Enhancement of Charge Carrier Mobility in Organic Semiconductor and their Gas Sensing Properties

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Introductions:

Semiconducting organic materials, both polymeric and small molecule based, have gained worldwide attention during last two decades owing to their several interesting electrical and optical properties, and therefore, are being used in various devices, such as, organic field effect transistor (OFET), organic photovoltaics, organic light emitting diodes (OLED) and bio- and gas sensors etc [1,2]. Presently some of these organic devices are available in the market. Although these devices are having low charge carrier mobility but still these can be used in some special cases like in low cost flexible electronics, large area devices application etc [3,4]. For better performance of these organic semiconductor devices, it is very important to understand the charge transport mechanism in these organic semiconductors. A considerable amount of efforts have been devoted to study the charge transport mechanism(s) in organic semiconductor thin films, particularly at low temperatures (300-4 K). However it is very difficult to measure electrical conductivity at temperatures below 150 K. This is because no measurable electrical current is obtained at low temperatures due to the very low mobility ($\mu$), which are usually in the range of 0.01-0.1cm$^2$V$^{-1}$s$^{-1}$. The low value of $\mu$ in organic semiconductor thin films mainly arises due to the weak van der Waals forces between adjacent molecules. In addition, the $\mu$ is also affected by energetic disorders (diagonal and non-diagonal), nature of molecular stacking (face-on or edge-on), adsorbed oxygen species and impurities [5].

Clearly, in order to investigate the lowtemperature charge-transport properties of organic semiconductor films, the major issue is how to improve the mobility of films. Similar to the conventional inorganic semiconductor films, the $\mu$ can be enhanced by improving the crystalline structure of the films and reducing the impurities. This work deals with growth and characterization of FePc and CoPc (chemical structure shown in figure 1a) thin films with a motivation of improving the charge carrier mobility and to study their charge transport and gas sensing properties.

Effect of substrate on the growth of organic semiconductor:

We have deposited metal-phthalocyanine (MPC) films using organic molecular beam epitaxy (OMBE) system on a variety of substrates viz. glass, (100) SrTiO$_3$, (100) LaAlO$_3$, (0001) Al$_2$O$_3$ and along the 38.6$^\circ$ bi-crystal boundary of bicrystal SrTiO$_3$. Generally, growth of MPC epitaxial films on inorganic substrates is difficult due to (i) large lattice mismatch between film and substrate, and (ii) extended (planar) nature of the MPC molecules. Nevertheless, it has been found that the chemical nature of substrate as well as its surface roughness strongly influences the growth of the MPC films. The growth mode of large planar molecules is governed by a competition between “molecule-molecule” and “molecule-substrate” interactions. If the molecule-substrate interaction is dominant then molecules arrange in the face-on stacking mode, otherwise the stacking mode will be edge-on.
The glass substrates are widely used to deposit organic films. Glass substrates are amorphous in nature and are chemically non-interactive to MPc molecule. Thus there is minimum substrate-molecule interaction between phthalocyanine and glass substrate. However, the morphology and the structure of the films strongly depend on various growth parameters, such as substrate temperature, film thickness, and deposition rate. For example, MPc molecule deposited with various substrate temperatures ranging from 25°C to 300°C, the morphology changes from amorphous to densely packed grains to nanowires [6]. Overall due to the less substrate-molecule interaction and high roughness, MPc molecules stack ‘edge on’ and results disordered films on glass.

On the other hand the (0001) sapphire surface has extremely low roughness and has aluminium termination which interact very strongly with the $\pi$-cloud of MPc molecules. This results ‘face on’ staking of molecules (shown schematically in figure 1b) on the sapphire surface upto certain thickness (~ 20 nm). However, as film thickness increases, the influence of molecule-substrate interaction becomes weaker and molecule-molecule interaction dominates, which allows edge-on stacking of molecules. As a result, the film grows in the polycrystalline form at higher film thickness. It may be added here that the thesepolycrystalline films are likely to be better in terms of the molecular packing as compared to the polycrystalline films grown on the glass substrate in which molecules randomly stack inthe edge-on configuration.

The high mobility along charge transport direction demands face to face staking of molecule which enhances the overlapping of charge clouds. Thus we need to deposit MPc molecule on such a substrate so that it can induce ordering in some direction as well as molecule stack face to face along charge transport direction. For this purpose we choose twined (001) LaAlO$_3$ which has very low roughness of less 1 nm and natural twin boundaries. These natural twin boundaries act as template for the molecule to order along the twin boundary with edge-on configuration. The high degree of ordering is confirmed by X-ray rocking curve of (200) Bragg peak. Taking a clue from the growth of MPc films on (001) LaAlO$_3$ substrate, we have selected a bi-crystal (001) SrTiO$_3$ substrate for the deposition of CoPc films. The bicrystal has a single boundary, which consists of periodic triangularly shaped grooves (depth of 2-3 nm). Since the bicrystal boundary has a very small width of 2-3 nm, therefore, in the film CoPc molecule grow with edge-on stacking along this narrow bi-crystal boundary (as schematically depicted in figure 1c.). At rest of the place the molecules will stack randomly similar to the glass substrate.

**Effect of molecular ordering on charge transport:**

The charge transport of MPc films depends on the molecular ordering which in turn depends on the substrate on which they are deposited. In this section, we will discuss the charge transport behaviour of MPc films on different substrates. The MPc films on glass substrate shows a hysteretic current-voltage characteristic ($J-V$) at room temperature. The hysteretic $J-V$ characteristic is explained by space charge limited conduction (SCLC) with deep charge traps created by chemisorbed oxygen. The presence of chemisorbed oxygen is confirmed by XPS. The amount of hysteresis in $J-V$ characteristic depends on the amount of chemisorbed oxygen which further depends on the crystallinity of the films [7, 8]. In these films, the transport at low temperature is governed by the Poole-Frankel mechanism which is nothing but the promotion of localized charge...
Table 1. Different parameters calculated from temperature dependent $J$-$V$ characteristics of CuPc films grown on glass and (0001) sapphire substrate.

<table>
<thead>
<tr>
<th>Films on</th>
<th>$n_0$ ($m^{-3}$)</th>
<th>$T_t$ (K)</th>
<th>$N_t$ ($m^{-3}$)</th>
<th>$P_0$ (eV$^{-1}$m$^{-3}$)</th>
<th>$\mu$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>2.5 x $10^{18}$</td>
<td>600</td>
<td>4.5 x $10^{21}$</td>
<td>8.7 x $10^{24}$</td>
<td>0.095</td>
</tr>
<tr>
<td>(0001)Sapphire</td>
<td>9.6 x $10^{18}$</td>
<td>236</td>
<td>9.8 x $10^{20}$</td>
<td>1.9 x $10^{22}$</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Fig. 2. Charge transport mechanism of CuPc films deposited on LaAlO$_3$ at different temperature and bias range

As seen in the previous section a highly ordered MPc films are grown along the twin boundary of (001) LaAlO$_3$, the same is manifested in the charge transport measurement along the twin boundary. The measured $J$-$V$ characteristics show no sign of hysteresis with improved mobility of around $\sim 7$ cm$^2$V$^{-1}$sec$^{-1}$. The improved mobility allow us to measure charge transport down to 25 K. Based on the nature of current dependence on bias and temperature, four distinct regions (marked as I to IV) have been identified and a proposed temperature bias phase diagram is presented in figure 2. Broadly, regions I and II belong to the temperature region of 300-100 K, whereas regions III and IV lie in the temperature zone below 100 K. In the high temperature region i.e. regions I and II, the transport is mainly dominated by bulk of the film. The linear variation of current density with voltage indicates that the transport is via Ohmic carrier to the transport level by the application of electric field. The mobility in these films is quite low and is calculated to be 0.095 cm$^2$V$^{-1}$sec$^{-1}$ which is due to the presence of large number of deep traps created by chemisorbed oxygen. On the other hand, the charge transport in MPc films on sapphire is governed by the shallow traps which yield non-hysteretic $J$-$V$ characteristics throughout the temperature range [9]. A comparison of different parameter for the MPc films deposited on glass and sapphire are presented in table I which clearly indicate enhancement of mobility in sapphire substrate over the glass. The enhanced mobility in MPc films on sapphire is due to the nature and decreased number of traps, which is owing to improved ordering in MPc films on sapphire substrate.
conduction in the region I, where as in region II, i.e.
high bias the transport is dominated by trap free
SCLC. For temperatures <100K, transport
characterises show very different behaviors in the
regions III and IV and that is mainly dominated by
electrode limited process. In the region III, i.e. at
low bias the transport is via Schottky conduction
and at high bias (region IV) the transport is
governed by multi step tunnelling from electrode to
transport level of the semiconductor [10]. Similar to
the previous one, CoPc molecule also form ordered
film along bi-crystal boundary of (001) SrTiO3 and
charge transport measurement indicate the same.
The mobility is calculated from temperature
dependent \( J-V \) characteristics and found to be \( \sim 150 \)
cm\(^2\)v\(^-1\)sec\(^-1\) and the charge conduction down to 30K
can be described by Ohmic conduction followed by
trap free SCLC at higher voltage [11].

![Graph](image.png)

Fig. 3: Typical response of 20 nm CoPc films grown
on glass, sapphire, twined (001) LaAlO\(_3\) and 36.8°
cut bicrystal (001) SrTiO\(_3\) for 2 ppm Cl\(_2\) gas.

**Gas sensing properties of metal Phthalocyanine
thin films:**
The efficient gas sensing of any MPc films depends
on two processes, (i) adsorption of gas molecule on
MPc films and consequently charge carrier
generation and (ii) efficient transport of generated
charge carrier to the respected electrodes. The first
process requires active sites in the films for the
interaction of gas molecules and MPc films. The
second process requires high mobility of the films.
These two parameters will depend on the
morphology of the films and ordering of CoPc
molecules. In previous section, we have seen that
CoPc films have different morphology and ordering
on different substrates. Thus these films have
different sensitivity for chlorine gas. The measured
response of 20 nm CoPc films grown on different
substrates, such as glass, sapphire, twined (001)
LaAlO\(_3\) and 36.8° cut bicrystal (001) SrTiO\(_3\), for 2
ppm Cl\(_2\) gas are shown in figure 3 and the calculated
sensor parameters are tabulated in the table – 2. The
conductivity of the films deposited on glass drifts
below initial base conductivity after the exposure of
Cl\(_2\) gas. This drift can be explained by the deep
traps created by chemisorptions of oxygen by CoPc
molecules. Although CoPc films on glass have
enough sites to interact with Cl\(_2\) molecule but due
to low mobility and drift in the conductivity these
films are not suitable for gas sensing application.
On the other hand the films deposited on the
sapphire do not have these problems, and therefore,
they show a reversible response with very high
sensitivity and fast response and recovery, which is
very essential for the sensor application. The highly
ordered CoPc films, grown along twin boundary of
(001) LaAlO\(_3\) and along bicrystal boundary of
(001) SrTiO\(_3\) have lower sensitivity for Cl\(_2\) gas as
compared to that grown on sapphire. This is due to
the ordering of CoPc molecules which reduces the
available interaction sites although they have very
high mobility. As the CoPc films grown on sapphire
substrate have highest sensitivity with very fast
response and recovery the chemi-resistive sensors
are made and have been demonstrated that these
sensors can detect any concentration of hazardous
Chlorine ranging from 5 ppb to 2000 ppb at an
operating temperature of 180°C (a typical response
shown in figure 4). These sensors are found to be
very stable but more importantly these sensors can
detect as low as 5 ppb of Cl\(_2\) gas with faster
response time (18 s), higher base line stability (<
5%) and enhanced response (80%) [12].
Table 2. Comparison of sensitivity of CoPc films (20 nm) grown on different substrate for 2 ppm Cl₂ gas.

<table>
<thead>
<tr>
<th>Sensors</th>
<th>Sensitivity (S in %)</th>
<th>Response time (s)</th>
<th>Recovery time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycrystalline CoPc films on Glass</td>
<td>7.2 × 10³</td>
<td>35</td>
<td>510</td>
</tr>
<tr>
<td>Polycrystalline CoPc films on Sapphire</td>
<td>9.2 × 10³</td>
<td>15</td>
<td>230</td>
</tr>
<tr>
<td>Ordered CoPc films on (001) LaAlO₃</td>
<td>7.8 × 10²</td>
<td>90</td>
<td>1440</td>
</tr>
<tr>
<td>Ordered CoPc films on (001) SrTiO₃</td>
<td>1.57 × 10²</td>
<td>55</td>
<td>480</td>
</tr>
</tbody>
</table>

Conclusions:

We have demonstrated that by choosing an appropriate substrate, the mobility can be enhanced (graphically shown in figure 5) from <0.5 cm²V⁻¹s⁻¹ (obtain for amorphous CoPc films on glass) to ~150 cm²V⁻¹s⁻¹ (for highly ordered CoPc films grown along the 38.6° bi-crystal boundary of bicrystal SrTiO₃). The electronic charge transports disordered and highly ordered MPC films have been investigated as a function of bias and temperature (down to 25K). We have generated a new bias-temperature phase-diagram for ordered Pc films on LaAlO₃ substrates. The Pc films have also been used for ppb level Cl₂ gas sensing application.

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Reference: