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Controlling the Early Stages of Pentacene Growth by Supersonic Molecular Beam Deposition

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The key role of the pentacene kinetic energy (Ek) in the early stages of growth on SiOx/Si is demonstrated: islands with smooth borders and increased coalescence differ remarkably from fractal-like thermal growth. Increasing Ek to 6.4 eV, the morphology evolves towards higher density of smaller islands. At higher coverage, coalescence grows with Ek up to a much more uniform, less defected monolayer. The growth, interpreted by the diffusion mediated model, shows the critical nucleus changing from 3 to 2 pentacene for Ek > 5–6 eV. Optimal conditions to produce single crystalline films are envisaged.

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Pentacene (Pen) is one of the most promising candidates for organic electronic applications [1] since it exhibits high hole mobility (up to 5.5 cm2/V s) [2] in organic thin film field effect transistors (OTFTs). Nonetheless, the difficulty to determine and to control key properties of the organic layer, such as structure, morphology, and interfaces, is still a major factor limiting electronic properties. In particular, further progress in device development requires highly ordered large size crystals [3], possibly eliminating grain boundaries [1,3]. Recent studies evidenced a viable and promising approach to these questions based on controlling the incident molecules’ energy by supersonic molecular beam deposition (SuMBD) [4–6]. Since the film quality is largely determined by the early stages of growth, and since the first few molecular layers are crucial for charge transport in OTFTs [7], we focused on the (sub)monolayer growth on a chemically inert, flat SiOx/Si surface. Recently, Killampalli et al. [8], who studied Pen monolayer deposition on SiOx/Si by SuMBD at various kinetic energies (1.5–6.7 eV), reported a decreasing adsorption probability for increasing incident kinetic energy (Ek), an island density that does not increase appreciably during island growth, and the smallest stable nucleus requiring four molecules. The same critical nucleus was found for thermal evaporation [9,10]. In this Letter, we show that, by tuning the impinging molecules’ flux and energy, one can achieve unprecedented control on the condensation nucleus, and on the island density at different growth stages and thus produce films of much better quality. In particular, we demonstrate that, at moderate fluxes, (i) the island density depends markedly on Ek, (ii) the critical nucleus, determined by applying the general scaling function [11] is composed of only two molecules, and (iii) the growth rate increases with Ek. Based on this approach, we established improved conditions for producing highly ordered Pen layers with minimum density of grain boundaries. The different island growth modes are rationalized, as a function of different Ek regimes, in terms of surface diffusivity and its effects on the growth model.

Pen was deposited on a native SiOx layer [12] prepared by a standard wet chemical oxidation process [10] on silicon. The typical root mean square surface roughness of ~0.5 nm was determined by atomic force microscopy in tapping mode (AFM), by which we also noticed a few bright spots (area density of ~2.5 × 107 cm−2), presumably due to contamination. All substrates were hydrophilic, with water contact angles of 35 ± 2° determined by the sessile drop method [13]. Pen (Sigma-Aldrich, 99.98%) was purified before use by gradient vacuum sublimation [14]. The SuMBD system was described previously [4]. Samples were prepared by exposure to the supersonic beam (~10 mm diameter), for different times (10, 20, 30, and 50 min), at room temperature. Ex situ AFM [15] was systematically carried out by scanning over multiple 10 × 10 μm2 areas at the sample center. The molecular beam was characterized on-line in terms of chemical purity, flux, and energy distribution by combining time of flight (TOF) mass spectrometry and multiphoton ionization spectroscopy. We chose an operating regime where no clustering effects [16] and contaminants were detectable. The typical flux was ≈ 2 × 1011 molecules/(s cm2), estimated by cross correlating the TOF spectra at different Ek of the beam with that of a Knudsen Pen source used as a standard.

The four different Ek explored here (3.3, 5.0, 6.4, and 6.7 eV) were achieved by varying the degree of seeding through changing the He carrier gas pressure. The highest Ek achievable in our experimental conditions using He is 6.7 eV.

Figure 1 shows the morphology evolution versus exposure time for two of the Ek’s explored. In all cases, as shown by a micrograph at higher resolution in Fig. 2, the shape of islands is uniform (lobular) with smooth borders and hence markedly different from the fractal shapes usually ob-
served for thermal evaporated layers [17,18]. The top two images in Fig. 1 compare samples produced at an exposure time of 10 min. There are relevant trends that have been systematically observed: at higher kinetic energies ($E_k/0.0136:0$ and 6.4 eV) the typical island size shrinks and the island density increases as shown by the molecular island size distributions [Fig. 3(a)]. In particular, samples prepared at 3.3, 5.0, and 6.4 eV exhibit distributions peaking at island sizes of 0.11, 0.10, and 0.09 $\mu m^2$, respectively. The broader distribution observed for $E_k = 3.3$ eV is likely related to a more thermal-like growth process, which is expected for this beam as its $E_k$ distribution is closer to thermal. Insight into the growth of Pen from hyperthermal beams can be achieved by considering that it is a diffusion limited process [9,10]. When colliding with the surface, the initial $E_k$ of Pen is converted (partially) into $E_k$ parallel to the surface via a complex mechanism involving inelastic molecule-molecule and molecule-surface energy transfer processes [19–22]. It is reasonable to assume, by extending consolidated growth models [9–11], that molecules with higher $E_k$ diffuse over longer distances before aggregating or being captured by preformed molecular islands. This would result in a more uniformly dispersed pattern of small islands. On the contrary, molecules with lower $E_k$ travel shorter distances and have a lower probability to form new islands by colliding with other freely diffusing molecules at empty sites. A quantitative assessment was achieved by determining the critical nucleus $i$ (number of molecules forming a stable nucleus), based on the general scaling function $f_i(u) = C_i u^i e^{-au^{1/4}}$ introduced by Amar and Family [11], extended to Pen growth by Ruiz et al. [9], and reproposed by Tejima et al. and Stadlober et al. [23,24]. $C_i$ and $a_i$ are constants determined by hypergeometrical equations for $i = 0, \ldots, 3$ that assure normalization and proper asymptotic behavior of $f_i(u)$. Figure 3(b) compares the normalized island size distributions of films grown at $E_k = 3.3$ and 6.4 eV with the predictions of the general scaling model calculated for $i = 1, 2, \text{ and } 3$. For the highest $E_k$, we systematically observed a much better agreement for $i = 2$, as confirmed by a $\chi^2$ criterion. At about $E_k \leq 5.5–6.0$ eV the experimental dis-

FIG. 2 (color online). High resolution (2.0 $\times$ 2.0 $\mu m^2$) AFM micrograph showing the typical island morphology of a film prepared by exposure to a beam of $E_k = 5.0$ eV for 10 min.

FIG. 1 (color online). AFM micrographs (10 $\times$ 10 $\mu m^2$) of pentacene grown by SuMBD at two kinetic energies: $E_k = 3.3$ eV (first column) and $E_k = 6.4$ eV (second column). The evolution of the deposition has been characterized at different exposure times: (a),(b) at 10 min; (c),(d) at 20 min; (e),(f) at 30 min; (g),(h) at 50 min.
distribution is better reproduced by the $i = 3$ distribution, as previously reported for thermally deposited films on similar substrates [9,23,24]. By analyzing different sets of data by best fitting procedures, we corroborated the critical nucleus decrease from 3 to 2 over a threshold of $E_k$ as shown in Fig. 4(a). The diffusion growth model confirms the important role played by $E_k$ in the diffusion mediated processes regulating island formation and growth. An understanding of the mechanism by which a smaller critical nucleus can generate a higher final correlation length can be gained by considering that it implies a much higher density of nucleation sites, which proportionally reduces the island-island distance. Since the growth is diffusion mediated, such higher density shifts the onset of the island-island coalescence process to a much earlier stage of island ripening. The final outcome is that smaller and more mobile islands can merge easier in a crystalline film with reduced grain boundaries and hence a higher surface correlation length.

As evidenced in Figs. 1(c) and 1(d) after 20 min exposure the samples prepared at the highest $E_k$ show island coalescence, not observed for the lower $E_k$. It appears that for samples prepared at 3.3 eV the competition between growth of preformed islands and nucleation of new islands is still important, as indicated by the increase of island density. This process continues as the exposure time increases [Figs. 1(e) and 1(f)]. At this stage one observes a higher coverage for the highest $E_k$ at the same flux, as also confirmed by x-ray photoelectron spectroscopy measurements on the same samples. Already only 30 min of
exposure to the 6.4 eV beam yields an almost complete monolayer.

Figures 1(g) and 1(h) present the films formed after 50 min exposure, where second layer islands are seen on top of the completed monolayer for the sample prepared at 6.4 eV. The latter shows a much better monolayer quality with a much lower defect density, quasicompletely coalesced islands, a flatter surface, and sharper island edges (where visible). For all samples the monolayer is (1.5 ± 0.2) nm thick, and the formation of a second molecular layer is observed only after the (near) completion of the first. This indicates that molecules landing on top of a molecular island have enough energy to overcome the edge barrier [10] and to move down onto the bare substrate. The samples prepared at 3.3 eV show more grain boundaries with a smaller average molecular island size (∼0.5 μm²). It appears that the coverage, and hence growth rate, increases with $E_k$, with a rate difference that becomes more evident at larger coverage [Fig. 4(b)]. This can be understood within the diffusion mediated growth model considering the higher corrugation of the molecular island surface compared to the bare substrate. Seemingly the higher $E_k$ becomes crucial when the probability of landing on top of molecular islands is larger and both the increase in diffusion length and the need to overcome the barrier at the island edges determine the growth regime. When comparing our findings to those of Killampalli et al. [8], the differences in the coverage dependence, the observed morphologies, and the critical nucleus are quite striking. Our results demonstrate that dissimilar growth regimes can be achieved in SuMBD by tuning $E_k$ and flux (the growth rates reported here are about a factor 50 lower than in [8]).

In conclusion, we have highlighted the key role of molecular kinetic energy in SuMBD, which we successfully used to control the early stage growth of Pen layers. By increasing $E_k$ we could decrease the area density of structural defects in the monolayer, a critical step in achieving optimal growth conditions for organic films of unprecedented crystalline quality. We interpreted the impact of $E_k$ in terms of the diffusion mediated model and found that the critical nucleus reduces from $i = 3$ (typical for thermal sublimation) to $i = 2$ for $E_k > 5–6$ eV. A next step will be to investigate how the growth by SuMBD is influenced by different surface properties, such as the hydrophilic-hydrophobic character of the substrates.

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[12] The thickness of the SiO$_2$ layer was determined from ellipsometry measurements (Imaging Ellipsometry, Nanofilm Technology GmbH, Germany).
[15] The AFM images were acquired with a multimode scanning probe microscope, Digital Instruments, Veeco Metrology Group, U.S. The detailed analysis of AFM data was carried by WSXM (version 7.71, Nanotec Electronica S.L.) software.