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h-BN on Rh(1 1 1): Persistence of a commensurate 13-on-12 superstructure up to high temperatures

D. Martoccia [a], S.A. Pauli [a], T. Brugger [b], T. Greber [b], B.D. Patterson [a], P.R. Willmott [a,*]

[a] *Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland*
[b] *Institute of Physics, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland*

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ABSTRACT

We present a high-resolution surface X-ray diffraction study of hexagonal boron nitride (h-BN) on the surface of Rh(1 1 1). The previously observed commensurate 13-on-12 superstructure for this system is stable in the temperature range between room temperature and 830 °C. Surface X-ray diffraction measurements up to 830 °C on the superstructure show no sign of a shift towards a different superstructure, demonstrating the high thermal stability and strong bonding between film and substrate. At lower temperatures, an anomalous thermal expansion behaviour of the topmost surface region of rhodium is observed, where the rhodium in-plane lattice constant remains invariant. This can be explained by the (h-BN) single-layer being compressively strained, whereby the strong bonding to the substrate causes the latter to be tensile strained.

1. Introduction

The technological goal of engineering template structures on the scale of a few nanometers for the purpose of creating regular two-dimensional arrays of molecules has important potential applications, e.g., in molecular recognition [1]. This task can be addressed by the formation of superstructures, which can act as nanotemplates. The size and stability in different physical environments of the superstructure cell is of fundamental importance. In 2004, a highly regular mesh was found to form when a clean Rh(1 1 1) surface was exposed to borazine, $(HBNH)_3$, at high temperature [2]. This so-called hexagonal boron nitride (h-BN) nanomesh has been shown to act as an ideal template for assembling nanoparticles [3] or trapping single molecules [4,1,5].

From low-energy electron-diffraction (LEED) measurements [2] (which show a surface reconstruction), ultraviolet photoelectron spectroscopy (UPS) measurements (which reveal a σ-band splitting [2]); scanning tunneling microscopy (STM) [3,4,6], and subsequently from density functional theory calculations [7–9], the structural model of the nanomesh has been deduced to be a single corrugated BN layer consisting of hexagonally arranged “high” and “low” regions formed by differences in the chemical bonding strength of the B and N atoms to the Rh atoms underneath. Surface X-ray diffraction (SXRD) experiments confirmed a large unit cell for the (h-BN) layer, consisting of (13 × 13) N and (13 × 13) B atoms above a substrate-surface unit cell of (12 × 12) Rh atoms [10] (referred henceforth as 13-on-12). The periodicity of the superstructure is 3.22 nm. Recently it was reported in a LEED study that (h-BN) grown on Rh–YSZ–Si(1 1 1), a system better suited for technological applications, exhibits a (14 × 14) (h-BN) on (13 × 13) Rh(1 1 1) superstructure [11]. It was argued that the different thermal expansion behaviours of the multilayer substrates and the single crystal substrate is the reason for the formation of the different sized superstructures. Similar structures were also found for (h-BN)/Ru(0 0 0 1) [3,12,13] and for graphene/Ru(0 0 0 1) [14–17].

The (h-BN)/Rh structure results as a consequence of a balance between repulsive forces acting on N and attractive forces acting on the B atoms. The strength of these forces varies with the lateral BN position relative to the underlying Rh-substrate atoms – the (h-BN) monolayer therefore deforms (corrugates) vertically [7,8]. This theoretically predicted, highly corrugated monolayer structure was later confirmed experimentally by STM [4]. Although there are several reports on the growth of this system, the explanations why the reconstruction adopts a 13-on-12 signature are rare [11].

To precisely assess the effect of the commensurate fit of the (h-BN) with respect to the substrate we performed high-resolution surface X-ray diffraction (SXRD) measurements. We measured the

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* Corresponding author.
E-mail address: philip.willmott@psi.ch (P.R. Willmott).

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dependence of the superstructure lattice constant on the temperature and compared it to expectations from the known thermal expansion coefficients of bulk Rh and (*h*-BN).

2. Experimental

The single-crystal Rh(1 1 1) surface was prepared in an ultra-high vacuum (UHV) system equipped with LEED, STM and UPS by the standard preparation method [2,12]. The growth temperature was 750 °C. UPS and LEED measurements after preparation and directly before transfer under UHV to the Materials Science beamline, Swiss Light Source, Paul Scherrer Institut, confirmed the presence of the (*h*-BN) nanomesh.

The nanomesh was investigated by SXRD using a beam energy of 12.398 keV (1.00 Å) by recording six peaks [given in reciprocal lattice units (r.l.u.) of the rhodium bulk] per temperature value, at the $h = 11/12$, $h = 1$, $h = 13/12$ and $h = -11/12$, $h = -1$ and $h = -13/12$ positions, whereby $k = 0$ and $l = 1.2$ remained constant. The angle of the incoming X-rays was fixed to the critical angle, $\alpha_{crit} = 0.315^\circ$ for Rh at this X-ray energy, where the X-ray evanescent wave intensity is strongest, and only penetrates the surface to a depth of a few nanometers. At each peak position a high-resolution scan covering at least a range of ±0.04 r.l.u. was performed. The background was fit with a polynomial function and was subtracted from the measured data. The resulting signal itself was fit using a pseudo-Voigt function. At each new temperature, enough time was allowed to ensure thermal equilibration (which was especially important at lower temperatures) before the sample was carefully realigned and crystallographically oriented. The integer Bragg-rod positions of the Rh-substrate were used to determine the substrate lattice constant. Previous temperature calibrations of the substrate heater ensured the accuracy of the temperature to better than ±20 °C.

3. Results and discussion

First we confirmed the 13-on-12 reconstruction of the (*h*-BN)/Rh(1 1 1)-system at room temperature (see Fig. 1). Importantly, in addition to the (10)-Rh-peak and the 13/12 principal (*h*-BN)-peak, we observe the 11/12 peak. We call this the "real reconstruction" peak – since SXRD is not affected by multiple scattering (it satisfies to a high degree of accuracy the kinematical approximation), this peak can only arise if the system exhibits a true commensurate superstructure, which in this case is due to a corrugation over 12 × 12 Rh-atoms. Such a signal would not be observed in a simple Moiré structure resulting from the coincidental overlay of a flat (*h*-BN) monolayer on a flat Rh-substrate. This peak is still observed at 780 °C, a sign that even at these high temperatures, the commensurate superstructure remains well defined.

The temperature-dependent in-plane lattice constant of bulk rhodium, a_{Rh} [18], and bulk (*h*-BN) [19] given in Angstrom are:

$$a_{Rh} = 3.8026/\sqrt{2} + 29.27 \times 10^{-6} \cdot T + 10.49 \times 10^{-9} \cdot T^2 + 0.54 \times 10^{-12} \cdot T^3 \quad (1)$$

$$a_{h-BN} = 2.504 - 7.42 \times 10^{-6} \cdot (T - 25) + 4.79 \times 10^{-9}(T - 25), \quad (2)$$

with the temperature T given in °C. However, in this system comprising of only a single monolayer of (*h*-BN) it is possible that the in-plane lattice constant may deviates significantly in its temperature dependence from that of bulk (*h*-BN). There is no literature on the lattice constant of free-floating (*h*-BN) monolayers, so we assume here that it follows a similar temperature dependence to the bulk lattice constant.

The measured in-plane Rh-lattice constant at room temperature is 2.689 Å, in agreement with the literature [18]. However, we should view this value with some caution. The controlling diffractometer software (SPEC) fits the lattice parameters a, b, c, α, β, and γ. After careful analysis of these values as a function of temperature, we estimate that the systematic errors for the lattice constants are ±0.01 Å. The statistical errors are at least an order of magnitude smaller.

In Fig. 2a we compare the expected lattice expansion (blue solid line) [see Eq. (1)] for the bulk rhodium with the measured lattice expansion (blue line with circles) of the topmost Rh surface region between room temperature and 830 °C. As explained above, the absolute measured lattice constant of the rhodium at room temperature is associated with a systematic error of ±0.01 Å, however the shape of the curve is reliable. Hence the boundaries of possible vertical displacement of the measured lattice constant of rhodium are given by the grey band.

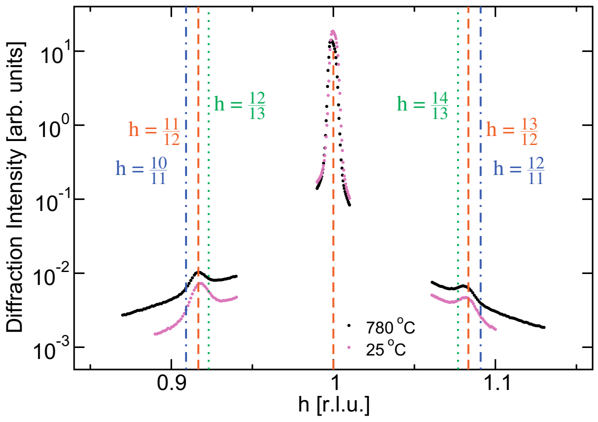

Fig. 1. Raw data for scans along h at $l = 1.2$, $k = 0$ r.l.u. measured at two different temperatures, 25 °C (black) and for 780 °C (magenta). The real reconstruction peak and the principal (*h*-BN) peak both unambiguously confirm a 13-on-12 commensurate superstructure (indicated by the red dashed line) at both temperatures. The 13-on-12 superstructure is unambiguous and well defined, as the peak-width is smaller than the separation between the $h = 13/12$ and the $h = 14/13$ positions (green dotted line) or between $h = 12/11$ (blue dash-dotted) and $h = 13/12$. Note that only the background increases with higher temperatures, the signals differ by less than 10% in peak height and integrated intensity.

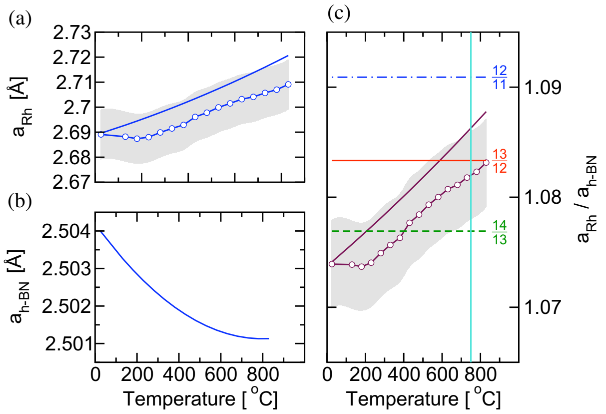

Fig. 2. (a) The temperature-dependent in-plane rhodium lattice constant, expected (solid blue line with grey error band) and measured (blue line with circles). (b) The expected (*h*-BN) lattice expansion as given in [19]. (c) The ratio of the plots given in Fig. 2a and b. At the growth temperature of 750 °C (vertical solid line) a 13-on-12 superstructure is expected, whereas at room temperature a 14-on-13 would seem more favourable. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

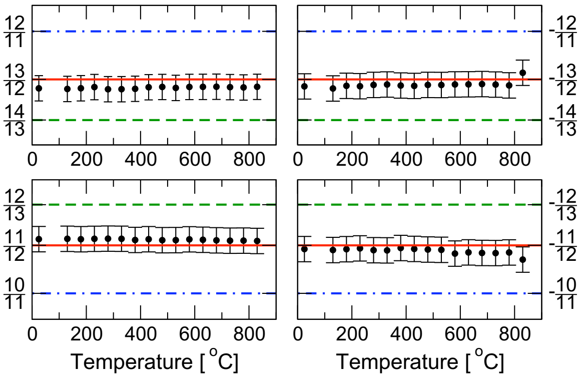

Fig. 3. Temperature dependence of the four superstructure peaks 13/12, −13/12, 11/12, and −11/12 r.l.u. The reconstruction remains stable even up to above 780 °C. This proves that the reconstruction is commensurate and that 13 × 13 BN in fact lock-in to 12 × 12 Rh-atoms. A 14-on-13 superstructure was never observed.

A plot of the temperature dependent lattice expansion of bulk (*h*-BN) given in Eq. (2) is shown in Fig. 2b. Note that the bulk rhodium lattice expands with temperature, whereas the (*h*-BN) exhibits a contraction up to 774 °C, and a dilation higher in temperature. In Fig. 2c we show the ratio of the plots shown in Fig. 2a and b. The ratio of the measured rhodium lattice expansion and the expected (*h*-BN) contraction between approximately 200 °C and the highest measured temperature of 830 °C has the same gradient as the predicted curve and therefore follows the expected behaviour given by Eqs. (1) and (2). Note, however, that between room temperature and 200 °C the experimental data disagrees with the predicted curve insofar that the in-plane rhodium lattice constant remains constant over this temperature range. From Fig. 2c, one can see that at the growth temperature of 750 °C the superstructure closest to both the predicted and experimentally determined lattice constant ratios is 13-on-12, whereas at room temperature a 14-on-13 would appear to be more likely.

The size of the measured superstructure as a function of the temperature is shown in Fig. 3. At all temperatures up to 780 °C the peaks were found to match a 13-on-12 superstructure within their experimental uncertainty. The errors associated with the peak positions were calculated from the standard deviation of the recorded positions and the error estimated from the pseudo-Voigt fit to the signal and found to be $\sigma = \pm 0.002$ r.l.u. No indication of a drift towards a 14-on-13 superstructure could be established, even at room temperature. This can be only explained by the fact that the (*h*-BN) layer is locked in with the rhodium atoms due to strong lock-in to the substrate, seen also by Preobrajenski et al. [20]. We know that the lock-in energy of the corrugated system is lower than the absorption energy [9], but larger than the strain energy. This latter is difficult to quantify for our corrugated system, but we can set a lower limit to this for a flat (*h*-BN) layer, which we have calculated to be 0.3 eV per superstructure cell. Corrugation will of course increase this value substantially.

As the temperature was raised from 780 °C to 830 °C, the (*h*-BN) superstructure and real reconstruction peaks started to irreversibly vanish, presumably due to thermal degradation. This caused the diffraction peak intensities of the last temperature measurement to be lower, although all the peaks still matched a 13-on-12 reconstruction. We propose that the anomalous lattice expansion behaviour of the rhodium seen in Fig. 2 up to 200 °C is explained as follows: when grown, the (*h*-BN) forms a commensurate superstructure, evident from the real reconstruction peak at 11/12 r.l.u. At this temperature, 750 °C, the lattice constants of rhodium and (*h*-BN) favour a 13-on-12 superstructure (see Fig. 2c). During subsequent cooling, the strong bonding of the (*h*-BN) to the Rh-substrate prohibits a change of the superstructure registry to 14-on-13, although this would be more relaxed for the (*h*-BN) as well as for the rhodium surface. The (*h*-BN) becomes more and more compressively strained, and at approximately 200 °C, this force is strong enough to hinder the upper region of the rhodium from further contraction, causing this latter to become tensile strained.

4. Summary and conclusions

In this report we have investigated the (*h*-BN)/Rh(1 1 1) structure as a function of temperature. The 13-on-12 superstructure is confirmed. The existence of a reconstruction peak at 11/12 r.l.u. proves that the system is a real commensurate superstructure caused by corrugation and not merely a flat Moiré pattern. The structure is remarkably thermally stable, with the 13-on-12 reconstruction peaks remaining clearly visible up to 830 °C.

Calculations based on the thermal expansion coefficients of (*h*-BN) and Rh lead to the conclusion that the superstructure is formed at the growth temperature. Moreover, it is proposed that the observation of a hindered thermal expansion of the topmost rhodium surface layers below 200 °C is caused by strain coupling from the increasingly compressively strained (*h*-BN) layer as the system is cooled to the upper region of the Rh-substrate, which in turn becomes tensile strained.

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