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Recent Developments in the Deposition of c-BN Coatings

Martynas AUDRONIS*, **Algirdas Vaclovas VALIULIS**, **Paulius SILICKAS**

Materials Science and Welding Department, Vilnius Gediminas Technical University,
Basanavičiaus 28, LT-2009 Vilnius, Lithuania

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Cubic boron nitride, c-BN, due to the high strength of its covalent inter-atomic bond, small bond distance, and high coordination number, is the second hardest (HV ≈ 50 GPa) material (the first is diamond with HV ≈ 70 – 90 GPa) available as single crystal. The fact that c-BN does not react readily with ferrous metals, cobalt and nickel; can be deposited in thin film form under standard conditions (1 bar, 298 K); and has a high resistance to oxidation in air to high temperatures of 1000 °C, makes it very attractive for tool applications. Unfortunately c-BN films due to high compressive stress, which can reach values up to 25 GPa and poor adhesion strength of the interface, still reveal themselves to be poor adherent to almost every substrate material. The cause of the high stress is the strong ion bombardment, which in turn is necessary to obtain the cubic modification of boron nitride. In this article brief review of the present status of the research and technological development in deposition of c-BN coatings is presented. The c-BN mechanism, its peculiarities, and mechanical properties are described.

Keywords: c-BN, thin film coatings, mechanical properties.

1. INTRODUCTION

Materials having Vickers hardness HV of 40 – 60 and >80 GPa are commonly called as super- and ultrahard, respectively. The only super- and ultrahard materials, which are available as single crystals, are cubic boron nitride (c-BN, HV ≈ 48 GPa) and diamond (HV ≈ 70 – 90 GPa) due to the high strength of their covalent interatomic bond, small bond distance, and high coordination number [1, 2]. It was also predicted, that C_3N_4 should have hardness comparable to that of diamond [3 – 5], but this prediction still has not been confirmed by experiments thus far (see review [6] and references therein). These materials and possibly some ternary compounds from the B–N–C triangle [7] are ascribed to intrinsic superhard materials.

Cubic boron nitride, c-BN, is a metastable, high pressure, high temperature (HPHT) phase and the second strongest and hardest material (H ≈ 48 GPa). Its data were confirmed and improved upon in several later papers [8, 9]. The fact that c-BN (i) does not react readily with ferrous metals, cobalt and nickel, (ii) can be deposited in thin film form under standard conditions (1 bar, 298 K, [10]), and (iii) has a high resistance to oxidation in air to high temperatures of 1000 °C, makes it even more attractive for tooling applications. Moreover, c-BN is suitable for a broad range of electronic applications, since it has the widest energy band gap of all III-V compound semiconductors and since it can be doped both p- and n-type, as was demonstrated with HPHT grown single crystals [11, 12].

Because of its properties c-BN is very attractive for many applications. Unfortunately there are still many problems associated with mechanical strength, adhesion, growth rate etc. This review summarizes the present status of the research and technological development in deposition of c-BN coatings paying the main attention to the mechanical properties and applications.

2. c-BN FORMATION

Whereas diamond occurs in nature, only synthetic c-BN is known. In analogy to carbon, boron nitride crystallizes mainly in two structures, sp^2 bonded hexagonal and sp^3 bonded cubic (Fig. 1), with similar physical properties to graphite and diamond. For more information on these and other (wurtzitic (w-BN), rhombohedral (r-BN) and turbostratic (t-BN)) BN phases see ref. [13].

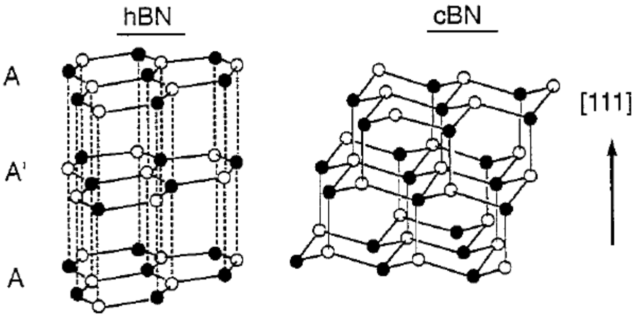

Fig. 1. Structures of the sp^2 bonded h-BN and sp^3 bonded c-BN phases

The formation of the fourfold coordinated network of the c-BN phase requires energetic ion bombardment. Inagawa et al. [14] observed that cBN film formation only occurred in a specific range of ion current (flux) and substrate bias (i.e. ion energy) values (Fig. 2). They observed that the process-parameter boundaries, as well as the maximum cBN content attained, were influenced by the ratio of Ar^+ to N_2^+ ions (i.e. ion mass). Later, Ikeda et al. [15] and Yokoyama et al. [16] found a narrow window of deposition rate and substrate bias in which cBN formed. With fixed ion mass and deposition rate, Kester and Messier [17], Ikeda [18], and Tanabe et al. [19] observed that cBN formed only for certain values of ion energy and

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[*] Corresponding author: Tel.: +44-77-46-731723; fax: +44-77-46-731723. E-mail address: *M.Audronis@pgr.salford.ac.uk* (M. Audronis)

ion flux. Thus, there are sharp thresholds for cBN formation in an experimental parameter space of (i) ion mass m, (ii) ion energy E, (iii) ion flux J (ions $cm^{-2}s^{-1}$), and (iv) deposition flux a (atoms $cm^{-2}s^{-1}$). The other important deposition parameter is the substrate temperature.

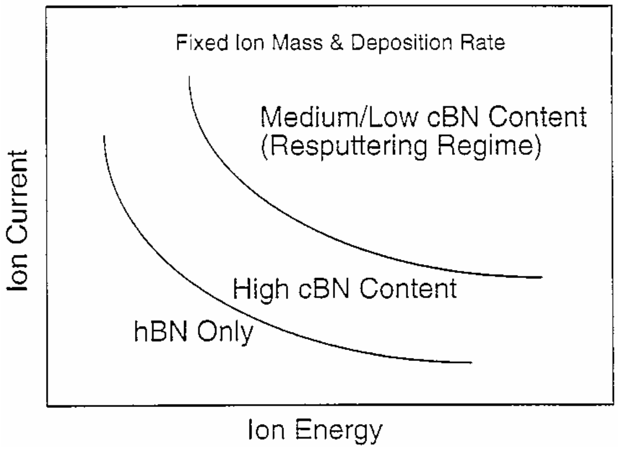

Fig. 2. Schematic diagram showing cBN content as a function of ion current energy at constant ion mass and deposition rate [14]. The transition to low/medium cBN content with increased ion current and energy is known to result from increased sputtering, which gives a thinner film and a no-growth condition

Ion assisted physical vapor deposition (PVD) and chemical vapor deposition (CVD) or pure ion beam deposition were used in a large number of studies to deposit c-BN thin films. It was shown that the nucleation and growth of c-BN films rely on the same principal mechanisms for all techniques and take place in well defined parameter ranges [14 – 22]. These films contain c-BN with an amount of up to 90 %. In recent years many investigations towards the understanding of the nucleation process have been made [14 –24].

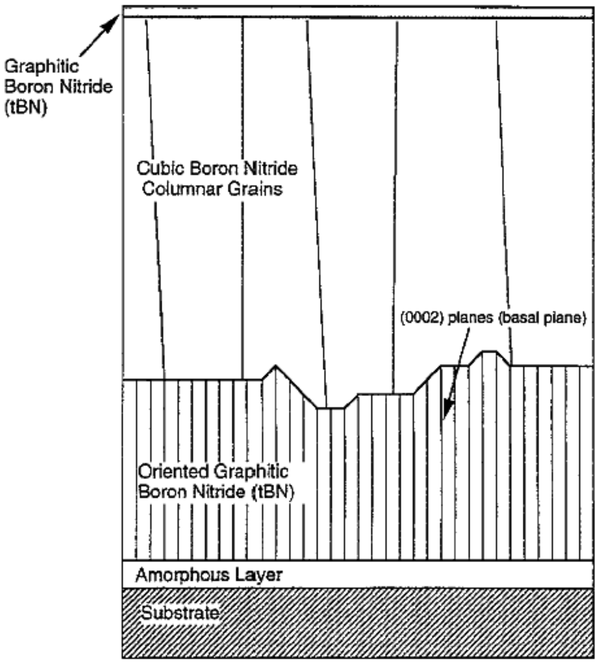

Fig. 3. Schematic diagram summarizing micro structural features of c-BN films [13]

A characteristic nucleation sequence (Fig. 3) a-BN → textured h-BN (c-axis parallel to the substrate) → c-BN has been established to precede c-BN growth, first observed by Kester et al. [25]. This unique sequence is observed almost independently of the deposition method and the substrate material [26]. Nevertheless, the thickness of the h-BN nucleation layer varies from 5 nm [25, 27] to 100 nm [28] depending on the deposition technique and parameters, but the reasons for this are still uncertain.

Characterization of BN films non-trivial and conclusive phase identification requires of several complementary techniques. In part this is because thin film c-BN is typically very small grained and highly defective. The most valuable techniques for phase identification of BN films are infrared spectroscopy, transmission electron diffraction and microscopy, and electron energy loss spectroscopy. Since distinguishing c-BN from graphitic BN can be difficult, use of complementary phase characterization methods along with stoichiometry analysis is prudent.

3. MECHANICAL PROPERTIES

Deposited cBN films showed extreme hardness such as 4000 kg/mm^2 as obtained by the micro Vickers hardness measurement [14, 29], 42.2 – 61.8 GPa for the Knoop hardness measurement load 100 mN [30], and 57.6 GPa for ultra low load indentation (load 10 mN) [31]. Since the cBN films have a limited film thickness of about a few hundreds nm due to delamination from the substrates caused by high compressive film stress and poor adhesion, the measurement of hardness by the conventional indentation method without substrate effect is very difficult. For such thin films, indent depths of less than 50 nm are required to keep the depth within the recommended value of roughly 10 – 20 % of the film thickness [32 – 34]. Such shallow indents can render spurious results even in nanoindentation. For indents beyond roughly 20 % of the film thickness, substrate effects can become substantial. It was shown [35] that the substrate begins to elastically deform at an indent depth to film thickness ratio of about 0.12. Such a substrate effect will alter the elastic modulus determined by indentation more than the measured hardness. Another possible difficulty is the elasticity of composite or layered BN films [13]. Nanoindentations with an extremely low load, a highly sharp tip and an extremely shallow penetration depth along with additional structural analyses are necessary to study the mechanical properties of such films. Recent study of nanomechanical properties of cubic boron nitride films [36] also showed, that due to the small thickness and layered structure of the cBN films, the evaluated hardness and elastic modulus changes with the film thickness and the penetration depth. The measurements of the mechanical properties of cBN films must be done carefully, considering the thickness of both the initial layer and the cBN layer.

In few recent reports [35, 37, 38] deposition of thick (0.7 – 5 µm) good quality cBN coatings by two step process described below, was published. Nanoindentation of mentioned coatings produced hardness and elastic modulus values to be 60 – 70 GPa and ≈ 800 GPa respectively, which are very close or even higher than

Table 1. Mechanical properties of bulk cBN

Hardness, *H*	45 – 55 GPa	Vickers — polycrystalline	[9, 39]
	≈ 55 GPa	Berkovitch / Nanoindentation — polycrystalline	[35]
	40 – 60 GPa	Knoop — polycrystalline	[40, 41]
	30 – 93 GPa	Knoop — single crystal (depending upon orientation) •	[42]
Young's modulus, *E*	800 – 900 GPa	Various Methods — polycrystalline	[35, 43 – 45]
Bulk modulus, *B*	370 – 385 GPa	Pressure dependence of lattice parameter	[46, 47]
Fracture toughness, *K*	2.8 MPa $m^{-1/2}$	Single crystal	[48]
	3.5 – 5.0 MPa $m^{-1/2}$	Polycrystalline	[39, 41]

these of bulk cBN. Mechanical properties of bulk cBN are listed in the Table 1.

Unfortunately c-BN films still reveal themselves to be poor adherent to almost every substrate material. The reasons for this poor adhesion are the high compressive stress, which can reach values up to 25 GPa [49], on the one side, and the poor adhesion strength of the interface, which cannot hinder the delamination of the film, on the other side [50, 51]. The cause of the high stress is the strong ion bombardment, which in turn is necessary to obtain the cubic modification. A very simple model proposed by Davis [52] assuming the stress to be caused by defects, mainly interstitials, relates the stress with the main deposition parameters. The resulting stress is given by the balance of ion induced defect generation and relaxation:

$$\sigma \propto \frac{n_i\left(E_{ion}, m_{ion}, \Theta_{ion}\right)}{E_{ion}^{5/3}}. \qquad (1)$$

The decisive parameter, the number of interstitials per incoming ion n_i, is a function of the ion energy E_{ion}, the ion mass m_{ion} and the angle of incidence Θ_{ion}. For the energy dependence Davis derived $n_i \propto E_{ion}^{1/2}$ [52], whereas S. Reinke's et al calculations yielded $n_i \propto E_{ion}$ [53]. Anyway both approaches lead to the result that the stress should decrease with increasing ion energy. Moreover, following this theoretical model, the stress can also be reduced by optimizing the ion mass and the angle of incidence, but theoretical as well as experimental studies are still missing.

In recent work R. Freudenstein et al. [24] determined that there are different mechanisms of the formation of the h-BN nucleation layer for different techniques. Under some conditions island growth can be observed leading to thick and rather rough layers with a poor adhesion, while under other conditions layer growth takes place, resulting in smooth, thin layers with good adhesion. Furthermore, it is suggested that the combination rough and thick nucleation layers/very poor adhesion are especially prominent for CVD films while PVD c-BN layers possess thinner and smoother nucleation layers and therefore the delamination behavior depends on the deposition method. This may be the reason for the experimentally observed significant differences in the thickness of the nucleation layer, its surface roughness and the delamination mechanisms of the c-BN films between the various deposition techniques.

Anyway the first aim is to minimize residual stress. This unwanted side effect can be reduced during growth by the choice of (i) high ion energies, (ii) substrate temperatures, (iii) suitable dopants, (iv) post annealing processes, (v) post-ion irradiation [54 – 58].

A. Klett et al. [59] in their systematic study of the influence of the ion energy and the ion mass on the stress of c-BN containing films, showed that the stress can be reduced down below 5 GPa by a proper choice of the deposition parameters, especially using high ion energies or low Ar/N_2 ratios, respectively. For further stress reduction of c-BN films they proposed a two-step process: first the deposition parameters should set to values providing a rapid nucleation of c-BN. Once c-BN nucleated, the deposition parameters should be switched to values enabling a low stress growth. The conditions of the second step led unfortunately also to a reduction of the c-BN content, but one should keep in mind that these conditions are far below the nucleation threshold of c-BN films. Therefore, a further optimization of the deposition parameters should enable an even more pronounced in situ stress reduction without too great a loss of the c-BN content. Further, the results of that work showed that stress favors rapid nucleation of c-BN, but also they proved that c-BN growth cannot be a stress-induced phase transformation.

It is naturally that the substrate material is an important factor affecting the film quality and adhesion. For example, good quality, adherent films on Ni substrate with c-BN content over 85 % have been obtained [60]. It was shown, that Ni having the lattice parameter of 0.352 nm what is close to that of c-BN – 0.362 nm, is very suitable for the nucleation and growth of c-BN. In order to enhance the film quality and adhesion on other substrates, Ni thin film (or other materials like B, BN, BCN, Ti etc. [15, 29, 61 – 63])can be used as a buffer layer. For more details using intermediate buffer layers see refs [15, 29, 56, 61 – 63].

Practical application of thin cBN coatings is still very problematic and there are very few trials of making this reported. One of such trials by M. Jin et al. was successful [64]. In an effort to provide an effective means of improving the performance of the tapping operation of beta titanium alloy, they fabricated a c-BN-coated tap by means of the magnetically enhanced plasma ion plating method [30] and carried out tapping experiments to evaluate the performance of the tap. It was found that the fabricated c-BN-coated tap was effective from the viewpoint of improving the tapped thread accuracy, reducing the tapping resistance and lengthening the tool life, compared with the commercially available conventional hard-film-coated taps.

4. CONCLUSIONS

The deposition of cubic boron nitride requires intense ion bombardment of the growing film during deposition in order to reduce the concurrent formation of the stable hexagonal soft h-BN. This results in large compressive stress, which limits the practically achievable thickness of c-BN coatings. For these reasons only c-BN based ceramics find wider application.

Nonetheless research is in progress and thick (0.7 – 5 μm), adherent and low stress coatings has been recently achieved. Thick cBN films can be as hard as bulk cBN. Combination of means of above described two step processes, proper post treatment, substrate choice and buffer layers opens the door for getting good quality and practically applicable coatings.

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