Chapter - 5

PHOTOLUMINESCENCE AND X-RAY DIFFRACTION ANALYSIS OF METAL NANOCOMPOSITES
5.1. INTRODUCTION

Luminescence is a non-equilibrium process for it needs excitation source, such as lamp or laser. Luminescence materials have drawn extensive attention over the past few decades due to their wide range applications. Luminescence in solids occurs by the phenomena of excitation of the electronic states by some energy from an external source and the excitation energy is released as light. When the wavelength of the emitted light falls in the shorter wavelength side of the electromagnetic spectrum, usually ultraviolet light, the phenomena is called photoluminescence.

Depending on the different excitation sources, we have photoluminescence (PL), which requires optical excitation, electroluminescence (EL), which needs excitation by electrical current, cathode luminescence (CL), which results from electron bombardment, thermo luminescence and the other kinds of luminescence.

The phenomenon of temporary light absorption and subsequent light emission is called photoluminescence. Each photoluminescence substance has its own excitation and emission spectra. The intensity of the Photoluminescence is proportional to its absorption, which in turn is proportional to the excitation light. The Photoluminescence emission of a substance is always at a higher wavelength than the light used to excite the substance (stokes-shift phenomenon). The Photoluminescence of a substance is sensitive to many factors and will change or even disappear under different conditions.
PL is one of the most widely used experimental methods for study of semiconductors, especially wide-band-gap materials [1-6]. PL is divided into two major types: intrinsic and extrinsic luminescence. The intrinsic luminescence has three kinds of luminescence, which are band-to-band luminescence, exciton luminescence, and cross-luminescence, respectively.

The recombination of an electron in the conduction band with a hole in the valence band generates band-to-band transition luminescence, which is sometimes shown in high purity crystals, such as Si, Ge and GaAs. At low temperatures, this luminescence is often replaced by the exciton luminescence. The light emission from bright light-emitting diodes and semiconductor lasers is also usually due to the band-to-band transition process.

Extrinsic luminescence is normally generated by the impurities which are intentionally or unintentionally incorporated. These kinds of impurities are normally called activators. There are two kinds of extrinsic luminescence in semiconductors. One is unlocalized type and the other is localized type.

Different luminescence studies are applied for semiconductor characterization. Defects in semiconductors are studied by the steady-state PL (SS-PL) spectra, time-resolved PL (TR-PL), or PL excitation (PLE) spectra. Optically detected magnetic resonance (ODMR), a modification of the PL technique, is also a very efficient method, especially in identification of the defects.

5.2. PHOTOLUMINESCENCE SPECTROSCOPY

Photoluminescence (PL) is a standard technique for characterization of semiconducting and lasing materials complementary to optical absorption. An examination of the difference between the lowest absorption peak and the
photoluminescence peak gives information about the nature of the emitting state. Temperature and intensity dependent steady-state PL [7-13] and time resolved PL measurements [14-16] yield the energies and life times of the trap sites involved in the radioactive combination. Particle size selection is accomplished by tuning the laser to the red edge of the absorption band. It excites only the largest particles in the different size distribution [17].

5.3. TIME-RESOLVED PHOTOLUMINESCENCE

Time-resolved photoluminescence is used for the direct measurement of the radiative recombination lifetime [18-20]. It requires the use of a pulsed laser excitation source and gated detection. The role of surface states in radiative recombination is studied by subjecting the colloidal particles to different passivation chemicals before they are dispersed in a polymer host [19] or by adding surface-active stabilizers to a semiconductor glass composite prepared by a sol gel process [14].

5.4. PHOTOLUMINESCENCE excitation SPECTROSCOPY

Photoluminescence excitation (PLE) spectroscopy is similar to PL except that in PLE a single luminescence band is monitored while the excitation wavelength is varied. The excitation source is either a tunable dye laser or high intensity arc lamp-monochromator combination. PLE can be used to effectively reduce the inhomogeneous width of the transitions by extracting information from a subset of the nanoparticle distribution. Only the smallest crystallites in the sample are probed in PLE when monitoring a narrow spectral region on the blue edge of the luminescence band [21]. PLE is also used to probe quantum dot size distribution as well as to study higher excited states [22,23]. In the present work we discuss the photoluminescence property of copper and silver ion exchanged glasses.
5.5. EXPERIMENTAL SETUP OF SPECTOROFLUOROMETER

All optical spectroscopic experiments require three basic elements viz., a light source, light dispersing element and a light detector. Although the characteristic features of these elements have changed over the years, the experimental principles yet remain the same. Photoluminescence spectra can be distinguished as excitation spectrum and emission spectrum.

a) Excitation spectrum

In the case of the excitation spectra the wavelength of the exciting light was varied and the intensity of the emitted light at a fixed emission wavelength was measured as a function of the excitation wavelength. The excitation spectrum gives information on the positions of excited states, just as the absorption spectrum does, except that the former reveals only absorption bands that result in the emission of light.

b) Emission spectrum

The emission spectrum was recorded by exciting the sample with xenon lamp and the emission was fed into a monochromator where the emission intensity is recorded as function of the wavelength. An emission spectrum provides useful information on the spectral distribution of the light emitted by the samples.

A schematic setup of the spectrofluorometer used for recording the excitation and emission spectra is shown below in the Fig. 5.1. The photoluminescence excitation and emission spectra were recorded using fluorescence spectrofluorometer (Spex Fluoro Max-3). It consists of an excitation source which is usually a xenon lamp for the excitation of the sample. An excitation monochromator which disperses the polychromatic exciting light into its component wavelength is coupled to the source. The sample
chamber is placed in between the excitation and emission monochromator. An emission monochromator, for dispersing the radiation emitted from the sample into its component wavelengths is placed next to the sample chamber. A detector which is a photomultiplier is interfaced to a personal computer through the software, is used for recording and analyzing the spectra. The emission spectra of the different excitation wavelength of copper and silver ion exchanged soda-lime glass samples were recorded at room temperature and are discussed in detail below.

![Fig. 5.1. Schematic setup of the spectrofluorometer](image)

5.6. RESULTS AND DISCUSSION

a) Photoluminescence spectra of copper ion exchanged and annealed glass

The emission spectra of the copper ion exchanged and different temperature annealed soda-lime glasses are shown in the Figs. 5.2 and 5.3. It is observed that for excitation at 250 and 285 nm the sample exhibited two broad luminescence emission bands at 425 and 700 nm. This observed broad emission band is due to the transition between the $3d^94s^1$ and $3d^{10}$ electronic configurations of the Cu$^{2+}$ and Cu$^+$ ions which has entered into the glass matrix during the ion exchange. Such kind of emission of Cu$^+$ ions has been reported earlier [24,25].
Fig. 5.2. Photoluminescence spectra of copper (Cu) ion exchanged and different temperature annealed soda-lime glasses with excitation wavelength of 285 nm

Fig. 5.3. Photoluminescence spectra of Cu ion exchanged and different temperature annealed soda-lime glasses with excitation wavelength of 250 nm
b) **Effect of annealing on the photoluminescence property of copper ion exchanged glasses**

The copper ion exchanged glasses were cleaned and then annealed in air for about 1 hour at four different temperatures (100-400°C) in steps of 100°C. The emission spectra of the copper ion exchanged and annealed samples clearly shows that the intensities of the emission spectra increased with increase in annealing temperatures. This is because annealing of the copper ion exchanged glasses resulted conversion of the Cu$^{2+}$ ions into Cu$^+$ ions as well the possible formation of metal copper [26].

At the excitation wavelength of 285 and 250 nm, the copper ion exchanged and different temperature annealed samples show a broad emission band at 430 and 700 nm respectively. The broad emission bands centered at around 430, 450 nm occurs two excitation wavelength 280 and 250 nm. The observed emission is attributed to S $\rightarrow$ d transitions of Cu$^+$ electronic configurations and the can be used as active laser host material. Another broad emission bands centered at around 700 nm, this emission occurs due to transitions of Cu$^{2+}$ copper ion exchanged soda-lime glasses annealed for high temperature.

A similar kind of vanishing of photoluminescence in the case of sequential implantation of Cu$^+$ and O$^+$ ions in silica glass was observed by Fumuki *et al.* [27], where the Cu$^+$ implanted silica exhibited photoluminescence with a good quantum yield, but on sequential implantation of O$^+$ ions into the same silica matrix resulted in the stabilization of the Cu$^+$ ions into metal copper and Cu$_2$O nanocrystallites, thus resulting in the decreasing the intensity of photoluminescence. This decreasing intensity and disappearance of photoluminescence is one of the interesting features observed in the present study.
c) Photoluminescence spectra silver ion exchanged and annealed soda-lime glasses

Silver ion exchanged glasses showed a broad emission band at 450 and 700 nm for two excitation wavelengths 280 and 285 nm. The emission is attributed to the electron transition from the 4d^{10} ground state to some levels of the 4d^95s^1 ion configuration. This kind of photoluminescence due to the presence of Ag^+ ions in various crystals and glassy matrices has been well established [28,29].

d) Effect of annealing on the photoluminescence property silver ion exchanged soda-lime glasses

At the excitation wavelength of 280 nm, the silver ion exchanged and different temperature annealed samples show a broad emission band at 460 and 670 nm respectively. Samples annealed at 200°C show two intense broad emission bands centered at around 460 and 683 nm, and the annealing temperature is increased to 300°C the emission bands are shifted to 446 and 667 nm. When the annealing temperature is further increased to 400°C the emission bands are shifted to 440 and 662 nm respectively, however these bands are less intense than the bands observed in the samples annealed at 200°C. This result shows that for higher annealing temperature the silver ion comes to stabilize silver metal.

At the excitation wavelength of 285 nm, the silver ion exchanged and different temperature annealed samples show a broad emission band at 448 and 660 nm respectively. Samples annealed at 100°C show two intense broad emission bands centered at around 451 and 663 nm, and then the annealing temperature is increased to 200°C the two bands are shifted to 450 and 668 nm.
When the annealing temperature is further increased to 300°C the two bands are shifted to 450 and 666 nm, the annealing temperature is further increased to 400°C the two bands are shifted to 455 and 669 nm; however these bands are less intense than the bands observed in the samples annealed at 100°C. It is well known that Ag$^+$ ions are luminescent in nature in both crystalline and glassy matrices [30].

The observed emission is attributed to $4d^{10} 5s \leftrightarrow 4d^{10} 5p$ transitions of (Ag$_2$)$^+$ pair which are the nucleation centers in the precipitation of silver nanoclusters. The another broad emission bands centered at around 680nm which are the origin of isolated Ag$^+$ and Ag$^+$-Ag$^+$ pairs observed the same excitation wavelengths.
Fig. 5.5. Photoluminescence spectra of Ag ion exchanged and different temperature annealed soda-lime glasses with excitation wavelength of 285 nm

In contrast, no PL emission due to Ag$^0$ atoms has been reported to the best of our knowledge. In view of this, we can say that increase in PL intensity at an annealing temperature of 100-400°C could be due to the increase of volume fraction of Ag$^+$ in the bulk of the glass matrix and the drastic decrease in PL intensity with further increase in annealing temperature can be due to the conversion of Ag$^+$ to Ag$^0$. Hence increase in annealing temperature from 100 to 400°C leads to the growth of silver nanoclusters of different size and different ions [Ag$^+$, Ag$^{2+}$ and (Ag$_2$)$_2$]$^+$, that might have resulted in the increase and diminishing of PL intensity. The excitation wavelength plays an important role in the PL spectra from silver nanoparticles. Hence effect of different excitation wavelengths on, PL spectra of Ag ion exchanged glass samples and different temperature annealed (100-400°C) have been studied extensively.
This shift in band emission to shorter wavelengths with increasing excitation wavelength may be due to the overlapping of different emission centers due to the presence of Ag$^+$$-$Ag$^0$ pairs. Also from these figures it is clear that as the excitation wavelength is increasing, the peak on higher wavelength side is evolving while peak at lower wavelength is diminishing. This typical behaviour of band emission can be explained by two mechanisms: a more effective internal relaxation from the photo-excited states to the lower emitting states, and/or energy transfer between the ions close to each other [31].

From the photoluminescence spectra confirmed that the broad emission for the two different excitation wavelengths were purely due to (Ag$_2$)$^+$ pairs inside the glass matrix. Annealing of the ion exchanged sample results in the movement of silver ions to the surface, increasing the surface silver concentration. But at higher temperatures silver evaporation takes from the surface [32] and the photoluminescence intensity falls rapidly due the reduction of silver concentration.

The PL spectra of copper ion exchanged and different temperature annealed soda-lime glasses exhibited two broad emission spectra with two excitation wavelength (285 and 250 nm). Similarly the silver ion exchanged and different temperature annealed soda-lime glasses also having the two broad emission spectra with different excitation wavelength (280 and 285 nm).
5.7. GRAZING INCIDENCE X-RAY DIFFRACTION (GIXRD) ANALYSIS OF EMBEDDED METAL NANOCCLUSTERS

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. It also gives information on deviations from a perfect particle. The XRD pattern of silver and copper ion exchanged and different temperature annealed soda-lime glasses were recorded using the X-Ray diffractometer (XRD-SMART Lab) - Rikagu, Japan.

**a) 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 Figs. 5.6-5.10. 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), Cu₂O (111), Cu (111) and Cu (200) nanoclusters.

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.
Fig. 5.6. GIXRD pattern of copper ion exchanged soda-lime glass

Fig. 5.7. GIXRD pattern of copper ion exchanged and 100°C annealed soda-lime glass
Fig. 5.8. GIXRD pattern of copper ion exchanged and 200°C annealed soda-lime glasses

Fig. 5.9. GIXRD pattern of copper ion exchanged and 300°C annealed soda-lime glass
This result indicates that 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.

b) GIXRD pattern of silver ion exchanged and different temperature annealed soda-lime glass

The XRD pattern of silver ion exchanged and different temperature annealed
soda-lime glass nanoparticles (Figs. 5.11 to 5.15). The silver ions as exchanged and
100°C soda-lime glass soda-lime glass have the five characteristic peaks for silver
nanoclusters appeared at 32.11°, 38.1°, 44.3°, 64.4°, 77.4° which correspond to crystal
faces (110), (111), (200), (220) and (311) of silver.
Fig. 5.11. GIXRD pattern of silver ion exchanged and Un-annealed soda-lime glass

Fig. 5.12. GIXRD pattern of silver ion exchanged and 100°C annealed soda-lime glass
Fig. 5.13. GIXRD pattern of silver ion exchanged and 200°C annealed soda-lime glass

Fig. 5.14. GIXRD pattern of silver ion exchanged and 300°C annealed soda-lime glass
This result indicates that the diffused silver (Ag) ions stay scattered inside the dielectric matrix as silver (Ag, Ag$^+$ and Ag$^{2+}$) particles and the cluster growth is induced by coagulation during annealing processes. Increasing the annealing temperature of silver ion exchanged (200, 300 and 400°C) soda-lime glasses have less number of peaks with lower intensity XRD pattern.

This result clearly shows that the size and structure of silver and copper nanocluster is varied during the annealing processes. It is also supported to the UV absorption spectra of silver and copper ion exchanged and different temperature annealed soda-lime glass with different clusters size. The XRD pattern of silver and copper nanoparticles confirm the presence of silver in pure form whereas copper is present as cuprite in the silver and copper ion exchanged different temperature annealed glasses.
REFERENCES


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