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Characteristics of CoPc/CdS hybrid diode device

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Abstract. **CdS/CoPc hybrid heterojunctions were fabricated and characterized. CdS films were deposited by the spray pyrolysis technique on indium tin oxide (ITO)-coated glass substrates and CoPc films coated on CdS by chemical precipitation. Ag contact metal deposited on CoPc by e-beam evaporation and glass/ITO/CdS/CoPc/Ag structures were fabricated. Rectification ratio, ideality factor, barrier height and junction parameters of the devices were determined. It is shown that device has diode characteristics with the ideality factor (*n*) of 4.8, rectification ratio of 4.5 and the built-in voltage (V_b) of 0.48 V. Absorption energy for CoPc was found as 1.57 eV. The results encourage utilizing CoPc as absorber organic material for solar cells.**

Keywords. **Asymmetric Co(II)phthalocyanine; CdS; organic; thin film; diode.**

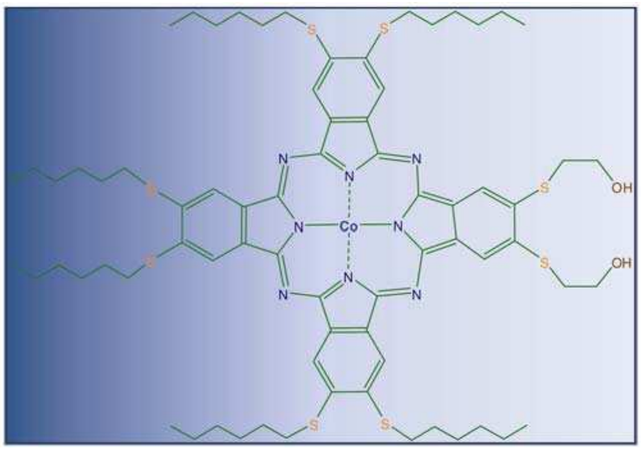
1. Introduction

During the last decades great efforts have been made to use organic materials in electronic devices.[1] Organic materials are cheaper and more easily utilizable compared to inorganic materials.[2] Among these organic materials, phthalocyanines (Pcs), which are well-known metal-organic complexes since the beginning of the last century, are important materials for organic-based electronic devices[1] such as rectifiers, gas sensors,[3] Schottky barrier diodes,[4] organic light-emitting diodes, optical recording materials and for photovoltaic devices.[5] Many works were directed to synthesize (metal-Pcs) MPcs such as CoPc, ZnPc, CuPc, etc. in order to optimize the properties of Pcs to convenient values.[1] Generally, MPcs materials were used by the accompaniment of an inorganic semiconductor in electronic devices. A group II–VI semiconductor CdS is very suitable inorganic material for the n-CdS/p-MPc heterostructures of inorganic- and organic-based materials due to its bandgap, transmission and resistivity properties, as well as its crystalline structure.[6–8] Many techniques and methods have been applied to deposit CdS films.[7] Vacuum evaporation,[6] chemical bath deposition,[9] electrochemical deposition,[10] close-spaced sublimation[11] and spray pyrolysis[12–14] are the mostly used methods. Among these methods spray pyrolysis have some major advantages. Spray deposition of CdS is a cost effective and easy method. Large area samples can be coated and this technique also allows doping the films.[7] Hybrid heterojunctions were fabricated by using inorganic CdS and organic MPcs are also promising structures for solar cell applications because of their reasonable conversion efficiency, long-term stability and low cost.[14] In this work, CoPc was used as organic material[15] (scheme 1). Thin film CoPc/CdS hybrid heterostructures were fabricated by easy, low-cost and effective deposition techniques such as spray pyrolysis and chemical precipitation.[7] Properties of the films and also device characteristics were investigated.

2. Experimental

2.1 *Materials*

All chemicals were purchased from Merck and Sigma-Aldrich and used as-received.



Scheme 1. Structure of CoPc.

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2.2 *Equipment*

UV–vis transmission spectra were obtained using the Perkin Elmer Lambda2 spectrometer. X-ray diffraction (XRD) data were taken by Philips Panalytical X-ray Diffractometer. Current–voltage measurements were held by Keithley Sourcemeter. Capacitance–voltage measurements were held by HP Impedance Analyzer. A hand-made system was used for spray pyrolysis deposition. Leybold electron beam system was used for metal deposition.

2.3 *Preparation of the device*

Commercially available glass/transparent conductive oxide (TCO) substrates first cleaned by methanol and then by ultrasonic bath. Clean substrates were washed by distilled water and dried in oven at 80°C. CdS films of thickness 500 nm were deposited on glass/TCO substrates by the spray-pyrolysis method at 400°C substrate temperature. Growing rate of the films was 100 nm min^{-1}. Fresh spraying solution was prepared by dissolving 0.025 M $CdCl_2$ and 0.025 M $(NH_2)_2CS$ in distilled water at 60°C. CoPc complex was synthesized as reported before.[15] Its concentrated solution was prepared in chloroform so that it can be used for thin film fabrication. The solution was spreaded out onto CdS film. Evaporation of chloroform was waited at room temperature. Then homogeneous CoPc thin film thickness of 1 μm was obtained. Ag was deposited onto CoPc as ohmic contact metal by electron beam vacuum evaporation under a pressure of 10^{-5} Torr. Finally, hybrid diode device was fabricated as glass/TCO/CdS/CoPc/Ag heterostructures.

Structural analysis of the CdS films was held by using XRD taken by XRD diffractometer. Conduction type of the CdS and CoPc films was determined by the hot probe technique. Resistivity measurements of the films and ohmic contacts were done by the two- and four-probe techniques. Absorption spectra of the films were obtained from optical transmission spectra and used for the energy bandgap calculations.[13]

3. Results and discussion

Hot probe technique was used in order to determine the conduction types of the deposited CdS and CoPc films. According to these measurements it was found that CdS film has n-type conductivity whereas CoPc film was p-type as expected.[6] Also, the resistivity of CdS film was measured as 10^2 Ω cm.

Figure 1 shows that CdS films were in wurtzite crystalline structure with the strong intensity for plane (101) at $2\theta° = 28°$.

Figures 2 and 3 show the absorption spectra of CdS film and CoPc film, respectively. Bandgap energy of CdS and absorption energy of CoPc were calculated as 2.47

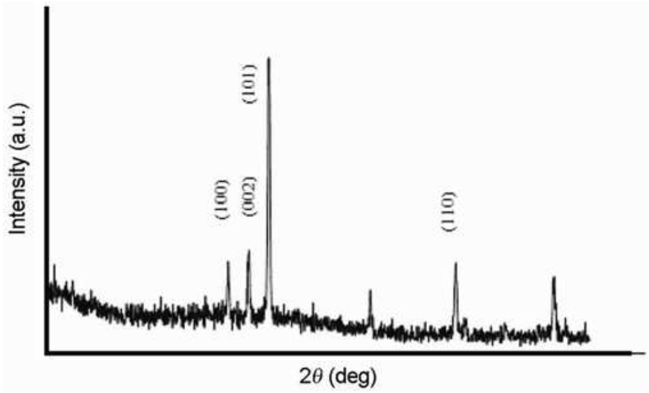

Figure 1. XRD pattern of CdS film.

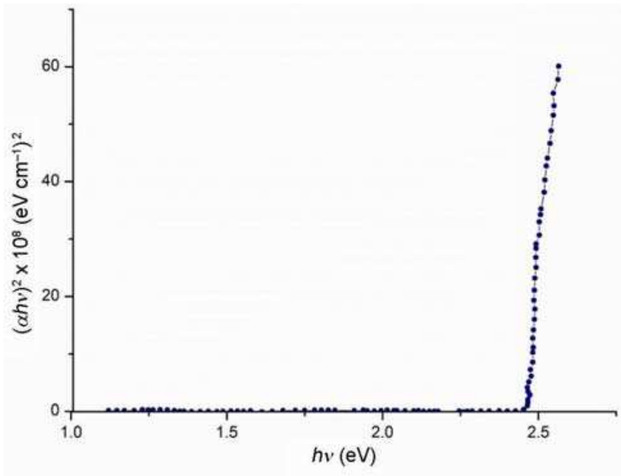

Figure 2. Absorption spectrum of CdS film.

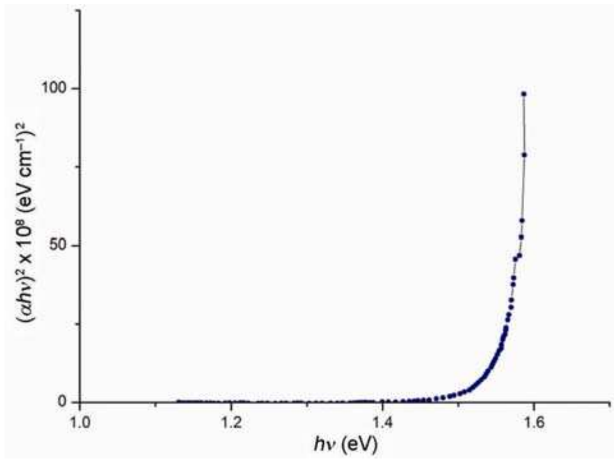

Figure 3. Absorption spectrum of CoPc film.

and 1.57 eV from equation (1)[13] using the absorption spectra, respectively

$$\alpha^2 (h\nu)^2 = B(h\nu - E_g), \quad (1)$$

where α is the absorption coefficient, h Planck's constant, ν the frequency, E_g the bandgap energy and B a constant.[13] Both CdS and CoPc have direct bandgap properties. Absorption energy of CoPc is good match for solar cell application in order to absorb broad solar spectrum.[6]

A metal ohmic contact needs to deposit onto the CoPc in order to conclude the fabrication of the diode device. Ag and Au are good ohmic contact metals, which prevent the Schottky barrier formation for p-type materials due to their high work functions. Hence, glass/Ag/CoPc/Ag and glass/Au/CoPc/Au sandwich structures were prepared under same conditions for choosing the convenient metal. These metals and CoPc layers were deposited as mentioned in experimental section. Current density–voltage (J–V) measurements of the structures are given in figure 4. Ag was chosen as it gives better ohmic contact property with CoPc.

Capacitance–voltage characteristics of the Ag/CoPc/CdS/ITO heterojunctions were measured at 1 MHz in dark (figure 5). This frequency is high enough to neglect the dielectric relaxation process in CoPc film,[2,3] so we can have information on the depletion region extended in the n-CdS side as calculated below. The built in voltage evaluated from figure 5 was $V_b = 0.48$ eV, which is in the limits of inorganic/MPc diode devices. This value and the typical diode characteristics, which can be seen from figure 5, support that the CoPc/CdS heterojunction works as a diode device.[1]

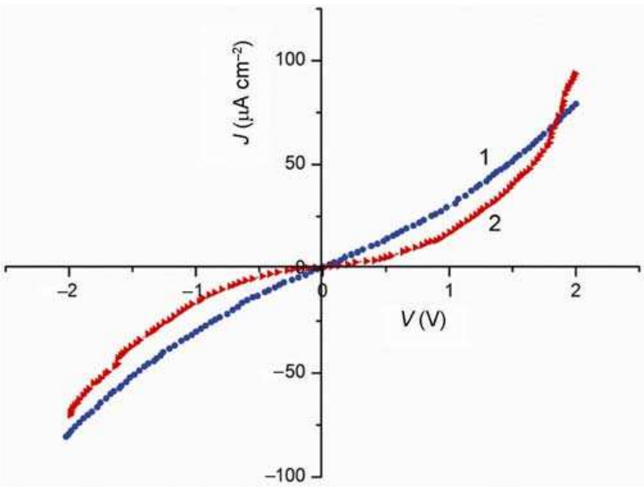

Figure 4. Current density–voltage characteristics of Ag/CoPc/Ag (1) and Au/CoPc/Au (2) structures.

Net carrier concentration is calculated using equation (2),[16] where V_b represents the built in voltage, C the capacitance of the junction measured at applied voltage V, k Boltzmann's constant and T the absolute temperature, e the electron charge, ε the dielectric constant, N the net carrier concentration and A the surface area of the junction

$$C^{-2} = \frac{2\left(V_b - V - \frac{kT}{e}\right)}{e\varepsilon NA^2}. \quad (2)$$

Net carrier concentration for CdS side of the junction was calculated as 4.9×10^{15} cm^{-3}. This value was typical for n-CdS semiconductor.[14]

Figure 6 shows the current density–voltage characteristic of the diode device measured in dark and at room temperature. From these data, rectification ratio was calculated as 4.5 for 2.5 V, which is appreciable for rectifying purpose. Ideality factor which is important to characterize diodes is calculated using[16]

$$n = \frac{e}{2.3kT}\frac{\partial V}{\partial \log(I)}. \quad (3)$$

In equation (3), n is the ideality factor, e the electron charge, k Boltzmann's constant and T the absolute temperature, while V and I are voltage and current, respectively. It is found that ideality factor of the CoPc/CdS diode

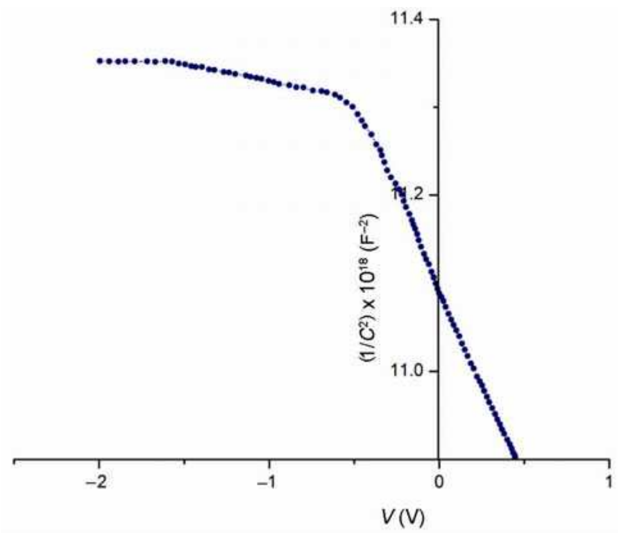

Figure 5. Variation if $1/C^2$ *vs.* V for CoPc/CdS diode.

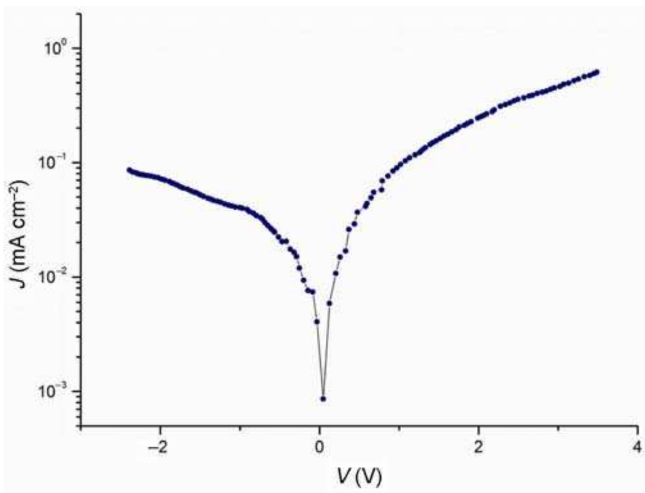

Figure 6. Current density–voltage characteristics of CoPc/CdS diode.

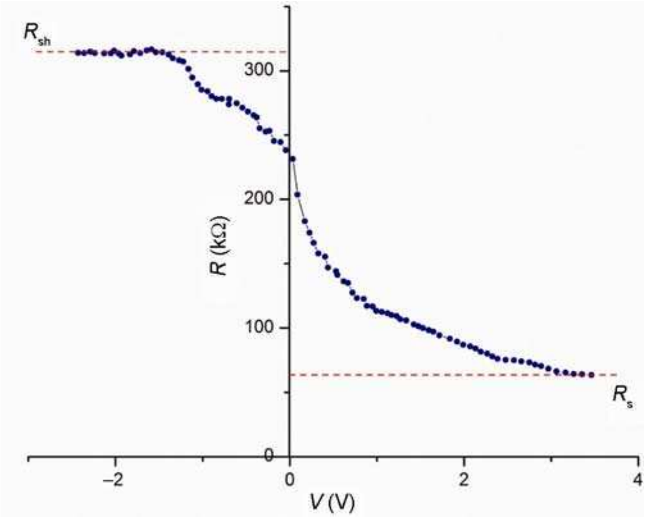

Figure 7. Junction resistance *vs*. applied voltage.

was $n = 4.8$. This result is consistent with the results mentioned above.

The series (R_s) and shunt resistances (R_{sh}) are very important parameters for many electronic devices.[17] Resistances voltage dependence of the junction resistance is given in figure 7. Series resistance of $R_s = 68$ kΩ and the shunt resistance of $R_{sh} = 315$ kΩ for the junction were calculated at room temperature using the method mentioned by Soliman *et al.*[1] These values are acceptable values for a heterojunction diode.

4. Conclusion

CoPc/CdS hybrid diode device was fabricated successfully by different, easy and cost-effective deposition methods. Spray pyrolysis, chemical precipitation and electron beam evaporation were used, respectively, for deposition of CdS and CoPc thin film layers and for Ag ohmic contact. Junction showed rectifying behaviour with the ideality factor of 4.8. Rectification ratio of the diode calculated for 2.5 V was 4.5, which is in the range of a rectifying electronic diode device. Capacitance–voltage characteristics also show that the junction works as a diode and built-in voltage calculated as $V_b = 4.8$ V. Therefore, there is no match problem with wurtzite crystalline structure of CdS film and CoPc film. Series resistance of $R_s = 68$ kΩ and shunt resistance of $R_{sh} = 315$ kΩ calculated were convenient values for a heterojunction diode. Good absorption property of CoPc is shown by plotting the absorption spectra. Absorption energy of CoPc is calculated as 1.57 eV, which is very convenient to absorb broad spectrum of sun. This value is very close to energy bandgap of inorganic absorbers, such as GaAs with E_g of 1.45 eV and CdTe with E_g of 1.5 eV used for efficient solar cells.[18] These values encourage the use of CoPc/CdS diodes also for organic-based hybrid solar cell applications.

Acknowledgement

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