

Hole-Trapping in Iodine-Doped Pentacene Films at Low Temperatures

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Abstract

Pentacene films, grown on polyethylene terephthalate (PET) substrates, were doped with Iodine. ESR measurements were made for the films in the temperature range of 100-300 K. Two regimes of doping stages were discernible: a light (intercalation) doping regime and a heavy doping regime. The light doping regime was concluded to be dominated by localized holes that were trapped at low temperatures, which indicated trap states near the valence band edge.

1. Introduction

Doping of pentacene is achieved through the inclusion of iodine and alkali atoms. The intercalated atoms donate either holes (iodine) or electrons (alkali) to the pentacene molecules. Iodine doping of pentacene films showed characteristic changes in electrical conductivity [1,2]. The increase of electric conductivity was related to intercalation of iodine with the form of I_3^- into pentacene molecular layers [3,4]. Further information about trap states near the valence band edge has been obtained by temperature dependent measurements of the thin film transistor (TFT) parameters [5]. Two stable phases, with different iodine concentrations, have been reported [6]: the intermediate intercalation phase with high conductivity; and the saturation phase associated with a significant lattice expansion. Conductivity of doped pentacene single crystals decreased in the heavy doping regime [7].

In this article we present the results of temperature-dependent ESR measurements of pentacene films doped with iodine, and show that the ESR measurements in light doping regime may reflect the hole trapping at low temperatures observed in the TFT mobility measurements [5].

2. Experiment

Pentacene powder was purchased from Sigma-Aldrich company. Pentacene films were grown on a PET

substrate by vapor transport of pentacene in a stream of nitrogen ($P=10$ mbar). The source temperature was 350 °C, and the substrate temperature was 180 °C. Film thickness was ~ 10 μm and the deposition rate was ~ 60 nm/min. Polycrystalline films were obtained, which were identified by X-ray diffraction and SEM measurements. The pentacene films were, then, doped at room temperature from a pure saturated vapor of iodine, after preliminary degassing of the samples in a vacuum. The iodine concentration of the sample was obtained from measuring the weight of the sample before and after doping. The ESR experiments were conducted between 100 K and 300 K with a Bruker EMX-8 spectrometer operating in the X-band.

3. Results and discussion

Figure 1 shows the SEM images of the pentacene films before doping. Doping levels of the films in relation to the doping time are shown in Fig. 2. It is seen that the iodine concentration in the films increased and reached some saturation levels for ~ 20 h and doping level ranges ~ 20 %.

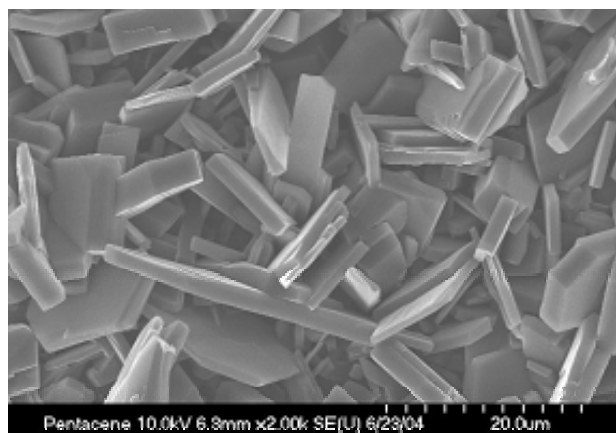


Figure 1. SEM image of a pentacene film

The ESR raw spectra at room temperature are depicted in Fig. 3. The ESR absorption lines for the doped samples were fitted using a Lorentzian. For undoped pentacene films, a small and broad signal (linewidth ≈ 10 G) was noticed in the air. This signal was neglected in the analysis, since the intensity was negligible compared to that of doped samples. We presumed the signal might have come from some impurity in the growth of pentacene films.

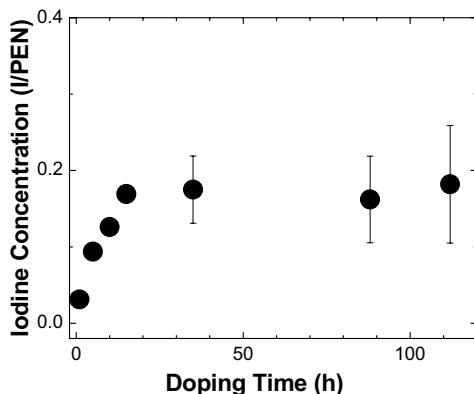


Figure 2. Iodine concentration vs. doping time.

Figure 4 shows the evolution of the ESR parameters of iodine-doped pentacene films with doping time.

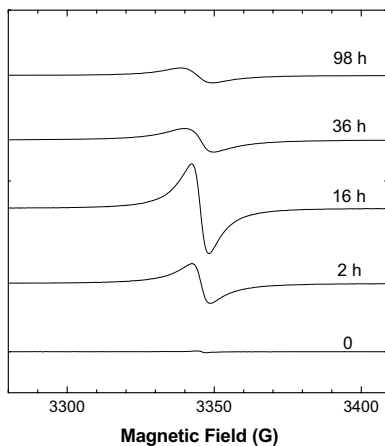


Figure 3. ESR spectra of the iodine doped pentacene films at different doping times.

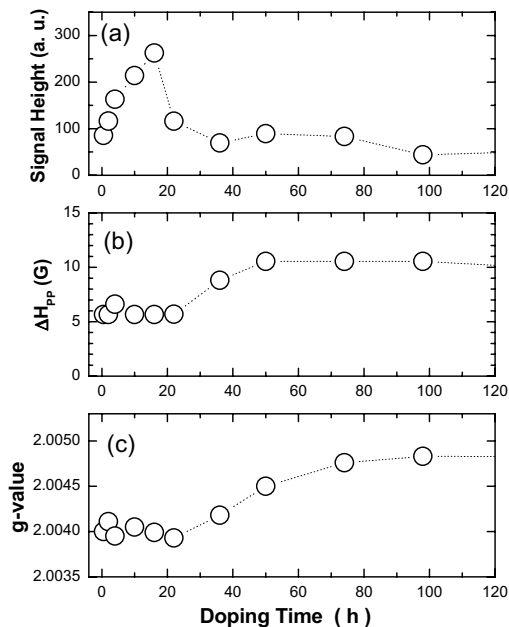


Figure 4. Variation of ESR signal height (a), line-width (b), and g-value (c).

In Fig. 4(a), it is seen that the ESR signal height increased to a maximum value for ~ 20 h, and then decreased again with further doping. We call the signal-increasing region the *light doping regime*. The ΔH_{pp} , defined as the linewidth between the derivative peaks, is shown in Fig. 4(b). The initial linewidth (~ 6 G) did not change for the light doping regime; then, it increased to a maximum value of ~ 10 G for the next saturation regime. In Fig. 4(c), the g-value showed a similar dependence on doping time.

Consequently, two distinctive doping regimes were discernible: a light doping regime and a heavily-doped saturation regime. In the light doping regime, the signal height increased, and linewidth and g-value remained unchanged. This implies that the increasing spin signals in the light doping regime may come from a same type of spin sites. It is known that the increase of ESR intensity in the light-doping regime is related to the increase of electrical mobility of the films [7]. The increased ESR signal upon doping was attributed to the PEN^+ ions [7,8]. A charge transfer from pentacene to iodine occurred due to the doping. Hole carriers were formed in the molecular column of pentacene [3].

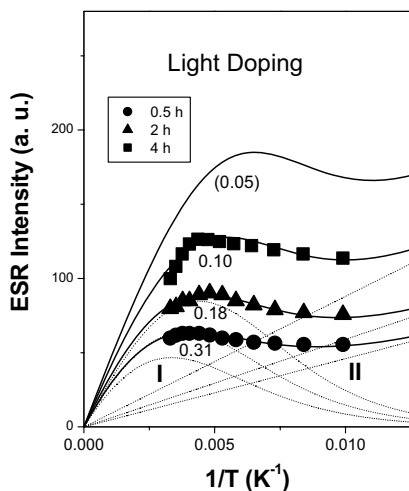


Figure 5. Temperature dependence of the ESR intensity at different doping times. The numbers represent the value of N_{TH}/N_{V0} .

It was also reported that cation dimers $(PEN^+)_2$ and related species were formed as the iodine concentration further increased [7]. In the heavy doping regime, the onset of conductivity decrease corresponded to the onset for the decrease of the total ESR susceptibility of the films.

In Fig. 5, the temperature dependence of the ESR intensity for the lightly-doped films is represented. In the light-doping regime, as the temperature was lowered from room temperature, the ESR intensity increased to begin with, and then decreased again. Meantime, it was reported that effective mobility in the pentacene films is the mobility of free carriers reduced by the fraction of holes that are trapped [5]. We presumed that the ESR signals in the light doping regime mainly come from the localized PEN^+ sites [7]. Therefore, we concluded that the decrease in ESR intensity at low temperature in Fig. 5 was an indication of trap states near the band edge. Thus, we fitted the temperature dependent ESR intensities by incorporating the model in the light doping regime:

$$\frac{\mu_{eff}}{\mu_o} = \frac{N_V}{N_V + N_{TH}} \approx \frac{1}{1 + \frac{N_{TH}}{N_{V0}} \exp\left(\frac{E_F - E_V}{kT}\right)}, \quad (1)$$

where N_{V0} is the effective density of states at the energy, E_V , of the valence band edge, and E_F is the

Fermi energy. N_{TH} is the number of trapped holes [5]. We presumed that $ESR \text{ Intensity} \propto [PEN^+]/T \propto [\text{free carriers}]/T$. Accordingly, the ESR intensity was modeled with two-components, a Curie component and a component typical for the spins subject to the hole trapping as given in equation (1). In Fig. 5, as the doping time increased (0.5 h, 2 h, 4 h), the ratio of N_{TH}/N_{V0} decreased (0.31, 0.18, 0.10), which indicated that N_{TH} decreased while N_{V0} remained constant. In Fig. 5, it is noticed that PEN^+ signals (*type-I*) were dominant at room temperature, while different localized spin signals (*type-II*) became dominant at low temperatures.

In particular, the best fit of the experimental data yielded an activation energy of the hole concentration of 42 meV; this value is in good agreement with the result determined by temperature-dependent measurements of mobility for iodine doped pentacene films [5]. It is apparent that the films have a trap distribution. The trap states are near the band edge. The traps can be caused by chemical impurities or the trap states may be influenced by the gas used in the vapor-phase growth.

The result that electric resistivity increases with decreasing temperature [2] may be consistent with the fact that *type-I* spins diminish at low temperature in the light-doping regime. In the heavy doping regime, it is known that the structural order vanishes, forming an amorphous-like material, which corresponds mainly to a population of localized spins. The role of disorder is believed to lower the mobility of the charges in the system. We may presume the *type-II* spins may be related to the high density of $(PEN^+)_2$ or I_5^- related structure. Full results will be published in a separate paper [9].

4. Conclusion

The ESR properties of iodine-doped pentacene films were investigated in the temperature range of 100-300 K. As the iodine doping proceeded, the ESR lineshape variation demonstrated the existence of two doping regimes: a light doping regime and a heavily-doped saturation regime. In the light doping regime, the dominant resonances were concluded to be from localized holes that were subject to hole-trapping at low temperatures. The estimated activation energy of the hole concentration was 42 meV. In the heavily-doped saturation regime, dominant spins were localized spins obeying the Curie law.

5. Acknowledgements

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6. References

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