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Chemical Physics 325 (2006) 178–184

Chemical Physics

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Influence of substrate morphology on organic layer growth: PTCDA on Ag(1 1 1)

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Received 30 November 2005; accepted 13 January 2006
Available online 7 February 2006

Abstract

By UV-excited photoelectron emission microscopy (UV-PEEM) we investigated the microscopic growth behavior of organic thin films using 3,4,9,10-perylene-tetracarboxylicacid dianhydride (PTCDA) on a Ag(1 1 1) single crystal substrate as example. Direct, real time observation allows to correlate the initial growth modes and the related kinetic parameters with substrate properties like terrace width, step density, and step bunches from the submonolayer range up to 5 layers or more. Above room temperature PTCDA grows in a Stranski–Krastanov fashion: after completion of the first two stable layers three-dimensional islands are formed. The nucleation density strongly depends on the temperature and the substrate morphology thus affecting the properties of the organic film.

Keywords: Photoelectron emission microscopy; OMBE; Growth kinetics; Nucleation

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1. Introduction

The electrical and optical properties of organic films strongly depend on their structural and morphological properties. Ideal epitaxial growth resulting in perfect, nearly defect-free films requires optimum conditions [1]. This is particularly difficult in the heteroepitaxy of very different materials like, e.g., organic–inorganic heterostructures [2,3]. The problem with the preparation of such systems lies in the nature of the involved substances. Whereas the structural periodicity in inorganic compounds is on the scale of few Ångström, the dimensions of organic unit cells are usually in the range of nanometers. In addition, the anisotropic shape and intermolecular interaction, the very different thermal expansion coefficients, and the (partly excited) internal degrees of freedom, e.g., the soft vibrational and phonon modes, of condensed molecules may result in different structural modifications (polymorphoism) in the condensed phase and in unexpected growth behavior. Thus, imperfections at the interface which may extend into the growing film are foreseeable.

In the rapidly growing field of molecular electronics these organic–inorganic hybrid systems play an extremely important role, for instance in organic field-effect transistors, light-emitting devices, transponders, and solar cells. Structural imperfections may very negatively affect the performance of such devices. This is for instance true for the charge carrier injection at the interface and for the carrier mobility within the film which is hindered by traps and scattering at grain boundaries and defects as well as by the hopping barriers between non-equivalent neighboring molecules. Moreover, the optical properties may suffer from imperfections causing non-radiative decay channels, traps, and scattering centers for exciton transport, and they may change by varying molecular orientation, geometric structure, and film morphology as a function of organic film preparation [4].

The structural imperfections within a thin film which affect its quality and properties arise from the dynamical

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0301-0104/$ - see front matter
doi:10.1016/j.chemphys.2006.01.006

growth behavior and from the properties of the interface. It is of course known from many studies of inorganic materials that imperfections of the underlying substrate may deteriorate the growth and structural properties of the film. However, the details and the extent of the influence of the substrate surface quality on organic layer growth have not been systematically investigated so far, and very few experimental results are yet available. In this paper, we particularly address the influence of the substrate on the initial growth of an epitaxial organic film. Emphasis is placed on the influence of the morphological properties of the metal substrate, in particular the effect of steps and step bunches on the growth behavior. The variation of the substrate temperature during adsorption of the molecules is another important parameter which directly affects the mobility and hence the growth behavior of the molecules.

For our investigation we have chosen the well-known model system 3,4,9,10-perylene-tetracarboxylicacid dianhydride (PTCDA) on a crystalline Ag(1 1 1) substrate. Due to the small (<2%) lattice mismatch between the (1 0 2) plane of the β-modification of the PTCDA single crystal and the commensurate superstructure of the PTCDA monolayer on the Ag(1 1 1) substrate, PTCDA can grow in a quasi-epitaxial manner [5]. In order to directly correlate the film properties with microscopic properties of the substrate we use photoelectron emission microscopy (PEEM), which is ideally suited to monitor in situ the properties of the substrate and the organic film during deposition of the molecules as already shown for a different organic system, pentacene on SiO_2 [6]. Monitoring the involved processes directly and in real time allows to observe metastable intermediate states and to extract kinetic parameters of the film at every growth state and to correlate them to mesoscopic distortions of the substrate surface.

2. Experimental

The photoelectron emission microscope (PEEM) used for the experiments was an intermediate setup of the energy-filtered and aberration-corrected SMART spectromicroscope [7,8], installed at the soft X-ray synchrotron radiation source BESSY-II (Berlin, Germany). This instrument enables a comprehensive in situ surface and thin film characterization in *real-time* by microscopic imaging, diffraction, and spectroscopy of photo-emitted and/or reflected electrons [9].

In the present study a mercury short arc lamp (Hg-lamp) was used as photon source ($h\nu = 4.9$ eV) for photoelectron excitation. In the case of a metal surface the intensity of the PEEM image and the image contrast are determined by two parameters: (i) the local work function; and (ii) the density of states (DOS) near the Fermi level. Since the clean Ag(1 1 1) surface has a work function Φ of 4.8 eV it appears bright in PEEM images.

The deposition of the first monolayer of PTCDA changes the PEEM intensity by three contributions: (j) it increases the work function to 4.9 eV (which is hardly changed upon further PTCDA deposition [10]) thus reducing the substrate emission by cutting off some fraction, (jj) it further reduces the substrate emission by elastic and inelastic scattering of the emitted substrate electrons (attenuation), and (jjj) it opens a new emission channel right below the Fermi level which arises from the hybridization (and partial filling) of the lowest unoccupied molecular level (LUMO) of PTCDA with the s-states of Ag [10]. Apparently, (j) and (jj) are the dominating influences on the PEEM contrast, as the first layer leads to a considerable reduction of the emission. The (intensity increasing) effect of (jjj) is apparently small which is most likely due to a low photoemission cross section in this photon energy range.

For the second and higher layers only contribution (jj) is applicable as the work function remains unchanged for these layers (j), and there is no occupied molecular orbital near the Fermi edge (jjj). For the second and thicker PTCDA layers the highest occupied molecular orbital (HOMO) has a binding energy of 2 eV [10] and hence cannot lead to photoemission using photons of $h\nu = 4.9$ eV taking the 4.9 eV work function into account. Thus, as seen in Figs. 1 and 2, the contrast of the different layers above the first layer is exclusively due to attenuation effects: most photoelectrons are excited in the Ag substrate and have to surpass the organic layers; due to scattering effects their intensity is almost exponentially attenuated by these layers. This monotonic decrease of the substrate intensity enables the identification of the local thickness up to about 8 layers

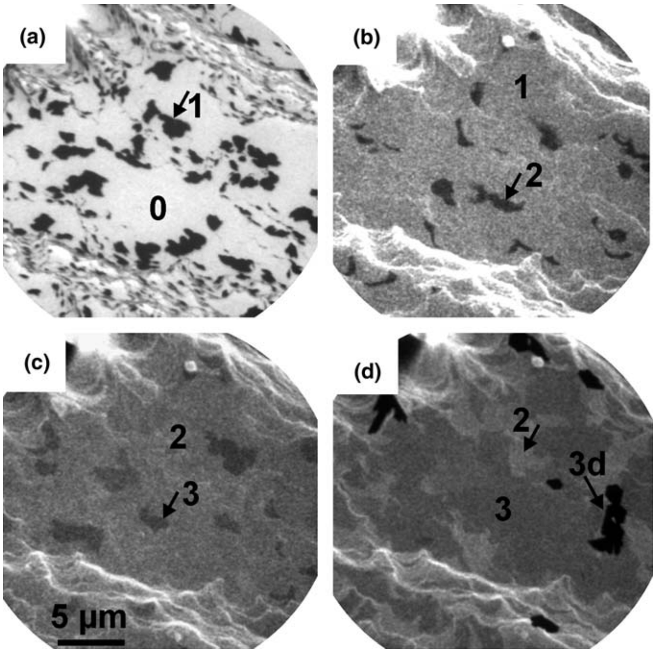

Fig. 1. In situ observation of the PTCDA growth on a Ag(1 1 1) surface at 378 K. The UV-PEEM images (a)–(d) show the identical area on the surface for the nominal coverages of 0.25, 1.05, 2.05, and 5 ML. The field of view is 23 µm × 23 µm. Only the intensity of image (a) was rescaled to optimize the contrast. The islands with the thickest PTCDA layer appear always darker than the surrounding. The labels 0, 1, 2, 3, and 3d indicate the pure substrate, the first to third layer, and the 3d-islands.