

Electrolytic in situ STM investigation of h-BN-Nanomesh

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Abstract

Single sheet boron nitride layers on thin rhodium (111) films were formed upon thermal decomposition of borazine under ultra-high vacuum (UHV) conditions. They were transferred and investigated in an electrolytic environment. In 0.1 M HClO₄, the presence and stability of the so-called nanomesh super structure with a lattice constant of 3.2 nm is established with electrochemical impedance spectroscopy, cyclic voltammetry and subsequent imaging with in situ scanning tunneling microscopy (STM) under potential control. In the electrolyte, the BN nanomesh acts as a dielectric layer with an unusual behaviour of the impedance, where the capacitive component is larger than on a Rh(111) reference sample. It exhibits reversible hydrogen adsorption and desorption at a potential of –600 mV vs. a saturated mercury sulphate reference electrode (MSE). The unit cell of the nanomesh is imaged by STM and shows hexagonally arranged two-dimensional pores with a diameter of 2 nm. At a fixed potential, the nanomesh was stable for long time, but after repeated potential sweeps between +260 and –540 mV vs. MSE, STM indicates roughening, though a 12 × 12 superstructure was recovered after annealing in UHV.

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1. Introduction

Nanostructured surfaces play a key role when it comes to the tailoring of nanometer-sized particles. The dimensions of interest here are far below 100 nm where lithographic methods are no longer applicable. Therefore, research focuses on regular self-assembled nano-templates that can trap molecules or lead to the nucleation of ultra-small metallic clusters [1]. An intriguing nanostructure has been reported recently for films of hexagonal boron nitride (h-BN) on Rh(111) [2] and Ru(0001) [3] prepared in ultra-high vacuum (UHV). The so-called boron nitride nanomesh is a two dimensional superstructure with a periodicity of 3.2 nm, which forms at 1050 K by thermal decomposition of borazine (HBNH)₃ [2]. It is now estab-

lished that it consists of a single sheet, i.e. a monolayer of hexagonal boron nitride which forms a 13 × 13 h-BN on 12 × 12 Rh coincidence lattice. The misfit and the site dependent lock in energy between the substrate and the overlayer cause a static transversal distortion wave in the boron nitride sheet, with a 0.05 nm corrugation [3–5]. The appearance and functionality of the distinct regions within the nanomesh were termed ‘holes’ or ‘pores’ for the locations with close contact to the substrate and ‘wires’ for the h-BN in the misfit dislocations. The pores with a diameter of 2 nm are surprisingly strong binding sites for single molecules, as it was e.g. demonstrated with the observation that in UHV at room temperature naphthalocyanine molecules selectively bind into the pores and thus form a two dimensional array of isolated molecules [5]. Together with the dielectric properties of boron nitride, which allow e.g. to decouple molecules from the metal support, h-BN/Rh(111), and h-BN/Ru(0001) [3] represent attractive templates for nanotechnology. These promises

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were further fuelled by the observation that nanomesh is stable in air [6] and that it survives immersion into water [5]. The solid–liquid interface is of special interest as electrochemical processes are increasingly applied for nano-structure fabrication as a relatively inexpensive, easy-to-handle and reliable method [7].

In this paper we demonstrate that h-BN/Rh(111) may also be immersed into an electrolyte and that it preserves its peculiar/unique structure within a relatively extended potential range. Electrolytic in situ scanning tunneling microscopy (STM) allows to visualize the nanomesh under potential control to explore its capabilities as a template for building two-dimensional arrays and as a model system to investigate fundamental electrochemical processes on nano-patterned surfaces. This paves the way for applications of boron nitride nanomesh as a lot for the construction of so far unknown supramolecular structures by means of electrochemical deposition.

2. Experimental

The h-BN nanomesh films were prepared in UHV with the recipe presented in detail elsewhere [2,5,8] on single-crystalline Rh(111) films of typically 80–150 nm thickness grown on $\text{Al}_2\text{O}_3(0001)$ [9]. Exposure of the hot sample surface, kept at a temperature of 1050 K, to 40 L (1 Langmuir = 10^{-6} torrs) of borazine leads to the self-saturating formation of a well-ordered, single h-BN layer covering the entire surface. The films were then transferred through air into the electrochemical setup. All experiments were performed in degassed (N_2) solutions of reagent grade chemicals in ultra pure water (18.2 M Ω , ELGA). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out using an Autolab PGSTAT30 in a conventional three-electrode cell with a saturated mercury sulphate reference electrode (MSE) and a Pt counter electrode. The exposed area of the substrates to the electrolyte is 0.283 cm². To investigate the clean Rh(111) surface, the nanomesh was removed by NH_3 -solution and thoroughly rinsed with ultra pure water. The electrolytic STM measurements were performed on a commercial scanning probe instrument (Nanoscope III Multimode from Veeco) enabling STM imaging with independent potential control of tunneling tip and electrode substrate in a homebuilt electrolytic STM cell. The STM scanner is calibrated with atomically resolved images of highly oriented pyrolytic graphite (HOPG) ZYB from Advanced Ceramics. Tunneling tips were prepared from Pt/Ir wire (90%Pt/10%Ir) by electrochemical etching in a salt melt [10] and subsequent insulation of most of the tip surface (except for the foremost part) with Apiezon wax.

3. Results and discussion

The cyclic voltammogram (CV) of the h-BN nanomesh on Rh(111) in 0.1 M HClO_4 , which is a non-specifically adsorbing electrolyte, is displayed in Fig. 1a. It shows an

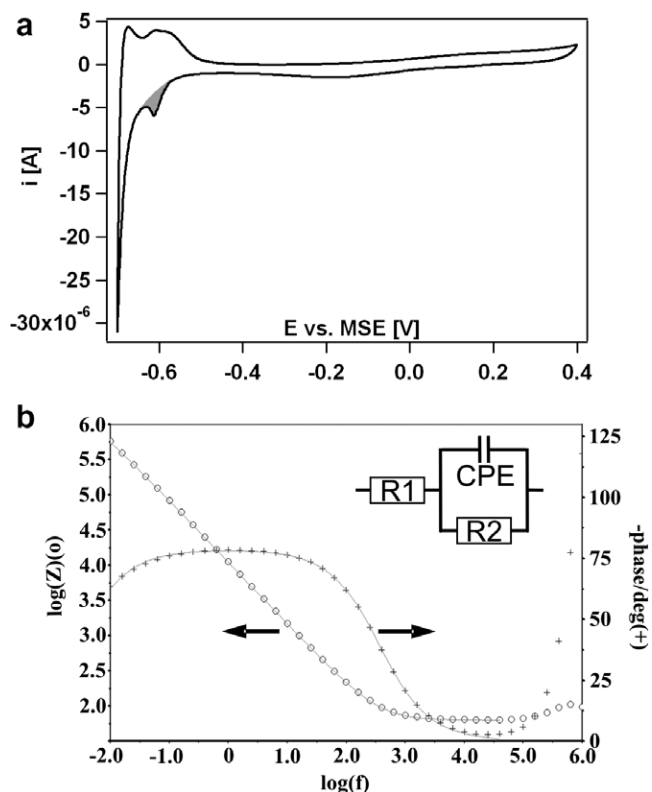


Fig. 1. h-BN nanomesh on Rh(111) in 0.1 M HClO_4 . (a) Cyclic voltammogram at 10 mV/s between -700 and $+400$ mV vs. a mercury sulphate electrode (MSE), with shaded region of hydrogen adsorption. (b) Impedance spectra at open circuit potential (OCP) of $+89$ mV vs. MSE, impedance Z (circles) and phase shift (crosses) are fitted (lines) using the equivalent circuit $R_1(R_2CPE)$ at upper right.

extended potential region, where no electrochemical reaction occurs, before hydrogen and oxygen evolves in the cathodic and anodic region, respectively. At -610 mV vs. MSE a small cathodic current peak is visible, while the equivalent anodic peak is located at -600 mV vs. MSE. These peaks are likely to be associated hydrogen adsorption/desorption according to the clean Rh(111) surface [11]. The charge density of ca. $80 \mu\text{C}/\text{cm}^2$ below the peak (shaded region in Fig. 1a) corresponds to the exchange of ca. 40 hydrogen ions on a 13×13 h-BN nanomesh unit cell ($3.2 \times 3.2 \text{ nm}^2$). This corresponds to about 1/4 of a monolayer hydrogen adsorbed on the surface where a full coverage (1 H per B, N) results in $310 \mu\text{C}/\text{cm}^2$. The CV in Fig. 1a also shows that the capacitive component of the electrical double layer regime is quite large (see below), which is not expected in the presence of an insulating layer [12]. The presence of the BN nanomesh is further evidenced by electrochemical impedance spectroscopy (EIS) data represented in Fig. 1b as a Bode plot. The spectra were recorded at open circuit potential (OCP) of $+89$ mV vs. MSE. The data can be fitted with a Randles equivalent circuit shown on the upper right of Fig. 1b. The fit was carried out with the frequency response analyser software by Eco Chemie, while frequencies above 60 kHz were rejected for analysis. The values for resistances R_1 , R_2 and CPE

(constant phase element) for the nanomesh on Rh(111) in comparison with the same Rh(111) film where the nanomesh was removed are summarized in Table 1. The two resistances R1 (electrolyte resistance) and R2 (charge transfer resistance) have the same order of magnitude. This is consistent with no significant change in the experimental geometry in going from the h-BN/Rh(111) to the clean Rh(111). The homogeneity described with the empirical exponent n in the CPE is also comparable for both systems. Essentially the imaginary part of the impedance is fitted with $1/(\omega C)^n$. As $n = 1$ represents an ideal capacitor, the homogeneity and the quality of the substrates are rather good. But there is a significant and counterintuitive difference in the magnitude of the CPE: The sample with the nanomesh is almost one order of magnitude larger than that for the Rh(111) reference sample. Even if one argues that the capacitive component of the in NH_3 -solution cleaned Rh(111) reference is smaller than published values for Rh polycrystals [13], the absolute value of the nanomesh CPE is fairly large. This is surprising for a dielectric overlayer, since the capacitance of the Helmholtz double layer at the electrode/electrolyte interface is expected to decrease with any dielectric ($\epsilon > 0$) which coats the electrode [12]. The observation of an increase in the double layer capacitance is compatible with a decrease of the effective Helmholtz double layer thickness. Such a decrease results e.g. from a stronger alignment of the dipoles in the electrolyte. In the present case, the extra alignment might be caused by the ionicity of the h-BN layer, where electron charge is transferred from the boron to the more electronegative nitrogen atoms [14,15].

The fact that the h-BN layer survives the transfer into an electrochemical environment and its stability over an extended potential range, encouraged us to investigate the h-BN nanomesh on Rh(111) by electrolytic in situ scanning tunneling microscopy (STM) and investigating the stability of the superstructure. Fig. 2 shows a large scale STM image at +120 mV vs. MSE with large monoatomic terraces and some screw dislocations. The profile in Fig. 2b along the line drawn in Fig. 2a clearly shows the step heights with multiples of 0.22 nm, which is the monoatomic step height on Rh(111). This overview image already indicates that no large scale surface roughening occurs under the electrochemical conditions stated above.

Table 1

Summary of the calculated values for the electrolyte resistance R1, the charge transfer resistance R2 and the constant phase element CPE (see inset Fig. 1b) of the electrochemical impedance spectroscopy (EIS)

Element	Nanomesh	Clean Rh(111)
R1	$62.8 \pm 0.25 \Omega$	$54.8 \pm 0.81 \Omega$
R2	$1.97 \pm 0.06 \text{ M}\Omega$	$1.85 \pm 0.11 \text{ M}\Omega$
CPE	$14.39 \pm 0.14 \mu\text{F cm}^{-2}$	$2.37 \pm 0.07 \mu\text{F cm}^{-2}$
n	0.875	0.819

The fit parameter n describes the homogeneity of the system.

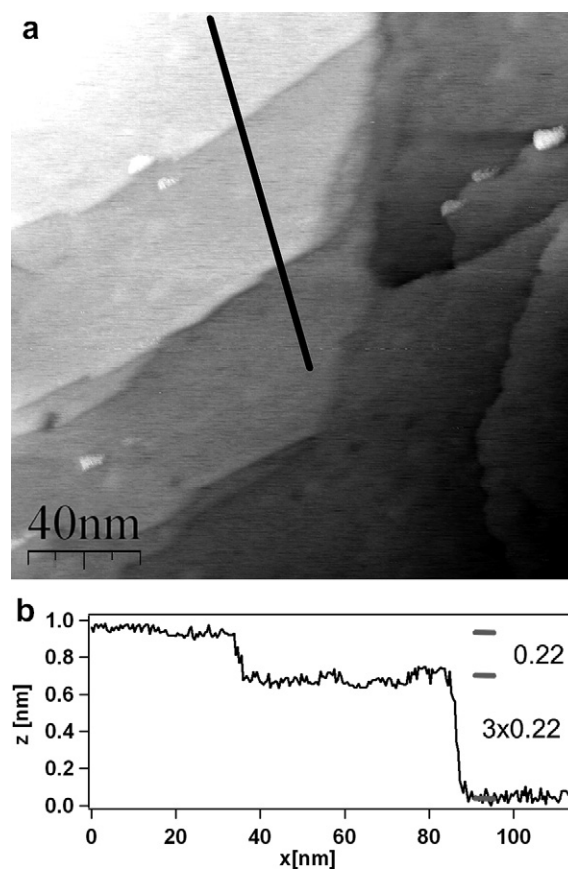


Fig. 2. (a) Overview STM image of h-BN nanomesh on Rh(111) in 0.1 M HClO_4 at +120 mV vs. MSE, $U_T = -50$ mV, $I_T = 150$ pA, $\Delta z = 3.5$ nm. (b) Profile along black line drawn in (a).

In Fig. 3a zoom-in into one of the large terraces of Fig. 2a identifies the h-BN nanomesh with its regular hexagonal pattern showing a periodicity of about 3 nm. Clearly, pores (dark) and wires (bright) are visible. Besides a slight thermal drift the STM image appears quite noisy, which is due to the very low tunneling current of 100 pA applied to image the nanomesh. The profile in Fig. 3b reveals a periodicity of the nanomesh of 3.2 nm and a depth of the pores of about 0.1 nm consistent with UHV-STM investigations [2,3,5]. The corresponding fast Fourier transform (FFT) of the STM image from Fig. 3a shows a hexagonal pattern and allows a quantification of the periodicity to 3.16 ± 0.15 nm. At the applied potential of +120 mV vs. MSE the nanomesh remains stable on the surface and no alteration in the STM appearance is observed for at least 2 h.

Upon successive sweeping the potential between +260 and -540 mV vs. MSE (within the region without substantial reduction or oxidation) a considerable roughening of the substrate is observed as displayed in Fig. 4a. This STM image is again recorded at +120 mV vs. MSE but the nanomesh is no longer discernible. Globular features appear with about the same size as the nanomesh pores displaying a much higher surface corrugation with $\Delta z = 2.15$ nm compared to $\Delta z = 0.15$ nm for the pure

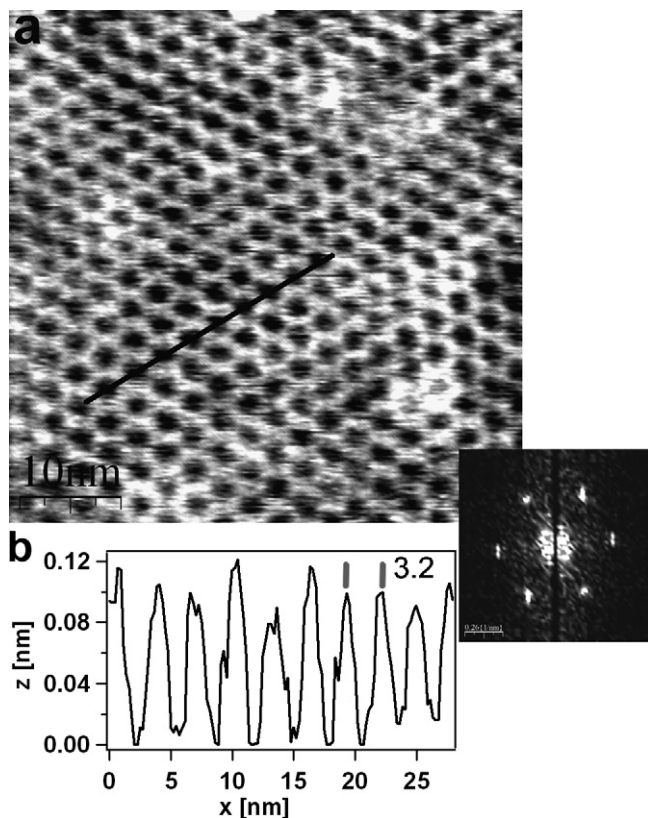


Fig. 3. (a) STM image of h-BN nanomesh on Rh(111) in 0.1 M HClO₄ at +120 mV vs. MSE, $U_T = -50$ mV, $I_T = 100$ pA, $\Delta z = 0.15$ nm, RMS = 0.03 nm. Pores map dark and mesh wires bright. (b) Profile line along black line drawn in (a). FFT of STM image from (a) at right panel.

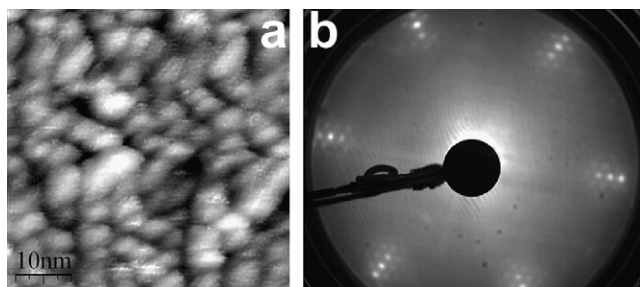


Fig. 4. (a) STM image (same scale as in Fig. 3) of h-BN nanomesh on Rh(111) after successive sweeping of the potential between +260 and -540 mV vs. MSE in 0.1 M HClO₄ at +120 mV vs. MSE, $U_T = -50$ mV, $I_T = 125$ pA, $\Delta z = 2.15$ nm, RMS = 0.28 nm. (b) LEED pattern at 92 eV of a 12×12 coincidence lattice which is recovered after UHV annealing of the roughened sample shown in Fig. 4a.

nanomesh. The roughness of the surface is also increased by almost a factor 10, from a RMS = 0.03 nm for the stable nanomesh to a RMS = 0.28 nm for the roughened sample. For pure metal surfaces, such a roughening is known to occur after several redox cycles [16]. A possible explanation in the case of the nanomesh could be an additional “intercalation effect” of ions in-between the Rh(111) surface and the h-BN layer at the slightly more reactive step edges as known from HOPG investigations [17]. The sam-

ple of Fig. 4 was then brought back into UHV, cleaned by annealing it to 1050 K for 30 min and analyzed by LEED. The LEED investigation evidences the presence of the nanomesh as the characteristic 12×12 coincidence lattice shown in Fig. 4b for the nanomesh superstructure is still present.

4. Summary and conclusions

The h-BN nanomesh on Rh(111) produced in UHV represents a nanopatterned sample of an insulating monolayer on a metal surface. The investigations presented in this paper disclose the possibility to transfer the nanomesh from UHV into an electrolytic environment and back to UHV. The applied electrochemical investigation techniques demonstrate the stability and the behaviour of the nanomesh under potential control and it was visualized by electrolytic STM. This paves the way for further experiments in different media. The unusual increase of the capacitive components of the system in presence of the nanomesh could be attributed to the ionicity of the h-BN monolayer. From ultra-violet photoelectron and scanning tunneling spectroscopy results in UHV it is known that the wires and pores reveal different electronic properties [5]. These differences should enable the nanomesh to serve as a template for the deposition of electrochemically active molecules and metal clusters to form large self-assembled arrays. Furthermore, the nanomesh is a very interesting model system for fundamental electrochemical investigations on a nanopatterned surface.

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