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h-BN/Ru(0001) nanomesh: A 14-on-13 superstructure with 3.5 nm periodicity

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ABSTRACT

The structure of epitaxially grown hexagonal boron nitride (h-BN) on the surface of a Ru(0001) single crystal was investigated using surface X-ray diffraction, which showed the system to form a commensurate 14-on-13 superstructure. This result disagrees with previous reports on superstructures of the same system and arguments based on simple thermal expansion coefficient calculations. We argue that the larger observed superstructure forms because of the strong bonding of h-BN to Ru. In comparison to h-BN/Rh(111) it can accommodate more induced lateral in-plane strain- or lock-in energy over larger regions (referred to as the holes) within the superstructure, which itself can consequently become larger.

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1. Introduction

The formation of large superstructures on the scale of a few nanometers, which act as nanotemplates [1] has great potential in future applications [2]. Ideally, such templates should remain stable and inert in air and up to high temperatures [3,4].

Borazine, (HBNH)$_3$, deposited on a transition metal surface at high temperatures decomposes and forms a single-layer h-BN [5]. Depending on the lattice mismatch to the transition metal substrate, the h-BN can be either flat, or form a corrugated nanomesh structure consisting of weaker bound regions, the wires, and stronger bound regions, the so-called holes. It has been shown that the formation of h-BN on 3d- and 5d- metals, like Ni(111) [6–9] and Pt(111) [10], leads to flat layers, which are weakly bound to the metal substrates. Also, on 4d-metals, the bond strength increases with the unoccupied states in the d-shell of the substrate [11,12]. Bonding is weaker for growth on Pd(111) [13], and stronger on Rh(111) [14] and Ru(0001) [15]. This, together with the lattice mismatch to Rh(111) and Ru(0001), results in the formation of a nanomesh, first observed by Corso et al. [14] on h-BN/Rh(111). The reported commensurate 13-on-12 structure was later confirmed by surface X-ray diffraction (SXRD) measurements [3,16]. In 2007, the formation of a nanomesh for h-BN on Ru(0001) was reported [15]. The periodicity of 13-on-12, as originally proposed by Paffett et al. [5], was considered to be the most likely.

In a recent study, h-BN was deposited on thin Rh(111)-films grown on yttrium stabilized zirconia on Si(111) [17]. A 14-on-13 structure was reported. It was argued that the slightly smaller lattice constant of the Rh-film compared to bulk Rh(111) and the slightly different thermal expansion coefficients are responsible for the formation of this larger superstructure. Extrapolating this line of argument to a Ru(0001) single crystal, it was predicted that either a 12-on-11 or a 13-on-12 nanomesh superstructure would be formed at the growth temperature of 900 K. Note that the difference in the linear dimensions of the hexagons of the h-BN between a 13-on-12 and a 12-on-11 structure is less than 2 pm, or 0.76 % of the unit cell size.

In order to resolve the question of the size of the h-BN/Ru(0001) superstructure we have performed high-resolution SXRD measurements. SXRD is uniquely capable of determining lattice constants of surface structures with picometer resolution [3,4,16,18].

2. Experimental

The Ru(0001) single crystal was prepared by several sputtering and annealing cycles. For the growth of the h-BN layer the crystal was heated to 1030 K in ultrahigh vacuum (UHV), and a single layer of h-BN was deposited by dosing borazine at a pressure of 6×10^{-7} mbar for 180 s. After the growth this temperature was held for another 60 s, after which, the crystal was cooled to room temperature over 10 min.

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The resulting structure was studied in situ by low-energy electron-diffraction (LEED) (Fig. 1). The LEED-image taken at an energy of 74.0 eV after the growth process shows clear satellite spots around the Ru Bragg-rod, demonstrating a well-ordered superstructure. The Ru Bragg-rod, labelled *Ru* in the figure, is henceforth referred to as the *Ru-peak*. The *h*-BN Bragg-rod, which we henceforth refer to as the *principal h-BN-peak*, is labelled *h-BN*, and at 74.0 eV it is the strongest LEED signal. In addition, several other signals in a hexagonal arrangement can be identified. We call these the *real reconstruction peaks* for reasons that will become evident below. An example of such a real reconstruction peak is labelled *rr* in Fig. 1.

Before we proceed, it is important to note that the weak elastic-scattering cross-section of X-ray photons with electrons means that SXRD very well satisfies the kinematical approximation of single scattering events. The low-energy electrons used in LEED, on the other hand, undergo multiple scattering and produce dynamical diffraction. One consequence of this is that while in SXRD real reconstruction peaks appear only for true commensurate superstructures, similar signals at the same positions can arise in LEED even for incommensurate overlayers. An example might be a flat structure with in-plane lattice constants marginally different from those of the substrate, which results in a flat moiré structure. Hence, from the LEED pattern of Fig. 1 alone, we are unable to state with confidence whether *h*-BN on Ru(0001) produces such a flat moiré structure or a true commensurate superstructure. SXRD can resolve this uncertainty.

The valence bands of *h*-BN/Ru(0001) recorded by ultraviolet photoelectron spectroscopy (Fig. 2) indicates splitting of the σ- and π-bands, both of which are due to a corrugation and consequent heterogeneous local environment (hole and wire regions) of the B and N atoms [15], the σ_α and π_α peaks refer to the more weakly bound wires of the corrugation, whereas the σ_β and π_β peaks are associated with the stronger bound holes.

The sample was prepared at the University of Zurich and was transferred inside a UHV-baby chamber (10^{-9} mbar) equipped with a hemispherical Be-dome. After the chamber was mounted on the surface diffractometer of the Materials Science beamline, Swiss Light Source, the nanomesh was investigated by SXRD using a beam energy of 12.398 keV (1.00 Å). The incident angle was 0.3°, close to the critical angle, thereby enhancing the surface sensitivity. The structure factors were recorded using the PILATUS 100 k pixel detector and the data were extracted and corrected using standard procedures, described elsewhere [19–21].
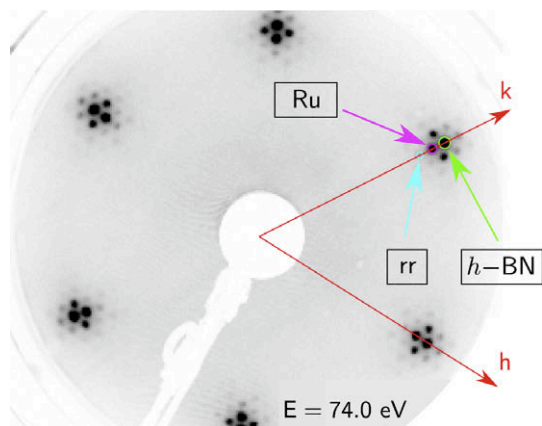
Fig. 2. He Iα ($h\nu$ = 21.2 eV) normal emission photoemission spectrum of *h*-BN/ Ru(0001). The σ- and π-band splitting of about 1 eV originate from a corrugated single-layer *h*-BN; σ_α and π_α refer to the wires, σ_β and π_β to the holes, which are more strongly bound.

A total of 18 scans were recorded, consisting of three peaks (one real reconstruction peak, the Ru-peak and the *h*-BN-peak) for each of the six high-symmetry directions, namely the $\{h, k\}$ = {1,0}. Each of the 18 high-resolution scans covered ±0.04 r.l.u. in the radial directions and were performed at an *l*-value of 0.4 r.l.u.

3. Results and discussion

Fig. 3 shows a *k*-scan over the (h, k) = (0, 1)-Ru-peak. Note that in addition to the Ru-peak, we observe the principal *h*-BN-peak and the real reconstruction peak. Representative scans are shown in Fig. 4. It can be seen that they lie at the positions (h, k) = (0, 14/13) and (h, k) = (0, 12/13), respectively. The width of both peaks of 6×10^{-3} r.l.u. is less than the separation between the superstructures under discussion (12-on-11, 13-on-12, and 14-on-13) and, from the Scherrer equation, the domain size is determined to be of the order of 45 nm or larger. The error associated with the peak positions was calculated from the standard deviation of the 12 peak positions and the error estimated from the pseudo-Voigt fit to the signal, and was found to be $\sigma = 1.4 \times 10^{-3}$ r.l.u. Eleven of the 12 peaks lie within ±σ of the nominal values. Therefore we can unambiguously state that *h*-BN on Ru(0001) grows as 14-on-13, with a superstructure size of 3.5 nm.

Fig. 1. LEED pattern of *h*-BN/Ru(0001) taken at an energy *E* = 74.0 eV. The reciprocal lattice vectors *h* and *k* are indicated in red. Hexagonally arranged satellite spots (one of which is labelled *rr*) can be seen around the Ru-peak, labelled *Ru*. The principal *h*-BN-peak is labelled *h-BN*. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
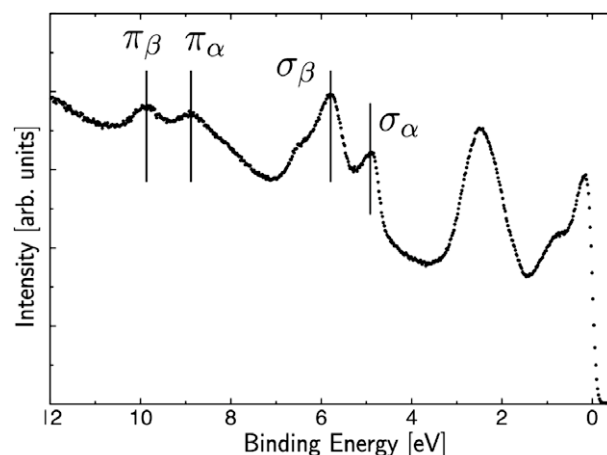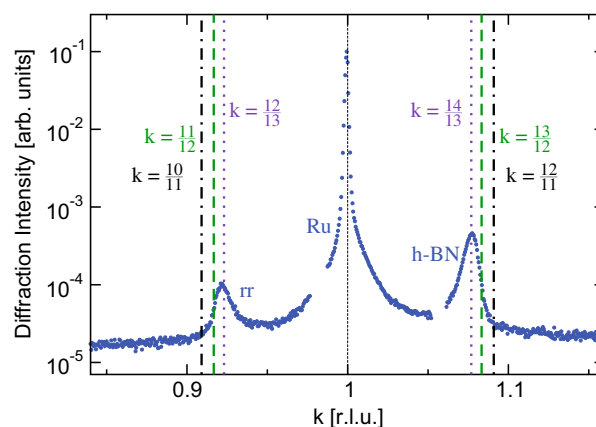
Fig. 3. Data of a *k*-scan around the (0 1)-peak at *l* = 0.4. The real reconstruction peak and the principal *h*-BN peak both unambiguously confirm a 14-on-13 superstructure. The appearance of a *k* = 12/13-peak shows that the unit cell of 13 Ru-atoms is well defined, most probably by a corrugation over this same period.

This result of a 14-on-13 superstructure is in disagreement with previous LEED studies on the same system [5,15,22] and also contradicts interpolation of data predicting a 13-on-12 or a 12-on-11 superstructure on this same system [17]. Using the thermal expansion coefficients for *h*-BN-bulk [23] and Ru-bulk [24] one would indeed expect the superstructure with the lowest in-plane strain at the growth temperature of 1030 K to be 13-on-12. On the other hand, at room temperature, one would expect the superstructure with the lowest in-plane strain to be 14-on-13. We have argued in another study [16] detailing temperature-dependent measurements on *h*-BN/Rh(111) that film and substrate lock in at the growth temperature and the strong bonding between film and substrate causes this superstructure to remain intact even after cooling to room-temperature. Interestingly, in the system presented here, where bonding between the *h*-BN and the Ru(0001) surface is thought to be even stronger than that between *h*-BN and Rh(111) [12], this argument fails – the observed 14-on-13 superstructure does not agree with that expected at the growth temperature. Even when we use the thermal expansion behaviour for Ru as given in [25], where an anisotropic thermal expansion of ruthenium is observed, the result remains the same.

The formation of the 14-on-13 structure may be related to the less perfect long range order of *h*-BN/Ru(0001) [15] compared to *h*-BN/Rh(111), though potential mechanisms for this remain obscure. Another more interesting possibility is that the formation of the 14-on-13 superstructure might be related to the theoretically predicted higher BN bond energy to Ru compared to that to Rh [12] and the consequently larger lock-in energy. The lock-in energy depends on the BN position with respect to the substrate atoms and is largest for N on top of a substrate atom. It is expected to be proportional to the bond energy to the substrate and is responsible for the formation of corrugated superstructures i.e., to the formation of a dislocation network with regions of tensile strained *h*-BN, in the holes, where BN is strongly bound to the substrate. This produces the opposite effect for the substrate atoms, which undergo lateral compressive strain in these strong bonding regions. The size of the holes depends on the lattice mismatch and the bonding strength [26]. As we propose here, it is the lock-in energy that allows a stronger bonding to the substrate, hence the formation of larger holes *and* a 16% larger superstructure. This offers an explanation for the formation of a larger unit cell in the case of *h*-BN/Ru(0001) compared to *h*-BN/Rh(111), whereby a larger BN lock-in energy is expected to induce the formation of a superstructure that is larger than that expected from the lattice

mismatch at the growth temperature. At the growth temperature, the ideal match of *h*-BN on the Ru surface would be a 12.7-on-11.7 structure. The strain energy associated with stretching from a 13-on-12 *h*-BN on Rh to a commensurate 1-on-1 structure has been calculated by Laskowski et al. [27] to be 0.5 eV per BN unit. Using the corresponding elastic constant, the energy needed for straining the *h*-BN lattice from an ideal match of 12.7 BN on 11.7 Ru cells to the observed 14-on-13 structure is calculated to be 4.3 meV per BN unit. The gain in lock-in energy for the whole superstructure cell must therefore be at least 0.8 eV, since this strain energy is a lower limit for the lock-in energy. Interestingly the calculated binding energy of *h*-BN to Ru, which was determined to be between 0.64 and 0.98 eV per BN unit [27] is of the order of the minimal BN strain energy needed for the 14-on-13 superstructure.

4. Summary and conclusions

In this report we have investigated the *h*-BN/Ru(0001) structure using surface X-ray diffraction. We have shown unambiguously that this is a 14-on-13 superstructure. The observed size of the superstructure contradicts previously reported studies [15,17,22] and cannot be simply explained by the formation of the superstructure at the growth temperature, as expected from the lattice mismatch of bulk materials. We argue that energy minimization from the stronger bonding of *h*-BN to the Ru in comparison to *h*-BN/Rh(111) overcomes the increased strain energy and leads to the formation of a larger superstructure, 14-on-13 rather than the smaller 13-on-12.

Acknowledgements

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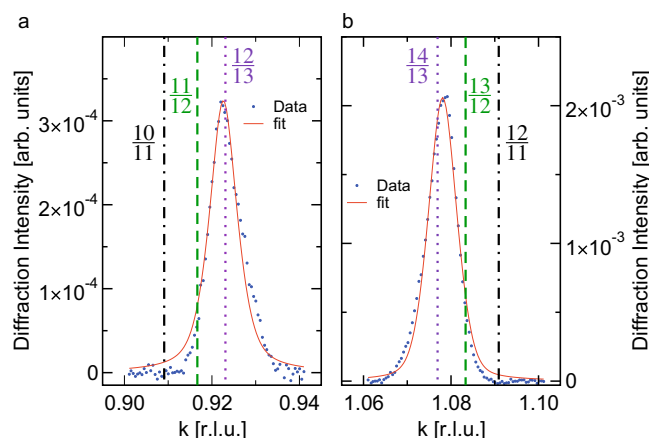
Fig. 4. The real reconstruction peak (a) and the principal *h*-BN-peak (b) in units of the experimentally determined Ru-reciprocal lattice unit. The signals were fit using a pseudo-Voigt-function.

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