STRENGTH AND PLASTICITY

Superhardness Effect in Transition-Metal Diborides Films

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Abstract—The structure, composition, and properties of transition-metal diboride films have been studied. It was shown that they are characterized by a wide range of structural states, namely from amorphous-like to nanocrystalline with crystallite sizes of 1−50 nm. The characteristic peculiarity of the structure of film transition-metal diborides with high physical and mechanical properties is the formation of a nanocrystalline (columnar) structure with the growth texture in plane [00.1] and a nanocrystallite size of 20−50 nm. The element composition of a superhard highly textured film transition-metal diborides was studied by ion mass spectrometry and Auger electron spectroscopy. The overstoichiometry effect in nanocrystalline transition-metal diboride films is explained. It was shown that this effect is related to the formation of an additional B−B covalent bond, which is realized at subgrain boundaries and leads to the appearance of superhardness in the formed coatings.

Keywords: films, texture, composition, properties, borides

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INTRODUCTION

At present, refractory-metal boride thin films are widely used as various anticorrosive and protective coatings [1, 2]. The interest in these films is also due to their high hardness and wear resistance. Moreover, it is of importance that the films maintain their physical and mechanical properties at high temperatures. In the course of the formation of transition-metal diboride films (TiB_2, CrB_2, TaB_2, VB_2, HfB_2, etc.), they were found to demonstrate a wide range of structural states, namely, from amorphous-cluster to nanocrystalline with the growth texture in plane (00.1) plane and columnar structure [1−16]. A distinctive feature of the structure of transition-metal diboride films with high physicomechanical characteristics is the columnar structure and growth texture in plane (00.1). In this case, the main factors that affect the formation of the structure, composition, and properties of film coatings are the deposition temperature and energy of film-forming particles [17]. Highly textured overstoichiometric transition-metal diboride films CrB_2, HfB_2, TaB_2, and TiB_2 exhibit superhardness H_V equal to 43.9 [7−9], 44 [6, 14, 15], 43.9 [12, 13], and 48.5 [5] GPa compared to those equal to 33, 36, 35, and 37 GPa for stoichiometric compositions, respectively.

A comparative analysis of the mechanical characteristics of overstoichiometric HfB_2 and TaB_2 films shows that they substantially exceed those of other materials and approach those characteristic of diamond. The H/E ratio for diamond is close to 0.1 and the elastic deformation during indentation is 100%.

Thus, according to the H/E ratios (0.111 and 0.13) and elastic recovery (87 and 88%) [13, 14], overstoichiometric hafnium and tantalum diboride films substantially exceed all films and differ in the structure and approach diamond. The high mechanical properties of diamond are known to be achieved due to its electron structure with the formed sp^3 bonds. The high level of the strength properties of the discussed nanocomposite coatings is substantially due to their nanosized grain structure. However, in a number of cases, the physicomechanical properties of nanosized films are worse than those of bulk samples; the hardness of the films is lower (sometimes by two to three times) than the maximum values for the corresponding bulk compound. Thus, the problem of the superhardnesss of synthesized films is not yet properly understood. However, the properties of the formed films undoubtedly depend on both their crystal and electron structures.

The aim of the present study is (1) to perform a comparative analysis of the composition and physicomechanical characteristics of transition-metal diboride films in different structural states and (2) to explain the superhardness effect in nanocrystalline transition-metal diboride films (based on the example of HfB_2).

EXPERIMENTAL

Tantalum and hafnium diboride films were prepared by HF nonreactive magnetron sputtering. Stud-

ies of the structure and physicomechanical properties are discussed in detail in [12, 15].

In the present work, the element composition of highly textured superhard transition-metal diboride films was studied by secondary-ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES). The composition of coatings prepared by sputtering TaB_2 and HfB_2 targets was determined by SIMS using a MC-7201 M spectrometer [12, 15]. The element concentration was determined by a standard procedure [18] using coefficients of relative sensitivity for boron and tantalum, which were determined for the powder of starting target.

In the case of AES, Auger electrons emitted from the surface layer (1–2 nm in depth) of samples are recorded. In the both cases (SIMS and AES), the standardizing method is used to determine the composition of the element. In terms of the method, samples with known concentrations that are similar to those under study are prepared. For comparison, we used an HfB_2 single crystal grown by electron-beam crucible-less zone melting. Samples were 5 mm in diameter and 0.6 mm in thickness. The sample base corresponds to the (0001) plane.

The composition of the hafnium diboride sample was studied by AES using a JAMP-9500F (JEOL, Japan) spectrometer. Before Auger-electron spectra were taken, the sample surface was purified by ion etching. The composition of the studied films was calculated using B_{KLL} and Hf_{MNN} lines with energies of 180 and 1624 eV, respectively.

RESULTS

Studies of the structure, composition, and properties of tantalum diboride films preliminarily prepared at different biases at the substrate (+75, 0, and −75 V) were performed [12]. It was shown that the bias substantially affects the structure and, therefore, the properties of the formed films. Since some problems were not explained in our previous study, we stated that the reported results are estimates and the problems call for further investigation.

Further studies of transition-metal diboride films were performed using an HfB_2 target. Results of a detailed study of the effect of deposition conditions (bias and substrate temperature) on the structure, composition, and physicomechanical characteristics of nanocrystalline hafnium diboride films are reported in [15]. We observed some differences in the sputtering conditions used for HfB_2 and TaB_2 films [11, 12]. It was shown that, in the case of a bias of ±50 V and substrate temperature of ~500°C, overstoichiometric highly textured films are formed, and their nanohardness and modulus of elasticity are 44 and 396 GPa, respectively. We also found the correlation between the composition and physicomechanical properties of hafnium diboride films in different structural states.
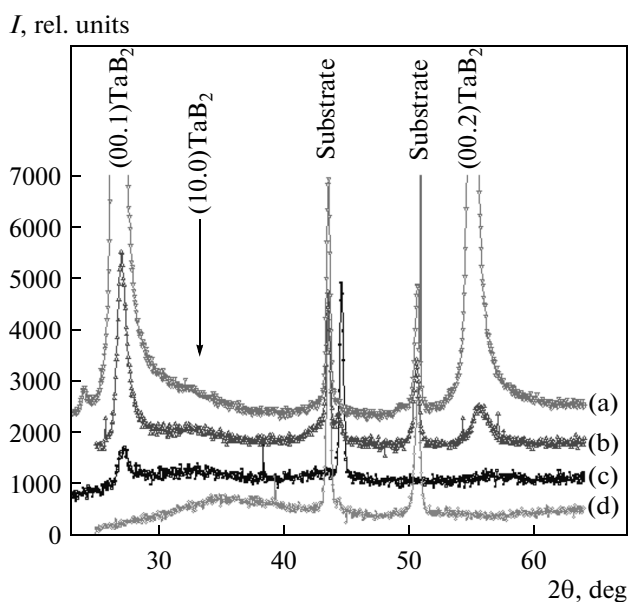

Fig. 1. X-ray diffraction patterns for tantalum diboride films in different structural states: (a) highly textured nanocrystalline; (b) weakly textured nanocrystalline; (c) amorphous-crystalline; and (d) amorphous-like.

Because of this, in the present work, we performed additional studies of the effect of sputtering conditions on the composition, structure, and properties of tantalum boride films.

X-ray diffraction studies of the phase composition of tantalum diboride films (Fig. 1) showed that, depending on the sputtering conditions, the structural state of formed films varies from amorphous-like to textured nanocrystalline. Studies of the physicomechanical properties of the films showed substantial differences in the characteristics of films that differ in the structure (Fig. 2).

The physicomechanical characteristics of amorphous-like films (Fig. 1d) differ substantially from those of nanocrystalline films. The hardness of coatings (prepared at a bias of −25 V) is 11.5 GPa. It was found to be substantially lower than that for stoichiometric bulk tantalum diboride (25 GPa [19]). The elastic modulus of films was also found to be lower (144 GPa) than that for bulk material (262 GPa). The boron-to-tantalum atomic concentration ratio for the amorphous-like films, which was determined by SIMS in [12], was 1.4–1.6.

Heating the substrate to 300°C leads to the crystallization of synthesized films and formation of mixed amorphous-crystalline structure with crystallites 5–10 nm in size (Fig. 1c). This is accompanied by an abrupt increase in the hardness to 29.4 GPa and modulus of elasticity to 232 GPa and an increase in the relative boron-to-tantalum concentration to 1.8. In the case of a grounded substrate holder and a substrate temperature of 500°C (Fig. 1b), the crystallization
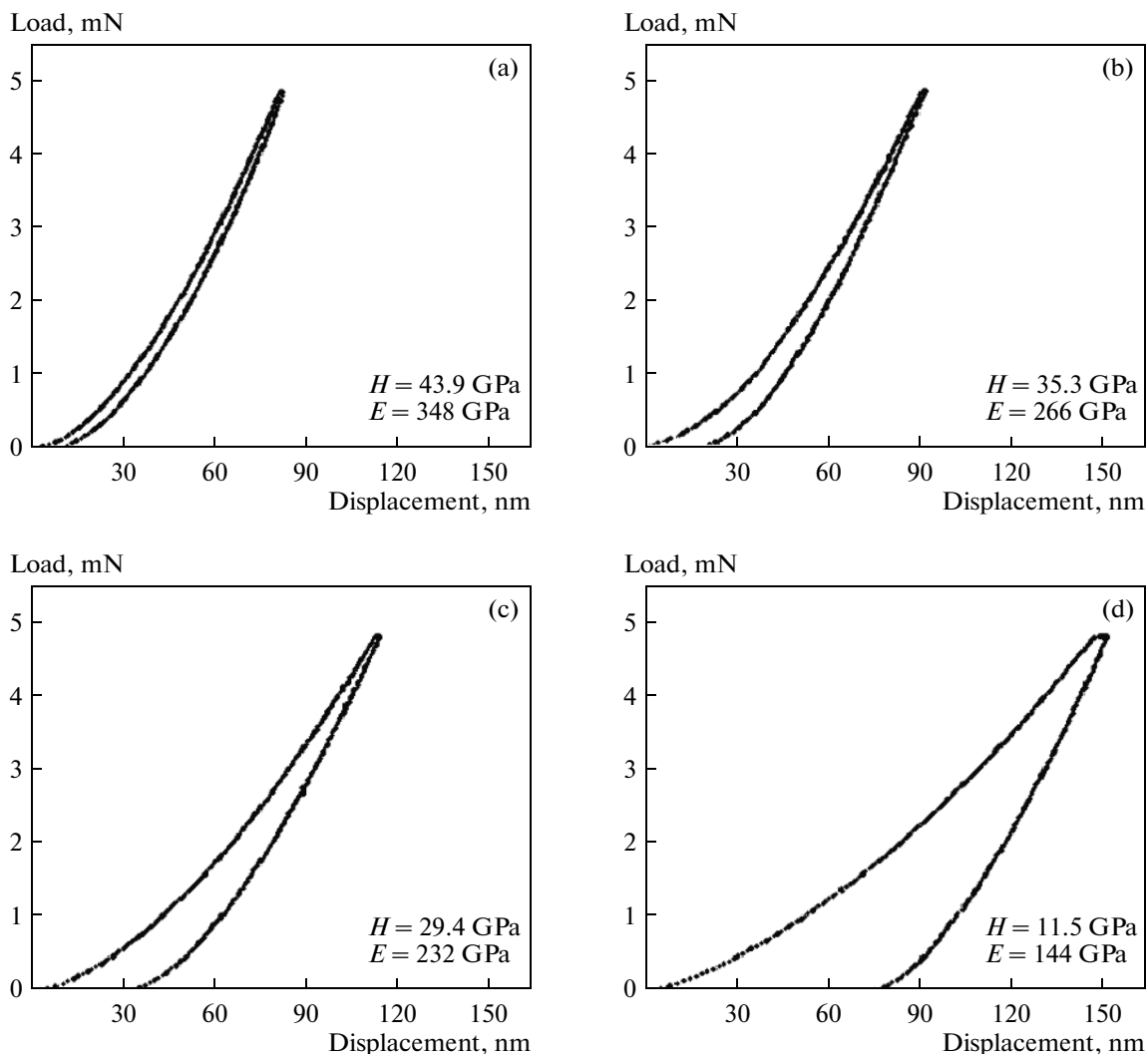
Fig. 2. Berkovich indentation curves for tantalum diboride films in different structural states: (a) highly textured nanocrystalline; (b) weakly textured nanocrystalline; (c) amorphous-crystalline; and (d) amorphous-like.

process continues and leads to the growth of crystallites 15–24 nm and the formation of growth texture in plane (00.1). In this case, the boron-to-tantalum ratio (determined by SIMS) is 1.96; within the determination error, the ratio corresponds to the TaB_2 phase. The increase in the substrate bias is accompanied by an increase in the degree of texture of coating and increase in nanocrystallite sizes. The prepared textured coatings with the columnar structure exhibit the increase in the nanohardness and modulus of elasticity from 35 and 266 GPa (for grounded substrate) to 44 and 348 GPa (at a bias of +50 V), respectively. These values agree completely with data on the nanohardness and modulus of elasticity of tantalum diboride films prepared previously at a bias potential of +75 V [12]. The boron-to-tantalum ratios measured for highly textured films are 10–30% higher than that for the starting target powder. The ratios are ~2.2–2.6 and similar to those found for hafnium diboride films [15].

Additional studies of the tantalum diboride films allowed us to analyze the effect of structure on the composition and physicomechanical properties of transition-metal (tantalum and hafnium) diboride films.

Table 1 shows results of studies of the composition, structure, and physicomechanical characteristics of tantalum and hafnium diboride films. A comparison of magnitudes of nanohardness and modulus of elasticity for the coatings, which range from amorphous-like to nanocrystalline structures with growth texture on plane (00.1), allows us to assert that the structural state is the determining factor in the formation of physicomechanical properties of the coatings. Results obtained in the present study indicate a direct correlation between not only the structure and physicomechanical characteristics, but also the composition of synthesized coatings (Table 1).

Table 1. Dependence of the composition and properties of tantalum and hafnium diboride films on their structural state

Structure	Crystallite size, nm	B/M ratio determined by SIMS	Nanohardness, GPa		Modulus of elasticity, GPa	
			TaB_2	HfB_2	TaB_2	HfB_2
Bulky condition			25 ± 0.42	29.1 [14]	262	584 ± 20 [14]
Strong growth texture [00.1]	20—40	2.2—2.4	43.9	44.0	348	396
Weak growth texture	10—15	2	35.6	36.0	266	340
Amorphous—crystalline	5—10	1.6—1.8	26.0	29.0	250	287
Amorphous-like	~1	1.4—1.6	11.5	13.0	144	174

Note that the increase in the boron concentration for highly textured tantalum and hafnium borides films [3—5] was also observed for TiB_2. The HfB_2, TaB_2, CrB_2 [8], and TiB_2 [5] films that have this structure exhibit the highest hardness magnitudes, namely, ~44, ~43.9, 43, and 48.5 GPa, respectively.

The films with less pronounced growth textures are characterized by stoichiometric boron-to-metal ratio equal to 2. This leads to a decrease in the mechanical characteristics, i.e., to the decrease in hardness and modulus of elasticity of CrB_2 films to $H_V = 33$ and $E = 276$ GPa [10], respectively. These results correlate with the data for the HfB_2 and TaB_2. A decrease in the degree of texture (Fig. 1b) leads to a decrease in the nanohardness of HfB_2 and TaB_2 to 36 and 35.4 GPa and a decrease in the modulus of elasticity to 340 and 266 GPa, respectively.

Films with the amorphous-crystalline structure (clusters) demonstrate the substantial broadening of diffraction peaks and decreases in their intensity; in this case, the crystallite size decreases to ~5—10 nm. The cluster films are characterized by understoichiometric boride composition; this fact was previously reported for TaB_2 [12] and HfB_2 [15] films. The transition to the cluster state leads to a further decrease in the hardness and modulus of elasticity to 26 and 254 GPa for HfB_2 and 29.4 and 232 GPa for TaB_2, respectively.

In the case of an amorphous state, halo-like diffraction peak profiles that correspond to (00.1) and (10.0) reflections (Fig. 1c) merged into a single line of reflection (Fig. 1d); a further decrease in the boron-to-hafnium ratio (to ~ 1.4—1.6) [12] takes place. This fact can be explained by a great amount of broken and unformed bonds typical of amorphous state, which lead to a substantial decrease in the hardness of HfB_2 and TaB_2 to 13 and 11.5 and, therefore, in the modulus of elasticity to 187 and 144 GPa, respectively.

Thus, the highly textured tantalum, hafnium, and titanium borides films exhibit the highest nanohardness equal to 43.9, 44, and 48.5 GPa, respectively. The nanohardness was determined by nanoindentation using the Oliver—Pharr technique. In our opinion [24], the difference between the nanonardness magnitudes obtained by Vickers measurements and nanoindentation (with a Berkovich indenter) is related to the fact that Vickers hardness measurements are performed under static conditions, whereas the nanohardness measurements are performed under dynamic conditions. It should be noted the anomalously high elastic recovery magnitudes obtained for the films of titanium (82%) [3], tantalum (88%) [12], and hafnium (87%) [14, 15] borides.

Films with these properties and structures are overstoichiometric; this fact is catching from the physical point of view.

A model is suggested in [20] (Fig. 3), according to which overstoichiometric films contain columns ~20 nm in width that comprise smaller TiB_2 subcolumns ~5 nm in average diameter. The subcolumns are separated by thin B-phase layers (one to two monatomic layers), which in the authors' opinion, explain the high hardness. The composition of overstoichiometric $TiB_{2.4}$ titanium diboride films was determined by electron microprobe analysis (EMA).

In our opinion, the problem of the formation of an overstoichiometric (in boron) composition remains open because the existence of excess boron it is not clear in the case of the sputtering of the stoichiometric target and the formation of stoichiometric TiB_2 subgrains by the scheme given in Fig. 3.

As is known, EMA, SIMS, and AES are based on different physical processes and are indirect, i.e., dependent on the electron structure and binding energy [18]. The study of the composition of superhard films of tantalum (43.9 GPa) and hafnium (44 GPa) borides allowed us to find the ~20%
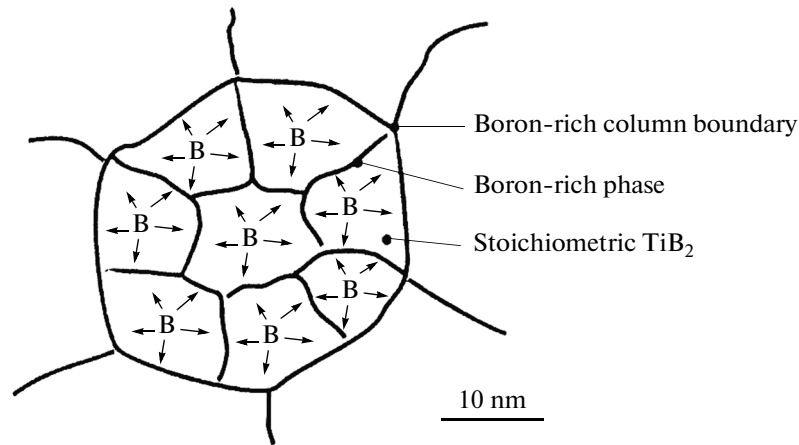
Fig. 3. Schematic diagram of (00.1) growth texture with a column 20 nm in width and formation of B−B bonds with the ⟨00.1⟩ orientation [20].
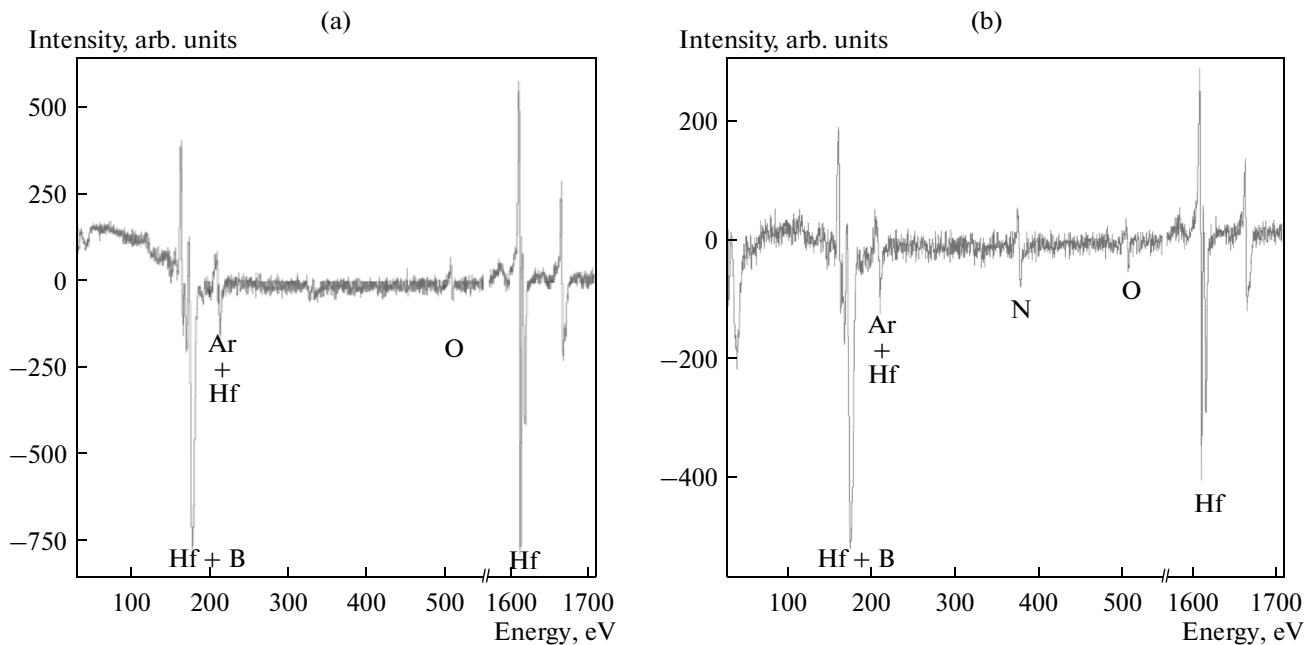

Fig. 4. Portions of high-resolution differential Auger electron spectra indicating groups of B and Hf peaks taken after ion etching (a) stoichiometric HfB_2 single crystal and (b) HfB_x superhard coating deposited on a steel (color "metallic")[14].

enhancement of secondary ion emission (SIE) for boron compared to that for the target (standard). In this case, the SIE for Ta^+ and Hf^+ ions for films and TaB_2 and HfB_2 targets were almost the same. As a result, the boron-to-metal ratio in the superhard films was more than 2; this contradicts the phase diagram (according to [22], the homogeneity range for the TiB_2 phase corresponds to 66−68% B).

The obtained results can be explained qualitatively in terms of the exchange theory of SIE using one of models [18], which shows that an increase in the degree of B^+ ionization is related to the strengthening of the B−B covalent bond. Thus, the observed increase

in the relative boron concentration is likely related to the peculiarities of the electron structure of transition-metal diborides. Because of this, to confirm the obtained data on the element composition of transition-metal diboride films, we used Auger electron spectroscopy. As a standard, we used an HfB_2 single crystal.

Figure 4 shows the portions of differential Auger electron spectra taken after ion etching of the stoichiometric HfB_2 single crystal and superhard HfB_x film (44 GPa) deposited on a steel. Table 2 shows the results of the quantitative processing of the spectra.
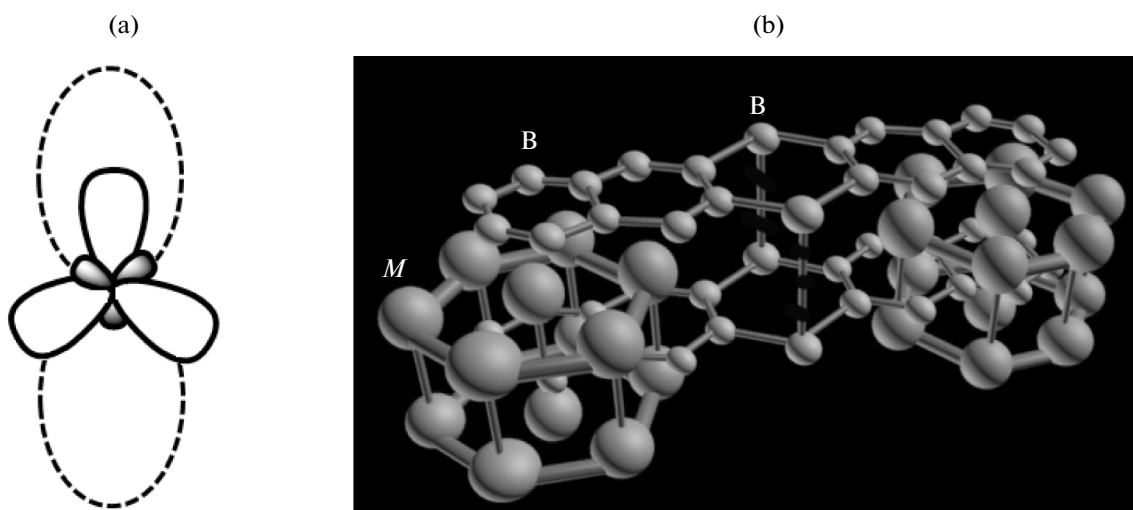
(a)   (b)

Fig. 5. (a) Formation of hybrid sp^2 orbitals and p_z vacant orbital of B atom and (b) scheme of chemical bonds in stoichiometric transition-metal diboride films and formation of B−B bonds.

The ratio of high-resolution Auger electron spectra B_{KLL} to Hf^+_{MNM} is 2.7, which correlates with results obtained by SIMS. We assume that the sputtering of stoichiometric MB_2 target at an applied voltage of ±50 V results in the formation of nanocrystalline superhard films with the columnar structure. To obtain these films, an additional energy is required, which can be supplied to the substrate by heating (to 500°C) or by an increase in the energy of particles that fall onto the growth surface (±50 V is supplied to the substrate).

Our measurements of the relative contents of boron to hafnium and boron to tantalum, which were preformed using AES and mass spectrometry, showed the excess boron content with respect to the stoichiometric composition of samples with the columnar structure. Such a result can be explained in assuming that boride phases with covalent bond are present between stoichiometric superhard columns, i.e., the superhigh strength of HfB_2 and TaB_2 borides, which are realized in films formed from high-energy falling particles, can be related to a change in the B−B binding energy.

The mechanism of the bond formation, which is similar to that in AlB_2 compound, is realized as follows. In the excited state, atoms of the component B with the s^2p^1 electron configuration form three sp^2 hybrid orbitals that make an angle of 120° with each other. The orbital overlap leads to the appearance of σ B−B bonds and the formation of planar hexagonal networks. These networks alternate with close-packed monoballs that correspond to metal (Hf, Ta) atoms.

The electron distribution in boron atom $1s^22s^22p^1$ (Fig. 5a) indicates the existence of a single unpaired $2p$ electron in the outer shell, which has three p^3 functions available for binding. This fact determines the ability of boron atoms to form strong covalent bonds in both boron crystals and in compounds with transition refractory metals; the ability manifests in the formation of characteristic boron-atom chains and networks coupled by strong covalent bonds [22].

When tantalum or hafnium diboride is formed, individual boron atom that have an s^2p valence electron configuration tends to form a stable sp^2 configu-

Table 2. Composition of the HfB_2 single crystal and thin HfB_x nanocrystalline film determined by AES

Sample	Concentration, at %					Hf/B ratio determined by AES
	B	C	N	O	Hf	
HfB_2 single crystal	66.7	–	–	–	33.3	2.0
Hf−B nanocrystalline film deposited on a steel substrate	70.8	–	2.2	0.9	26.1	2.7

ration by single-electron transition $s \rightarrow p$. This results in the formation of stoichiometric transition-metal diboride films.

We assume that the increase in the energy of ions (hafnium, boron) that fall onto the surface favors their transition to excited state $Hf^*(6s^1 4f^{14} 5d^3)$ and $B^*(2s^1 2p^2)$. The valence electrons of hafnium atom in the excited state $(6s^1 5d^3)$ can transfer to the $2p_z$ shell of boron atom (Fig. 5a) in accordance with the classic Grigorovich−Bil'ts theory [23]. In this case, the strong covalent bond is formed between metal and boron and the preference crystal growth direction coincides with the z axis; the B−B covalent bond is formed at the subgrain boundaries.

Thus, the effect of the overstoichiometry is related to the formation of additional B−B (or/and B−M) bond realized within the intergrain space. This leads to the superhardness of formed coatings. This hypothesis was supported also in [25]. Magnetron sputtering of a composite target with a boron-to-niobium ratio of ~1.6 to form Nb−B films leads to the formation of a film with a boron-to-niobium ratio of ~1.8. The NbB_2 films with the weakly pronounced (00.1) texture were formed at a substrate temperature of 300°C and a bias of −50 V. Results of nanoindentation of NbB_{2-x} film exhibit the very high hardness (42 ± 4 GPa) and modulus of elasticity (580 ± 40 GPa). X-ray photoelectron spectroscopic studies of chemical bonds showed the existence of a weak peak corresponding to B−B bond; this agrees with our hypothesis. This hypothesis calls for further studies of electron structure, which will be the matter of our investigations.

CONCLUSIONS

The explanation of the superhardness of transition-metal borides films has been suggested. The formation of superhard stoichiometric films with the columnar structure takes place with increasing energy of boron and metal particles and is caused by changes in the binding energy. The overstoichiometry (in boron) effect, which was observed for films with columnar structures by SIMS and AES, is due to the presence of amorphous-crystalline phase formed within intergrain space.

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