

Characterization of Cu / PAr / CdS MIS structure for sensor applications

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In this study, electrical characterization of the Cu/PAr/CdS MIS structures were made for sensor application. The main electrical parameters of MIS structure such as the ideality factor (n), barrier height (Φ_B), series resistances (R_s) and interface state density (N_{ss}) were determined at various environments. The series resistance of structures was found 696 Ω and 818 Ω respectively at atmosphere and chloroform environments. It is observed the structure is suitable for sensor applications. Examination of gas sensing property of diode, I-V measurements were done in chloroform atmosphere and constant voltage measurements were done at different gas atmosphere. With the exposure of chloroform, the resistance of diode increases and with discontinuation of gas flow, diode was reverted back to its initial. Therefore, it was understood that the diode was suitable for the sensor applications.

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1. Introduction

The sensors have been known as such devices which provide information on environment by monitoring gas, humidity, contaminants, etc. They have been fabricated by using inorganic and organic materials. In the last decade, as the polymers have been understood to have comparable advantage to inorganic types they are considered much attractive materials in the sensor technology field on account of their high selectivity, high sensitivity and short response time, thus room temperature operation ensurance, [1-3] for detection of most of the different gases and vapors. Polymers are known (i) low cost materials, (ii) can be used to make device by the various fabrication techniques such as electrochemical deposition, dip-coating, spin-coating, Langmuir-Blodgett (LB), Layer-by-layer (LBL) self-assembly, thermal evaporation, vapor deposition polymerization, drop-coating etc., (iii) various types of substrates can be used to deposition on it, (iv) can be chemically or electro-chemically synthesized as easy way (v) their molecular chain structure can be modified to obtain a variety of them (vi) they can be deposited as thin films and (vii) their electrical properties can be changed by doping remarkably, all of these which enable us to make sensing devices.

Polymer films can be used to make sensing devices such as capacitance sensor, temperature, pressure sensors, chemical sensor, gas sensor, relative humidity, biosensors, etc. [4-16]. As the interaction with the polymers and gaseous molecules can cause changes on their electrical characteristics, they have been found to be good candidate for fabrication of the devices to use in sensor applications [17-23].

Schottky diode devices have been fabricated based on polymers. As they provide more information about various parameters and therefore more detailed information of the polymer behavior as sensing layer, characterization of junction parameters of Schottky MIS diodes are of prime importance for their technological applications such as field effect transistors, diodes and sensors. For this reason, the characterization of ideality factor, barrier height, interface states and series resistance in Schottky diode structure has become a very intensive research subject [24-28].

In this paper, PAr was used as organic layer and Cu/PAr/CdS MIS structure was fabricated for sensor applications. The responses of Cu/PAr/CdS MIS structure to chloroform atmosphere and different gas atmosphere are presented and discussed.

2. Experimental

Cu/PAr/CdS (MIS) diodes were fabricated on the ITO coated glass substrates with a dimension and resistivity, 10 mm - 15 mm and 2.10^{-4} Ω .cm, respectively. The n-type semiconductor CdS was produced with spray pyrolysis (SP) method. Crystal has (101) H orientation and 2.11 μ m film thickness. Before the SP procedure, ITO substrates were degreased with ultrasonic bath in distilled water and ethanol solution. The degreasing procedure was performed 20 min. at 80°C temperature. Thereafter substrates were rinsed in distilled water and after that cleaning procedure towed in N_2 atmosphere. 0.02 M $CdCl_2$ and 0.02 M $CS(NH_2)_2$ solution was prepared in 400 ml distilled water for the deposition of CdS layer with spray pyrolysis technique. The solution was stored 1 day for precipitation

of impurities. The prepared solution was sprayed on the ITO substrates at 400°C. Whereafter the n type semiconductor film deposition process, film was polished with 5 µm diamond paste and polyarylate (PAr) film coated on as insulator layer with drop-casting method. Thickness of polyarylate film was found as 190 nm.

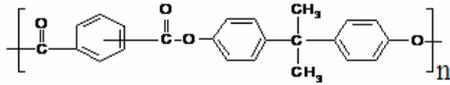


Fig. 1. Chemical structure of polyarylate.

Cu metal was evaporated by e-beam technique with a thickness of 100 nm and a radius of 1.5mm at a deposition rate of 2.5 A/s, as the top ohmic contact. All evaporation process was carried out in 10^{-5} Torr vacuum atmosphere using suitable masking.

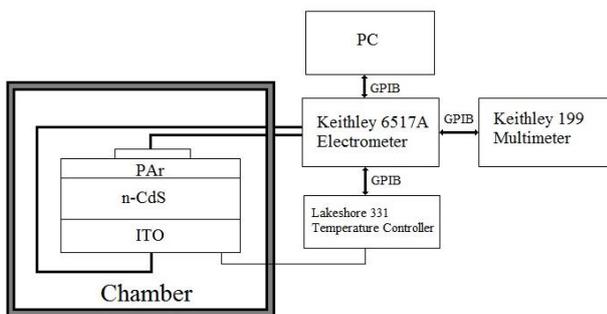


Fig. 2. Measurement setup used.

The electrical measurements of Cu/PAr/CdS (MIS) diodes were carried out in chloroform and atmosphere environment affirmingly. A Programmable Keithley 6517A electrometer / voltage source, a Keithley 119 multimeter and a Lakeshore Temperature Controller 331 were used as the measurement set-up by connecting to the computer interface by GPIB (Fig. 2).

3. Results and discussion

CdS crystal orientation was appointed from the XRD pattern which performed by using GCA-MMA X-Ray diffractometer (Fig. 3). Lattice spacing (d_{lat}) and lattice constants parameters were determined from this patterns for CdS crystal.

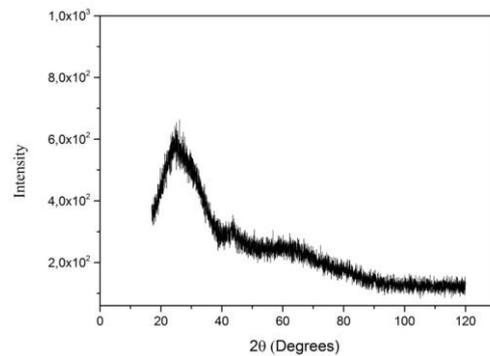
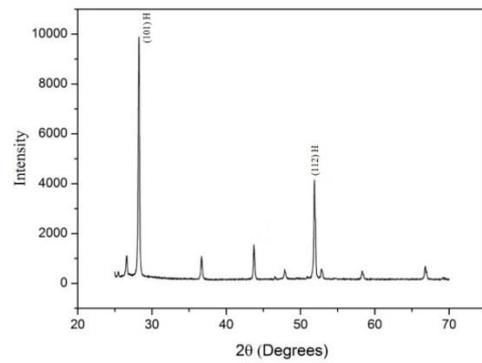


Fig. 3. XRD pattern of a) CdS and b) Polyarylate.

The grain size values (D) were calculated using Debye-Scherer formula.

$$D = 0.94 \cdot \lambda / B \cdot \cos\theta \quad (1)$$

where λ is the wavelength of the X-ray and B is the width of the half of the X-ray diffraction pattern maximum.

For the PAr films, crystalline structure has been observed but could not be identified in 10° - 120° range. Similar structural parameters have been reported for CdS crystal [29-32].

Table 1. Structural parameters of n type CdS film.

2θ (Degree)	(hkl)	d_{lat} (Å)	Grain Size (nm)
28.26	(101)	3.16	42.85
51.86	(112)	1.79	46.58

The changes on the Cu/PAr/CdS MIS diodes characteristics were investigated due to the chloroform (CHCl_3) gas, under constant voltage and temperature conditions. Fig. 4 shows the current - voltage (I-V) characteristics of CdS at room temperature under atmosphere and chloroform gas environment, using copper electrodes. As seen in Fig. 4, characteristics are symmetric and ohmic, but the current increases due to the exposure to chloroform gas.

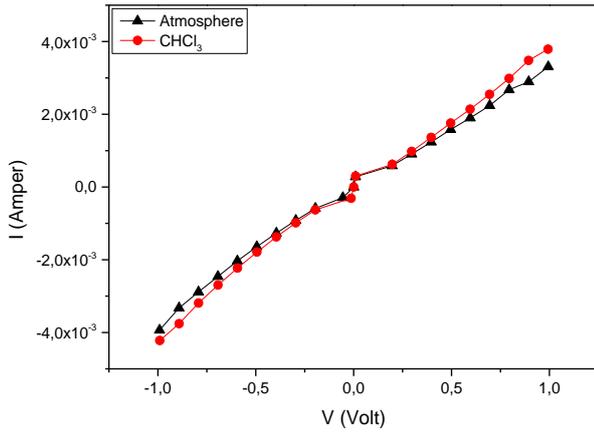


Fig. 4. I-V plot of Cu/CdS junction on chloroform and atmosphere environment.

Similarly, the current-voltage characteristic of the polyarylate (PAr) under the chloroform environment are also given in Fig. 5. The figure shows the positive current - voltage range and current axis of the graph is given on a logarithmic scale. From the inner graphics, the structure used for the measurement can be said that shows the ohmic behavior.

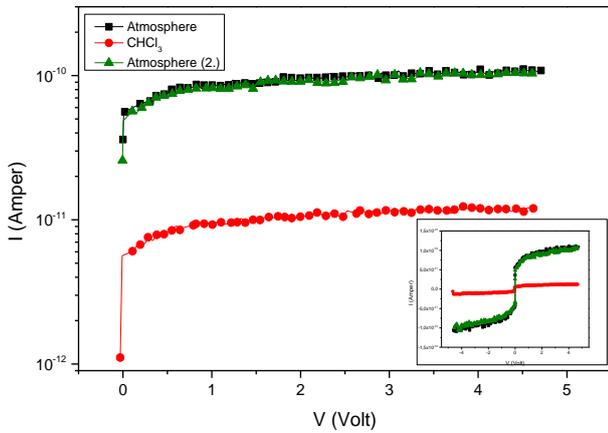


Fig. 5. Current vs. applied voltage plot of Cu/PAr at chloroform and atmosphere environment.

The majority of the microelectronic device working principle of metal-semiconductor contacts depends on the physical characteristics of them. In the junction region of such contacts, the potential barrier occurs. Formation of the potential barriers depends on re-dispersion of the concentration of charge carriers at the metal-semiconductor. The current and the capacitance values of the contacts vary with the value and direction of the externally applied voltage. Nonlinear characteristics of semiconductor contacts are used for rectification, conversion and amplification of electrical current or the generation of electrical signals. From this type of joint rectifier, diodes and transistors are made. The transfers of

electrons from metal to semiconductor is controlled by potential barrier height, the difference in contact potential and the energy of the Fermi level. When a reverse bias is applied to semiconductor side, because the contact resistance is to be too large from the resistance of the circuit, the applied voltage is distributed on the contact of the side semiconductor. In this case, the energy levels in the semiconductor band slide down by a few eV. Under the effect of externally applied negative voltage, the potential barrier height is increased, the thickness of the space charge region increases. When a forward bias is applied to metal / semiconductor contacts, all energy levels at the semiconductor moves up. Thus the height of the potential barrier is reduced, the thickness of the space charge region is decreased and the electron current increases.

The interface states at the insulator-semiconductor arising from unsaturated bonds or impurities and while the occurring the presence of moving the ions, traps and interfacial charges depending on the method during growth of the insulating layer, modify the properties of the MIS structure, so that deviations from the ideal characteristics of the MIS structure causes.

According to the standard thermionic emission theory, current usually is controlled by the transfer of carriers through the contact interface for rectifying J-V behavior of Schottky barrier devices, [33]. For the electrical characterization of a Schottky diode with an interfacial insulator layer and series resistance, the most important parameters of the structure, such as barrier height (ϕ_B), ideality factor (n) and series resistance (R_s) are determined. To determine the diode parameters of the Schottky structure, I-V characteristics were used with Thermionic Emission and Cheung functions as given respectively [33, 34]:

$$J = A^*T^2 \exp(q(V - IR_s)/nkT) \cdot \exp(-q\phi_B/kT) \quad (2)$$

where J is the current density, q is the electronic charge, V is the applied forward-bias voltage, n is the ideality factor, A^* is the effective Richardson constant and equals to $25 \text{ A cm}^{-2}\text{K}^2$ for CdS and ϕ_B is the effective barrier height at zero bias.

$$H(J) = V - \frac{n}{\beta} \ln(J/A^*T^2) \quad (3)$$

where $\beta = q/kT$ for Cheung functions.

Using these current - voltage (I-V) characteristics, we calculate the ideality factor, series resistances and barrier heights in both cases. According to the Thermionic Emission Theory, the ideality factor and series resistance were found to be 3.46 and $696.53 \text{ } \Omega$ respectively for atmosphere environment. This ideality factor indicate the deviation from ideality to be attributed the presence of an interfacial layer having the high interface state density (N_{ss}) in it and high series resistance. Under the same conditions, barrier height and series resistance were obtained as 0.56 eV and $672.74 \text{ } \Omega$ by using Cheung functions. The series resistance values are consistent with

each other which were obtained by TE and Cheung functions. The changes in the barrier heights observed are consistent with the change in the $J-V$ curves.

The current - voltage ($I-V$) measurements of Cu/PAr/CdS structure were realized as shown in Fig. 6, where the characteristics imply an asymmetric, non-ohmic rectifying behavior. As we can see from figure, the forward and reverse-bias currents of Cu/PAr/CdS MIS diode decrease due to exposure to chloroform CHCl_3 . With the exposure to chloroform gas for the diode structure, it has been seen that their electrical characteristics were changed, therefore it can be said this structure can be used as gas sensor.

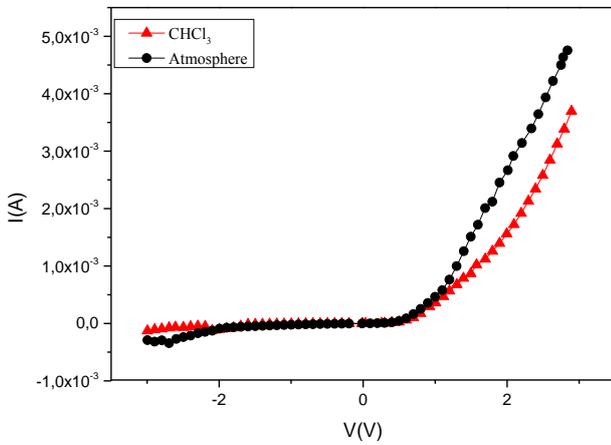


Fig. 6. Current-voltage characteristics of Cu/PAr/CdS MIS diode in chloroform and atmosphere environment.

The changes of MIS diode parameters with the chloroform, CHCl_3 environment effects are shown Table 2. As the presence of chloroform at environment, the diode series resistance value is increased remarkably. And also, it was seen the barrier height does not change due to the presence of chloroform.

Table 2. Electrical parameters of MIS diode due to the environment.

Environment	$dV/d\ln(J) - J$		$H(J) - J$	
	n	R_s	Φ_B	R_s
Atmosphere	3,467	696,532	0,562	672,746
CHCl_3	3,869	818,268	0,562	743,821

The interface state profile of diodes is known as significant factor for their performance and characteristic parameters. By using the forward bias region of current – voltage characteristics, interface states density (N_{ss}) distribution was procured for both environments.

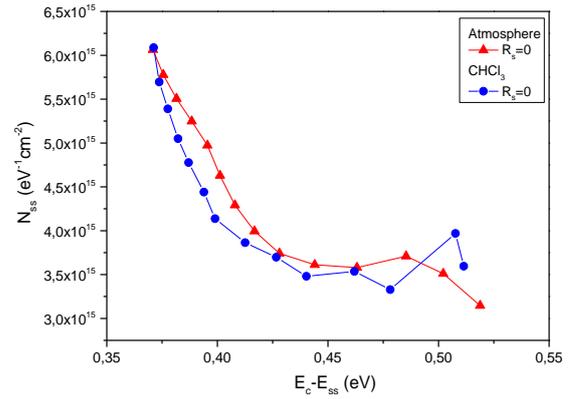


Fig. 7. Interface states density distribution of MIS sensor both at atmosphere and chloroform environment.

The distribution graphs were calculated for without R_s conditions. As can be seen in the Fig. 7, there were a slight difference between two curves which were measured under the environment with and without chloroform gas. Effect of diffusion of chloroform gases in to structure especially in to the PAr polymer interlayer reduces the density of states. The magnitude of the N_{ss} without the R_s has changed from 3×10^{15} to $6 \times 10^{15} \text{ eV}^{-1} \text{ cm}^{-2}$ at $E_c - 0.37(\text{eV})$ for the structure, respectively. The energy values of the density distribution of the interface states of the Schottky diode is in the range of $E_c - 0.37$ and $E_c - 0.54 \text{ eV}$.

To investigate the repeatability of MIS sensor, we measured resistance change of the structure by applying the chloroform gases periodically at a constant voltage (Fig. 8). 1V steady voltage applied to structure and chloroform gas inserted to chamber for 500 seconds period then disconnected, repeatedly. The resistance of the diode increases by gas flow started and after that during the discontinuation of chloroform gas, the resistance of MIS diode was reverted back to its initial state.

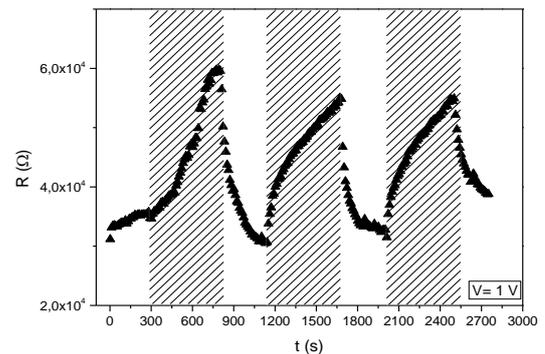


Fig. 8. Resistance vs time, $R-t$, measurement graph.

4. Conclusions

In this study, Cu/PAr/CdS Schottky barrier MIS diodes have been fabricated by depositing spray pyrolysed of CdS onto an ITO substrate and gas-sensitive characteristics of the diodes were observed for different environment. The examination of gas sensing property of

the Schottky diodes, I-V measurements were done in chloroform atmosphere and constant voltage measurements were done at different gas atmosphere. We observed that the Cu/PAr/CdS diode has an unsymmetric, non-ohmic rectifying characteristics. As a characteristic rectifying interfaces behaviour property, the exponential increase of the forward bias current and a weak voltage dependence of the reverse bias current were observed. The nonideal forward bias J-V behaviour and the higher ideality factor attributed to the series resistance, observed in the structure is attributed to a change in the barrier height due to the interface states, the interfacial insulator layer and series resistance. The values of ideality factor and series resistance have been calculated as 3,467; 696,532 Ω and 3,869; 818,268 Ω and the barrier height and series resistance have been determined as 0,562eV for both environments and 672,746 Ω and 743,821 Ω under the chloroform, CHCl₃ and atmosphere according to Thermionic Emission Theory and Cheung functions, respectively

The detection of chloroform for MIS diode was examined under the constant voltage and the forward and reverse-bias current were found to be decreased with the voltage and series resistance of the diode was increased by exposure to chloroform. As a result of exposure to chloroform for PAr film, the reason can be attributed to the realization of a lower levels of charge transfer with the increasing of the distance between molecules and the changes of bond length of PAr. From the current- voltage, I-V graphs, the PAr is understood to be active film layer and of Cu/PAr/CdS diode show the sensor feature.

To determine the sensing behaviour of the diode, the resistance measurements depending on the time were realized under the chloroform atmosphere. With the exposure to chloroform, the resistance of diode were observed to be increased and with discontinuation of gas flow, diode was reverted back to its initial, periodically.

In summary, in the present study, the prepared Cu/PAr/CdS Schottky diodes have been concluded to be suitable for the sensor applications.

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