

Surface and interface analysis of iodine-doped pentacene structures for OTFTs

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We investigated the impact of iodine doping on structural properties of pentacene layers as a function of iodine concentration, which is controlled by the diffusion time. Furthermore, also the storing history of the samples is examined. We found that the iodine doping properties of pentacene samples strongly depend on the storing conditions (ambient atmosphere, time) before diffusion. We observed that the iodine diffusion process into pentacene layers is much faster for new recently prepared samples in contrast to old samples that were stored a few months at atmospheric ambient condition in the dark box before iodine diffusion. Copyright © 2010 John Wiley & Sons, Ltd.

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Introduction

Organic semiconducting thin films have been intensely studied due to their potential applications in organic electronics.^[1,2] One of the main issues is the lifetime of organic devices, which can be significantly reduced by the influence of oxygen and moisture. In addition, a small contamination during device preparation also affects the semiconducting properties and the resulting device properties.^[3,4] Contaminations can also influence the doping process of organic semiconductors. Here we focus on the iodine doping of pentacene films. Although pentacene films are one of the most intensely investigated organic films^[5] for iodine doping, still significant differences in iodine diffusion times can be found in the literature (from several minutes to several hours).^[6–10]

This finding led us to study the doping properties of iodine into pentacene layers and its impact on the structural and electronic properties of different pentacene layers and structures as a function of iodine concentration and different storing time and conditions. We report on surface, interface and structure characterization of doped pentacene layers by SIMS, micro-Raman, X-ray diffraction and AFM methods.

Experimental

For studying the iodine diffusion into pentacene layers we used two different types of samples, A and B. The substrate treatment before film growth, as well as the storage conditions after film growth (before iodine diffusion) differs for both samples. In both cases, heavily doped silicon wafers were used with a 40-nm-thick thermally grown silicon dioxide insulating layer (supplier: ON Semiconductor). One substrate was covered with 40 nm parylene C (C₈H₇Cl)^[11] on top of the oxide (sample B), while the other substrate was treated in Hexamethyldisilazane (HMDS) vapor for 50 h (sample A).^[12] The pentacene films with a thickness of 100 nm (sample A) and 130 nm (sample B), respectively, 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 0.030 nm/s. No further purification was performed for the commercially available pentacene material (Acros Organics).

For comparing the iodine diffusion process, the structural quality of both pentacene layers (sample A and B, 'as deposited') should be similar before iodine diffusion. This was confirmed by micro-Raman spectroscopy and XRD measurements that showed similar results for both samples. It is known that the ratio of the integrated Raman band intensities at 1155 and 1158 cm⁻¹ (A₁₁₅₅/A₁₁₅₈) corresponds to the structural quality of the layer.^[14] This ratio was determined to be very similar for both samples, namely 1.1 for sample A and 1.2 for sample B.^[13] Furthermore, XRD spectra showed that in both samples (A and B) the so-called thin-film phase dominates.^[15]

The iodine doping of the pentacene films was performed by exposure to a mixture of iodine vapor and a very small amount of ambient atmosphere at room temperature in a self-made apparatus utilizing a glass container.^[15] The container stored two Petri dishes, one with the iodine crystals, and the second with the pentacene samples. Apart from the substrate treatment, the lifetime and storage condition differed between sample A and B. While sample B was stored for 9 months at atmospheric ambient

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condition (temperature $\approx 25^\circ\text{C}$, humidity 35–60%) in the dark box, sample A was prepared shortly (stored only several hours in the dark box in nitrogen atmosphere) before iodine diffusion. In order to support that the substrate treatment before film growth does not affect our results, we reproduced, later, the measurements with fresh and three-month-old samples of the same type (sample A), which will be discussed at the end of this manuscript.

After iodine diffusion the samples were analyzed using a time-of-flight-based SIMS instrument (Ion-TOF, SIMS IV) equipped with a high-energy Bi^+ primary source in combination with a low-energy sputter gun (Cs^+). The SIMS investigations were performed in order to obtain surface and depth profile chemical information, i.e. in order to resolve the composition of the layer interfaces. Micro-Raman spectroscopy (Jobin Yvon HR800) investigations at room temperature in backscattering geometry using He-Ne (633 nm) and Nd: YAG (532 nm) lasers were performed to estimate qualitatively the iodine doping by the presence of iodine ions I_3^- and I_5^- . Standard AFM investigations were done using a Park System XE100 in noncontact mode with conductive Cr–Au cantilevers to study the surface morphology and the thickness of the pentacene layers. XRD measurements were carried out using a Bruker D8 DISCOVER diffractometer equipped with a rotating Cu anode operating at 12 kW.

Results and Discussion

The structure of pentacene layers is usually characterized by the presence of the thin-film and the bulk phase.^[14] One way to enhance the structural quality of the pentacene layer is to dope it with iodine ions by diffusion.^[10] According to our previous experiments^[15] where we used pentacene layers that were stored for 9 months at atmospheric ambient condition in the dark box before iodine diffusion, we now used fresh pentacene samples (sample A) for iodine diffusion, starting with a diffusion time of 48 h (sample A48). During this long time the so-called intermediate regime of diffusion should be obtained.^[8] We found that after iodine diffusion for 48 h, the pentacene structure was completely changed. We confirmed this by XRD measurements where the XRD peak corresponding to the thin-film phase (Fig. 1(a), curve A) nearly vanishes, even if the data are scaled by a factor of 15 (Fig. 1(a), curve A48).

This finding was confirmed by micro-Raman spectroscopy (Fig. 1(b) top spectrum). The peak corresponding to I_5^- ions dominates, i.e. its intensity is much higher than that of the peak associated to I_3^- ions. This part of the Raman spectrum is capable of characterizing the saturation regime of the iodine diffusion. The results suggest that the I_5^- ions are the dominating species in the diffusion process. They diffuse between the pentacene molecules and cause distortions of the pentacene structure and, thus, they cause irreversible damage to the transport properties.^[9] Additionally, the high intensity of the iodine Raman bands supports the presence of high iodine concentration in the pentacene layer. This is also supported by SIMS measurements (Fig. 2), where we detect high iodine concentration in the first third of the layer thickness. Also, AFM measurements show strong morphological differences between 48 h doped and untreated pentacene layers (data not shown). A significant increase of the film roughness (from 4 to 20 nm) as well as a swelling of the pentacene microcrystallines after iodine doping was observed. Therefore, we decided to decrease the diffusion time gradually from days to hours and minutes, thus reducing the iodine concentration accordingly.

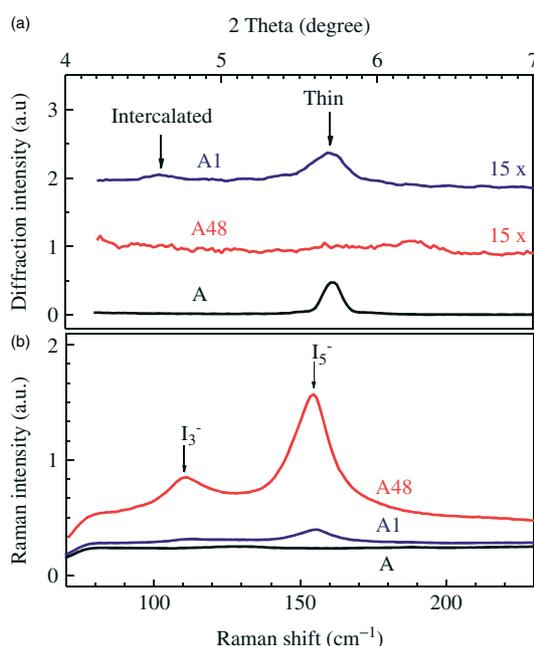


Figure 1. X-ray diffraction pattern (a) and Raman spectra (b) of sample A: as deposited (A), after 48 h (A48), and after 1 h of iodine diffusion (A1). The peaks denoted as I_3^- and I_5^- are associated with the stretching frequencies of the iodine ions I_3^- and I_5^- , respectively.^[9] For better view, the A1 and A48 XRD spectra are shifted to higher diffraction intensity values.

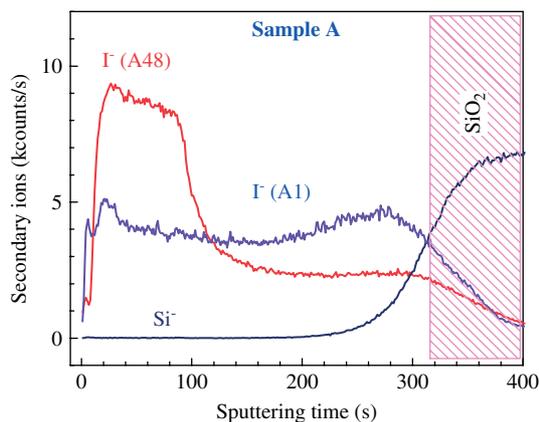


Figure 2. SIMS depth profile of silicon and iodine ions for pentacene samples after 1 h (A1) and after 48 h (A48) of iodine diffusion. The underlying SiO_2 layer is schematically shown by a rectangle.

In the following, we present the data of films doped for 1 h (sample A1) and compare the results with those of films doped for 48 h (sample A48). The presence of two small peaks at 5.7° and 4.6° in the XRD spectrum (Fig. 1a, top spectrum) documents a slight improvement of the pentacene structure in sample A1. The position of these peaks corresponds to the thin-film phase and the intercalated phase.^[6] Nevertheless, the peak intensities are significantly smaller than for the untreated layer (Fig. 1a) bottom spectrum), which shows that the structural quality of the pentacene layer is still decreased by iodine diffusion.

Additionally, SIMS depth profiles (Fig. 2) show differences in the iodine distribution within the pentacene layer for sample A1 and A48. In sample A1 the iodine profile is relatively constant over the film thickness, but it decreases slightly within the film

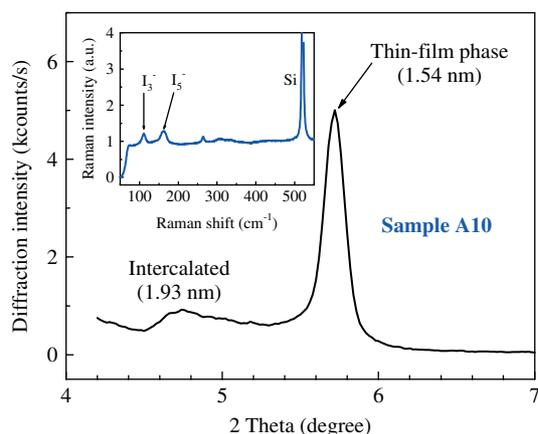


Figure 3. X-ray diffraction pattern of sample A, after 10 min of iodine diffusion (A10). The lattice spacing of both phases is shown in brackets for the corresponding Bragg peak. The insets show the Raman spectrum of sample A10 where the two peaks corresponding to I_3^- and I_5^- iodine ions are marked with arrows.

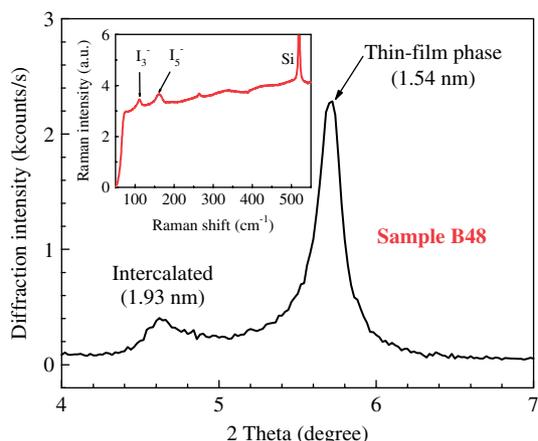


Figure 4. X-ray diffraction pattern of sample B, after 48 h of iodine diffusion (B48). The lattice spacing of both phases is shown in brackets. The inset shows a Raman spectrum of I_3^- and I_5^- iodine ions that are present in the layers after iodine diffusion.

and it increases near the SiO_2 interface. This type of depth profile of iodine ions in pentacene layers was also observed by other authors.^[15] It indicates a regular spreading of iodine ions into the pentacene bulk with the highest ion concentration at the surface. The corresponding Raman spectrum (Fig. 1(b) – spectrum in the middle) shows lower intensities of the I_3^- and I_5^- peaks compared to the spectrum of sample A48 (top spectrum), due to the lower concentration of iodine ions.

A further reduction of the iodine concentration leads to still better structural film properties: After decreasing the time of iodine diffusion to 10 min (sample A10) we obtained the so-called intermediate regime of diffusion^[8] which is characterized by the presence of the thin-film phase and also its intercalate phase in the layer. Both the measured XRD peaks corresponding to these phases are plotted in Fig. 3. The small width of the peak at 5.7° , corresponding to the thin-film phase, indicates a good crystallographic quality of the pentacene layer. The ratio of iodine ions I_3^-/I_5^- (approximately = 1.0) derived from Raman measurements (Fig. 3, inset) demonstrates that the diffusion took place in the intermediate regime.^[9]

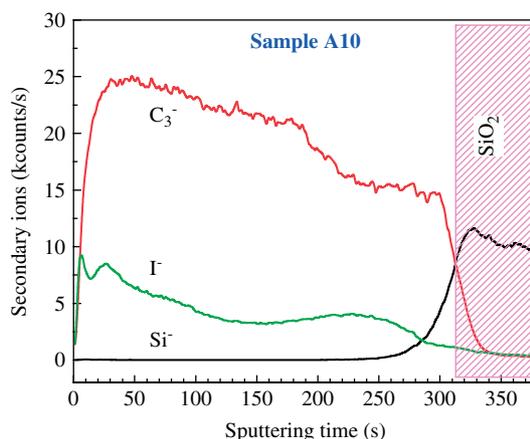


Figure 5. SIMS depth profiles of iodine and C_3^- ions in sample A after 10 min of iodine diffusion (A10). The pentacene/ SiO_2 interface is determined by the sharp increase of Si. A rectangular shaded area schematically shows the underlying SiO_2 layer.

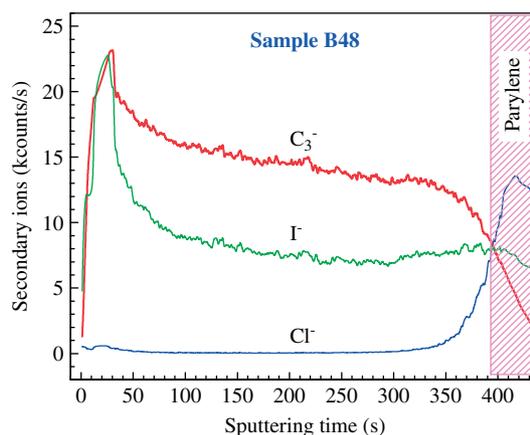


Figure 6. SIMS depth profiles of iodine and chlorine in sample B after 48 h of iodine diffusion (B48). The interface pentacene/parylene is determined by the sharp increase of chlorine. A rectangular shaded area schematically shows the underlying parylene layer.

In order to investigate the impact of the storage condition of the sample, we compare the results obtained for samples A with those obtained for samples B that were stored for 9 months in a dark box. Figure 4 shows the XRD spectrum for sample B48, which was doped for 48 h by iodine diffusion, which is very similar to the spectrum of sample A10 (compare Fig. 3). Also, the Raman spectra agree qualitatively (Figs 3 and 4, insets), as well as the depth profile determined by SIMS measurements, which are shown in Figs 5 and 6 for fresh (A10) and long-time stored samples (B48), respectively. In both samples, the highest iodine concentration is at the sample surface, which decreases slowly down to the substrate interface. This interface is determined for sample A10 (pentacene/ SiO_2 -interface) by the sharp intensity increase of Si ions and for sample B48 (pentacene/parylene interface) by the sharp intensity increase of chlorine ions (Parylene C is detected by chlorine ions^[12]).

These similar properties between sample A10 and B48 indicate that the same diffusion regime, namely the intermediate diffusion regime, is achieved although the samples were prepared with significant different diffusion times. This leads to the conclusion

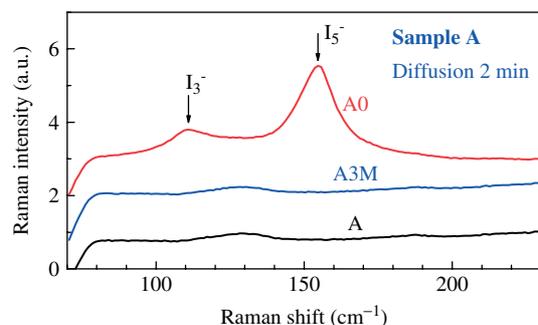


Figure 7. Raman spectra of sample A: as deposited (A) and after 2 min of iodine diffusion into a fresh sample (A0) and into a sample stored for 3 months at atmospheric ambient condition (A3M). The peaks denoted as I_3^- and I_5^- are associated with the stretching frequencies of the iodine ions I_3^- and I_5^- , respectively.^[9]

that for long-time stored samples the iodine diffusion time for obtaining the intermediate diffusion regime is significantly increased. While for fresh samples it is only 10 min, for long-time stored samples it is 48 h, which is approximately 300 times longer.

In order to further test the effect of substrate treatment, we repeated the experiments with the same type of substrate (sample A) but different lifetime after film growth. We used a fresh sample (sample A0) and a sample stored for 3 months at atmospheric ambient condition, which was similar to sample B (sample A3M). Figure 7 shows Raman spectra of these samples after 2 min of iodine diffusion. Only for the fresh sample the presence of iodine peaks I_3^- and I_5^- is visible, which supports the strong effect of storing condition onto the iodine diffusion process.

A possible reason for the phenomenon observed and described above can be deduced from SIMS measurements. In long-time stored samples we detect a significant increased amount of additional chemical elements that were present in the sample environment during storage, e.g. oxygen, sulphur and OH bonds. These elements modify the surface of the long-time stored pentacene layers. It was shown that in particular, water–pentacene complexes are created.^[4] This type of surface decreases strongly the diffusion coefficient for iodine into pentacene. Hence, it increases the time to obtain a certain regime of iodine diffusion.

Conclusion

In order to study the significant differences of published results characterizing the iodine diffusion process into pentacene layers which varies from minutes to several hours, SIMS, micro-Raman, XRD and AFM measurements have been used to investigate the mentioned process and to identify its nature. The differences obtained could be rationalized by different storing conditions of pentacene layers. The so-called intermediate regime of diffusion

is characterized by the presence of the thin-film phase and also the intercalate phase in the pentacene layer. We observed that for “old” samples, which were stored for 9 months under atmospheric ambient conditions in the dark box at room temperature, the diffusion time is approximately 300 times longer (48 h) compared to “new” (recently prepared) samples (10 min). Based on SIMS results, we believe that ambient conditions significantly modify the surface properties and lead to an aging effect. The different sample storing conditions (new and old samples) are therefore believed to be the major reason for the substantial variation of published data concerning the diffusion time of iodine into pentacene layers.

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