CHAPTER - I

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1.1. PHOTOCONDUCTIVITY PHENOMENA

With the transition from electronic era to photonic era, the photons (light) are being called upon to play more of the key roles previously played by electrons /1/. The ongoing transformation of the telecommunication network from copper wires to fibre-optics communication lines (FOCLs) is the main evidence of this change. The basis of FOCLs transmission are the light radiators, fibre-optic conductors and photodetectors.

The photodetectors are photo-electronic devices which convert the energy of optical radiation to electrical energy. These are indispensable not only in FOCLs, but also in image processing, in establishing optical links between electrical circuits, in radiation detectors from far infrared region to high frequency nuclear particles, in contactless remote acting devices etc. A solar cell can operate as a photodetector. However, other type of photodetectors, photothyristors and photoresistors (or photoconductors) may be more suitable for a variety of applications. These devices rely on the internal photoelectronic effect observed in semiconductor materials.

Two forms of phenomenon are observed in internal photoelectric effect. These two phenomena are : The photovoltaic effect and photoconductive effect. The photovoltaic effect is used in photodiodes, phototransistors, photothyristors and other pn junction devices, the photoconductive effect is used in photoresistors. Despite the rapid advances in the domain of pn junction photodetectors, photoresistors still hold an important place in optoelectronics /2/. In the present investigations the preparation technique of Cadmium telluride (CdTe) thin film photoconductors and the photoconduction mechanism in these films are described, in terms of structural and other thin film characterizations as some of the variable parameters.

1.2. CdTe THIN FILMS

The prominent members of II-VI family compound semiconductors are ZnS, ZnO, ZnSe, ZnTe, CdTe, CdS, CdSe, HgTe and HgSe. Out of these compound semiconductors HgTe has the smallest intrinsic band gap of $\sim 10^{-2}$eV while that of ZnS has the maximum band gap of more than 3.0eV. Therefore this group of semiconductors have the wide range of band gap because of which each individual members of this group behaves much differently for photoresponse properties. Due to the pecular characteristics, this group of compound semiconductors have the potential applications in different fields. Investigations of the transport properties of II–VI compound semiconductors have attracted considerable interest due to their high potential for producing photovoltaic devices at low cost and with large areas /3/.

In recent years considerable attention has been paid to the growth of CdTe thin films and the control of their properties by different ways. CdTe possesses a wide range of applications ranging from photovoltaic conversion, high energy flux detectors — such as x-ray and γ-ray detectors /4/, to electronic and opto-electronic devices. With a band gap of approximately 1.5eV, CdTe is well matched to the solar spectrum. Accordingly, CdTe based thin film solar cells have been fabricated and efficiences upto 15.8% have already been achieved /5/. Cadmium Telluride has been long recognised as a leading thin film photovoltaic material due to its suitable band gap as mentioned above and high absorption coefficient. CdTe absorbs over 90% of available photons ($h\nu > 1.5$eV) in a 1 μm thickness, so that films of only 1—3 μm are sufficient for thin film solar cells /6/. In view of economic considerations of CdTe thin films, the detail electrical characterization and photoconduction mechanism in such films is a prime objective.

1.3. PHOTOCONDUCTION MECHANISM IN CdTe THIN FILMS

In general the conductivity (σ) of a semiconductor thin film can be expressed as —

$$\sigma = e\ (n_e\mu_e + n_h\mu_h) \qquad \ldots (1)$$

where e is the charge of the carrier, n_e and n_h are the densities of free electrons and holes respectively while μ_e and μ_h are the respective mobilities.

The change in conductivity due to the illumination of light is called as photoconductivity. The corresponding change in the conductivity can be expressed as —

$$\Delta\sigma = e\Delta\ (n_e\mu_e + n_h\mu_h) \qquad \ldots (2)$$

The change in σ due to the change in n_e or n_h is called (a) Carriers modulation and due to the change in μ_e or μ_h is called (b) Barriers modulation. So in the case of photoconduction mechanism in semiconductors or more particularly in CdTe thin films the above two processes may equally be possible.

In carriers modulation, photoconductivity is caused by the light generated electrons in the conduction band or light generated holes in the valence band /7/. Different transitions caused by illumination included intrinsic (valence band to conduction band) transition and extrinsic (donor to conduction band or acceptor to valence band) transitions. It is also obvious that Δn_e and Δn_h depend on time and level of illumination. The change in conductivity whether due to intrinsic or extrinsic absorption, can be studied by observing the variation of photocurrent (I_{ph}) with wavelength of light for constant number of photons incident upon the film. The most important characteristic of intrinsic photoconductivity of a semiconductor is its band gap, which determines the longest wavelength of light $\lambda_g(\mu m) = \frac{1.24}{E_g(eV)}$ where E_g is the optical energy band gap.

In crystalline thin films there exist potential barriers between the grain boundaries. When the film is exposed to light illumination, the height of the potential barriers are reduced and there by the mobility of the carriers increase. Due to this increase of mobility, the conductivity increases.

In addition to the above two processes of photoconduction mechanism, the change in conductivity under the illumination may be the result of the contribution from a variety of photosensitive defect centres. In this films however without incorporation of impurity there may be certain imperfection levels produced within the band gap due to native defects formed during the time of growth of the films. Such defects also contribute to the change of conductivity under illumination. The process of release of electrons and holes under the influence of illumination from these defect levels accompanied by their recombination determine in general the photoconductivity growth and decay. The current reaches the steady state only when the rate of recombination becomes equal to the rate of generation of new carriers under which condition the concentration of holes and electrons attains some constant value. In many cases the dominant recombination mechanism is recombination via electron or hole traps. When a photogenerated carrier say an electron is captured by an empty trap and then a hole is captured by the trap already filled by the electron, the electron-hole pair recombines resulting in change of conductivity. The inverse processes are the release of an electron from a filled trap into the conduction band and the emission of a hole from an empty trap into the valence band. The rate of electron capture by the trap is proportional to the number of electrons and to the number of empty traps. Thus the presence of trapping centres in the band gap of a semiconductor thin film play important role in the change of photoconductivity.

1.4. PRESENT STATUS OF THE WORK ON THE PHOTOCONDUCTION MECHANISM OF CdTe

Due to the technological importance of CdTe thin films as a potentially rich material for different photoconversion devices, considerable attention has been given in recent years by the research workers for characterization of its various physical attributes particularly in its thin film form. The choice of thin film over the bulk is due to the drastic change in properties depending upon the variety of thin film growth parameters.

From the survey on the works of CdTe it is found that extensive studies have already been done on growth, structure and composition of CdTe thin films deposited by different techniques /8—15/. Regarding the optical, electrical and electronic properties of good quality CdTe thin films researches are still going on in many centres world over /16—23/. Annealing effects of As^{+} implanted CdTe epilayers have been reported /24/ recently. Effect of laser annealing on the structural, electrical as well as the optical properties have been studied by another group of workers /25/. The misfit stress relaxation mechanism, the substrate effect on CdTe layers have also been studied by different group of workers /26, 27/. Reports are available on the works of CdTe thin film solar cells with the studies of different properties in connection with different growth parameters such as source to substrate distance, source temperature and substrate temperature etc /28—32/. Reports on the growth and carrier transport mechanism in CdTe thin films are also available /33—37/. Again reports have been made by very many workers on the electric and photoelectric conductivities and also the correlated studies of impurity levels of the polycrystalline CdTe thin films under different ambient conditions /38—42/. Some other researchers studied the d.c. conduction mechanism under different applied electric fields on CdTe thin films of sandwich structure. The results of these works lead to the conclusion that a Poole-Frenkel type of conduction mechanism is dominating at high fields /43, 44/. In these works a high value of the Poole-Frenkel coefficient (β) was found and therefore an explanation was also forwarded in terms of the operation of a modified Poole-Frenkel effect.

1.5. MOTIVATION OF THE PRESENT WORK

From the recent literature it is observed that a lot of people are still engaged in the studies of the properties of CdTe thin films under different ambient conditions all through out the world. Again from the available literature it is seen that the studies on the CdTe thin films of gap type cell configuration is much less in comparison with the studies on sandwich type configuration. Moreover a systematic and correlative studies on the dark and photoconductivity mechanism and photosensitivity with the growth parameters such as thickness of the film, substrate temperature, nature of substrate etc seen to be not adequate. Therefore still there are much scope and necessity for the studies of CdTe thin films on these lines.

The aim of the present work is to make an experimental study on the effect of structure of the thin film on the photoconduction mechanism and the photoactivation processes in CdTe thin films of gap type cell geometry. In other words the various experiments performed, are motivated to assess the nature and extent of the modulation effects that illumination may cause in the potential barriers present at the grain boundaries of the film. The grain size and the grain boundary potential barriers are functions of the substrate temperature, film thickness, source to substrate distance and other growth parameters. In the present study keeping other parameters fixed, the substrate temperature and film thickness have been choosen as the independent variable for obtaining films of different grain sizes. Photo and dark conductivities are studied at different ambient temperatures, applied fields, various intensities of both white and monochromatic light covering a wide range of wavelengths. In addition to that the photoconductivity rise and decay processes are also studied. In all these films used for the study of optical and other properties, the XRF, XRD and SEM studies are also performed. The different experimental data corresponding to the composition and structural properties are analysed in the light of relevant theoretical formulations. Finally results of all the various experiments will be summerised and correlated to find the optimum parameters for maximum photosensitivity and reproducible device quality CdTe thin films.

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