JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 11, No. 10, October 2009, p. 1412 - 1415

Electrical properties of Langmuir-Blodgett thin films using calixarene molecules♣

Z. ÖZBEK, R. ÇAPAN*, H. SARI[a], T. UZUNOĞLU[a], F. DAVIS[b]
Balıkesir University, Faculty Of Science, Department Of Physics, 10100 Balıkesir, TURKEY
[a]Ankara University, Faculty Of Engineering, Department Of Engineering Physics, 06100 Tandogan, Ankara, TURKEY
[b]Cranfield Health, Cranfield University, MK43 0AL, UK

Calix[8]acid/calix[4]amine alternate layer Metal-Langmuir-Blodgett film-Metal (M/LB/M) structures were fabricated onto an aluminized glass substrate. Film deposition results indicated that these molecules are suitable to deposit with a highly ordered alternate layer structure. Studies were made of the nano-layer structures' electrical properties such as I-V and C-f. By analyzing I-V curves and assuming a Schottky conduction mechanism, the barrier height was found to be 0.67 eV.

(Received November 5, 2008; accepted December 15, 2008)

Keywords: Calixarene, Langmuir-Blodgett thin films, Electrical properties

1. Introduction

Calix[n]arene derivatives are extensively studied for their possible applications as sensors, because these materials are highly selective moleculer receptors for various metal ions and organic compounds for separation and analyses applications [1]. The Langmuir–Blodgett (LB) thin film deposition technique allows us to produce ultra-thin films using organic materials. In this technique, a floating monolayer at the air/water interface can be transferred onto a substrate, which is raised and dipped through the monolayer.

It has also attracted considerable interest in the fabrication of electrical and electronic devices, e.g. metal-insulator-metal (MIM) structures because of the precise controlled thickness and molecular architecture of the device [2]. A polar aluminum surface was used for the investigation of the electrical transport mechanism through LB films [3]. These materials are a class of macrocyclic compounds of fundamental interest and growing technical importance in different fields. The calixarenes are cyclic, cavity containing oligomers, built up from phenol units linked together via alkylidene groups to ring systems [4]. One important characteristic of calixarenes is the great conformational mobility, which increases with the degree of condensation. The calixarenes are mobile at room temperature; for example in solution, *p*-tert-butylcalix[4]arene exists in four conformations: 'cone', 'partial cone', '1,2- alternate' and '1,3 alternate' which differ for the respective orientations of the aromatic rings [5-6]. A similar class of molecules are the calixresorcinarenes, formed by the condensation of various aldehydes with resorcinol. These have also shown potential for sensor applications when deposited as LB films [7].

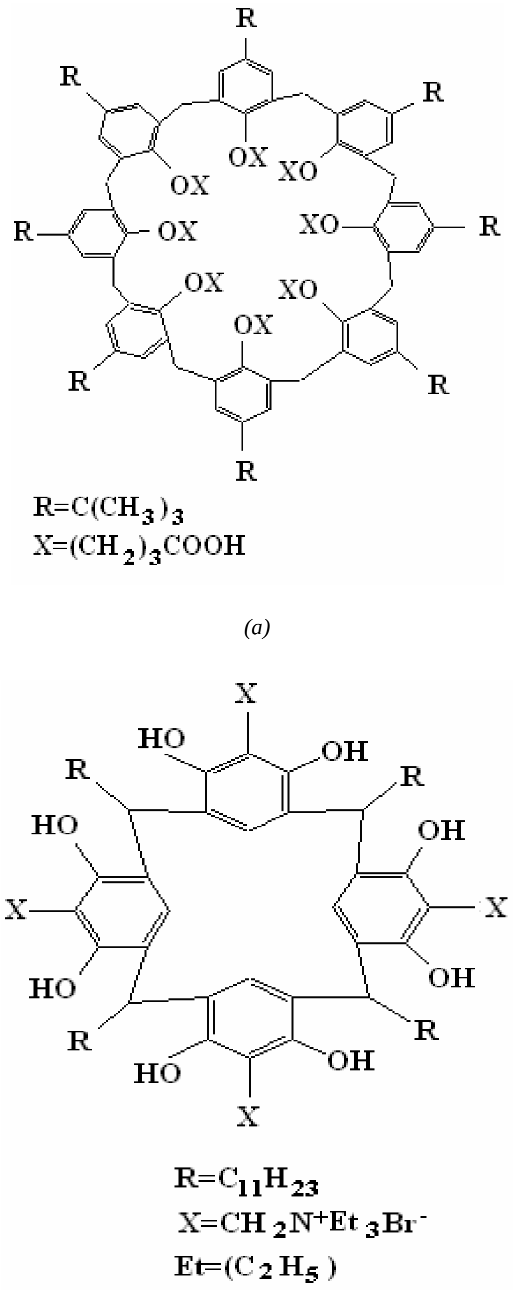
2. Experimental

The chemical structure of the materials used in this work is shown in Figs. 1(a) and (b). The calix[8]acid 1a is based on a cyclic phenol formaldehyde octamer [8], whereas the calix[4]amine is based on a cyclic calixresorcinarene tetramer (formed from resorcinol and dodecanal which has been substituted at the 2 position of the resorcinol units using a Mannich type procedure [6].

Initial information about the structure of mixed monolayers on the water surface was obtained from pressure/surface area isotherm measurements which also allowed us to choose the processing window for LB deposition. These measurements as well as LB thin film deposition were performed with a computer controlled two-barrier LB trough equipped with a Wilhelmy microbalance containing deionized water at room temperature. The compound was spread from a 0.25 mg ml^{-1} concentration in chloroform on the subphase, enabling monolayer study following complete evaporation of the solvent (10-15 min).

♣ Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008

A device structured as A1 / LB film /Al was used in order to measure the electrical properties of the LB thin films. The composite LB thin film was deposited on the bottom and top electrode prepared by the evaporation of A1 onto a slide glass substrate. The aluminum oxide layer was inserted by dipping the Al/glass substrate in the LB trough, and the thickness of the aluminum oxide layer was taken to be 50 nm.



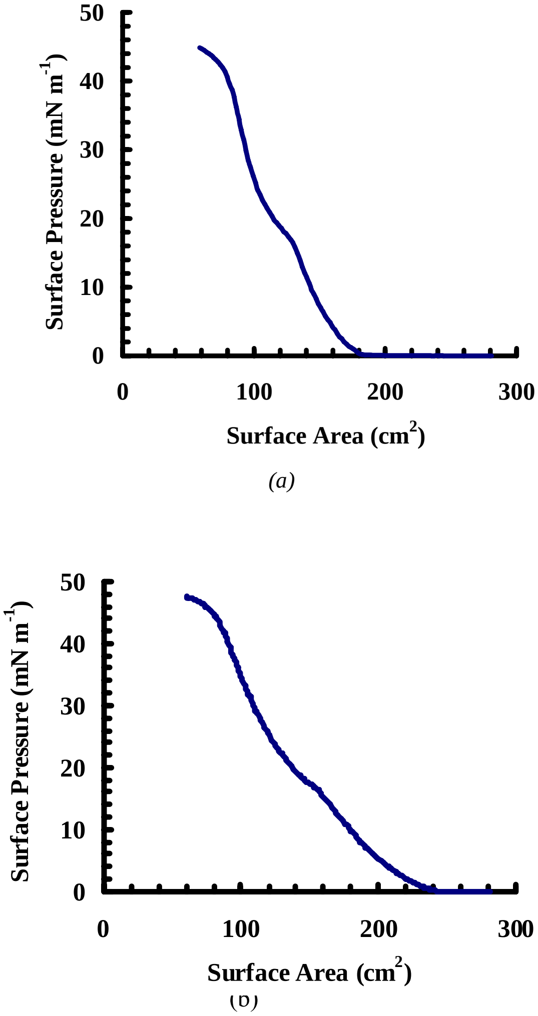
(a)

(b)

Fig. 1. Chemical structure of (a) Calix[8]acid (b) Calix[4]amine.

3. Result and discussion

Fig. 2 shows pressure/area isotherms of calix[8]acid and calix[4]amine monolayers at the air-water interface at room temperature. From the results of the isotherm studies, the LB thin films were transferred onto aluminized (Al-coated) glass slides at a constant surface pressure of 22.5 mN m^{-1} for electrical experiments.



(a)

(b)

Fig. 2. Isotherm graph of (a) Calix[8]acid (b) Calix[4]amine at the air-water interface.

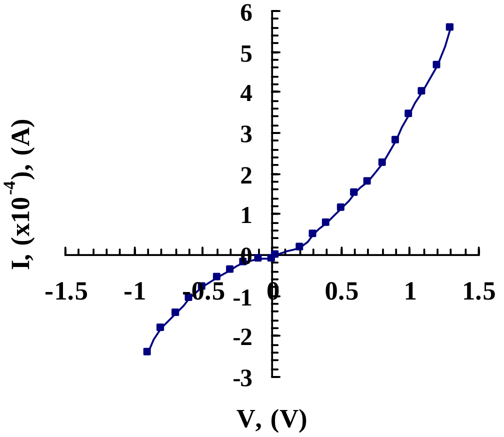


Fig. 3. I-V characteristic of an Al/LB film/Al structure.

The I-V characteristics of the calix[8]acid/calix[4]amine LB thin films deposited onto the Al electrode were investigated by measurements at room temperature, as shown in Fig. 3. Using these graphs, the ohmic part of the conductivity at low voltage values was calculated to be 11.5×10^{-7} S m^{-1}.

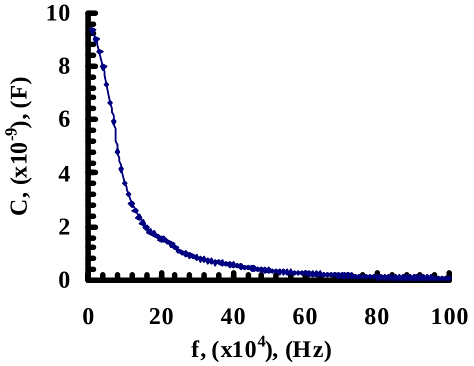


Fig. 4. The capacitance measurements of calix[8]acid/calix[4]amine as a function of frequency.

Fig. 4 shows the capacitance measurement as a function of frequency for 21 monolayers of alternate layer-type calix LB thin films at room temperature. The capacitance significantly decreased when the frequency increased. The dielectric constant of the LB thin film was calculated, using this graph (Fig. 4) and utilising Eq. 1:

$$C=\left(\frac{\varepsilon_{calix}\varepsilon_o S}{Nd}\right) \tag{1}$$

where C is the capacitance of calix[8]acid/calix[4]amine, N is the layer number, d is the thickness of calix[8]acid/calix[4]amine and S is the Al electrode area. Using the thickness value of the calix molecules [9], the dielectric constant is estimated to be 3.03. This value shows a similarity to that of 2.80 calculated for calixarene [10].

The Schottky mechanism arises from the injection of carriers from the electrodes over the potential barrier formed at the insulator-metal interface. The relationship between the current and applied voltage can be described as:

$$I = AST^2 \exp\left(-\frac{\phi_s}{kT}\right)\exp\left(\frac{\beta_s V^{1/2}}{kTd^{1/2}}\right) \tag{2}$$

where A is the Richardson constant, T is the absolute temperature, k is the Boltzmann constant, ϕ_s is the Schottky barrier height at the injecting electrode interface, and β_s is Schottky coefficient given by:

$$\beta_s = \frac{1}{2}\left(\frac{e}{\pi\varepsilon_r\varepsilon_o}\right)^{1/2} \tag{3}$$

where is ε_r the dielectric constant of the film, ε_o is the permittivity of free space, d is the film thickness. Using the slope of Fig. 5, the experimental Poole-Frenkel and Schottky coefficients were calculated, and are given in Table 1.

Table 1. Theoretical and experimental values of β.

Calix[8]Acid/ Calix[4]amine	Theoretical value *(eVm $^{1/2}$V $^{-1/2}$)*		Experimental value *(eVm$^{1/2}$V $^{-1/2}$)*
	β_{PF}	β_S	β_{exp}
21 layers	4.36×10^{-5}	2.18×10^{-5}	1.55×10^{-5}

In order to determine the barrier height, (ϕ_s), of the alternate layer LB film, the value of I_o must be known. The potential barrier can be described as:

$$\phi_s = \frac{\left[kT\ln\left(\frac{AT^2}{I_o S}\right)\right]}{e} \tag{4}$$

The theoretical value of β_s is found to be 2.18×10^{-5} eVm$^{1/2}$V$^{-1/2}$, using Eq. 3. The experimental value of β is calculated 1.55×10^{-5} eVm$^{1/2}$V$^{1/2}$, using the gradient of the lnJ-V$^{1/2}$ curve given in Fig. 5. The experimental β value for the Al-type calix LB film is very close to the theoretical β_s value.

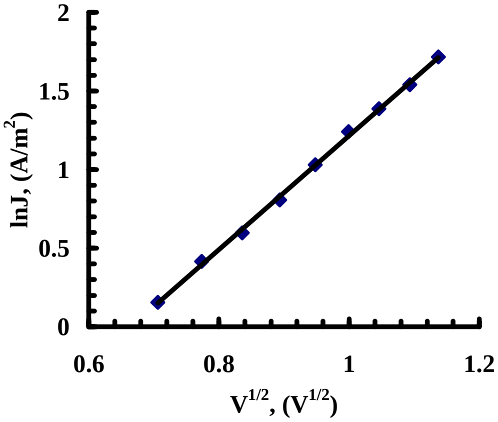


Fig. 5. Plot of lnJ versus $V^{1/2}$ *for 21 layers.*

4. Conclusions

Uniform alternate layer calix[8]acid/calix[4]amine LB thin films were prepared using the LB thin film deposition procedure, and the electrical properties for these LB thin films were evaluated. The I–V characteristic shows a symmetrical and highly non-linear behaviour, with an ohmic regime at low voltage values of 11.5×10^{-7} S m^{-1}. The conduction obeys the Schottky conduction mechanism at high voltage values. The potential barrier height for the Al/LB film/Al was found to be 0.67 eV using dc measurements.

Acknowledgements

Z. Özbek would like to thank Murat Evyapan for help.

References

[1] Aouni, A. Rouis, H. Ben Ouada, R. Mlika, C. Dridi, R. Lamartine, Materials Science and Engineering: C **24**, 491 (2004).
[2] R. Capan, T. H. Richardson, D. Lacey, Thin Solid Films **468**, 262 (2004).
[3] A. V. Nabok, Iwantono, A. K. Hassan, A. K. Ray, T. Wilkop Materials Science and Engineering C **22**, 355 (2002).
[4] R. Mlika, H. B. Ouada, M. A. Hamza, M. Gamoudi, G. Guillaud, N. Jaffrezic-Renault, Synthetic Metals **90**, 173 (1997).
[5] R. Milka, H. B. Ouada, R. B. Chaabane, M. Gamoudi, G. Guillaud, N. Jaffrezic-Renault, R. Lamartine, Electrochimica Acta **43**, 8, 841 (1998).
[6] R. B. Chaabane, M. Gamoudi, B. Remaki, G. Guillaud, O. El Beqqali, Thin Solid Films **29**, 648 (1997).
[7] F. Davis, C. J. M. Stirling. Langmuir **12**, 5365 (1996).
[8] M. W. Sugden, T. H. Richardson, F. Davis, S. P. J. Higson, C. F. J. Faul, Coll. Surf. A **321**, 43 (2008).
[9] Z. Özbek, R. Çapan, H. Sarı, T. Uzunoğlu, F. Davis, Submitted to J. Optoelectron. Adv. Mater. (2008).
[10] J. H. Yim, J. Kim, D. W. Gidley, R. S. Vallery, H. Peng, D. K An, B. K. Choi, Y. K. Park, J. K. Jeon, Macromol. Mater. Eng. **291**, 369 (2006).

---

[*] Corresponding author: rcapan@gmail.com