Impact of low 6,13-pentacenequinone concentration on pentacene thin film growth

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Thin films of pentacene (P) have been vacuum codeposited on SiO_2 with low concentrations of 6,13-pentacenequinone (PQ) in order to investigate the impact on the pentacene thin film structure. Within a range of 2%–20% PQ concentration no intercalation of the compounds can be observed by means of x-ray diffraction and infrared absorption spectroscopy. The crystalline quality of the P films stays unchanged by the presence of PQ, whereas P bulk phase contributions are being suppressed at PQ concentrations $\geq 5\%$, which could be confirmed by means of atomic force microscopy. From the results the authors suggest phase-separated PQ growth as well as PQ nucleation at P grain boundaries. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2767972]

Thin films of conjugated organic molecules such as pentacene (P) ($C_{22}H_{14}$) have been widely investigated during the last years due to the applicability in organic field effect transistors (OFETs).[1–3] The charge carrier mobility in P thin films is governed by structural defects, the density of grain boundaries,[4,5] and the purity of the material. It was found that 6,13-pentacenequinone ($C_{22}H_{12}O_2$) is a main impurity in commercially available P and can reduce the charge carrier mobility in P single crystals.[6] In addition, it was suggested that PQ can form deep traps of 0.2–0.75 eV for electrons within a P matrix, depending on the mutual molecular orientation.[7,8] In a recent study it was shown that P and PQ exhibit pronounced phase separation if codeposited in a molar ratio of 1:1.[9] However, up to now no attention has been directed to possible structural changes of P thin films due to the presence of low concentrations of PQ during P thin film growth. We address this issue by controlled vacuum codeposition of P and PQ.

Pentacene (Fluka, purum grade 99.9%) and 6,13-pentacenequinone (Sigma-Aldrich Co., purity 99%) were used without further purification. Films of nominally 30 nm thickness were obtained by vacuum codeposition (base pressure of 3×10^{-7} mbar, 1 nm/min total deposition rate) from resistively heated ceramic crucibles. The nominal film thickness was measured *in situ* by a quartz microbalance. Substrates were (100) p-doped silicon wafers (Siegert Consulting, prime grade) with a thermally grown oxide layer of 50 nm, cut into 10×10 mm coupons. The root mean square roughness of the substrates was determined to 0.2 nm by atomic force microscopy (AFM) (all AFM investigations were done on Veeco Nanoscope III in TappingMode®); the substrates were used as received; the cleanliness was confirmed prior to organic film deposition by AFM investigations. X-ray diffraction (XRD) measurements were performed at the beamline W1.1 at the synchrotron radiation source HASYLAB (Hamburg, Germany); the wavelength was set to $\lambda = 0.11808$ nm. The upper limit of instrumental broadening of this setup was estimated by the 2Θ width of the (111) reflection of a Ag(111) single crystal $(0.0382 \pm 0.0003)°$. Fourier transform infrared absorption spectroscopy measurements (FTIR) (resolution of 2.0 cm^{-1},

near-normal transmission geometry) were performed with a Bruker IFS-66v spectrometer (liquid N_2 cooled mercury cadmium telluride (MCT) detector); reference scans were done on SiO_2 substrates covered with the powder of the respective pure materials.

We performed specular x-ray diffraction on P/PQ codeposited films with PQ concentrations of 50%, 20%, 10%, 5%, and 2%, as well as on a reference film of pure P (see Fig. 1). It is known that P can grow in different polymorphs depending on the film preparation conditions.[10,11] In all spectra we found primarily the 00*l* series of a P structure characterized by a (001) net plane spacing of 1.55 ± 0.01 nm, which is commonly referred to as *P thin film phase*,[12] indicating a nearly upright standing molecular orientation. For the pure and P film containing 2% PQ we found additionally two reflections originating from the $(1-10)$ and (022) net planes of another polymorph[13] (referred to as *bulk phase* in the following). Here the long molecular axes are parallel with respect to the substrate plane. In the latter case, the intensity of the bulk contributions is reduced by 25%, and vanishes at PQ concentrations $\geq 5\%$. Interestingly, no peaks
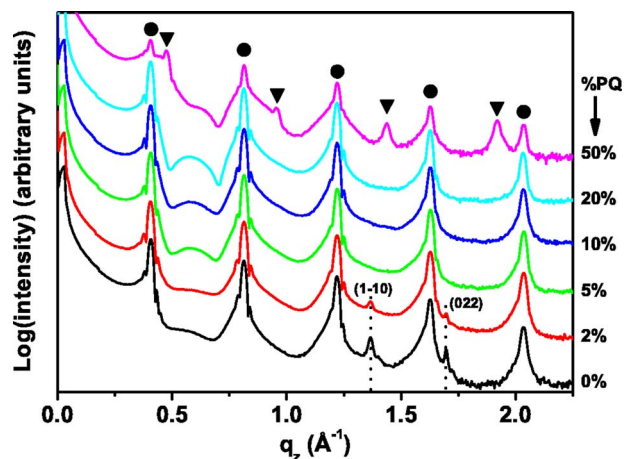

FIG. 1. (Color online) Specular x-ray diffraction scans of P/PQ codeposited films on SiO_2 at various molar ratios, $q_z = 4\pi \sin \Theta / \lambda$ denotes the momentum transfer normal to the surface at the Bragg angle Θ; the plots are vertically shifted for clearness. Peaks assigned to the P and PQ thin film phases are marked with a circle and triangle, respectively; peaks assigned to the P bulk phase are labeled with the corresponding indices.

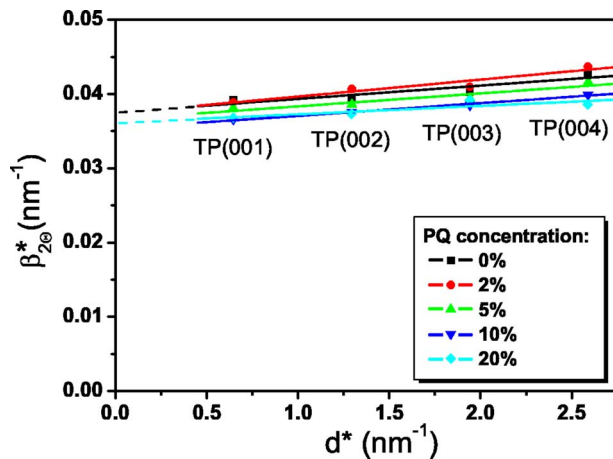a)Electronic mail: norbert.koch@physik.hu-berlin.de

FIG. 2. (Color online) Williamson-Hall plot of P films codeposited with different amounts of PQ. The lines connecting the peak series are linear least-squares fits.
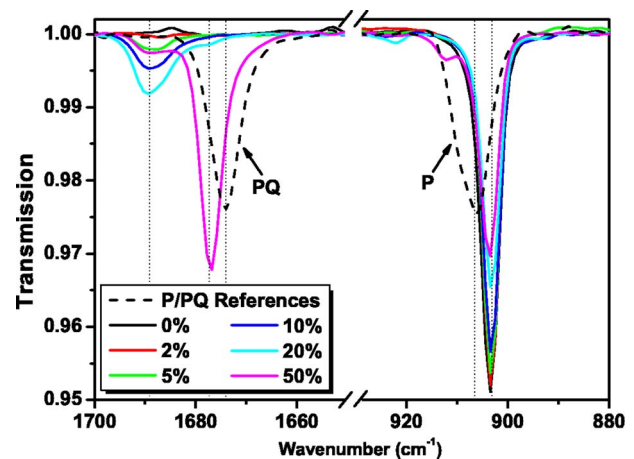

FIG. 3. (Color online) FTIR spectra of P/PQ blended films of different PQ percentages compared to reference scans of the respective source materials used for evaporation.

originating from PQ can be found even at concentrations as high as 20%. Instead, a broad feature arises between the P (001) and (002) reflections, which may be due to scattering from amorphous PQ. However, in a 1:1 codeposited film P and PQ grow in phase separated crystallites, exhibiting the two distinct series of the respective thin film phase peaks [the (00*l*) lattice spacing of the PQ thin film phase[9] was determined to 1.32 ± 0.01 nm].

In order to investigate the microstructure of the mixed films a Williamson-Hall analysis[14,15] (WHA) has been performed. The total integral breadth ($\beta_{2\Theta}$), (i.e., the ratio of peak area and height) is attributed to three distinct line-broadening factors:[16] (i) instrumental broadening, (ii) diffraction order-independent broadening (β_S) due to the average finite size of the crystallites, and (iii) order dependent broadening (β_D) due to lattice distortions (microstrains). This allows to separate (ii) from (iii) after correction of (i), by plotting $\beta_{2\Theta}$ [expressed in reciprocal units: $\beta_{2\Theta}^* = \beta_{2\Theta} \cos(\theta)/\lambda$] versus $d^* = 2 \sin(\theta)/\lambda$,

$$\beta_{2\Theta}^* = \beta_S^* + \beta_D^* = 1/\langle L \rangle_V + 2ed^*, \quad (1)$$

where $\langle L \rangle_V$ denotes the volume weighted average thickness of the crystallites along the direction [*hkl*] (Ref. 15) and *e* denotes the *maximum (upper limit) strain*, which is proportional to the distortion of the crystal lattice.[16] Being aware of the limitations of this simple model in deriving absolute values for the above quantities,[17] we applied WHA to explore *changes* within the P lattice due to low concentrations of PQ. The line profiles of the P (00*l*) reflections were fitted using pseudo-Voigt functions; the result is shown in Fig. 2. For pristine P we found a value of $\langle L \rangle_V = 26.6 \pm 0.6$ nm, which is only slightly increased to 27.7 ± 0.5 nm for the film containing 20% PQ. The value of the maximum strain remains essentially constant for all P:PQ ratios. The slight increase of $\langle L \rangle_V$ can be attributed to the decrease of the P bulk phase amount, as the PQ ratio is increased (see Fig. 1). This demonstrates that the P thin film phase crystallites grow essentially *undisturbed* despite the presence of 2%–20% PQ, which is being corroborated by the constant strain value.

In contrast to XRD, where only contributions of crystalline volume portions can be detected, FTIR provides information also on less ordered sample volumes. For instance, FTIR can be used to study polymorphism of organic molecu-

lar crystals.[9,18] It allows even to observe amorphous regions and can be highly sensitive to changes of the molecular environment, as would be induced by intercalation of P and PQ. We performed FTIR on the same set of samples that were investigated by XRD; characteristic parts of the spectra are shown in Fig. 3 in comparison to reference spectra of the pure materials. In the region of C–H out-of-plane bending and stretching modes,[19,20] we found that the most intense P absorption (903.5 cm^{-1}) was shifted by -3.0 cm^{-1} with respect to the P reference. This is explained by the different molecular arrangements in the P powder and the vacuum deposited films (substrate induced P thin film phase).[21] No shift of this mode was observed for PQ ratios up to 50%, which is further evidence for unchanged P growth in the presence of PQ. The same holds for other P vibrations (not shown). In the spectrum of the 50% PQ film the C=O stretching mode at 1676.9 cm^{-1} is blueshifted by 2.7 cm^{-1} compared to the PQ reference,[22,23] which is explained by growth in the thin film polymorph,[9] as found by XRD (Fig. 1). However, at lower PQ concentrations, the intensity of this vibration is strongly reduced and a peak at 1689.2 cm^{-1} emerges, which has not been reported before. This indicates a different molecular environment of PQ (compared to the bulk and thin film phases) in the low-concentration cases. However, we rule out considerable PQ intercalation into the P lattice, since this would alter the P lattice, and therefore also change the P absorption frequencies (which we did not observe).

In addition, all samples have been investigated by AFM; Fig. 4 displays micrographs of the pure P and the 20% PQ ratio sample. Apparently, the P island density increased for PQ concentrations $\geqslant 20\%$ (e.g., 0% PQ: 0.4 μm^{-2}, 20% PQ: 0.9 μm^{-2}). Both films showed the expected morphology of the P thin film phase with characteristic steps of 1.6 ± 0.2 nm height. Apart from P thin film phase islands we found small areas of different morphologies in both cases, which we assign as follows: Areas of P bulk phase (pure P film) and PQ areas (codeposited film with 20% PQ ratio).[24] As the features assigned to PQ in the codeposited film (Fig. 4) are being found at P grain boundaries, we expect these sites to be preferred nucleation positions for PQ, since our findings from XRD and FTIR provide strong evidence against intercalated
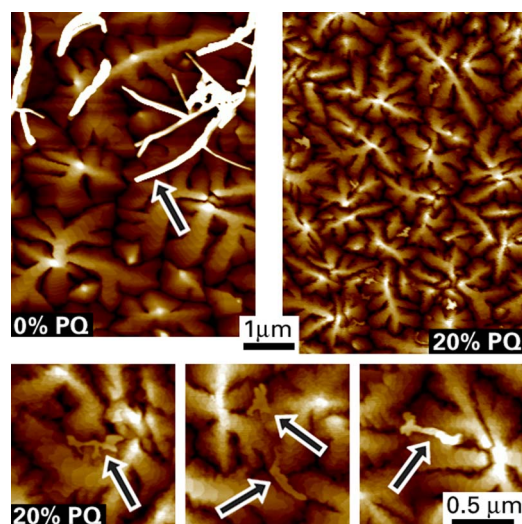
FIG. 4. (Color online) AFM micrographs of a pure P film compared to a codeposited P/PQ film with 20% PQ ratio. The colors indicate a height range of 30 nm; arrows point to areas of interest (see text).

growth of P and PQ, and a reduction of the lateral extension of the P islands was observed.

In conclusion, we have investigated the influence of low-concentration PQ presence on P thin film growth. Upon codeposition with PQ, the proportion of the P bulk phase is reduced and even absent for PQ concentrations $\geq 5\%$. Within the investigated PQ concentration range, the crystalline quality of the P structure remains unchanged and no evidence for intercalated growth was found. Instead, we suggest that PQ accumulates at P grain boundaries thus leading to additional complexity of grain boundary energetics with an expected impact on charge transport, which could now be studied systematically as function of PQ content. Moreover, it should be interesting to investigate possible charge confinement on single P grains due to barriers provided by PQ.

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