Controlling Geometric and Electronic Properties of Highly-Ordered CuPc Thin Films

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Abstract

Geometric and electronic properties of ordered copper phthalocyanine (CuPc) thin films grown on hydrogen and antimony passivated Si(111) surfaces have been studied using near edge x-ray absorption fine structure (NEXAFS) and photoemission spectroscopy. The H- and Sb-passivations of vicinal Si surfaces resulted in different molecular orientation in thick films, namely upright and near lying molecules, respectively. In the absence of the vicinality, the molecules on the Sb-passivated surface changed towards upright orientation. The work function of the films was monitored during the growth and correlated with the molecular orientation. © 2007 Elsevier Science. All rights reserved.

1. Introduction

Controlling the stacking axis of molecules is a key factor in the optimization of electronic properties of organic devices. While an upright geometry of molecules is rather commonly observed especially if the molecules grow on oxidized surfaces, the lying-down orientation is difficult to achieve for most molecules for device-relevant film thicknesses. Even if molecules lie down during the onset of the film growth, they typically change their orientation towards upright when going to thicker films [1-5] unless a specific template film is employed [6].

In this study, the growth of copper phthalocyanine ($C_{32}H_{16}CuN_8$) films on either hydrogen- or antimony-passivated vicinal Si(111) surfaces was examined. We will demonstrate the influence of the vicinality on the molecular orientation of the CuPc films.

2. Experimental Details

For the growth studies, 0.35°-offcut n-Si(111) wafers (7.5 Ωcm) with the miscut angle tilted toward the [1-10] direction were used as vicinal surfaces, i.e. with regular step arrays. First, the stepped 7×7 reconstructed surfaces were prepared [7]. Secondly, surface bonds of the reactive 7×7 surface were passivated either (a) by hybridization through the

exposure by atomic hydrogen or (b) via deposition of 2 monolayer thick Sb layer and subsequent annealing. While the former passivation retains the 7×7 reconstruction, the latter changes the surface reconstruction to 1×1. Experimental details can be found in Ref. [8].

On such surfaces, CuPc films were sequentially grown at RT with an evaporation rate of about 0.2 nm/min. During CuPc growth the pressure was better than 2×10^{-9} mbar. The samples were characterized by both NEXAFS and photoemission spectroscopy after each growth step. The entire sample preparation and its characterization by electron spectroscopies were performed *in situ* at the Russian-German Beam Line in BESSY using the MUSTANG experimental station. After finalization of the growth, the samples were inspected by atomic force microscopy (AFM).

3. Results and Discussion

Figs. 1 (a-c) present angle-resolved NEXAFS spectra for CuPc films with nominal thicknesses of 1.2, 1.8, and 10 nm grown on the vicinal H-Si(111)-7×7 surfaces. The photon incidence angle θ was changed with respect to the [1-10] azimuth. The experimental intensities of the π*-resonance normalized with respect to the π*-resonance taken at θ = 90° are presented in the insets along with calculated dependences. The thick curves present the best fits for α, the average angle between the π-orbital vector, which is orthogonal to the molecular plane, and the surface normal. The analysis suggests that the molecules gradually change their orientation with CuPc film thickness; the average molecular angle with respect to the substrate surface was detected to be 51±2° (1.2 nm), 65±3° (1.8 nm), 67±3° (3.6 nm), and 85±5° (10 nm).

Fig. 2 shows the evolution of the work function and ionization energy of the H-Si(111)-7×7 surface upon the CuPc growth. Note that the work function gradually decreases over the investigated range up to the thickness of about 4 nm. Such gradual decrease is not related with the interfacial dipole, which manifests itself via an *abrupt* work function change due to the dipole confinement within first 1-2 monolayers. Since the CuPc film has grown in the laminar mode, as evidenced by the evolution of the
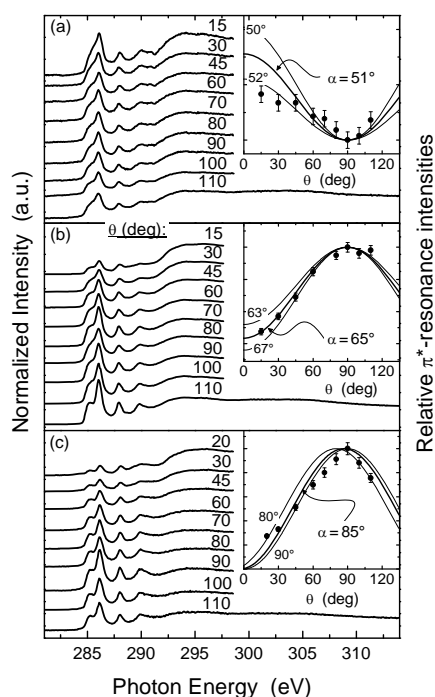

Figure 1a-c. NEXAFS spectra of the 1.2, 1.8, and 10 nm thick CuPc films grown on the vicinal H-Si(111)-7×7 surface. The insets show calculated intensity ratios of π*-orbital vector as the function of its tilt angle α with respect to the surface normal and the x-ray incidence angle θ. The best fits illustrated by thick lines in the insets correspond to molecular orientations of 51±2° (1.2 nm), 65±3° (1.8 nm), and 85±5° (10 nm) with respect to the substrate surface.
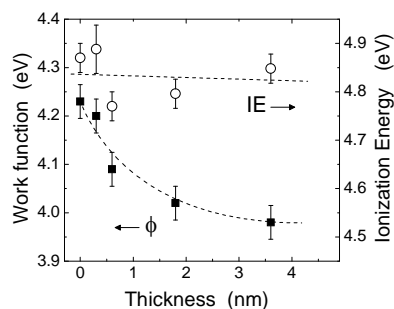

Figure 2. Evolution of the work function (solid squares) and ionization energy (open circles) of the H-Si(111)-7×7 surface upon the CuPc growth. The error bars are not statistical, but express the confidence level of the parameter identification.

Si2p and C1s intensities with the film thickness, we assume that the work function decrease is related with the gradually increased tilt angle (with respect to the surface) of molecules which form the outer, i.e. probed film surface [2, 3, 9, 10]. We note that the 10 nm thick film displayed charging effects and thus its electronic properties could not reliably be assessed.

Fig. 3a shows the NEXAFS spectra and the corresponding calculated intensity ratios for about 10 nm thick CuPc films grown on the vicinal Sb-Si(111)-1×1 surface. The best fit corresponds to an average molecular orientation of 28±4° with respect to the substrate surface. The same passivation procedure of the Si(111) surface, however with the absence of the vicinality, has resulted in a significantly modified molecular orientation, namely an average angle of about 60±2° (Fig. 3b).

Thus, the vicinality of the substrate surface seems to enhance the lying-down geometry of molecules. The mechanism is presumed to be induced via the directed diffusion imposed by unioriented step edges. The unioriented diffusion of molecules over the surface during the film growth has been recently proposed to play an essential role for achievement of

the lying molecular geometry [11].

4. Summary

On vicinal H-passivated Si(111)-7×7 surfaces, the molecules gradually change their orientation towards upright position with increasing film thickness. The gradual reorientation of molecules resulted in the drop of the film work function.

On vicinal Sb-passivated Si(111)-1×1 surfaces, the CuPc molecules assumed a near lying geometry also in thick films. In the absence of the vicinality, however, the molecular orientation changed towards the uprightness. The finding suggests that the unidirectional diffusion of molecules during the film growth imposed here by the vicinality of the substrate surface may be the essential factor for development the lying-down molecular orientation in thick films.

Acknowledgement

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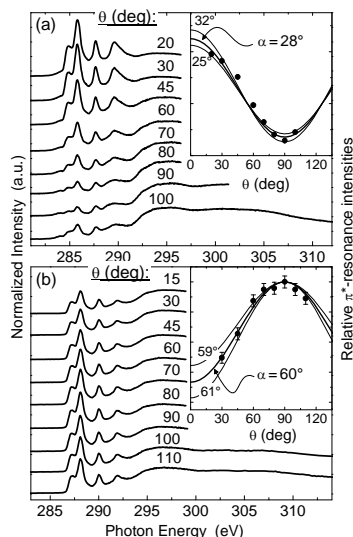
Figure 3a,b. NEXAFS spectra of about 10 nm thick CuPc films grown on the vicinal (a) and flat (b) Sb-Si(111)-1×1 surfaces. See Fig. 1 for the description of parameters. The best fits illustrated by thick lines correspond to molecular orientations of 28±4° (vicinal surface) and of 60±2° (flat surface) with respect to the substrate surface.