One-dimensional structure of boron nitride on chromium (110) – a study of the growth of boron nitride by chemical vapour deposition of borazine

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

[a] Institut für Anorganische Chemie, Naturwissenschaftlich-Technische Fakultät III – Chemie, Pharmazie und Werkstoffwissenschaften, Universität des Saarlandes, 66041 Saarbrücken, Germany
[b] Institut für Experimentalphysik, Naturwissenschaftlich-Technische Fakultät II – Physik und Mechatronik, Universität des Saarlandes, 66041 Saarbrücken, Germany

ABSTRACT

The nucleation and growth of boron nitride films on a chromium (110) surface by thermal decomposition of borazine $(HBNH)_3$ was investigated by low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS) and X-ray photoelectron diffraction (XPD). The boron nitride film forms a chemically non-uniform one-dimensional superstructure with short range order along the $[1\bar{1}0]$ direction and long range order along [001]. Moreover, the thermal stability of the resulting BN film was investigated and a chemical reaction with the substrate was observed leading to the formation of Cr–B– and Cr–N– bonds at the interface and indicating the onset of the formation of hard boride and nitride phases in the system Cr–B–N.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Regarding the synthesis of boride, carbide and nitride based coatings of refractory metals (e.g., $MB_xC_yN_z$; M = Ti, Cr and Mo) by deposition techniques based on CVD and PVD methods, there is a continuous interest regarding the hardness and wear resistant properties of these materials. To obtain those films in high quality and suitable crystallinity, a detailed understanding of gas phase reactions during film formation, interactions and reactions within the substrate-film interface as well as the stability of the phases and their chemical reactivity is necessary to tune the film quality and crystallinity. Such an interface reaction can occur by thermal treatment of a nitride-based coating like BN on a substrate enabling the formation of intermediate phases.

Depending on the material, the film properties can be enhanced by means of annealing, which becomes a complex process in the case of multinary composites because of phase stability and phase segregation phenomena. Irrespective of the deposition of films of a distinct stoichiometry and composition, covered by kinetic aspects of the synthesis, the study of phase segregation by chemical reactions induced by annealing is not well understood and can be attributed to the thermodynamic aspects of the stabilities of the phases. Such phase segregation behaviour is reported as a general problem in the Cr–B–N system because of the formation of hard chromium boride and nitride phases like CrB_2 and CrN, and soft h-BN with lubricant properties [1–4]. Investigations dealing with growth kinetics and thermodynamic aspects of the chemical reactivity of the deposited phases are of general interest to understand the mechanisms leading to the film formation of individual phases. This topic is still under investigation regarding the boron nitride system, which is of general importance for all multinary nitride-based composite systems [5–8]. For these reasons, the CVD reactions of borazine as a molecular precursor were investigated on chromium (110). Such nucleation and growth reactions of hexagonal boron nitride (h-BN) on transition metal surfaces from borazine as a molecular BN source gained new interest since the discovery of the formation of self-organized superstructures (called "nanomesh") on a Rh(111) surface by Corso et al. [9], actually consisting of a corrugated monolayer of h-BN [10,11].

So far, the growth of boron nitride has been investigated for a large variety of transition metal surfaces, as, e.g., Ni [12–18], Pt [19–21], Pd [22,23], Ru [24], Mo [25] and Ag [26].

Most of these investigations were focussed on the growth on the (111) surfaces of face centred cubic (fcc) crystals, because in that cases, the point symmetry of the surfaces coincides with the symmetry of the hexagonal boron nitride lattice (h-BN), for which different domain types were observed.

In the case of Ni(111), e.g., there is nearly a vanishing lattice mismatch ($a(h\text{-BN}) = 0.250$ nm vs. $a_{111}(\text{Ni}) = 0.249$ nm) and the h-BN lattice forms domains with the unit cell of the h-BN lattice being aligned parallel to the in-plane unit cell of the Ni(111)

* Corresponding author. Tel.: +49 681 3022465; fax: +49 681 3023995.
 E-mail address: h.sachdev@mx.uni-saarland.de (H. Sachdev).
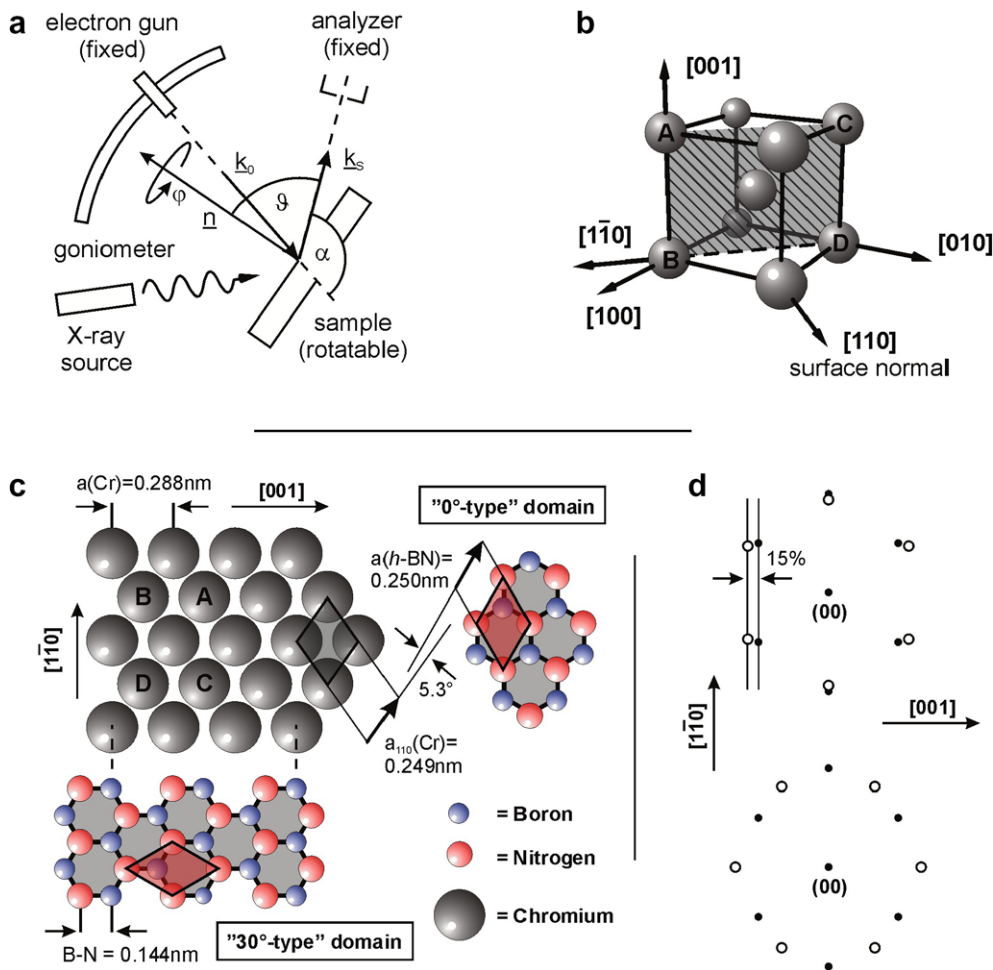
Fig. 1. (a) Experimental setup, as described in the text, (b) lattice structure of the Cr bcc crystal and lattice directions used in the text. The (1 1 0) surface is given by the shaded plane, (c) comparison of the Cr(1 1 0) surface with the h-BN lattice for 0°-type and 30°-type domains. For orientation, four atoms of the Cr(1 1 0) surface are labelled as in the previous three-dimensional representation. The oblique unit cells of the surfaces are indicated by the shaded areas, (d) reciprocal lattice of the rectangular Cr(1 1 0) surface (black dots) and the h-BN (open circles) for 0°-type domains (top) and for 30°-type domains (bottom).

substrate (0°-type domains, lattice mismatch $\delta_{0°} = 0.4\%$). The domains are different with respect to the stacking along the surface normal, i.e., they differ by boron occupying the fcc or hcp sites of the Ni(1 1 1) substrate [13].

In the case of Pt(1 1 1) [20] or Pd(1 1 1) [22], the lattice mismatch is in the intermediate range ($a(h\text{-BN}) = 0.250$ nm vs. $a_{111}(Pt) = 0.277$ nm, $\delta_{0°} = 11\%$ and $a_{111}(Pd) = 0.275$ nm, $\delta_{0°} = 10\%$, respectively) and also h-BN domains of different orientation have been observed. If the h-BN unit cell is aligned perpendicular to the Pt(1 1 1) or Pd(1 1 1) in-plane unit cell (30°-type domain), the lattice mismatch is reduced to $\delta_{30°} = 4\%$ (Pt) and $\delta_{30°} = 5\%$ (Pd), respectively.

In addition to the hexagonal (1 1 1) surfaces, the growth of BN was also investigated for surfaces of different point symmetries, as, e.g., Ni(1 1 0) [16] and Pd(1 1 0) [21]. For such surfaces, a large variety of superstructures have been observed, among which some exhibit large $a:b$ aspect ratios of the rectangular supercells due to the enhanced anisotropy of the substrate lattice. For example, BN/Pd(1 1 0) is assumed to represent a "tunable system". In Ref. [23], the authors suggest that the contributions of the various domains can probably be tuned via the preparation procedure. For future applications in micro- or nanoelectronic devices, the preparation of BN layers with preferred directions may represent an interesting task. If, e.g., the growth of such layers would result in a corrugation similar as for the BN/Rh(1 1 1) system [11], then their one-dimensional topography would provide templates for

the alignment of other nano-scaled modules, as, e.g., carbon nano-tubes. Some visionary concepts are suggested in Ref. [10].

In this paper, we report on the growth of boron nitride on the (1 1 0) surface of chromium via the evaporation of benzene-like borazine (HBNH)$_3$. In contrast to most of the examples listed above, Cr forms a body centred cubic (bcc) lattice and the (1 1 0) surface of a bcc crystal represents the particular case that it provides a pseudo-hexagonal symmetry with only a slight distortion. On the one hand, the bcc (1 1 0) surface forms a rectangular lattice with a preferred direction, similar to the case of an fcc (1 1 0) surface, on the other hand, the point symmetry of a bcc (1 1 0) surface is very close the hexagonal point symmetry of h-BN, similar to the case of an fcc (1 1 1) surface. For Cr, the (1 1 0) surface additionally exhibits two special distances (cf. Fig. 1): with respect to the formation of "0°-type" domains,[1] the situation is similar to Ni(1 1 1), i.e., the Cr(1 1 0) in-plane lattice constant nearly matches witch the lattice constant of h-BN ($a(h\text{-BN}) = 0.250$ nm vs. $a_{110}(\text{Cr}) = 0.249$ nm, $\delta_{0°} = 0.4\%$), but the angles of the oblique unit cells deviate by about 5°. With respect to the formation of "30°-type" domains, the bulk lattice constant ($a(\text{Cr}) = 0.288$ nm) is exactly twice the B–N distance, i.e., there is exactly a 6:4 commensurability along the [0 0 1] direction.

---

[1] Although the Cr(1 1 0) lattice deviates by about 5° from a hexagonal lattice, we use the terms "0°-type" and "30°-type", that originally refer to a hexagonal surface.