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Influence of deposition conditions and annealing temperature on phase composition and structure of W–B system ion-plasma condensates

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Effects of condensation temperature and subsequent annealing on composition and structure of tungsten boride condensates obtained by ion-plasma sputtering have been studied. In the condensation temperature range 300 to 900°C, the formation of condensates with amorphous/nanocrystalline structure has been found to take place. As compared to the material being sputtered, the condensate composition is characterized by boron atomic deficiency. High-temperature vacuum annealing (T_{ann} = 1100 to 1230°C, $P < 7{\cdot}10^{-4}$ Pa) results in crystallization into lower boride phases, among which the γ–W_2B is most stable. The causes of observed effect are discussed.

Исследовано влияние температуры конденсации и последующего отжига на состав и структуру ионно-плазменных конденсатов борида вольфрама. Установлено, что в исследуемом температурном интервале осаждения 300...900°С происходит формирование конденсатов с аморфно-нанокристаллической структурой. По сравнению с распыляемым материалом состав конденсатов характеризуется недостатком по атомам бора. Высокотемпературный вакуумный отжиг ($T_{отж}$ = 1100...1230°С, $P < 7{\cdot}10^{-4}$ Па) приводит к кристаллизации в фазы низших боридов, из которых при высоких температурах наиболее стабильной является γ–W_2B-фаза. Проанализированы причины наблюдаемого эффекта.

Tungsten borides are among the most prospective materials for industrial applications in machine building and microelectronics [1, 2]. For tungsten borides, very rigid interatomic covalent-metallic bonds are typical, which cause high level of elastic constants, infusibility, high hardness, and chemical stability. Among the known phases of tungsten borides, the most studied is W_2B_5, which possesses a high chemical stability, high thermo-conductivity (28.4 to 30.3 W/m·deg in temperature range 300 to 1300°C) and a relatively high hardness (26 GPa) [3]. The boride W_2B_5 has a hexagonal type lattice (space group D^4_{6h}–$P6_3/mmc$) with layers of metal and boron atoms alternating along the axis c [3]. The metal atoms in W_2B_5 lattice form closely packed layers, while boron atoms, flat and partially bidimensional hexagonal nets [4, 5].

Unfortunately, tungsten boride ceramics in coarse crystalline bulk state is very brittle, that limits its wide application in engineering. One of the promising directions for strength increase and cracking resistance is decreasing the sizes of structural components down to nanometer range, where the prevailing role for improving the strength and crack resistance is played by the atoms positioned at interphase and intergrain boundaries. A substantial content of atoms which do not form a long range order and are positioned in inter-crystallite layer of nano-material, results in formation of a bi-

structural state, i.e. crystalline ordered state and inter-crystallite without long range order one [6]. A high specific contribution of surface atoms may result in change of crystalline ordering type in nanocrystallites, that would stimulate formation of a crystalline structure with minimum surface energy (for instance, going to structural formations containing less than 5000 atoms, the most stable are configurations with fcc lattice or with more sphere-like decahedral and icosahedral ones [7, 8]). The mentioned features allow to expect the borides in ion-plasma nanocrystalline condensates having an unusual structure state, phase composition and functional characteristics. It is worth to note as well that the intended applications of tungsten boride coatings as protective ones including protection of construction elements working at elevated temperatures (1000 to 1300°C), require to study the stability of condensed boride coating composition and structure in this temperature range. Thus, the aim of this work was to study the effects of condensation conditions and high temperature annealing on phase composition and structure of W–B ion-plasma condensates prepared by sputtering the target of the most thermodynamically stable W_2B_5 stoichiometric phase.

The 4–8 μm thick samples were prepared by magnetron sputtering of W_2B_5 stoichiometric target. A planar magnetron sputtering system was used. The substrate was positioned at 55 mm above the anode, and anode-to-target distance was 4–5 mm. During the ceramic film deposition, argon pressure (P) in vacuum chamber was $6 \cdot 10^{-1}$ Pa. The target average sizes were: diameter d = 50 mm, thickness t = 4 mm. The deposition rate was about 0.5 nm/s. As substrates, polished single-crystalline silicon (111) plates were used as well as polycrystalline tantalum plates with melting temperature higher than maximum experimental temperatures in this work. Before the coating deposition, the substrates were held in vacuum $3 \cdot 10^{-4}$ Pa at 950°C to remove any gaseous impurities from the surface. The films were deposited on the substrates heated up to 300–900°C. The films were annealed in a modernized vacuum system at 900–1230°C for 40–60 min under residual gas pressure lower than $7 \cdot 10^{-4}$ Pa (the working vacuum was provided using diffusion pumps). The main components of residual gas were molecular H_2O as well as oil decomposition products from pumping system (C_xH, $CO_x(N)$, etc.).

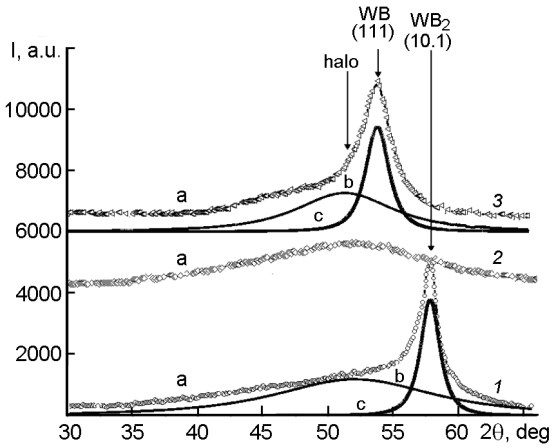

Fig. 1. X-ray diffraction patterns for tungsten boride films obtained at substrate temperatures (T_s, °C): 300 (*1*), 500(*2*) and 900 (*3*) (Fe–K_α radiation). The initial diffraction curve (a) and the diffraction profile separation results into components (b, c).

X-ray diffraction was studied using a DRON-3 diffractometer with Fe–K_α and Cu–K_α radiation, the scattered beam being registered in discrete regime with scanning step in the range $\Delta(2\theta) = 0.01–0.05°$, depending on half-width and intensity of diffraction lines. The exposure duration for a step was 20 to 100 s. The diffraction profiles separated using the overlapped line separation software package "New_profile" developed at NTU "KhPI". The phase volume fractions were calculated using standard technique taking into account both integral intensity and reflectivity of several lines for each phase [9].

Condensation temperature effect on phase composition of tungsten boride films. The scanning in the large-angle X-ray diffraction mode ($2\theta > 10°$) have shown (Fig. 1) that as the single-phase stoichiometric hexagonal α–W_2B_5 target is sputtered, a characteristic feature of condensates deposited on relatively low heated (300–400°C) silicon and tantalum substrates is a diffraction peak of nano-crystalline phase with hexagonal crystalline lattice of *P6/mmm* space group typical of transition metal borides MeB_2 on the "halo-like" profile background of amorphous-cluster component (Fig. 1, curves *1*a, b, c). In the case of W–B system, such a phase may be WB_2, its existence in bulk equilibrium state being evidences by some contradictory data [3]. At the same time, under annealing up to 900°C of non-stressed films separated from the substrate,

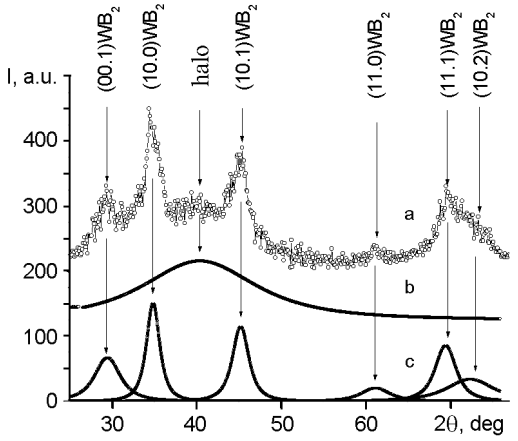

Fig. 2. X-ray diffraction spectrum for annealed (900°C, 1 h) bi-structure films containing amorphous-like matrix and nano-crystalline WB_2 inclusions (Cu–K_α radiation). The initial diffraction curve (a) and diffraction lines separated by computerized processing (b, c).

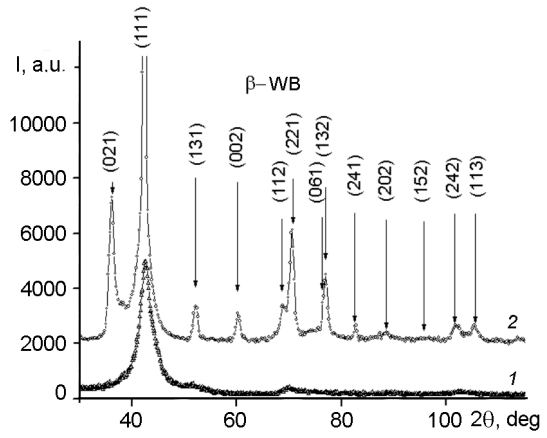

Fig. 3. X-ray diffraction spectrum for a film obtained by magnetron sputtering of a W_2B_5 target at the condensation temperature 900°C prior to annealing (*1*) and after 1 h annealing in vacuum at 1050°C (*2*) (Cu–K_α radiation).

the whole spectrum of diffraction lines typical of this phase is revealed. In Fig. 2, a typical part of diffraction pattern (obtained using more hard Cu–K_α irradiation in order to compress the spectrum) is shown. The calculation of WB_2 phase crystalline lattice parameters using 7 main lines has resulted in $a = 0.3044$ nm, $c = 0.3030$ nm.

The substrate temperature elevation up to $T_{sub} = 500$°C under condensation results in formation of the only amorphous-cluster structure with characteristic angular position of intensity maximum $2\theta \approx 51°$ in diffraction curve obtained in Fe–K_α radiation (Fig. 1, curves *2*a, *1*b, *3*b). It is well known that amorphous-like state is characterized by local short-range chemical ordering similar to crystalline structure [10]. Thus, for layered systems based on tungsten, having no long range, a diffraction maximum is typical positioned close to ordering length $d_a = 0.225$ nm (in Fe–K_α radiation, $2\theta \approx 51°$) corresponding to the first interatomic distance $R_{w-w} = 7.73d_a/2\pi = 0.277$ nm for crystalline tungsten [11].

The condensation temperature elevation up to 800–900°C results in formation of a new type of bi-structural state in the films, where along with amorphous-cluster component, β–WB boride nano-crystallites are present [12] with the (111) strongest diffraction line (Fig. 1, curves 3a, c). The crystallite sizes estimated from the diffraction line broadening (Selyakov-Scherrer equation [13]) are 12–14 nm.

A much more complete spectrum of diffraction lines inherent in high temperature β–WB phase was revealed in diffraction spectra of the films annealed for an hour at $T_{ann} = 1050$°C (Fig. 3, Cu–K_α radiation). Calculation of formed orthorhombic β–WB lattice parameters has given the following values: $a = 0.313$ nm, $b = 0.931$ nm, $c = 0.3071$ nm which differed a little from reference values ($a = 0.319$ nm, $b = 0.840$ nm, $c = 0.307$ nm) [12]. It is seen that the main difference is increased b value. It is to note that, according to equilibrium diagram [14], the β–WB phase has a relatively large homogeneity area that, under boron atomic non-stoichiometry, makes it more stable as compared to α–WB.

Annealing temperature effect on tungsten boride condensate phase composition. After annealing of the samples prepared at relatively high T_{sub} of 500 to 900°C for an hour at 1100°C the lines from the stable phase γ–W_2B most depleted of boron atoms with tetragonal lattice [15] are appeared in the diffraction spectra. The lines of W_2B_5 phase typical of the sputtered target were not revealed under high temperature annealing as well, while, besides of γ–W_2B phase, the lines were registered identified as β–WB ones, the content thereof in the film being dominating for $T_{sub} = 500$°C and commensurable with γ–W_2B phase concentration for annealed sample deposited at $T_{sub} = 900$°C (Table 1). Increasing of annealing temperature above 1200°C did not caused qualita-

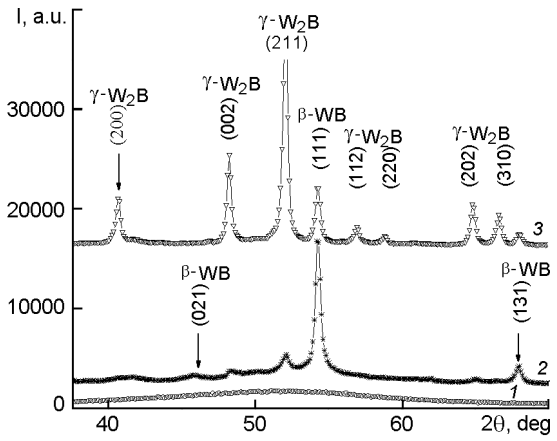

Fig. 4. Changes in the condensate diffraction spectrum due to high-temperature annealing: initial state (T_s = 500°C) (*1*); annealed at 1120°C (*2*); and at 1230°C (*3*).

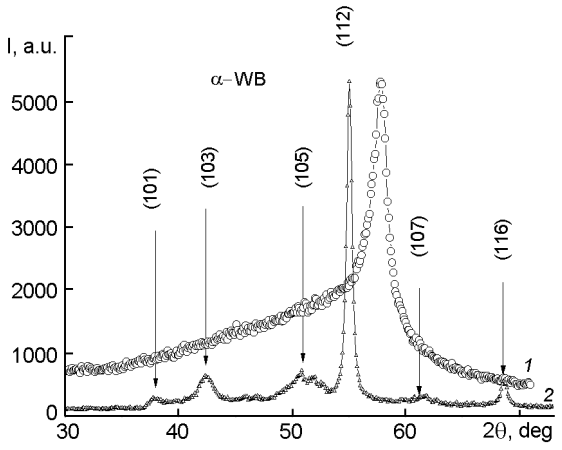

Fig. 5. Sections of the diffraction spectra for condensate obtained at T_s = 300°C: initial state (*1*); annealed at 1230°C for 1 h (*2*).

tive variations in the film phase composition; however, it was accompanied by changes in the quantitative correlations towards stabilization of γ–W_2B phase with the lowest boron content. This is the most pronounced for the samples initially deposited at higher T_{sub} = 900°C (Table 1). In Fig. 4, typical diffraction patterns for different annealing stages of the condensates prepared at T_{sub} = 500°C are shown. It is seen that in the temperature range 1050–1150°C, the crystallization of initial amorphous-cluster structure occurs with formation of the β–WB crystallites with preferential orientation parallel to (111) crystallite plane growth surface.

Annealing at 1200–1250°C results in changing of the crystalline phase ratio with preferential formation of non-textured γ–W_2B-crystallites (Fig. 4, curve 3*)*. Lattice parameters of γ–W_2B-phase were a = 0.5578 nm, c = 0.4745 nm, the c being close to nominal value (0.4744 nm [15]), while a exceeding a little the nominal value (0.5568 nm).

Table 1. Influence of T_{ann} effect on volume content of phases in the films condensed at T_s = 500 and 900°C

T_s, °C	T_{ann}, °C					
	1050		1120		1230	
	β–WB	γ–W_2B	β–WB	γ–W_2B	β–WB	γ–W_2B
500	100 %	–	90 %	10 %	15 %	85 %
900	100 %	–	45 %	55 %	5 %	95 %

In the condensates prepared at lower T_{sub} = 300°C, high temperature annealing gives other results. In this case, the annealing both to 1120°C and to 1230°C stimulates the formation of practically single-phase sample. This is the low-temperature α–WB phase with tetragonal lattice [3] (in some other references, the notation δ–WB is used [16]). In Fig. 5, the areas of diffraction patterns obtained before and after high-temperature annealing are shown for the sample deposited at T_{sub} = 300°C. Considering the causes of α–WB phase formation under high-temperature annealing, the main feature which should be noted is a rather weak influence of thermal factor on the coating structure and elemental composition at relatively low condensation temperature, while the preparation conditions being close to equilibrium. As is seen from Fig. 5, such preparation conditions result in formation of phases structurally close to the hexagonal W_2B_5 being sputtered. Perhaps this is the main cause of phase transition to more stable low-temperature α–WB modification under high-temperature annealing [14], which is accompanied by the simplest reconstruction of initial crystallite hexagonal lattice into tetragonal $I4_1/amd$ type one of the α–WB [3, 16]. It is to note that the α–WB lattice is obtained from hexagonal MeB_2 one by rotation and translation of the layers of triangular prisms formed by tungsten atoms and centered at boron ones [17].

Basing on the results obtained for phase compositions of as-prepared and annealed condensates, it could be supposed that, due to high diffusion mobility characteristic

typical of nano-crystalline materials (especially for grain-boundary diffusion) [18], boron atom deficiency in the coating takes place already during the formation process, which is increases as the condensation temperature is elevated. Indeed, as the time-of-flight secondary ion mass spectrometry (as described in [19]) has shown, the increase of substrate temperatures results in changing the atomic ratio boron/tungsten in the samples. The change of B/W signal ratio as compared to reference value indicates a decrease of boron atoms content in the films condensed at higher substrate temperatures. While the atomic ratio corresponds to $WB_{2.19}$ formula for the samples prepared at $T_{sub} = 300$°C, this is described by $WB_{1.39}$ for the films deposited at $T_{sub} = 900$°C (Table 2). It should be noted that the atomic ratio remains almost constant over the film thickness (of the order of microns) except for a thin (5–7 nm) subsurface layer near.

It is well known that formation of interstitial phases of transition metals results in transformation of the metal electron spectrum [20]. However, in the direction TiX → WX (X is a non-metal atom: C, N, B), d^5 state stability degree increases sharply while that of *sp* configuration, for instance, boron atoms, drops, i.e. the covalent component of Me–X bond decreases [20]. Thus, thermal stability of tungsten based interstitial phases is relatively low. This feature manifests itself most clearly under vacuum annealing of coatings and films of micrometer scale thickness. It was found that under annealing of the tungsten carbide coatings at $T > 1100$°C in vacuum $(0.13 \text{ to } 1.3)\cdot 10^{-1}$ Pa, intense decarbonization takes place as a result of easy carbon diffusion to the surface and formation of volatile carbon compounds with residual gas atoms [21–23]. For such subsurface oxidation and formation of volatile carbon compound, a water vapor pressure as low as 10 ppm is sufficient [21].

In the bulk state, a relatively weak bond between tungsten and interstitial atoms (C, N, B) was revealed when studying the tungsten boride stability in nitrogen atmosphere. It was found that already at 800 to 900°C, nitrogen starts to react intensely with tungsten borides (W_2B, WB, WB_2) and form boron and tungsten nitrides [24]. The results obtained in this work indicate as well that already at the W–B film formation stage, depletion of light boron atoms occurs. In this case, the bonding between tungsten and boron atoms in obtained "amorphous-cluster" and "amorphous-nano-crystalline" ion-plasma condensates remains weak enough to cause a further film depletion of boron atoms under high-temperature annealing. Thus, the annealing is followed by film phase composition variation towards low-boron compounds with one-dimensional isolated arrangement of boron atoms in tetrahedral voids of metal lattice (γ–W_2B-phase). It should be noted that the decrease of boron concentration in tungsten boride lattice is stimulated by compressive macrostresses developing in the films during their condensation [25]. The starting temperatures of intense boron diffusion in tungsten boride corresponding to the first (800–900°C) and second (1100–1230°C) stages of phase transformations associated with decreasing boron content in condensates, namely, with the lowest boride γ–W_2B formation, correspond to energy range 0.10 to 0.12 eV. The average energy of the film-forming atoms deposited from ion-plasma beams (for the deposition conditions used in this work, the average energy is 10 to 17 eV [26]) is one order higher than the calculated values necessary for high boron diffusion mobility in tungsten boride. Moreover, heavy tungsten atoms bombarding the growing coating intensify the depletion effect of light boron atoms in subsurface layers due to their ballistic sputtering from the growth surface [27]. The action of both factors may explain the decreasing boron/tungsten atomic ratio under condensation. Thus, the condensates formed by a W_2B_5 target ion-plasma sputtering have amorphous-cluster, or amorphous-nanocrystalline structure. The phase composition of formed nano-crystallites corresponds to tungsten borides lower than the target material. The formation of the lowest borides under condensation is caused by decrease of relative boron atomic concentration in the film during its formation as a result of physicochemical and radiation stimulated processes. The annealing of the condensates

Table 2. T_s effect on boron/tungsten atomic ratio in condensates obtained by W_2B_5 target sputtering

Substrate temperature at condensation, T_s, °C	B/W ratio in the films
300	$WB_{2.17}$
500	$WB_{2.09}$
700	$WB_{1.69}$
900	$WB_{1.38}$

in the 1100 to 1230°C range results in predominated formation of γ–W_2B crystallites with isolated boron atomic arrangement in tetrahedral voids of tetragonal tungsten atomic lattice. Among the transition metal borides, such structure corresponds to the strongest Me–Me bond.

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Вплив умов одержання і температури відпалу на фазовий склад та структуру іонно-плазмових конденсатів системи W–B

О.В.Соболь

Досліджено вплив температури конденсації та подальшого відпалу на склад і структуру іонно-плазмових конденсатів бориду вольфраму. Встановлено, що досліджується, температурному інтервалі осадження 300...900°C відбувається формування конденсатів з аморфно-нанокристалічною структурою. У порівнянні з матеріалом, що розпилюється, склад конденсатів характеризується браком атомів бору. Високотемпературний вакуумний відпал ($T_{від}$ = 1100...1230°C, $P < 7{\cdot}10^{-4}$ Па) призводить до кристалізації у фази нижчих боридів, з яких за високих температур найбільш стабільною є γ–W_2B-фаза. Проаналізовано причини ефекту, що спостерігається.