Hyperthermal Molecular Beam Deposition of Highly Ordered Organic Thin Films

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We use a seeded supersonic molecular beam to control the kinetic energy of pentacene ($C_{22}H_{14}$) during deposition and growth on Ag(111). Highly ordered thin films are grown at low substrate temperatures (~ 200 K) at kinetic energies of a few electron volts, as shown by low energy He diffraction and x-ray reflectivity spectra. In contrast, deposition of thermal molecules yields only amorphous films. Growth at room or higher temperature substrates yields films of poorer quality irrespective of the depositing beam energy. We find that after the first wetting layer is completed, a new ordered phase is formed, whose in-plane lattice spacings match one of the bulk crystal planes. The high quality of the films can be interpreted as the result of local annealing induced by the impact of the impinging high-energy molecules.

The growth of highly ordered thin films of planar, aromatic organic molecules, like pentacene ($C_{22}H_{14}$), is at present an active area of research as the semiconducting electrical properties of these materials make them promising candidates for plastic electronic device applications [1–3]. Because charge mobility and injection in organic crystals depend strongly on molecular orientation and packing, controlling the structure and the morphology of organic thin films may lead to useful applications. For the widely studied inorganic materials, growth is controlled by the balance between kinetics (impingement rate and surface diffusion) and thermodynamics (surface and interface energies) [4–6]. Fast surface diffusion and low impingement rates favor the formation of large islands and layer-by-layer growth, while poor adhesion (low interface energy) promotes aggregation and 3D growth modes. For nonreactive organic molecules, like pentacene, adhesion is relatively small on most surfaces, although it can be adjusted by optimizing the choice and the preparation of the substrate. For example, chemical treatment of the Si(001) surface allows the growth of large size (up to 0.1 mm) single-crystal pentacene grains [7] with "standing-up" molecules [8]. The standing up is the only thin films phase observed for pentacene on inert substrates (for example, on SiO_2 [10]). Alternatively it has been proved that a smooth surface of a weakly chemically active substrate, as Ag(111), allows for the epitaxial growth of commensurate, laying-down, highly ordered films of large, π-conjugated organic molecules, like PTCDA (3,4,9,10-perylenetetracarboxylic dianhydride) and oligothiophenes [11,12]. On the other hand, attempts to grow laterally ordered thin films of molecules with no reactive groups like pentacene on any weakly interacting (111) metal surface have been unsuccessful [13].

In this Letter, we present direct structural evidence of the validity of a completely different approach to the growth of organic thin films [14]. Instead of tailoring the substrate properties, we show, using mainly low energy atom diffraction (LEAD), that the quality of the film can be dramatically improved by controlling the kinetic energy of the impinging molecules. Molecules are accelerated to a few eV using a seeded supersonic free jet expansion from a molecular beam source (SuMBE) of 0.1 mm diameter in which different inert gases (He, Ar, and Kr) can be used as a carrier gas. Spectroscopic, morphologic, and powder pattern x-ray evidence of the soundness of this approach has been provided in the case of oligothiophenes [14–16]. However, the structure of the first interfacial layers and of the topmost surface were not determined. Most importantly no differential measurements were reported showing directly the structural consequences of controlling the velocity of the impinging molecules.

Varying the nature, or the pressure, of the carrier gas and/or the temperature of the organic material, the average mass of the flowing gas and, as a consequence, the translational kinetic energy (E_t) of the pentacene molecules, change according to $E_t = 5(m/\bar{m})kT/2$ where k is the Boltzmann constant, T is the temperature of the nozzle (~ 200–$220\,°C$), and m and $\bar{m}$ are the pentacene and average (pentacene plus carrier gas) molecular mass, respectively [17]. In particular, given a carrier gas pressure of about 300 Torr and being 1.2×10^{-3} Torr the vapor pressure of pentacene at $220\,°C$ (our typical working conditions), $\bar{m}$ is approximately that of the carrier gas. Taking into account the deceleration of pentacene molecules due to the velocity slip [17], E_t can be calculated to vary between 5 and 0.4 eV by changing the carrier gas from He to Kr. These values are in good agreement with time-of-flight measurements [18].

LEAD measurements were performed *in situ* with a surface scattering apparatus extensively described before

[19], using a monoenergetic He beam with energy of 14 meV ($T_{nozzle} = 70$ K) and $\Delta E/E \sim 2\%$. The reciprocal space of the surface was mapped by detecting the angular distribution of the diffracted atoms at different azimuthal orientations of the substrate crystal. The detector is a liquid helium cooled bolometer rotating in the plane that contains the incident beam direction and the normal to the surface. The angle-to-momentum conversion is then performed using the equation $\Delta K_{\parallel} = k_i(\sin\theta_f - \sin\theta_i)$, where $\Delta K_{\parallel}$ is the parallel momentum transfer, k_i is the incident wave vector, and θ_i and θ_f are the incident angle and the detector angular position, respectively. The Ag(111) surface was cleaned in UHV by repeated Ar^+ sputtering (1 keV) and annealing (800 K) cycles, until the $(0, 1)$ diffraction peak, which defines the Ag(111) $\langle 11\bar{2} \rangle$, or next nearest-neighbor direction, was clearly visible and a specular peak with intensity of at least 25% of the intensity of the primary He beam was detected at the crystal temperature of 80 K. Complementary *ex situ* x-ray reflectivity measurements have been carried out at the beam line X10B of the NSLS at Brookhaven on one of the pentacene films grown at 200 K.

In Fig. 1 we show the decay of the He specular reflection peak intensity (I) monitored during pentacene deposition as a function of the exposure time, normalized to the signal at zero exposure (I_0), at a substrate temperature of 200 K. Because of the large size of adsorbate and defect cross sections for diffuse He scattering, He reflectivity is a sensitive method to study lateral interactions between adsorbates and ultimately the film growth mode [20,21]. Here the specularity of the clean surface I_0 is mainly limited by the number of steps (we measured a surface miscut of $\sim 0.56°$, corresponding to an average terrace width of ~ 380 Å). Because of the high kinetic energy of the molecules, and to the low barrier for diffusion (typically ~ 0.5 eV) on the flat silver terraces, pentacene admolecules can migrate even at temperatures as low as 200 K to reach the steps, which they find energetically favored [22]. As long as the adsorbed molecules are found only at steps, the total diffuse scattering probability is similar to that of the bare stepped surface (slower initial decay regime; see the inset of Fig. 1). After step saturation pentacene islands grow from the steps, in parallel with some island nucleation and growth on the terraces. The completion of the first layer is then associated with the maximum of the first oscillation of the specular reflectivity shown in Fig. 1 [20,21].

LEAD data along the Ag(111) $\langle 11\bar{2} \rangle$ direction relative to 1 ML of pentacene deposited at the substrate temperature of 200 K (± 10 K) at $E_t = 5$ eV are shown in Fig. 2(a). Data were taken after cooling the film at 40 K in order to reduce both the attenuation of the elastic signal deriving from thermal motion of the surface atoms and the thermal radiation transfer from the crystal onto the bolometer, which decreases the detector sensitivity. These data clearly show that along the Ag $\langle 11\bar{2} \rangle$ direction the periodicity of the monolayer is 6 times that of the substrate corresponding to 15.0 ± 0.1 Å which is about 2 times the short van der Waals dimension of the molecule (16.6 Å $\times$ 7.4 Å [23]). Along the Ag $\langle 1\bar{1}0 \rangle$ instead peaks are not clearly resolved. The same monolayer structure was observed for all the temperatures and pentacene velocities investigated in this work (150 to 350 K), but the narrowest diffraction peaks were obtained between 200 and 250 K.

Further pentacene deposition at 200 K results in the appearance of a second, damped, specular intensity oscillation (see Fig. 1), attributed to the completion of the second layer. This observation suggests a layer-by-layer growth mode for pentacene on Ag(111) [5]. Because of the noise in our detection system at the temperature of deposition (see above), and of the large Debye-Waller factor of pentacene multilayers, no further oscillation can be clearly observed during the growth. Moreover, the second oscillation was observed only at a substrate temperature of 200 K [24]. The diffraction pattern, measured at this second maximum in the reflectivity curve, shows peaks at different positions than the first layer. Further increasing the pentacene dosing does not cause any major structural change while the diffraction patterns become sharper. Azimuthal scans relative to the surface of ~ 50 ML (~ 170 Å) thick pentacene film deposited at 200 K with high kinetic energy are shown in Fig. 2(b). The multilayer in-plane diffraction pattern fits well with the unit cell (u.c.) shown in Fig. 2(c), with dimensions of 6.1 ± 0.1 Å $\times 16.5 \pm 0.6$ Å, in which the molecular long axis is tilted 20° with respect to the the Ag(111) $\langle 1\bar{1}0 \rangle$ direction. This u.c. gives a molecular assembly similar to the *b-c* plane of the bulk phase ($b = 6.06$ Å, $c = 16.01$ Å [9]). Although the molecular tilting angle could be optimized to yield a better fit, we think that the proposed structure is the best choice as it retains the bulk molecular assembly. Since no measurable effects were found after room temperature annealing of the film grown at 200 K, *ex situ* x-ray reflectivity measurements were successively
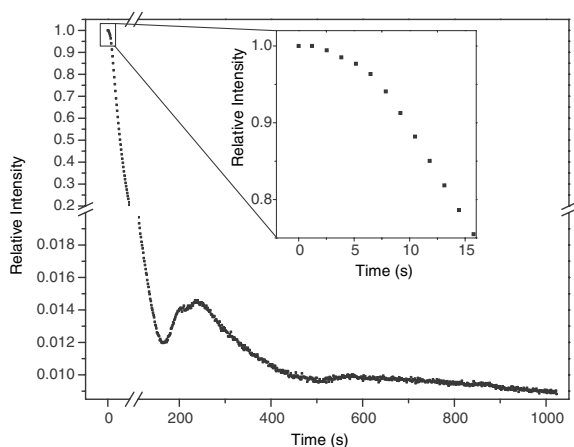

FIG. 1. Surface specular reflectivity as a function of deposition time, relative to the clean Ag(111) specular reflectivity I_0. Inset: expanded view of the initial decay.
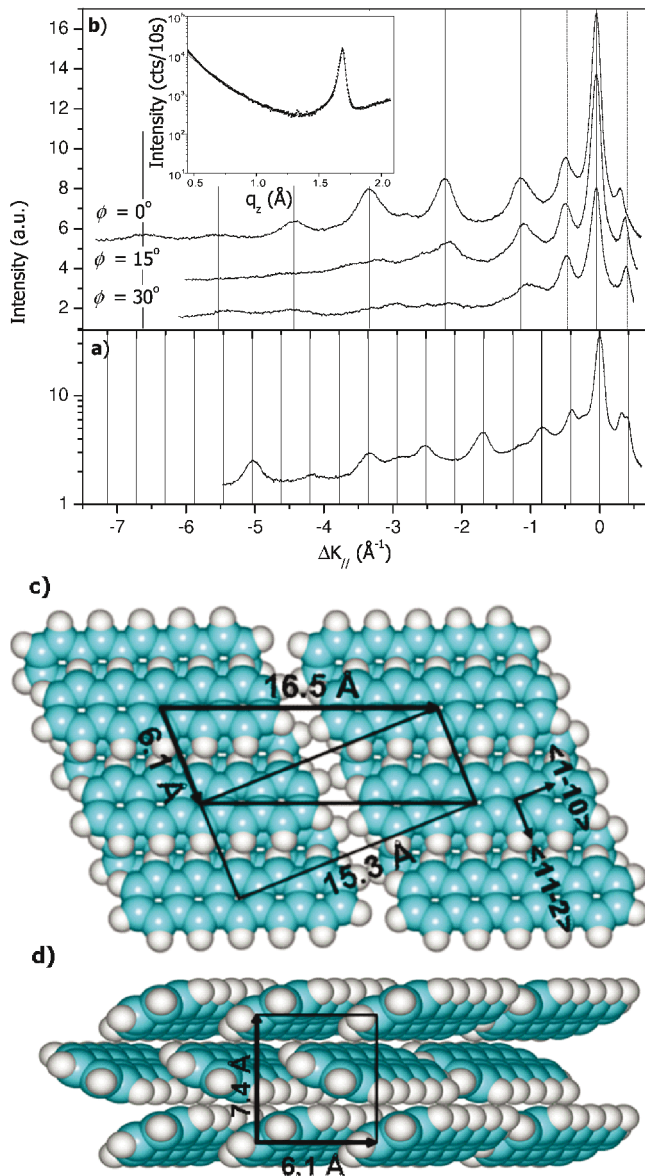
FIG. 2 (color).   (a) He diffraction spectrum along the Ag(111) $\langle 11\bar{2}\rangle$ direction (defined here as $\phi = 0°$) for 1 ML pentacene deposited with $E_{trasl} = 5$ eV. Expected peak positions relative to the $(6\times)$ periodicity (see text) are indicated by full lines. (b) Diffraction spectra from $\sim$50 ML pentacene/Ag(111) deposited with $E_{trasl} = 5$ eV. Full (dashed) lines correspond to a periodicity of 6.1 ± 0.1 Å (15.3 ± 0.6 Å) along Ag(111) $\langle 11\bar{2}\rangle$ ($\langle 1\bar{1}0\rangle$) direction. Inset: *ex situ* x-ray reflectivity spectrum from the same film. Structural model of the film: (c) top view; (d) side view.

performed on the same film. X-ray intensities recorded in reflection geometry are shown in the inset of Fig. 2(b). At $q = 1.68$ Å^{-1} a highly asymmetric peak is observed, which is associated with a z_{film} interplanar spacing of 3.72 ± 0.01 Å, i.e., only 5% less than half the a spacing of the bulk u.c. (7.9 Å [9]), which further supports the similarity of the growing phase with the bulk. In Fig. 2(d) the proposed structure of the film along the a axis is shown. The compression in the interplanar spacing

is compensated by the expansion along the c axis. Our model gives a monoclinic crystal structure with the same u.c. volume of the triclinic bulk phase (692 Å^3 for the bulk phase, 690 ± 40 Å^3 in our case).

Asymmetries in x-ray reflectivity curves [see inset of Fig. 2(b)] have been reported in previous works [25,26] and shown to be related to the interference of the scattering amplitude of the film with that of the underlying substrate. The best least-squares fit of the reflectivity curve in Fig. 2(b) was obtained by inserting a flat pentacene layer between the tilted film and the silver surface, as expected in order to maximize the interaction of the pentacene π electrons with the underlying surface. The result of the fit indicates a distance of 7.8 ± 0.3 Å between the silver surface and the first *tilted* pentacene layer.

In the case of films grown at 150 and 250 K the diffraction peaks were quite broad, and no diffraction was detected after a few monolayers, as shown in Fig. 3. No structural order was found at temperatures of 300 K and higher. Annealing the films grown at temperatures other than 200 K improved slightly the diffraction pattern and resulted in a partial decrease in the peak widths, indication of increasing domain size, but the structural quality of the film grown at 200 K could never be reached. No measurable effects were instead found after annealing of the film grown at 200 K up to the sublimation temperature of the film itself that we found to occur at $\sim$400 K. The thermal stability of the film grown at 200 K clearly shows that a long-range ordered phase of pentacene thin films was produced and that this phase represents energetically a global minimum of the system.

In order to prove that the high quality of the thin film structure at 200 K is strictly connected to the kinetic
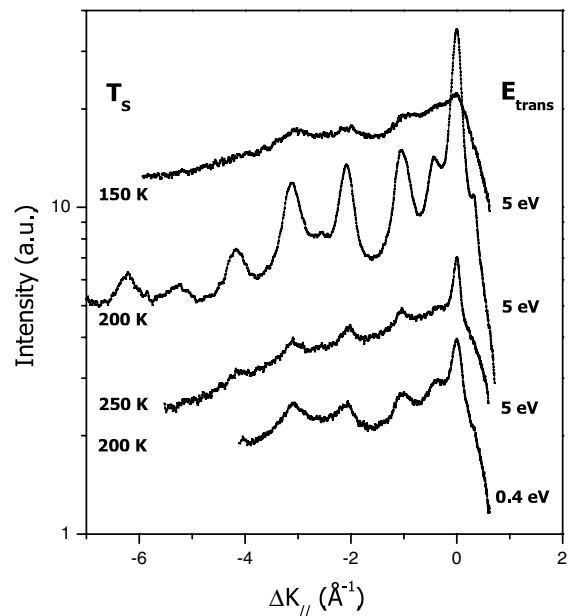

FIG. 3.   LEAD data taken along the surface $\langle 11\bar{2}\rangle$ direction for films grown at different temperatures and kinetic energies.

energy of the hyperthermal beam, we investigated the film growth at a pentacene kinetic energy of about 0.4 eV, by changing the carrier gas from He to Kr, while keeping the molecular flux almost constant ($\sim$0.4 ML/min). Diffraction data along the Ag(111) $\langle 11\bar{2} \rangle$ direction for films grown at 200 K with 0.4 eV kinetic energy are shown in Fig. 3 (bottom spectrum): multilayer diffraction peaks are considerably broader for films grown with Kr carrier gas. Similar improvements of the film morphology with increasing deposition energy at low substrate temperatures have been recently demonstrated for the epitaxial growth of β-SiC on Si(100) [27].

The growth of good quality pentacene thin films at relatively low substrate temperature points to the fact that the local annealing induced by the impact of the hyperthermal molecules is a more efficient route to order than either the global annealing of the film, where competing processes like dewetting can play an interfering role, or higher substrate temperatures, where competing disordering processes, connected, for instance, to the growth of different crystal polymorphs [28], become relevant. Quasi layer-by-layer growth at low substrate temperatures (up to 70 K) has been observed by reflection high-energy electron diffraction (RHEED) and LEAD for other homo-epitaxial metal systems [21,29]. Since layer-by-layer growth is an adatom diffusion-mediated process, and since at 70 K thermally activated diffusion is not relevant, RHEED data were explained with a diffusion mechanism driven by the energy gained by the adatoms from the latent heat of condensation. In the case of molecular crystals like pentacene, the heat of condensation is lower than for metals, and crystallization involves more complex rearrangements [30], so that it is reasonable that for organic molecular films an extra amount of energy is required to activate a layer-by-layer type of growth.

In summary, we have reported here the first successful *in situ* structural determination of pentacene thin films grown on a solid metal surface using a hyperthermal organic-molecule seeded source. A long-range ordered monolayer structure has been produced, which mediates the growth of a new thin film phase, which matches that of bulk pentacene when growing from the b-c face of the bulk crystal. Our results suggest that hyperthermal beam sources may be useful in thin film growth for electronic applications.

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