ABSTRACT

This thesis presents the results of investigation of vacuum evaporated Cu$_2$S film and the process involved during deposition. Cu$_2$S is an interesting semiconductor material with electrical, optical and physical properties varying significantly as a function of composition. It is a suitable material to be used in solar cell because it has very high absorption coefficient for wavelength constituting the solar spectrum. Semiconducting copper sulphide (Cu$_2$S) thin films were deposited on glass substrates at room temperature by vacuum evaporation method with four different thicknesses. Films were deposited under a pressure of 10$^{-6}$ Torr at an evaporation rate of 3Å/sec. Rotary drive was employed to obtain uniformity in film thickness. Thicknesses of the film were measured by using quartz crystal monitor. Characterization of the film has been carried out using X-ray diffraction (XRD) and Raman spectroscopy. The two point probe method was used for the investigation of electrical properties and four point probe was used for resistivity analysis. Hall effects measurements were carried out to determine the size dependent electrical properties of the film.

X-ray diffraction studies show that lower thickness films are a mixture of amorphous and polycrystalline while, higher thickness films bear polycrystalline nature. It was also observed that at lower thickness the formed film is a mixture of either or both phases of chalcosite (Cu$_2$S) and covellite (CuS), whereas higher thickness Cu$_2$S film changes its crystal structure from
Cu$_2$S to CuS and exhibit deviation in the composition of the film. Raman spectroscopy was used as a rapid identification of the composition of the film. Raman shifts at 472 cm$^{-1}$ and 474 cm$^{-1}$, indicates that the films deposited at lower thickness were chemically close to Cu$_2$S (copper-rich phase), while higher thickness films were CuS (sulphur-rich phase). This change in the composition of the film at higher thickness meant that the films were deposited as layers, with those layers next to substrate having a composition with a higher Cu:S ratio than outer layers.

Optical spectra of the films were studied in the UV-VIS-NIR region. Cu$_2$S exhibits high transmission in the visible region and high absorption throughout the near infrared region. Transmission decreased for the higher thickness film as the chemical composition approached CuS that was found to be high absorptive in nature. Optical absorption of the film also revealed the phase transformation of Cu$_2$S film at higher thickness. Optical band gap of the film was studied and it was found that the values decrease with increasing film thickness. It was also observed that both real and imaginary part of dielectric constant decreases with the increase in photon energy. Refractive index, extinction coefficient, optical conductivity and dielectric properties of the film were also reported. Some practical applications of the film were also discussed.

The electrical properties of Al- Cu$_2$S -Al (MSM) structures were studied using current-voltage characteristics. Conductivity was found to exhibit two distinct mechanisms within the applied field ie, ohmic in the low bias region and non-ohmic in the high bias region. The conduction
mechanism prevailing in Cu$_2$S film was found to be Poole-Frenkel effect. Activation energy of Cu$_2$S film decreases with an increase in film thickness. From the capacitance voltage measurements it was observed that at low frequency the capacitance shows larger value, whereas at higher frequency the frequency dispersion of capacitance was almost constant. The influence of thickness on carrier concentration, carrier mobility, conductivity and Hall coefficient were also investigated.

The resistivity properties of Cu$_2$S thin films was measured in the temperature range 303K-453K and was found between $10^{-8}$ to $10^{-6}$ ohm cm. Cu$_2$S film exhibits p-type conductivity and this low resistivity is due to degenerative nature of the film. Resistivity was found to increase with thickness upto 5000Å and further decreases with increase in thickness for all the films. It was found that the band gap energy of Cu$_2$S film decreases with increase in film thickness. The voltage dependence of photo current was measured in dark with three different illuminations for Cu$_2$S film. It was observed that photocurrent increases with film thickness and photo sensitivity also increases with light intensity and film thickness.

The effect of annealing in air at 100$^0$C, 200$^0$C on structural, optical and resistivity properties of Cu$_2$S films deposited at room temperature was also investigated. It was relevant from XRD studies that as-deposited lower thickness Cu$_2$S film was high chalcocite (Cu$_2$S) phase however after annealing, the phase obtained has comparatively a high content of sulphur ie, covellite (CuS). This was evidenced by the changes in the transmission spectra. Moreover, for the film deposited at higher thickness the initially
formed phase was CuS and after annealing the sample at 200°C results in copper-rich phase (Cu₂S). Grain size of the film was calculated using Scherer’s formula and is found to increase with the increase in annealing temperature. Annealing effects on resistivity properties reveal that lower thickness Cu₂S films exhibit increase in resistance when annealed at 100°C, at the same time resistance decreases when annealed at 200°C. Moreover higher thickness Cu₂S film exhibits increases in resistance with an increase in annealing temperature. Optical studies also reveal that after annealing lower thickness Cu₂S films display phase transformation from Cu₂S to CuS at 200°C, whereas higher thickness film results in phase transformation from CuS to Cu₂S. It was observed that thermally treated higher thickness Cu₂S film has high transmittance with the least reflectance of about 80% than compared to the lower thickness film. Annealing Cu₂S film results in a decrease in resistivity with an increase in current values. It was also found that the band gap energy decreases with an increase in annealing temperature.