Surface X-ray Diffraction Study of Boron-Nitride Nanomesh in Air

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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 diffrac-
tion utilizing synchrotron radiation. This unique structure has been found to be
stable under ambient atmosphere which provides an important basis for techno-
logical applications like templating and coating. The previously suggested (12x12)
periodicity of this reconstruction has been unambiguously confirmed and structural
features are discussed in the light of the x-ray diffraction results.

Key words: surface x-ray diffraction, boron nitride, rhodium, nanomesh

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19 **1 Introduction**

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

30 Related but different structures of hexagonal boron nitride have been reported
31 for other surfaces like for example Ru(001), Pt(111) [2,3], Cu(111), Ni(111)
32 [4] and Pd(110) [5]. From a fundamental and an applied point of view is it im-
33 portant to disentangle the delicate balance in the surface free energy between
34 h-BN and substrate contributions and the processes that lead to the forma-
35 tion of this fascinating structure and related structures on other substrates.
36 For applications, it is mandatory to have detailed knowledge of the atomic and
37 electronic structure of the surface for utilizing it as an oxygen- and carbon-free
38 template, e.g., for the production of nanocatalysts and nanomagnets.

39 To solve the structure of a reconstruction involving several hundred atoms the
40 best technique currently applicable is surface x-ray diffraction (SXRD) [6–8].
41 X-rays easily penetrate the surface and are therefore sensitive to the structure
42 of an extended surface region rather than only the topmost layer. The data

43 can be analyzed within the kinematical framework and this facilitates solving
44 such large reconstructions. However, due to the low scattering cross-sections
45 of boron and nitrogen, is it necessary to perform such an experiment at a
46 3rd-generation synchrotron source.

47 With applications like templating and ordering of liquids in mind, we studied
48 the nanomesh structure on Rh(111) under ambient conditions. It turned out
49 that the nanomesh is stable even under these extreme conditions, in contrast
50 to typical surface reconstructions, which normally require ultra-high vacuum
51 to be preserved.

52 **2 Experimental**

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

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

60 Freshly prepared samples for the x-ray experiments were transferred to the
61 beamline and mounted under ambient conditions inside a chamber with Kap-
62 ton windows. The chamber was flushed by a constant overpressure of helium
63 to reduce the background scattering. The x-ray photon energy was set to
64 15.0 keV and the glancing angle of incidence to 0.20° . A dataset consisting of
65 816 fractional order and 17 integer order in-plane reflections was recorded. De-

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 hours 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.

66 tails about the beamline, the surface diffractometer and the data acquisition
 67 using a novel 2D pixel detector can be found elsewhere [10,11].

68 The integrated intensity of the recorded reflections was determined and the
 69 standard geometrical correction factors applied [11]. Averaging reflections
 70 which are equivalent due to the p3m symmetry of the substrate yielded 402
 71 fractional and 9 integer order reflections. The systematic error determined in
 72 this standard averaging procedure [7] was as high as 74 %, rendering a quanti-
 73 tative data analysis impossible. Among other things is the use of the stationary
 74 geometry without sample rocking scans [12] and scattering from the sample
 75 holder responsible for this. Nevertheless, valuable qualitative structural infor-
 76 mation can be obtained from the SXRD data.

77 In the following we use the conventional surface coordinate system with $\mathbf{a} =$
 78 $1/2[10\bar{1}]_{\text{cubic}}$, $\mathbf{b} = 1/2[\bar{1}10]_{\text{cubic}}$ and $\mathbf{c} = 1/3[111]_{\text{cubic}}$. The cubic coordi-
 79 nates are in units of the rhodium lattice constant, 3.80 Å at 300 K.

Fig. 2. SXR D 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.

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 hour 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.

The Patterson function is the auto correlation function of the electron density.

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(111) unit cell.

93 The peaks in the Patterson function correspond to interatomic distances. The
 94 projection of this function in the surface plane can be calculated from the
 95 near in-plane reflections which have a small momentum transfer perpendicular
 96 to the surface [6–8]. A contour plot of this projection is shown in Fig. 3.
 97 Taking both integer and fractional order reflections into account, the Patterson
 98 function is sensitive to both the bulk-like substrate and the reconstructed
 99 surface region. The resulting contour plot is shown in Fig. 3(a). The plot is
 100 dominated by peaks originating from interatomic distances between bulk Rh
 101 atoms since these atoms scatter significantly more than h-BN.¹ A regular
 102 mesh of 12×12 peaks over the (12×12) unit cell is observed.²

103 The Patterson function calculated from the fractional order reflections alone is
 104 only sensitive to the reconstructed surface region, i.e., to the h-BN nanomesh
 105 and any Rh atoms showing in-plane deviations from their bulk positions, see
 106 Fig. 3(b). Again a hexagonal structure can be observed but this time with
 107 13×13 peaks within the (12×12) unit cell. This is a clear fingerprint of the
 108 nanomesh, which has been interpreted as a coincidence structure of 13 h-BN
 109 per 12 Rh units [1]. The internal structure of the nanomesh cannot be deduced
 110 from the Patterson function. However, one more important point can be made:
 111 The Rh substrate does not exhibit significant relaxations since otherwise the
 112 Patterson function calculated from the fractional order reflections, Fig. 3(b),
 113 would be dominated by the Rh signal in the vicinity of points corresponding

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.

114 to bulk distances, i.e., peak positions in Fig. 3(a). Therefore we can conclude
115 that the adsorbate-substrate interaction is sufficiently strong to yield a com-
116 mensurate and long-range well-ordered structure but does not induce strong
117 relaxations of the Rh atoms from their bulk-like positions in the surface plane.

118 4 Summary and outlook

119 We have investigated the nanomesh structure of hexagonal boron nitride on
120 Rh(111). This unique surface reconstruction has been found to be stable under
121 prolonged exposure to ambient atmosphere and x-ray radiation. The initially
122 proposed (12×12) unit cell has been confirmed by the SXRD results. As a
123 preliminary result indications have been presented that the nanomesh is a
124 coincidence structure of 13 h-BN units per 12 Rh substrate units and that
125 no major deviations from the in-plane bulk positions occur for the bulk Rh
126 atoms.

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

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