BIAS AND TEMPERATURE DEPENDENT CHARGE TRANSPORT IN HIGH MOBILITY COBALT-PHTHALOCYANINE THIN FILMS

Technical Physics and Prototype Engineering Division

M. Senthil Kumar
Department of Physics, Indian Institute of Technology, Mumbai

The paper was awarded the First Prize in the category of Best Poster at the International Symposium on Nanostructured Materials: Structure Properties and Applications, held at Jalandhar, during Oct. 28-29, 2009

Abstract

The temperature dependent current-voltage ($J-V$) characteristics of highly-oriented cobalt phthalocyanine films (rocking-curve width = 0.11°) deposited on (001) LaAlO$_3$ substrates are investigated. In the temperature range 300-100K, charge transport is governed by bulk-limited processes with a bias dependent crossover from ohmic ($J\sim V$) to trap-free space-charge-limited conduction ($J\sim V^2$). The mobility ($\mu$) at 300 K has a value of $\sim 7$ cm$^2$V$^{-1}$s$^{-1}$ and obeys Arrhenius-like ($\ln \mu \sim 1/T$) behavior. However, at temperatures <100 K, the charge transport is electrode-limited, which undergoes a bias dependent transition from Schottky ($\ln J \sim V^{1/2}$) to multistep-tunneling (conductivity varying exponentially on the inverse of the square-root of electric field).

Keywords: Phthalocyanine, rocking curve, mobility, multistep tunneling

Introduction

In recent years, phthalocyanines (Pc’s) have received increasing attention as a promising molecular semiconductor for low cost and large area electronics$^1$ due to their advantageous properties, such as, high stability up to 400°C, unaffected by strong acids and bases, chemical tunability (achieved by replacing metal atoms at the center of the Pc ring and functionalizing their side groups) and commercial availability at cheap price. For electronics applications, thin films of Pc’s offer unique advantage over other molecular semiconductors (e.g. pentacene etc.) in terms of a very small charge injection barrier at the electrode/film interface. Ultraviolet photoemission spectroscopy (UPS) measurements carried on Au/Pc film interface revealed that the barrier height for the hole injection - difference between the Au Fermi level and the highest occupied molecular orbital (HOMO) of Pc - is $\sim 0.8$ eV.$^2$ However, the results of inverse photoemission spectroscopy indicated that Au Fermi level gets pinned at the energy gap of the Pc’s, which lowers significantly the interface barrier height.$^3$ Despite of several advantages Pc’s offer, their use in electronics applications is limited by the low charge carrier mobility ($\mu < 0.1$ cm$^2$V$^{-1}$s$^{-1}$) of thin films.$^4$ This is in contrast to a high $\mu$ (75 cm$^2$V$^{-1}$s$^{-1}$) reported for Pc single crystals.$^5$ The low $\mu$ in Pc films arise mainly due to their poor crystallization. Different substrates were employed for the growth of oriented Pc films and stepped sapphire substrates were found suitable for this purpose.$^6$ From the viewpoint of basic physics, a major disadvantage of low $\mu$ Pc films is that their low temperature (<100K) charge transport properties cannot be measured. This is because the charge carriers are trapped at disorders, and therefore, no measurable current is obtained.$^7$ In this letter, we report growth of high $\mu$ ($\sim 7$ cm$^2$V$^{-1}$s$^{-1}$ at 300 K) cobalt phthalocyanine (CoPc)
films on (001) LaAlO	extsubscript{3} substrates and investigate their charge transport properties down to 24 K.

**Experimental**

CoPc films (thickness: 20 nm) were deposited on (001) LaAlO	extsubscript{3} substrates using molecular-beam epitaxy, MBE, (RIBER system, model EVA 32) under a base vacuum of better than 10	extsuperscript{−8} Torr. The growth temperature and deposition rate were respectively, 200°C and 2Å/s. Structure of grown films was determined by x-ray diffraction (XRD) using CuK\textalpha radiation. The surface morphology of the films was imaged by atomic force microscopy, AFM, (Nanonics: MV4000) using tapping mode. The charge transport measurements were carried out using in-plane electrode geometry. For this purpose, two planar gold electrodes (size: 3mm x 2mm) separated by 7 μm were thermally deposited onto films using a metal mask. The current-voltage (J-V) measurements were carried out using Keithley 6487 voltage-source/picoammeter and computer based data acquisition system. The measurements in the temperature range 300-24 K were carried out using a closed cycle cryostat in dark ambient to avoid any possible contributions from photocconductivity.

**Result and Discussion**

Fig. 1 shows a typical XRD spectrum recorded for the 20 nm CoPc films grown on (001) LaAlO	extsubscript{3} substrate. Presence of a highly intense Bragg peak at 6.7°, corresponding to the (200) peak of the α-CoPc phase, indicates that the film is highly crystalline with a-axis normal to the substrate. This is further confirmed by recording the rocking curve of (200) Bragg peak, as shown in the inset of Fig. 1, which has an intense peak at 3.35° (exactly at half the value of Bragg peak position) with a full-width-half-maximum (FWHM) value of only 0.11°. The possible reasons for high crystallinity could be the chemical reactivity between CoPc molecules and (001) LaAlO	extsubscript{3} surface and/or presence of natural twins in LaAlO	extsubscript{3} substrate that might act as a template for the growth of ordered CoPc films. Typical AFM image of 20 nm CoPc films, as shown in the inset of Fig. 1, reveal that film consists of highly dense CoPc grains.

Typical J-V characteristics recorded for 20 nm CoPc films, as shown in Fig. 2, indicates that variation of current depends on both applied bias as well as the temperature. Based on the nature of J dependence on V and T, four distinct regions (marked as I to IV) have been identified. The analyses of these regions are described below. As shown in Fig. 3 (a), a transition from region I to region II takes place as a function of applied bias. In the region I, the slope of the linear fit to data is ~1, indicating an ohmic conduction. In molecular semiconductors, an ohmic conduction normally occurs if the thermally generated carriers exceed that of injected carriers through the electrode, and the J in this case is given by:

\[
J = n_0 e \mu \frac{V}{d},
\]

where \(n_0\) is the thermally generated hole concentration, \(e\) is electronic charge, \(\mu\) is the hole mobility and \(d\) is the electrode separation. However, the slope value in region II is ~2, indicating that the charge transport is via trap-free space-charge limited characteristics (SCLC). SCLC occurs if the injected carrier density is higher than the thermally generated carrier density and the J depends on applied bias using the relation:

\[
J = \frac{9}{8} \varepsilon \mu \frac{V^2}{d^2},
\]

where \(\varepsilon\) is permittivity of the film. The experimentally determined...
value of $\alpha$ for our films is $2.75\times10^{-11}\text{F/m}$. Using data of Fig. 3(a), we have calculated the values of $n_0$ and $\mu$. The values of $n_0$ is determined from the crossover voltage ($V_c$), as shown in Fig. 3(a), using the relationship:

$$V_c = 8n_0 e d^2 / 9\varepsilon.$$ 

The estimated value of $n_0$ at 300 K is $1\times10^{20} \text{m}^{-3}$, which is in agreement with reported literature. The $\mu$ values at different temperatures were calculated from the slopes of $J-V^2$ plots. The temperature dependence of $\mu$ is plotted in Fig. 3(b), which is found to obey the Arrhenius behavior i.e. $\ln \mu = 1/T$. Since in the temperature range 300-220 K, we have only ohmic region in the entire bias, the value of $\mu$ at 300K was obtained by the extrapolation of data, which is found to be $-7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. This $\mu$ value is higher by two orders in magnitude as compared to that reported for disordered films. Arrhenius-like dependence of $\mu$ has been predicted using a polaron effective mass approach that considers intermediate electron-phonon interactions. The temperature dependence of $\mu$ in this case is given by: $\mu(T) = \mu_0 \exp\left(-E_{pol} / 2kT\right)$, where $E_{pol}$ is the polaron binding energy. From the slope of Fig. 3(b), we estimate the value of $E_{pol}$ equal to 30 meV, which is in agreement with the reported value.$^{10}$

As shown in Fig. 2, for temperatures <100K, the $J-V$ characteristics show very different behaviors in regions III and IV. In region III i.e. at low bias, $J$ drops sharply with lowering $T$; whereas in region IV i.e. at very high bias, $J$ shows a very weak $T$ dependence. These data, as analyzed below, indicate that the electrode-limited processes govern the charge transport at low temperatures. In region III, a linear fit of $J$ vs $V^{1/2}$ data, as plotted in Fig. 3(c) in a semi-log scale, indicates that charge transport is governed by Schottky model$^8$:

$$J = AT^{-2} \exp\left(-\phi / kT\right) \exp\left(-\frac{\beta_s}{kT} \sqrt{V} / \sqrt{J}\right),$$

where $A$ is Richardson constant $(1.2 \times 10^6 \text{Am}^{-2})$, $\phi$ is barrier height at the Au/CoPc interface and $\beta_s = (e^2 / 4\pi\varepsilon\varepsilon_0)^{1/2} \phi$ is the field lowering coefficient. For Au/CoPc interface, the obtained values of $\beta_s$ and $\phi$ are respectively, $1.8 \times 10^5 \text{ eVm}^{-1/2} \text{V}^{-1/2}$ and $-0.2 \text{ eV}$. The experimentally determined value of $\beta_s$ is close to its theoretical value $(2 \times 10^5 \text{ eVm}^{-1/2} \text{V}^{-1/2})$, which supports Schottky-barrier limited conduction.

---

![Fig. 2: Log-log plots showing current-voltage ($J-V$) characteristics of 20 nm CoPc films in the temperature range 300-24 K. Based upon dependence of current on applied bias and/or temperature, four regions I to IV have been identified (marked by thick solid curves).](image)
A smaller value of $\phi$ (0.2 eV) as compared to 0.8 eV measured experimentally using UPS, supports Au Fermi level gets pinned at the energy gap of Pc’s. A weak $T$ dependence of $J$ in the region IV indicates a possibility of tunneling mechanism. It has been shown that if localized states are present in the gap, then these states assist sequential tunneling of charge carries (i.e. from the Fermi level of the electrode to the conduction level of the film) and this process is termed as multi-step tunneling (MUST). It has been shown that if localized states are present in the gap, then these states assist sequential tunneling of charge carries (i.e. from the Fermi level of the electrode to the conduction level of the film) and this process is termed as multi-step tunneling (MUST).11,12 It has been demonstrated that MUST is observed only in high $\mu$ devices and this mechanism leads to an inverse square-root field dependence of conductivity, i.e. 

$$\sigma \propto \exp \left( -\frac{E_0}{E} \right)$$

where $E_0$ is related to the material through the potential barrier ($\phi$) and a parameter $\alpha$ given by $\alpha = \ln(\rho^{-1})$, where $\rho$ is the probability of forming N-step tunneling path. As shown in Fig. 3 (d), in region IV the conductivity varies as the inverse square-root of the field, confirming the MUST mechanism. By least square fitting of data at 24 K, the obtained value of $E_0$ is 800 kV/cm. Using $\phi = 0.2$ eV and $\rho = 0.95$, the theoretically calculated value of $E_0$ is 780 kV/cm, which is consistent with experimentally observed value. MUST mechanism have experimentally been reported in organic field effect transistors and organic light emitting diodes. However, the experimentally observed $E_0$ value in these cases was much higher (~6400 kV/cm), which is expected as the interface barrier is also high (i.e. $\phi = 0.5$ eV).

**Conclusion**

In conclusion, we have demonstrated growth of high mobility (~7 cm$^2$V$^{-1}$s$^{-1}$ at 300 K) CoPc films on LaAlO$_3$ substrates. The various charge transport mechanisms operating in these films are summarized in the Fig. 4. In the temperature range 300-100 K, Au/CoPc interface is ohmic in nature and the charge transport is bulk-limited. A bias dependent crossover from ohmic to space-charge limited conduction is observed. At temperatures <100 K, a barrier of 0.2 eV has been estimated at the Au/CoPc interface. It has been shown that at lower bias the transport is governed by Schottky-barrier limited conduction mechanism; whereas at higher bias multistep tunneling is the dominant mechanism.

**References**


