Surface Science 630 (2014) 22–27

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Nucleation and evolution of zinc phthalocyanine thin films on the deactivated Si(111)-B $\sqrt{3} \times \sqrt{3}$ $R30°$ surface

Sean R. Wagner, Pengpeng Zhang *

Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824-2320, USA

ARTICLE INFO

Article history:
Received 8 April 2014
Accepted 27 June 2014
Available online 4 July 2014

Keywords:
Scanning tunneling microscopy
Phthalocyanine
Moiré pattern
Ehrlich–Schwöebel barrier
Grain boundary
Self-assembly

ABSTRACT

We report the growth evolution of thermally evaporated zinc phthalocyanine (ZnPc) on the deactivated Si(111) surface using scanning tunneling microscopy (STM). We find that the Ehrlich–Schwöebel barrier (ESB) associated with the ZnPc step edges is negligible, while the formation of molecular domain boundaries provides an activation barrier and additional nucleation sites which increases the film roughness and interrupts the anisotropic step-flow growth. By increasing the substrate temperature, the grain boundary density is significantly reduced, resulting in a well-controlled surface morphology. This study provides insight into the influence of the ESB and the grain boundary crossing barrier on the growth dynamics of organic thin films.

1. Introduction

Organic semiconducting materials have begun to emerge into the electronics market as a cost-effective template for flexible devices [1,2], with tunable properties owing to their functionalities [3–5]. Since the electronic properties of organic thin films, such as charge transport and exciton diffusion, are intrinsically coupled to the film structure, one would like to control the molecular orientation, grain distribution, density of grain boundaries, as well as the roughness of the film [6]. However, in contrast to inorganic thin films, there still remains a lack of understanding of the growth mechanisms that ultimately determine the organic molecular structures.

It is known that the growth dynamics of inorganic thin films depends on the initial deposition condition along with the atomic processes such as diffusion and nucleation. The presence of an additional activation barrier, the Ehrlich–Schwöebel barrier (ESB), which is associated with the downward mass transport at the step edges due to the loss of coordination [7–9], can restrict adatoms to a given terrace [10–14], giving rise to the formation of deep trenches that cannot be filled, i.e., Zeno effect [13–15]. In addition, grain boundaries occur as the film growth evolves which often act as activation barriers and introduce nucleation sites for adatoms. The combination of the ESB and the grain boundary crossing barrier inevitably results in a rough film [10]. Although the same considerations can be applied to organic molecular thin films [16–22], the anisotropic nature and internal degrees of freedom of the organic molecules often complicate the diffusion and nucleation processes, thus directly affecting the magnitudes of the ESB and the grain boundary crossing barrier [16–18,23–28]. So far the ESB has been described as one of the dominant factors in determining the organic molecular film morphology [16–27,29–31], with fewer studies discussing the effect of the grain boundary crossing barrier on the molecular diffusion [10,32] and nucleation [33,34]. Thus, it is demanding to achieve a comprehensive understanding of the growth dynamics of organic molecular thin films. Note that although the ESB was originally defined in inorganic systems using an atomistic picture, the same nomenclature has been adopted to describe the organic molecular thin film growth.

In this study, we report on the growth dynamics of ZnPc on the deactivated Si(111)-B $\sqrt{3} \times \sqrt{3}$ $R30°$ surface. We find that the grain boundary crossing barrier leads to the film roughening, while the ESB associated with ZnPc step edges is negligible. We show that elevating the substrate temperature during growth reduces the nucleation density and consequently the number of grain boundaries, yielding a smoother film. This work illustrates the need and the significance of considering both the ESB and grain boundary crossing barrier in order to accurately assess the evolution of the organic film morphology.

2. Experimental methods

Experiments were carried out in an Omicron NanoTechnology GmbH ultrahigh-vacuum (UHV) system consisting of two different

---

Abbreviations: ZnPc, zinc phthalocyanine; CuPc, copper phthalocyanine; STM, scanning tunneling microscopy; ESB, Ehrlich–Schwöebel barrier; UHV, ultrahigh-vacuum.

* Corresponding author. Tel.: +1 517 884 5630; fax: +1 517 353 4500.
E-mail address: zhang@pa.msu.edu (P. Zhang).

http://dx.doi.org/10.1016/j.susc.2014.06.025
0039-6028/© 2014 Elsevier B.V. All rights reserved.

chambers for sample preparation and characterization by scanning tunneling microscopy (STM). Heavily boron doped Si(111) substrates were cleaned ex situ by standard RCA1 and RCA2 wafer preparation procedures, leaving a thin (1–2 nm) surface oxide. These substrates were transferred into the UHV system with a base pressure below 1.0×10^{-10} mbar. The sample was then in situ annealed by direct current heating at 1200 °C to remove the surface oxide followed by extended annealing at 800 °C to induce the sub-surface boron segregation. The sub-surface boron segregation depletes electrons from the surface dangling bonds of the adatoms [35, 36] forming an atomically smooth and deactivated Si(111)-B $\sqrt{3} \times \sqrt{3}$ $R30°$ surface for self-assembly of organic molecules (see Fig. 1(a)). The surface quality was checked using STM prior to the deposition of organic molecules.

ZnPc thin films were prepared using high purity ZnPc molecules obtained from Sigma-Aldrich that were further purified by sublimation processing before being transferred into the UHV system. The ZnPc molecules were thoroughly degassed in the organic evaporator prior to being thermally evaporated from a boron nitride crucible on to the deactivated Si surface with the substrate held at room temperature or at elevated temperatures by resistive heating. A typical chamber pressure of $\approx 1.0 \times 10^{-9}$ mbar was maintained during the deposition process. After deposition, samples were transferred in situ to the STM for data acquisition.

3. Results and discussion

3.1. Defects and initial nucleation of ZnPc on the Si (111)-B $\sqrt{3} \times \sqrt{3}$ R30° Surface

In order to prevent localization of ad-molecules due to their strong covalent interaction with Si dangling bonds [37], the deactivated Si(111)-B $\sqrt{3} \times \sqrt{3}$ surface is utilized where molecules are allowed to fully explore the energy landscape and intermolecular interactions to form organized structures [35,36]. Meanwhile, the deactivated Si(111)-B provides a large-scale atomically smooth surface, as shown in Fig. 1, thus offering a robust template for investigating the mechanisms of molecular thin film growth.

Fig. 1(a) and (b) presents a prototypical "pristine" Si(111)-B surface at different scales, where the atomic structure of the surface and the straight step edges are illustrated. Once ZnPc molecules are deposited on such a surface, they are able to diffuse over a long distance to preferentially nucleate at the lower Si step edges even at room temperature [38–40]. The thus formed step-flow growth further induces an effective reduction in the growth symmetry. This, combined with the favored π–π stacking between ZnPc molecules, leads to a single dominate stripe growth direction, as seen in Fig. 2(a). Interestingly, once these ZnPc molecular stripes extend across the Si terraces, they terminate at the upper Si step edges, suggesting that the ESB associated with the Si step edges is

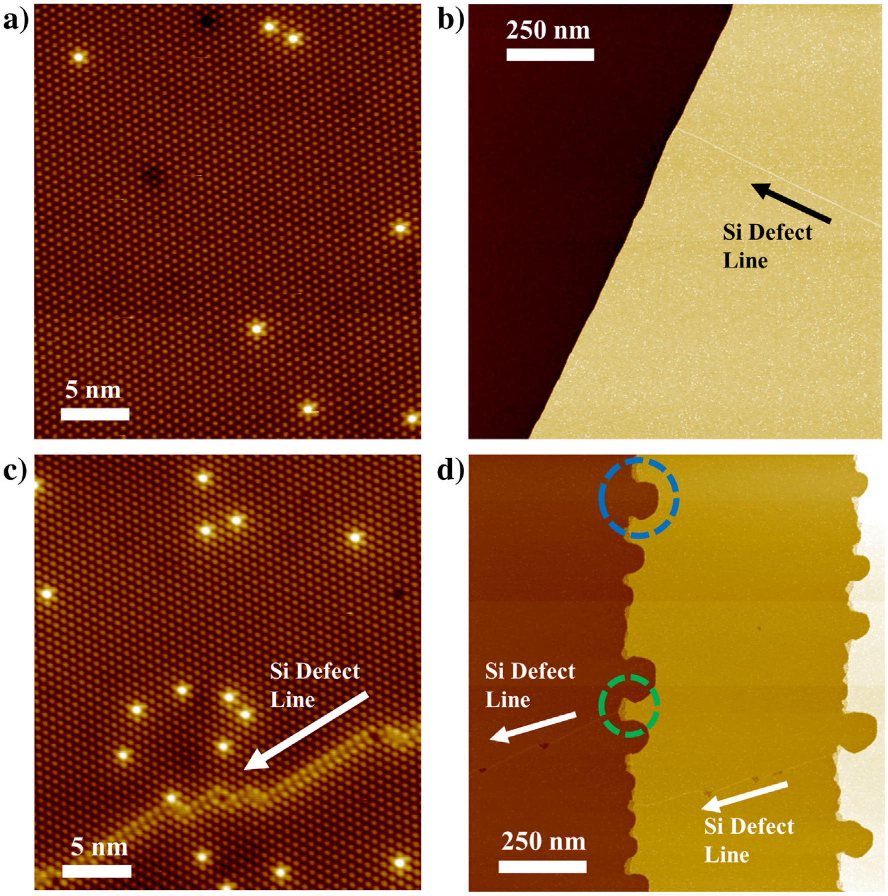

Fig. 1. STM topography images ($V_s = +2.0$ V, $I_t = 50$ pA) of the Si(111)-B $\sqrt{3} \times \sqrt{3}$ R30° surface, obtained at 77 K. (a) The surface is hexagonal with lattice parameter $a = 6.65 \pm 0.02$Å. Bright features correspond to Si dangling bonds with the absence of underlying boron atoms. Dark features correspond to individual Si adatom vacancies or Si adatoms not occupying their corresponding energetic minimum sites. (b) A large scale image of a pristine Si(111)-Bsurface. Atomic Si defect lines are still present on the terraces (highlighted by the black arrow) despite the high surface quality. A zoomed in STM image of a defect line is shown in (c). (d) A defected Si(111)-B surface that displays deformation of the Si step edges forming "bowl" shaped structures (dashed blue circle) and the distinct surface reconstruction near the "bowls" (dashed green circle). Si defect lines are marked by the white arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)