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Structure of the Boron Nitride Films Obtained by RPECVD from Borazine

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Abstract

In this paper study and characterization of the composition and structure of BN films deposited from borazine are reported. The films were deposited using remote plasma enhanced CVD process (RPECVD). Compared to conventional CVD process which shows amorphous BN, the films synthesized from borazine by the RPECVD method at low temperatures (473–873 K) show nanocrystalline structure. These films consist from the mixture of h-BN and c-BN. The quantity of cubic phase is considerably less (near 15 %) than that of hexagonal one. Microstructure of the films depends on conditions of deposition: the mixture of cubic and hexagonal phases was observed in the films deposited at T_{su}=473 K in the system with excited nitrogen, as the single phase of h-BN was observed in the films obtained in the system with excited helium. The size of grains depends on borazine pressure. There are two distinct layers in the film microstructural evolution: the initial amorphous layer near the interface (2 nm), and the second layer consisting of nanocrystalline phases of h-BN and c-BN or single h-BN.

INTRODUCTION

Various chemical precursors such as BCl_3 and B_2H_4 with ammonia or nitrogen [1–4], thrimethylborazine [5], and borazine [6–9] have been used for the boron nitride films deposition. Borazine is molecular precursor for boron nitride films possessing the correct boron-nitrogen stoichiometry. It should be emphasized that there are a few publications concerning the process using borazine as starting substance for boron nitride films deposition. Comparison of two different reactants such as mixture B_2H_4 with NH_3, and borazine contradicted that stable BN films may be obtained for both deposition chemistries, depending on deposition conditions [8].

Earlier [10, 11] we found the conditions of stable BN films synthesized from borazine using plasma excited helium, argon or nitrogen in the deposition process, and reported their physical and electrophysical properties.

Nguen *et al.* [9] comprised the structure of BN films using diborane and borazine as starting substances. They found that with diborane as a precursor, the obtained films were amorphous. With borazine as a precursor, the films consisted of the mixture of crystalline phases, such as hexagonal, wurtzite and cubic. Kouvetakis *et al.* [8] carried out structural characterization of BN films using transmission electron microscopy. The films were deposited from borazine using PECVD process. Electron diffraction patterns consisted of several rings which were interpreted as hexagonal layered boron nitride structure. In addition to the hexagonal boron nitride rings, a set of weak spots with an interplanar spacing of d = 2.06 Å patterns was observed. This d spacing has been assigned to diffraction from cubic boron nitride {111} orientation. In [7] the structure of BN synthesized by pyrolysis of borazine at a temperature between 523 and 973 K under 100 MPa pressure was investigated. It was

TABLE 1

Conditions of the films deposition

Sample No.	Chemical system	Temperature of deposition, K	Pressure of borazine, Pa	Pressure of excited gases, Pa	Input power, W	Thickness, nm	Deposition rate, nm/min
942	$B_3N_3H_6$ + He*	873	2	4	9.4	88.6	0.4
917	$B_3N_3H_6$ + He*	873	4	4	9.4	140	2
927	$B_3N_3H_6$ + He*	873	7	4	9.4	349	4
949	$B_3N_3H_6$ + He*	873	5	4	23	92	0.5
926	$B_3N_3H_6$ + He*	873	5	4	23	253	0.5
918	$B_3N_3H_6$ + He*	873	5	4	125	65	1
975	$B_3N_3H_6$ + N_2*	473	4	8	9.4	75	1
977	$B_3N_3H_6$ + N_2*	473	4	5	9.4	174	3
863	$B_3N_3H_6$ + $\bar{e}$	473	4	–	125	170	2

found that the product showed diffuse rings which characterized turbostatic BN of hexagonal symmetry.

So, it may be concluded that with diborane as a precursor, the films deposited by the PECVD process were amorphous. Mixed hexagonal, wurtzite, and cubic nanocrystallinity were observed for borazine BN films. Conventional pyrolysis process at low temperature gives amorphous (turbostatic) structure of BN.

In this paper we wish to report a more thorough study and characterization of composition and structure of BN films deposited from borazine.

EXPERIMENTAL

Borazin used in this study was synthesized and purified at the Institute of Inorganic Chemistry, SB RAS, and was stored at a temperature below 0 °C. Single crystal silicon plates were used as wafers. They were degreased in organic solution and dipped in HF. For the investigation of chemical structure by the IR spectrometry method single crystal germanium wafers were used. The RPECVD process was used for the films deposition. Deposition technique was described in detail in [10]. Conditions of the films deposition are presented in Table 1. The film thickness and refractive index were measured ellipsometrically, using photoelectronic ellipsometer LEF-3M, equipped with 632.8 nm He-Ne laser. The identification of the deposited films was primarily based on the observed IR spectra, recorded with a Philips PU-9512 spectrophotometer. The surface morphology was studied using a scanning electron microscope LE 0982. Cross-sectional and dark-field (DF) images as well as selected area diffraction pattern were recorded using a transmission electron microscope JEOL 2010.

RESULTS AND DISCUSSION

IR spectroscopy

IR spectrum of the film deposited at T_{su} = 873 K on Ge wafers is depicted in Fig. 1. There is a sharp and strong absorption at 1370 cm^{-1}, attributed to a stretching of the B—N bond between the basal planes. This mode is related to the IR active mode of h-BN. Secondary peak around 1080 cm^{-1} can be used for the identification of c-BN [11]. No absorption bands can be observed in the curve assigned to N—H and B—H groups (at 3440 and 2490 cm^{-1}, respectively). The spectrum of the film deposited at T_s = 473 K was shown in [10]. It was observed that the hydrogen concentration (only N—H

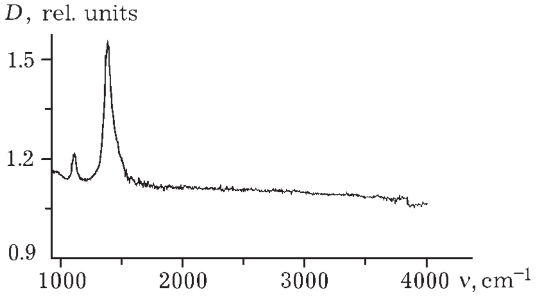

Fig. 1. IR spectrum of the films deposited on Ge wafers. T_s = 873 K, $P_{B_3N_3H_6}$ = 4 Pa, P_{N_2} = 5 Pa, input power 50 W.

groups) was very low. From IR data (see Fig. 1) it may be concluded that the films deposited at $T_s = 873$ K consist of h- and c-BN. Absorption intensity of h-BN is stronger than that of c-BN. The data of IR spectroscopy may be used for determining relative amounts of c-BN in the films. One of the approaches for phase quantification is as follows: volume fraction c-BN $\approx I_{1080}/(I_{1080} + I_{1370})$. Here, I_{1080} and I_{1370} are the normalized transmitted intensities of the IR absorbances at wavenumbers of 1080 and 1370 cm^{-1}. From the IR spectrum (see Fig. 1) it follows that the volume fraction of c-BN is about 15 %.

Morphology and structure

The plan-view images obtained by SEM method are shown in Fig. 2. The structure of the films may be characterized as scaled. Comparison of the morphology of films obtained with various deposition rate (samples No. 927, 942, 949) shows that the size of microcrystallites increases with the deposition rate as the borazine pressure is increased. The other parameters of process were kept constant. As it is evident from [10], this process involves the formation of polymeric precursors in the gas phase. The polymeric precursors provide the structural unity of the growing film. It may be concluded from Fig. 2 that larger polymeric precursors formed when the borazine pressure was increased. The films deposited at $T_{su} = 473$ K in the system with excited nitrogen (sample No. 975) had a lower size of scales on the surface of the film. The film morphology changed with the increase in thickness (compare samples No. 975 and 977).

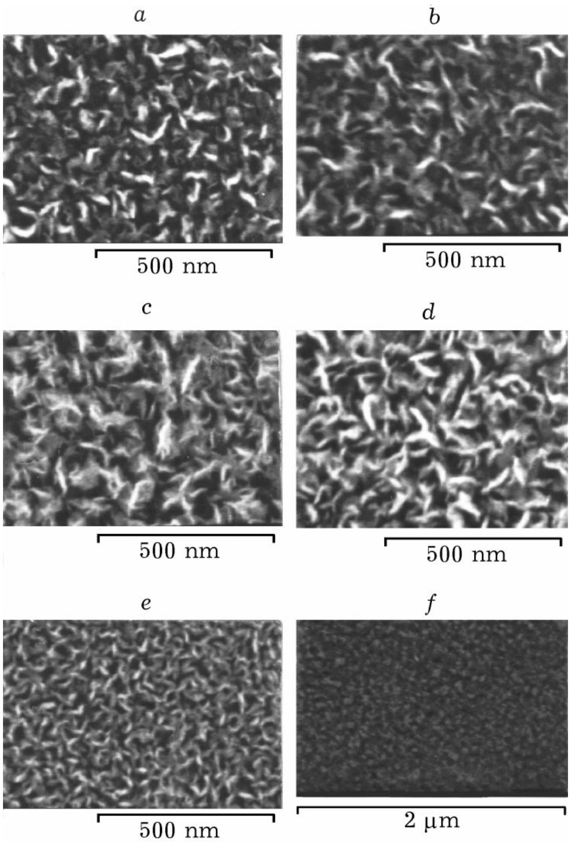

Fig. 2. In-plane SEM images of the films. Deposition conditions see in Table 1. Samples: 942 (*a*), 949 (*b*), 927 (c), 926 (*d*), 975 (*e*), and 977 (*f*).

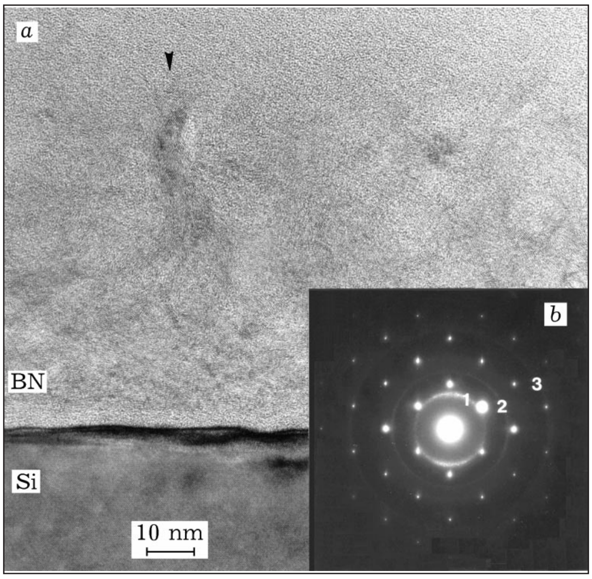

Fig. 3. The TEM image and SAD pattern of the film. The SAD characterizes the area designated by a black needle (sample No. 918): 1–3 – the diffuse rings corrrespond to {0002}, {1010}, and {1120}, respectively.

Cross-sectional transmission electron microscopy (TEM) images and selected area diffraction (SAD) patterns of samples No. 918, 863 and 975 (see Table 1) are shown in Figs. 3–5.

In Fig. 3 the TEM image and electron diffraction pattern of the film deposited at $T_s = 873$ K in the system with excited helium (sample No. 918) are shown. The TEM image characterizes the point designated by a black needle. From the TEM image it follows that there are two distinct layers in the microstructural evolution. There is an initially amorphous layer near the interface. The thickness of this layer is near 2 nm. We have no analytical determination of the chemical composition of this layer,

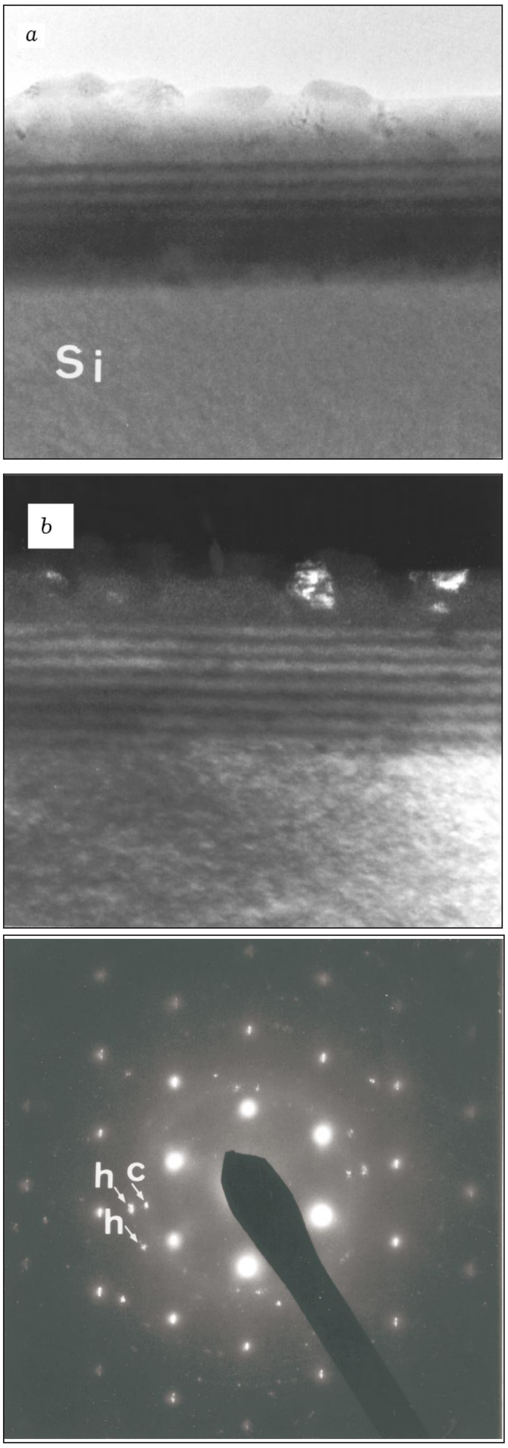

Fig. 4. The TEM bright-field (*a*), dark-field (*b*) images, and SAD pattern (*c*) of the film deposited in systems without excited inert or noble gas (sample No. 863). Here and in Fig. 5: c – cubic BN, (110); h – hexagonal BN, (1010)

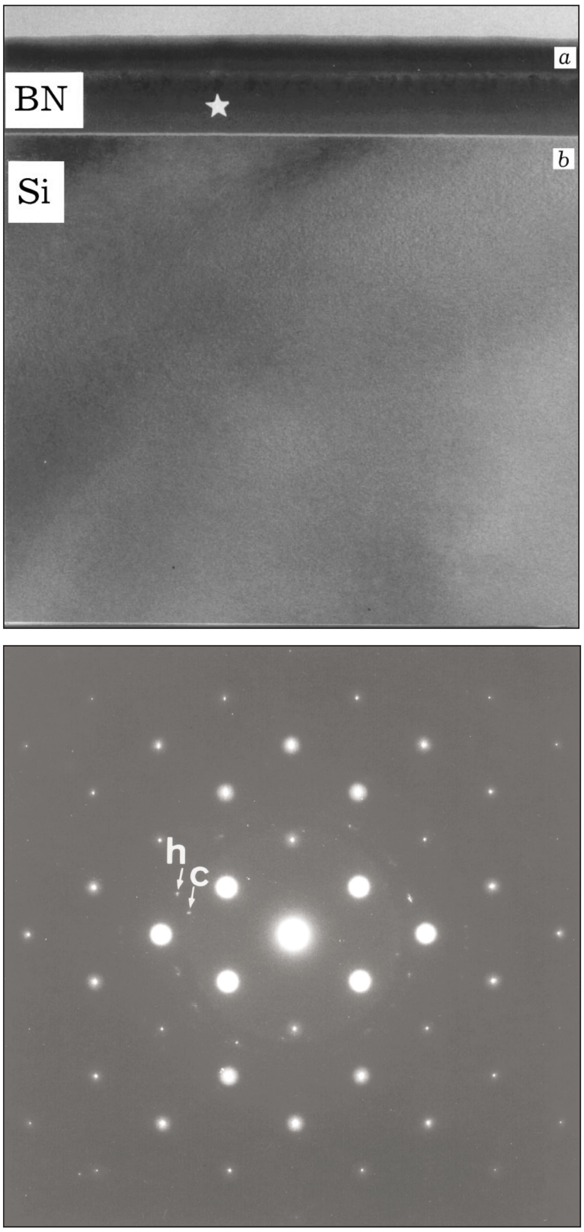

Fig. 5. The TEM image (*a*) and SAD pattern characterizing the area designated by a star (*b*) of the film deposited in the system with excited nitrogen (sample No. 975).

but we suppose that it may be described as an amorphous boron nitride. The SAD pattern shows sharp spots from the Si substrate and diffuse rings from the deposited layer. The diffuse rings correspond to {0002}, {1010}, and {1120} reflections of hexagonal layered boron nitride structure. The observed contrast shows that the structure of this layer is distorted and extends only over a short distance.

It should be emphasized that the layered BN films microstructure has not been universally observed, but some authors also observed layered structure of BN films deposited with plasma or ion-assisted processes. Speculated explanations of such film structure were discussed in [12].

A representative TEM image and SAD patterns of the film deposited in systems without excited inert or noble gas are shown in Fig. 4. There are many grains in the volume of the film. The size of the crystallites was measured to be 30 nm or less. The SAD pattern shows diffuse rings and spots (indicated by arrows) due to deposited layer together with the SAD pattern of Si [110] incidenced from the substrate.

The rings are indexable as hexagonal h-BN{1010} (d = 2.17 Å). There can be also observed the spots indexable as c-BN{110} out-of-plane orientation. From published data it follows that {111} in-plane texture is common in c-BN films. Ballet *et al.* [13] showed that {110} out-of-plane orientation might arise if c-BN grows on a non-polar face since the {110} planes have an equal density of boron and nitrogen atoms.

The film synthesized at $T_s = 473$ K in the system with excited nitrogen (see Fig. 5, sample No. 975) also consists of the mixture of h-BN {1010} and c-BN {110}. So, the appearance of cubic phase at $T_{su} = 473$ K in the system with excited nitrogen was found to be possible. It may be proposed that the phase composition and structure of the films depend on system chemistry, and conditions of deposition. It takes a more detail investigation of influence of these factors on the structure of films for understanding the mechanism of the film structure formation.

CONCLUSIONS

1. Compared to conventional CVD process which gives amorphous BN, the films synthesized from borazine by the RPECVD method show nanocrystalline structure. The films consist of the mixture of h-BN and c-BN. The quantity of cubic phase is considerably less (near 15 %) than that of hexagonal one.

2. Microstructure of the films depends on deposition conditions: in the system with excited nitrogen the mixture of cubic and hexagonal phases was observed in the films deposited at $T_{su} = 473$ K, as in the system with excited helium the single phase of h-BN was observed.

3. The size of grains depends on pressure of borazine.

4. There are two distinct layers in the film microstructural evolution: the initial amorphous layer near the interface (2 nm), and the second layer consisting of nanocrystalline phases of h-BN and c-BN or single h-BN.

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