Electrical Properties of Metal/Langmuir–Blodgett Layer/Semiconductive Devices

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SYNOPSIS

Metal–insulator–semiconductor (MIS) structures were fabricated by vacuum deposition of various metals like indium, aluminum, and tin on Langmuir–Blodgett (LB) films of cadmium stearate ($CdSt_2$) obtained on polypyrrole (PPY) films electrochemically deposited on indium–tin–oxide glass. Junction parameters such as rectification ratio, barrier height, and work function of such devices were experimentally determined. Passivation of semiconducting polypyrrole film is seen to result in a lower value of the ideality factor. For example, measured ideality factors of $CdSt_2$ LB layer/semiconducting PPY structures are 6.63, 6.57, and 6.54 for various metals like Sn, Al, and In, respectively, in comparison to the values of 8.85, 8.82, and 8.20 obtained with semiconducting PPY interface with same elements. The value of the dielectric constant of the insulating $CdSt_2$ LB film was calculated as 1.84 and this is in reasonable agreement with the value (2.13) reported earlier. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The Langmuir–Blodgett (LB) technique is an excellent method for deposition of ultrathin uniform insulating layers comprising fatty acids and polymeric materials with a controllable thickness for fabrication of metal–insulator–semiconductor (MIS) devices.[1-5] Many investigations pertaining to the metal–LB layer-semiconductor (MLS) configuration based on silicon, amorphous silicon, and compound semiconductors have been conducted.[6,7] An MLS capacitor is a convenient device for the characterization of an insulating layer and the semiconductor–insulator interface.[8]

Conducting polymers like polypyrrole (PPY), polythiophene, and polyaniline are beginning to be used for fabricating semiconducting devices.[9-19] Schottky devices based on electrochemically deposited PPY and the desired metal (Ag, Sn, Al, and In) have been shown to exhibit interesting electrical characteristics. For such devices, the value of the ideality factor (also referred to as the diode quality factor) has been reported to vary from 10.11 to 10.67.[18] The presence of an artificial barrier layer usually causes the ideality factor to exceed unity, resulting in the observed currents to be lower than otherwise expected at lower forward voltages. The passivation of semiconducting PPY film with an insulating layer has been shown to result in the improvement of the junction characteristics of such a device.[12] The use of an LB film as a gate dielectric for the fabrication of MLS devices has been reported.[20] In this article, we report the results of our systematic studies performed on silver–cadmium stearate ($CdSt_2$) LB layer–PPY, tin–($CdSt_2$) LB layer–PPY, aluminum–($CdSt_2$) LB layer–PPY, and indium–($CdSt_2$) LB layer–PPY devices.

EXPERIMENTAL

PPY films (thickness ~ 2.5 μm) have been electrochemically prepared on indium-tin-oxide (ITO) glass (sheet resistance, 15–20 Ω/cm) using a cell containing deionized water, pyrrole ($0.1M$), and p-toluene sulfonate ($0.1M$). These films are rinsed several times with deionized water.[18,19] The electrical

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Journal of Applied Polymer Science, Vol. 60, 407–411 (1996)
CCC 0021-8995/96/030407-05

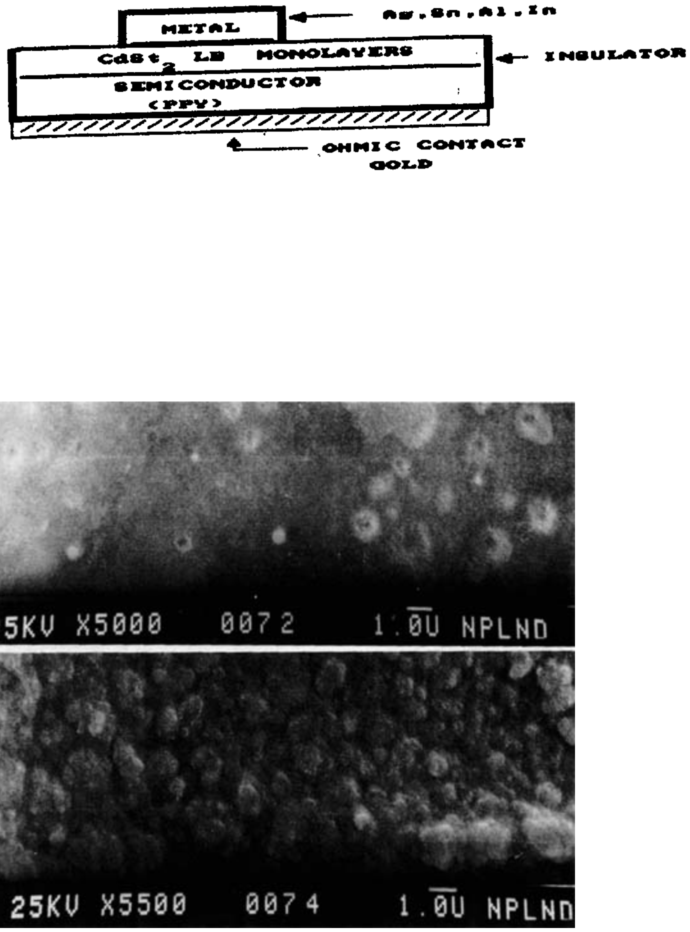

Figure 1 (a) Schematic of cross section (not to scale) of a metal (0.5 μm-thick)-insulator ($CdSt_2$ LB layer, 2.7–81 nm thick)-semiconducting PPY (2.5 μm thick) device. (b) SEM pictures of (top) 9 and (bottom) 20 $CdSt_2$ LB monolayers on polypyrrole surface.

conductivity of annealed (70°C) PPY films measured using the four-points-probe method was 30 S/cm. Stearic acid (10–20 μg) dissolved in chloroform is dropped onto the surface of water (pH 5.6) contained in a trough (Joyce Loebl Model 4). The $CdSt_2$ monolayers formed at the air–water interface at a surface pressure of 25 mN/m and at a barrier compression speed of 0.3 cm^2/mol/min were transferred to annealed PPY films deposited on ITO glass inserted/withdrawn at a rate of 1 mm/min. The surface morphology of such $CdSt_2$ LB films (thickness of one monolayer was 2.7 nm [Ref. 20]) was investigated using a scanning electron microscope (Model JSM 35 CF). UV-visible spectra of $CdSt_2$ monolayers were recorded on a spectrophotometer (Shimadzu Model 160 A).

MIS structures were fabricated by thermally evaporating pure (99.99%) metals (Ag, Sn, Al, and In) of about 0.5 μm thickness on $CdSt_2$ LB film/PPY structures using a vacuum evaporator (10^{-6} Torr). The effective junction area in each case is about 10^{-3} cm^2. Gold contacts were made after carefully removing various metal/$CdSt_2$ LB layer/PPY structures from the respective ITO glasses. A schematic showing a cross section of such an MLS device is given in Figure 1(a). Current (I)-voltage (V) measurements of various MLS devices were conducted using a Keithley electrometer (Model 610). Capacitance (C)-voltage (V) measurements on In/$CdSt_2$ LB layer/PPY devices were carried out using an impedance analyzer (HP 4192-A).

RESULTS AND DISCUSSION

SEM pictures [Fig. 1(b)] of $CdSt_2$ LB films (9 and 20 monolayers) deposited on annealed PPY films indicate the absence of any pinholes. Nearly pinhole-

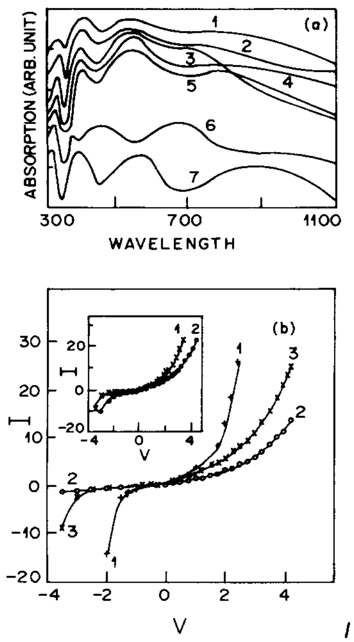

Figure 2 (a) UV-visible spectra of $CdSt_2$ LB films on polypyrrole/surface. Curves 1–7 are, respectively, for 30, 20, 15, 10, 8, 6, and 4 monolayers. (b) I (mA)–V (volts) characteristics of metal/10 $CdSt_2$ LB monolayers/PPY devices. Curves 1–3 are for Ag, Sn, and Al, respectively. Inset shows the I–V plot for In/10 $CdSt_2$ LB monolayers/PPY (curve 1) and unannealed (curve 2) In/15 $CdSt_2$ LB monolayers/PPY (curve 1) and In/PPY devices (curve 2).

free layers are appropriate for fabrication of the MLS devices.[21] The results of UV-visible studies [Fig. 2(a)] carried out in the reflection mode show that the magnitude of absorption increases with increase in the number of monolayers, indicating the uniform nature of the $CdSt_2$ LB films. Such $CdSt_2$ LB layer/PPY structures were used for the fabrication of the desired MLS devices.

Figure 2(b) shows the results of I–V measurements performed on silver/10 $CdSt_2$ LB monolayers/PPY (curve 1), tin/10 $CdSt_2$ LB monolayers/PPY (curve 2), and aluminum/10 $CdSt_2$ LB monolayers/PPY (curve 3) devices, respectively. The inset in Figure 2(b) exhibits the I–V data obtained both for indium/10 $CdSt_2$ LB monolayers/PPY (curve 1) and indium/PPY (curve 2) devices. The I–V characteristics are similar to those reported for metal/PPY junctions.[18] The values of the junction parameters shown in Table I for various MLS devices were calculated using the following Schottky equation[12]:

$$J = J_0 \exp(qV/nkT) \tag{1}$$

where j_0 is the saturation current density that can be obtained from eq. (2):

$$J_0 = A^{**}T^2 \exp(-qx_b/kT) \tag{2}$$

where A^{**} is the Richardson constant (1.2×10^{-6} $Am^{-2}T^{-2}$); n, the ideality factor; x_b, the barrier height; T, the temperature; and K_B, the Boltzmann constant. Values of the rectification ratio obtained for each of the devices were measured at 2 V.

The values of the rectification ratio, barrier height, and ideality factor determined as 2, 0.406, and 7.729, respectively, for the silver/10 $CdSt_2$ LB monolayers/PPY device point to its non-ohmic behavior resulting from application of the $CdSt_2$ LB monolayers.

A decrease in the value (6.63) of the ideality factor determined for the tin/10 $CdSt_2$ LB monolayers/PPY device over a value (8.85) for the tin/PPY device once again demonstrates the role played by the $CdSt_2$ LB monolayers. However, the observed lower value (5.0) of the rectification ratio limits its application as a Schottky diode.

The values of the rectification ratios for aluminum/10 $CdSt_2$ LB monolayers/PPY devices were determined as 10 and 8, respectively. Moreover, the lower values of the ideality factors coupled with the

Table I Junctions Parameters Such as Barrier Height (X_b) and Ideality Factor (n) of Various Metal (Ag, Sn, Al, In)/$CdSt_2$ LB Monolayers/PPY and Metal (Ag, Sn, Al, In)/PPY Structures

Metal	Method	Barrier Height (x_b) Without LB Film (eV)	Barrier Height (x_b) With LB Film (eV)	Ideality Factor, n, Without LB Film	Ideality Factor, n, With LB Film	Work Function ϕ[a] (eV)
Ag	I-V	—	0.406 ± 0.001	—	7.729	4.74
Sn	I-V	0.37 ± 0.001	0.381 ± 0.001	8.85	6.43	4.42
Al	I-V	0.39 ± 0.001	0.398 ± 0.001	8.82	6.57	4.28
In	I-V	0.39 ± 0.001	0.393 ± 0.001	8.0	6.63	4.12

[a] ϕ is the work function of the annealed PPY film.

higher values of the barrier heights found for both these MLS devices clearly indicate that these can be used as excellent Schottky diodes. Short-term stability of the aluminum/10 $CdSt_2$ LB monolayers/PPY device compared to that of indium/10 $CdSt_2$ LB monolayers/PPY was attributed to the oxidation of aluminum in air.

Figure 3 shows the results of the C-V data undertaken on the indium 15 $CdSt_2$ LB monolayers/PPY device obtained at 10 kHz, 100 kHz, and 1 MHz, respectively. It can be seen that the interface comprising the semiconducting PPY and cadmium stearate LB layer undergoes a transition from accumulation to depletion as the voltage is swept (20 mV/s) from negative to positive values. The inset in Figure 3 exhibits the results of similar measurements performed on such annealed (50°C) and unannealed devices. The decrease in the magnitude of hysteresis (originating due to the presence of Cd^{2+} ions in the $CdSt_2$ LB film and *p*-toluene sulfonate in semiconducting polypyrrole) in Figure 3 can be understood to arise from annealing of this device, resulting in a reduced trap density at the semiconducting PPY/$CdSt_2$ LB monolayers' interface.

Figure 4(a) is the 1 MHz C-V plot of such a device containing 9 and 15 $CdSt_2$ LB monolayers, respectively. These results demonstrate that the decrease in the number of $CdSt_2$ LB monolayers results in the higher value of the capacitance, which is likely to lead to the improved functioning of the MLS device.

Figure 4(b) shows the variation of the capacitance of the indium/$CdSt_2$ monolayers/PPY device with increase in the number of $CdSt_2$ LB monolayers. The decrease in the value of capacitance with the increase in the number of $CdSt_2$ LB monolayers can be attributed to the variation in the dielectric characteristics of $CdSt_2$ that have been shown to be a function of its thickness.[11] The effective dielectric constant of cadmium stearate LB film was estimated by plotting the reciprocal film capacitance with the number of LB monolayers. From the results shown in Figure 4(a) and employing the relationship

$$C = C_s C_0 A/w \tag{3}$$

where w is the thickness of the material; A, the area; C_0, the space charge permittivity, the value of the effective dielectric constant, C_s, of cadmium stearate (gate dielectric) was estimated at 1.84. This is in reasonable agreement with the reported value (2.13).[5]

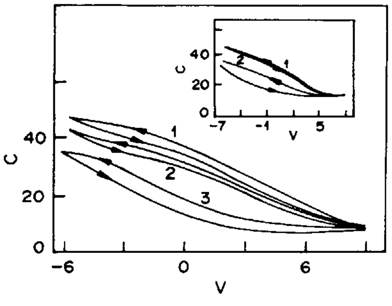

Figure 3 (a) C(pF)-V (volts) plot for In/15 $CdSt_2$ LB monolayers/PPY device obtained at 10 kHz (curve 1), 100 kHz (curve 2), and 1 MHz (curve 3). Inset shows 1 MHz C (pF)-V (volts) plot for annealed (50°C, curve 1) and unannealed (curve 2) In/15 $CdSt_2$ LB monolayers/PPY devices.

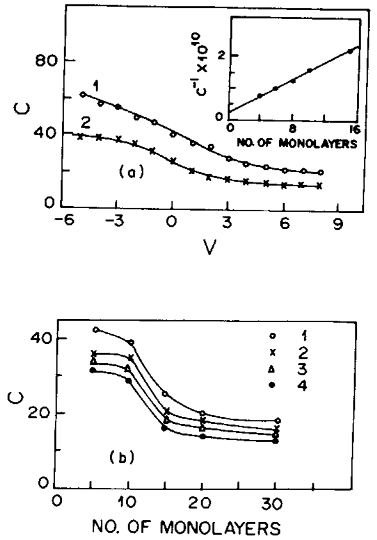

Figure 4 (a) C (pF)-V (volts) plot for In/10 $CdSt_2$ LB monolayers PPY device (curve 1) and In/10 $CdSt_2$ LB monolayers/PPY device (curve 2). Inset shows variation of 1/C(pF) as a function of the number of the $CdSt_2$ LB monolayers for the In/$CdSt_2$ LB monolayers/PPY device. (b) Variation of C (pF) as a function of the number of $CdSt_2$ LB monolayers for the In/$CdSt_2$ LB layer/PPY device.

CONCLUSIONS

In summary, we have shown that MLS devices can be fabricated by thermal evaporation of metal (Ag/Sn/Al/In) onto $CdSt_2$ LB films deposited on electrochemically prepared PPY films. It has been shown that the use of the low-temperature Langmuir–Blodgett film deposition technique compared to the other methods of MIS preparation (which invariably cause the damage of surface layer) results in the improved junction parameters. However, the values of ideality factors are higher than those based on inorganic semiconductors (Si/GaAs). The value of the work function of the annealed PPY film has been estimated to lie in the range of 4.12 to 4.74 eV. Annealing of indium/$CdSt_2$ LB monolayers/PPY devices has been shown to result in the reduced trap density of the semiconducting PPY/$CdSt_2$ LB film interface. It should now be interesting to conduct studies in relation to applications of these MLS devices to electroluminescent displays and photovoltaic and photonic devices.

The authors are grateful to Professor E. S. R. Gopal, Director, NPL, New Delhi, for constant encouragement and his interest in this work. We are thankful to Dr. Subhas Chandra for his interest during the course of this work. Thanks are also due to Dr. N. S. Sundaresan and Dr. B. C. Chakravarti for their suggestions during the preparation of the revised manuscript. Financial assistance from the Commission of the European Community (Contact No. CII-CT92-0102) is gratefully acknowledged.

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Received July 10, 1995
Accepted November 3, 1995