

PR0362

The growth morphology of ultrathin films of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on rutile (110) titanium dioxide.

○Richard Murdey¹, Naoki Sato²

¹Kyoto University Pioneering Research Unit for Next Generation

²Kyoto University Institute for Chemical Research

Introduction

Epitaxial growth of sexithiophene on rutile TiO₂ (110) surfaces has been recently observed.¹ The sexithiophene molecules were oriented with the primary axis in the same direction as the oxygen and titanium rows of the substrate. It has also been noted however that surface defects on the (110) terraces can act as anchor points for perylene derivatives, and possibly nucleation sites for the formation of larger clusters.² In our work, we examine the influence of the substrate on the morphology and electrical properties of PTCDA thin films and consider possible methods to chemically deactivate the nucleation sites in order to improve film quality. Dienols are tested to discover if they can be made to selectively bind to the surface defect sites as they are known to effectively bind to nanoparticle surfaces.^{3,4} Finally, we look at whether this treatment has a measurable effect on the growth mode of vacuum deposited PTCDA thin films.

Experimental

Rutile TiO₂ (110) single crystals were obtained from Shinkosha. The offcut was specified to be a maximum of 0.05°. The crystals were washed in acetone, ethanol and hot ultrapure water before being annealed to 1273 K for 5 hours under atmosphere and washed again in either ultrapure water or acidified 10 mM solutions of L-ascorbic acid (Aldrich) or ascorbic acid palmitate (Aldrich). AFM measurements were made on a Molecular Imaging Picoscan II+ instrument operated in contact mode. Contact angle measurements were performed at room temperature using 10 mL droplets of ultrapure water. Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) was obtained from Aldrich and purified by vacuum sublimation before use. Thin films were deposited from resistively heated quartz crucibles in a UHV chamber with a base pressure of 10⁻¹⁰ mbar.

Results and Discussion

The AFM image of the annealed TiO₂ (110) surface is shown in Figure 1. Regular, flat terraces are observed consistent with the manufacturers stated offcut angle. The contact angle measurements in Figure 2 clearly show the effect of the adsorbed dieneol molecules.

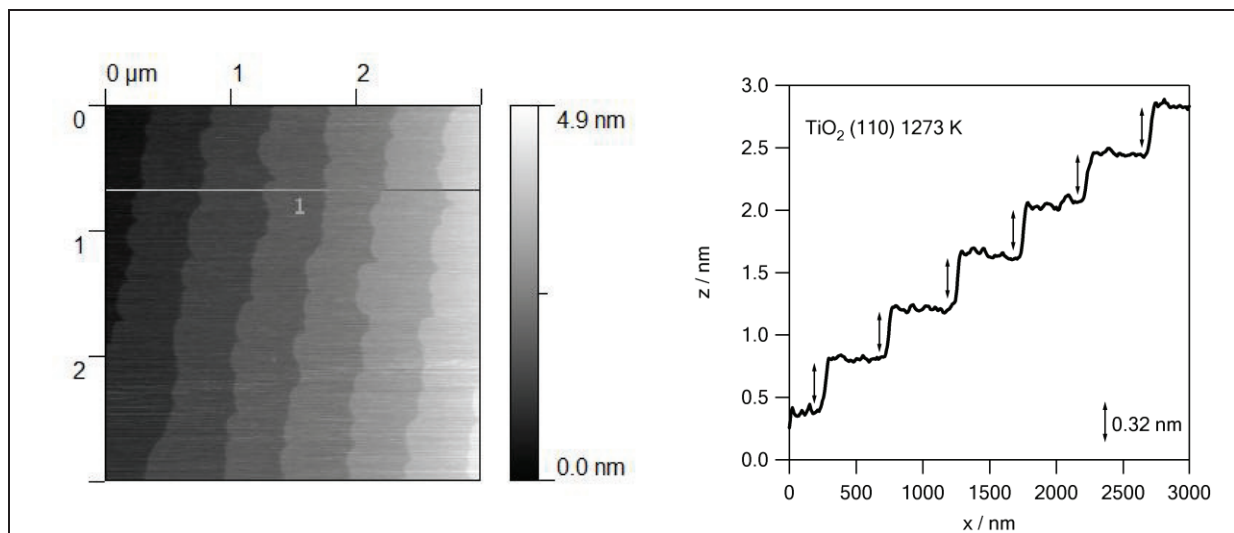


Fig. 1. Contact mode AFM image (left) of the TiO₂ (110) rutile surface after annealing at 1273 K in air for 5 hours. The profile (right) shows that the atomically flat, 400 nm wide terraces have a step height corresponding with the (110) axis repeat distance of 0.32 nm.⁵

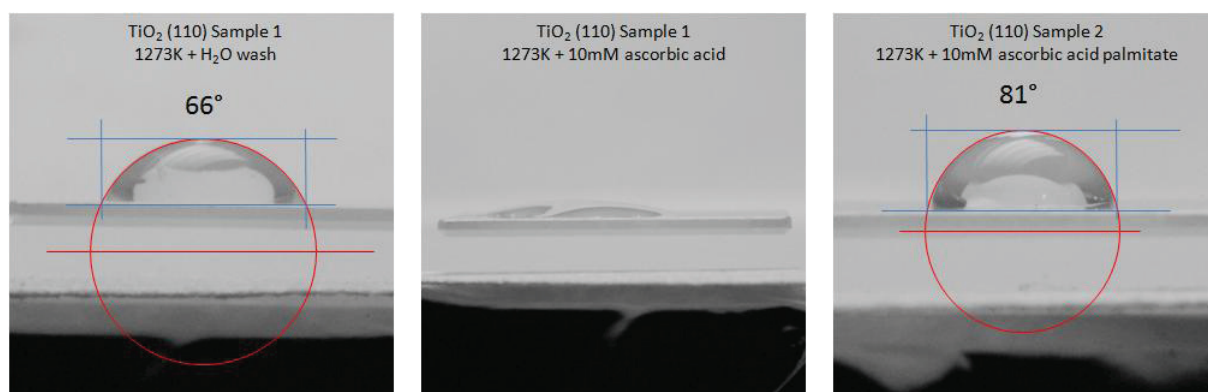


Fig. 2. Contact angle measurements of TiO₂ (110) surfaces showing the effect of exposure to aqueous solutions of hydrophobic and hydrophilic dieneol molecules.

References

1. T. Haber, J. Ivanco, M.G. Ramsey, R. Resel, *J. Cryst. Growth*, **310** (2008) 101.
2. J. Schütte, R. Bechstein, P. Rahe, et. al. *Phys. Rev. B*, **79** (2009) 045428.
3. T. Lana-Villarreal, A. Rodes, J. M. Perez, R. Gomez *J. Am. Chem. Soc.*, **127** (2005) 12601.
4. L. de la Garza, Z. V. Saponjic, N. M. Dimitrijevic, et. al. *J. Phys. Chem. B*, **110** (2006) 680.
5. H. Onishi, Y. Iwasawa, *Surface Science* **313** (1994) L783.