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Solvent-induced phase transition in thermally evaporated pentacene films

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We report a solvent-induced phase transition in pentacene thin films, from a ''thin film'' phase to a bulk-like phase. X-ray diffraction indicates that as-deposited thermally evaporated pentacene films consist mainly of (001)-oriented pentacene with an elongated (001) plane spacing of 15.5 ± 0.1 Å, and a minor amount with a (001) plane spacing of 14.5 ± 0.1 Å. When such films are exposed to solvents such as acetone, isopropanol, or ethanol, the plane spacing of the entire layer shifts abruptly from the elongated (001) plane spacing to the bulk value and this shift is accompanied by a macroscopic change in film morphology. While molecular ordering is maintained as indicated by x-ray diffraction, thin film transistor performance is severely degraded, most likely as a result of the morphological changes in the film. *© 1999 American Institute of Physics.* [S0003-6951(99)03322-7]

Recent reports of pentacene thin film transistors (TFTs) with performance comparable to hydrogenated amorphous silicon TFTs have increased interest in organic-based TFTs for large-area electronic applications on flexible plastic substrates.[1–4] We have shown previously that pentacene TFTs can have field-effect mobility as high as 1.5 cm^2/V s, current on/off ratio as large as 10^8, near-zero threshold voltage, and subthreshold slope as low as 1.6 V/decade when fabricated on heavily doped thermally oxidized silicon substrates treated with octadecyltrichlorosilane, a silane coupling agent.[5] One problem in fabricating more advanced organic-based integrated circuits is that it is difficult to pattern the organic active layer using photolithography and etching, or to pattern layers deposited on top of the organic active layer. While bulk pentacene is relatively insoluble and nonreactive in the typical solvents used in photolithographic processing, TFT performance is dramatically degraded after exposure to solvents. In this letter we investigate solvent interaction with thermally evaporated pentacene films.

Pentacene was purchased commercially with an initial purity of >97% and purified by temperature-gradient vacuum sublimation.[6] Films were deposited by thermal evaporation onto heavily doped thermally oxidized (100)Si substrates in a turbomolecular-pumped vacuum system with a typical base pressure of less than 7×10^{-5} Pa. The substrates were held at 60 °C and the pentacene was deposited at 0.15–0.2 nm/s, with a final average thickness of 50 nm.

For this work, after the active layer deposition we fabricated TFTs by thermally evaporating gold through a shadow mask to form source and drain contacts. The as-deposited TFT characteristics are shown in Fig. 1 (solid lines), where we have plotted the drain current as a function of drain-to-source voltage for several values of gate-to-source voltage. This device had a channel length of 35 μm, a channel width of 220 μm, and a gate dielectric thickness of 300 nm. A field-effect mobility of 0.36 cm^2/V s was extracted from a plot of the square root of the drain current as a function of gate-to-source voltage for the TFT biased in saturation.

The film morphology was characterized using a Park Scientific M5 scanning probe microscope. Figure 2 is an atomic force microscope (AFM) image of the topology of the pentacene film. This 10 μm $\times$ 10 μm scan shows the film is highly textured with large dendritic grains extending over several microns. Smaller area scans show the dendrites are terraced, with a step height of approximately 1.5–2.0 nm.

Molecular ordering was investigated by θ–2θ x-ray dif-

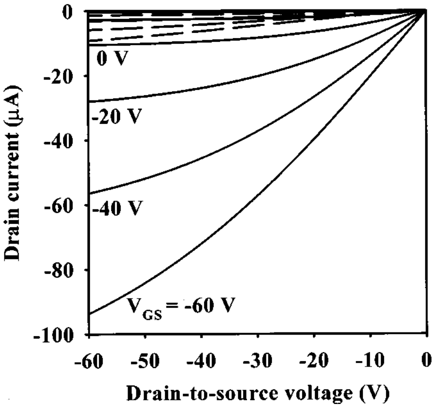

FIG. 1. A plot of the pentacene TFT characteristics as-deposited (solid lines) and after ethanol exposure (dashed lines). The TFT has a channel length and width of 35 and 220 μm, respectively, and a gate dielectric thickness of 300 nm.

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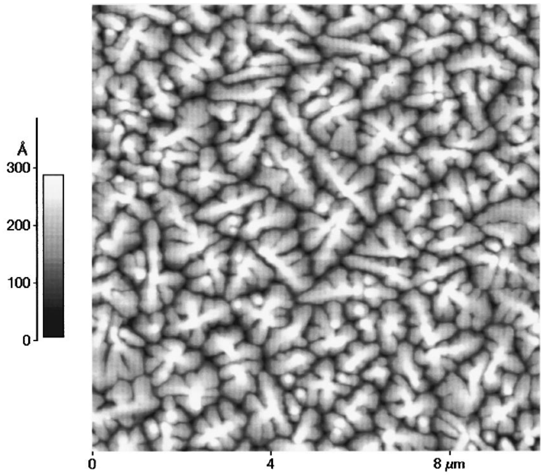

FIG. 2. A 10 μm×10 μm AFM image of a pentacene film. The film is highly textured, with micron-sized, terraced dendritic grains.

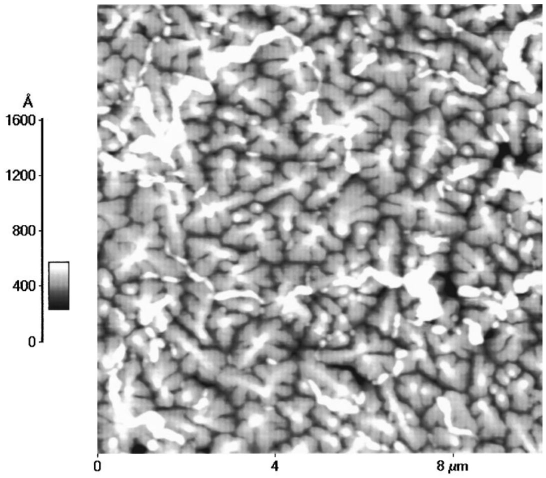

FIG. 4. A 10 μm×10 μm AFM image of a pentacene film after exposure to isopropanol. The layered, dendritic features are maintained, although regions appear that are significantly elevated above the average film height.

fraction scans using a four-circle diffractometer with Cu $K\alpha$ radiation. The diffraction vector was aligned perpendicular to the substrate surface. The θ–2θ scan for the as-deposited film is shown in Fig. 3. The peaks in Fig. 3 indicate that the as-deposited film consists of a phase with a d spacing of 15.5 ± 0.1 Å, and a small component of a second phase whose d spacing of 14.5 ± 0.1 Å closely matches the (001) spacing of bulk pentacene.[7] The triclinic crystal structure of bulk pentacene does not have any interplanar spacing that matches the 15.5 ± 0.1 Å spacing present in our film. The greatest interplanar spacing in bulk pentacene is d_{001} with a spacing of 14.52 ± 0.1 Å, followed by $d_{10\bar{1}}=7.84$ Å. However, a similar elongated interplanar spacing has been observed in pentacene thin films and even pentacene single crystals by others.[2,8] This extended spacing has been attributed to the (001) interplanar spacing of a metastable ''thin film'' phase, denoted by $d_{001'}$ to distinguish it from the d_{001} bulk spacing.[2]

After characterizing the electronic, morphological, and structural properties of the as-deposited films, the films were exposed to acetone, isopropanol, or ethanol, by dipping them into a beaker containing the solvent and blowing them dry. These solvents were chosen because they are common laboratory solvents in which pentacene is nominally insoluble, and they can be useful in photolithographic processing. The TFT performance was severely degraded after solvent exposure. Figure 1 shows the TFT characteristics after exposure to ethanol (dashed lines). The extracted field-effect mobility was reduced by almost a factor of 10, from 0.36 to 0.037 cm^2/V s. The effect in the extrapolated value of threshold voltage after solvent exposure was negligibly small.

Figure 4 is an AFM image of the same film shown in Fig. 2 after isopropanol exposure. Many of the original film features are maintained. The film texture is similar to the unexposed film, with terraced, micron-sized dendrites remaining. However, regions appear that are significantly elevated above the average film height. Figure 5 is a θ–2θ x-ray diffraction scan of an isopropanol-exposed film; the sharp diffraction peaks indicate that microscopic film ordering is maintained after solvent exposure. However, the (001) interplanar spacing of the entire layer after solvent exposure has shifted to the bulk pentacene spacing. Since this shift would cause an increase of the in-plane film area, this indicates that the raised areas shown in Fig. 4 are regions where

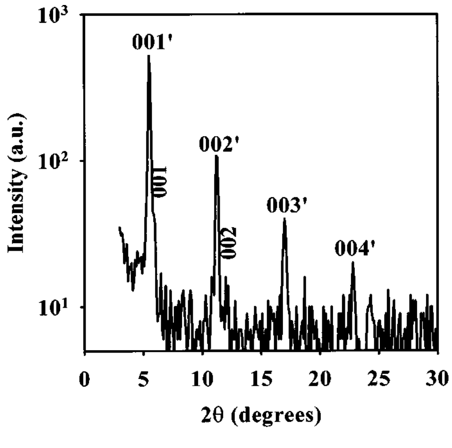

FIG. 3. The θ–2θ x-ray diffraction scan of a pentacene film as-deposited. The peaks labeled $00l$ correspond to the spacing observed in bulk pentacene, while those labeled $00l'$ correspond to an elongated (001) interplanar spacing.

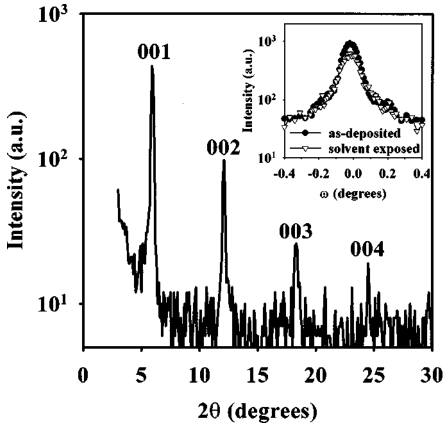

FIG. 5. The θ–2θ x-ray diffraction scan of a pentacene film after exposure to isopropanol. Not only is the film ordering maintained after solvent exposure, the plane spacing of the entire layer has shifted to the bulk pentacene spacing. The inset shows the rocking curve of the 001′ majority peak from Fig. 3 (circles) and the shifted 001 majority peak after isopropanol exposure from Fig. 5 (triangles). Note that the peak width and intensity are similar.

the film has buckled. The inset of Fig. 5 shows the rocking curve of the 001 majority peak of the pentacene film as-deposited and after isopropanol exposure. Despite the macroscopic film movement with solvent exposure the peak width and diffracted intensity are similar for the shifted and unshifted peaks. For this measurement the sample was not removed from the x-ray diffraction sample mount nor was it realigned after solvent exposure. We believe the small decrease in intensity of the shifted peak is due to film area lost to the buckled regions. Similar results were observed for films exposed to acetone or ethanol.

The difference between the elongated $d_{001'}$ spacing and the d_{001} spacing corresponds to an out-of-plane strain of approximately 6%. If we assume volume is conserved, this gives an in-plane compressive strain of approximately 6% or about 2.5% if we assume biaxial strain. From our AFM scans of films after solvent exposure, we find that the surface area of the buckled regions (estimated from the length, width, and height of the buckled regions) for a given scan size corresponds well with the expected change in surface area. This leads us to believe the film buckling is the result of in-plane compressive stress failure and not a delamination and reattachment of the film to the substrate after the solvent has evaporated.

Our observations that solvent exposure causes the $d_{001'}$ spacing to shift to the d_{001} spacing suggests that the elongated interplanar spacing is due to a slight rotation of the pentacene molecules making them more perpendicular to the (001) pentacene plane (and the SiO_2 interface) than occurs in bulk pentacene. In addition to a solvent-induced phase transition from a metastable ''thin film'' phase to a bulk-like phase, solvent exposure causes a change in film morphology, manifesting itself as film buckling most likely due to compressive stress failure. Since the typical TFT device size is greater than the average grain size of the pentacene, the device properties are influenced by both intragrain and intergrain transport. While x-ray diffraction indicates that molecular ordering is maintained after solvent exposure, TFT performance, most notably field-effect mobility, is severely degraded. This observed degradation is most likely a result of morphological changes which significantly degrade the intergrain transport. Intragrain transport effects due to the solvent-induced phase transition are also possible, but would likely be masked by intergrain effects in these measurements.

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