ELSEVIER

Surface Science Letters

Surface X-ray diffraction study of boron-nitride nanomesh in air

O. Bunk [a,*], M. Corso [b], D. Martoccia [a], R. Herger [a], P.R. Willmott [a], B.D. Patterson [a],
J. Osterwalder [b], J.F. van der Veen [a,c], T. Greber [b]

[a] *Research Department Synchrotron Radiation and Nanotechnology, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*
[b] *Physik-Institut, Universität Zürich, 8057 Zürich, Switzerland*
[c] *ETH Zurich, 8093 Zürich, Switzerland*

Abstract

The hexagonal boron-nitride 'nanomesh' surface reconstruction on Rh(111) [Corso et al., Science 303 (2004) 217–220] has been investigated using surface X-ray diffraction utilizing synchrotron radiation. This unique structure has been found to be stable under ambient atmosphere which provides an important basis for technological applications like templating and coating. The previously suggested (12×12) periodicity of this reconstruction has been unambiguously confirmed and structural features are discussed in the light of the X-ray diffraction results.
© 2006 Elsevier B.V. All rights reserved.

1. Introduction

At elevated temperatures borazine decomposes on Rh(111) to form a self assembled surface reconstruction of thermally very stable hexagonal boron-nitride (h-BN) [1]. The unit cell of this highly regular structure is, at 32 Å, huge by surface science standards. The detailed geometry of this 'nanomesh' is still under debate but major efforts are being taken to further investigate and utilize this unique system. This is attested, for example, by the formation of a specific targeted research project 'NanoMesh' supported within the sixth framework program (FP6) of the European Commission, a recent NanoMesh workshop, and the successful use of the nanomesh as template for the ordering of fullerenes [1].

Related but different structures of hexagonal boron-nitride have been reported for other surfaces like for example Ru(0001), Pt(111) [2,3], Cu(111), Ni(111) [4] and Pd(110) [5]. From a fundamental and an applied point of view is it important to disentangle the delicate balance in the surface free energy between h-BN and substrate contributions and the processes that lead to the formation of this fascinating structure and related structures on other substrates. For applications, it is mandatory to have detailed knowledge of the atomic and electronic structure of the surface for utilizing it as an oxygen- and carbon-free template, e.g., for the production of nanocatalysts and nanomagnets.

To solve the structure of a reconstruction involving several hundred atoms the best technique currently applicable is surface X-ray diffraction (SXRD) [6–8]. X-rays easily penetrate the surface and are therefore sensitive to the structure of an extended surface region rather than only the topmost layer. The data can be analyzed within the kinematical framework and this facilitates solving such large reconstructions. However, due to the low scattering cross-sections of boron and nitrogen, is it necessary to perform such an experiment at a 3rd-generation synchrotron source.

With applications like templating and ordering of liquids in mind, we studied the nanomesh structure on
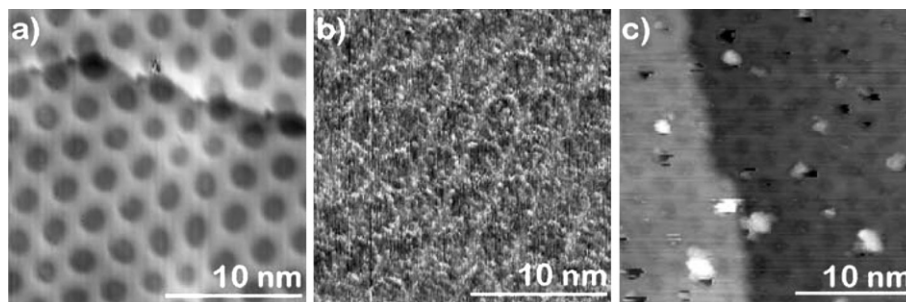
Fig. 1. Constant current STM images measured at $I_t = 1$ nA and $V_s = -1$ V. (a) STM image of the h-BN on Rh(111) nanomesh taken after preparation in UHV. The nanomesh survived 60 h air exposure as demonstrated by (b) STM and LEED images. (c) A short annealing up to 950 K is enough to remove a relevant part of the contaminants (as H_2O, O_2, CO_2, and CO) from the surface and bring the nanomesh back to its initial (pre-air exposure) configuration.

Rh(111) under ambient conditions. It turned out that the nanomesh is stable even under these extreme conditions, in contrast to typical surface reconstructions, which normally require ultra-high vacuum to be preserved.

2. Experimental

The samples were prepared in an ultra-high vacuum (UHV) system equipped with low energy electron diffraction and a scanning tunneling microscope (STM) [9]. The Rh(111) surface has been cleaned by repeated sputtering and annealing cycles. The surface was held at 1070 K and exposed to borazine at a pressure of 3×10^{-7} mbar, then subsequently cooled down to room temperature.

As a pre-study of the stability of the reconstruction STM investigations have been performed before and after a 60 h air exposure, see Fig. 1.

Freshly prepared samples for the X-ray experiments were transferred to the beamline and mounted under ambient conditions inside a chamber with Kapton windows. The chamber was flushed by a constant overpressure of helium to reduce the background scattering. The X-ray photon energy was set to 15.0 keV and the glancing angle of incidence to 0.20°. A dataset consisting of 816 fractional order and 17 integer order in-plane reflections was recorded. Details about the beamline, the surface diffractometer and the data acquisition using a novel 2D pixel detector can be found elsewhere [10,11].

The integrated intensity of the recorded reflections was determined and the standard geometrical correction factors applied [11]. Averaging reflections which are equivalent due to the p3m symmetry of the substrate yielded 402 fractional and nine integer order reflections. The systematic error determined in this standard averaging procedure [7] was as high as 74%, rendering a quantitative data analysis impossible. Among other things is the use of the stationary geometry without sample rocking scans [12] and scattering from the sample holder responsible for this. Nevertheless, valuable qualitative structural information can be obtained from the SXRD data.

In the following we use the conventional surface coordinate system with $\mathbf{a} = 1/2[10\bar{1}]_{cubic}$, $\mathbf{b} = 1/2[\bar{1}10]_{cubic}$, and

$\mathbf{c} = 1/3[111]_{cubic}$. The cubic coordinates are in units of the rhodium lattice constant, 3.80 Å at 300 K.

3. Results and discussion

One of the main results of our investigations is the stability of the nanomesh reconstruction under ambient atmosphere. As an example, the effect of a 60 h exposure to air is shown in Fig. 1. The basic structural elements can still be recognized after this prolonged exposure. After removing the adsorbates by a short annealing at 950 K, the original structure is restored. This means that this unique surface reconstruction is an ideal candidate for practical applications, such as its use as a template for the production of nanomaterials.

That the nanomesh structure is a commensurate reconstruction with a (12×12) unit cell has been confirmed by in-plane scans along directions of high symmetry. An example is shown in Fig. 2. The (13/12 0) peak of the reconstruction is of course weak but clearly observable and exactly at the expected position.
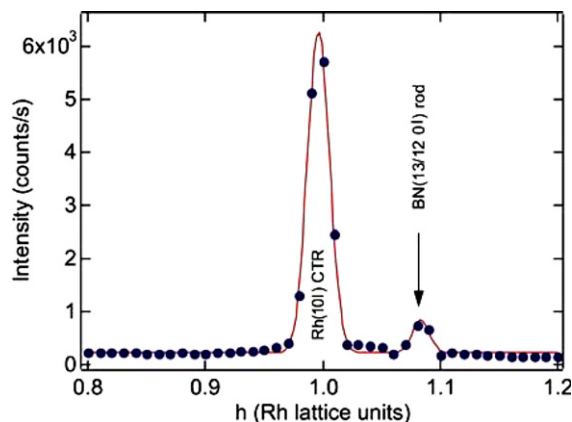

Fig. 2. SXRD intensity profile recorded in the plane of the surface ($l = 0.07$) at constant, $k = 0$. The (1 0 0.07) peak of the Rh(111) substrate and the (13/12 0 0.07) peak of the nanomesh reconstruction are observed, thereby confirming a commensurate superstructure with a (12×12) Rh(111) unit cell.
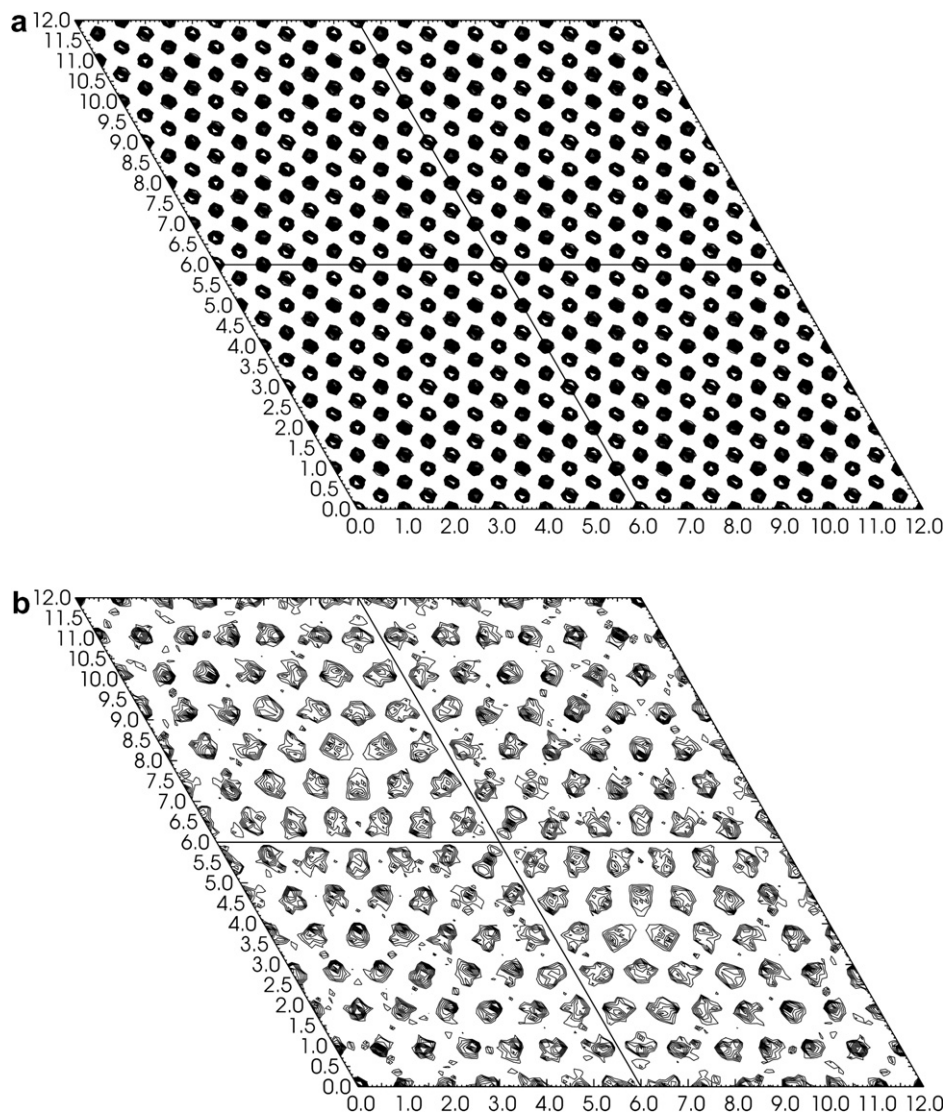
Fig. 3. Patterson functions of h-BN on Rh(111). Each peak of these contour plots of the Patterson function calculated from the in-plane reflections corresponds to an important interatomic distance projected in the surface plane. (a) The Patterson function calculated from all and (b) only from the fractional order reflections is shown. The observed distances show a clear fingerprint of a (13×13) coincidence lattice of h-BN on a (12×12) Rh(1 1 1) unit cell.

The Patterson function is the auto correlation function of the electron density. The peaks in the Patterson function correspond to interatomic distances. The projection of this function in the surface plane can be calculated from the near in-plane reflections which have a small momentum transfer perpendicular to the surface [6–8]. A contour plot of this projection is shown in Fig. 3. Taking both integer and fractional order reflections into account, the Patterson function is sensitive to both the bulk-like substrate and the reconstructed surface region. The resulting contour plot is shown in Fig. 3a. The plot is dominated by peaks originating from interatomic distances between bulk Rh atoms since these atoms scatter significantly more than h-BN.[1]

A regular mesh of 12×12 peaks over the (12×12) unit cell is observed.[2]

The Patterson function calculated from the fractional order reflections alone is only sensitive to the reconstructed surface region, i.e., to the h-BN nanomesh and any Rh atoms showing in-plane deviations from their bulk positions, see Fig. 3b. Again a hexagonal structure can be observed but this time with 13×13 peaks within the (12×12) unit cell. This is a clear fingerprint of the nanomesh, which has been interpreted as a coincidence structure of 13 h-BN per 12 Rh units [1]. The internal structure of the nanomesh cannot be deduced from the Patterson function. However, one more important point can be made: The Rh substrate

---

[1] Rh has $Z = 45$ electrons compared to $Z = 5$ for B and $Z = 7$ for N, i.e., Rh scatters about $45^2/5^2 = 81$ times stronger than B and ~ 41 times stronger than N.

[2] The shift vector from one to the following bulk Rh layer is $(1/3\,2/3\,-1)$ and the Patterson function is sensitive to the projection of all these layers in the surface plane.

does not exhibit significant relaxations since otherwise the Patterson function calculated from the fractional order reflections, Fig. 3b, would be dominated by the Rh signal in the vicinity of points corrsponding to bulk distances, i.e., peak positions in Fig. 3a. Therefore we can conclude that the adsorbate–substrate interaction is sufficiently strong to yield a commensurate and long-range well-ordered structure but does not induce strong relaxations of the Rh atoms from their bulk-like positions in the surface plane.

4. Summary and outlook

We have investigated the nanomesh structure of hexagonal boron-nitride on Rh(1 1 1). This unique surface reconstruction has been found to be stable under prolonged exposure to ambient atmosphere and X-ray radiation. The initially proposed (12×12) unit cell has been confirmed by the SXRD results. As a preliminary result indications have been presented that the nanomesh is a coincidence structure of 13 h-BN units per 12 Rh substrate units and that no major deviations from the in-plane bulk positions occur for the bulk Rh atoms.

A detailed three-dimensional structure determination of the nanomesh structure in UHV is planned to gain a detailed picture of the structure including all atomic positions.

Acknowledgements

References

[1] M. Corso, W. Auwärter, M. Muntwiler, A. Tamai, T. Greber, J. Osterwalder, Science 303 (2004) 217.
[2] M.T. Paffett, R.J. Simonson, P. Papin, R.T. Paine, Surf. Sci. 232 (1990) 286.
[3] F. Müller, K. Stöwe, H. Sachdev, Chem. Mater. 17 (2005) 3464.
[4] A.B. Preobrajenski, A.S. Vinogradov, N. Mårtensson, Surf. Sci. 582 (2005) 21.
[5] M. Corso, T. Greber, J. Osterwalder, Surf. Sci. 577 (2005) L78.
[6] R. Feidenhans'l, Surf. Sci. Rep. 10 (1989) 105.
[7] I.K. Robinson, Surface crystallography, in: G.S. Brown, D.E. Moncton (Eds.), Handbook on Synchrotron Radiation, vol. 3, North-Holland, Amsterdam, 1991, p. 221 (Chapter 7).
[8] H. Dosch, Critical Phenomena at Surfaces and Interfaces – Evanescent X-ray and Neutron Scattering, Springer, New York, 1992.
[9] W. Auwärter, T.J. Kreutz, T. Greber, J. Osterwalder, Surf. Sci. 429 (1999) 229.
[10] B.D. Patterson, R. Abela, H. Auderset, Q. Chen, F. Fauth, F. Gozzo, G. Ingold, H. Kühne, M. Lange, D. Maden, D. Meister, P. Pattison, T. Schmidt, B. Schmitt, C. Schulze-Briese, M. Shi, M. Stampanoni, P.R. Willmott, Nucl. Instr. Meth. Phys. Res. A 540 (2005) 42.
[11] C.M. Schlepütz, R. Herger, P.R. Willmott, B.D. Patterson, O. Bunk, C. Brönnimann, B. Henrich, G. Hülsen, E.F. Eikenberry, Acta Cryst. A 61 (2005) 418.
[12] E. Vlieg, J. Appl. Cryst. 30 (1997) 532.