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Ordering of PVBA on amorphous SiO_2 and Pd(110)

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Abstract

Organic thin films made of 4-trans-2-(pyrid-4-yl-vinyl) benzoic acid are produced by molecular beam deposition under ultra-high vacuum conditions. We demonstrate by optical transmission measurements and second harmonic generation that oblique incidence of the molecular beam results in thin films with a preferential orientation of the organic molecules on amorphous substrates. Using Pd(110) as crystalline substrate, our STM images reveal improved ordering due to preferential adsorption at specific lattice sites. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Organic thin films with second order non-linear optical properties promise to open new frontiers for realizing high-speed, large capacity information transmission and processing [1,2]. Their controlled fabrication, however, is difficult because the non-centrosymmetric molecules in the film have to exhibit a preferential orientation in order to produce a macroscopic non-linearity. At a first glance, one would expect that the dipolar molecules tend to align antiparallel, and a macroscopic non-linearity cannot be found any more. However, processes far from thermal equilibrium such as molecular beam deposition (MBD) might be useful to fabricate films with oriented molecules. The most promising way to induce an in-plane anisotropy in MBD, we see so far, is the oblique incidence of the molecular beam. From growth studies employing inorganic materials, it is known that oblique incidence of the molecular beam can lead to structural, magnetic and optical anisotropies [3–5]. This is expected to work equally well for organic materials, although no experimental studies have been reported so far. Probably, the films are unstable due to the weak interaction at the film-substrate interface and within the organic thin film. Metals such as palladium are appropriate substrate materials because they form strong π-bonds with some conjugated organic molecules [6,7]. However, one problem, the weak interaction within the film, still remains. Therefore, we have developed special molecules which form strong intermolecular hydrogen bonds. The non-centrosymmetric molecule, i.e. 4-trans-2-(pyrid-4-yl-vinyl) benzoic acid (PVBA), has a pyridyl ring on one end and an acidic group on the other one (Fig. 1). Hence, the different ends can form a hydrogen bond and are connected to each other in a head-to-tail fashion leading to linear polymer-like structures as we have shown by solid state ^{15}N-NMR [8]. These structures are thermally and mechanically more stable than traditional non-linear optical organic materials [9]. Thus, the hydrogen bonds are expected to stabilize an alignment of organic molecules, possibly realized by MBD at oblique incidence.

Another important feature of these materials is that they can be easily sublimated in vacuum. Here, the hydrogen bonds are broken while the molecules themselves remain intact. At the film surface, the hydrogen bonds between the molecules are formed again.

2. Experimental

As amorphous, non-reactive substrates, simple glass (microscope slides) and fused silica (Suprasil®) are used. The deposition was carried out in an ultra-high vacuum chamber equipped with low temperature effusion sources. PVBA was sublimated from such a source at a temperature of 220°C resulting in deposition rates typical for molecular beam epitaxy (1 monolayer/s). Before first deposition,

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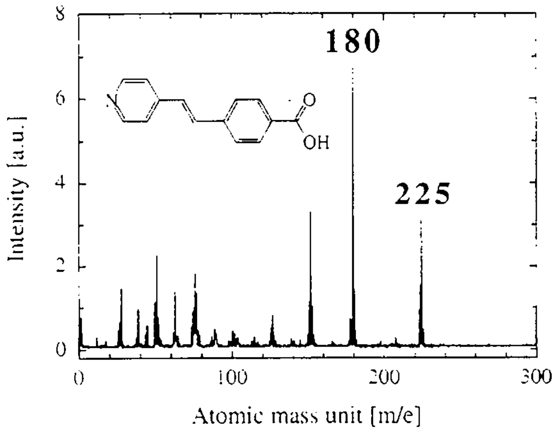

Fig. 1. Mass spectrum of PVBA obtained by a quadrupole mass spectrometer with a cross-beam source at a base pressure of 10^{-9} mbar. Inset: molecular structure of PVBA.

adsorbed water and some residual chemicals are removed from PVBA by heating the source to 120°C for at least 12 h. A low base pressure during deposition ($< 6 \times 10^{-9}$ mbar) guaranteed high purity thin films. The deposition rate was controlled by a quartz microbalance stabilized at 30°C and calibrated by in situ and ex situ film thickness measurement techniques [9].

The optical transmission measurements ranging from ultraviolet to infra-red light were performed by a Spectrophotometer (Lambda-9, Perkin-Elmer). The second harmonic generation (SHG) experiments in transmission mode were carried out ex situ using a BMI Nd:YAG laser (wavelength 1064 nm, pulse duration 25 ns, repetition rate 30 Hz).

In order to characterize the growth of PVBA on a single crystal metal surface at the atomic level, experiments employing a Pd(110) substrate were performed by variable-temperature scanning tunneling microscopy (VT-STM) under UHV conditions (2×10^{-10} mbar) [10]. The STM measurements are performed in situ right after deposition. The Pd(110) sample preparation followed the procedures outlined in [11].

3. Results and discussion

A quadrupole mass spectrum of PVBA is reproduced in Fig. 1. The mass of PVBA corresponds to 225 amu. The presence of 225 amu in the spectra ensures PVBA evaporation as intact molecules. The main peak, however, is found at 180 amu. The difference (45 amu) corresponds to the carboxylic group, signaling a weak bond of the latter which can be broken by ionization.

PVBA was deposited on amorphous SiO_2-substrates by an angle of about 30° with respect to the normal surface. This relatively small angle guarantees good thickness homogeneity and modest roughness, but gives rise to a remarkable anisotropy in optical transmission spectra. Changing the angle of the polarizer in front of the sample, the transmission of the UV-light shows a sinusoidal behavior (Fig. 2). The maximum is within the plane of incidence of the molecular beam or shifted by 90°. This optical in-plane anisotropy can be described as linear dichroism [12], which is defined as the difference in the absorbance parallel and perpendicular to an orientation axis. The curves shown in Fig. 2 are obtained from a thin film with a thickness of 270 nm grown at 100°C with a deposition rate of 0.10 nm/s. The characteristic peak in linear dichroism is found at a wavelength of 373 nm with the same amplitude for PVBA/glass and PVBA/fused silica. A similar organic material deposited on fused silica exhibits the peak at a different wavelength [9]. Therefore, the peak at 373 nm should be characteristic for PVBA. It is attributed to an excitation parallel to the long axis of aligned PVBA molecules (see below).

The transmission data show the anisotropic alignment of the organic molecules. Linear optical phenomena, however, cannot be used to distinguish between parallel and antiparallel molecular configurations. Second harmonic generation (SHG) - the frequency doubling of light, however, is only observed if the centrosymmetry is broken, i.e. if the molecules exhibit a preferential orientation with a resulting macroscopic dipole. The PVBA thin films generate second harmonic light with a strong polarization dependence (Fig. 3). This dependence is used to derive the ratio of the most important non-linear optical coefficients

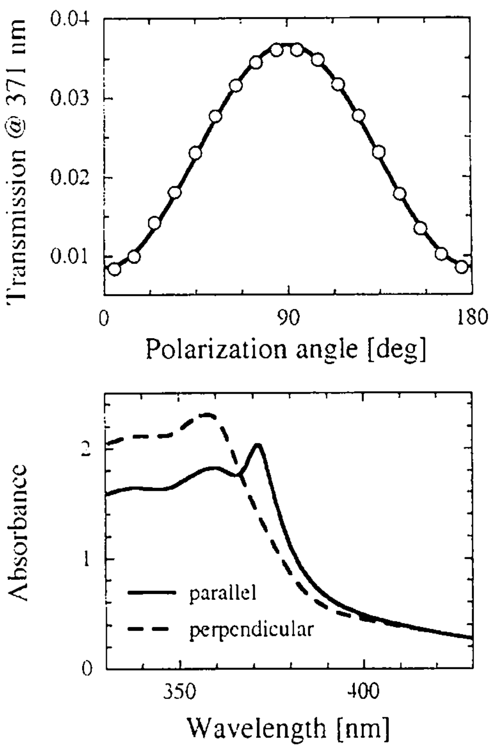

Fig. 2. Sinusoidal polarization dependence of the optical transmission at a wavelength of 371 nm (upper part). Optical transmission spectra of a PVBA thin film parallel and perpendicular to the plane of incidence of the molecular beam (lower part).

$d_{333}/d_{311} = (2.8 \pm 0.3)$. Using the standard Maker-fringe technique, $d_{333} = 0.5$ pm/V is determined (calibration reference: d_{11} of quartz 0.3 pm/V) [13]. This value is quite low but it should be raised considerably by the use of stronger donor-acceptor end groups or improved ordering by optimized growth conditions.

The maximum of SHG intensity $I_{2\omega}$ is found when both polarizers are parallel to the plane of incidence of the molecular beam. That means there is an in-plane component of the effective charge transfer with maximum in direction 3, a consequence of the symmetry of deposition geometry. Experimentally, this has been verified by sample rotation of 180° after deposition of half film thickness. Due to the induced sign reversal of the non-linearity the SHG signal disappears.

A significant contribution from the interfaces of the film to the SHG intensity can be definitely excluded because of the quadratic thickness dependence of the intensity [14,15]. An alignment of the molecules due to substrate morphology is also ruled out. For that, a substrate was cut into four pieces which were rotated by 90° to each other before deposition. The maximum SHG signal is always parallel to the plane of incidence of the molecular beam. In addition, the variation of the angle of incidence of the molecular beam from 10 via 20 to 30° with respect to the normal surface results in a considerable increase of SHG intensity. Thus, the ordering of PVBA molecules due to the oblique incidence of the molecular beam has been proven.

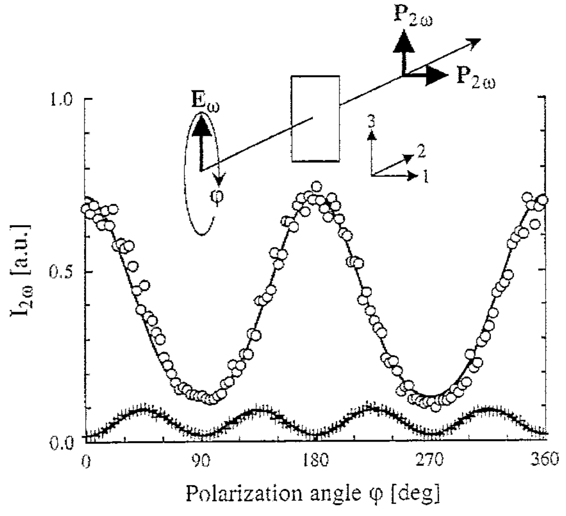

Fig. 3. SHG intensity as a function of the polarization angle to demonstrate the preferential orientation of the PVBA molecules. The data are obtained from a 180-nm thick PVBA film deposited on fused silica at a substrate temperature of 100°C and a deposition rate of 0.09 nm/s.

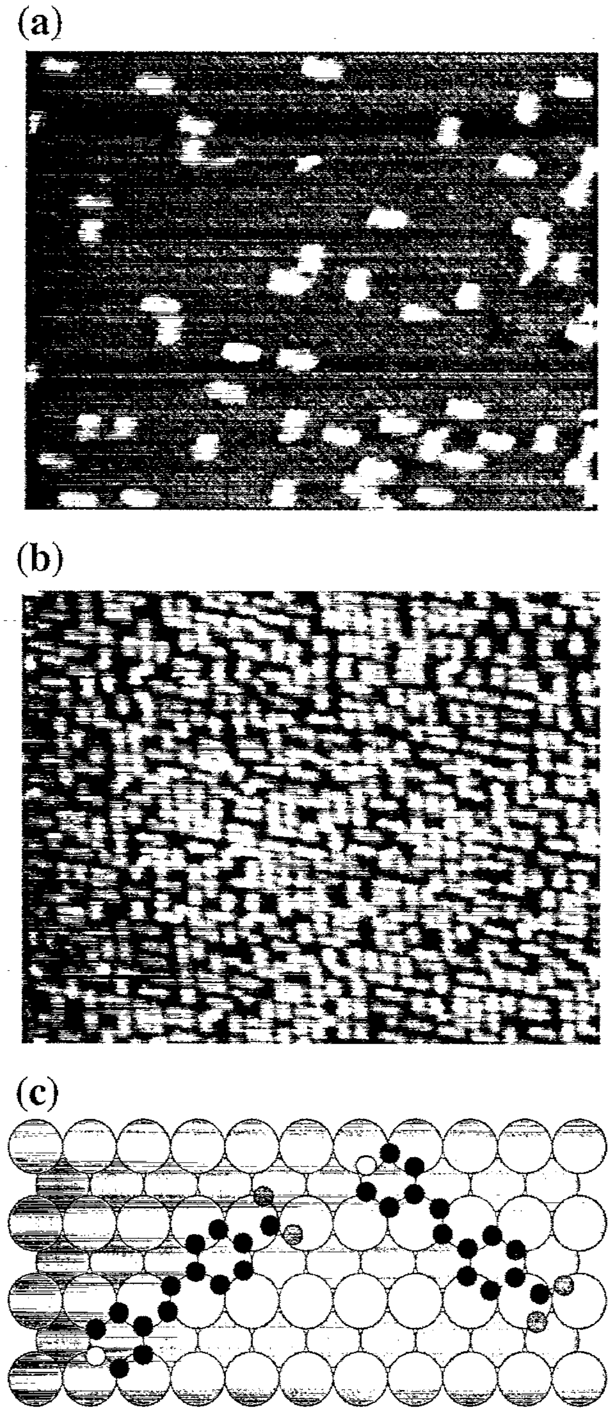

Fig. 4. STM images of PVBA molecules on Pd(110) with (a) submonolayer coverage ($T = 360$ K) and (b) monolayer coverage ($T = 410$ K); image sizes: 210 × 170 Å (c) ball model of the adsorption geometry. The PVBA molecules may be shifted by half an atom along the Pd rows.

Crystalline surfaces are expected to substantially improve the ordering since the organic molecules are preferentially adsorbed at specific lattice sites. A single-crystal metal surface was chosen because the arrangement and the internal structure of organic molecules can be detected by STM [16]. Pd(110), an anisotropic fcc(110) surface, is used to facilitate the expected linear chain formation of PVBA molecules. Surprisingly, such chains of H-bonded molecules do not evolve. Instead, STM data show isolated protrusions consisting of two rings (Fig. 4). Each of these protrusions is attributed to one organic molecule. Even with increasing coverage, the molecules do not form any islands. They are clearly separated and oriented towards two specific directions. Interactions between molecule and substrate are thus rather strong, whereas intermolecular interactions are weak. The absence of molecular chain formation might also be related to the chemical activity of the Pd substrate inducing a decomposition of the molecule. The PVBA acidic group could be detached, a hypothesis which would be in accordance with experiments demonstrating formic acid decomposition on Pd(110) [17]. More likely, however, the acidic group is not imaged, as found for the carboxylic group of formic acid on graphite [18].

VT-STM investigations demonstrate that, at submonolayer coverage, the molecules are highly mobile for temperatures exceeding about 350 K [19]. At monolayer coverage, space limitations prevent the molecular surface diffusion, and the adsorbate lattice is well ordered even at higher temperatures, as demonstrated by the image in Fig. 4b. Nevertheless, it is impossible to grow films thicker than a monolayer. This behavior indicates strong interactions at the interface, inhibiting H-bond formation. Under all conditions, the organic molecules are adsorbed at well-defined lattice sites, as illustrated by the model in Fig. 4c (based on STM images with simultaneous resolution of the protrusions and the atomic structure of the substrate, such as Fig. 4a). The model describes both the angles between the molecules and the Pd rows (about ± 35°) and the separation between the two rings. Thus, organic molecules can be, in principle, perfectly aligned by the choice of an appropriate crystalline substrate. For applications, however, where thicker films are necessary, the ordering must be extended to multilayer coverages.

4. Conclusion

We have demonstrated that MBD at oblique-incidence can result in ordered organic thin films with anisotropic properties even on amorphous substrates. The in-plane orientation of the molecules is given by the direction of the molecular beam. The growth of the organic thin films can be monitored in situ and precisely controlled down to the atomic scale. The ordering may be improved by the choice of crystalline substrates. The interaction between the organic molecules and the substrate, however, has to be precisely characterized.

Acknowledgements

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