Revealing the buried interface: para-sexiphenyl thin films grown on TiO₂(110)

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Received 26th October 2009, Accepted 11th January 2010
First published as an Advance Article on the web 10th February 2010
DOI: 10.1039/b922285e

The thickness dependent optical and electronic structure of para-sexiphenyl thin films grown on TiO₂(110) at around 400 K reveals that the substrate is first wet by one monolayer of molecules lying with their long axis parallel to the [001] direction of the substrate, while the molecules in subsequent layers are almost standing upright. Whilst ultraviolet photoemission spectroscopy (UPS) is sensitive to the molecules in the outermost layer, reflection difference spectroscopy (RDS) shows that the molecules at the buried interface do not dewet and maintain the orientation of the original wetting monolayer.

1. Introduction

Arguably the two dominant factors for organic device performance are the orientation of the molecules within the films and their interfaces with the contacts. As the molecules are highly anisotropic, their orientation will control the charge transport in the films as well as the direction of light absorption/emission. The geometry and the electronic level alignment of the molecules at the interface is important for charge injection into the films. Moreover, this first monolayer can act as a template, controlling further film growth. Whether a wetting monolayer of molecules lying flat (a “lying monolayer”) is initially formed and whether it is significantly changed or disappears during the dewetting process upon film growth is difficult to ascertain, as most techniques are either too surface-sensitive or too bulk-sensitive to reveal the buried interface. This buried interface is particularly important in gate dielectrics for OFETs (organic field-effect transistors) where the channel order have been grown on single crystal substrates such as TiO₂(110), Cu(110)-(2x1)O, Al(111), and KCl(001) via physical vapor deposition in ultra-high vacuum (UHV). What has also been recognized is that the orientation of the p-6P molecules within the films can, on some substrates, be selected through growth temperature allowing the growth of films containing molecules with the desired orientation for different applications. On TiO₂(110), growth at room temperature or below leads to films in which the molecules are exclusively lying on the substrate surface with their long molecular axes parallel to the atomic corrugation of the substrate, from sub-monolayer coverages up to thick films (monolayer thickness ≈ 3.5 Å). In contrast, growth at elevated temperatures leads to epitaxial (001) oriented p-6P films containing near-uptight molecules with their long axes nearly parallel to the surface normal (monolayer thickness ≈ 23 Å). For these films of upright molecules some basic questions are still open, namely, is there a wetting layer of lying molecules and, if so, how does this wetting layer evolve upon the growth of upright molecules on top of it? In this communication, we present a combined in situ study on the growth of p-6P on TiO₂(110) at 430 K using optical and electronic probes, namely, reflectance difference spectroscopy (RDS) and ultraviolet photoemission spectroscopy (UPS), with particular focus on the initial stages of the growth. The valence band photoemission suggests the presence of a lying interfacial monolayer, but cannot prove that it remains due to the inherent surface sensitivity of the technique. In contrast, RDS, being sensitive to molecular orientation throughout the film, can also probe the buried interface and thus unambiguously reveal that the lying interfacial monolayer maintains its orientation and does not dewet upon the growth of upright molecules on top of it.

2. Experimental

The experiments were carried out in situ under ultra high vacuum (UHV) conditions. The TiO₂(110) single crystal order have been grown on single crystal substrates such as TiO₂(110), Cu(110)-(2x1)O, Al(111), and KCl(001) via physical vapor deposition in ultra-high vacuum (UHV). What has also been recognized is that the orientation of the p-6P molecules within the films can, on some substrates, be selected through growth temperature allowing the growth of films containing molecules with the desired orientation for different applications. On TiO₂(110), growth at room temperature or below leads to films in which the molecules are exclusively lying on the substrate surface with their long molecular axes parallel to the atomic corrugation of the substrate, from sub-monolayer coverages up to thick films (monolayer thickness ≈ 3.5 Å). In contrast, growth at elevated temperatures leads to epitaxial (001) oriented p-6P films containing near-uptight molecules with their long axes nearly parallel to the surface normal (monolayer thickness ≈ 23 Å). For these films of upright molecules some basic questions are still open, namely, is there a wetting layer of lying molecules and, if so, how does this wetting layer evolve upon the growth of upright molecules on top of it? In this communication, we present a combined in situ study on the growth of p-6P on TiO₂(110) at 430 K using optical and electronic probes, namely, reflectance difference spectroscopy (RDS) and ultraviolet photoemission spectroscopy (UPS), with particular focus on the initial stages of the growth. The valence band photoemission suggests the presence of a lying interfacial monolayer, but cannot prove that it remains due to the inherent surface sensitivity of the technique. In contrast, RDS, being sensitive to molecular orientation throughout the film, can also probe the buried interface and thus unambiguously reveal that the lying interfacial monolayer maintains its orientation and does not dewet upon the growth of upright molecules on top of it.
in situ absorption of 5.5 eV covering the most interesting range of the optical can be recorded in the photon energy range between 1.5 and 4.5 eV at normal incidence with the polarization axis oriented parallel to the surface and the lower with upright molecules. While the angle resolved UPS clearly indicate a difference in the molecular orientation between the monolayer and thicker films grown at elevated temperature, it cannot rule out that the lying monolayer dewets and evolution of the optical anisotropy as a function of p-6P film thickness was obtained. As demonstrated recently, RDS is extremely sensitive to the HOMO to LUMO electronic transition of organic molecules which are highly polarization dependent for elongated molecules like p-6P. Therefore, RDS is not only sensitive to the orientation of molecules in thicker films but also to the initial stage of growth. Based on the measured intrinsic anisotropy of the organic films, the orientation and crystalline properties can be determined by RDS.

3. Results and discussion

The growth of p-6P on TiO$_2$ has been followed with UPS both in normal emission and 45° off-normal emission and workfunction measurements for substrate temperatures of 100, 300 and 430 K. Fig. 1 displays a UPS growth series showing the development of the upper π band for a substrate temperature of 430 K during exposure. In the insert the full valence band is shown which reveals that by a film thickness of 3.5 Å the strong TiO$_2$ emission features are almost totally suppressed and the p-6P features almost fully developed. Given the low exposure, this clearly indicates that a wetting monolayer of lying molecules must be formed. Workfunction measurements corroborate this conclusion and show that the change in workfunction saturates at this exposure ($\Delta \phi = -0.4$ eV). In all respects the p-6P monolayer grown at elevated temperature is identical to the monolayer grown for substrate temperatures of room temperature or below (300 to 100 K). For room temperature growth, beyond the 3.5 Å monolayer no significant changes in the valence band spectra, or their behavior with electron emission angle, are observed. In contrast, as can be seen in Fig. 1, large changes are observed in the π band spectra for exposures beyond 3.5 Å for growth at elevated temperature. The molecular emission features of the monolayer are different to those of higher coverages both in terms of energy position and intensity behavior with electron emission angle. In the monolayer the highest occupied molecular orbital (HOMO) has an ionization potential of 6.2 eV, while for higher coverages it appears at 5.6 eV. These two ionization potentials have been observed on a number of different substrates and are indicative of the molecular orientation within the films. The higher ionization potential is associated with molecules oriented parallel to the surface and the lower with near vertical orientation.2,11 For the monolayer at off-normal emission geometry HOMO and HOMO-1 are visible while the emissions from the six inter-ring non-bonding orbitals are weak, appearing only as a shoulder at around 8 eV. In normal emission (not shown) the intensity relationship is reversed, with the non-bonding emissions being intense while HOMO and HOMO-1 are undetectable. Such behavior is associated with films of lying molecules whose axes are all parallel.19 In contrast, for high coverages all features are intense with little intensity variation with experimental geometry, consistent with upright molecules. While the angle resolved UPS clearly indicate a difference in the molecular orientation between the monolayer and thicker films grown at elevated temperature, it cannot rule out that the lying monolayer dewets and
becomes incorporated in the layers of upright molecules at higher coverage.

Fig. 2 shows RD spectra (\(\Delta R/R\)) recorded after each step of p-6P deposition till a nominal thickness of 60 Å at a substrate temperature of 380 K. In order to follow the evolution of the molecular orientation, the deposited amount of p-6P in each of the first 12 steps was controlled to be a nominal thickness of 1 Å. Depositions at higher substrate temperature up to 430 K show the same behavior. As a reference, the RD spectrum of a p-6P film with a thickness of 60 Å grown at room temperature (RT) is also plotted. For the p-6P films with identical thickness of 60 Å the optical anisotropy around 3.5 eV of the p-6P film grown at RT is much larger than that grown at 380 K. The orientation of the p-6P molecules in the grown layer can be deduced from the sign and the energetic position of the \(\Delta R/R\) peak related to the HOMO to LUMO transition of the molecule.\(^6,20\) The positive sign and the \(\Delta R/R\) peak position at 3.5 eV is a fingerprint of lying p-6P molecules which are oriented with their long axis parallel to the [001] direction of the TiO\(_2\)(110) substrate. In contrast the standing p-6P molecules, which are orientated near upright with their long axis inclined by about 17° to the surface normal,\(^6\) will not contribute to the RD signal at 3.5 eV.\(^6,20\) The spectra in Fig. 2 thus reveal that in the films grown at RT, p-6P molecules are lying, whereas the films deposited at 380 K contain mainly standing p-6P molecules.\(^6\) This conclusion agrees with the UPS results above and with recent grazing incidence X-ray diffraction,\(^3\) which reveal that p-6P films grown at elevated temperatures form four equivalent crystalline domains with the p-6P (001) plane being parallel to the substrate surface.

To emphasize the spectral evolution, the RD spectra around 3.5 eV are plotted on a smaller scale in the inset of Fig. 2. During the initial stage of growth, the RD signal at 3.5 eV increases linearly till a thickness of about 4 Å which corresponds exactly to one monolayer of lying p-6P. The large optical anisotropy at 3.5 eV for the first monolayer results from the molecules in the first monolayer being uniaxially aligned along the [001] TiO\(_2\) azimuth. Indeed, the line shape and amplitude of the RD spectra in this regime is identical to that obtained for growth at RT\(^6\) and is due to a wetting monolayer of lying p-6P molecules. As can be seen in Fig. 2, for further growth beyond the first monolayer, the incremental increase of the optical anisotropy as a function of the p-6P coverage becomes much smaller in the whole energy range of measurement. In particular, almost no change in the optical anisotropy is observed in the region around 3.5 eV. This result implies that the molecules grown on top of the lying monolayer do not display a strong in-plane anisotropy, as would be expected for standing molecules.\(^6,20\) Of particular importance is the observation that no reduction of the anisotropy at 3.5 eV appears at any stage during the growth at elevated temperatures. Since the standing molecular layers are optically transparent around 3.5 eV,\(^20\) the optical anisotropy of the wetting layer is still accessible even when it is buried. If the molecules of the lying monolayer changed their orientation upon further growth, such as if they were incorporated into the film of upright molecules, the strong positive signal at 3.5 eV would decrease and thoroughly disappear in the subsequent RD spectra. This is clearly not the case and it can be concluded that the lying molecular monolayer does not dewet or significantly reorient upon the growth of layers of standing molecules on top of it.

4. Conclusion

In conclusion, we have studied the thickness dependence of the electronic structure and optical anisotropy of p-6P thin films grown on TiO\(_2\)(110) at elevated temperatures. As illustrated in Fig. 3, the substrate is first wet by one monolayer of lying p-6P molecules with their long axes parallel to the [001] direction of the TiO\(_2\)(110) substrate. After completion of the wetting layer, from the second monolayer onwards, the p-6P molecules adopt a near upright orientation, consistent with p-6P(001) crystalline orientation. Of particular significance is that the orientation of p-6P molecules in the buried wetting layer remains unchanged when they are covered by subsequently deposited layers in which the molecules are standing up. The experimental observation reflects the fact that the molecular orientation of organic thin films is determined by the delicate balance between molecule–molecule and molecule–substrate interactions. In the present case, the lying orientation of the p-6P molecules in the first layer suggest a strong binding to the TiO\(_2\)(110) substrate. On the other hand, the standing orientation of p-6P in the subsequent layers can be viewed as the result of the interaction between molecules, only. In fact, for a p-6P molecular crystal, Nabok et al.\(^{21}\) have shown by \textit{ab initio} calculations that the surface free energy is lowest for the (001) plane. Consequently, the formation of p-6P crystallites with the (001) plane parallel to the substrate and, hence, nearly upright standing p-6P molecules is expected to be energetically favored during the later stage of growth. Our experiment now reveals that the nucleation and growth of the films of upright standing molecules occurs on top of the p-6P wetting layer but not directly on the TiO\(_2\)(110) surface. The growth mode beyond the first monolayer is thus controlled by the diffusion and nucleation properties on the p-6P wetting layer which are obviously different from those on the bare substrate. Previously, the epitaxial orientation of the p-6P(001) films has been argued to result from a commensurability to the
rows of the TiO₂ substrate. We suggest here that the argument may still be valid as the molecules in the interfacial lying monolayer discovered here by RDS are most probably commensurate with the surface corrugation.

Acknowledgements

We are grateful for financial support by the Austrian Science Fund (FWF).

References


Fig. 3 Schematic model showing the lying molecular orientation in the wetting layer and the near-upright one in the second layer on the TiO₂(110) substrate.