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New Stage Structure of Iodine Doped Pentacene Film (II)

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In pure pentacene film and iodine doped pentacene film, X-ray and electric conductivity measurements were performed. It was found from X-ray diffraction data that the iodine doped pentacene possess the stage-2 structure in addition to the stage-1 structure. The c axis lattice constant of the stage-2 structure, which is the length of the interval between the layers, was determined to be 33.2 Å. Moreover, electric conductivity was measured in pentacene doped with iodine at the various doping temperatures T_d. This result was compared with the results obtained from X-ray diffraction data.

Keywords: pentacene; electric conductivity; intercalation compound; X-ray study

INTRODUCTION

It has recently been shown that pentacene (PEN; $C_{22}H_{14}$) film doped with both acceptors and donors formed new molecular conductor[1,2]. Especially, PEN films doped with iodine (which is acceptor dopant) show interesting characteristics of crystal structure and electric conductivity. It is known from X-ray studies that pure PEN forms the layer structure. The *c* axis lattice constant which is the length of the interval between the (001) planes is 15.3 Å[3]. On the other hand, in iodine doped PEN, the lattice constant of *c* axis increases to 19.3 Å,

because iodine is intercalated between the molecular layers of PEN[3]. This structure is the same as the stage-1 structure of graphite intercalation compounds, GICs, which exhibit the high in-plane conductivity[4]. Moreover, it was found from electric conductivity measurement that iodine doped PEN film with the stage-1 structure exhibited the high conductivity above 100 $S \cdot cm^{-1}$ with highly ordered structure at room temperature, although electric conductivity of pure PEN film is below 10^{-8} $S \cdot cm^{-1}$[1]. It is also known that a variety of physical properties such as electric conductivity and lattice dynamics, etc. depend on the stage structure[4]. However, physical properties of iodine doped PEN film with higher stage structure were not clear. Therefore, it is interesting to investigate crystal structure and electric conductivity on various stage structures.

In the present study, iodine doped PEN films were prepared by a two-bulb method with various doping temperatures and then the stage dependence of lattice constant and of electric conductivity was examined.

SAMPLE PREPARATION AND EXPERIMENTAL

Specimens were prepared on glass substrates in a vacuum of 3×10^{-4} Pa. Pure PEN was thermally evaporated from a sublimation cell. Both film thickness and deposition rate, monitored by a quartz oscillator, were controlled by the heating temperature of the sublimation cell. Pure PEN was deposited at a rate of 5 Å/s with a substrate temperature T_s = 30 ℃. Both PEN film and iodine were sealed in a vacuum of 6×10^{-4} Pa. The temperature of pure PEN film was kept at room temperature. The doping temperature of iodine, T_d, was controlled in the temperature region between 0 ℃ and 20 ℃. The reaction time was 20 h.

The stage structures on iodine doped PEN film were observed with Rigaku Rint-1500 X-ray diffraction meter (Cu-Kα radiation). The stage number and the *c* axis lattice constant of films were determined from the diffraction angle 2 θ of the (00*L*) Bragg peak. Specimens were wrapped with thin polyethylene film to prevent their decomposition by air and moisture.

Electric conductivity was measured at a frequency of 1 MHz with an LCR meter (HP4284A). The specimens used in the electric conductivity measurement were 400 nm in thickness.

RESULTS AND DISCUSSION

X-ray diffraction patterns of pure PEN film and iodine doped PEN films are shown in Fig. 1. In pure PEN film, the X-ray diffraction peaks appear at 5.83°, 11.7° and 17.6° (Fig. 1(a)). These peaks correspond to (001), (002) and (003) diffractions of pure PEN film. The *c* axis lattice constant was calculated to be 15.1 Å from the angle of these peaks. This value is in good agreement with the value of 15.3 Å which was reported by Minakata, *et al.*[3]

Fig. 1(b) and (c) show X-ray diffraction patterns of iodine doped PEN film at the doping temperature T_d = 20 ℃ and 5.2 ℃, respectively. In the case of T_d = 20 ℃, the peaks of pure PEN film disappear and the new peaks appear at 4.64°, 9.27°, 13.9° and 18.6° (Fig. 1(b)). These diffraction angles correspond to (001), (002), (003) and (004) of the stage-1 structure, respectively. This result agrees with the result of Minakata, *et al.*[3] From this result, the *c* axis lattice constant of the stage-1 structure was determined to be 19.0 Å.

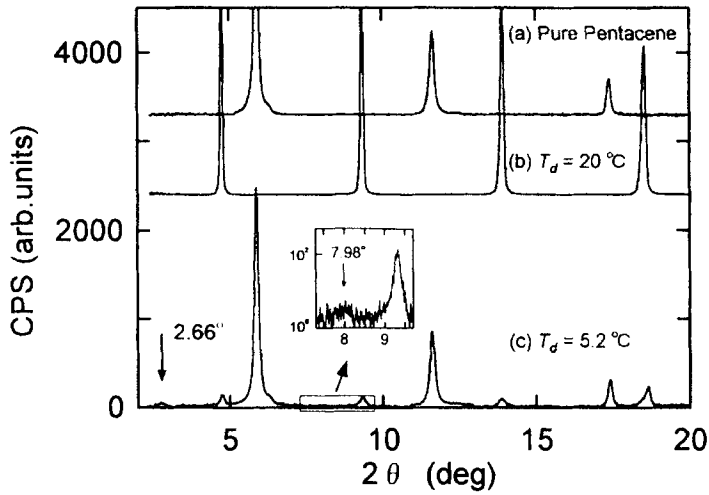

FIGURE 1 The doping temperature dependence of the X-ray diffraction pattern. The inset figure shows the enlarged figure near 2 θ = 8° in Fig. 1 (c).

Fig. 1(c) show the result of X-ray diffraction at T_d = 5.2 ℃. As shown in Fig. 1(c), new diffraction peaks are observed at 2.66° and 7.98°, in addition to the diffraction peaks of pure PEN film and of the stage-1 iodine doped PEN film. It is noted that in this doping condition one of the new diffraction peaks appeared at the lowest angle, 2.66°, and that this diffraction peak was not observed in pure PEN film and the stage-1 iodine doped PEN film. This fact suggests the existence of the new stage structure in iodine doped PEN film. We can determine the *c* axis lattice constant of the new stage structure to be 33.2 Å from the diffraction peak angle, 2.66°. This value is close to the value, 34.1 Å, of the stage-2 structure which is estimated from the lattice constants of the pure PEN film and the stage-1 iodine doped

PEN film (As well known in GICs, for the most acceptor compounds the c axis lattice constant of the stage-2 obtained from the experiment is shorter than that calculated from the structure of HOPG and the stage-1 structure). Moreover, there is no diffraction peaks below 2 θ= 2.66° . In addition, the new diffraction peak of 7.98° corresponds to (003) diffraction peak of the stage-2 structure, when the diffraction peak of 2.66° corresponds to (001) diffraction peak of the stage-2 structure. These results indicate that this new stage structure would be the stage-2 structure.

Fig. 2 shows the doping temperature T_d dependence of electric conductivity σ.

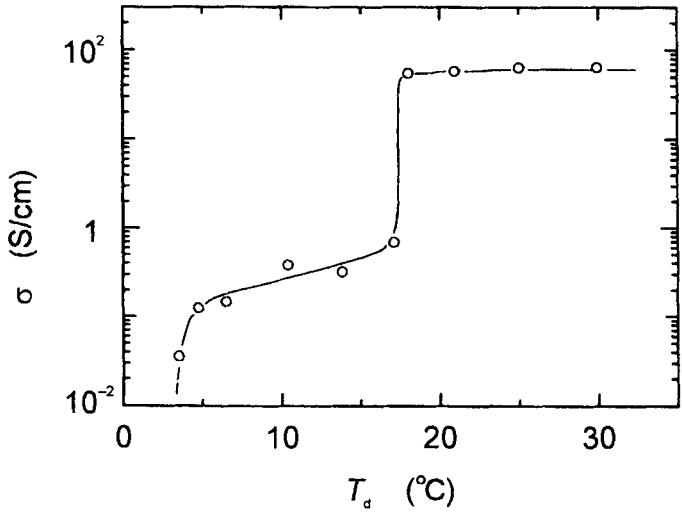

FIGURE 2 The T_d dependence of σ

With increasing T_d, σ increases rapidly up to T_d = 4.8 ℃, increases gradually up to T_d = 18 ℃, increases rapidly at T_d = 18 ℃, and then saturates. This result indicates that iodine begins to be intercalated

between PEN molecular layers at T_d = 4.8 ℃, and that above 18 ℃ the amount of iodine intercalated between PEN molecular layers is not changed. Taking into account this result and the results of X-ray studies, we considered that large increase of conductivity at T_d = 4.8 ℃ results from the change of the crystal structure to the stage-2 structure and the increase at 18 ℃ results from the formation of the single phase stage-1 structure.

CONCLUSION

We have shown that on linear acenes family the new stage structure exists, as seen in GICs. The stage-2 structure would be obtained by adjusting the doping temperature at 5.2 ℃. Moreover, we determined the *c* axis lattice constant of stage-2 structure to be 33.2 Å from (001) and (003) diffraction angles.

It was also found that the electric conductivity of iodine doped PEN increased suddenly up to T_d = 4.8 ℃ and that increased rapidly at T_d = 18 ℃. We concluded from present results that the increase of conductivity at T_d = 4.8 and 18 ℃ results from the change the crystal structure to the stage-2 structure and from the formation of the stage-1 single phase. It will be expected that the higher stage structures are obtained in iodine doped PEN. We are now preparing the specimen with the higher stage structure by more precise temperature control.

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