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Influence of Preparation Conditions on Electrical Properties of the Al/Alq$_3$/Si Diode Structures

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Hybrid organic-inorganic diode structures, Al/Alq$_3$/n-Si and Al/Alq$_3$/p-Si based on thin films of tris(8-hydroxyquinoline) aluminum (Alq$_3$) have been investigated. The Alq$_3$ films were evaporated in vacuum and spin coated onto patterned areas of crystalline n- and p-type Si substrates with chemically removed native SiO$_2$ layer. Current-voltage characteristics of the diode structures demonstrated improved rectification property compared to similar Al/n-Si and Al/p-Si device structures. Increased barrier height values (0.90 eV ÷ 1.1 eV and 0.77 eV ÷ 0.91 eV for the Al/Alq$_3$/n-Si and Al/Alq$_3$/p-Si device structures, respectively) certified presence of an interface dipole induced by the organic interlayer. Non-ideal behavior of forward current-voltage characteristics has been explained assuming non-uniformity of barrier height, presence of interface states, and influence of the organic film on diode series resistance and space charge limited current.

Keywords: organic-inorganic heterostructures, vapour deposition, spin coating, Alq$_3$ thin film, Schottky thermionic emission.

1. INTRODUCTION

During the last few years, interest in organic semiconductors and their thin films increased rapidly due to their potential application in solar cells, field effect-transistors, organic light emiting diodes (OLEDs) and other electronic and optoelectronic devices [1].

Metal-semiconductor (M-S) junction known as Schottky barrier diode is one of the most important device structures used in semiconductor device technology. Electrical properties of the M-S diodes and particular their rectification properties depend on interface formation and particurar on height of a potential barrier, Φ_b, occuring at the interface. One can expect that this parameter should depend on difference between work functions of metal and that of a semiconductor. However, in most cases the barrier height is governed by defect states occuring in a semiconductor at the interface. As a result, barrier height is restricted to within 0.6 eV ÷ 0.8 eV and 0.5 eV ÷ 0.7 eV ranges for n-Si and p-Si, independently on metal [2]. Formation of high-quality junctions with a certain fixed Schottky barrier height is one of essential process to improve electrical properties of the diodes.

An organic thin film inserted between semiconductor and metallic electrode was found to modify electrical properties of the M-S junctions. Number of authors [3 – 6] have used thin film interlayers of various organic compounds to introduce a controlled dipole layer at the semiconductor/organic interface in order to modify the effective Schottky barrier height. Either increase or decrease of the effective Schottky barrier by using an organic thin layer on an inorganic semiconductor have been reported.

Tris(8-hydroxyquinoline) aluminum (Alq$_3$) is one of the most stable organic semiconductor used widely for the fabrication of OLED and other electronic devices [7, 8]. Our goal was to investigate contribution of the interlaying Alq$_3$ film on electrical parameters of the hybrid Al/Alq$_3$/p-Si and Al/Alq$_3$/n-Si device structures. Effects of Alq$_3$ film thickness on photoluminescence and electrical properties of the Al/Alq$_3$/p-Si structures have been investigated recently [9]. Here in this work, we concentrate on thickness and preparation conditions of Alq$_3$ films on electrical properties of the Al/Alq$_3$/p-Si and Al/Alq$_3$/n-Si hibrid device structures. The characteristic parameters as barrier height, ideality factor and series resistance evaluated from the current–voltage (*I–U*) plots have been compared with those of conventional M-S junctions.

2. EXPERIMENTAL

2.1. Preparation of the device structures

Alq$_3$ compound of 98 % purity, purchased from Aldrich company have been used in this work for thin film preparation. Wafers of boron-doped p-type Si (d ~350 nm) with polished (100) surface and electrical resistivity of (3 – 5) Ωcm as well as phosphor-doped n-Si(100) with resistivity $\rho = (0.5 – 1.0)$ Ωcm were used as conducting substrates. Aluminum exhibiting relatively low work function value (4.2 eV) was used as a top electrode material for the prepared device structures.

The substrates were cleaned in acetone to remove organic contaminants. In following, insulating SiO$_2$ overlayer (d of about 200 nm) was grown onto the substrates by their oxidation in a dry air at $T \cong 1100$ °C. The substrates were coated by a positive photoresist to be patterned using a standart optical photolithography technique. Sets of squares (1×1 mm^2) with chemically

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removed insulating SiO_2 layer were formed both on n- and p-type Si substrates. Just after chemical etching, the wafers were rinsed thoroughly in distilled water followed by drying in N_2 atmosphere.

2.2. Device fabrication

The substrates were installed into the deposition chamber just after chemical etching. Alq_3 thin films were thermally evaporated in vacuum under residual gas pressure of 8×10^{-4} Pa. Tanthalum boat was used for evaporation of the powdered organic material. Temperature of the boat was increased gradually up to a maximal value of 250 ºC to avoid decomposition of the organic compound. Evaporation ratio of the organic film was of about 0.03 nm/s. Distance between the evaporator and the substrates of about 10 cm has been chosen to reduce possible heating of the films during their deposition. preparation conditions of the evaporated organic Alq_3 films as substrate temperature (T_s), evaporation ratio (ER) and film thickness (d), are summarised in Table 1.

Table 1. Preparation conditions of the evaporated Alq_3 and Al films

Film	T_s ºC	ER, nm/s	d, nm
Alq_3	20	0.03	80 ÷ 220
Al	20	0.4 ÷ 0.6	100 ÷ 150

For a comparison, in this work Alq_3 films ($d = 300$ nm ÷ 400 nm) were also prepared onto the the patterned Si wafers by spin coating technology (rotation spead ~1000 rpm) using formaldehide-based Alq_3 solution. Finally, these coatings were dried by keeping the substrates at 150 ºC in a dry air atmosphere.

Morphology of the organic films was investigated by Scanning probe atomic force microscope (AFM) „Dimension 3100“ (Digital Instruments) operating in a taping mode regime while their thickness was measured by Dektak 6M profillometer.

To prepare top electrodes for electrical measurements, Al coatings were evaporated onto non-heated organic films in vacuum at a residual pressure $P \sim 8\cdot10^{-4}$ Pa (see Table 1). Special mask was used to form series of electrical contacts onto top surface of the device structures while liquid In-Ga alloy applied to a grooved back side of the substrates ensured low resistance ohmic contacts to the conducting n-Si and p-Si wafers. Special electrical measurements revealed ohmic behaviour of the In-Ga/Si interface with relatively low values of contact resistivity ($\rho_c < 1.0\ \Omega cm^2$) due mainly to high defect density occuring on mechanically damaged Si surface.

2.3. Measurement setup

The device structures were mounted onto a holder stage with two probing needles connected to the top and bottom electrodes. *I–U* characteristics of the prepared diode structures were measured at room temperature in an atmosferic ambient under dark condition. Schematic structures of the device structures without and with the organic layer (Al/Si and Al/Alq_3/Si) are shown in Fig. 1.

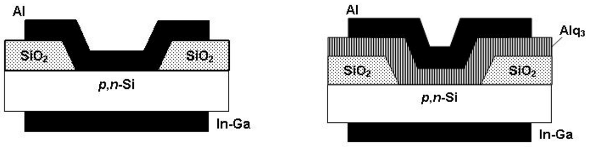


Fig. 1. Schematic drawings of cross-sectional views of the Al/Si and Al/Alq_3/Si device structures

3. RESULTS AND DISCUSSIONS

3.1. Surface morphology of the Alq_3 films

AFM surface images of the organic Alq_3 films prepared onto Si substrate by vacuum evaporation and spin coating are shown in Fig. 2, a, and Fig. 2, b, respectively. The average surface roughness (RMS) was found to be of about 3.1 nm for the evaporated Alq_3/Si film while relatively flat surface with less pronounced island-like features resulting reduced surface roughness (RMS of about 1.2 nm) has been indicated for similar spin coated films.

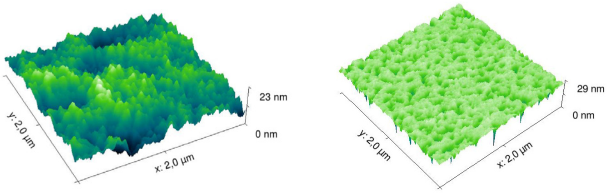
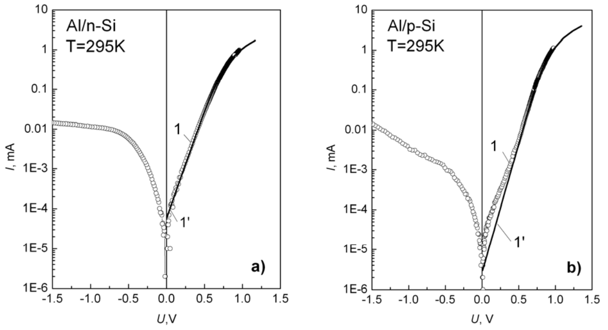


Fig. 2. AFM surface image of the Alq_3 thin films deposited on Si substrates by vacuum evaporation (a) and by using spin coating technology (b)

3.2. Electrical properties of the diode structures

Fig. 3, a, b, shows typical semi log plots of *I–U* characteristics measured at $T = 295$ K for the fabricated Al/n-Si (Fig. 3, a) and Al/p-Si (Fig. 3, b) diode structures in a case of forward and reverse bias. Note that forward bias for the Al/n-Si and Al/p-Si diode structures corresponds, respectively, to a positive and negative voltage applied to the top Al electrode. Relatively low values of zero bias resistance indicated for the diode structures show that thickness of native dielectric SiO_2 oxide occurring at the Al/Si interface should be rather small and have only negligible influence on the *I–U* curves.



a b

Fig. 3. Typical *I–U* characteristics measured for the Al/n-Si (a) and Al/p-Si (b) heterostructures at 295 K in a case of forward and reverse bias. Fitting curves (1') have been obtained using Schottky thermoionic emission model

Following Fig. 3, a, b, we point out exponential growth of current with forward bias in a range of relatively low U values ($U_F < 0.8$ V). Exponential growth of current with forward bias and clearly defined rectification behavior is typical for Schottky junction and demonstrate presence of a potential barrier in the interface between semiconductor and metal (Al).

Certain saturation behavior of current with U_F increasing seen from Fig. 3, a, b, for the diode structures at higher forward bias values show that current at high U values is limited by a series resistance of the diodes while deviation from exponential low at low forward voltages (see Fig. 3, b) demonstrates shunting behavior due to tunneling or a possible demage of the potential barrier.

Typical forward *I–U* characteristics measured for the prepared Al/Alq$_3$/n-Si and Al/Alq$_3$/p-Si diode structures containing interlaying Alq$_3$ films of different thickness are displayed in Fig. 4, a, and b, respectively. Exponential growth of the current with forward voltage has been indicated both for the Al/Alq$_3$/n-Si and Al/Alq$_3$/p-Si heterostructures (see clearly defined linear portions over several orders of forward bias values in the semi log *I–U* plots). Thus, one can conclude that all the heterostructures behave like a conventional Schottky diode (M-S junction).

Comparing results for the diode structures displayed in Fig. 3, a, b, and Fig. 4, a, b, one can certify that insertion of Alq$_3$ film results noticeable modification of electrical properties. Certainly, we point out reduced forward and reverse current values, increased zero bias resistance and improved rectification property of the hybrid organic-inorganic diode structures in comparison to Al/n-Si and Al/p-Si diodes (see Fig. 3, a, b).

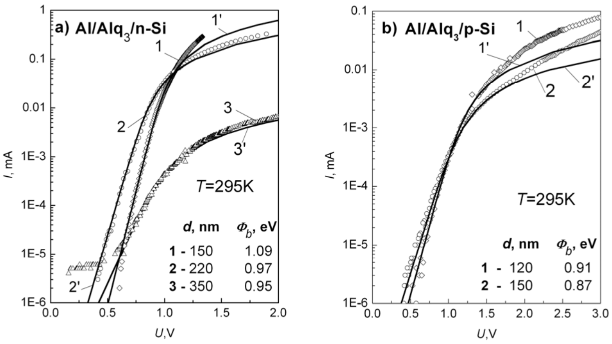


Fig. 4. Forward *I-U* characteristics measured at 295 K for the Al/Alq$_3$/n-Si (a) and Al/Alq$_3$/p-Si (b) heterostructures with thermally evaporated (1, 2) and spin coated (3) interlaying Alq$_3$ film. The corresponding fitting curves (1'–3') have been calculated using Schottky thermionic emission model

3.3 Modelling of the I-U characteristics

Carrier transport in the diode structures has been modeled assuming presence of a potential barrier at the M-S interface and taking into account dominating role of Schottky thermionic emission. Current flowing through a uniform M-S interface due to the thermionic emission in a case of applied forward bias can be expressed as [2]:

$$I = I_0\left[\exp\left(\frac{q(U - IR_s)}{nkT}\right) - 1\right], \qquad (1)$$

where U is the applied voltage, q is the electron charge, R_s is the series resistance of the diode, k is Boltzman constant, n (≥ 1) is the ideality factor, T is the absolute temperature and I_0 is the saturation current defined as:

$$I_0 = AA^*T^2 \exp\left(-\frac{q\Phi_b}{kT}\right), \qquad (2)$$

here A is the diode area, A^* is the effective Richardson constant, ($A^* = 32.0$ Acm^{-2}K^{-2} and 120 Acm^{-2}K^{-2} for p-Si, and n-Si, respectively) and Φ_b is zero bias barrier height.

I_0 has been evaluated by extrapolating linear regions of the semi log forward *I–U* curves to zero applied voltage. The Φ_b values were calculated from Eq. (2) while n values have been estimated from the slopes of linear regions in semi log forward *I-U* plots.

Major electrical parameters of the junctions, namely, the ideality factor, the saturation current and zero bias barrier height estimated for the prepared hybrid organic-inorganic heterojunctions by fitting their experimental *I–U* dependences to those calculated from Eq. (1) and Eq. (2) are summarized in Table 2. For a comparison, in the same table similar values for the conventional Al/n-Si and Al/p-Si diodes each averaged over 8 device structures are displayed.

Table 2. Electrical parameters of the diode structures: thickness of the interlaying Alq$_3$ film, d_{Alq3}, zero bias barrier height, Φ_b, ideality factor, n, series resistance, R_s, and the rectification ratio K ($U = \pm 1$ V) estimated from the measured *I–U* plots

Structure	d_{Alq3}, nm	Φ_b, eV	n	R_s, kΩ	K
Al/Alq$_3$/n-Si	85	1.10	1.5	0.4	1800
	100	0.92	2.3	0.4	1200
	110	1.00	1.9	0.6	2600
	150	1.09	1.6	1.4	700
	220	0.97	2.1	3.2	2100
	170	0.97	1.7	1.0	860
	180	0.95	2.0	1.4	1100
	200	0.90	2.0	1.8	3200
Al/Alq$_3$/n-Si (spin coating)	350	0.93	3.3	150.0	340
Al/Alq$_3$/p-Si	80	0.77	2.8	12.0	270
	90	0.80	2.7	23.0	500
	100	0.77	3.2	40.0	380
	120	0.91	3.5	50.0	400
	150	0.87	3.8	110.0	400
	200	0.82	3.5	110.0	250
Al/n-Si	0	0.77	2.2	0.18	180
Al/p-Si	0	0.68	2.4	0.16	250

One can see from Table 2 that insertion of Alq$_3$ film resulted increased barrier height values both for Al/Alq$_3$/n-Si (0.90 eV ÷ 1.1 eV) and Al/Alq$_3$/p-Si (0.77 eV ÷ 0.91 eV) diode structures when compared to similar data obtained for the Al/n-Si (0.77 eV) and Al/p-Si (0.68 eV) diodes. Noticible increase of Φ_b caused by Alq$_3$ film insertion certifies formation of a dipole layer by polar organic Alq$_3$ molecules [3, 4].

Note that all the diode structures prepared in this work (either with or without Alq$_3$ interlayer) showed non-ideal

$I–U$ behaviour with $n > 1$. Moreover, significant variation of both n and Φ_b values have been indicated.

Relatively large n values can be attributed to a number of factors, namely, to an interfacial insulator layer (SiO_2), presence of surface states, possible influence of series resistance and formation of barrier inhomogeneities at the M-S interface [10, 11].

It is important to note also rather high R_s values of the hybrid organic-inorganic diodes compared to those estimated for the Al/n-Si and Al/p-Si structures as well as an increase of R_s values with Alq_3 film thickness (see Fig. 5). Higher R_s values estimated for the Al/Alq_3/p-Si diode structures may be understood taking into account that Alq_3 demonstrates preferiantially n-type conductivity and thus it is highly resistive in a case of forward biased Al/Alq_3/p-Si structures when holes are injected from p-Si. This property may be supported by the fact that Eq. (1) with R_s as a constant value is not a good approximation to explain $I–U$ behaviour of the Al/Alq_3/p-Si device structures at high forward bias values. Significant deviation between yhe experimental points at numerical data seen for the heterostructures in Fig. 4, b, at high U values ($U > 1$ V) show, probably, importance of space charge limited current ($I \sim U^2$) in the organic interlayer [1].

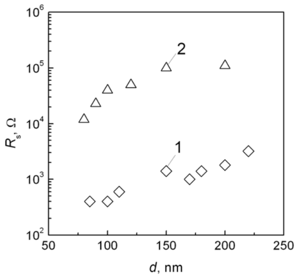


Fig. 5. Series resistance of the Al/Alq_3/n-Si (1) and Al/Alq_3/ p-Si (2) heterostructures versus thickness of the evaporated Alq_3 film

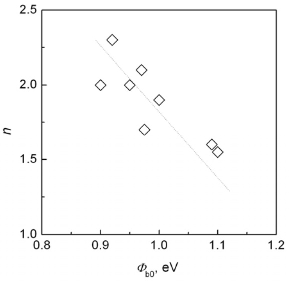


Fig. 6. Correlation between ideality factor and barrier height values for the Al/Alq_3/ n-Si heterostructures

n values estimated in this work for the diode structures with Alq_3 films (see Table 2) are typical for similar device structures containing various organic interlayers. Non-ideal behavior of the structures can be understood taking into account a role of inhomogeneity on formation of Schottky barrier [7, 10 – 12].

In Fig. 6 one can notice certain correlation between n and Φ_b values for the prepared Al/Alq_3/n-Si diodes. It is worth noting, however, that in a case of large n values ($n > 2$) the barrier height can not be estimated precisely. Thus, we conclude that the observed increase of n values with d as well as certain correlation between n and Φ_b for the Al/Alq_3/n-Si diodes (see Fig. 6) should be related either to barrier inhomogeneity or high R_s values caused by highly resistive organic interlayer.

4. CONCLUSIONS

1. Hybrid organic-inorganic Al/Alq_3/n-Si, Al/Alq_3/p-Si diode structures with thermally evaporated Alq_3 film demonstrated increased barier height values and improved rectification property compared to similar Al/p-Si and Al/n-Si device structures.

2. Increased barrier height values: 0.9 eV ÷ 1.1 eV and 0.77 eV ÷ 0.91 eV estimated for the Al/Alq_3/n-Si and Al/Alq_3/p-Si device structures, respectively, certify presence of an interface dipole induced by polar Alq_3 molecules.

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