



Evidence of pentacene bulk and thin film phase transformation into an orthorhombic phase by iodine diffusion

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ABSTRACT

We present evidence for 130 nm thick pentacene films ordered in the orthorhombic phase obtained by iodine diffusion into the film deposited by classical thermal evaporation. After desorption of iodine by vacuum annealing the crystallographic properties of the investigated pentacene films resemble those of very thin thermal evaporated films that exhibit an orthorhombic phase with high electrical performance. Therefore, the results presented in this work are believed to be important for the development of organic field-effect transistors.

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1. Introduction

Pentacene (PEN) is one of the leading candidates of many available organic materials for use in current organic field-effect transistor (OFET) architectures, because of its excellent electrical characteristics [1–3]. It is known that chemical doping can increase the electrical conductivity of molecular semiconductors. For instance, iodine is an efficient acceptor for doping of PEN increasing the conductivity in this material by eleven orders of magnitude [4]. Structural characterization based on X-ray methods [4,5] indicated that iodine atoms tend to intercalate between PEN layers, and for high iodine vapor concentration also between PEN molecules [6]. Experiments performed on powder, single crystals, and thin-films doped with iodine have been already published [4,5]. Different substrates such as quartz, CaF₂, polytetrafluoroethylene, Si/SiO₂, etc. were used for the preparation of PEN thin-films. The PEN layers were doped in different ways e.g. by saturated vapor of pure iodine, by a mixture of iodine vapor with inert gas or ambient atmosphere, or by immersion into solution of iodine in acetonitrile [4–9]. It was shown that in the first stages of the iodine doping the PEN structure does not change significantly. In the intermediate doping regime interlayers of iodine between PEN layers are formed, which coexist to some extent with undoped PEN regions in the crystals. In the high

doping regime iodine diffuses between PEN molecules within one layer causing structural disorder, which leads thus to a decreased conductivity. By X-ray diffraction (XRD) it was shown that intercalated iodine ions cause an increase of the interlayer spacing by about 0.40–0.43 nm [4,5]. Over time, the XRD peaks corresponding to the pristine layer disappear and the intercalated phase becomes visible.

It is known that at least five different polymorphs, corresponding to different lattice d_{001} spacings (shortly d-spacing) ranging between ~1.41 and 1.60 nm, can be obtained in thin-films [10–14]. Evidence for an orthorhombic phase is given by a lattice spacing of d_{001} ~ 1.57–1.60 nm. It evolves in the first stage of layer preparation and it is of crucial importance because of its high influence on the electrical properties of OFETs. This is due to the fact that charge transport in these devices takes place at the first few monolayers near the interface with the gate dielectric [15].

In this Letter, we present iodine doping of PEN layers, prepared on Si/SiO₂ and Si/SiO₂/polyethylene C substrates. Based on the evidence of X-ray reflectivity data and measured d-spacings we observe on Si/SiO₂ substrates an unusual transformation from the thin film and the bulk phase into the orthorhombic phase of PEN films. Until now, this phase has been only observed for very thin PEN layers (5–16 nm) at the beginning of growth [12]. The preparation of thick (130 nm) PEN layers in the orthorhombic phase would open new perspectives for studying this phase by different methods and for controlling the preparation of electronic devices with new promising properties.

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2. Experimental details

For studying the iodine diffusion into PEN layers we used two different film structures, J161 and J162 induced by different kind of substrates. In both cases heavily doped silicon wafers with a 40 nm thick thermal grown silicon dioxide insulating layer were used (Supplier: ON Semiconductors). One substrate was prepared with a 70 nm parylene C layer [16] on top of the oxide (J161), while the other substrate was treated in oxygen plasma for 2 min (J162) [17]. The 130 nm thick PEN films were deposited on top of the substrates by thermal evaporation at a pressure of 10^{-3} Pa at 30 °C and a deposition rate of 0.045 nm/s. No further purification was performed for the commercially available PEN material (Acros Organic). The iodine doping of the PEN films was obtained by exposure to a mixture of iodine vapor and a very small amount of ambient atmosphere at room temperature in a self-made apparatus consisting mainly of a glass container. This container is divided in two parts. In the bottom part two Petri boats are placed, one for the iodine powder and the second for the samples. The upper serves as cover of the container. The container is evacuated before the iodine powder is inserted. Since the specific weight of iodine vapor is higher than air the bottom part of the container infiltrates only a very small volume of air by the insertion of new samples. Due to this fact we believe that mainly vapor of iodine and only a very small amount of air reaches the sample.

A Jobin Yvon HR800 monochromator equipped with a CCD detector was used to record the micro-Raman spectra at room temperature in backscattering geometry. The spectra were obtained with excitation wavelengths of a He–Ne laser (laser line 633 nm) and of a Nd:YAG (laser line 532 nm). The incident laser beam was focused on a spot size diameter of about 2.0 μ m. XRD analysis was carried out using Bruker D8 DISCOVER diffractometer equipped with a rotating Cu anode operating at 12 kW. All measurements were performed in parallel beam (i.e. reflectivity) geometry with a parabolic Goebel mirror in the primary beam.

The samples were analyzed using time of flight based secondary ion mass spectroscopy (SIMS) instrument (Ion-TOF, SIMS IV) with high-energy Bi^+ primary source with combination of low energy sputter gun (Cs^+). The SIMS investigations were used to get chemical information of the surface and depth profile resolving the layer interfaces.

3. Results and discussion

Fig. 1 shows the XRD spectra A and B of the PEN layer J162 before and after iodine doping, respectively. Two peaks characterize the XRD spectrum of the as-deposited film, which are consistent with the d-spacing of the thin film phase (1.54 nm) and of the bulk phase (1.44 nm) [12,18,19]. Spectrum B in Fig. 1 represents the PEN film after 48 h of iodine diffusion. Both pristine peaks (corresponding to the thin film and the bulk phase) are disappeared and a new peak at 5.6° is created corresponding to a d-spacing of 1.58 nm. According to recent publications this value is consistent with the orthorhombic phase, which exists in thin-films deposited on SiO_2 or on polymer surfaces [12,13]. Apart from the main peak in spectrum B we observe also a low intensity peak at 4.5°. Angle positions of both peaks were determined by Lorentzian function fitting. The broad peak at 4.5° most likely represents the iodine intercalated phase, which is characterized by the vertical periodicity spacing of 1.98 nm. The difference of 0.4 nm between the d-spacing of the orthorhombic and the iodine intercalated phase is in good agreement with the ionic parameter of iodine [20]. Similar results for iodine intercalate of the thin film or bulk phase of PEN were obtained by also other authors [4–7]. We present for the first time

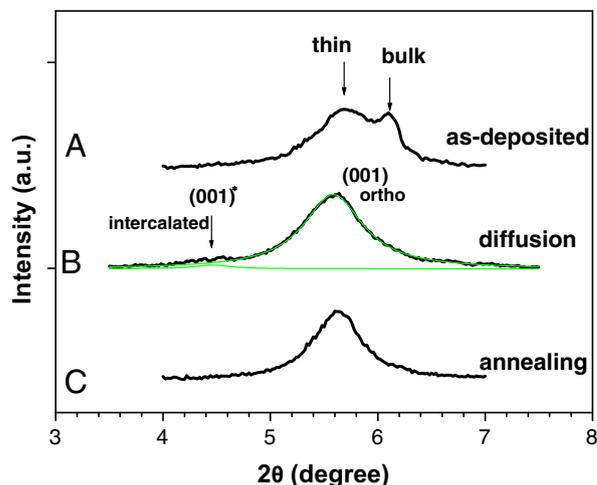


Fig. 1. XRD spectra for sample J162 (PEN on SiO_2): as-deposited (A), after 48 h of iodine diffusion (B) and after annealing in vacuum (C). The two peaks in spectrum A correspond to the thin and the bulk phase of PEN. In spectrum B the peaks at 4.5° and 5.6° correspond to the intercalated orthorhombic phase, denoted as (0 0 1)ⁱ and to the pure orthorhombic phase of PEN, denoted as (0 0 1), respectively. The Lorentzian fits used for the deconvolution are shown as a thin solid lines in spectrum B. The thick solid lines represent experimental data. The peak in spectrum C corresponds to the pure orthorhombic phase.

evidence for the preparation of the orthorhombic phase and its iodine intercalate in thick PEN films.

In the literature [7,8] intercalation/desorption experiments are reported (not shown), where PEN films consisting mainly of the bulk phase were transformed almost entirely into the thin film phase. The complete desorption of iodine from the PEN films was achieved at temperatures above 80 °C and vacuum pumping. We have performed similar experiments of desorption for the sample J162.

Fig. 1 spectrum C shows XRD measurements of the sample J162 after annealing in vacuum and after increasing the temperature between 50 and 113 °C for 2.5 h. During annealing the XRD spectra were recorded in situ. We observe a disappearance of the peak consistent with the intercalate phase. Only the peak matching the pure orthorhombic phase remains in the sample. We note, that by annealing up to 105 °C the FWHM of this peak slightly decreases, meaning that the structural quality is possibly enhanced by the transformation of two phases into one phase, i.e. into the orthorhombic phase. In contrast, for temperatures above 105 °C the FWHM increases slightly, which is probably due to a small partial degradation of the PEN film and its transformation to the bulk phase. This cannot be detected in form of a new XRD-peak due to the small part of the transformed film. For preventing further transformations the annealing process was stopped at a temperature of 113 °C. Similar phase transformations of PEN films from the thin film to the bulk phase were published by Mattheus et al. [10]. They observed the evolution of the bulk phase above an annealing temperature of 121 °C. A similar effect would be expected for our samples. To prevent the degradation of PEN films and the creation of the bulk phase it is necessary to adjust the desorption temperature carefully between 105 and 121 °C.

It is known [12] that PEN films grown on polymer surfaces exhibit a higher degree of structural order than those grown on SiO_2 . Here, both films are grown with a thickness of 130 nm. The FWHM of the XRD-peak corresponding to the orthorhombic phase after iodine diffusion and annealing is 0.53 °C. This is very similar to results obtained for PEN on a polymer surfaces, where also the peak of the orthorhombic phase was observed with 0.5–0.7° [12]. This means that the crystalline quality of the PEN films after iodine

diffusion and annealing is comparable to those deposited on polymer surfaces. Our experimental finding was obtained for films thicker than 100 nm, which is suitable for bulk investigations of the orthorhombic phase (e.g. by micro-Raman measurements) as well as using it in OFETs for improving their electrical properties. It was known that the orthorhombic phase grows in the first monolayers of PEN films, until about 16 nm [10]. Here, we present for the first time evidence for a 130 nm thick PEN film completely arranged in the orthorhombic phase.

For a deeper understanding of the structural changes due to iodine diffusion and annealing we have performed similar measurements (XRD) and sample treatments (iodine diffusion and annealing) to the sample J161. In our previous experiments we showed [21] that PEN layers deposited on a parylene C surface exhibit a better crystalline quality in comparison to PEN layers deposited on a SiO₂ surface meaning that the bulk phase is much less pronounced. Therefore, PEN was deposited on parylene C giving rise to the structure J161. By comparison of Figs. 1 and 2a we see that our assumption is fulfilled; in sample J161 we have detected a much lower intensity of the XRD-peak corresponding to the bulk phase compared to sample J162. In Fig. 2b XRD three dif-

ferent XRD spectra are plotted for J161, A as-deposited, B after iodine diffusion and C after annealing in vacuum. After 48 h of iodine diffusion into the sample we detected similar structural changes as they were reported earlier by other authors [5,6,9], i.e. iodine ions are intercalated between PEN layers and a diffraction peak corresponding to the intercalated phase instead of the thin film phase is observed. The stars in Miller indices indicate peaks corresponding to the intercalated phase. Their position corresponds to a lattice spacing of 1.94 nm. The increase of the d-spacing due to iodine diffusion is about 0.4 nm, which is in good agreement with the ionic parameter of iodine [20], similar as in the sample J162. We note that due to iodine diffusion XRD peaks corresponding to the bulk phase have disappeared and only those of the thin film phase and of the intercalate phase remain (Fig. 2b). We believe that the bulk phase is transformed into the thin film phase and then simultaneously to the intercalated phase. This is supported by the increasing order of the film given by the peak width in the XRD spectrum in the pristine and in the diffused layer (from 4 to 6 order, respectively). Other researchers observed even higher order peaks of XRD spectra after iodine diffusion [4]. In our opinion the transformation of the bulk phase into the thin phase is the main reason for the improved structural order of the PEN films after diffusion, observed in many papers [4,5,7], but it is not explained so far. It was shown [22] that the bulk phase in PEN layers nucleates at very thin thicknesses shadowed by the growth of the thin film phase. This bulk phase in small portion is often not detected by XRD. Our XRD data suggest that the bulk phase is transformed into the thin film phase and simultaneously into the intercalate phase by iodine diffusion. Due to this phenomenon the whole volume of PEN layer is transformed partly or fully into the intercalated phase.

After iodine diffusion sample J161 was annealed in vacuum in the temperature range of 50–85 °C. Simultaneously, the XRD spectra were recorded in situ. After 4 h of annealing the intercalated phase vanished and the annealing procedure was stopped. The XRD spectrum after annealing is shown in Fig. 2a (spectrum C) and in magnified form in Fig. 2b. From the comparison of the spectra A and C in Fig. 2 we see stronger intensities of thin film phase peaks and vanishing of bulk phase peak after annealing. According to the paracrystal theory [23,24] we have estimated the reduction of the degree of structural disorder of the annealed sample J161 in comparison with the as-deposited layer. The above mentioned observations show an improving of the crystallographical quality of the PEN layer in sample J161 after annealing.

From the diffusion and annealing procedures of samples J161 and J162 we are able to make these important findings: (i) The structural quality of both PEN films was improved compared to the pristine layers. (ii) In both films only one phase seems to be present after annealing, i.e. the orthorhombic or the thin film phase. These findings are very important and promising for the enhancement of carrier mobility in OFETs prepared from these modified layers, because the presence of more phases in PEN layers greatly decrease its transport properties [1].

For further investigation of the new kind of iodine diffusion in sample J162, we have performed micro-Raman and SIMS measurements that allow to determine the valence of the iodine ions and their depth profile respectively. Fig. 3 shows micro-Raman spectra of both samples (J162 and J161) after 48 h iodine diffusion (two spectra in the middle of the figure). For both samples we detect new peaks at 111 cm⁻¹ and 163 cm⁻¹ in comparison with as-deposited (bottom) or annealed (top) spectra. It was presented [5,6] that these peaks are associated with the stretching frequencies of I₃⁻ and I₅⁻ ions [25,26]. We have detected no peak near 200 cm⁻¹ which is associated with iodine I₂ [25,26]. Therefore, all iodine inside the PEN layer is composed of I₃⁻ and I₅⁻ ions.

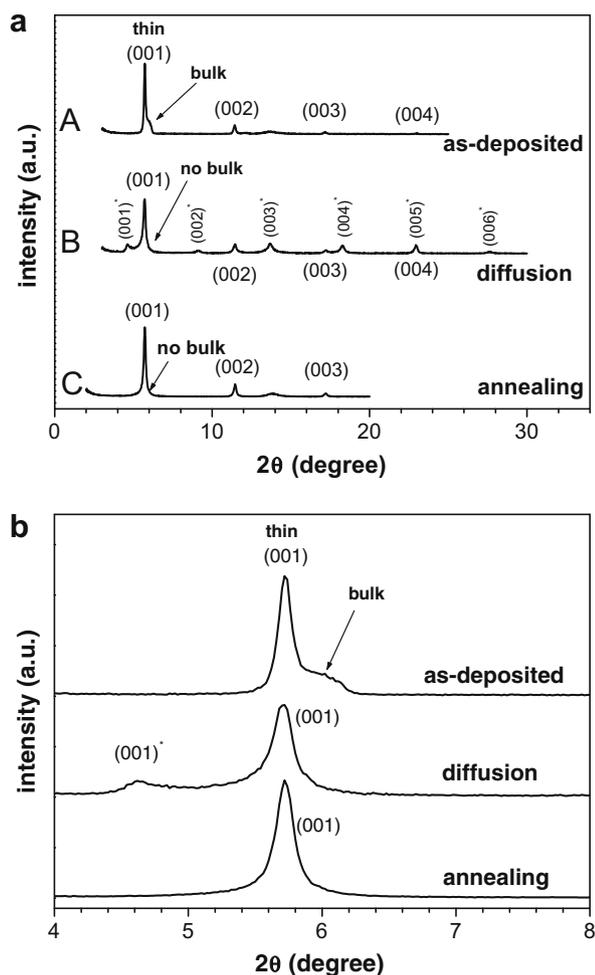


Fig. 2. (a) XRD spectra for sample J161 (PEN on Parylene): as-deposited (A), after 48 h of iodine diffusion (B) and after annealing in vacuum (C). Spectrum A shows two coexisting phases, the thin and the bulk phase of PEN. The order of diffraction of the thin film phase is denoted by (001)–(004). Peaks marked with a star correspond to the iodine intercalate thin film phase. The broad peak at 13.6° belongs to the parylene C layer. (b) First order of XRD spectra of sample J161, magnified from (a) allowing to observe the presence of the bulk phase peak in the as-deposited layer and its disappearance after iodine diffusion and after annealing.

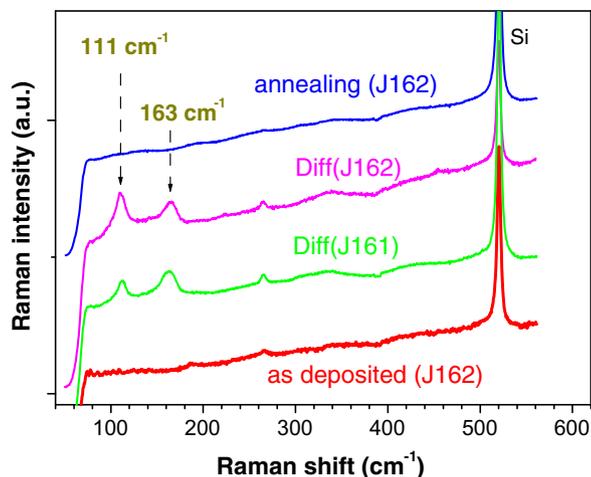


Fig. 3. Micro-Raman spectra of iodine doped PEN films J161 and J162 (middle spectra). For comparison the spectrum of J162 is plotted at the bottom for pristine films and on top after iodine diffusion and vacuum annealing. The peaks at 520 cm^{-1} come from the Si substrate.

The ratio of Raman intensities of the iodine ion peaks is approximately the same (about 1.0) in both samples. This corresponds to the intermediate region of iodine diffusion [5,6]. High intensities of I_{5-} [5] are associated with the degradation of PEN molecules. The existence of the intermediate diffusion region is confirmed also by XRD measurements for both samples (Figs. 1 and 2), because both peaks for the intercalated and the pristine phases, are visible in the XRD spectra.

We have seen above, that Raman measurements show only small differences between the properties of the samples J161 and J162, therefore we have performed SIMS measurements to determine the depth profile of iodine in the samples. In Figs. 4 and 5, SIMS profiles are shown for iodine in both samples. Together with the iodine profile also Si (presented in SiO_2 layer) and chlorine (presented in Parylene C layer) depth profiles are shown for the samples, to determine the position of the PEN–substrate interface. In sample J162 (Fig. 4) we can observe a huge increase of iodine near the interface of the PEN layer/substrate. We believe that this accumulation of iodine species causes the unusual phase transformation in this sample. Most likely, iodine ions I_{3-} and I_{5-} diffuse to this interface causing a decreased bonding strength between substrate and PEN molecules which could result in a decreased

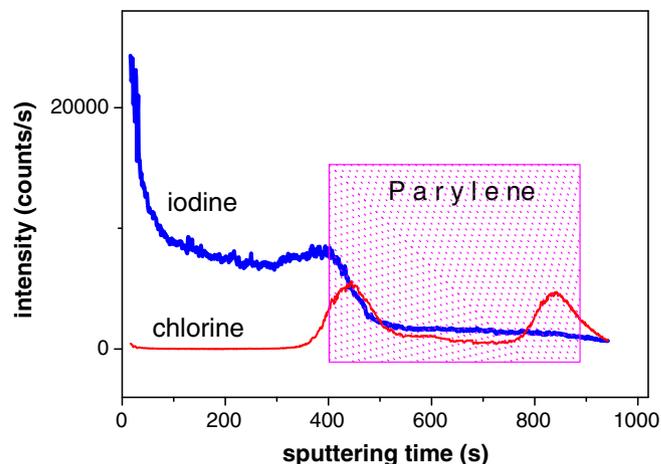


Fig. 5. SIMS depth profile of iodine and chlorine in the sample J161 after 48 h of iodine diffusion. The parylene C layer is schematically denoted by a rectangle.

molecular tilt angle of the molecules relative to the substrate normal giving possibly rise to the phase transformation (from the bulk and the thin film phase to the orthorhombic phase). In sample J161 also an accumulation of the iodine near the interface is observed, but with much lower amount than in sample J162 (Fig. 5). Nevertheless, we believe that the phase transition from the bulk to the thin film phase is also caused by the interfacial iodine accumulation. A similar phase transformation of PEN molecules was observed in [7,8]. We detect this small increase of iodine concentration near the interface PEN/substrate also in other iodine diffused samples, in which the bulk peak at pristine layers was very small or not detected by XRD. We believe that the phase transformation by iodine diffusion took place in many of the experiments of others researchers, e.g. [4–6], but it could not be observed by XRD since the transformed volume was small.

4. Conclusion

For the first time we have presented evidence for a phase transformation in pentacene layers from the thin film and the bulk phase into the orthorhombic phase by iodine diffusion. The thickness of the layer was 130 nm, which is much higher than in previously published results, where the orthorhombic phase was also detected in PEN films. Additionally, we have confirmed earlier observations of other authors regarding the transformation of the bulk phase into the thin film phase by iodine diffusion. The preparation of a single phase of pentacene in the complete film is promising for improving the electrical of OFETs.

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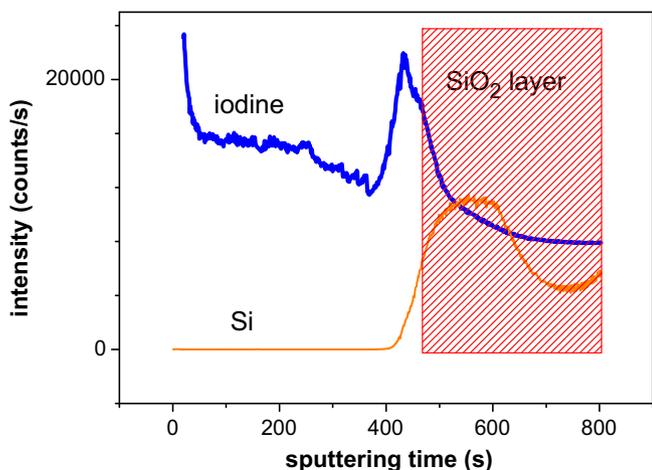


Fig. 4. SIMS depth profile of iodine and Si in the sample J162 after 48 h of iodine diffusion. The SiO_2 layer is schematically denoted by a rectangle.

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