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Electrical conductivity properties of boron containing Langmuir–Blodgett thin films

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Abstract Electrical characterisations of Mesitylene-2-boronic acid (MBA), Phenylboronic acid (PBA) and 1-Naphthylboronic acid (NBA) are investigated using C-f and I–V measurements. All materials are used to fabricate Langmuir–Blodgett (LB) thin film by vertical dipping method. Metal/LB film/Metal sandwich structure is prepared to investigate electrical properties of boron containing LB films. For evaluation of electrical measurements, the theoretical thickness is determined using ChemDraw software and experimental thickness value is calculated from surface plasmon resonance (SPR) curves. Dielectric measurements are used to determine the dielectric constant (ε) and to compare refractive index value which is determined from SPR results. The values of ε are determined as 2.79, 2.70, 2.82 for MBA, PBA and NBA respectively. The refractive indexes of three materials are calculated to be around 1.6. I–V results are used to study the conduction mechanism of these LB films. The low voltage region shows an ohmic characteristic for each LB film and conductivity values are calculated as 0.55×10^{-11} S m^{-1}, 0.42×10^{-11} S m^{-1} and 3.62×10^{-11} S m^{-1} for MBA, PBA and NBA respectively. In the high voltage region of I–V curves that show Schottky type conduction mechanisms with the barrier heights estimated for each LB film as 0.77, 0.79 and 0.76 eV respectively.

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1 Introduction

Physical and sensing properties of boron containing thin film materials [1–5] have been extensively studied because of their potential application in many areas such as transistors [6], nanoscale electronic devices [7], protein detection [8], sugar sensing [9] and gas sensors [1]. There are two ways of producing boron containing thin films. The first is doping a thin film with boron atom [3, 4] and the second is producing a thin film with boron containing material. When a thin film is doped with boron atom, free electron density increases. Doping boron in a thin film decreases the electrical resistivity and gains better electrical stability [3] and increases electrical conductivity [4]. Poly(3-thiophene-boronic acid) was selected for use as a semiconductor structure by polymerisation method and the study concluded that this boronic acid containing organic thin film can be used as an organic transistor [10].

Langmuir–Blodgett (LB) thin films are widely used in different fields and subjects for a large number of potential applications due to nonlinear optic properties [11], sensitivity properties [12–14] and electrical conductivity properties [15, 16]. Different organic thin film materials can contribute special properties to LB films depending on their speciality. Hence; molecular structure is important for physical properties of LB films. There are some widely used organic molecules for LB film preparation, but not enough studies exist on boron containing materials as an LB film. The few studies in the literature have been done by Pietraszkiewicz et al. [17], Ludwig et al. [18] and Miyahara and Kurihara [19]. They showed that boronic acid containing LB thin films can be fabricated in a nanoscale area. Pietraszkiewicz used Langmuir technique and studied the recognition of carbonhydrates by boronic acid containing cavitands. Ludwig experimented with several phenylboronic acids to produce LB films and investigated their saccharide sensing system. In addition, Kurihara produced electrically conductive LB films using boronic acid containing amphiphile and studied their sugar recognition. In the present study, Mesitylene-2-boronic acid (MBA), Phenylboronic acid (PBA) and 1-Naphthylboronic acid (NBA) with structural differences were chosen to produce LB films. These three molecules all include a boronic acid group but have some structural differences. With only six valence electrons and a consequent deficiency of two electrons, the sp^2-hybridized boron atom possesses a vacant p orbital. This low-energy orbital is orthogonal to the three substituents, which are oriented in a trigonal planar geometry. Unlike carboxylic acids, their carbon analogues, boronic acids are not found in nature. These compounds are usually prepared from borate esters which are the main precursors for boronic acid derivatives. At ambient temperature, arylboronic acids are chemically stable and most of them display shelf-stability for long periods. Moreover, their low reactivity, stability and ease of handling, makes boronic acids a particularly attractive class of synthetic intermediates. Due to their low toxicity and ultimate degradation into the environment boronic acids can be regarded as "green" compounds. In this study, the electrical properties of boronic acid containing LB films with structural differences were investigated and compared.

2 Experimental details and measurement systems

The synthesis details of MBA, PBA and NBA materials were given in the literature [20, 21] and chemical structures of the materials are shown in Fig. 1. They were dissolved in chloroform with a concentration ratio of $\sim$0.6 mg ml^{-1}. Each solution was separately spread onto pure water surface using a Hamilton syringe at a value of pH 6 to yield Π-A isotherm graphs using NIMA 622 type alternate layer LB trough. The solvent was allowed to evaporate for 15 min before the area was enclosed by moving barriers. The barriers were closed with a compression speed of 1,000 mm min^{-1} as a function of a reduced surface area. The isotherm measurements were repeated several times and the results were found to be reproducible. All the experiments were carried out at room temperature by a Lauda Ecoline RE 204 temperature control unit. Using the isotherm graphs, deposition pressures were found to be 15 mN m^{-1} for MBA, 17 mN m^{-1} for PBA and 17 mN m^{-1} for NBA to produce non centrosymetric Z-type LB films. The Z-type LB films were obtained using vertical dipping method which is upwards from water-monolayer-air direction with a speed of 10 mm min^{-1}. LB film layers were transferred onto 50 nm aluminium coated glass substrates for electrical measurements. In order to carry out the electrical measurements, a sandwich structure was prepared between two aluminium electrodes. The bottom and top electrodes were deposited on a glass substrate using thermal evaporator under 7 × 10^{-7} mbar vacuum. The thicknesses of these electrodes are 50 nm. The top electrode is 1 mm × 15 mm. In order to prevent the evaporation of top electrodes onto organic thin film, the deposition was carried out with a slower speed of 3 Å s^{-1}. The sandwich structure of the metal/LB film/Metal configuration is shown in Fig. 2. The electrical measurements were performed in room temperature using HP 4192A impedance analyser, GPIB computer board and 2420 Keithley 3A Sourcemeter. Electrical properties were investigated by measuring C-f and I–V curves at room temperature. The I–V measurements were

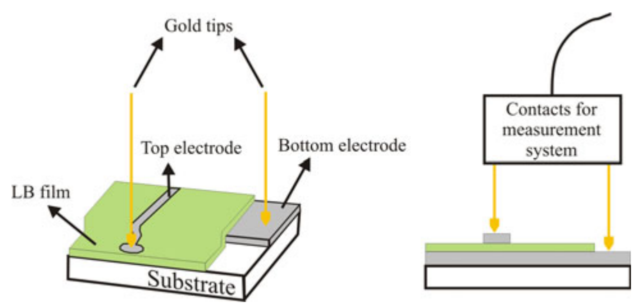
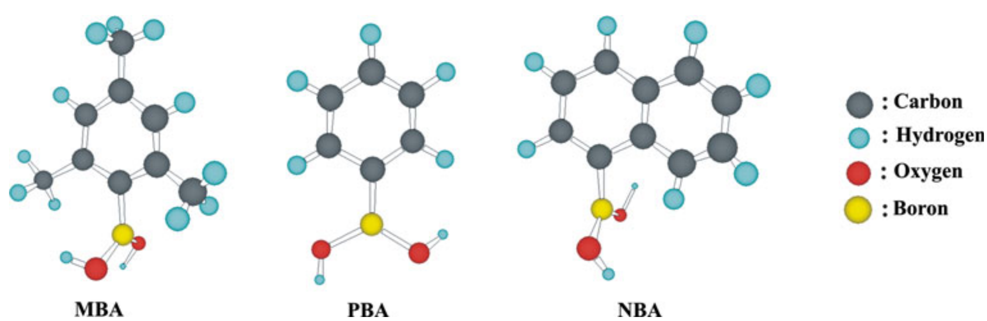


Fig. 2 Metal/LB film/metal device structure

Fig. 1 Chemical structures of Mesitylene-2-boronic acid (MBA), Phenylboronic acid (PBA) and 1-Naphthylboronic acid (NBA)



performed in the range of ±4 and the C-f measurements' range limit was between 10 kHz and 1 MHz.

Surface plasmon resonance (SPR) technique allows us to evaluate the thickness and the refractive index of dielectric layer on the gold surface. Dielectric measurements also can be used to determine the refractive index values of LB films. SPR measurements were carried out using Kresmann configuration SPR system of Biosuplar 6 Model 321. 20 mm × 20 mm × 1 mm sized, 50 nm homogeneous gold coated slides were commercially purchased in order to monitor SPR spectra of gold surface. A glass prism (n = 1.62) was mounted with a sample into the spectrometer and 633 nm source was employed to perform the SPR measurement. Reflected light intensity was recorded as a function of the incidence angle of light which depends on the surface morphology and thickness of the LB film. LB films with different layer numbers were prepared onto gold substrates and SPR curve changes were investigated.

3 Results and discussions

3.1 Analysis of LB film thickness

Figure 3 shows the SPR curves of MBA, PBA and NBA LB films, given as variation of reflected light intensity as a function of angle of incidence. When the number of layers increased, SPR curves shift to the higher angles for all LB films. This shift proves the presence of LB films on the gold substrate [22]. Table 1 gives the angle shifts versus number of layers for three materials. When Fig. 3 and Table 1 is investigated, the most linear change of Δθ value as a function of layer number belongs to MBA material. Up to 10 layers, every two MBA layers create a shift of about 0.2°. 10 layer MBA film creates only about 0.04° angle change after 8 layers. In Fig. 3, SPR curve of 10 layer MBA film has a larger reflectivity value than other layers that results in a decrease in resonance depth. The change of resonance depth can be attributed to absorption of light by organic film [23]. Similar explanations can be given for PBA materials, however more broadened SPR curves for PBA than MBA layers. Broadening of SPR curves and rising of the reflected light intensity can be attributed to damping of resonance with increasing number of layers [24, 25]. A decrease in resonance depth can be seen for 8 and 10 layer PBA films. They are results of surface roughness of thicker PBA films. Angle shifts for NBA films are in the range of about 0.1°, but 10 layer NBA film makes a smaller shift of about 0.06°. Furthermore, the SPR curve shifts to the higher angles with increasing number of layers. The broadening of SPR curves also increases as the number of layers increase.

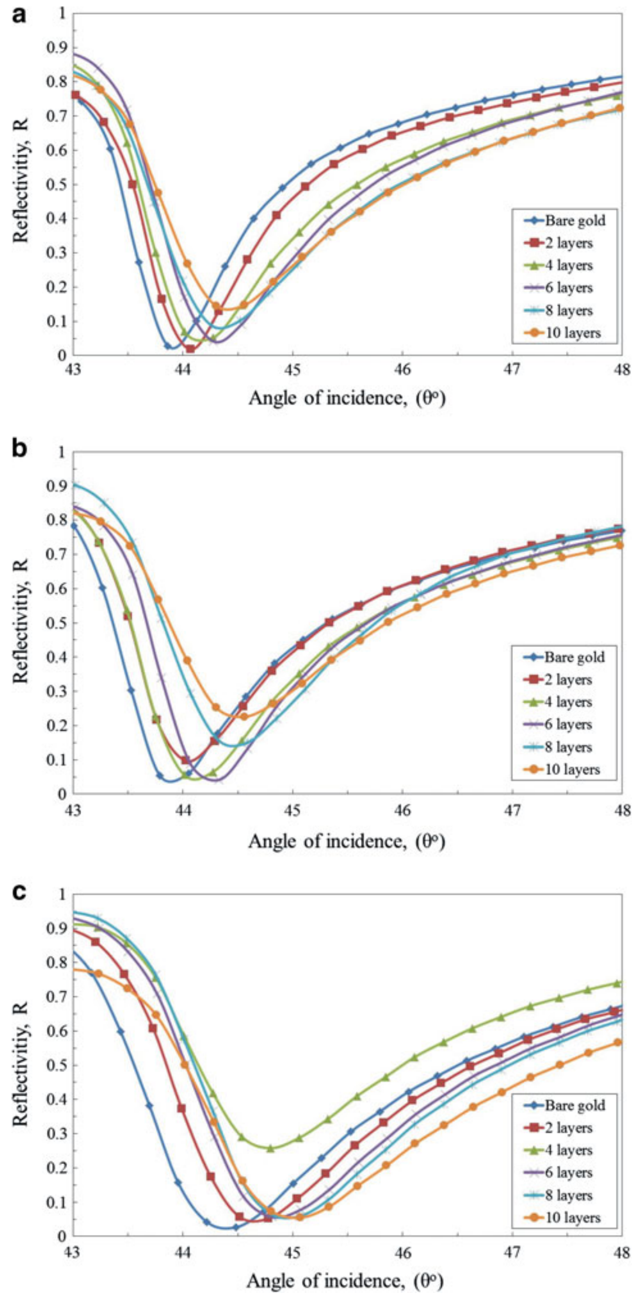


Fig. 3 SPR curves of **a** MBA, **b** PBA and **c** NBA LB films

An examination of the changes in full width at half maximum (ΔFWHM) in Table 1 reveals that NBA LB films have minimum changes compared to others due to the small angle shifts of NBA layers. Additionally, the refractive indexes of LB films can be estimated using Fresnel reflection theory [26]. The experimental thickness and refractive index of these films were evaluated by fitting the SPR curves. The SPR curves of bare gold substrate and LB films were fitted using Winspall 3.01 software which is based on Fresnel equations and developed by Max-Planck Institute [16]. Based on the SPR results, MBA, PBA and

Table 1 SPR angle shifts

Number of layers	MBA			PBA			NBA		
	Δθ (°)	ΔFWHM (%)	ΔR	Δθ (°)	ΔFWHM (%)	ΔR	Δθ (°)	ΔFWHM (%)	ΔR
2	0.206	5	0	0.236	12	0.06	0.294	3	0.02
4	0.414	31	0.02	0.486	25	0.01	0.373	13	0.23
6	0.672	31	0.02	0.539	25	0.01	0.413	7	0.03
8	0.922	57	0.06	0.798	50	0.11	0.527	10	0.03
10	0.964	68	0.11	0.869	75	0.19	0.586	28	0.03

NBA refractive indexes were found to be 1.66, 1.63 and 1.66 respectively.

The investigation of the theoretical thickness of LB films were performed via ChemOffice 5.0 software developed by CambridgeSoft Corporation. It is used to find out the monolayer thickness using the ideal bond lengths. The theoretical film thickness assumption is given by;

$$d = N\ d_m \quad (1)$$

where d is the LB film thickness, N is the number of LB film layers and d_m is the monolayer thickness calculated by ChemOffice.

Figure 4 shows how thickness changes with different number of layer LB films. It is clear in Fig. 4 that theoretical and the experimental values are in good agreement in the beginning. As number of layers increases, the deviation of values increases as well. Theoretical values are higher than experimental values due to a non-uniform film transfer occurred.

3.2 Dielectric properties

The dielectric properties of LB films were investigated by measuring the capacitance versus frequency. The capacitance of a parallel plate capacitor is directly related with the distance between two parallel plates. This relation can be attributed to the thickness of LB film between the two metal electrodes. The capacitance of LB film should decrease with increasing number of layers. In order to check the producibility of LB film layers, 1/C versus number of layers graph is investigated. The graph of 1/C versus number of layers usually gives a linear relationship for reproducible LB film layers [27].

C-f measurements can be used to determine the refractive index of LB thin films and for monitoring the deposition properties of thin films. Al_2O_3/LB film/Al structure shows parallel plate capacitor characteristics and the capacitance of LB film can be calculated as:

$$C_{LB} = \frac{\varepsilon_0\ \varepsilon_{LB}\ A}{d} \quad (2)$$

where $\varepsilon_0$is the dielectric constant of free space, ε_{LB} is the dielectric constant of LB film, A is the overlap area of LB film and d is the thickness which was estimated from SPR curves. In order to calculate the capacitance of LB film, the oxide layer which is formed onto bottom aluminium

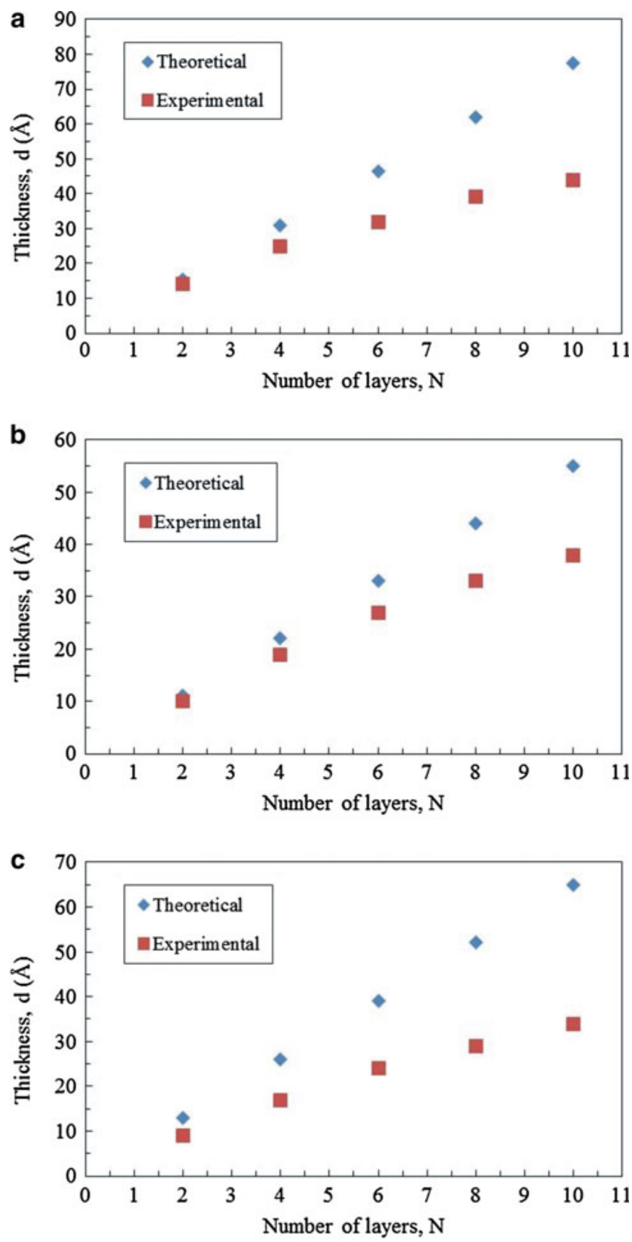


Fig. 4 Thickness change of **a** MBA, **b** PBA and **c** NBA LB films versus number of layers

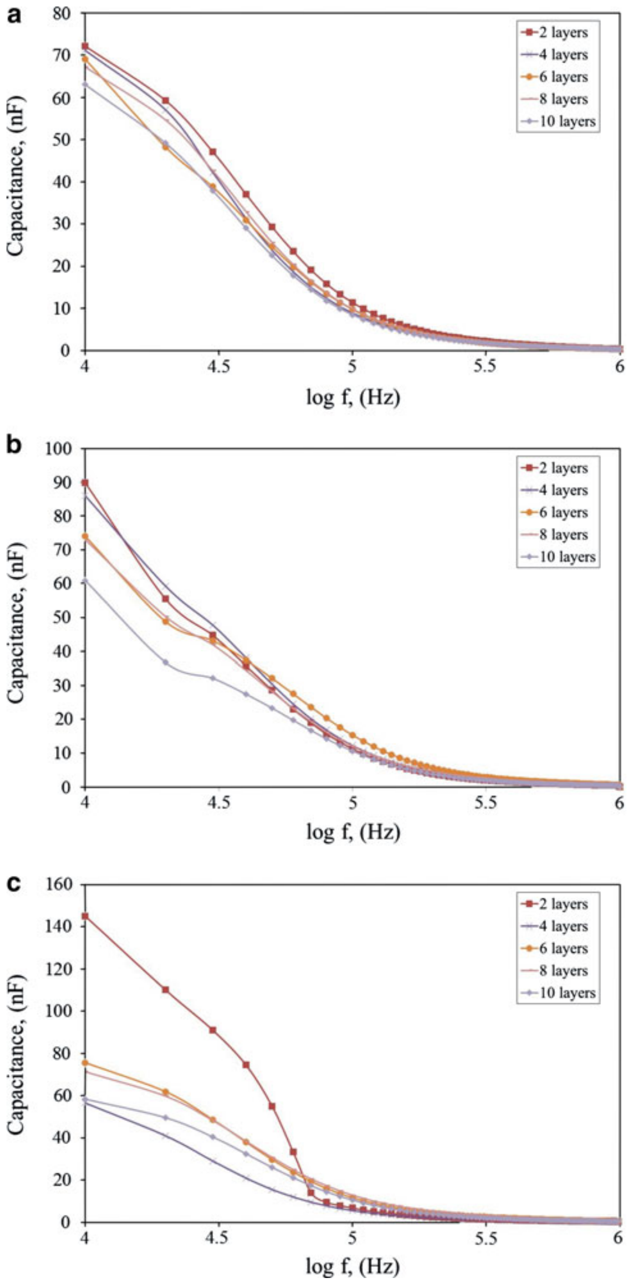


Fig. 5 Capacitance change of **a** MBA, **b** PBA and **c** NBA LB films versus log f

electrode needs to be considered. The total capacitance (C_T) of structure is a combination of metal oxide layer capacitance (C_{Ox}) and LB film capacitance (C_{LB}). The relationship is given by [28]:

$$\frac{1}{C_T} = \frac{1}{C_{Ox}} + \frac{1}{C_{LB}} \tag{3}$$

$$\frac{1}{C_T} = \frac{1}{C_{Ox}} + \frac{1}{\left(\frac{\varepsilon_0\, \varepsilon_{LB}\, A}{d}\right)} \tag{4}$$

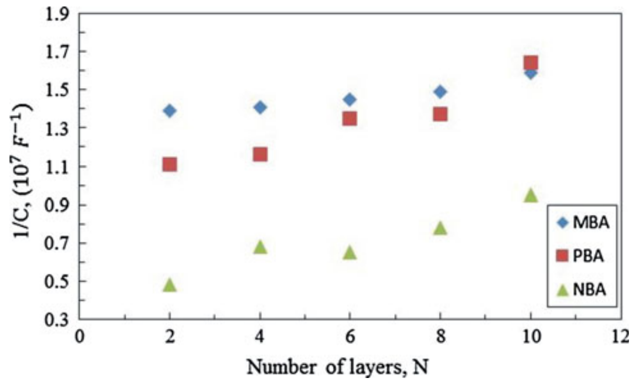


Fig. 6 Reciprocal capacitance of LB films against number of layers

If oxide layer value is very small, this value can be ignored. Therefore the slope of $(1/C_T)$as a function of LB film thickness gives the capacitance of LB film.

The variation of capacitance versus log f for M/LB film/ M structures were plotted in Fig. 5. With increasing number of layers, the capacitance shows a decreasing behaviour for all three LB films. In order to check this relationship between capacitance and number of layers, 1/C versus number of layer change at 10 kHz is shown in Fig. 6. The behaviour of the plots shows an increasing tendency with the increasing number of layers. These relations indicate that dielectric layer thickness increase and prove the producibility of LB film layers [27]. The gradients of plots were used to determine the dielectric constant of LB films.

The refractive index of LB film can be calculated by two different measurements: Dielectric and SPR. In the first, the refractive index of LB film is directly dependent on the dielectric constant (ε_{LB}) and the relation is given by [29]:

$$n = \sqrt{\varepsilon_{LB}}. \tag{5}$$

These values were estimated as 1.67, 1.64 and 1.68 from dielectric measurements. The details of the second calculation using SPR results and WINSPALL fitting programme has been given in Sect. 3.1. These two experimental techniques' results give an opportunity to compare refractive index values. From the results of SPR, MBA, PBA and NBA refractive indexes were evaluated as 1.66, 1.63 and 1.66 respectively. The results are in a good agreement with the organic materials refractive index values [30, 31]. Also, the estimated dielectric constant of boron carbon nitride films is 2.4 [32] and methyl group containing boron carbon nitride films is 2.5 [33]. This is around 2.6 in our results.

3.3 Conductivity measurement

Electrical conductivity properties of LB films were investigated by measuring the I–V characteristics. Figure 7 shows the I–V graphs of different number of layer boron

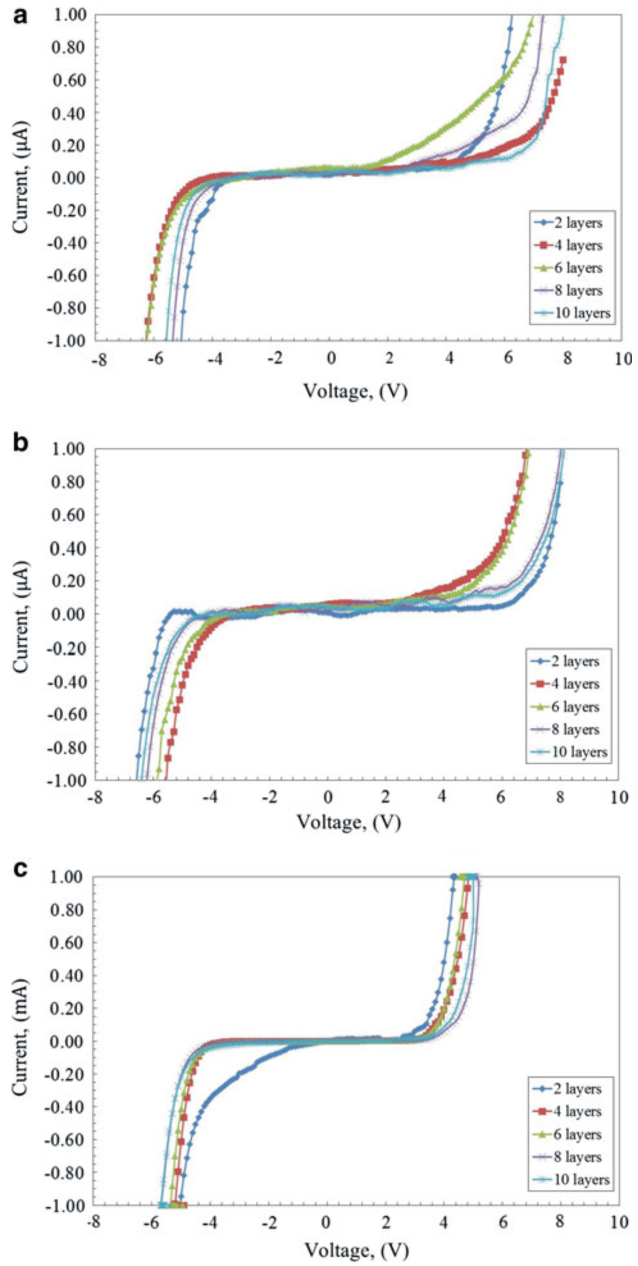


Fig. 7 I–V curves of the metal/LB film/metal devices of **a** MBA, **b** PBA and **c** NBA LB films

containing LB films. All samples show an ohmic behaviour in the low voltage region between 0 and 5 V for MBA and PBA, 0 and 3 V for NBA films. Calculated ohmic conductivity values are given in Table 2. These conductivity values are acceptable for organic thin films and similar values can be found in literature for other LB films such as stearic acid and eicosylamine alternate layer LB films yield 3.87×10^{-13} S m^{-1} and 7.75×10^{-12} S m^{-1} [34] and a calixarene LB film gives a conductivity value of 1.34×10^{-13} S m^{-1} [16]. In the literature there is a limited number of studies on boronic acid organic thin films using other thin film fabrication methods for electrical characteristics. A boronic acid containing polimer thin film was reported to have a conductivity value in the 10^{-4}–10^{-7} S m^{-1} range [10] and in a different study borazine derivative of phthalocyanine thin film had a conductivity in the 10^{-5}–10^{-6} S m^{-1} range [5]. In Table 2, highest conductivity values belong to NBA LB films in the ohmic region. Because this material has two benzene rings and these rings can have a positive contribution effect to the charge transition. This contribution was shown in literature as increasing conjugation system results with decreasing band gap [35]. The comparison of MBA and PBA films' ohmic conductivity shows that the average value of MBA LB films is slightly higher than the average value of PBA films. This can be a result of molecular order of MBA in LB film. SPR results indicate that MBA LB films have a better quality than others. When the relationship between layer number and ohmic conductivity is investigated, it can be said that there is no remarkable change.

For the higher voltage values, determination of the conduction process through LB film is theoretically difficult. However, it can be obtained by making certain expressions via making some assumptions. The result of calculation, dominant conduction mechanism can be obtained. The current density of LB film (J) can be obtained using the current values from Fig. 7. Figure 8 shows the relation between natural logarithm of current density (lnJ) and square root of voltage ($V^{1/2}$) that is linear. The linear dependence suggests that the conduction mechanism obeys either Poole–Frenkel or Schottky mechanism [36–38].

In our study, conduction processes through LB films were explained by plotting of lnJ versus $V^{1/2}$ graph and the expressions given by [39]:

$$I_{Poole-Frenkel} = I_0 \exp\left(\frac{\beta_{PF} V^{1/2}}{kTd^{1/2}}\right) \quad (6)$$

$$I_{Schottky} = A^{*}A\,T^2 \exp\left(\frac{-e\varphi}{kT} + \beta_S V^{1/2}\right) \quad (7)$$

where A^* is the Richardson constant, A is the metal contact area, T is absolute temperature, e is the electronic charge, k is the Boltzmann's constant and φ is band gap of thin film. β_{PF} and β_S are Poole–Frenkel and Schottky coefficients respectively and Poole–Frenkel field-lowering coefficient is given by [39]:

$$\beta_{PF} = \frac{e}{kT}\left(\frac{e}{\pi\varepsilon_0\varepsilon_{LB} d}\right)^{1/2}. \quad (8)$$

The Schottky coefficient is $1/2\beta_{PF}$. In order to determine conduction mechanism, theoretically and experimentally β coefficients are compared. Table 2 gives the β values for all LB films. β_{LB} is almost closed to the value of β_S. Therefore the dominant conduction mechanism through LB

Table 2 Conduction and conduction mechanism of LB films

Number of layers	Ohmic conductivity ($S\ m^{-1}$)	β coefficients ($eV\ m^{1/2}\ V^{-1/2}$)		
		Poole–Frenkel	Schottky	Experimental
MBA				
2	1.40×10^{-12}	7.10×10^{-5}	3.55×10^{-5}	1.08×10^{-5}
4	5.00×10^{-12}	5.23×10^{-5}	2.62×10^{-5}	1.43×10^{-5}
6	9.60×10^{-12}	5.25×10^{-5}	2.63×10^{-5}	1.46×10^{-5}
8	2.20×10^{-12}	4.15×10^{-5}	2.08×10^{-5}	1.72×10^{-5}
10	9.60×10^{-12}	4.17×10^{-5}	2.09×10^{-5}	1.79×10^{-5}
PBA				
2	7.00×10^{-12}	7.53×10^{-5}	3.77×10^{-5}	1.02×10^{-5}
4	1.90×10^{-12}	5.58×10^{-5}	2.79×10^{-5}	1.47×10^{-5}
6	5.40×10^{-12}	5.05×10^{-5}	2.53×10^{-5}	1.53×10^{-5}
8	3.30×10^{-12}	4.59×10^{-5}	2.30×10^{-5}	1.69×10^{-5}
10	3.80×10^{-12}	4.69×10^{-5}	2.35×10^{-5}	1.60×10^{-5}
NBA				
2	1.80×10^{-9}	5.21×10^{-5}	2.61×10^{-5}	1.01×10^{-5}
4	3.40×10^{-11}	4.51×10^{-5}	2.26×10^{-5}	8.53×10^{-6}
6	4.80×10^{-11}	3.72×10^{-5}	1.86×10^{-5}	1.39×10^{-5}
8	2.90×10^{-11}	3.70×10^{-5}	1.85×10^{-5}	1.95×10^{-5}
10	3.40×10^{-11}	3.77×10^{-5}	1.89×10^{-5}	2.60×10^{-5}

film can be Schottky effect. Similar results can be found in the literature for other LB films [16, 34, 39, 40].

φ can be estimated using the lnJ value at V = 0 and given by:

$$\varphi = \frac{kT}{e}\left[\ln(A^{*}T^{2}) - \ln J\right]. \quad (9)$$

Using Fig. 8 and Eq. 9 the obtained barrier heights are found around 0.67–0.81 eV and given in Table 3. There is no correlation between number of LB film layers and barrier height. There are slightly different barrier heights of our LB film samples. NBA LB films' barrier heights are between 0.67 and 0.76 eV and that shows the narrower band gap amongst our materials. In Table 2, it can be seen that the highest conductivity values at the lowest voltage region belong to NBA LB films. In literature, some LB films have been reported to have barrier heights between 0.18 and 0.26 eV [41]. In addition, a boronic acid containing organic material which was named Poly(3-thiophene-boronic acid) has been investigated with a conductivity value of 2.0×10^{-9} $S\ m^{-1}$.

Due to the empty p orbital on the boron atom, aryl boronic acids act as Lewis acids. While boron atom directly bonded to the aromatic ring, the conjugation between the aromatic π electrons and neighbouring empty p orbitals of the boron atom will increase the electron delocalization on the whole molecule just like the aromatic carbocyclic acid shown in Fig. 9. On the PBA molecule, the C–B$(OH)_2$ plane is quite coplanar with the benzene ring, while the two methyl groups on the ortho-position force the OH groups out of the aromatic plane due to the steric hindrance. This rotation results in decreasing conjugation of the p electrons in the aromatic ring with the empty p orbitals on the boron atom. The three methyl groups slightly donates the electron to the aromatic ring by the inductive effect but the decrease in resonance effect the electron delocalization more than inductive electron donation. In the naphthalene boronic acid, there are two opposing effects, the conjugation of the second joined aromatic ring in naphtyl group should increase the delocalisation of the electron on the molecule, and steric hindrance of joined ring may force to rotate the boronic acid (OH) site out of the naphthyl plane. Comparing the PBA, MBA, and NBA the stearic hindrance is not as much as the two methyl group but the delocalisation effect seems much more effective according to the conductivity results.

4 Conclusion

In this paper three boronic acid containing organic materials were used for the first time in the characterization of LB films and investigation of electrical properties. Boron is an important element that can improve the electrical stability and conductivity when it is doped in an organic material. SPR technique was used to check the reproducibility of multilayer LB film structure and to find out the thickness and refractive index of LB films which were used for the calculation of conductivity parameters. The average conductivities at the

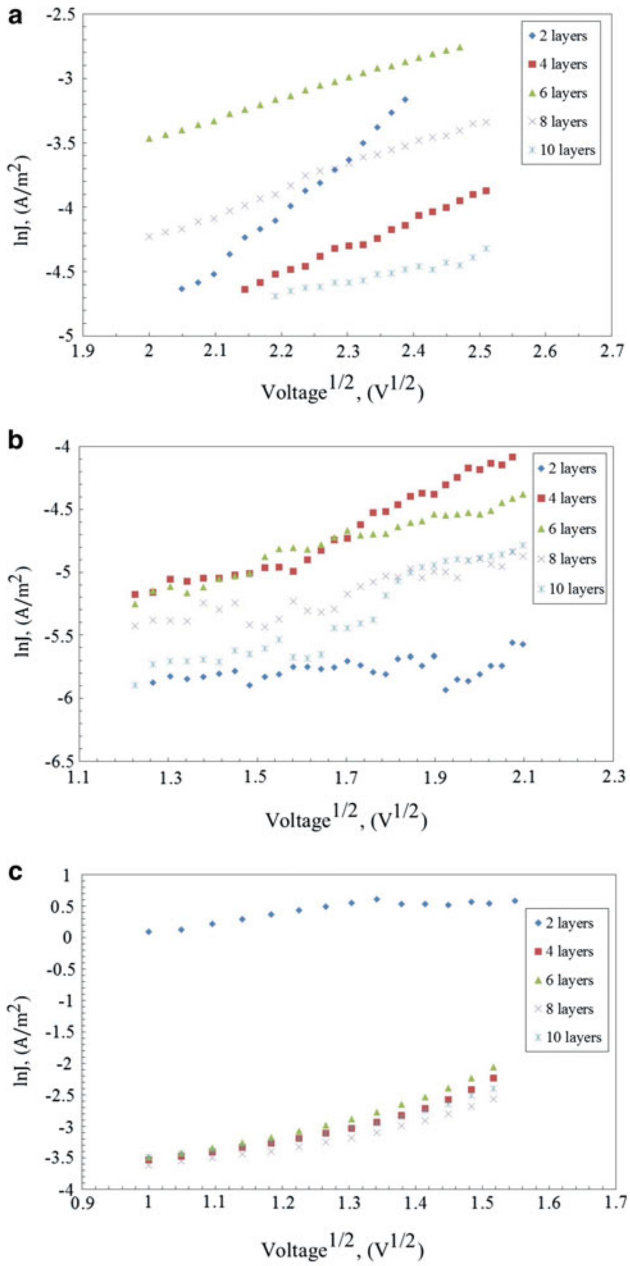


Fig. 8 Relationship between lnJ and $V^{1/2}$ of **a** MBA, **b** PBA and **c** NBA LB films for the applied voltage

Table 3 Barrier height of LB films

	φ (eV)				
	2 layers	4 layers	6 layers	8 layers	10 layers
MBA	0.79	0.79	0.75	0.77	0.78
PBA	0.81	0.79	0.79	0.79	0.81
NBA	0.67	0.76	0.76	0.76	0.76

low voltage values were found to be 0.55×10^{-11} S m^{-1}, 0.42×10^{-11} S m^{-1} and 3.62×10^{-11} S m^{-1} for MBA, PBA and NBA respectively. The conductivity measurements

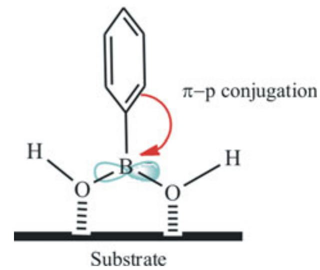


Fig. 9 π–p conjugation of molecule

indicated that the Schottky type conductivity occurred at the high voltage values. Using the Schottky type analysis method, the barrier heights of LB films were estimated to be 0.77, 0.79 and 0.76 eV for MBA, PBA and NBA respectively. The results of our study showed that the three boronic acid molecules can be candidates as LB film materials and can be used for electrical applications in the field of thin film devices.

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