

RUBRENE & PENTACENE BASED 2-TERMINAL ORGANIC ELECTRONIC DEVICES

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ABSTRACT

We present the study of both Ohmic and Schottky junction in metal/organic semiconductor/metal sandwiched devices based on two promising organic semiconductors, Pentacene and Rubrene. Two types of devices have been considered, one with carrier injecting contacts on both sides and other with carrier blocking contact on one side and carrier injecting contact on the other side (Schottky diode). The Current-Voltage characteristics show the difference in transport properties of the two types of devices. In the Schottky diode, the presence of depletion region due to band bending at metal/organic interface is established in reverse bias. For devices with both side flat band contacts, the J-V characteristics is symmetrical for forward and reverse bias. Further from the fitting parameters the value of lattice constant 'a' obtained is also close to that obtained by experimental methods.

I. INTRODUCTION

The transport properties of charge carriers in organic molecular semiconductors (OMS) have been studied extensively in recent years in order to understand the fundamental phenomena which control the operation of the devices based on these materials [1-6]. This is of great importance for synthesizing better materials so as to improve the performance of the devices. One of the most important parameters which determine the performance of OMS based devices is the mobility of the charge carriers. Since the organic molecules are held together loosely by weak Van der Waals type of intermolecular coupling and long range order is absent in these molecules, therefore the electronic wave functions are localized on molecular sites. Hence charge carrier transport occurs by hopping among the molecular sites which have energy distribution assumed to be Gaussian in shape [3,5]. Consequently, the mobility is strongly dependent on temperature, electric field and also concentration of charge carriers. The non-Arrhenius temperature dependence of mobility and Poole-Frenkle behavior for field dependence of mobility has been described by many researchers and several models have been put forward [7-15]. But in many cases these two factors become insufficient for explaining the charge carrier mobility in organic semiconductors. Hence the effect of the third factor i.e, dependence of carrier density on charge carrier mobility has to be included which has been done by very few groups [10]. Further to establish any microscopic charge transport model, macroscopic measurable quantities have to be correlated with some microscopic parameter. In most of the works current transport has been



modeled by a single parameter i.e, width of the Gaussian density of states (GDOS), σ . But the transport properties in organic materials are also sensitive to molecular arrangement i.e, solid state packing in thin films, which have been overlooked in these works. It is therefore essential to study the dependence of transport properties on microscopic parameters such as molecular packing and lattice parameter. To have a proper understanding of the microscopic charge carrier transport in molecular systems, it is of great importance to carry out experimental studies of current-voltage (J-V) characteristics and their theoretical interpretation taking into account the effects of carrier concentration, electric field and temperature with correlation to microscopic parameters such as lattice constant.

Among the molecule-based organic semiconductors Pentacene and Rubrene are the most promising materials with very high carrier mobility required for all organic active matrix light emitting displays and organic integrated circuits. Both Pentacene and Rubrene are hole transport materials with HOMO lying at 5.0eV and 5.4eV respectively. Moreover Pentacene and Rubrene have a typical thin film morphology controlled by diffusion limited aggregate (DLA) [16-18] which is suitable for measuring microscopic lattice parameter. In this paper we have carried out an extensive study of the charge transport in Pentacene and Rubrene based organic diodes through the quantitative understanding of the dependence of J-V characteristics on microscopic parameters. The J-V characteristics of both ohmic contact and Schottky contact diodes in forward and reverse bias condition have been studied through experiments and theoretical interpretation of the J-V characteristics including the effects of carrier concentration, electric field and temperature, has also been presented in this paper.

II. THEORY

Recently, it has been realized that the parameter, carrier density p , which has been overlooked, is extremely important for the explanation of large difference of carrier mobility in diode and transistor. Hence, to explain J-V curves, in addition to temperature and electric field, carrier density dependence of μ i.e. $\mu(p, F, T)$ has to be invoked. It is desirable to put forward a unified description of F , T and p dependence of μ for the description of SCLC in diode. It has been shown by Pasveer et al [10] that μ can be parameterized as

$$\mu(T, p, F) = \mu(T, p) f(T, F) \quad (1)$$

It has been shown, based on numerical simulation of master equation for variable range hopping,

$$\sum_{i \neq j} [w_{ij} p_i (1 - p_j) - w_{ji} p_j (1 - p_i)] = 0, \text{ where } p_i (p_j) \text{ is the probability that site } i(j) \text{ is occupied and } w_{ij} (w_{ji}) \text{ is}$$

the transition rate from site i to j (j to i), that $\mu(T, p)$ can be parameterized as

$$\mu(T, p) = \mu_0(T) \exp \left[\frac{1}{2} (\hat{\sigma}^2 - \hat{\sigma}) (2pa^3)^\delta \right] \quad (2)$$



Where a is lattice constant $\hat{\sigma} = \sigma / k_B T$, $\mu_0(T) = \mu_0 c_1 \exp[-c_2 \hat{\sigma}^2]$, $\delta = 2 \frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln(\ln 4)}{\hat{\sigma}^2}$ and

$\mu_0 = \frac{a^2 v_0 q}{\sigma}$ with $c_1 = 1.8 \times 10^{-9}$, $c_2 = 0.42$ and q is the electronic charge. Based on Bassler's GDM for non-

Arrhenius temperature dependence of μ , $f(T, F)$ can be parameterized as

$$f(T, F) = \exp \left\{ 0.44 (\hat{\sigma}^{3/2} - 2.2) \left[\sqrt{1 + 0.8 \left(\frac{Fqa}{\sigma} \right)^2} - 1 \right] \right\} \quad (3)$$

Where a is the lattice constant. In the limit of low carrier density, $\mu \propto \exp[-c_2 \hat{\sigma}^2]$, which is nothing but Bassler's results for temperature dependence of μ under GDM. Once the deconvolution of $\mu(p, F, T)$ can be obtained, using the Eq. (1)-(3) the J-V curves can be simulated by solving the following equations self consistently

$$J = qp(x)\mu[T, p(x), F(x)]F(x) \quad (4)$$

$$\frac{dF(x)}{dx} = q \frac{p(x)}{\epsilon_0 \epsilon_r}, \quad (5)$$

$$V = \int_0^L F(x) dx \quad (6)$$

III. EXPERIMENTAL DETAILS

High purity (>99.999%) triple sublimed Pentacene and Rubrene, procured from Sigma Aldrich Chemical Co. USA has been used for this study to avoid any Chemical impurity induced traps. A very low evaporation rate ($\sim 0.1 \text{ \AA/sec}$) and high growth temperature ($\sim 90^\circ\text{C}$) are needed to obtain surface morphology required for the investigation [19-21]. The devices studied consist of Pentacene and Rubrene sandwiched between ITO and Au or Al and Au. The Organic layers were deposited in an oil free evaporation system at a base pressure of 2×10^{-6} Torr on ITO grown on glass or SiO_2/Si substrate and then top metal electrode was evaporated on organic layer. The J-V characteristics were measured in rough vacuum (10^{-2} mbar) using Keithly picoammeter and Keithly voltage sources. All the experimental data have been obtained from School of Physical Sciences, JNU, New Delhi.

IV. RESULTS AND DISCUSSION

As stated earlier, the J-V characteristics of two types of devices have been studied in this work. The first type is ohmic contact type where ITO and Au having work functions of 4.8eV, 5.1eV respectively are used for making metal contacts. Pentacene and Rubrene have HOMO at 5eV and 5.3eV. Therefore ITO/Pentacene/Au and ITO/Rubrene/Au structure will not form any barrier for hole injection at the Pentacene/Au or Rubrene/Au interface but there will be a small barriers of 0.2eV and 0.5eV for hole injection at ITO/Pentacene and ITO/Rubrene interface respectively. The results of all 20 devices with active layer grown under almost identical conditions on same

substrate are almost same, with variation smaller than 2-3 times of the current density. This may be due to the variation in the contact electrode area.

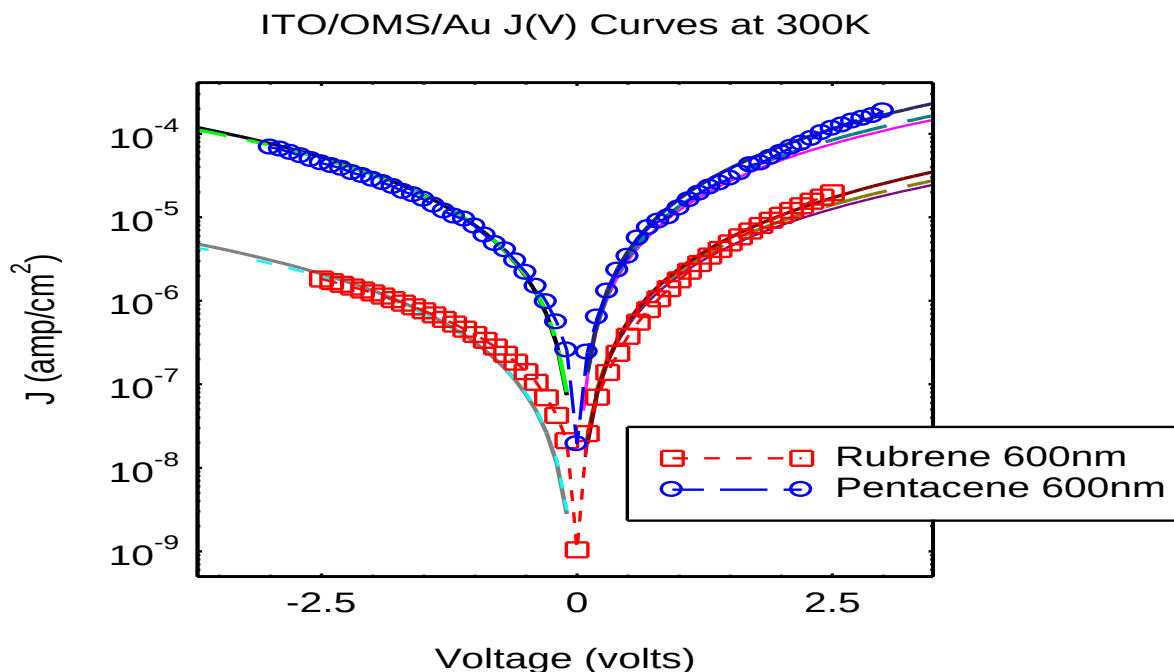


Fig 1. J(V) curves of ITO/Pentacene600nm/Au and ITO/Rubrene600nm/Au at 300K for both forward and reverse bias. The markers show the experimental data. Thick solid lines show the theoretical fitting using $J \propto \mu(p,T,F)$ and dashed lines are for $J \propto \mu(T,F)$ and thin solid lines are for $J \propto V^2$.

Fig. 1 shows the J(V) characteristics of ITO/Pentacene/Au and ITO/Rubrene/Au hole only diodes at 300K. The current was measured for both positively biased Au and ITO electrode. It is observed that ITO/Pentacene/Au and ITO/Rubrene/Au devices show weak asymmetric behavior i.e., a difference of about one order of magnitude in currents when bias polarity is reversed at a bias voltage of 2.5V. The asymmetric behavior is little more prominent in Rubrene because the barrier at ITO/Rubrene interface is more than that of ITO/Pentacene interface. In both the devices J(V) characteristics are non-linear and show $J \propto V^n$ with $n \geq 2$. Further, Fig. 2 shows that in the low bias region (0.1-1V), current vary quadratically indicating space charge limited conduction (SCLC) but beyond this region slope increases gradually reaching close to 3 around 3V. It is to be noticed that ohmic in the low bias region is absent indicating absence of leakage path for current through organic layer and intrinsic conduction due to impurities. Departure from $n=2$ was initially attributed to field dependence of mobility but recently it has been shown that enhancement of SCLC is due to combined effect of electric field and carrier concentration dependence of mobility. With the increase in carrier density, the lower energy sites are gradually filled leading to lowering of hopping barrier to neighboring sites and hence in increase of carrier mobility. To show the effect of carrier

concentration the $J(V)$ characteristics have been theoretically fitted and compared using three different models: (i) $J \propto V^2$ (ii) $J \propto \mu(F,T)$ and $f(T,F)$ given by equation (3) and (iii) using Pasveer[10] model with $J \propto \mu(p,F,T)$ given by equation (1), (2), and (3). It can be seen that in both cases i.e., current either being injected from Au or from ITO, $J-V$ characteristics can be fitted with $J \propto V^2$ in low bias region. But at higher bias voltages the fitting is poor. When current is injected from Au electrode the whole range of data is best fitted by taking the dependence of μ on both electric field F and carrier density p . There are three fitting parameters μ_0 , σ and a which are determined by optimizing the fitting that are given in TABLE I. When current is injected from ITO electrode, it is clear that the whole range of data can be well fitted with field dependent mobility only. To account for the lower value of current at the same bias compared to forward direction, an extra factor has been introduced in the Pasveer model shown in equation (7).

$$\mu(T, p, F) = \mu(T, p) f(T, F) \exp\left(\frac{-\phi_B}{K_B T}\right) \quad (7)$$

Where ϕ_B is a factor depending on the barrier at ITO/Pentacene or ITO/Rubrene interface and K_B is the Boltzmann constant. The value of ϕ_B obtained from optimized fitting that is given in TABLE II. All other fitting parameters are kept same as in forward condition.

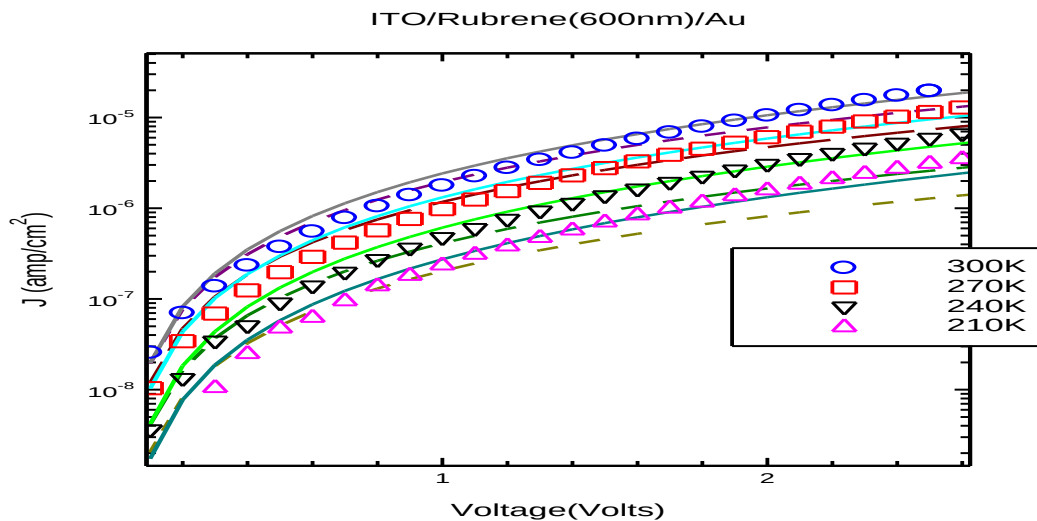


Fig 2. $J(V)$ curves of ITO/Pentacene/Au in forward bias. The markers show the experimental data, solid lines show the theoretical fitting using $J \propto \mu(p, T, F)$ and dashed lines are for $J \propto \mu(T, F)$.

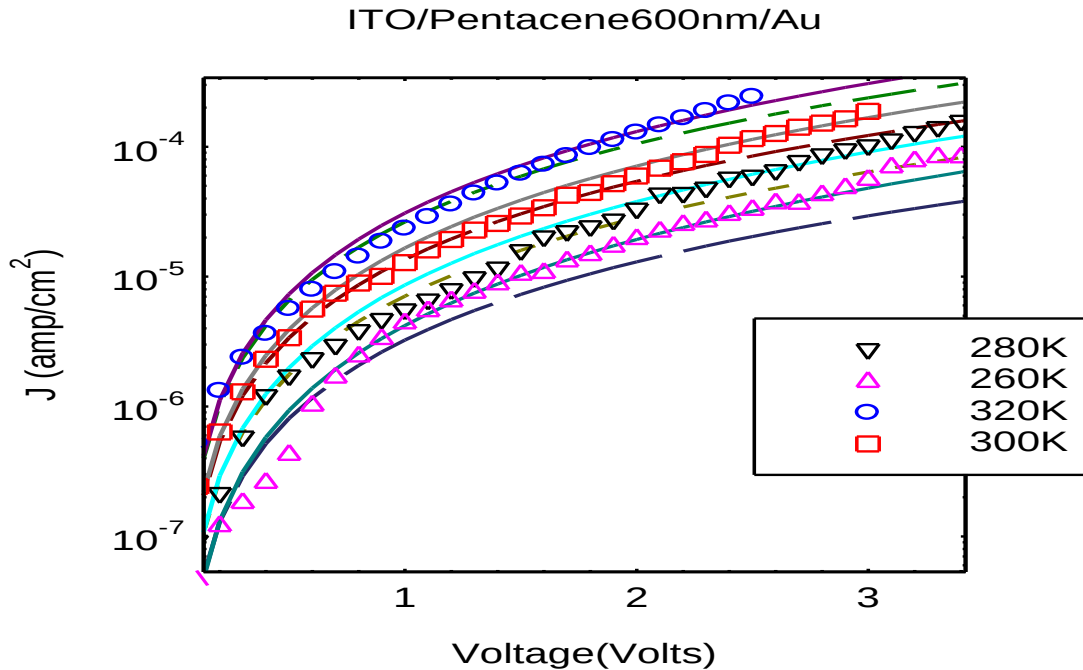


Fig 3. $J(V)$ curves of ITO/Rubrene/Au. The markers show the experimental data, solid lines show the theoretical fitting using $J \propto \mu(p, T, F)$ and dashed lines are for $J \propto \mu(T, F)$.

Fig. 2 and Fig. 3 show the temperature dependence of J-V characteristics of ITO/Pentacene/Au and ITO/Rubrene/Au hole only diodes respectively. All the devices have a length of 600nm and the experimental J-V curves have been obtained with Au positively biased and ITO negatively biased. The theoretical fitting has been shown for both $J \propto \mu(F, T)$ and $J \propto \mu(p, F, T)$ models. It is clear that quality of the fit is improved substantially including carrier density dependence of μ . Three fitting parameters μ_0 , σ and a which are determined by optimizing the fitting and are given in TABLE I. The fitting of J-V curves gives almost same values of the fitting parameters at all temperatures which show the consistency of fitting. The lattice constant a is the minimum hopping distance of carriers while going from one electrode to another. It is interesting to note that the theoretical fitting of J-V curves using equations (4)-(6) generates values of a lying between 1.5-1.7nm which is very close to the value obtained by GIXRD [22]. The values of σ for different temperatures lie between .113eV to .107eV for Pentacene and .122eV to .100eV in Rubrene and these values are close to values obtained directly from temperature dependent mobility ($J \propto V^2$ model) at low bias. A comparison of the values of mobility at different temperatures obtained from $J \propto V^2$ model and $J \propto \mu(p, T, F)$ is also given in TABLE I.

Table I

Device	T (K)	μ_0 (m ² /Vs) from fitting	a (nm)	σ (eV)		$\mu(T)$ (cm ² /Vs)	
				From Fitting	From Fitting	From Fitting	From $J \propto V^2$
ITO/Pentacene/Au	320		1.7	.113		1.7×10^{-5}	2.4×10^{-5}
	300		1.7	.111		8.5×10^{-6}	9×10^{-6}
	280	1000	1.5	.109	.103	3.8×10^{-6}	4.1×10^{-6}
	260		1.5	.107		1.4×10^{-6}	2.1×10^{-6}
ITO/Rubrene/Au	300		1.5	.122		1.0×10^{-6}	3.0×10^{-6}
	270		1.5	.114	.1104	5.1×10^{-7}	5.3×10^{-7}
	240	600	1.5	.107		1.6×10^{-7}	1.5×10^{-7}
	210		1.5	.100		5.6×10^{-8}	7.0×10^{-8}

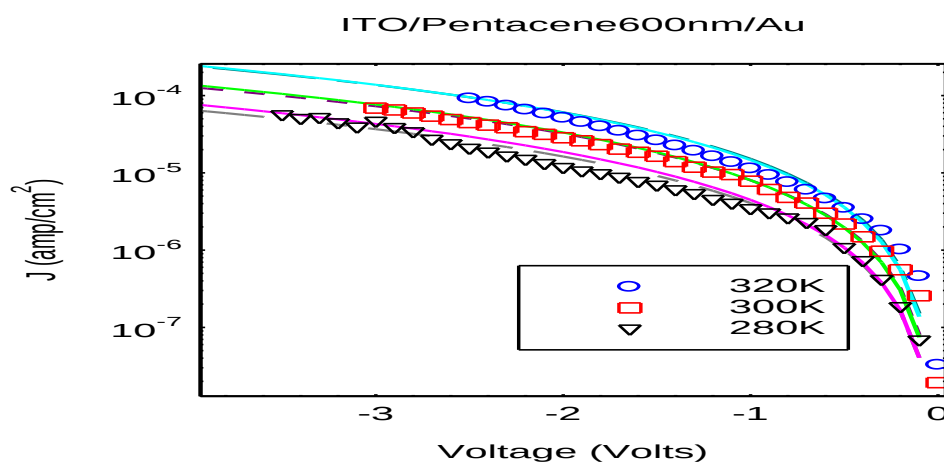


Fig 4. J(V) curves of ITO/Pentacene/Au in Reverse bias. The markers show the experimental data, solid lines show the theoretical fitting using $J \propto \mu(p, T, F)$ and dashed lines are for $J \propto \mu(T, F)$.

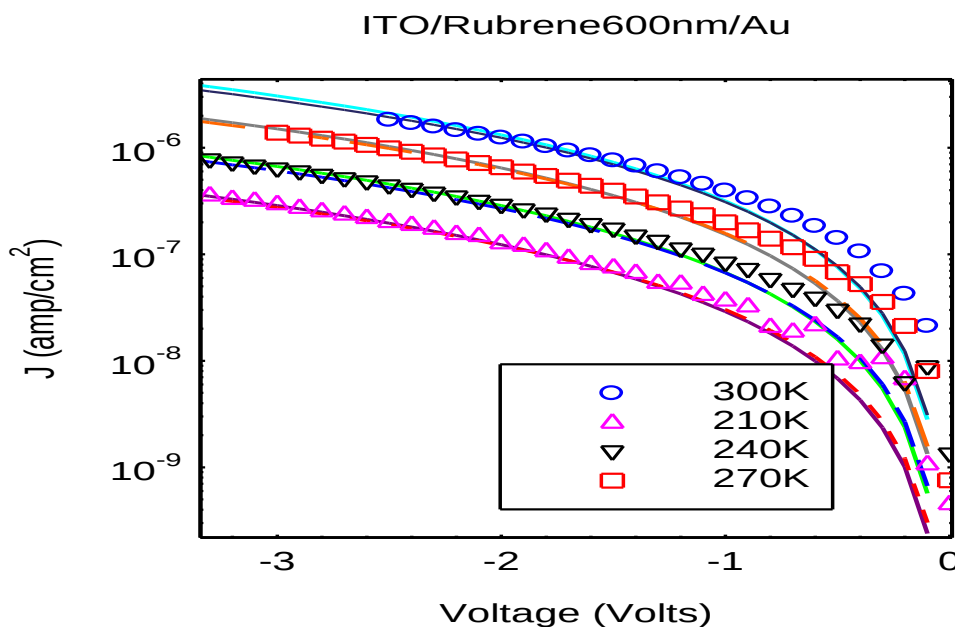


Fig 5. $J(V)$ curves of ITO/Rubrene/Au in Reverse bias. The markers show the experimental data, solid lines show the theoretical fitting using $J \propto \mu(p,T,F)$ and dashed lines are for $J \propto \mu(T,F)$.

In Fig. 4 and Fig. 5 the temperature dependence of J-V curves of ITO/Pentacene/Au and ITO/Rubrene/Au diodes for negatively biased Au electrode and positively biased ITO electrode is shown. In these curves also the theoretical fitting has been compared for both models using $J \propto \mu(p,T,F)$ and $J \propto \mu(T,F)$ [23,24]. As observed earlier the whole range of data can be well fitted with field dependent mobility only. The fitting parameters are given in TABLE II. It is observed that all the fitting parameters remain same as forward bias condition and the lowering of the current in reverse bias can be explained by the extra factor given in equation (7).

Table II

Device	Temperature (kelvin)	Φ_B in eV	
		$J \propto \mu(p,F,T)$	$J \propto \mu(F,T)$
ITO/Pentacene/Au	320		.012
	300	.015	.01
	280		.006
	300	.045	.04

ITO/Rubrene/Au	270		.035
	240		.025
	210		.017

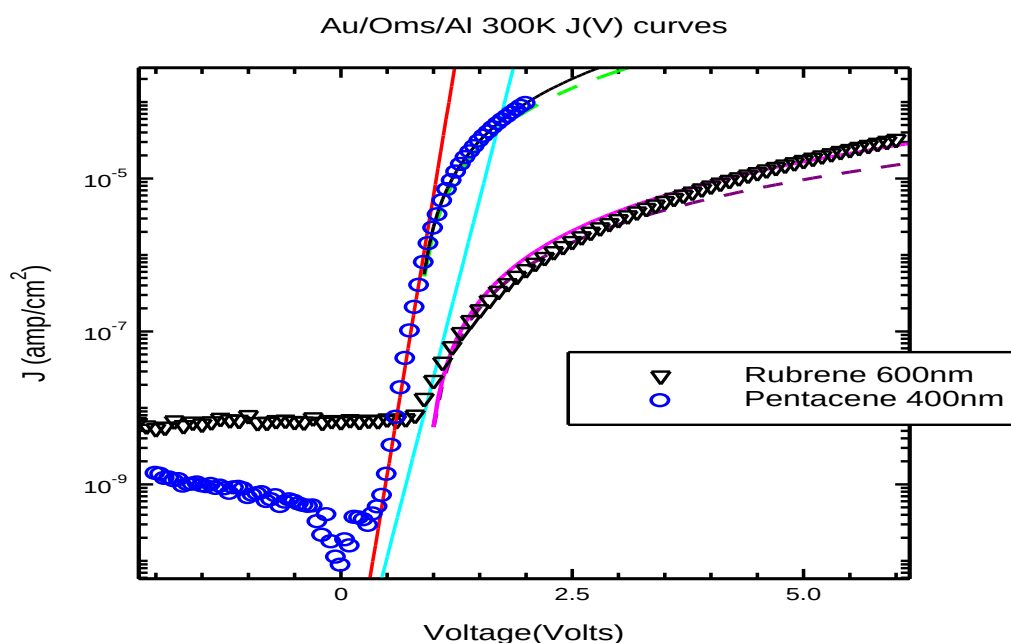


Fig 6. J(V) curves for Au/Pentacene400nm/Al and Au/Rubrene600nm/Al Schottky diodes for both forward and reverse bias. The markers show the experimental data, solid lines show the theoretical fitting using $J \propto \mu(p,T,F)$ and dashed lines are for $J \propto \mu(T,F)$. The straight line shows $J \propto \exp\left[\frac{qV}{gK_B T}\right]$ with g as the ideality factor.

factor.

The second type of devices used for studying the charge transport properties of Pentacene and Rubrene are Al/Pentacene/Au and Al/Rubrene/Au Schottky diodes. According to Mott-Schottky scheme for energy level alignment there would be no barrier at Pentacene/Au and Rubrene/Au interface, but a barrier of 0.8eV and 1.1eV will exist for holes at Al/Pentacene and Al/Rubrene interface [25,26]. Fig. 6 shows the J-V curves in Al/Pentacene/Au and Al/Rubrene/Au hole only diodes. The current due to hole injection from positively biased Au was measured and then current due to hole injection from Al was measured by reversing the polarity of the bias voltage. As expected, the J-V characteristics of both Al/Pentacene/Au and Al/Rubrene/Au devices show asymmetric



behavior with rectification properties. There is a difference of five orders of magnitude in currents when the bias polarity is reversed. When Al is positively biased the current is injection limited and is reduced due to the existence of a Schottky energy barrier at Al/Pentacene and Al/Rubrene interface. When Au is positively biased the current increases exponentially for bias voltage $V < 1V$ due to effective lowering of the Schottky barrier in the forward bias. In this region the current follows Mott-Schottky relation

$$J_H = J_0 \left[\exp \left(\frac{qV}{gK_B T} \right) - 1 \right] \quad (8)$$

Where J_0 is the saturation current, g is the ideality factor and V is the applied bias. For bias voltages above 1V, J-V characteristics show power law dependence i.e., $J \propto V^n$ due to SCLC. Here also the theoretical fitting has been done for both $J \propto \mu(p,T,F)$ and $J \propto \mu(T,F)$ models. It is evident from the fitting that at low bias i.e., upto 1.5V for Pentacene and 2V for Rubrene the fitting is equally well with both the models but at higher bias $J \propto \mu(p,T,F)$ fits better than $J \propto \mu(T,F)$. TABLE III gives the fitting parameters for optimized fitting. Here also the value of $a = 1.5nm$ gives very good agreement with the experimental data. A comparison of the value of $\mu(T)$ obtained in Pentacene and Rubrene from fitting with $J \propto \mu(p,T,F)$ at 300K and values obtained directly from temperature dependent mobility ($J \propto V^2$ model) at low bias is also given in TABLE III. Therefore from all the theoretical fittings it is evident that the dependence of carrier mobility on charge carrier concentration has a substantial effect on the J-V characteristics of both ohmic and Schottky diodes in the forward bias SCLC region.

Table III

Device	T(K)	μ_0 (m^2/Vs)	a (nm)	σ (eV)	$\mu(T)$ (cm^2/Vs)	
					From Fitting	From J $\propto V^2$
Au/Pentacene/Al	300	1000	1.5	.11	9.78e-6	1.2e-5
Au/Rubrene/Al	300	600	1.5	.13	2.53e-7	3e-7

The charge carrier transport in Pentacene and Rubrene have been analyzed by correlating structural parameters with current-voltage characteristics. In this work a charge transport model has been implemented which describes the dependence of macroscopic parameter on microscopic parameter. The effect of carrier density on mobility of charge carriers has been studied by quantitative analysis of the current-voltage characteristics of different Pentacene and Rubrene based two-terminal devices.

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