ROOM TEMPERATURE OPERATED FLEXIBLE AMMONIA SENSOR

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Abstract

The structural, charge transport and chemi-resistive gas sensing characteristics of cobalt phthalocyanine (CoPc) films deposited on flexible bi-axially oriented polyethylene terephthalate (BOPET) substrates were investigated. CoPc films exhibited a preferential (200) orientation with charge carrier mobility of \(-118 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}\) (at 300 K). Charge carrier mobility in these films systematically decreases upon bending, which implies that bending reduces \(\pi-\pi\) interactions among molecules. At room temperature, these films exhibited a reversible change in resistance on exposure to ammonia (5 – 50 ppm) along with high sensitivity and selectivity as well as fast response and recovery. The sensing properties were found to improve significantly under bend conditions owing to creation of more numbers of interaction sites.

Introduction

Development of high mobility flexible organic semiconductor devices is highly desired for the fast and low cost next generation flexible electronic applications. Metal phthalocyanines, which have shown tremendous potential as a key component in organic photovoltaic and gas sensing devices, have never been investigated for flexible devices. In this work, we demonstrate very high charge carrier mobility of 118 cm² V⁻¹ s⁻¹ (at 300 K) in cobalt phthalocyanine (CoPc) films grown on transparent flexible bi-axially oriented polyethylene terephthalate (BOPET). These high mobility flexible CoPc films are found to be suitable for detection of ammonia gas in parts per million (ppm) range.

Experimental details

CoPc films (thickness: 20 nm) were deposited on pre-cleaned flexible BOPET substrates by molecular beam epitaxy (vacuum – \(2 \times 10^{-8} \text{ mbar}\)). After film deposition, four pairs of planar gold electrodes (size: 3mm x 2mm) separated by 12 \(\mu\text{m}\) were thermally evaporated onto films using a metal mask. Subsequently, silver wires were attached to the gold electrodes using silver paint. The bending measurements were performed by attaching the flexible samples to curved surfaces of different radius. Current-voltage (J-V) measurements were carried out using Keithley 6487 voltage-source/picoammeter and computer based data acquisition system.

Results and discussions:

The atomic force microscope (AFM) image of 20 nm thick CoPc films grown on BOPET substrate, Fig. 1(a), reveals that film consists of elongated grains with rms
surface roughness of 1.1 nm. Presence of Bragg peak at 7.8° in the XRD pattern shown in Fig 1(b) suggest the (200) orientation of the α-CoPc phase i.e. film is crystalline with a-axis normal to the substrate plane.¹

A typical 2-dimensional pole figure contour recorded for the (200) Bragg peak (2θ = 6.9°) is shown in Fig. 2(a). From pole figure data it can be seen that the intensity is maximum at the center which decreases sharply with increasing azimuthal angle (Ψ) and the contour is highly symmetric with respect to the polar angle (Φ). This suggests that the grown films have reasonably good out-of-plane texturing but there is no preferential texturing in the plane of the films.¹

A good texturing of CoPc films on BOPET is attributed to the presence of polar groups i.e. C=O and O-C=O in the PET molecular chains, as shown in the inset of Fig. 1(b), that can electrostatically interact with CoPc molecules and a relatively stronger π-π interaction among CoPc molecules.¹

A photograph showing the flexible nature of CoPc films with deposited gold electrodes and schematic of our bending set up along with the charge transport measurement arrangement is shown in Fig. 3(a). Typical room temperature J-V characteristics measured for CoPc films under flat (without bending i.e. bending radius \( r \to \infty \)) and for \( r \) are shown in Fig. 3(b). It can be seen that with an increase in bending (i.e. a decrease in \( r \)) the J decreases. In the inset of Fig. 3(B), the J-V data’s are plotted in log-log scale, it is seen that J-V characteristics are non-linear, and exhibits two different power law behavior (\( J \sim V^\alpha \)) as a function of applied bias with varying \( \alpha \) values. At room temperature, for low bias (< 15V) \( \alpha \sim 1 \) indicates ohmic conduction. For ohmic conduction the J-V characteristics can be described by \( J = n_e \mu d \); where \( n_e \) is the concentration of thermally generated holes, \( \epsilon \) is the electronic charge, \( \mu \) is the hole mobility, and \( d \) is the electrode separation. For high bias (>15V), \( \alpha \sim 2 \) indicates the shallow trap mediated space charge limited conduction (SCLC). SCLC occurs if the injected carrier density is higher than \( n_0 \) and \( J \) depends on applied bias through the relation:

\[
J = \frac{9 \epsilon \theta}{8 d^2} V^2,
\]

where \( \epsilon \) is permittivity (experimentally determined value of \( \epsilon \) for our films is \( 2.45 \times 10^{-11} \text{F/m} \)) and \( \theta \) is the ratio of free to total (trapped and free) charge carrier density. The \( \mu \) values were estimated from the slopes of J-V² plots for different \( r \), and the results are plotted in the Fig.1(c). The value of \( \mu \) in the flat condition of the films was found to be \( \sim 118 \text{cm}^2\text{V}^{-1}\text{s}^{-1} \), which systematically decreases on bending.²

Metal phthalocyanines (MPc) are intrinsically insulators under high vacuum environment and turn semiconductors only when exposed to ambient conditions. This is because ambient oxygen gets chemisorbed at the surface, which in turn, induces hole carriers in the films via the process:²

\[
\text{MPc} + O_2 \leftrightarrow \left( \text{MPc} + h^+ \right) + O_2
\]
MPc films acts as chemiresistive sensors because the analyte gases (both reducing and oxidizing) can interact with O₂ as well as metal surface sites, which results in a change of electrical resistivity. The interaction of MPc with the reducing gases (such as NH₃) shows an increase in resistivity, which is attributed to the hole trapping within the films by the electrons donated from reducing gas.

Condition, CoPc molecules are arranged in edge-on configuration, which results in improved π-π interaction, and hence high charge carrier mobility is observed. In this case, NH₃ molecules can only interact with surface of the films as Co metal sites are unavailable owing to close packing. Under the bend condition, as shown in Fig. 4(d), the stress enhances the separation among CoPc molecules, which facilitates NH₃ molecules to interact with chemisorbed oxygen present on Co metal sites. An increase in the numbers of interaction sites under bend condition is responsible for high sensitivity as well as fast response/recovery. Due to high toxicity of the gas, any leak in the system can result in a life threatening situation. Traditional method of detection of presence of ammonia by chemical analysis is a time-consuming and complicated process. However the sensors based on metal oxides are sensitive to NH₃ but require high temperatures for operation. In this respect, highly flexible CoPc films exhibiting high sensitivity and fast response/recovery under bend condition makes them an attractive candidate for ppm level of NH₃ sensing.

Conclusion

In conclusion, we have demonstrated the growth of highly ordered CoPc films on transparent flexible BOPET substrates with a charge carrier mobility of ~118 cm²V⁻¹s⁻¹ at 300 K. These flexible films show excellent response/recovery for ammonia in the concentration range of 5 to 50 ppm at room temperature. The low cost, room temperature operation, high sensitivity, fast response/recovery of CoPc flexible films makes them attractive candidates for flexi-gas sensor devices.

References