Diamond & Related Materials 19 (2010) 1027–1033

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

BN analogues of graphene: On the formation mechanism of boronitrene layers — solids with extreme structural anisotropy

Hermann Sachdev [a],*, Frank Müller [a,b], Stefan Hüfner [b]

[a] Allgemeine und Anorganische Chemie FR 8.1, Universität des Saarlandes, Postfach 151150, D-66041 Saarbrücken, Germany
[b] Experimentalphysik, Naturwissenschaftlich-Technische Fakultät II - Physik und Mechatronik, Universität des Saarlandes, D-66041 Saarbrücken, Germany

ARTICLE INFO

Available online 8 April 2010

Keywords:
Boron nitride
Formation mechanism
Monolayers
Growth of graphene-like BN monolayers
Low energy electron diffraction (LEED)
X-ray photoelectron spectroscopy (XPS)
Nucleation
CVD

ABSTRACT

Boron nitride is an extremely useful material for applications in material sciences and appears in a manifold of crystalline modifications, with hexagonal and cubic boron nitride as most prominent substances. In hexagonal boron nitride, threefold coordinated boron and nitrogen atoms form two-dimensional layers, which resemble the boron nitride analogue of graphene layers, and we refer to this two-dimensional network as boronitrene layers. So far, there is little knowledge about the elementary growth reactions of these boronitrene layers.

Here we show that it is possible to regenerate a previously prepared 14×14 BN/13×13 Rh(111) superstructure [obtained by CVD of borazine ($B_3N_3H_6$)] after an oxidation step from an unordered monolayer of a boron–oxygen compound by chemical reactions induced by ammonia as nitrification agent on the surface. The individual steps of the experiment were controlled by a LEED- and XPS- analysis and indicate that the original BN superstructure can be recovered without traceable amounts of oxygen in the film. The presented results indicate that highly mobile species from the B–N–O–H system can be considered as surfactants in the elementary formation and degradation reactions of highly ordered boronitrene layers. An understanding of these reactions is a fundamental issue in tuning the crystal growth and quality of the BN phases.

1. Introduction

Phenomena based on self-organization have continuously been gaining interest in material research since domain structures of the size of nanometres can be obtained by substrate–film interactions. A recent example represents the formation of a superstructured monolayer of boron nitride on a transition metal substrate. The formation of a highly regular self-assembled BN nanostructure with a periodicity of 3.22 nm on Rh (111) by CVD of borazine ("NanoMesh") was first obtained by Corso et al. [1] and the BN monolayer structure was modelled by Laskowski et al. [2]. Such BN layers represent a two-dimensional quantum barrier with a polar surface [3]. Subsequently, the ability of this periodic nanostructure to act as a template was demonstrated [4]. The variation of the lattice mismatch between the BN lattice and the lattice of the substrate crystal offers the possibility to tune the size of nanostructures for applications in technology, e.g. in nano-electronic devices [5]. In the current literature there are several reports regarding the syntheses of BN monolayers on transition metal substrates based on borazine [6–11], but there is little information regarding the stability and chemical reactivity of such BN monolayers [4,12]. Nucleation and growth reactions of hexagonal boron nitride (*h*-BN) on transition metal surfaces from borazine as a molecular precursor are of general interest to understand the *h*-BN crystal growth as a solid with high structural anisotropy (cf. *h*-BN structure in Fig. 1). These aspects are also important regarding the syntheses of boron nitride modifications by various means of deposition techniques based on CVD- and PVD-methods [13–17], high-pressure-high-temperature synthesis [18–21], or synthesis at ambient pressure [22], and there is a continuous interest in these materials due to their electronic properties [23–25]. For applications, it is of general interest to achieve sp^2-type coordinated boron nitride monolayers in high quality and even with an undulated superstructure ("NanoMesh") which can act as a template with lateral confinement for trapping molecules [3,4]. In recent years there have been numerous reports regarding some concepts of CVD, where volatile molecular precursors contain structural motifs also present in the solid material to be built up. According to these concepts, such a provision of structural subunits of the finally desired crystal lattice by a volatile molecular precursor shall enable a more facile formation of the desired solid material due to a pre-existing connectivity of atoms which is deemed not to be restructured again during the growth of the solid. For this reasons borazine, $B_3N_3H_6$, was generally considered as a suitable candidate for CVD of sp^2-type BN phases (cf. refs. [1,6–11]). The mechanistic details

---

* Corresponding author.
E-mail address: h.sachdev@mx.uni-saarland.de (H. Sachdev).

0925-9635/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2010.03.021

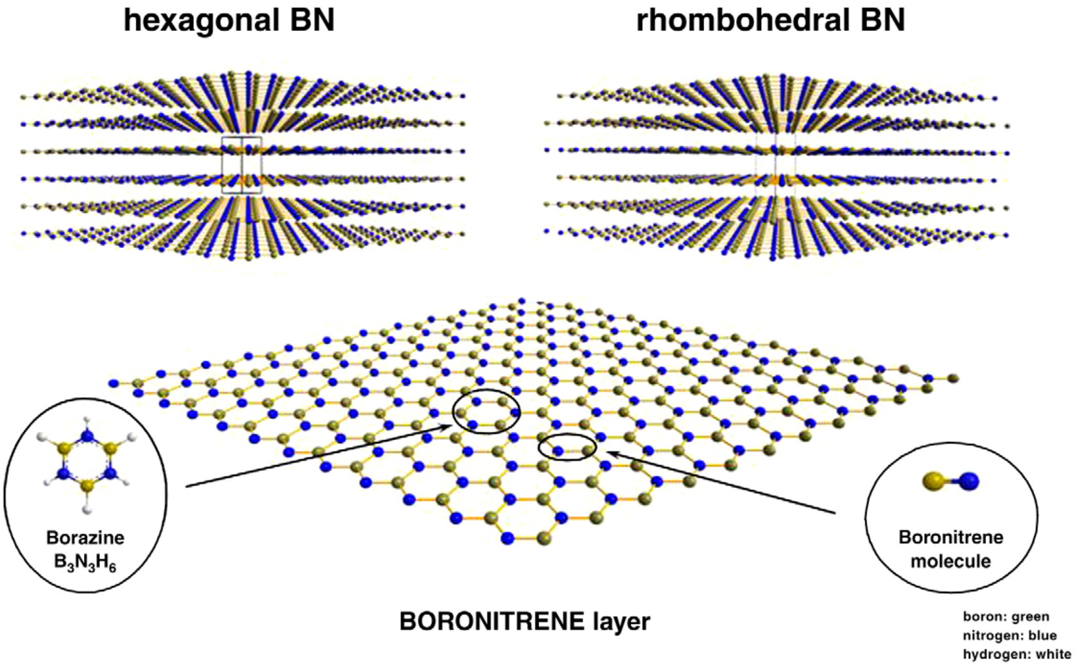

Fig. 1. Hexagonal and rhombohedral BN: Threefold coordinate sp^2-type BN-modifications with extreme structural anisotropy. top left: crystal lattice of hexagonal boron nitride (structural data: SG: P 63/m m c (194), $a = 2.5040$ Å, $c = 6.6612$ Å [28]; top right: crystal structure of rhombohedral boron nitride (SG: R 3 m (160), $a = 2.5040$ Å, $c = 10.0000$ Å [29]; bottom center: boronitrene layer; bottom left: borazine molecule as a molecular building block for a boronitrene layer; bottom right: single boronitrene molecule formally acting as a diatomar building block for polymer two-dimensional boronitrene layers. A structural model for a free boronitrene layer consists of a 2 dimensional, hexagonal 2 atomic basis of similar dimensions as given above for h- or r-BN.

regarding the formation of well-ordered BN monolayers in general are still unknown and a major question is whether substrate effects like epitaxial interactions or precursor issues are responsible for the built up of BN layers (e.g., with respect to the question whether a pre-existing structural motif delivered by a molecular precursor, like a six membered B_3N_3-ring in borazine, is necessary for a CVD formation of a specific material, like, e.g., sp^2-type BN phases). Therefore, investigations elucidating potential chemical reactions at the substrate–film interfaces, surfaces and rims of the formed solids and phases are of general interest to understand, model and tune the growth of the resulting films [13,26,27]. Furthermore, it has to be noted that superstructured BN monolayers are generally referred to as hexagonal boron nitride (*h*-BN) monolayers in the literature up to now, but these monolayers do not really represent a structural unit of a hexagonal boron nitride crystal, since they can be bulged and undulated (leading to larger superstructures) or corrugated (dislocation of B– and N– atoms in opposite directions from the mean plane), and even a monolayer of rhombohedral BN (r-BN) has the same connectivity as a monolayer of hexagonal boron nitride (cf. Fig. 1). The analogous building blocks of a graphite crystal are referred to as graphene layers. The two-dimensional graphene-like BN monolayers are built up by a two-dimensional array of BN units, leading to a graphene isostructural motif. For reasons mentioned above, and since the individual building unit of a two-dimensional BN layer of hexagonal (or even rhombohedral) boron nitride is a boronitrene unit (a molecular unit linking a borylene with a nitrene), we will refer to these layers as boronitrene layers, which resemble the analogy to graphene layers.

To understand the stability of boron nitride bulk materials or BN monolayers, a testing of the reactivity towards reactive gases and the study of the remaining material will lead to an insight in the molecular species involved during the degradation process. This aspect is also of great importance regarding selective etching reactions for the individual BN phases for the gas phase deposition of c-BN [13,26,27]. In this report, the reactivity and chemical stability of a boronitrene film grown by CVD of borazine on a Rh(111) multilayer substrate [30] towards oxidation and nitrification of the obtained intermediate was investigated by LEED and XPS with respect to gain information of the nature and stability of the intermediates. The configurational binding forces according to Ref. [2] and a model of the corresponding boronitrene superstructure are schematically depicted in Fig. 2.

2. Results and discussion

It could be commonly observed that the oxygen content of the BN monolayers prepared from borazine determined by XPS drops significantly even beyond the detection limit, after a BN layer had been formed [1,4–10,30]. For these reasons it may be assumed that oxygen containing compounds in the B–N–O–H–system can act as surfactants delivering mobile species responsible for the BN-layer formation. In order to validate this aspect, the following experimental sequence using LEED and XPS analysis was performed to learn more about the stability and growth of BN. The results of the sequence (LEED polar intensity plots and relevant XPS signals) are depicted in Fig. 3. They indicate the formation of a superstructured BN monolayer as described in Ref. [30] by CVD of borazine, the formation of an unstructured film containing boron and oxygen after oxidation, and the reformation of a BN superstructure after adding ammonia to the system.

In the first step, a boronitrene monolayer was prepared by CVD of borazine as previously described [1,4–9,30] and the formation of the BN superstructure is confirmed by LEED and XPS data (Fig. 3, 1st row). In the second step, oxygen was added at 900 K to see whether the obtained BN superstructure remains stable. Since this was not the case, but the formation of an unstructured boron oxide species was detected on the substrate as indicated by LEED and XPS measurements (Fig. 3, 2nd row) [only the Rh(00) and (01) substrate signals on an enhanced background are present without any superstructure satellites], the question of the reversibility of such a reaction sequence has arisen. Therefore, in the next step, ammonia was added at 900 K and remarkably, XPS signals for BN-related boron B1s and nitrogen N1s appeared again, while the intensity for O1s had decreased and the