
STUDY OF MULTILAYER CdS THIN FILMS

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ABSTRACT

Polymers are generally known for their insulating property because of covalent bond present in saturated carbon compounds. Since desirable properties can be conveniently attained by tailoring the polymer structure and also by incorporating additives, scientists have been enthusiastic to explore the possibility of transforming insulating polymers into conducting or semiconducting materials envisaging such special characteristics like low density, ease of fabrication, flexibility of design, low energy and labour requirements for fabrication and processing.

Key words: Semiconduction, low energy, fabrication

INTRODUCTION

The sulphide semiconductors are one of the most extensively investigated semiconductor in thin film form and a large variety of deposition techniques have been utilized to obtain solar cells.

The Cadmium sulphide films grown by vacuum evaporation technique have been used as gas sensors for detection of oxygen and with a direct bandgap it serve as a window material for heterojunction solar cells.

Sharma, R.P. et al, [30] showed that CdS / polyaniline composite thin films can form tunable band gap heterostructure with vacuum evaporation CdS thin film on to glass substrate.

Jayachandran, M. et al,[23] prepared polyaniline layers onto porous structure by in-situ electrodeposition and showed photoluminescence at room temperature with a maximum current density 20 mA/Cm², a possibility of polyaniline as ohmic contact.

Schlamp, M.C. et al, [29] demonstrated improved efficiency in LED's made with CdS and CdSe core / shell type nanocrystal incorporated in semiconducting polymers.

Advincula, R.C et al, [33] reported improvement in performance of LED's which incorporated polyaniline coated on to ITO glass polyelectrolyte layer for heterostructure.

N.F. Foster et al, [38] prepared the polycrystalline CdS films and found that the structural, electrical and optical properties of vacuum coated thin films of Cadmium Sulphide are very sensitive to the deposition conditions e.g. the degree of vacuum, the rate of deposition, the substrate temperature and the subsequent heat treatment. He also found that the CdS films have excess of Cadmium owing to the dissociation of CdS during evaporation, and concluded that the stoichiometry can be restored by codepositing Sulphur together with CdS.

The Porous structure was prepared on P-Si single crystal wafers by anodizing route at low current densities. They also gave the X-R-D studies which indicate that an optimum pore size is found at this anodizing condition and the crystal structure is cubic. They observed porous structure using SEM Hitachi 530011. The (I-V) study also gives both porous silicon surface and porous silicon surface coated with Polyaniline. The result shows the polyaniline incorporation into the pores which is capable of making good electrical contact for device applications.

JUNCTION BEHAVIOR OF POLYANILINE

The Polymers has taken an up swing to their requirements for fabrication of semiconductor devices for optoelectronics and microelectronics photovoltaic. It become possible due to substantial improvements and advancements in the stability and processing characteristics of available polymeric materials. It is

also universally accepted that exactions play an important role in the optical properties of conjugated polymers. There is still an on going debate about the absolute magnitude of charge carrier binding [118-122], where as the polaron pair generation clearly occurs in conjugated polymers film [123].

Polyaniline (Pani) is unique among conducting polymers, it is environmentally stable, but its conductivity can be reversibly controlled both by charging level.

The conductivity of Pani is controlled by complete protonation. The wide range of electrical properties coupled with thermal and environment stability makes Pani potentially attractive as a printable conductor. Pani is superior to other conducting polymers for application due to its chemical and oxidative stability in both the undoped and doped forms. These possess good tunable electrical conductivity and are organic electro chromic materials with chemically active surfaces. They are chemically sensitive but have poor mechanical properties. Pani is also one of the most widely studied conducting polymers because of its good conductivity. Its well defined electro-chemical (redox) response, easy preparation, and possible application in rechargeable batteries, corrosion protection, light emitting diodes, molecular sensors electrochromic devices and microwaves, screening, and photovoltaics[124].

Polyaniline is not charge conjugate symmetric i.e., the valence and conduction bands are asymmetric to a great extent.

The conductive polymers are inexpensive, abundantly available and can be fabricated over a large area in the form of thin film and the properties can be almost tailored to suit specific requirements for their use in particular applications. It is one of the most promising polymers which can be used for device fabrications such as photonic devices, opto electronic device, microelectronic, civil, communication and strategic applications.

The semiconducting polymers are to be used in the following configuration:

- (a) The conducting polymer being used as metal in conjunction with inorganic semi conductor.
- (b) The semi conducting polymers being used as the p-type material on which a metal is deposited and the configuration is called as schottky type.
- (c) If a polymer and a inorganic semi conductor is used then a heterojunction is formed at the interface of the two.
- (d) In the form of p-n homojunction on the same semi conductive polymer.

The important factor for device fabrication is the electrical conductivity and the interface behavior of the polymer with different metals. The semi conducting polymers are p-type and except for poly-acetylene it has not been possible to prepare the n-type for polymers like Pani etc. It is hence not possible to prepare a pn junction for device fabrication. Another alternative is to fabricate a heterojunction of the polymer (assumed to behave a p-type solid) with other material, e.g. a material or a semi conductor of n type. We have taken P-polyaniline and n-CdS for the fabrication of a heterostructure and the electrical characterization of such type of samples have been studied completely by using Keithly S M U 236 source measure unit.

When the polymer is brought in to electronic contact with a metal then the three types of junction formation is possible after contact which is follows.

(i) Ohmic Contact

In such type of contact there is a free flow of charges from the polymer to metal and metal to polymer.

(ii) Rectifying Contact

In such type of contact, unidirectional flow of charges takes place.

(iii) Blocking Contact

In such type of junction there is no injection or extraction of charges from the polymer.

For the heterojunction, an electronic interface subsequently builds up at heterojunction having depletion region in the polymer.

If the metal having a work function = ϕ_m

and the polymer having a work function = ϕ_p

then,

if $\phi_m > \phi_p$, (ohmic contact)

if $\phi_m < \phi_p$, (Rectifying contact)

The current through such type of heterojunction is mainly thermionic controlled and current voltage characteristics can be explained on the basis of theories for Schottky emission.

The current density J across the junction is given by the equation

$$J = J_0 \exp\left(\frac{eV}{nKT}\right). \quad \dots\dots\dots 1.1$$

and
$$J_0 = A^* T^2 \exp\left(\frac{-e\chi_b}{KT}\right) \quad \dots\dots\dots 1.2$$

- J_0 = Saturation current.
- A^* = Richardson constant,
- e = Electronic charge
- χ_b = Barrier height.
- K = Boltzman's constant.
- T = Absolute temperature,
- n = Ideality factor.

For the sample preparation Pani is prepared by redox polymerization as discussed in previous chapter obtained in powder form.

This powder is evaporated by vacuum coating unit at a vacuum of 10^{-5} mm Hg. Vacuum deposition technique followed by using a Molybdenum boat at a constant vacuum evaporated speed on highly cleaned glass substrate. The glass substrate was cleaned in aquaregia washed in distilled water and Isopropyl Alcohol (IPA).

Characterization of CdS and Pani on CdS Film.

The prepared films have been subjected for different characterization, as a result of which the following properties have been observed.

STRUCTURAL CHARACTERIZATION;

(i) X-Ray Diffraction

The X-ray-diffraction of the sample gives the valuable information about the nature and structure of the film.

The X-ray diffractogram of different samples have been used to characterize the sample of vacuum deposited CdS on glass and Pani on to same CdS/Glass as shown in fig. (1.1) and fig. (1.2) of the sample CdS/Glass indicates the amorphosity of the film with occasional crystallization.

It can also be illustrated from the fig. (1.1) that for CdS/Glass sample X-ray intensity of the hexagonal (101) reflection peak is stronger in comparison to (110) reflection.

The thin film of CdS has a high degree of preferred crystallographic orientation. The characteristics strong peak at ($2\theta = 24^\circ$) correspond to the (101) plane, other peak can be seen at ($2\theta = 44^\circ$) correspond to p hexagonal (110) reflection.

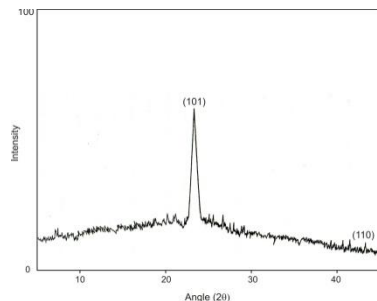


Fig. 1.1 X-Ray diffraction pattern of CdS/Glass thin film

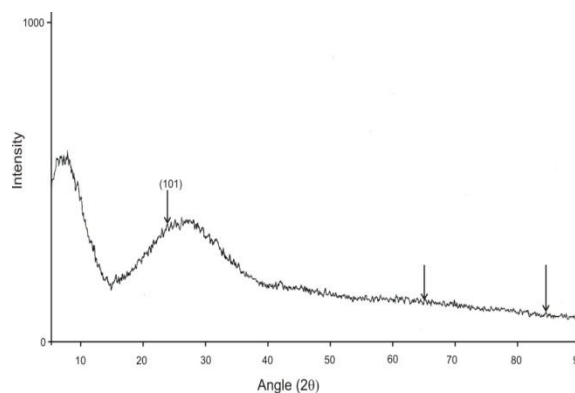


Fig. 1.2 X-Ray diffraction pattern of Pani/CdS/Glass multilayer thin film.

Table 1.1

2 \square , d values and lattice parameters for the sample CdS/Glass and sample Pani/CdS/Glass.

S.No.	2θ	JCPDS/ASTM d(A $^\circ$)	d(A $^\circ$)	(h, k, l)
1	24	3.58	3.56	(101)
2	44	2.07	2.06	(110)
3	24	3.58	3.55	(101)
4	61.2	1.54	1.42	*
5	70.0	*	1.34	*

On the other hand the sample fig. (1.2) in which Pani and CdS multilayer thin film have been deposited on the same glass substrate indicate many peaks besides oriented peaks. The preferred orientation is not lost correspond to (101) reflection but the decrease in intensity is observed which indicate the hexagonal type of structure. Other peak have also been identified and their corresponding diffraction angle and d values also been given in table (1.1).

(ii) Scanning-Electron Microscopy (SEM)

Scanning Electron Microscopy provides a direct structural evidence of the growth and perfection of the film. This is one of the most useful methods for the investigation of the surface topography, microstructural feature etc. It is based upon the fact that the electron are absorbed or diffracted at inhomogenities and thus reveals these inhomogenities as contrast effect. The secondary electrons are generated by the interaction of loosely bound electrons of the surface atoms. The emission of

secondary electrons is sensitive to the incident beam direction and the topography of the surface layer. The contrast hence depends on the rate of secondary electron yields and the incident angle of primary beam to the surface being examined.

The surface morphology of the samples has been investigated by scanning electron microscopy. To access the size and morphology the electron beam of 15 KV have been used, the SEM image of CdS on glass substrate is shown in fig. (1.3). This indicate that the surface is smooth and grain boundaries are widens which are seen as thick black lines between the grains which are connecting together.

On the other hand when the thin film of Pani is coated on to the same sample as described above and different type of surface morphology can be seen in the fig. (1.4) Which shows a large surface area and comparative higher degree of crystallinity.

OPTICAL CHARACTERISATION

(i) Energy Band Gap

The fundamental and basic optical properties which can be investigated are reflectance, transmittance and absorption of light at various wavelengths. The different samples have been characterized using Varian Cary 5000 U-3400 and on basis of these studies the energy and band gaps for different samples have been calculated.

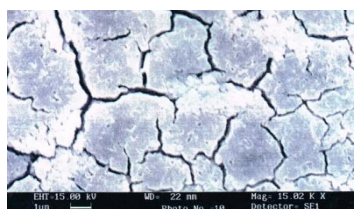


Fig. 1.3 SEM image of CdS thin film on to glass substrate.



Fig. 1.4 SEM image of Pani/CdS thin film on to glass substrate.

A Varian Cary 5000 spectrophotometer was employed to record the reflection spectra of these films in the wavelength range of 300-800nm, at room temperature. The energy bandgap of films were determined by reflection spectra. To measure the energy bandgap of CdS, we use the Tauc relation in which a graph between $(\alpha hv)^2$ Vs (hv) is to be plotted, where α is the absorption coefficient and hv is photon energy. The absorption coefficient α is proportional to $\ln[(R_{\max}-R_{\min})/(R-R_{\min})]$, Where reflectance falls from R_{\max} to R_{\min} due to absorption of photons by the material, R is the reflectance for any intermediate energy photons. Hence we have α in terms of reflectance as $\ln[(R_{\max}-R_{\min})/(R-R_{\min})]$. When we plot a graph between $(\alpha hv)^2$ Vs (hv) , a straight line is obtained. The extrapolation of this straight line to $(\alpha hv)^2 = 0$ axis, gives the value of bandgap of the films material. The band gap measurement of such type of sample in which CdS is vacuum evaporated on to highly cleaned glass substrate in a vacuum of 10^{-6} torr, the reflection spectra is shown in fig, (1.5). Fig. (1.6)

shows the band gap determination of vacuum evaporated CdS thin film of approximately thickness on to highly clean glass substrate. When the thin film of polyaniline is deposited onto the above discussed sample, the different type of reflection spectra is obtained as shown in fig. 1.6

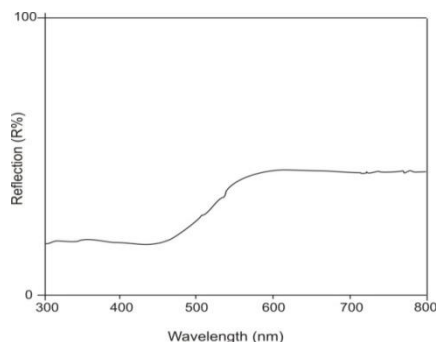


Fig. 1.5 Reflection spectra of CdS film on Glass Substrate

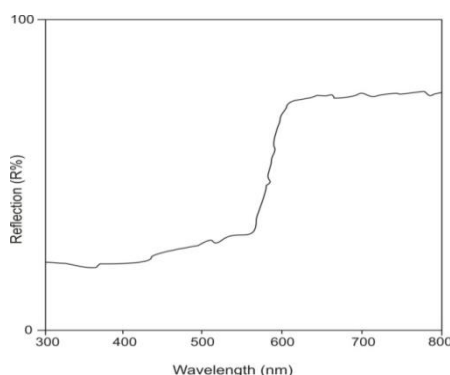


Fig. 1.6 Reflection spectra of Polyaniline CdS heterostructure on Glass Substrate

Polyaniline Pallet/Cds Thin Film Junction

In addition to the work done on polyaniline/CdS thin films as discussed above we have also tried junction of CdS thin film and polyaniline pallet. The I-V characteristics of Pani and CdS/Pani junction are shown in fig. (1.12).

Conducting polyaniline (PANI) has been synthesized using Sol-Gel technique with chemical oxidation process. Thermal and environmental stability of the synthesized sample of PANI is investigated by measuring the thermal transport properties of the samples at different temperatures and time using Transient Plane source (TPS) technique. The results indicate that the PANI shows excellent thermal and environmental stability. Chemically prepared cadmium sulphide has been printed on a pallet of conducting polyaniline (of 1.2 cm diameter and 2 mm thickness). This pallet of CdS coated conducting polyaniline has been sintered at 150° for six hours for ensuring better adhesion. I-V characteristics of CdS, conducting polyaniline and CdS coated conducting polyaniline have been recorded at room temperature using Keithley electrometer. The results indicated that I-V of CdS is ohmic whereas that of conducting polyaniline is observed to be non-ohmic. PANI is a p-type material and CdS is an n-type material. The junction formed in CdS coated PANI is a p-n junction. I-V characteristic of this junction shows diode characteristic. This confirms that a good diode can be fabricated by using such a simple technique.

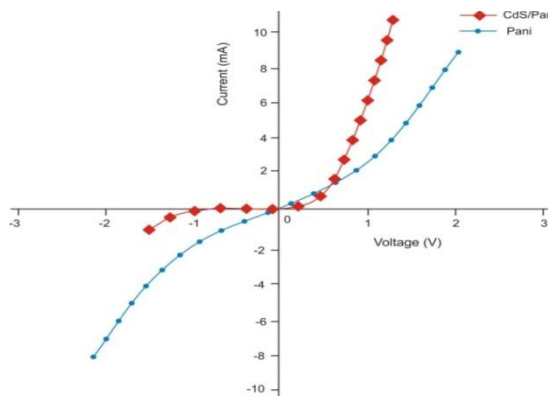


Fig. 1.7 V Characteristics of Pani & CdS/Pani heterojunction

CONCLUSION

In PANI/ CdS junction the conduction of charge across the junction is typically a mixture of electron from n-CdS side a polaron and bipolaron from p-Pani side. In addition to observing a thermionic emission, Schottky I-V characteristics are also observed, a pool frenkely and trap assisted field emission, a non-linear behavior. The junction characteristics of Pani/CdS thin film are complex of many conduction mechanisms and can not be explained by simple theory.

The n-CdS and p-Pani heterojunction also holds the promises of being studied and converted in to an active device. The low value of fill factor and conversion efficiency can be attributed to the polycrystallinity of the CdS thin film and vacuum deposited Pani thin film, as they do not make an extremely sharp perfect heterojunction. Also the substrate has a strong influence on the surface morphology of the films.

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