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Morphology of perylene thin films on $SiO_x/Si(1 \ 0 \ 0)$ and $SiO_2/Si(1 \ 0 \ 0)$: A spectroscopic and microscopic study of the influence of the preparation parameters

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ABSTRACT

Thin films of perylene on $SiO_x/Si(1 \ 0 \ 0)$ and $SiO_2/Si(1 \ 0 \ 0)$ substrates have been studied by X-ray photoelectron spectroscopy and atomic force microscopy. These investigations reveal that structure, morphology, and growth modes depend on the preparation parameters. By varying the deposition rate between 0.8 and 16 nm/min, a transition from island growth mode, with large and isolated crystallites, to a homogeneous film growth is observable.

We can predict the growth of perylene on technologically relevant substrates: homogeneous smooth films at lower substrate temperature (below 200 K) and single grains, enough for single nanodevices, when the film is grown at higher substrate temperature.

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1. Introduction

Organic electronic devices offer an interesting alternative to inorganic semiconductor electronics due to low-cost deposition methods, flexible substrates, and simple packaging [1–4]. Organic field effect transistors (OFETs) are part of this rapidly developing field, but remain a technological challenge [5-8]. The most important part of an OFET is represented by the organic layer. Organic single crystals of tetracene [9] and pentacene [10] have been used in OFETs, reaching relatively high room temperature mobility values of $0.4/0.5 \text{ cm}^2/\text{V}$ s. However, the growth of single crystals for use in OFETs is not an easy task. Organic single crystals are often fragile and small. Their integration in a device is difficult, in particular regarding the organic/insulator interface and the organic/metal contacts. A promising alternative is given by thin films of small molecules [7]. Usually, in a thin film transistor, the molecules can be vapor-deposited under vacuum, spin-coated, dip-coated, or printed on the insulator material. All of these deposition techniques are of significant importance for low-cost electronics.

An appropriate choice of the insulator, i.e., one that optimally fulfils the main role of insulating the gate contact from the active layer, is very important. The most commonly used insulators are silicon-based [7-11], some alternatives are given by organic insulators [12,13] or metal oxides mixed with transition or rare-earth

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metals such as zirconium or lanthanum [14,15]. In a bottom-gate device, the organic semiconductor is deposited on the insulator; therefore, it is very important to gain detailed knowledge of the interface between an organic layer and its insulator substrate. In particular, an understanding of the growth mechanisms is necessary in order to control the preparation of optimized devices.

Perylene $(C_{20}H_{12})$ is one of the simplest aromatic hydrocarbons and its crystal and molecular structure has been thoroughly studied already in the 1960s [16,17]. Today, its high room temperature (RT) hole $(0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ and electron mobility $(5.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ when the electric field is parallel to the crystallographic *b* axis) [18] make perylene an interesting model system. In a recent paper we have analyzed the growth mechanisms of perylene on $Si(1 \ 1 \ 1)$ and Si(100) using a multi-technique approach [19]. In the present Letter we report an investigation of perylene thin films on $SiO_x/$ Si(100) and SiO₂/Si(100) substrates. Particular emphasis will be on the morphology of the perylene films, as investigated by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Apart from the investigation in [19], only a few works have studied the perylene thin film growth dynamics or the interaction with different metal substrates [20-24], and very little work has been done on oxide substrates [25-27].

2. Experiment

Substrate preparation and organic thin film deposition were performed in an ultra-high vacuum (UHV) chamber (base pressure



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 5×10^{-10} mbar) equipped with an ion sputter gun, two separate gas dosing systems for argon and oxygen, respectively, a low energy electron diffraction (LEED) optics, a standard twin anode X-ray source (the presented spectra are taken with Al K_{\alpha} radiation), and a hemispherical electron analyzer (VG CLAM II). The preparation section of this chamber contains a home-made Knudsen cell and is separated from the measuring section by means of a shutter to preserve the base pressure.

The substrates were single-side polished p-Si(100) wafers (CrysTec, Germany) with an undoped resistivity of $2 \text{ k}\Omega \text{ cm}$. The cleaning of the Si(100) surface was performed according to a standard recipe [28]. Without any previous ex situ treatment, it was outgassed in UHV below the temperature at which the oxide is removed. Then the temperature was raised rapidly to 1520 K for 1-2 min. Finally, the substrate was slowly cooled down to room temperature. The obtained clean Si(100) surface is flat and the disorder is minimized, as found in our AFM and LEED characterization. We prepared two different types of oxidized substrates. One was prepared by exposing the cleaned Si(100) surface to molecular oxygen (partial pressure 1×10^{-6} mbar) at RT for 1 min. This gives a very thin oxide layer (denoted SiO_x in the following) in which more than one sub-oxide component is present [29]. The preparation of the silicon dioxide on Si(100) was carried out by exposing the substrate to molecular oxygen (partial pressure 1×10^{-3} mbar) at 870 K for 30 min. This method gives oxide layers that are about 2 nm thick (denoted SiO₂ in the following). Each step of the substrate preparation was checked by XPS, LEED, and AFM.

Perylene (Aldrich) was purified using thermal gradient sublimation and deposited *in situ* under UHV conditions on SiO_x/Si(1 0 0) and SiO₂/Si(1 0 0) by organic molecular beam deposition (OMBD). The deposition was monitored by XPS and the nominal thickness was determined using the attenuation of the Si 2p substrate signal and calibrating the Knudsen cell. Furthermore, the homogeneity of the film thickness was probed by XPS, checking simultaneously the C 1s and the Si 2p core level spectra. The deposition rate (Φ) was varied in the range between 0.8 and 16 nm/min. The substrate temperature (T_{sub}) was varied between 200 K and 400 K in order to probe a wide range of different preparations and their influence on the film morphology.

The AFM measurements were performed under ambient conditions in non-contact mode with a Topometrix scanning probe microscope.

3. Results

3.1. Perylene thin films on $SiO_x/Si(1 \ 0 \ 0)$

Fig. 1 shows 10 μ m × 10 μ m AFM images of nominally 120 nmthick perylene films deposited on SiO_x/Si(1 0 0) at various substrate temperatures and using different deposition rates. Fig. 1a shows a typical AFM image of a film grown with $\Phi = 1$ nm/min and a substrate temperature of 200 K. Perylene forms very small grains. The maximum peak-to-valley height is 701 nm and the average film roughness is 118 nm. An increase of the deposition rate ($\Phi = 5$ nm/min) at the same substrate temperature (Fig. 1b) leads to smaller and more numerous grains, indicating a larger number of nucleation sites. The maximum peak-to-valley value is 130 nm (average roughness = 7 nm). Further increase of the deposition rate to 17 nm/min gives a smooth and homogeneous film (the maximum peak-to-valley height and the average roughness are 67 and 7 nm, respectively).

AFM images are different when the substrate is kept at RT (Fig. 1d–f). The grain size is relevantly larger in comparison with the previous preparation and the film growth shows a different behavior. The film grown with 1.6 nm/min deposition rate (Fig. 1d) is characterized by a maximum peak-to-valley variation of 1268 nm, while this value decreases to 1181 and 585 nm for evaporation rates of 5 and 11.6 nm/min, respectively (Fig. 1e and f). In the film shown in Fig. 1f, the island density is significantly higher than for the other two films prepared at RT.

The AFM micrograph of perylene thin films deposited on a heated substrate (400 K) are shown in Fig. 1g and h. At first glance, it seems that the growth at lower deposition rate (Fig. 1g)



Fig. 1. Ten square micron AFM images of 120 nm-thick perylene films on SiO_x/Si(1 0 0), grown at $T_{sub} = 200$ K with deposition rates of: (a) 1 nm/min, (b) 5 nm/min, (c) 17 nm/min, respectively; at $T_{sub} = 300$ K and deposition rates of: (d) 1.6 nm/min, (e) 5 nm/min, (f) 11.6 nm/min, respectively; at $T_{sub} > 300$ K and deposition rates of: (g) 0.8 nm/min, (h) 2.5 nm/min, respectively. The grey scale corresponds to the first derivative to better represent the grain structure. The *z*-axis is expanded in comparison to the *x*- and *y*-axes.



Fig. 2. Mg K_{α} XPS Si 2p signal attenuation versus film thickness for perylene on SiO_x/Si(1 0 0): (a) T_{sub} = 200 K, (b) T_{sub} = 300 K, and (c) T_{sub} > 300 K. The relative deposition rates are indicated in each figure. All graphs have the same ordinate scale. The lines connecting the data points are intended as a guide to the eye.

resembles the mechanism of the films shown in Fig. 1d and e. However, the details are actually quite different: the grains are larger; their average lateral size is several μ m. The grains grown with deposition rate of 2.5 nm/min exhibit flat top facets (the maximum peak-to-valley value is 1000 nm), while the grains in Fig. 1d and e do not.

XPS measurements performed on the films grown at 200 K corroborate these observation (Fig. 2a). The substrate signals are rapidly and completely attenuated for higher deposition rates, i.e., for nominal film thicknesses of 18 and 25 nm, respectively. The growth mode is Stranski–Krastanov, as will be discussed below.

The relative Si 2p line intensity versus the film thickness obtained from the XPS measurements performed on the films grown at RT is shown in Fig. 2b. The Si 2p intensity decreases as the perylene film covers the substrate. The decrease is quite gradual in comparison with the case of the substrate kept at 200 K, indicating a strong tendency for three-dimensional (3D) growth, in agreement with the respective AFM micrographs. The same holds true for the films grown at higher substrate temperature. Also in this case, the intensity of the Si 2p signal decreases very gradually (Fig. 2c), indicating strong island growth. Comparing the attenuation behavior of the substrate signal as a function of thickness, we observe a different decay for the three substrate temperatures. Under the present experimental conditions, the inelastic mean free path (λ , IMFP) of the Si 2p photoelectrons is about 3.7 nm and the sampling depth is about 11.1 nm. In case of layer-by-layer growth, 95% of the collected photoelectrons come from a thickness within 3λ below the surface. Thus, the signal should be completely attenuated above the thickness corresponding to three times the IMFP. None of the films exhibits such XPS signal attenuation, indicating that only Stranski–Krastanov and 3D island growth modes are present in our study. The different ('slower') exponential decay for the films grown at substrate temperatures \geq RT indicates a strong tendency towards 3D growth with increasing substrate temperature.

3.2. Perylene thin films deposited on $SiO_2/Si(100)$

Fig. 3 shows 10 μ m × 10 μ m AFM images of 100 nm thick perylene films deposited on SiO₂/Si(1 0 0) varying the substrate temperature and using different deposition rates. The films grown at a substrate temperature of 200 K are smooth and homogeneous. The film grown with 0.8 nm/min deposition rate (Fig. 3a) is characterized by a maximum peak-to-valley variation of 70 nm, while this value decreases to 40 nm when the evaporation rate is 10 nm/min (Fig. 3b). The relative Si 2p line intensities versus the film thickness are shown in Fig. 4a. The Si 2p intensity decreases to zero as the perylene film covers the substrate. For the higher



Fig. 3. Ten square micron AFM images of 120 nm-thick perylene films deposited on $SiO_2/Si(1 \ 0 \ 0)$ at $T_{sub} = 200$ K with deposition rates of: (a) 0.8 nm/min, (b) 10 nm/min, respectively; at $T_{sub} = 300$ K and deposition rates of: (c) 3.1 nm/min, (d) 13.3 nm/min, (e) 16 nm/min, respectively; at $T_{sub} > 300$ K and deposition rates of: (f) 0.8 nm/min, (g) 10 nm/min, respectively. The grey scale corresponds to the first derivative to better represent the grain structure. The *z*-axis is expanded in comparison to the *x*- and *y*-axes.



Fig. 4. Mg K_{α} XPS Si 2p signal attenuation versus film thickness for perylene on SiO₂/Si(1 0 0): (a) T_{sub} = 200 K, (b) T_{sub} = 300 K, and (c) T_{sub} > 300 K. The relative deposition rates are indicated in each figure. All graphs have the same ordinate scale. The lines connecting the data points are intended as a guide to the eye.

deposition rate, the process is quite fast, leading to an almost complete extinction of the Si 2p signal when the adlayer is 17 nm thick.

As in the case of perylene deposited on $SiO_x/Si(100)$, AFM images are significantly different when the substrate is kept at RT (Fig. 3c-e). Fig. 3c shows a typical AFM image of a film grown with a deposition rate of 3.1 nm/min. Perylene forms large grains, their lateral size extends to several µm. The maximum peak-tovalley value is 1800 nm. Increasing the deposition rate to 13.3 nm/min (Fig. 3d) leads to a size reduction of the voids, while the grain size is also smaller (in average about $1.7 \,\mu\text{m}$). As in the case of the $SiO_x/Si(100)$ substrate, this again indicates a larger number of nucleation sites. The maximum peak-to-valley height is 1300 nm. Further increase of the deposition rate up to 16 nm/ min gives a smoother (the average roughness is 225 nm) but again grain-like film (Fig. 3e). XPS measurements performed on these films confirm these coverage observations (Fig. 4b). For all deposition rates the substrate signal remains very strong after the various deposition steps, despite the coexistent presence of a strong C 1s signal (not shown here). This is in agreement with the AFM images that indicate an island growth mode.

AFM micrographs of perylene films deposited on the heated substrate are shown in Fig. 3f and g. Also in this case, it seems that the growth at lower deposition range (Fig. 3f) resembles the mechanisms of the film shown in Fig. 3c. Once more, the details are quite different: the grains are smaller; they exhibit sharp edges and flat top facets. Their average lateral size is about 1.4 μ m. The XPS Si 2p signal does not decrease very fast (Fig. 4c), in agreement with an island growth mode. Increasing the deposition rate up to 10 nm/ min leads to a higher nucleation density. The grains again show flat top facets and sharp edges. It is also possible to distinguish the formation of long grains that grow along two preferential directions. The size of the grains ranges from 1.3 to 2.7 μ m.

4. Discussion

The present results give a detailed picture of the growth mechanisms of perylene thin films on $SiO_x/Si(1 \ 0 \ 0)$ and $SiO_2/Si(1 \ 0 \ 0)$. The AFM images show the film morphology as a function of the preparation parameters. Looking at Figs. 1 and 3, it is evident that for substrate temperatures equal to or above RT, the typical growth mode is substantially an island-type growth mode (Volmer–Weber and/or Stranski–Krastanov) with formation of large islands. In contrast, for a cooled substrate, the films are homogeneous and completely closed. By changing the deposition rate it is possible to modify the film morphology, as is easily seen comparing Fig. 1d– f. Here, the morphology slowly changes from a film with a strong three-dimensional character to a film that, still grain-like, presents large domains with the substrate completely covered.

Substrate temperature and deposition rate are among the parameters that affect the deposition process in the classical the-

ory of nucleation when looking at the thermodynamic aspects of thin film growth [30,31]. In particular, they affect the change in the free energy of the adsorbate. This influence has several consequences: (1) the higher the substrate temperature, the bigger the size of the critical nucleus, i.e., the size at which the island becomes stable with the addition of only one more molecule. (2) A nucleation barrier may exist at higher substrate temperature. (3) The number of supercritical nuclei decreases with temperature, i.e., there are fewer nuclei at higher temperature. (4) Increasing the deposition rate results in smaller islands. (5) A continuous film can be grown at lower film thicknesses [30,31]. These are exactly the phenomena shown by the sequence of micrographs in Figs. 1 and 3. The growth mechanisms in the case of perylene deposited on $SiO_x/Si(100)$ and $SiO_2/Si(100)$ have different energy barriers to overcome in order to reach the stage of the film formation. The associated inhomogeneous growth is clearly evidenced by the different attenuation of the Si 2p signal versus the film thickness for the films grown at the different temperatures (see Figs. 2 and 4

In addition to the thermodynamic and kinetic aspects, the substrate-molecule interaction has to be taken into account. Pervlene growth on $SiO_{v}/Si(100)$ resembles that of pervlene adsorbed on Si(100) [19]. The low exposure (45 L) used to prepare the SiO_{v} / Si(100) surface gives rise to a two-dimensional island nucleation of the oxide layer and, therefore, the $Si(1 \ 0 \ 0)$ is not completely covered [29]. Thus, we may reckon that the Si(100) regions play the major role in the film growth, under these conditions. By interpreting the attenuation behavior of the Si 2p substrate signal in Figs. 2 and 4, it can be seen how it is apparently energetically more favorable to obtain a closed film on $SiO_x/Si(100)$, compared to deposition on $SiO_2/Si(1 \ 0 \ 0)$. This is due to the different interaction strengths between molecule and substrate in the two cases. In perylene films deposited on SiO_x /Si(100), the influence of the Si(100), although not so strong to constitute a template for the film, is still sensible, lowering the barrier necessary for two-dimensional growth. On the other hand, the strength of the interaction molecule-substrate is definitely quenched by the closed oxide layer in $SiO_2/Si(100)$. This leads to a higher probability for a three-dimensional growth over a larger range of preparation conditions.

The findings presented in this Letter are important also from a technological viewpoint. By using an appropriate set of preparation conditions for the perylene thin films, the morphology can be varied, ranging from the growth of homogeneous smooth films to big single grains. This indicates that, in principle, it is possible to grow high quality organic thin films matching the exact requirements of specific devices, opening the way towards a film-engineering approach for the optimization of organic-based devices. We can predict the growth of perylene on technologically relevant substrates as: (i) homogeneous smooth films at lower substrate temperature (≤ 200 K), and (ii) single large grains, with dimensions big enough

to build a single nanodevice for higher T_{sub} . Consequently, this recipe has recently been applied to build an OFET based on a microcrystallite of diindenoperylene on sapphire [32].

5. Conclusion

The presented results give insight into the growth mechanisms of perylene thin films on $SiO_x/Si(1 \ 0 \ 0)$ and $SiO_2/Si(1 \ 0 \ 0)$. The films grown at room temperature or above are characterized by large grains. By varying the preparation conditions, the island density can be increased, leading to an improvement of the homogeneity of the films. These findings constitute the basis for organic thin film engineering and thus can have a strong impact in technologically relevant applications. Matching the requirements for the development of a certain device, the film morphology can be designed, ranging from the growth of single, very large grains that can be used for a complete nanodevice, to homogeneous films for application in large displays.

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