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h-BN on Pd(1 1 0): a tunable system for self-assembled nanostructures?

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Abstract

A one-monolayer thick covalent network of hexagonal boron nitride (*h*-BN) forms on Pd(1 1 0) upon thermal decomposition of borazine $(HBNH)_3$. Due to the weak interfacial bonding, the different symmetries of overlayer and substrate, and the lattice mismatch, a variety of rotated domains are created. Several Moiré patterns appear in STM images, which can be well explained by simple atomic models. Rings in LEED manifest domain averaging. Non-uniform intensity distributions along these rings measure the abundance of certain domains, depending on particular preparation procedures. The individual Moiré domains represent interesting periodic nanostructures that can be imprinted in an adsorbed layer of C_{60} molecules.

Keywords: Hexagonal boron nitride (*h*-BN); Palladium; Moiré pattern; Scanning tunneling microscopy (STM); Low energy electron diffraction (LEED)

1. Introduction

Ultra-thin insulating films weakly bonded to flat metal surfaces may offer interesting applications in the construction of future microelectronic devices due to the abrupt change of the electronic structure at the interface. In the search of materials with these properties, hexagonal boron nitride (*h*-BN) has proven to be an excellent candidate. *h*-BN monolayer films were produced on a variety of transition metal surfaces, in most cases with a hexagonal symmetry [1–5] or in one case on a square lattice (Ni(1 0 0) [6]). The layers are weakly interacting with the metal but they are stable at high temperatures (up to 1000 K) and to air exposure. These important features are due to the

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strong lateral inter-atomic bonds within the *h*-BN layers. The strength of these bonds plays a key role in the process of formation of *h*-BN layers on different metal surfaces, but the geometry and the lattice constant of the substrate make every system unique. In the case of *h*-BN films on Rh(1 1 1), for example, the large tensile lattice mismatch of −6.7% between the overlayer and the substrate leads to the formation of a bilayer nanomesh with a periodicity of 32 ± 2 Å [5]. Two monolayer meshes of *h*-BN with a hole diameter of 24 ± 2 Å and a wire thickness of 9 ± 2 Å grow one on top of the other, shifted such as to cover most of the substrate surface. In contrast, when *h*-BN is grown on Ni(1 1 1), the small compressive lattice mismatch of +0.4% between the two systems leads to the formation of a (1 × 1) commensurate single atomic layer. Ordered and flat terraces of one monolayer thickness are found over large areas [7,8].

In this paper we report on the rich and peculiar structural elements found when *h*-BN is formed on the (1 1 0) surface of a palladium single crystal, which does not match the hexagonal symmetry of a *h*-BN layer. Scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) measurements illustrate that the *h*-BN units do not find a unique way to register with the Pd(1 1 0) surface. A large variety of domains is formed in which the *h*-BN unit cells assume different orientations with respect to the substrate crystallographic directions while preserving their original inter-atomic distances. The weaker bonding to the substrate manifests itself by producing, for each domain, a characteristic Moiré pattern resulting from the superposition of substrate and film periodicities. A number of regular nanostructures is thus formed, with different periodicities and symmetries. There are indications that the domain distribution depends on details of the sample preparation.

2. Experimental

The experiments were performed in three ultra-high vacuum (UHV) chambers (base pressure $<10^{-10}$ Torr) connected through a low vibrational noise coupling. In this way the same sample can be transferred under UHV conditions between the LEED chamber, the STM chamber (which hosts a Park Scientific Instruments VPII STM) and the photoemission chamber (with a modified VG ESCALAB 220 spectrometer) [9,10]. STM images were recorded in constant current mode. NaOH etched W tips were used. All the data were taken on the same Pd(1 1 0) single crystal at room temperature. It was prepared by repeated cycles of Ar^+ ion bombardment (750 eV), exposure to 10 L (1 Langmuir = 10^{-6} Torr × s) of O_2 while keeping it at 750 K, and subsequent annealing to 1000 K. The *h*-BN monolayers were obtained by exposing the clean and hot (1000 K) Pd(1 1 0) surface to a borazine $(HBNH)_3$ vapor with a pressure reading of 2.3×10^{-6} Torr for 40 s (90 L). The B and N coverages were quantified by means of STM and X-ray photoelectron spectroscopy (XPS), and the cleanliness of the sample was checked with XPS (less than 1% carbon contamination was found).

3. Results and discussion

The STM pictures of *h*-BN/Pd(1 1 0) (as e.g. those in Figs. 1a and 2a) show various Moiré patterns that arise from the incommensurate growth. The domains extend up to 100 nm regardless of the presence of steps (Fig. 1a). On the other end, two different domains (a "stripe-like" and "dot- like") can coexist on the same terrace (Fig. 1a). They are separated by a line of white features that are 0.13 ± 0.02 nm high, 1.7 ± 0.1 nm wide and with lengths between 2.0 nm and 3.8 nm. The nature of this domain boundary is unknown. In atomically resolved STM images within a single domain only one elemental species is imaged (as in the insert of Fig. 2).

It is possible to reproduce the Moiré contrast with a model in which the sublattice of one kind of atoms in the *h*-BN layer is considered. A similar observation was made for the Moiré patterns created by NaCl adsorbed on Cu(1 1 1) [11] and on Al(1 0 0) [12], where only the Cl^- ions were imaged appearing as protrusions. Theoretical calculations for *h*-BN/Ni(1 1 1) show that the local density of states (LDOS) of N atoms around the Fermi level