CHAPTER-II
2.1. INTRODUCTION

Metal doped glasses are formed by the conventional methods, such as for example, melt-quenching techniques, but a major breakthrough in the Metal Nanocluster Composite Glass (MNCG) technology occurred with the invention of the multi step methodologies for the fabrication of MNCGs. Emphasis was made on the above process, as they are found suitable for controlling the cluster structure inside the glass matrix. The first step in the two-step process is the introduction of the metal ion into the glass matrix either by ion-exchange or by direct implantation of the metal ion of interest. Secondly, the glasses are subjected to proper combination of treatments like irradiation with low-mass ion or electron beams, heat treatments in reducing atmosphere or pulsed laser irradiation. Nano dimension cluster growth, through metal aggregation is promoted with several degrees of freedom by the above multi step process, defining the cluster structure and the composite’s optical performance. The main advantage of this sequential method is the possibility of tailoring the cluster formation within the waveguiding layers, selecting small clusters for which the absorption cross section is extremely small. The materials and various experimental methods involved in the fabrication of MNCGs are explained in this chapter.
2.1. MATERIALS CHOSEN FOR THE STUDY

As the study is mainly aimed at the synthesize and optical characterization of noble metal nanocluster like Copper, Silver and Gold in soda-lime glass matrix, commercial ("MARIENFELD" German make) soda-lime micro slides of composition (Weight. %, 72.90 SiO₂, 14.50 Na₂O, 6.72 CaO, 4.10 MgO, 1.40 Al₂O₃, 0.03 SO₃, and 0.08 Fe₂O₃) and dimension 76X26X1 mm were bought. The glass slides were cleaned using the Ultronix glass cleaner to remove any surface impurities and then dipped in the molten salt bath solution of respective metal salt for ion-exchange. The different compounds selected for doping soda-lime glasses with metal ions through ion-exchange, their ratios, processing temperatures and dipping time and they are shown in the Table. 2.1.

Table. 2.1.

Salt form of metal, ratio, processing temperature and dipping time of the three metal species of experimental interest

<table>
<thead>
<tr>
<th>Metal species</th>
<th>Salts chosen</th>
<th>Ratio</th>
<th>Temperature of baths (°C)</th>
<th>Dipping time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>CuSO₄ : Na₂SO₄</td>
<td>1 : 1</td>
<td>560 - 570</td>
<td>1 min</td>
</tr>
<tr>
<td>Silver</td>
<td>AgNO₃ : NaNO₃</td>
<td>1 : 2</td>
<td>350 - 360</td>
<td>1 min</td>
</tr>
<tr>
<td>Gold</td>
<td>HAuCl₄ : NaNO₃</td>
<td>1 : 5</td>
<td>370 - 380</td>
<td>1 min</td>
</tr>
</tbody>
</table>
2.2. ION-EXCHANGE PROCESS

Ion-exchange reaction involves equivalent substitution of one ion for another. It is a chemical process occurring in surface layers of glasses in different media. Also, it is one of the promising techniques for doping glasses with metal ions in a controllable way. It forms the first step in the multistep process of MNCG preparation. During the ion-exchange process, the monovalent alkali ions on the surface layers of the glass are replaced with the metal ion from the molten salt bath as shown schematically in the Figure. 2.1.

![Figure 2.1: Schematic diagram of Cu\(^{+}\)-Na\(^{+}\) ion-exchange in the molten salt bath of (CuSO\(_4\) : Na\(_2\)SO\(_4\))](image)

The following conditions need to be satisfied for ion-exchange to take place:

- The ionic radius of the dopant metal should be smaller than or nearly equal to that of the alkali sodium ions.
Salt form of the metal of interest is required for ion-exchange process.

The melting point of the metal salt bath should be less than the glass softening temperature of soda-lime glass.

Table. 2.2. shows the various ionic radii for sodium and the three noble metals choosen for the present study.

Table. 2.2.

Ionic radii of sodium and some noble metals

<table>
<thead>
<tr>
<th>METALS</th>
<th>Ionic Radii pm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>102</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>77</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>73</td>
</tr>
<tr>
<td>Cu³⁺</td>
<td>54</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>115</td>
</tr>
<tr>
<td>Ag²⁺</td>
<td>94</td>
</tr>
<tr>
<td>Ag³⁺</td>
<td>75</td>
</tr>
<tr>
<td>Au⁺</td>
<td>137</td>
</tr>
<tr>
<td>Au²⁺</td>
<td>85</td>
</tr>
<tr>
<td>Au³⁺</td>
<td>57</td>
</tr>
</tbody>
</table>

The respective salt mixture of given ratio were taken in a silica crucible and then heated using a temperature controlled electric Bunsen burner till the salt mixture turns into solution. The melt was stirred well using glass rods for
uniform mixing and the temperature was maintained during the dipping process for ion-exchange. Pre-cleaned soda-lime glass slides are dipped in the salt bath solution for about 1 minute for ion-exchange. In the bath the alkali metal ions coming out of the glass matrix from the surface layers are replaced by the metals ions entering into the glass from the bath. The temperatures of the melts for the different salt solutions are as detailed in the Table. 2.2.

The glass composition plays an important role in the ion-exchange process with the addition of alkali like Na₂O to the interconnected SiO₄ of fused silica resulting in the modification of the structure as follows:

The oxygen in the molecule of Na₂O is accommodated by breaking an existing bond in the Si–O–Si linkage and thus forming two dangling SiO bonds, i.e., Si–O O–Si, with the Na being loosely bound in the near vicinity. Other network modifiers, such as CaO also enter into the soda-lime glass formation along with the Al₂O₃, which can act either as a network modifier or as a network former. Addition of the above compounds have an important property of opening up the glass structure, resulting in a larger void volume and a consequently an easier path for diffusion of alkali and for the counter flow of the metal ion during the ion-exchange process. The structure of soda-lime glass with the loosely bound sodium is shown in the Figure 2.2.

The mechanism that governs the diffusion of metal ions into glass by ion-exchange has not been described fully, with even the Ficks law finding limited validity and applications. As copper is very sensitive to glass composition, it is
difficult to control the equilibrium between the two different copper oxidation states like \( \text{Cu}^+ \) and \( \text{Cu}^{2+} \) as well as possible formation of Cu or \( \text{Cu}_2\text{O} \) involved in the exchange process [1].

\[ 
\text{Si} \quad \rightarrow \quad \text{O} \\
\text{Na} 
\]

Fig. 2.2. Structure of soda-lime glass with the loosely bound sodium
Binary ion-exchange has been extensively used for the fabrication of passive integrated-optical devices [2]. Ion-exchange used in the chemical strengthening is studied by Bartholomew et al. [3]. High performance single and multi mode waveguides were also fabricated by Ag⁺-Na⁺ ion-exchange [4], with an index increase of about (0.1). A considerable amount of work has been done on ion-exchange with the effect of glass composition on the exchange process [5-8].

After the exchange process, the copper ion-exchanged glasses turned to brick red, the silver ion-exchanged glasses into pale yellow accordingly but in the case of gold, the ion-exchanged glasses showed a faint pink color due to embedded gold particles as reported [3]. For the sequential CuAg and AgCu ion-exchange process the copper ion-exchanged glasses were again dipped in the silver bath for the same time of dipping and vice versa. The CuAg ion-exchanged glasses turned dark yellow after dipping in the silver bath and the AgCu ion-exchanged glasses changed into dark reddish brown. Thus the prime step in the multi step process of MNCG preparation is achieved by ion-exchange with the ion-exchanged glasses themselves forming optical waveguides.

The various methods involved in the treatment of the ion-exchanged glasses to form MNCGs are ion irradiation of the doped samples with low mass ions using accelerators, light irradiation using lasers and heat treatment techniques etc. In the present study, He⁺ ion irradiation and thermal annealing
in air of the metal doped glasses are the two different methods utilized to promote the growth of clusters in the metal doped glasses.

2.3. TYPES OF ACCELERATORS

Accelerators had their development from the cathode ray tubes, which J.J. Thompson used for accelerating electrons. The accelerators used in materials research are normally in the energy range from a few hundred keV to recent GeV. The requirements like ion current, energy and ion species vary depending upon the application. Helium and Hydrogen ions are the most used in the ion beam analysis. Ions in the energy range of a few keV are used in the surface modification and in the study of irradiation effects of materials. Van-de-Graaff accelerators and pelletrons with terminal voltage of 1-2 MeV are conventionally used for medium energy ion implantation, where as higher energy accelerators like cyclotron which provide beams in the energy range of 5-10 MeV are used for the simulation of reactor damage. The role of accelerators in materials research is discussed below.

2.3. ROLE OF ACCELERATORS IN MATERIALS RESEARCH

Accelerators are finding increasing application in materials research in different areas such as ion beam analysis, ion beam modification of materials, ion implantation and in the study of ion irradiation effects in materials.

a) Ion beam analysis

Ion beams are extensively used in the analysis of surface and subsurface regions. The Rutherford Backscattering Spectroscopy, where the energy distribution and intensity of the back scattered ion from a target gives
information regarding the surface composition of materials. Ion induced characteristic X-rays are used for elemental analysis. Proton Induced X-ray Emission (PIXE) is a well established technique for the analysis of trace elements. Accelerators are also used in the nuclear reactant and elastic recoil detection analysis.

b) Ion implantation

Ion implantation is a superb method for surface modification of materials since it offers accurate control over the dopant composition and structural modification at any selected temperature. A judicious choice of implant energies and current allows the incorporation of any desired atomic species in the target with precise control of depth and concentration. In the semiconductor industry it is the primary technology to introduce impurities in semiconductors to form devices and integrated circuits. Ion implantation also introduces high density defects, which have adverse effects on the electrical properties, but they can be annealed out by suitable heat treatments. Optical properties of semiconductors are also influenced by the production of defects, resulting in a reduction of optical band gap and an increase in optical absorption coefficient [9]. Introduction of radiation damage into certain semiconductors like CdS give rise to photoconductivity [10, 11].

c) Ion irradiation

Apart from the various technological importances, study of irradiation effects is also of basic interest. Materials under ion irradiation experience defect accumulation, chemical disordering, irradiation enhanced
atomic mobility or overall change in the chemical composition due to ion implantation. During ion irradiation energetic ions falling on the material transfer kinetic energy to the target atoms causing displacements from their equilibrium positions. The displaced atoms might end up at an interstitial site, leaving behind a vacancy in the original site. The defects thus produced might recombine or migrate to sinks like surfaces, grain boundary and dislocations. The defects produced with ion beams are of several orders of magnitude higher than that of fast neutrons.

Order-disorder transformations, precipitation of thermally unstable phases and inverse Ostwald ripening are some of the other interesting effects observed during ion irradiation [12]. Thus it can be concluded that ion irradiation influences materials properties through various processes like segregation, irradiation induced phase transformation, enhanced diffusion and formation of defect clusters.

2.4. EFFECT OF ION IRRADIATION ON METAL DOPED GLASSES

Ion irradiation of metal doped glasses has drawn considerable interest in the last few years due to their controlled promotion of metal particle growth. The process involves the establishment of effective models for metal diffusion and aggregation under various irradiation conditions. Irradiation of insulators gives rise to various effects [13] such as sputtering, enhanced diffusion, breakup of clusters of precipitated atoms and electric fields formation by promotion of electronic excitation. Cluster formation actually depends strictly on the metal atoms present in the glass matrix to migrate and aggregate [14]. Hence the
mechanism of diffusion under irradiation plays an effective role in the particle synthesis and moreover as diffusion takes place via defects, the production of such defects by irradiation will come into play in determining the particle formation. In the present study He\(^+\) ions of energy 100 keV are used to irradiate the ion-exchanged glasses. The schematic diagram of irradiation of the ion-exchanged glass with He\(^+\) ions for cluster growth is shown in Figure 2.3.

![Schematic representation of He\(^+\) irradiation of ion-exchanged soda-lime glass](image)

**Fig. 2.3. Schematic representation of He\(^+\) irradiation of ion-exchanged soda-lime glass**

### 2.5. EXPERIMENTAL SETUP OF THE ACCELERTOR USED

The irradiations were carried out using J-15 sames, 150 kV accelerator. In the 150 kV accelerator, the positive ions are accelerated from the high voltage terminal, the potential of which is varied from 40-150 kV, to the target, which is kept at ground potential. Figure 2.4(a) shows the schematic representation and Fig. 2.4(b) the photograph of the 150 keV accelerator used for irradiation of samples in present study. The details of the different parts are briefed as follows:
Fig. 2.4(a) Schematic representation of the 150 keV Accelerator
Fig. 2.4(b) Photograph of the 150 keV accelerator used for irradiating the ion-exchanged glasses
i) Ion source

The ion source consists of a radio frequency ion source followed by the extraction and focusing systems. A controlled gas feed of about 10-20 cc/hour into the ion source is maintained. A 100 MHz, 100 W RF power supply is capacitatively coupled to the ion source bottle to ionize the gas. Applying an extraction potential of 0-6 kV, the ions are extracted from the source. Applying a voltage of 0-14 kV to the focus electrode at the exit of the ion source, the extracted beam can be focused. The ion source can give intense beams of gaseous ions, with a yield as high as 1 mA.

ii) Mass analyser

A 10 stage accelerating tube accelerates the extracted ion beam. A vacuum of $10^{-6}$ mbar is maintained inside the accelerator using an oil diffusion pump (100 mm diameter). The accelerated ion beam is mass analyzed using an in-house designed H shaped magnet producing a saturation field of 1.5 Tesla in the pole gap of 30 mm. Square section hollow copper conductor is used as the magnetizing coil. An in-house built 200 ampere 100 ppm stabilized power supply is used to energize the magnet coil. A two port magnet chamber is used for the ion beam transport. The 45° port is used for the analyzed evacuation to the magnet chamber.

It is essential to maintain the sample surface clean, as the range of the implanted ions with low incident energy is only a few Angstroms. Hence the beam line starting from the mass analyzing magnet chamber and the implantation chamber are made compatible with ultra high vacuum (UHV).
turbo molecular pump evacuates the magnet chamber to a pressure of the order $10^{-6}$ mbar. A liquid nitrogen trap is provided in the beam path to reduce contamination of hydrocarbon vapours emanating from the oil diffusion pump used for pumping the accelerator.

iii) Irradiation chamber (Target chamber)

The irradiation chamber is of small volume, evacuated separately by a turbo molecular pump to maintain a pressure of $10^{-8}$ mbar. It is provided with multiports having facilities for beam entry, beam viewing and vacuum measurements. The beam entry port has provision for fixing a demountable collimator of varying size to define the beam, falling on the target.

The sample holder is attached to the top flange of the implantation chamber by means of mini DNPS 35 UHV manipulator, capable of linear (±10 mm) and rotary (360°) motions. The sample holder is a 25x25x40 mm copper block, fixed to the manipulator shaft. The samples are fixed on the faces of the copper block by silver paste. The copper block is electrically insulated from the manipulator shaft by a ceramic disc, so that the current and the integrated charge is carried out using a digital beam current integrator. The accumulated irradiation dose in term of ions/cm² can be calculated by knowing the integrated charge and diameter of the incident beam.

When energetic charged particle impinges on a target, emission of secondary electrons takes place which introduces errors in the dose measurement, essentially giving rise to an overestimate of the dose. This occurs because the current integrator senses the emission of the each secondary
electron from the target as the arrival of a positive ion. In order to eliminate this error, a secondary electron trap is used. This essentially consists of a thin walled stainless steel cylinder suspended from the top flange around the target. It is insulated from the top flange as well as the target. The cylinder is maintained at -60 to -70 V with respect to the target, in order to repel the secondary electrons back to the target. Openings are provided in the secondary electron trap for the beam entry and beam viewing.

The ion-exchanged glasses are cleaned well to remove any surface impurities and then are mounted on a copper block kept inside the irradiation chamber maintained at vacuum. The samples were irradiated with a mass analyzed beam of He+ ions of energy 100 keV at room temperature. The beam current was maintained around ~1.5µA/cm² to minimize beam heating of the sample. In the irradiation process, the dose parameter is varied in order to study the effect of it on the cluster size. Metal clusters of nano size are thus formed in the ion-exchanged and irradiated soda-lime glasses.

2.6. THERMAL AIR ANNEALING

Thermal annealing is another 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. In the present work pre-cleaned ion-exchanged glasses are taken in porcelain boats and kept inside the furnace for annealing. The samples were maintained at the same temperature
for about 1 hr for the different heat treatment temperatures. During annealing migration and aggregation of the metal particles takes place resulting in the formation of clusters.

Metal nanocluster composite glasses are thus formed by the above multi step techniques. The optical absorption, Raman scattering and Phtoluminescence properties of these MNCGs are discussed in the following chapters.
REFERENCES


