Surface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Surface Science

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

Switching orientation of adsorbed molecules: Reverse domino on a metal surface

C.R. Braatz [a], T. Esat [c,d], C. Wagner [b,c,d], R. Temirov [c,d], F.S. Tautz [c,d], P. Jakob [a,*]

[a] Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität Marburg, 35032 Marburg, Germany
[b] Leiden Institute of Physics, Universiteit Leiden, Niels Bohrweg 2, 2333 CA Leiden, The Netherlands
[c] Peter Grünberg Institut, Forschungszentrum Jülich, 52425 Jülich, Germany
[d] Jülich Aachen Research Alliance (JARA), Fundamentals of Future Information Technology, 52425 Jülich, Germany

ARTICLE INFO

Available online xxxx

Keywords:
Infrared absorption spectroscopy
STM
Metal organic interface
NTCDA
Ag(111)
Organic semiconductor

ABSTRACT

A thus far unknown phase of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA) on Ag(111), characterized by an all perpendicular orientation of the planar molecules and bound to the Ag substrate through the carboxyl oxygen atoms has been identified using infrared absorption spectroscopy and scanning tunneling microscopy. Its formation process requires second layer NTCDA to squeeze into empty spaces between relaxed monolayer NTCDA molecules. Remarkably, this process causes initially parallel oriented NTCDA to likewise adopt the new, highly inclined adsorption geometry. According to our SPA-LEED and STM findings, the new phase displays a distinct long range order and shows a pronounced tendency to form 1D rows or narrow islands. We suggest that extra NTCDA preferentially transforms into the upright configuration close to existing islands and attaches to them, i.e. the transformation process proceeds in a directed and recurrent manner (reverse domino scenario). Identical processing starting with a compressed NTCDA/Ag(111) monolayer leads to a purely parallel oriented bilayer, that is, the NTCDA monolayer phase is retained and merely acts as a passive template for bilayer NTCDA. The new vertical NTCDA phase represents an unusual molecular system with π–orbitals oriented parallel to a metal surface. A substantially reduced coupling of these orbitals to Ag(111) electronic levels is conjectured, which will have a major impact on intermolecular couplings and electronically excited state lifetimes.

1. Introduction

Molecular constituents of organic films quite naturally represent anisotropic entities, and accordingly, intermolecular interactions and physical properties are expected to display directional dependencies [1,2]. For 2D layers, the formation of ordered arrays over extended distances represents a common testimony thereof. In terms of electronic coupling, coplanar adsorbed molecular species behave very much like isolated objects with negligible lateral coupling. Band structure effects of molecular states are expected primarily in case of hybridization with substrate electronic levels [3–7]. The reason for the weak intermolecular coupling despite their close vicinity lies in the closed shell character of electronic orbitals at the molecules' perimeter. For stacked arrays, the direction perpendicular to the molecular plane with its aromatic π–electron system represents a natural pathway for excited electron/hole migration between adjacent molecules, and it is usually associated with distinct energy dispersions of molecular levels [2,8, 9]. According to the literature [10,11], electron mobilities for π–stacked single crystals of rubrene or pentacene may reach values of 20–50 $cm^2V^{-1}s^{-1}$, that is, well beyond those of amorphous silicon.

As planar molecular species with π–electron systems tend to grow with their molecular planes oriented parallel to the substrate surface, charge transport or, alternatively, band structure formation primarily concerns the normal direction. Vertical molecular orientations in the first layer (while maintaining parallel stacking) usually involve weakly interacting substrates (oxides, sulfites, graphite, …) [12–14]. Considering the (often) sensitive energy balance associated with surfaces, interfaces, and bulk crystalline structures [1,15], inclined molecular orientations may also be encountered for functionalized or precovered surface layers [16–19]. By means of specific surface decoration, molecular orientations and thin film morphology can thus be controlled so that ionization potentials and molecular level alignment (e.g. accessed by means of detecting core level shifts [20]) may be adjusted through internal or induced molecular dipoles within grown layers [21,22]. Generally speaking, the local adsorption geometry has a notable influence on charge transport properties and band structure formation within grown molecular films.

In the present study, NTCDA layers in excess of one monolayer have been analyzed under conditions of a constrained thermodynamic equilibrium on Ag(111). NTCDA is a planar molecule with D_{2h} symmetry, i.e. the long and the short ends are different but opposing ends are identical (cf. inset of Fig. 2 for the chemical structure formula of NTCDA). Besides the π–electron system associated with the aromatic

---

* Corresponding author.
E-mail address: peter.jakob@physik.uni-marburg.de (P. Jakob).

http://dx.doi.org/10.1016/j.susc.2015.06.016
0039-6028/

Please cite this article as: C.R. Braatz, et al., Switching orientation of adsorbed molecules: Reverse domino on a metal surface, Surf. Sci. (2015), http://dx.doi.org/10.1016/j.susc.2015.06.016

naphthalene core, the carboxyl and anhydride groups located at the long ends of the molecule introduce another potential interaction mechanism between NTCDA and the underlying substrate. The intriguing role of NTCDA and related molecules as a model system arises from the combined action and/or competition of these two functionalities. For example, it is well-known that the π–metal interaction and oxygen–metal interaction together lead to a distortion of the molecule when adsorbed at the surface [23–27].

According to the literature [1,18,27–29], the dominance of the π–electron interaction seems symptomatic for NTCDA (as well as for the related PTCDA species), as the parallel orientation is commonly reported for monolayers in direct contact to a metal substrate, even on the weakly interacting Au(111) surface [30]; NTCDA multilayer growth, on the other hand, quite commonly yields inclined or perpendicular orientations [12,31], in accordance with the bulk crystal structure [32] (note that π-stacking of planar molecules favors lamellar arrangements). We like to discriminate our work from similar studies on very weakly interacting substrates such as graphite, oxides, sulphites, or passivated substrates for which intermolecular interactions exceed adsorbate–substrate interactions and, depending on total coverage, orientation changes from parallel to non-parallel, bulk-like arrangements are likely [12,19]. Molecular layers on metals are different as compared to non-conducting substrates as covalent bonding may lead to the formation of hybrid orbitals by mixing of metal states and molecular orbitals [27,31]. Generalizing this finding, we expect that for most such functionalized aromatic species, the energy gain associated with π-bonding to a metal surface exceeds alternative bonding schemes. One notable exception is NDCA deposited onto oxygen precovered Ni(111). Here, the particularly strong Ni–oxygen bond exceeds π-bonding via the naphthalene core, especially once the latter interaction is weakened by preadsorbed oxygen [33]. This exceptional case notwithstanding, π-bonding generally appears all the more favorable as van der Waals interactions additionally provide an appreciable extra energy gain for flat lying molecules as opposed to inclined or vertically orientated species. Thanks to its relatively compact size and a relatively small-scale aromatic core, NTCDA appears as an ideal candidate to challenge this unwritten rule.

To do so, we take advantage of specific kinetic constraints, that is, we apply a defined sequence of individual preparation steps (deposition, annealing) to launch or suppress processes selectively, depending on the respective activation energies. This way, thermal equilibration within grown layers can be restricted to a local section of the phase space only. A comprehensive spectroscopic characterization in conjunction with adequate control of grown layers thereby proved essential to succeed in preparing films with desired properties. In our study, infrared absorption spectroscopy (IRAS) has been used to identify and discriminate different phases of NTCDA on Ag(111), as well as to follow their formation and decay in detail. In a previous work, we have demonstrated our capability to reproducibly prepare such well-defined organic monolayer films using spot profile analysis low energy electron diffraction (SPA-LEED) and thermal desorption spectroscopy (TDS), besides IRAS [34].

A key parameter of organic films involving planar molecular species is the inclination angle assumed by these, and it is one of the foremost questions in thin film growth to derive a fundamental understanding as to why the one or the other geometry is adopted. In the present work, we have taken advantage of the polarization dependencies of the various vibrational modes to identify changes in molecular orientation within deposited monolayer and bilayer films using IRAS: Vibrational modes are generally associated with characteristic displacement patterns of molecular bonds and can be classified in terms of irreducible representations of the symmetry group. Analysis of their intrinsic polarizations represents a complementary approach, besides the NEXAFS method [31,35] to determine molecular orientations.

The studied system, NTCDA on Ag(111), is well-known from the literature, and models regarding the structural properties of its monolayer phases have been suggested [36,37]. Specifically, adsorption geometries have been analyzed by NEXAFS, and it has been invoked that mono- and bilayers cannot be prepared in a perpendicular orientation at any preparation temperature [31], a long-standing statement which we will invalidate in the present work.

By applying refined processing, an unusual phase comprising ordered arrays of vertically standing planar NTCDA molecules on a Ag(111) surface has been identified. We will refer to it as NTCDA-vert from now on. Despite extensive research on this model system, the new phase has eluded discovery thus far, which exemplifies the beneficial combination of spectroscopic and real space microscopic techniques. Our IRAS and STM data further reveal that substrate bonding proceeds via the bottom side oxygen atoms, while the twin upper side points towards the vacuum and may serve as an attractive docking site for higher layers. Based on low temperature STM data, a model for its formation is presented which may be best described as a reverse domino effect, as growth proceeds in a directed and self-sustaining fashion (producing extended rows of the vertically aligned molecules) and in particular involves reorientation of initially parallel oriented NTCDA towards the vertical.

2. Experimental

The IRAS and SPA-LEED experiments were carried out in a UHV chamber at a base pressure of 5×10^{-11} mbar. The Fourier-transform infrared spectrometer (FTIR) was a Bruker IFS 66v/S with evacuable optics. For the IR measurements, the sample was positioned in a specially designed cell. The spectra were recorded using a liquid N_2-cooled Mercury-Cadmium-Telluride detector (spectral range 600–5000 cm^{-1}). We used polarized light throughout and selected a spectral resolution of 2 cm^{-1}; the number of coadded scans typically was $n_{scan} = 1000$. IRAS as well as SPA-LEED (Omicron Nanotechnology) measurements were obtained at a sample temperature of 77 K. Temperature measurements used a K-type thermocouple welded to the edge of the Ag(111) sample. The Ag(111) crystal was cleaned by Ar^+ sputtering (30 min at $U_{ion} = 700$ eV, $I_{ion} = 3$ μA, and $T_{sample} = 373$ K) followed by annealing to 773 K for 5 min. NTCDA was evaporated from a home-made thermal evaporator at $T_{NTCDA} = 390$ K (deposition rate of 0.2 ML/min) controlled by a Pt1000 temperature sensor. During evaporation, the background pressure typically increases by $\Delta p = 1 \times 10^{-10}$ mbar. All layers were grown at $T_{ads} = 77$ K.

STM experiments were performed in a separate UHV chamber, using a low temperature scanning tunneling microscope by CREATEC GmbH. Typical temperatures at which experiments were carried out have been at 8–9 K. Samples were prepared in a preparation chamber ($p \approx 4 \times 10^{-10}$ mbar), following procedures applied in the IRAS chamber, and transferred in vacuo to the cold STM. STM images were obtained with a tungsten tip. WSxM software [38] has been used to analyze STM images.

3. Results and discussion

In our study, we will take advantage of the delicate balance of binding and configuration energies associated with the various bonding schemes and geometries of NTCDA on Ag(111) to realize a novel binding configuration involving highly inclined NTCDA species bound to the Ag(111) metal substrate by means of carboxyl oxygen. IRAS is primarily used to characterize prepared NTCDA layers spectroscopically and to follow their thermal evolution in detail. Thereby, the high spectral resolution of infrared absorption spectroscopy discriminates sensitively between different phases, binding geometries, and local environments. Modifications in the overall molecular structure or of the local binding geometry to the substrate are directly reflected in the vibrational spectrum and can be deduced from the presence or absence of characteristic modes with specific polarizations. These provide direct access to molecular orientations within organic films. Note that such a structural characterization is not restricted to the tilting of the

Please cite this article as: C.R. Braatz, et al., Switching orientation of adsorbed molecules: Reverse domino on a metal surface, Surf. Sci. (2015), http://dx.doi.org/10.1016/j.susc.2015.06.016