Adsorption of thioether molecules on an alumina thin film

Yi Pan [a], Niklas Nilius [a,b,*], Wolf-Dieter Schneider [a,c], Hans-Joachim Freund [a]

[a] Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany
[b] Institute of Physics, Carl von Ossietzky University Oldenburg, 26111 Oldenburg, Germany
[c] École Polytechnique Fédérale de Lausanne, Institute of Condensed Matter Physics, CH-1015 Lausanne, Switzerland

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ABSTRACT

Low-temperature scanning tunneling microscopy has been employed to study the adsorption of (bis(3-phenylthio)-phenyl)sulfane (BPPS) molecules on an aluminum-oxide film grown on NiAl(110). Large variations in the molecular coverage on incompletely oxidized samples indicate substantial differences in the binding strength of BPPS to metallic (NiAl) versus dielectric (alumina) surfaces. From atomically resolved images, we obtain possible BPPS adsorption geometries on the oxide, in which the sulfur centers and not the phenyl rings of the molecule govern the interaction. A local hexagonal ordering of BPPS, as deduced from pair correlation functions, suggests a preferential binding of the BPPS sulfur atoms to Al ions with distorted pyramidal coordination in the oxide surface. Our work provides insight into rarely explored binding schemes of organic molecules on wide-gap oxide materials.

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1. Introduction

The interplay between organic molecules and metal surfaces has been already in the focus of research for several decades [1,2]. This continued interest is driven by various applications of molecular–metal interfaces, e.g. for new electronic, light-emitting and photovoltaic devices based on organic materials. The interaction of organic molecules and non-metallic surfaces, on the other hand, has attracted much less attention, although the technological relevance of this combination is equally large [3]. Interfaces between organic matter and oxide supports, for example, are of crucial importance for liquid–solid solar cells, in which the optical excitation occurs in molecular sensitizers, while separation and transport of the photo-generated carriers are realized by an oxide [4]. The most prominent example in this regard is the Grätzel cell, consisting of a TiO_2 powder covered with Dye-molecules, which has reached conversion efficiencies of 15% to date [5]. Molecule–oxide interfaces are of interest also in the widespread field of heterogeneous catalysis, where oxides are typically used as cheap and robust support materials [6–8].

The significance of molecule–oxide interfaces is in contrast to the limited research activities in the field. Despite a vital technological interest, fundamental studies on such systems are rare, a discrepancy that arises from several experimental difficulties. First of all, the binding between wide-gap insulators and common organic molecules is weak, as the interaction arises mostly from van-der-Waals and Coulomb forces and not from chemical bonds [9,10]. As a consequence, molecule–oxide junctions exhibit high structural flexibility at room temperature and defined interfaces only develop at cryogenic conditions. More relevant is the poor electrical conductivity of most molecule–oxide systems, which limits the applicability of electron-mediated spectroscopic and microscopic techniques [11]. Especially, the use of scanning tunneling microscopy (STM) for structural characterization at the nanometer scale is challenging, as the tip easily perturbs the weakly bound adsorbates [12–15]. Closely related to the issue of finite conductivity are the unusual imaging properties of molecules in the STM. In many cases, molecular orbitals contribute only weakly to the STM image contrast, as they poorly overlap with the substrate electronic states and cannot serve as initial or final state in a tunneling process.

In this study, we have overcome these restrictions by using an oxide film, thin enough to maintain a finite conductivity, to support the organic molecules. Our model system is alumina, an archetypical ionic insulator with 8 eV band gap, grown on a NiAl(110) substrate [16,17]. Our probe molecule, a thioether compound consisting of four phenyl rings linked by sulfur atoms, has recently attracted attention as it was found to act as re-dispersion agent for metal nanoparticles [18,19]. On the basis of atomically resolved STM images, we will determine the binding behavior of the molecules on the oxide surface and analyze general aspects of molecule–oxide interactions.

* Corresponding author at: Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany.
  E-mail address: nilius@fhi-berlin.mpg.de (N. Nilius).

2. Experiment

The experiments have been performed with a custom-built ultra-high vacuum STM operated at 4.5 K. The alumina films were prepared by oxidizing a sputtered and annealed NiAl(110) single crystal in 5 × 10^{-6} mbar of oxygen at 550 K, followed by a vacuum-annealing step at 1000 K [17]. The film quality was routinely checked with low-energy-electron-diffraction, exhibiting a complex yet sharp spot pattern, and STM measurements revealing wide, atomically-flat oxide terraces. The main properties of the NiAl-supported alumina films have been discussed in several papers before and shall only be sketched at this point [20,21]. The film comprises four atomic layers; (i) an interfacial Al$_i$ plane consisting of atoms in pentagonal and heptagonal configuration, (ii) a hexagonal O$_i$ plane, (iii) an iso-structural Al$_s$ plane and (iv) a terminating O$_s$ plane made of triangular and square units (Fig. 1a). While each interface Al$_i$ ion has three O neighbors, the Al$_s$ coordination number varies between four and five due to ions in tetrahedral and pyramidal sites [20]. The oxide lattice is composed of rectangular unit cells (10.7 × 17.9 Å^2), being arranged in two reflection domains rotated by ±24° against the lattice of the NiAl support [22]. The oxide has a commensurate relationship with the substrate only along the NiAl[1$\bar{1}$0] direction, while no commensurability exists along the orthogonal NiAl[001]. In order to release misfit strain in the commensurate direction, a periodic network of dislocation lines is inserted into the film, comprising both antiphase and reflection boundaries between equal and mirrored surface domains, respectively [23]. The boundaries appear as protruding lines in empty-state STM images, as they possess a set of unoccupied defect states in the oxide band [24].

The adsorption experiments were carried out with (bis(3-phenylthio)-phenyl)sulfane (referred to as BPPS in the following), synthesized in the group of Prof. Blechert at the Technical University Berlin [18,25]. The compound consists of four phenyl rings linked via three sulfur atoms in meta-positions. Due to facile rotation about the C-S-C axes, a variety of configurations of the molecule can be realized upon adsorption, e.g. the chain-like and folded conformers shown in Fig. 1b–d. The molecules were purified by extensive degassing at 430 K and dosed from an alumina crucible onto the fresh oxide film at 300 K. Immediately after deposition, the samples were transferred into the cryogenic microscope to avoid contamination.

3. Results and discussion

On incompletely oxidized surfaces, the BPPS molecules show a high preference for binding to the metallic NiAl, while the coexisting oxide patches remain essentially empty (Fig. 2a). This difference in sticking indicates a much stronger BPPS adhesion onto metallic than dielectric surfaces, reflecting the chemical inertness of the latter. The observed variations in local coverage demonstrate also the high mobility of the molecules that are always able to reach a nearby NiAl patch at 300 K. By evaluating the mean distance between adjacent metal areas on samples with different metal–oxide surface ratio, we have determined the lower bound for the BPPS diffusion length on the oxide film to be of the order of 500 nm [26]. A detailed discussion of thioether molecules interacting with a NiAl surface can be found in the literature [18].

On fully oxidized samples, a molecular fingerprint becomes detectable also on the alumina film (Fig. 2b). Atom-sized protrusions of ~0.5 Å height and 5–7 Å diameter are found on defect-free oxide domains and, less abundant, along the domain boundaries (bright lines in Fig. 2b). Already a crude image inspection reveals that the maxima are not randomly distributed, but form a hexagonal pattern on the surface. Typical distances are derived from pair-correlation functions, calculated on the basis of STM images as shown in Figs. 2b. Three characteristic separations between the maxima are revealed, namely (10 ± 1), (22 ± 5) and (45 ± 5) Å (Fig. 3). Also the connecting lines between the protrusions have distinct orientations, following the diagonals of the unit cells in the two oxide domains (see arrows in Fig. 2b for one domain). Note that molecules located directly on the domain boundaries have been excluded from this statistics, as their positions might be altered by the line defects.

The adsorption pattern observed on the alumina film seems incompatible with the structure of the BPPS molecules at first glance. Assuming that either the phenyl rings or the sulfur atoms become visible in the STM, we would expect to find either four or three maxima in linear, triangular or rhomboidal configuration to represent a single molecule (Fig. 1b–d). In contrast, most protrusions appear in pairs with either 10 or 22 Å distance, suggesting that only some of the molecular entities actually contribute to the contrast. In a possible scenario, two sulfur atoms might be detected in the STM, while the third one remains invisible. A separation of 22 Å between adjacent maxima would then correspond to the first and last sulfur atom in linear BPPS
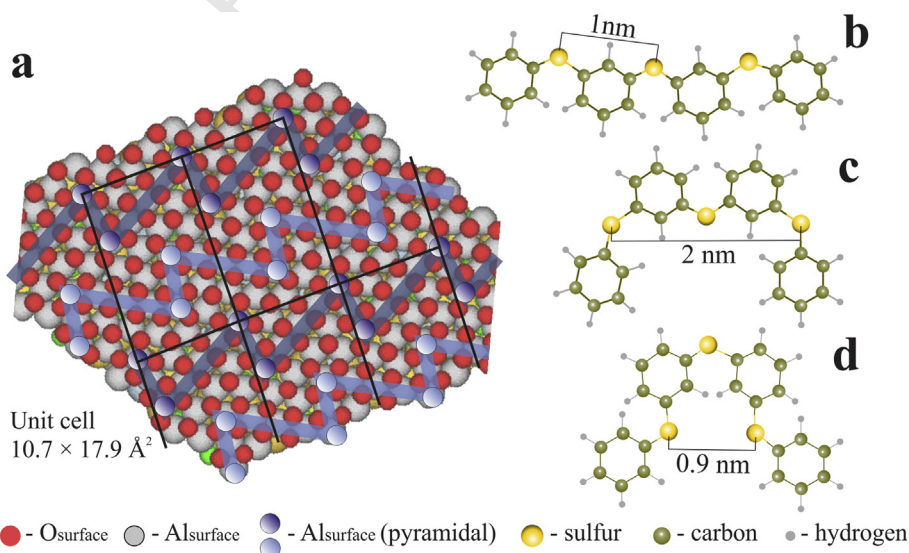

Fig. 1. (a) Ball model of the Al$_s$ and O$_s$ planes of the alumina film grown on NiAl(110). The Al$_s$ ions in distorted (regular) pyramidal configuration are highlighted by blue balls (zig-zag lines), as they dominate the image contrast seen in STM. (b-d) Three planar conformations of the (bis(3-phenylthio)-phenyl)sulfane molecule. Note that various other 2D and 3D conformers exist and our selection is not exhaustive. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).