CHAPTER- V

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The physical methods such as vacuum depositon and cathodic sputtering and the chemical methods such as anodization, electrolytic, electroless, controlled, chemical vapor deposition etc. have been used to prepare the thin films. The physical methods are applicable to all the substances and to a great range of thickness. Though the physical methods result in the formation of very pure and welldefined films, their main drawbacks include requirement of high temperature, sophisticated instrumentation and extreme cleaning of substrates. Also the large area depositoon is not possible. The advantages of chemical methods over the physical methods are-ability to form the films on large area, low cost of materials and equipments, low temperature process, easily controlled parameters etc. Chemical bath deposition method is presently attracting a considerable attention as it is relatively inexpensive, simple and convenient for large area deposition.

Chemical deposition of silver has been carried out by using electroless depositon in which sensitizers and activators are used and deposition on metallic, semiconducting and plastic substrates have been reported.

However, the deposition of silver on the amorphous glass substrates has not been reported as the surface of the amorphous glass substrate could not be sensitized and activated. In the present work, silver films have been prepared onto the glass substrate using 'adsorption-reduction' mechanism in which silver ions are adsorbed on the glass surface which are then reduced to the metallic silver in thin film form. The work is divided into five Chapters. **Chapter-I** gives brief introduction to the subject of thin films. **Chapter-II** describes the deposition of Ag films in detail. **Chapter-III** and **IV** relate the conversion of silver films into silver sulphide and silver selenide films respectively. A detailed summary of the work undertaken has been described in this chapter.

Chapter-I describes the general, survey of literature on silver and purpose of the dissertation.

Chapter-II describes the deposition of silver films. To deposit silver films onto the glass substrates, the glass substrates are first dipped in warm ($80^{o}C$) alkaline 0.1 M silver nitrate solution. Then these glass substrates are dipped in warm ($80\ ^{o}C$) 37.41% of formaldehyde solution so as to form the silver films onto the glass substrates. For 0.1 M concentration of $AgNO_3$, the films

are thin. The reducing agent such as 37.41% of formaldehyde and complexing agent sodium-potassium-tartarate are suitable as the films are continuous and well adherent to the substrates.

X-ray diffraction revealed that the Ag films deposited are polycrystalline since it shows sharp peaks corresponding to the Ag. The scanning electron microscope showed that the films are uniform all over the surface. The average grain size of Ag film is 0.1 micron and the agglomeration in such films is observed.

The Hall effect of Ag films is studied by using Vander Pauw's configuration. In order to avoid the contact and voltage drop problem, we prepared the sample holder using PCB technique by making four point contacts A,B,C,D at arbitarily places along the circumference. For unannealed Ag films, the electrical resistivity (ρ) exhibits monotonically decrease with increasing the film thickness (t). The $\rho = 1.12 \times 10^{-5}$ ohm-cm at t=1246 A^{o} reduces to $\rho = 0.60 \times 10^{-5}$ ohm-cm at t=3260 A^{o}. The mobility (μH) increases with increasing the film thickness (t). The $\mu H = 2.0 \times 10^{3}$ cm^{2} V^{-1} S^{-1} at t=1246 A^{o} increases to $\mu H = 2.75 \times 10^{3}$ cm^{2} V^{-1} S^{-1} at t=2210 A^{o}. The carrier concentration (n) from 2.6×10^{20} cm^{-3} at t=1246 A^{o} increases to $n=3.1 \times 10^{20}$ cm^{-3} at t=2210 A^{o}. The Hall

coefficient (R_H) decreases linearly with increasing the film thickness (t). The $R_H = 2.4 \times 10^{-2} cm^3 C^{-1}$ at t=1246 A^o reduces to $R_H = 1.5 \times 10^{-2} cm^3 C^{-1}$ at t=3260 A^o. The thermoelectric power (S) increases monotonically with increasing the film thickness (t). The $S=1.7 \mu V\ ^oC^{-1}$ at t=1246 A^o increases to $S=4.2 \mu V\ ^oC^{-1}$ at t=3260 A^o.

For annealed Ag films, the $\rho = 1.1 \times 10^{-5}$ ohm-cm at t=1246 A^o reduces to $\rho = 0.56 \times 10^{-5}$ ohm-cm at t=3260 A^o. The $\mu H = 1.7 \times 10^3 cm^2 V^{-1} S^{-1}$ at t=1246 A^o increases to $\mu H = 2.7 \times 10^3 cm^2 V^{-1} S^{-1}$ at t = 2210 A^o. The $n=3.1 \times 10^{20} cm^{-3}$ at t=1246 A^o increases to $n=3.3 \times 10^{20} cm^{-3}$ at t = 2210 A^o. The $R_H = 2.2 \times 10^{20} cm^3 C^{-1}$ at t=1246 A^o reduces to $R_H = 1.4 \times 10^{-2} cm^3 C^{-1}$ at t = 3260 A^o. The $S=1.6 \mu V\ ^oC^{-1}$ at t=1246 A^o increases to $S=3.6 \mu V\ ^oC^{-1}$ at t=3260 A^o.

The electron mean free path (U) and the Fermi surface area (V) vary with the film thickness.

Thus, by using 'adsorption-reduction' method Ag films have been deposited onto the glass substrates. The films are polycrystalline, continuous and well adherent to the glass substrate. The effect of annealing the films in vacuum improves the mobility, Hall coefficient and thermoelectric power.

Chapter-III descibes the conversion of silver into silver sulphide (Ag_2S) by a simple chemical method. The Ag films are deposited onto the amorphous glass substrates by 'adsorption-reduction' method and are converted into Ag_2S films just by dipping Ag films in 0.1 M sodium sulphide (Na_2S) solution. The Ag_2S films are annealed in vacuum at 200°C for 2 hours to study the electrical properties.

X-ray diffraction revealed the total conversion of Ag into Ag_2S . The Ag films have orientations in (111), (200), (220) and (311) planes whereas the converted Ag_2S films have orientations in (110), (023) and ($\bar{1}$05) planes. The XRD pattern of annealed Ag_2S films show increase in intensity of peaks of Ag_2S. The optical absorption of converted Ag_2S films shows that the band gap energy, Eg for unannealed and annealed films is about 0.88 eV. The scanning electron micrograph of Ag film shows that films are uniform and the films consist of closely packed round grains whereas the converted Ag_2S films show hairlike structure and the film surface is rough.

For unannealed Ag_2S films, the electrical resistivity (ρ) decreases montonically with increasing the film thickness (t). For Ag films, the $\rho = 1.12 \times 10^{-5}$ ohm-cm at t=1246 Å was reduced to $= 0.60 \times 10^{-5}$ ohm-cm

at t=3260 A^{o} whereas for the converted Ag_2S films, the $\rho = 1.38 \times 10^{2}$ ohm-cm at t=1330 A^{o} reduces to $\rho = 0.53 \times 10^{2}$ ohm-cm at t=3210 A^{o}.

For annealed Ag films, the $\rho = 1.1 \times 10^{-5}$ ohm-cm at t=1246 A^{o} was reduced to $\rho = 0.56 \times 10^{-5}$ ohm-cm. at t=3260 A^{o} whereas for the converted Ag_2S films, the $\rho = 1.26 \times 10^{2}$ ohm-cm at t=1330 A^{o} reduces to $\rho = 0.47 \times 10^{2}$ ohm-cm at t=3210 A^{o}.

The thermoelectric power measurement of unannealed and annealed Ag_2S films reveals that the films are having n-type electrical conductivity. For Ag films, the thermoelectric power (S) was of the order of $\mu V\ ^{o}C^{-1}$ whereas for the converted Ag_2S films 'S' is of the order of $mV\ ^{o}C^{-1}$.

Thus, the metallic silver films have been converted into semicoducting silver sulphide films by using a simple chemical conversion method. The Ag_2S films have optical band gap energy, Eg equal to 0.88 eV and the electrical resistivity is of the order of $10^{2} - 10^{3}$ ohm-cm. The effect of annealing the Ag_2S films in vacuum improves the electrical properties.

Chapter IV describes the conversion of silver into silver selenide (Ag_2Se) by chemical method. Both unannealed and annealed Ag films are converted into Ag_2Se

by dipping Ag films into 0.1M selenium oxide (SeO_2) solution for 70-80 minutes. The Ag_2Se films are annealed in vacuum for 2 hours at 200°C.

X-ray diffraction revealed the conversion of Ag into Ag_2Se. The Ag films have orientations in (111), (200), (220) and (311) planes whereas the converted Ag_2Se films have orientations in (002), (111), (210) and (204) planes. The optical absorption of Ag_2Se film shows that the band gap energy for unannealed and annealed films is about 1.31 eV. The SEM of Ag film shows that film consist of closely packed round grains whereas converted Ag_2Se film shows the rough surface.

For unannealed Ag_2Se films, the electrical resistivity (ρ) decreases monotonically with increasing the film thickness. For Ag films, the $\rho = 1.12 \times 10^{-5}$ ohm-cm at t=1246 A° reduced to $\rho = 0.56 \times 10^{-5}$ ohm-cm at t=3260 A° whereas for converted Ag_2Se films, the $\rho = 1.1 \times 10^{3}$ ohm-cm at t=1370 A° reduced to $\rho = 0.45 \times 10^{3}$ ohm-cm at t=3850 A°.The free charge carrier density for converted Ag_2Se films is 3.9×10^{20} cm^3.

The TEP measurement revealed that Ag_2Se films are having n-type electrical conductivity. It is of the order of $mV°C^{-1}$. The TEP increases rapidly with increasing the film thickness about 2314 A° and thereafter

increases slowly with a further increase in thickness, attaining saturation. The variation of TEP with the reciprocal of film thickness showed that curves are linear at lower thicknesses and become scattered at higher thicknesses indicating inverse relation between TEP and film thickness.

Thus, the Ag films are converted into semiconducting Ag_2Se films by chemical method. The Ag_2Se films have optical band gap energy, Eg equal to 1.31 eV and the electrical resistivity is of the order of 10^3 ohm-cm. Annealing Ag_2Se films in vacuum improves the electrical properties.

Thus by a simple chemical method silver films have been deposited and are converted into silver sulphide and silver selenide films.

The Fig.5.1 (a),(b),(c) show the chemically deposited silver, converted silver sulphide and silver selenide films respectively.

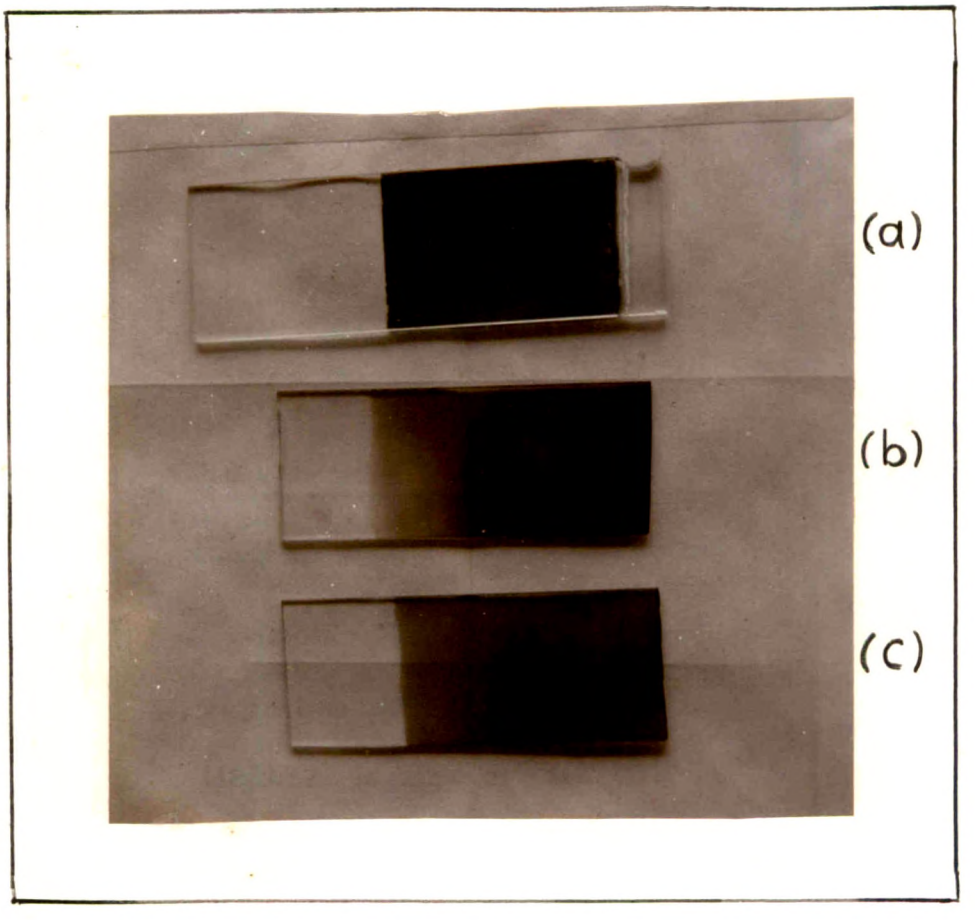

Fig.5.1 : Chemical Deposited Films of
a) Silver (Ag) (b) Silver Sulphide (Ag_2S) (c)Silver Selenide (Ag_2Se)