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Structure of tantalum diboride thin films deposited by RF-magnetron sputtering

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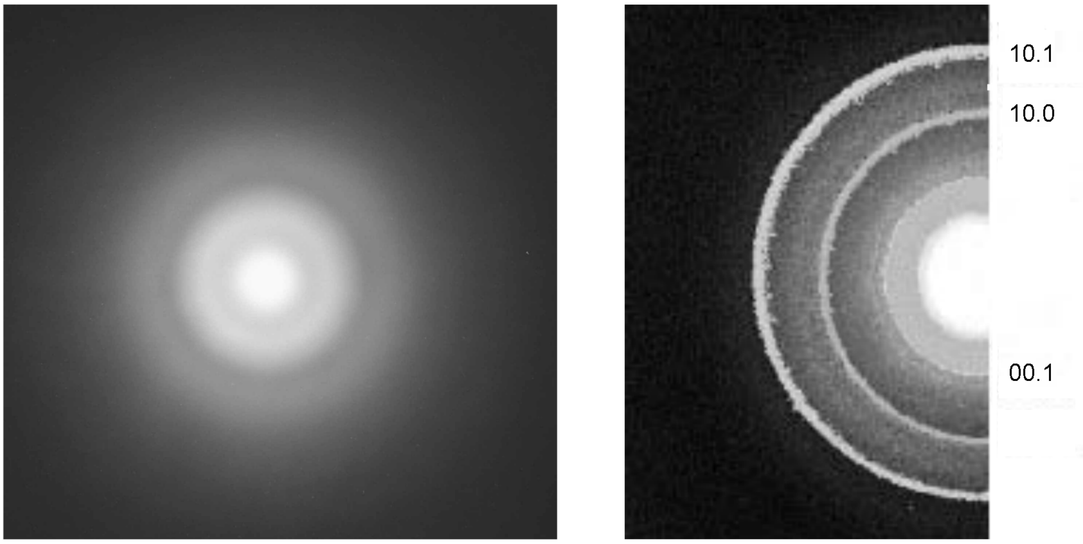
The tantalum diboride films have been deposited in various conditions by non-reactive RF magnetron sputtering. The film phase compositions and structures have been determined by X-ray diffraction, secondary ion mass spectrometry, and electron microscopy. The effect of the substrate temperature and of positive bias potential value on the texturing extent and phase composition has been defined. Some general regularities of the film growth have been established: the formation of quasi-amorphous structure and its transition to textured condensate with various texturing extent.

Методом нереактивного ВЧ-магнетронного распыления при различных условиях осаждения получены пленки диборида тантала. С помощью рентгеновской дифрактометрии, вторичной ионной масс-спектрометрии и электронной микроскопии исследованы их фазовый состав и структура. Изучено влияние температуры подложки и величины положительного потенциала смещения на изменение степени текстурированности и состава получаемых покрытий. Установлены некоторые общие закономерности роста пленок: образование квазиаморфной структуры и ее переход в текстурированный конденсат различной степени совершенства.

Borides of transition metals are rather attractive materials for wide scale application in various fields of machine-building, metallurgy, instrument-making, chemical industry, etc., due to their high thermodynamic stability, hardness, electric conductivity in combination with high melting temperatures. Thin films prepared on the basis of those materials provide a still larger application field thereof, in particular, as diffusion barriers in micro-electronics. Titanium, zirconium, wolfram and chromium diborides [1–6] have been studied most comprehensively and find practical application. The formation peculiarities of thin films of tantalum diboride (TaB_2) being typical representative of transition metal boride class (melting point 3037°C, microhardness 25 GPa [7]) have been studied insufficiently till now. The growth peculiarities of tantalum boride thin films prepared by RF magnetron sputtering on silicon substrates have been investigated in [8]. A strong influence of negative bias potential applied to the substrate on the structure, phase composition, and electrical properties of the coatings is noted. In this work, the structure and composition of TaB_2 films prepared on steel substrate by RF magnetron sputtering in argon atmosphere are studied depending on the deposition conditions.

A sintered TaB_2 disk of 120 mm diameter was used as the target. The operating pressure was 0.32 Pa, the generator power 500 W, the bias voltage being varied in the range of 0 V (earthed base) to +75 V, deposition time being 10–90 min. The film thickness was determined by multi-beam in-



a b

Fig. 1. Microdiffraction patterns for various areas of TaB_2 thin films.

terference technique on a MII-4 microscope, the structure and phase composition were examined by X-ray diffraction (DRON-3) using CuKα radiation (Ni filter). The coherent dispersion area value (CDA) was calculated using improved approximation method (Smyslov-Mirkin). The coating composition was checked by SIMS method (MS-7201M). The relative atomic concentration (boron to tantalum) was determined by standard technique [9] using the relative sensitivity coefficient of boron to tantalum found for powder of initial target. Electron microscopic studies were carried out using a JEM-200A apparatus. The texturing extent of the coatings was evaluated using orientation factor f_{hkl},

$$f_{hkl} = \frac{I_{hkl}}{F_{hkl}} \Big/ \sum_{hkl} \frac{I_{hkl}}{F_{hkl}} \quad ,$$

I_{hkl} being diffraction peak intensity from the chosen surface; F_{hkl}, dispersion factor for that surface, determined for the powder of target (untextured sample).

The most essential factors stimulating the ordering processes in growing film are known to be thermal heating and radiative influence of high-energy particles (atoms and ions) bombarding the film. The method of RF magnetron sputtering is characterized by a rather low energy (1 to 50 eV) of particles being condensed. At the same time, any growth surface contains numerous dangling atomic bonds, which define the mobility of particles in the adsorbed layer. Therefore, in these conditions, it is just the thermal factor that contributes most considerably to the ordering processes.

The heating of the substrate surface layer and growing film may also occur under bombarding with electron flow. Hence, the studied films were prepared in different techniques:

I — on earthed substrates without preheating;

II — on earthed substrates heated to 773 K (the heater power remaining constant during the whole deposition time);

III — under positive bias potential U = +75 V and without preheating;

IV — under positive bias potential U = +75 V on the base heated to 773 K (the heater power remaining constant during the whole deposition time).

The coating thickness was varied depending on the deposition time and technique and amounted 0.05 to 1.5 μm. The other conditions being the same, the greatest thickness values were obtained using the technique I, the least ones, by the IV one. The characteristic feature of all studied films is that till a certain thickness (h_c), all of them had quasi-amorphous structures (by X-ray diffraction data). At the same time, besides of diffuse rings typical of the case (Fig. 1a), areas with micro diffraction pictures typical of ordered tantalum diboride polycrystals (Fig. 1b) have been revealed. Such results allow to conclude the existence of an amorphous-crystalline structure typical of thin films obtained under heavy supercooling (and consequently under high supersaturation in the absorption layer), that

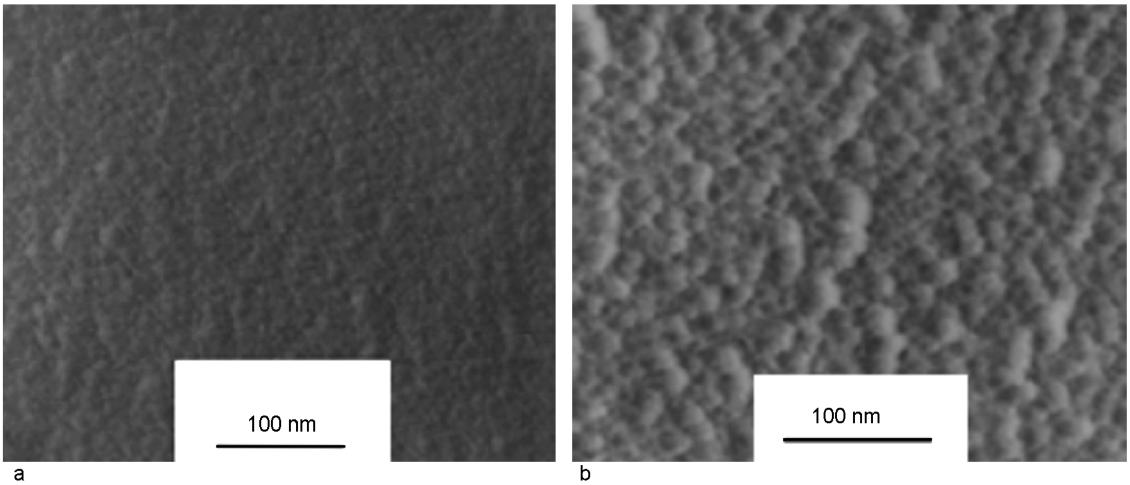


Fig. 2. Microphotos of film surface: a) thickness less than h_c; b) thickness exceeding h_c.

structure being due also to the dimension factor influence [10, 11].

The "critical" thickness values h_c vary depending on the preparation technique (see the Table). The films with thickness exceeding h_c are characterized by the presence of clear reflexes allowing to identify TaB_2 phase reliably. Such structural rebuilding may occur under the influence of high internal stresses and is accompanied by appreciable increasing grain size and more pronounced three-dimensional growth character (Fig. 2). Another characteristic feature of films having thickness exceeding h_c is the presence of a texture. The texture was grown in the <00.1> direction perpendicular to the coating growth front for all preparation methods. The texture extent varied depending on the preparation method: the greatest one was observed in films deposited by the III method, the least one, in those obtained by the method II (Fig. 3). X-ray diffraction patterns of films deposited by the I and IV methods looked like that shown in Figure 3b, only absolute peak heights of reflections from (00.1) and (00.2) planes and their ratio being varied.

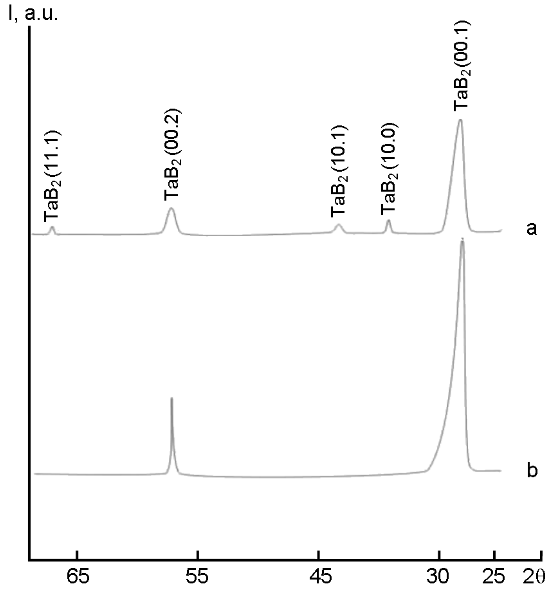


Fig. 3. Typical X-ray diffraction patterns of coating obtained by: a) II method, b) III method.

Variations in structural characteristics of obtained films depending on the method of preparation has been noted, first of all, differences in CDA size and lattice parameters (see Table). The latter could indicate variations in defectness degree of studied film coatings and, as a result, deviations from stoichiometric composition [12]. The

Table.

Deposition method	T, K	Bias voltage, V	h_c, nm	CDA, nm	Δa, nm	Δc, nm	h, nm	C_B/C_{Ta}
I	273	0	35	35	–	+0.0052	850	1.9
II	773	0	15...20	24	+0.00621	+0.0001	800	2.0
III	273	+75	20...25	25	–	+0.0040	820	1.8
IV	773	+75	10...15	28	+0.01489	+0.0052	750	1.9

increase of the lattice parameter "*c*" could be induced, besides of high macroscale stresses, by large number of vacancies in non-metal sublattice, while increase of "*a*", by vacancies in metal one. This is confirmed by the results of SIMS examination.

Summarizing the study results, it could be concluded that the substrate heating in the course of the coating deposition favors a reduction in the texture extent and reduces the structure defectness. A positive bias potential applied to the substrate, though reducing the defectness, increases considerably the texturing of coatings obtained. During the experiments, the substrate temperature monitoring has shown the temperature to be set in the range 343–353 K during 10:15 min and not to be changed further when depositing film by the I method. When depositing by the III method, the temperature was being set in the range 363–373 K during the same time. The electron bombardment in the involved energy range seems to cause only heating of the upper surface layers of growing film and do not result in producing some visible radiation-induced damage. As a result, lowering of the stress level in condensate occurs, atomic mobility in adsorbed layer being increased somewhat as well, that is reflected in reduced defectness of obtained structures. The texture formation in tantalum diboride films seems to be due to the presence of temperature gradient on condensation surface and to its value (the greater is the gradient, the higher is the texturing extent). Considering the results obtained, it is possible to make the following conclusions. The substrate heating promotes formation of least textured coverings with simultaneous increase of the grain size and decrease in the structure defectness. The effect of positive bias potential corresponds as a whole to the effect of thermal factor. However, some radiation effect is also possible resulting in increased structure defectness, number of the nucleation centers on the growth surface, and in the total structure thinning of the coatings.

Thus, the structure characteristics of tantalum diboride films depend essentially on the sputtering conditions and are due to the effect of radiant heating factors. The structures closest to equilibrium are formed at additional heating of substrates up to at least 500°C. The quasi-amorphous structure is formed at an initial stage of film growth in all cases. It transits into textured condensate with various texturing extent as the coating thickness increases. Distinctions in film structures should certainly influence their physical and mechanical properties.

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Структурні характеристики тонких плівок диборида танталу, одержаних ВЧ-магнетронним розпиленням

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Методом нереактивного ВЧ-магнетронного розпилення при різних умовах осадження отримано плівки диборида танталу. За допомогою рентгенівської дифрактометрії, вторинної іонної мас-спектрометрії та електронної мікроскопії досліджено їхній фазовий склад і структуру. Вивчено вплив температури підкладки і величини позитивного потенціалу зсуву на зміну ступеня текстурованості і склад одержаних покриттів. З'ясовано деякі загальні закономірності росту плівок: утворення квазіаморфної структури та її перехід у текстурований конденсат різного ступеня досконалості.