Chapter VI

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The primary objective of the work has been to investigate the electrical and the optical properties of crystalline and amorphous semiconductors. As far as the crystalline silicon is concerned, the x-ray diffractogram clearly reveals its lattice structure. The theoretical evidence that the crystal is a perfect one is proved by the calculation of its lattice spacing which agrees with the reported value. Studies on optical transmission spectroscopy was instrumental in determining the optical band gap of the crystalline silicon. The optical band gap is slightly lower compared to the reported value but it is within the experimental error. The measurement of the electrical properties of crystalline germanium has been done by the Four Point Probe and Hall-Effect techniques. The Four-Point Probe technique was applied to measure the conductivity of germanium and its band gap. As in the case of the optical gap, the band gap value obtained by this method is within the experimental error. The Hall-Effect measurement for crystalline germanium with n-type and p-type yields carrier density, electron mobility, Hall coefficient and resistivity. These values are also found to be within the experimental error. The conductivity for crystalline silicon was measured directly using the Keithley Source Measurement Unit. The oxide layer formed on its surface during the deposition of aluminium electrodes hinders with the accurate estimation of the conductivity and the energy gap of the material. Finally, for the crystalline silicon, the a.c .conductivity results gave the variations of conductance, series and parallel capacitance as a function of the frequency. The similar set of studies were also repeated for hydrogenated amorphous silicon. The a.c. studies on crystalline Si was found to be interesting because of a sort of resonance phenomena in the variation of electrical parameters with frequency was observed. Furthermore, such a resonance frequency for electrical parameters (except C_p) first increased with the annealing temperature and later it was found to decrease. For C_p, exactly opposite results was observed. For amorphous materials the resonance phenomena, as mentioned earlier could not be detected. But, the electrical parameters did vary with the changes in the a.c. frequency. These effects requires further investigations.

There are two primary areas of interest in studying the hydrogenated amorphous silicon (a-Si:H) prepared by using the home built horizontal plasma glow discharge technique. First the annealing effect on the structure is investigated and secondly, the role played by the hydrogen on its electrical and optical properties are analysed. When the film is annealed at a moderately high temperature, evolution of hydrogen are from the weak or $(SiH_2)_n$ bonds. However, when annealed at a higher temperature, more hydrogen atoms are evolved from the Si-H and SiH_2 bonds at the surface and in the bulk. Hydrogen removed from the Si-H bonding configurations alter the electrical and the optical properties of the film.

The hydrogen content calculated from the optical and the FTIR transmission spectrum are different in magnitude for both samples as-prepared and annealed. The hydrogen content derived from optical spectrum includes all hydrogen at all bonding sites whereas the hydrogen content calculated from the FTIR transmission spectrum accounts for hydrogen at Si-H bonding sites only but it also includes microvoid content in the film. Oxygen contamination is more significant in the high silane flow-rate a-Si:H. Oxygen bonded to silicon atoms forms orthorhombic silicon oxide microcrystallite structures in the film. The higher deposition rate due to the higher silane flow-rate results in more residual oxygen atoms in the preparation chamber being trapped into the film structure. The grain size are significantly larger in the high silane flow-rate sample. Thus, when annealed the grain size decreases in the high silane flow-rate sample but becomes amorphous for the low silane flow-rate sample. The parameter R calculated from the integrated intensities at the Si-H and Si-H_2 stretching mode depends strongly on the intensity of the Bragg peak corresponding to the <200> plane for both the low and the high silane flow-rates. This parameter is proportional to the hydrogen bonded in some sort of microstructure. Thus, the increase in the grain size in the film could be due to the increase in microstructure concentration in the film.

The optical energy gap, E_g for both the low and the high silane flow-rate samples is dependent on the hydrogen content calculated from the FTIR spectrum. The optical energy gap is related to matrix defect in the film structure. Since the hydrogen content from the FTIR spectrum represents hydrogen in Si-H bonding sites only, thus hydrogen removed from these bonding sites create matrix defects in the film. Decrease in the hydrogen content from these sites results in the decrease in E_g. Analysis of Urbach tail band width values which quantifies disorders in film structure shows that larger grain sizes in film produces a more ordered structure. Increase in microstructure concentration which produces columnar structures in film also results in a more ordered structure.

Annealing at higher temperature increases the density of states in the mid gap near the fermi level. These states are created when hydrogen is removed from $(SiH_2)_n$ bonding sites. Increase in the states in the gap increases the possibility of electrons being trapped in these states when excited, thus shifting the fermi level closer to the conduction band.

These reduces the activation energy and correspondingly increases the conductivity of the film. The results obtained from this work shows that the manner in which the hydrogen incorporated into the film determines the structural, optical and electrical properties of the film. Annealing results in hydrogen being removed from different bonding sites and thus effect these properties.

To obtain a more comprehensive understanding on the effects of annealing on the properties of a-Si:H film, studies must be carried out on samples prepared under different preparation conditions. Samples prepared at different silane flow-rates and deposition temperatures could be studied to get a more conclusive result. In this work, the a-Si:H is prepared from pure silane with no diluent gas. Film prepared from the discharge of silane diluted in hydrogen, argon or helium could be also be studied. The effect of these diluents on the properties is certainly very interesting to investigate.

The tools used in this study are not adequate to obtain a clearer picture on the structural, optical and electrical properties of amorphous materials concerned. Other tools such as X-Ray Photoelectron Spectroscopy/Auger Electron Spectroscopy (XPS/AES), Atomic Force Microscopy (AFM), Tunnelling Electron Miccroscopy (TEM), Electron Spin Resonance (ESR), Nuclear Magnetic Resonance (NMR) and Raman Spectroscopy could also be utilised for further investigations in enhancing our understanding of the properties of this materials.

The X-ray Photoelectron Spectroscopy(XPS/AES) provides the medium to analyse the film surface for elemental compositions. Applications of a-Si:H in electronic based devices may be enhanced with an in-depth study in this area. Tunnelling Electron Microscope (TEM) is a tool used for the study of structural defect analysis and useful in studying the microstructures in the thin films. Apart from that, it assists in the study of morphology and chemical compositions of nanometer particles. The TEM, would be useful in understanding the form of structural transformations caused by annealing. It also gives an in-depth look at the film's structural, electrical and optical properties. The study on the effects of annealing on the film's surface structure may be enhanced with the aid of the AFM. It depicts contamination, columnar structures and voids in the film. Electron Spin Resonance (ESR) would be a vital tool to study and to detect the density of surface defects in the form of dangling bonds. It also sheds some light on the link between the dangling bonds and the SiH and $(SiH_2)_n$, configurations which are inferred from the infra-red measurements. The Nuclear Magnetic Resonance (NMR) spectrum would also be able to provide informations on molecular hydrogen in the hydrogenated amorphous silicon. The amount hydrogen in various molecular states can be obtained for different annealing temperatures. Finally, the Raman Spectroscopy is an important tool to analyse the character of the SiH configuration in nanocrystalline a-Si:H. Such studies also can be used to determine the average grain size of the crystallites by observing the phonon peak position shift as the sample is annealed at higher temperatures.