out using 6MeV electron irradiation. The process of diffusion is ensured with the help of UV Visible spectroscopy, XRD and SEM techniques.
5.2.2.1: U-V Visible Spectroscopy

The optical absorption spectrum for the virgin and 6MeV electron assisted diffused soda lime glass is shown in figure 5.2.

![Graph showing UV-Visible Spectra of virgin and 6MeV electron assisted silver diffused soda lime glass.](image)

**Figure 5.2**: UV-Visible Spectra of virgin and 6MeV electron assisted silver diffused soda lime glass.

It is observed that the virgin soda lime glass does not show any absorption peak in the spectrum. However, irradiated samples with fluences of $10 \times 10^{14}$ electrons/cm$^2$, $20 \times 10^{14}$ electrons/cm$^2$, $30 \times 10^{14}$ electrons/cm$^2$ show peaks at 485 nm. This peak corresponds to the point defect known as non-bridging oxygen hole centre (NBOHC)[17]. The intensity of the peaks also increases with increase in the electron fluence. This shows that the concentration of the NBOHC increases with increase in the electron fluence. However, for the fluence of $40 \times 10^{14}$ electrons/cm$^2$, the peak at 485 nm is not observed, but another peak is observed at 425 nm. This peak attributes to the diffusion of Silver[18]. It is also observed that the absorption intensity of this peak is decreased. This decrease in the absorption intensity is due to the decrease in the concentration of NBOHC and diffusion of silver [19]. In the process of diffusion, the...
vacancy concentration of NBOHC helps to enhance the diffusion of silver in the sodalime glass. High concentration of vacancies at 30 X10^{14} electrons / cm^2 are now displaced by diffusion of silver.

![Figure 5.3: A plot of (\alpha h\nu)^2 against h\nu (eV).](image)

To find the energy band gap, and the defects concentration Urbach graph is plotted as shown in figure 5.3.

It is a plot of (\alpha h\nu)^2 against h\nu (eV). It has three different regions viz. (i) The low absorption region, (ii) Urbach region and (iii) high absorption region. The slope of the graph in the Urbach region gives Urbach energy, greater the Urbach energy, greater will be the disorder in the system and greater will be the defect concentration. Urbach plot clearly indicates that, the defect concentration increases with increase in the electron fluence, which enhances the process of diffusion of silver.

The exponential region of the Urbach plot is extrapolated to X-axis, the intercept of this line on the X-axis gives energy band gap of the sodalime glass. The plot clearly shows that the energy band gap decreases with increase in the electron fluence. However, for the fluence 40 X 10^{14} e/cm^2, it regains its original band gap. The decrease of the energy band gap is due to the increase in the defects concentration and the formation of defect centers or defect levels in the band structure. However, when
the diffusion of silver takes place, the defect centers are occupied by the silver atoms. Therefore, energy band gap is reestablished due to the silver diffusion and further increase in the band gap is due to blue shift of the absorption curve and size of the nanoparticles[20].

5.2.2.2: XRD analysis

The XRD pattern of virgin and 6MeV electron assisted Ag diffused sodalime glass is shown in figure 5.4. For the virgin sodalime glass as well as for the samples irradiated with 10X10^{14} ele/cm^2, 20X10^{14} ele/cm^2, 30 X10^{14} ele/cm^2 no diffraction peaks are observed. However, for the sample irradiated with 40 X10^{14} ele/cm^2, the diffraction peaks appearing at 2θ values 38.19° and 64.41° are found to match well with (111) and (220) crystalline planes of the face centered cubic silver crystal structure[21]. This clearly indicates that silver is diffused into the sodalime glass matrix by 6 MeV electron irradiation at the fluence of 40 X10^{14} ele/cm^2.

![XRD pattern of (a)Virgin and (b) 6 MeV electron irradiated Sodalime glass at 40X10^{14} e/cm^2 fluence in AgNO_3](image)

Figure 5.4: XRD pattern of (a)Virgin and (b) 6 MeV electron irradiated Sodalime glass at 40X10^{14} e/cm^2 fluence in AgNO_3
5.2.2.3: SEM and EDAX

The morphology and elemental analysis of the sample has been observed using Scanning electron microscopy (SEM) and Energy Dispersive X ray (EDAX). The 6 MeV electron irradiated samples were coated with thin layer of platinum to avoid any charging problem due to high energy electron bombardment during SEM/EDAX analysis.

![SEM image of Virgin and 6 MeV electron irradiated Sodalime glass at 40X10^{14} e/cm^2 fluence in AgNO_3](image)

Figure 5.5: SEM image of (a)Virgin and (b) 6 MeV electron irradiated Sodalime glass at 40X10^{14} e/cm^2 fluence in AgNO_3

SEM image of Virgin and 6 MeV electron irradiated Sodalime glass at 40X10^{14} e/cm^2 in AgNO_3 is shown in figure-5.5. It clearly shows that Virgin sample does not show any dispersed particles. However, for the 6MeV electron irradiated sodalime glass at 40X10^{14} ele/cm^2, silver particles with a high degree of polydispersivity and a wide size distribution is shown in figure 5.5(b). The size of the Ag nanoparticles found to be varying from 40 to 80 nm, with an average size of ~ 60 nm. Moreover, it can also be seen that the Ag nanoparticles of lower sized are also present in the sample. These results indicate that the silver particles of random size are produced at higher electron fluence.
The percentage concentration of Ag atom in the sodalime glass is confirmed by EDAX shown in figure 5.6. It shows that the concentration of Ag atoms in sodalime glass is enhanced by 3.11% at the fluence of 40 X10⁴² electron/cm².

5.2.2.4: Mechanism of formation of nanoparticles

The formation of silver nanoparticles and the respective diffusion in the glass matrix is because of the energetic electrons deposit energy in the medium through various processes, among which the prominent processes are ionization and excitation of atoms, breaking of chemical bonds, etc. During electron irradiation, the following electron induced radiolytic reactions and disintegration processes can be initiated in an aqueous mixture of the metal salt, PVA and 2-propanol solution

\[ n \cdot H_2O \sim \sim \rightarrow e^{-}_{aq}, H^+, OH^-, H_2, H_3O^+, H_2O_2, \ldots \text{etc.} \quad \ldots \ldots \ldots (5.1) \]

\[ MS \rightarrow M^+ \quad \ldots \ldots \ldots (5.2) \]
Where MS is the metal salt, $M^{x+}$ is the metal ion produced in the solution due to dissociation of the metal salt under electron irradiation. The metal salt used here are AgNO$_3$ which releases the $M^+$ ions such as Ag$^+$, Au$^{3+}$ and Cu$^{2+}$ in the solution[22].

For the $M^+$ ions the electron capture cross section is very high and, therefore, a large number of neutral ($M^0$) metal atoms can be produced in the solution through the following reaction,

$$M^+ + e^-_{aq} \rightarrow M^0 \quad \cdots \cdots \cdots \cdots \cdots \cdots (5.3)$$

The neutral $M^0$ atoms can encounter with the excess $M^+$ ions then they tends to associate with ions and coalesce into the dimmers and vacancies. These dimers progressively grow into vacancies followed by a large cluster which eventually precipitates out in the solution through the following reactions,

The neutral $M^0$ atoms can encounter with the excess $M^+$ ions then they tends to associate with ions and coalesce into dimers.

$$M^0 + M^+ \rightarrow M^+_{2} \quad \cdots \cdots \cdots \cdots \cdots \cdots (5.4)$$

$$M_{n-1} + M^+ \rightarrow M^n_+ \quad \cdots \cdots \cdots \cdots \cdots \cdots (5.5)$$

$$M^n_+ + e^-_{aq} \rightarrow (M)_n \quad \text{(Metal nanoparticle)} \quad \cdots \cdots \cdots \cdots \cdots \cdots (5.6)$$

In this manner, during electron irradiation, the size of the metal particle can grow and subsequently forms metal particles of nanometric dimensions [23].

The presence of bombarding particles at a particular temperature also adds mobility to the atom of the solid giving them some chance to rearrange themselves. Three effects may be anticipated

(a) An energetic primary knock-on produces in medium and heavy elements at least a high concentration of displaced atom and also propagates replacement collision sequences. It is to be expected that such a spike would destroy some of the order present in the spike region.
(b) Enhanced nucleation of phase changes may occur in the damage region produced by particle bombardment. The effect may be due to the need to relax large lattice strains or the presence of vacancies may also assist nucleation.

(c) Diffusion occurs in most solids by the motion of thermal vacancies, and thus the presence of irradiation induced vacancies in general enhanced diffusion. The magnitude of this effect is discussed below.

The diffusion coefficient \( D \) is given by the equation

\[
D = a\nu_0 a^2 C_v \exp\left(-\frac{Em\nu}{K}\right) \\
\text{----------}(5.7)
\]

Where \( K \) is Boatman’s constant, \( \nu_0 \) is the Debye frequency of the lattice, \( a^2 \) is the mean square jump length, \( A \) is constant, usually \( \sim 10 \), involving geometrical and entropy factors, and \( C_v \) is the vacancy concentration. The thermal equilibrium value of \( C_v \) is given by

\[
C_{veq} = B \exp\left(-\frac{E_{f\nu}}{K}\right) \\
\text{----------}(5.8)
\]

As we have seen previously. The effect of irradiation is to increase the vacancy concentration above \( C_{veq} \) and thus to increase \( D \). The rate of production of irradiation induced vacancies is fixed by the bombarding particle flux, and the equilibrium concentration depends upon the rate of production of vacancies. The thermal vacancy concentration increases exponentially with temperature and thus at low temperature the irradiation induced concentration will be much the greater. It is to be expected, therefore, that the diffusion coefficient would be enhanced at low temperature but unchanged at high temperature [24].

**5.2.2.4: Conclusion**

The results of XRD, UV-Vis and SEM EDAX revealed and confirmed that sodalime glass responds to the diffusion of Ag atoms by electron irradiation at higher fluence.
5.3 Diffusion of Silver in Ion exchanged Soda Lime glass and nanoparticles formation by 6MeV electron irradiation

5.3.1: Introduction

The coloring of glasses by the controlled introduction of appropriate metallic nanoclusters is one of the older techniques known to humankind and their optical properties are related to the existence of nanoclusters, for potential applications to photonics [25]. Research on precipitation control has involved many techniques [26]. Among these methods involving the use of ionizing radiation (photons, electrons, ions) have repeatedly drawn interest because control is envisaged, via the irradiation fluence, over the amount of precipitated metal, the density and average size of the metallic nanoclusters. For example, adequate control is indeed observed via photon irradiation in so-called photosensitive glasses [27], and rather precise control via ion irradiation is recently demonstrated [28]. However, in radiation induced diffusion of silver, the percentage of diffused silver is very feeble. The present work aims at improving the diffusion of silver and to envisage the control over average size of the metallic nanoclusters.

5.3.2: Experimental

Optically polished commercial soda lime glass slides of composition (weight %) 72.90 SiO₂, 14.50 Na₂O, 6.72 CaO, 4.90 MgO, 1.40 Al₂O₃, 0.03 SO₃, 0.08 Fe₂O₃ were taken for the experiment. The plane slides were then cut into many pieces of the dimensions 1cm X 1cm X 0.1cm. The samples were washed with acetone and then with distilled water and finally with methyl alcohol to remove any surface ambiguities. These samples were then dried with absorbent papers as well as wrapped into aluminium paper and stored in the dust free environment in a thin polythene. A salt bath of AgNO₃ : NaNO₃ in the molar ratio 1:2 is kept in the furnace and the temperature of the bath was maintained at ~ 350°C for about 45 minutes. The molten bath was then taken out of the furnace for few minutes and the glass samples were put into it, and it was then placed into the furnace for 30 minutes. During the immersion, silver ions of the salt bath diffuse...
into the glass and replaces the sodium ions. The samples were isolated from molten salt, cleaned with acetone, and were mounted on the Faraday cup and irradiated with 6 MeV energy pulsed electron beam having 2 µsec pulse width and 50 pps repetition rate. The output of the Faraday cup was connected to the current integrator for the measurement of electron fluence received by the sample. The samples were then irradiated at different fluences in the range from 10×10^{14} to 40×10^{14} electrons/cm^2. The irradiation was carried out at room temperature and atmospheric air pressure. The thermal annealing of the ion exchanged samples were also carried out in air for one hour at the temperature of 450 °C. These ion exchanged synthesized metal nanoparticles were characterized by UV-Vis absorption spectroscopy, XRD, SEM and Energy dispersive spectroscopy (EDS) techniques.

5.3.3: Results and Discussion

5.3.3.1: Visual observations and UV-Visible spectroscopy

UV-Visible spectra of virgin and ion exchanged with 6 MeV electron irradiated soda lime glass for different fluences is shown in figure 5.7. A virgin glass (plain glass before reaction) did not show any characteristic peak. However, ion exchanged soda lime glasses of faint yellow color are changed into dark brown color after the electron irradiation at different fluences from 10×10^{14} to 40×10^{14} ele/cm^2. These thermally annealed samples show characteristic peaks of silver nanoparticles at 438 nm and reduced to 417 nm [29], with increase in electron fluences from 10×10^{14} to 40×10^{14} ele/cm^2. This blue shift of ~ 21 nm suggesting that size of the Ag nanoparticles decreases with increasing electron fluence [30].
It is also observed that the peak intensity of the spectrum increased with increase in electron fluence. Similarly, the full width half maxima (FWHM) of the spectrum also increased with increase in electron fluence. Average cluster radii (R) of Ag nanoparticles have been calculated from the full width half maximum, \( \lambda \) (FWHM) of the optical absorption peaks by using a formula given below:

\[
R = \frac{V_f \lambda_p^2}{2\pi c \Delta \lambda} \quad \text{.........(5.9)}
\]

Where \( V_f \) is the Fermi velocity of the electrons in bulk metal (for silver \( 1.39 \times 10^8 \) cm/s), \( \lambda \) is the full width at half maximum of the absorption band and \( \lambda_p \) is the characteristic wavelength at which SPR occurs. Both \( \lambda_p \) and \( \lambda \) depend on the glass substrate and size of the metal nanoclusters forming the composite [31]. The calculated average cluster radii of silver nanoparticles were in the range of 7-29 nm. It is observed that average cluster radius of nanoparticles decreases with increase in electron fluences.
5.3.3.2: X-ray diffraction (XRD) analysis

Figure 5.8 shows the XRD spectra for Ion exchanged and Ag doped Soda lime glass Irradiated with 6Mev electrons for different electron fluences. It shows characteristic peaks at 2θ position of 38.08°, 44.28°, 64.57° and 77.26° corresponds to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of a faced centre cubic (fcc) lattice of silver [32]. The XRD patterns displayed in this study are consistent with earlier reports. Some more peaks have been observed with increase in electron fluence from 10 x 10^{14} to 40 x 10^{14} e/cm². Moreover, the intensity of the XRD peaks found to be increased with the fluence, and is mainly attributed to the increase in crystalline volume fraction [33].

![XRD spectra of Ion exchanged and Ag doped Soda lime glass Irradiated with 6Mev electrons at different electron fluences](image)

The average size of the silver nanoparticle is calculated by using the Scherrer’s formula[34].

\[
t = \frac{0.9\lambda}{\beta \cos\theta}
\]

\[........(5.10)\]
Where, $t$ is a size of Ag nanoparticles in $\text{Å}$; $\lambda$ is wavelength of X-rays; $\beta$ is full width half maxima and $\theta$ is called angle of diffraction. The calculated average size of Ag nanoparticles is in the range of 15 to 62 nm.

5.3.3.3: SEM and EDAX Analysis

SEM image of virgin and ion exchanged with 6MeV electron irradiated soda lime glass at different fluences from $10 \times 10^{14}$ e/cm$^2$ to $40 \times 10^{14}$ e/cm$^2$ is shown in figure 5.9. Virgin sample does not show any evidence of silver nanoparticles. Ag nanoparticles have been observed in sodalime glass after electron irradiation (figure B, C, D & E). It also shows that the presence of clusters of Ag nanoparticles at a electron fluence of $10 \times 10^{14}$ e/cm$^2$ and they are observed mainly due to the high surface energy of nanoparticles. However, at an electron fluence of $20 \times 10^{14}$ e/cm$^2$ and $30 \times 10^{14}$ e/cm$^2$, size of silver nanoparticles further reduced to $\sim 90-110$ nm, (figure C & D) and at a fluence of $40 \times 10^{14}$ e/cm$^2$, the size of Ag nanoparticles observed within the range $\sim 20-80$ nm (figure 2E). Figure5.10 is a representative EDS profile of ion exchanged with 6 MeV electron irradiated soda lime glass. The presence of Ag peaks indicated that percentage of Ag in the glass composition is $3.37\%$ at the fluence $40 \times 10^{14}$ electrons /cm$^2$ and is considerable amount.
Figure 5.9: SEM images of ion exchanged with 6MeV electron irradiated soda lime glass for different fluence (A) Virgin (B) $10 \times 10^{14}$ ele/cm$^2$ (C) $20 \times 10^{14}$ ele/cm$^2$ (D) $30 \times 10^{14}$ ele/cm$^2$ (E) $40 \times 10^{14}$ ele/cm$^2$

Figure 5.10: EDS of Ion exchanged with 6MeV electron Irradiated Soda lime Glass at $40 \times 10^{14}$ ele/cm$^2$ fluence.
The representative histogram shown in the figure 5.11 indicates the particle size distribution of Ag nanoparticles at a electron fluence of $40 \times 10^{14}$ e/cm$^2$ and is in between 10nm to 80nm with maximum at 40nm. Thus, obtained result revealed that the size of Ag nanoparticles can be controlled by using electron irradiation with different fluences.

5.3.3.4: FTIR analysis

The FTIR spectra of virgin and ion exchanged with 6 MeV electron irradiated soda lime glass is shown in figure-5.12. The virgin soda lime glass shows a broad shoulder with prominent peaks at 1066 and 1192 cm$^{-1}$ as well as centered at 1122 cm$^{-1}$. This band is the characteristic of the vibrational motion of oxygen atoms in SiO$_2$ [35]. This vibration has been described as rigid bodies in which the oxygen and silicon atoms move in the opposite directions. The differences in motion at the two edges in the oxygen stretching band reflect the differences in the relative IR activity at the peak of the stretching band near 1075 cm$^{-1}$, and at broad shoulder centered at about 1150 cm$^{-1}$ [36].
Figure 5.12: FTIR spectra of ion exchanged with 6 MeV electron irradiated soda lime glass for different fluences. (a) virgin (b) $10 \times 10^{14} \text{ele/cm}^2$ (c) $20 \times 10^{14} \text{ele/cm}^2$ (d) $30 \times 10^{14} \text{ele/cm}^2$ (e) $40 \times 10^{14} \text{ele/cm}^2$

There is no distinct shift in the spectrum of virgin sodalime glass and the ion exchanged electron irradiated soda lime glass. This indicates that the chemical environment at each one of the silicon atoms of the Si-O-Si linkage is not involved to make changes in the Si-O-Si vibrational frequency and the Si-O-Si bond angle remain same [37]. However, there is a broadening of the band and the shoulder disappears which indicates a statistical distribution of different bonding arrangements at each silicon atom site [38]. The disappearance of the shoulder is an effect that is driven by symmetry considerations. A distinct peak is observed at 995 cm$^{-1}$ in control soda lime glass did not observe in fused silica glass indicates that there is no composition of Na$_2$O. This peak corresponds to Si-O-Na$^+$ none bridging bond [39]. The intensity of this peak decreases with increasing electron fluences. However, the higher fluences ($40 \times 10^{14} \text{ele/cm}^2$) the peak is disappeared due to the diffusion of Ag and formation of Si-O-Ag$^+$ bond.
5.3.3.5: Mechanism of formation of nanoparticles

The mechanism behind the formation of nanoparticles is illustrated as follows:

\[ \text{Electron Irradiation} \]

Glass \( \rightarrow h^+ + e^- \) \hspace{2cm} (5.11)

\[ \text{Ag}^+ + e^- \rightarrow \text{Ag}^0 \] \hspace{2cm} (5.12)

At high electron fluence, Ag ions will be regenerated due to the recombination of electrons in Ag atoms with hole centres.

\[ \text{Ag}^o \rightarrow \text{Ag}^+ + e^- \] \hspace{2cm} (5.13)

\[ e^- + h^+ \rightarrow \text{recombination} \] \hspace{2cm} (5.14)

In this manner, Ag nanoparticles have been formed due to the diffusion and aggregation of Ag atoms in the glass matrix. Further, treatment with high temperature at 500°C for 15 min results dissolution of the silver particles. This dissolution of Ag particles is of interesting because Ag particle dissolution is normally observed under high electron fluence, but not by high temperature annealing. These Ag nanoparticles exist in the glass. The reason for particle dissolution may be similar to the dissolution of Ag atoms shown in reactions (5.12) and (5.13). The hole centers in the glass matrix plays a crucial role as an oxidizing agent also studied previously [40].

5.3.3 : Conclusion

In conclusion, the method used method in which size of Ag nanoparticles can be effectively controlled in ion-exchanged soda-lime glass using 6 MeV electron irradiation. The Ag nanoparticles synthesized by electron irradiation have been characterized by a variety of standard analytical techniques and size obtained around 50 to 80nm at a electron fluence of 40X10^{14} ele/cm². This study can be applied in the fields of microelectronics, medical, sensing and imaging.
5.4: Diffusion of Copper in Ion exchanged Soda Lime glass and nanoparticles formation by 6MeV electron irradiation.

5.4.1: Introduction

Metal-alkali ion exchanged in glass has been widely used to dope silicate glasses [41]. The process is realized by immersing silicate glass slides in a molten salt bath containing the dopant ions, which replace alkali ions of the glass matrix. Ion exchanged with copper has in particular attracted new attention for the blue-green luminescence properties of copper-doped glasses [42], useful for laser technology as well as for the third-order nonlinear optical features of copper nanoclusters in glass [43]. The blue-green luminescence property is due to the copper ions dispersed in the glass matrix in the Cu$^+$ oxidation state [44]. Therefore, the knowledge of the distribution of copper oxidation states inside the treated glass is an important issue for the understanding of the applications of the glass technology. Because of the possible presence of different oxidation states, namely, Cu$^+$, Cu$^{2+}$ and Cu$^0$, copper distribution within the matrix follows a rather complex behavior [45], critically depending on both glass and bath composition as well as on the process parameters. At present, only a few studies have been dedicated to ion exchange with copper [46] but no report available on size control of copper nanoparticles in soda lime glasses irradiated by 6 MeV electrons. Hence, this chapter deals with 6MeV electron assisted and ion exchange diffusion of copper and synthesized copper nanoparticles and the combined use of these analytical tools allowed us to define the microscopic structure reached after the doping process.

5.4.2: Experimental details

5.4.1.1: Preparation of samples

Optically polished soda lime glass slides of composition (weight %) 72.90 SiO$_2$, 14.50 Na$_2$O, 6.72 CaO, 4.90 MgO, 1.40 Al$_2$O$_3$, 0.03 SO$_3$, 0.08 Fe$_2$O$_3$ (Melting temperature to 1560$^0$C for half an hour, Annealing temperature 560$^0$C, for two hours) were used for the experiment. The plane slides were then cut into many pieces of the dimensions 1cm X 1cm X 0.1cm. The samples were washed with acetone and then with distilled water and finally with methyl alcohol to remove any surface ambiguities. These samples
were then dried with absorbent papers as well as wrapped into aluminum paper and stored in the dust free environment. Further, these fused silica glasses were placed in a thin polythene.

**5.4.1.2: Ion Exchange:**

A salt bath of CuSO$_4$ : Na$_2$SO$_4$ in the molar ratio 54:46 is kept in the furnace and the temperature of the bath was maintained at ~ 545°C for about 30 minutes. The molten bath was then taken out of the furnace for few minutes and the glass samples were immersed into it. The molten bath was loaded in the furnace and kept for 10 minutes. During the immersion, copper ions of the salt bath diffuse into the glass and replaces by the sodium ions. The samples were isolated from molten salt, cleaned with acetone and wrapped in the aluminum foil.

**5.4.1.3: 6 MeV electron Irradiation and thermal annealing**

Ion exchanged soda lime glass samples were then mounted on the Faraday cup and irradiated with 6 MeV energy electrons using Race-Track Microtron. The output of the Faraday cup was connected to the current integrator for the measurement of electron fluence received by each sample. In a similar manner, samples were irradiated at the different fluences in the range from 10 × 10$^{14}$ to 40 × 10$^{14}$ electrons/cm$^2$. The irradiation was carried out at room temperature and atmospheric air pressure. The thermal annealing of the ion exchanged samples was carried out in air for one hour at the temperature of 450°C.

**5.4.2: Results and Discussion**

**5.4.2.1: Visual observations and UV-Visible spectroscopy**

The UV-Visible spectra for virgin and ion exchanged soda lime glass irradiated with 6 MeV energy electrons for different fluences from 10 × 10$^{14}$ to 40 × 10$^{14}$ ele/cm$^2$ is shown in figure 5.13. The ion exchanged soda lime glasses were light green in color before the irradiation but observed to be dark green with reddish tinge in color after the electron irradiation. The optical absorption spectra of the ion-exchanged sample
showed peak around 774 nm as the copper particles, but the ion exchanged with electron irradiated and further thermally annealed samples shows distinct peak at 560 nm.

![UV-Visible absorption spectra of Ion exchanged and Cu doped Soda lime glass Irradiated with 6MeV electrons for different electron fluences](image)

Figure 5.13: UV-Visible absorption spectra of Ion exchanged and Cu doped Soda lime glass Irradiated with 6MeV electrons for different electron fluences (appended).

These absorption peak at 774 nm corresponds to the surface plasmon resonance (SPR) of copper Cu$^{2+}$ and the peak around 533 nm represents Cu$^{0}$ clusters [47]. It is also observed from the figure that the absorption peak shifts to lower wavelength from 560 nm to 533 nm, with increasing electron fluence from $10 \times 10^{14}$ to $40 \times 10^{14}$ ele/cm$^2$. This observed blue shift around 27 nm in the absorption edge clearly indicates an decrease in the size of the Cu nanoparticles in the glass with increase in the electron fluence. Moreover, it is also found that the peak intensity and the full width half maxima (FWHM) of the respective peak increases with increase in the electron fluence. The average cluster radius is calculated from the full width half maximum $\Delta \lambda$ (FWHM) of the absorption band using the formula.

$$ R = \frac{V_f \lambda^2 p^2}{2\pi C \Delta \lambda} \quad \ldots\ldots(5.15) $$
Where λp is the characteristic wavelength at which SPR occurs and V_f is the Fermi velocity of the electrons in bulk metal (for copper it is 1.57 X 10^8 cm/s).

5.4.2.2: X-ray diffraction (XRD) analysis

XRD spectra of the copper ion-exchanged soda lime glass with 6 MeV electron irradiated sample is shown in figure 5.14. It is observed from the figure that, copper ions inside the glass matrix, stabilizes to form metal copper nano crystallites through electronic energy transfer mechanism. The spectra shows peaks at 2θ position of 43.40^0 corresponding to FCC (1 1 1) plane of nano crystalline copper [48]. Thus, the change in the chemical state and structure of the embedded copper ions are confirmed from this study.

![Figure 5.14: XRD of Ion Exchanged copper doped Sodalime glass Irradiated with 6MeV electrons at different fluences (appended)](image)

One can calculate average size of the crystallites using the Scherrer’s formula given by equation 5.15. The estimated average size of copper nano particles found to be around 20nm for the fluences of 10 X 10^{14} e/cm² and shows crystalline plane of copper. However, with further increase in the electron fluence up to 40 X 10^{14} e/cm², the XRD
peak observed to be more broadened. Therefore the average size of the nanoparticles decreases from 20 to 15 nm. Moreover, the increase in the intensity of the XRD peaks with electron fluence reveals an increase in the number of copper nanoparticles. Thus, the results revealed that size of the Cu nanoparticles can be controlled using electron irradiation.

5.4.2.3: FTIR analysis

The FTIR spectra of virgin and ion exchanged with 6 MeV electron irradiated soda lime glass at different fluences in the range 700–1400 cm\(^{-1}\) is shown in figure 5.15. The spectrum is the percentage transmission against wavenumber in cm\(^{-1}\). The virgin soda lime glass shows a broad shoulder with two prominent peaks at 1069 cm\(^{-1}\) and 1201 cm\(^{-1}\) centred at 1126 cm\(^{-1}\). This band is the characteristic of the vibrational motion of oxygen atoms in SiO\(_2\)[49]. The motion of oxygen atoms is coupled with silicon atom, and this in turn serves to maximize the coupling between the electric field of the IR radiation and the dipole moment of the structure. This vibration has been described as a rigid bodies in which the oxygen and silicon atoms move in opposite directions. The oxygen atoms around a given silicon atom of the basic SiO\(_2\) building block move
Figure. 5.15. FTIR Spectra of Ion Exchanged copper doped with 6MeV electron irradiated Soda lime glass at different fluences (appended)

with the same phase and the silicon atom moves with opposite phase and in order for the center of mass to remain at rest, it follows the low frequency band edge, which is accompanied by silicon motion and the in-phase motion of the oxygen atoms. The high frequency edge, is the out-of-phase motion. These differences in motion at the two edges in the oxygen stretching band account for the differences in the relative IR activity at the peak of the stretching band near 1073 cm$^{-1}$, and at broad shoulder centered at about 1167 cm$^{-1}$ [50]. There is a distinct shift in the spectrum of virgin sodalime glass and the ion exchanged soda lime glass by 50 cm$^{-1}$ towards higher wave number which shows stretching of the Si-O-Si bond angle. The shift of the peak position is an indicator of a change of the average bond angle. [51]. The electron irradiated soda lime glass shows disappearing shoulder which indicates the chemical environment at each one of the silicon atoms of the Si-O-Si linkage can promote changes in the Si-O-Si vibrational frequency keeping the Si-O-Si bond angle is same [52]. Moreover, the broadening of the band indicates a statistical distribution of different bonding arrangements at each silicon atom site[53]. The disappearance of the shoulder is an effect that is driven by symmetry considerations. A distinct peak is observed around 1000 cm$^{-1}$ in virgin soda lime glass. This peak does not appear in fused silica glass where there is no composition
of Na₂O. This peak corresponds to Si-O-Na⁺ non bridging bond.[54]. This peak disappears when the electron fluence of 40 X 10¹⁴ ele/cm² due to diffusion of copper and formation of band.

5.4.2.4: Scanning electron microscopy (SEM-EDS)

The SEM images of the virgin and copper ion exchanged with 6 MeV electron irradiated soda lime glass at different fluences from 10 X 10¹⁴ e/cm² to 40 X 10¹⁴ e/cm² is shown in figure 5.16. At each electron fluence, the particles can be classified in two groups viz; small size and large size. A comparison reveals that at an electron fluence of 40 X 10¹⁴ e/cm², the number of the copper particles of sizes in the range of ~ 17 nm is greater in number. These SEM results clearly reveal that the size of the copper particles decreases with increase in the electron fluence. The EDAX analysis of the virgin and 6 MeV electron irradiated samples is carried out in order to check the ion exchanged diffused copper and is shown in figure 5.17. This indicates that the virgin soda lime glass does not show the peak of copper, however ion exchanged glass irradiated at 40 X 10¹⁴ ele/cm² shows 8.17 atom% of copper. It is quite clear that copper is present in the ion exchanged irradiated soda lime glass.
Figure 5.16: SEM images of ion exchanged with 6MeV electron irradiated soda lime glass for different fluence (a) Virgin (b) $10 \times 10^{14}$ ele/cm$^2$ (c) $20 \times 10^{14}$ ele/cm$^2$ (d) $40 \times 10^{14}$ ele/cm$^2$

![Figure 5.16: SEM images of ion exchanged with 6MeV electron irradiated soda lime glass for different fluence]

Figure 5.17: A typical EDAX of ion exchanged copper doped with 6MeV electron irradiated sodalime glass at a fluence of $40 \times 10^{14}$ e/cm$^2$

![Figure 5.17: A typical EDAX of ion exchanged copper doped with 6MeV electron irradiated sodalime glass at a fluence of $40 \times 10^{14}$ e/cm$^2$]
The mechanism of the precipitation of copper nanoparticles inside the glass by 6MeV energy electrons is the reduction of copper ions to atoms. Copper exist in the ion exchanged glass in our case is in the form of Cu\(^{2+}\) ions. These ions can capture electrons generated by an electron accelerator and causing reduction of these ions which forms Cu\(^0\) and therefore Cu\(^0\) atoms aggregates to form copper nanoparticles[55]

**5.4.3: Conclusion**

Overall, in conclusion 6MeV electrons used for the synthesis of copper nanoparticles in the ion exchanged copper doped soda lime glass. UV-Visible spectra show characteristic of copper nanoparticles. The glass is further characterized by standard FTIR, XRD, SEM and EDS analytical techniques. FTIR spectra show the Si-O-Si stretching and Si-O-Na\(^+\) non bridging bonds. XRD shows the existence of copper in the matrix and has fcc structure. The size of the nanoparticles found to be around 15nm and same is confirmed in SEM analysis. Moreover, the incorporation of copper in the sodalime glass is confirmed by EDAX measurement, where it shows increase of copper atomic percentage by 8.17%.

**References**:


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