OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 6, No. 11-12, Nov. – Dec. 2012, p. 1164 - 1167

Stabilized Langmuir layers based on silver stearate, carbon nanotubes and porphyrins additives for UV-sensor applications

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Langmuir films based on silver stearate, carbon nanotubes and porphirins have been prepared on the water surface of the Langmuir trough. By several compression-extension cycles the films were stabilized. The multilayer thin films were deposited on special ceramic body provided with platinum comb configured electrodes. The measurements of the electrical resistance of the deposited thin films, at illumination in UV light, showed a strong effect of UV light on the electrical resistivity of the material. This effect suggests a potential application of these thin films in UV sensors.

(Received October 20, 2012; accepted October 30, 2012)

Keywords: Barrium stearate, UV sensor, Ageing

1. Introduction

Special properties of Langmuir films based on fatty acid have been observed since the preparation in 1935 by Katherine-Blodgett at General Motors (USA) of the first controlled layers and supported multilayers [1]. Films of different composition have been prepared and a special phase transition in stearic acid was identified as a consequence of ultra-sonication [2]. Recently, we reported the preparation of Langmuir-Blodgett films bassed on barium stearate and carbon nanotubes [3].

In this paper are presented the results obtained during the study of stable Langmuir films based on a new composition (silver stearate, carbon nanotubes and porphyrins). We have used silver stearate because the molecule has one valence and we wanted to investigate the diference form barium stearate valence two. The Langmuir thin films were subjected to several compression-expansion cycles to find the experimental conditions leading to a stable structure. After preparation of LB thin films, their electrical resistance at illumination in UV range was measured, in order to investigate the effect of ultraviolet rays on multilayer films based on this new composition. Particulary, the sensibility of a sensor prepared with the multilayer films deposited on a ceramic body as substrate, has been measured.

2. Experimental

The Langmuir and Langmuir-Blodgtett films were prepared in a KSV 5003 apparatus. The system is provided with double trough, fully controlled by computer. The compression curves have been measured for both types of films (Cu(II)- porphyrin and Ni(II)- porphyrin. The measurements were carried out in several runs. Compression up to deposition surface tension was followed by decompression and after reaching the initial point a new compression was started followed by relaxation and a final compresion. The compression and decompression was achieved by moving the teflon barrier on the water surface with a speed of 7.5 mm per minute. The similarity in the behaviour of the Langmuir layers with Cu(II)- porphyrin and that with Ni(II)- porphyrin nanotubes consists in the pronounced irreversible effect of hysteresis.

The formation of the films was followed by the registration of the π-A curves. Deposition of the multilayer samples (5 monolayers) were made on the glass slide and on the ceramic body provided with platinum electrods in a comb configuration. The rate of deposition was 1 mm/min. The deposition surface pressure was of 25 N/m. Various parameters that govern the formation of Langmuir films have been monitored: pH of the water, temperature during deposition, atmosheric pressure and humidity of the air above the trough.

Fatty acids are from Fluka. Dodecylbenzene sulfonate was from Merck, the carbon nanotubes are from Alpha Aesar and the metalo-porphyrinins are from Sigma Aldrich. The solution for deposition was prepared in purity p.a. benzene. The final solution was ultrasonicated in an ultrasonication bath at 37 kHz.

3. Results

The curves π-A have been recorded with the parameters: rate of compression 7.5 mm/min, room temperature: 25 °C, relative humidity of the air: 60%. Fig. 1 shows the curves pressure-area for the measured compositions: compositions with Cu(II)- porphyrin and Ni(II)- porphyrin.

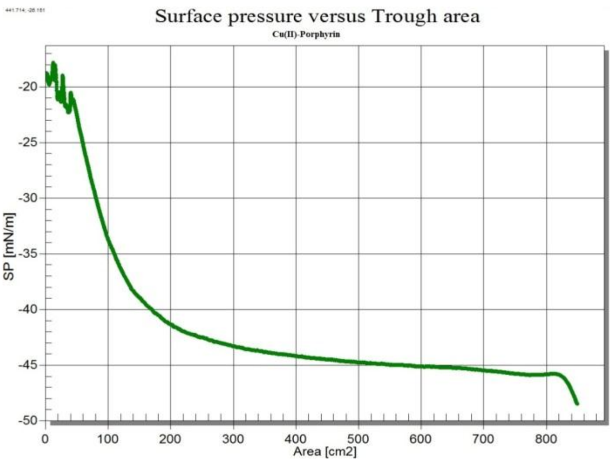

Fig. 1a. The pressure-area curve for the deposition of 5 Langmuir Blodgett thin films based on Cu(II)- porphyrin, silver stearate and SWCNT.

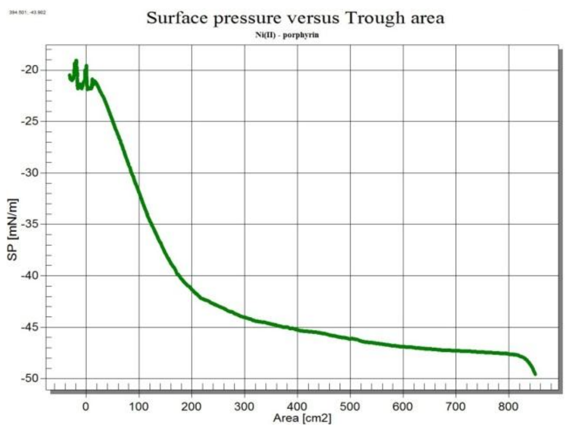

Fig. 1b. The pressure-area curve for the deposition of 5 Langmuir Blodgett thin films based on Ni(II)- porphyrin silver stearate and SWCNT.

The π-A curves show signidicant differences in the middle region and at the first part of the compression. It is remarkable that the compression of the multilayers with Ni-porphirins is larger than that of the Cu-porphiriun layers.

In order to evidence more clearly various regions of ordering we calculated the derivative of the π– A curves. All the curves show three distinct zones: gas-like, intermediary(Liquid) and solid-like zone. (Fig. 2).

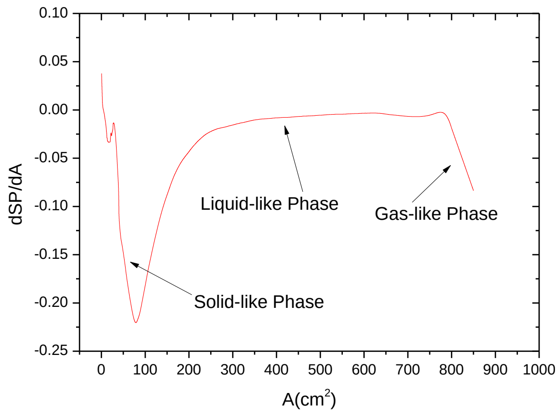

Fig. 2a. Derivate of the presure area deposition curve for Cu(II)- porphyrin silver stearate and SWCNT.

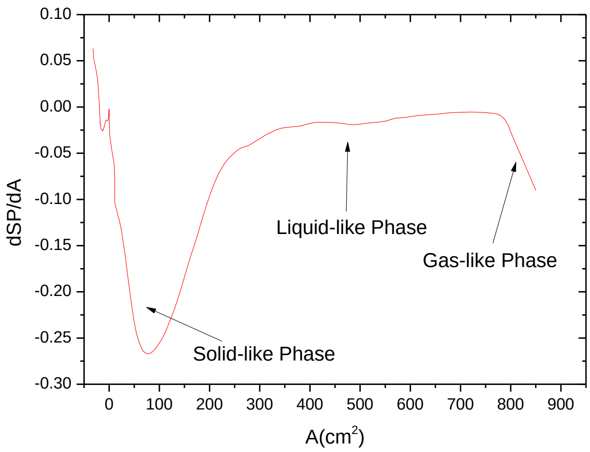

Fig. 2b. Derivative of the presure-area deposition curve for Ni(II)- porphyrin silver stearate and SWCNT.

The derivative curves show that the compression of Cu-porphirin layer is more abrupt than in Ni-porphiurin layer. This means that solid state of the films is reached more rapidly in the layer with Ni-porphirin.

In a further experiment we evidenced the sensitivity of the material deposited as 5 multilayers on a ceramic body provided with comb electrodes. The measurements of electric resistance have been made in a special device built especially for this type of measurements connected to a Keithley Multimeter unit.The curves of variation of the electrical resistance versus time of irradiation are presented in Fig. 3 for copper porphirin sample. UV irradiation has been carried out with a medical UV lamp made by Electrotehnica-Bucharest, having the main emission lines in the range of 330-340 nm at the power density of 116 $\mu W/cm^2$.

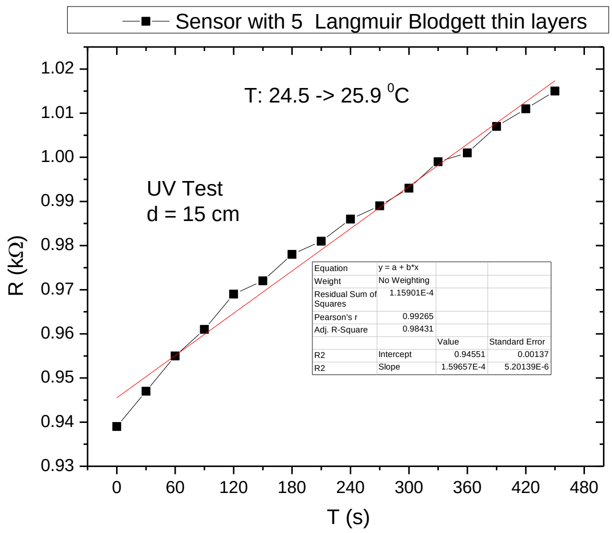

Fig. 3. The effect of UV radiation of the sensor based on Cu(II)- porphyrin silver stearate and SWCNT.

The change of electrical resistance under UV irradiation cannot be due to soaking of the multilayer films because the rsistance come back to the initial value after switching-off the UV-light.

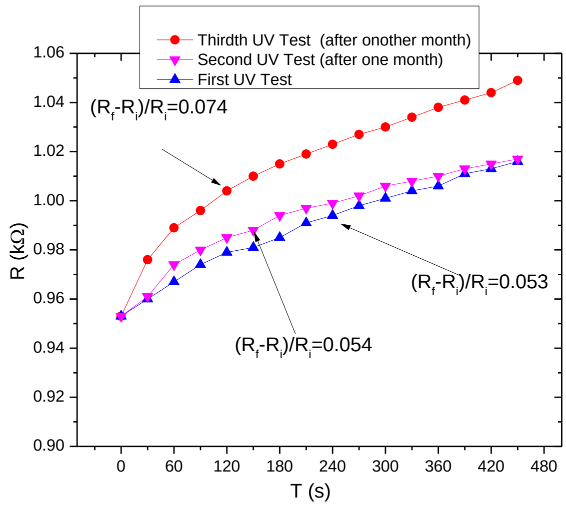

Fig. 4. The effect of UV radiation of the sensor based on Cu(II)- porphyrin silver stearate and SWCNT in the time period of three monts. R_f is the final resistance on the sensor and the R_i is the initial resistance of the multilayered material.

Fig. 4 shows the behaviour of the electrical resistivity of the sensor after storage for various time duration. The sensitivity of the sensor is evaluated with the help of the parameter (Rf-Ri)/Ri. The sensitivity increases significantly with the time of storasge.

4. Discussion

Using stabilized layers of fatty acids (Ag-stearate) and porphirins as additive we have obtained a sensitive material for detection of the UV radiation. The sensitive material, deposited layer by layer using the Langmuir Blodgett technique, based on SWCNT, silver stearate and Cu(II) porphyrin is carrefuly selected because the stearate has the roll of a matrix in which the nanotubes are dispersed, 33% from the used nanotubes have metallic character, thus exibits the electric resistance of the layer and the porphyrin is considerd to be a good activator of conductivity in the presence of light.

We can observe from the plot of electrical resistence vs. time of UV irradiation that the sensitive material has a good and linear response from wich we have calculated the sensitivity of the sensor for Cu(II)-porphirins: 0.15 Ω/s.

We can assume that probably the UV irradiation lead to evaporation of liant between the nanotubes and then decreasing the conductive paths between them or with other words increasing of the barriers between CNTs results the decreasind of the hopping mobility. The sensor is not fully reversible and therefore, the effect is useful for cummulative dose sensors applications. A sensor able to measure eventualy the power of incident flux of UV light is possible. Further experiments are required for the understanding of the phenomena and improvemernt of the sensitivity of the material. It was observed that during ageing the sensitivity of the sensor slighly increases. (Fig. 4).

5. Conclusions

The surface properties of the complex layers with porphyrins.silver stearate and SWCNT have been studied. We have obtained the optimum surface tension at which a thin film can be deposited successfully. We have tested the sensitivity of the material for ultraviolet radiation. On the basis of the above described complex material we have developed a cummulative sensor for UV-radiation.

Acknowledgement

This paper is suported by the Sectorial Operational Programme Human Resources Development (SOP HRD), financed from the European Social Fund and by the Romanian Government under the contract number SOP HRD/107/1.5/S/82514.

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