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Effect of RF-magnetron Sputtering Parameters on the Structure of Hafnium Diboride Films

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The study reports about effect of energy factor on the structure formation of nanocrystalline hafnium diboride films. It was shown, that in the magnetron sputtering the change of energy density $\mathcal{E}_{bi}$ delivered to growing film by bombarding ions occurring due to changing in substrate bias potential U_s and ion current density j_s, leads to the formation of hafnium diboride films with various structural states from nanoclustered to nanocrystalline with a growth texture in plane (0.01) and nanocrystallites size from 2.3 to 20 nm respectively.

Keywords: Magnetron discharge, Hafnium diboride, Bias potential, Structure, Ion current.

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1. INTRODUCTION

Deposition of refractory compounds nanocomposite coatings [1] including nanostructured coatings of transition metals diboride (TiB_2, CrB_2, TaB_2, HfB_2, e.t.c.) causes high interest due to their high hardness, thermal stability and corrosion resistance [2, 3].

As a rule, transition metals diboride coatings (TMB_2,) are obtained by ion-plasma methods, often DC- and RF-magnetron sputtering in argon medium from a composite sintered target.

The influence of the sputtering parameters in obtaining these coatings plays a decisive role in the formation and growth of the films.

Changing the external parameters of the magnetron sputtering processes (working pressure, discharge power, substrate temperature, target-to-substrate distance, substrate bias potential) makes it possible to vary the plasma parameters in a wide range [4]. Accordingly, the fluxes of charged and neutral particles change taking part in the deposition and formation of films on the surface of substrate are changed, which makes it possible to obtain coatings of different structure and composition with different physico-mechanical properties [5].

In review [4] J. Musil generalized the tasks that must be solved for development of new promising superhard nanocomposite coatings.

Some of them are a detailed study of the relationship between the properties of the coating and the energy delivered by the ions to the growing surface.

According to the results [6], the main parameters that effect on the atoms mobility and determine the mechanism of growth and structure of the film deposited by DC-magnetron sputtering is the heating of the substrate i.e. ratio T_s/T_m (where T_s and T_m – the substrate temperature and the melting point of the film material, respectively) and ion bombardment of the growing film. shows Dependence of the film structure on the energy density $\mathcal{E}_{bi}$ delivered to the growing surface by bombarding ions was studied iIn the paper [7], The contribution of the thermal component can be neglected in this case, since its value is comparatively small.

Energy density $\mathcal{E}_{bi}$ delivered to growing film by bombarding ions has a major influence on the structure, microstructure, elemental and phase composition and physical properties. In magnetron sputtering systems, according to the formula proposed in [7], the value of $\mathcal{E}_{bi}$ can be controlled by the bias potential supplied to the substrate U_s and ion current density j_s.

The aim of this paper is the study of the effect of the substrate bias potential U_s and ion current density j_s on the formation of HfB_2 films structure deposited by RF–magnetron sputtering.

2. EXPERIMENTAL METHODS

A horizontal RF-sputtering system based on a planar magnetron have been used in this work for the deposition of HfB_2 films, designed to use standard round targets with a diameter 120-125 mm and thickness up to 10 mm. The magnetic field of the magnetron with intensity about 4×10^3 A/m on the surface of the target have been created by a set of annular permanent magnets (Co-Sm) with a steel polar tip. The generator UV–1 (13,56 MHz, 1 kW) was used as a source of RF power, connected to the load by means of a matching device, which is an L-circuit of tunable reactive elements, and a blocking capacitor, providing for the appearance on the target of negative self-bias. The substrate holder electrically insulated from the housing of the installation by ceramic insulators and is intended for fastening plate-like substrates. A DC-voltage source connected to the substrate holder through the high-pass filter, allowing a bias potential on the substrate in the range from – 100 to +100 V. The values of the bias potentials and ion currents on the target and substrate are monitored by pointer instruments (measurement error ±5%). The samples heated by means of a tungsten glowing spiral with a diameter 2 mm. The chromel-alumel thermocouple provides temperature control up to 1100 K. A schematic diagram of the sputtering system is shown in Fig. 1.

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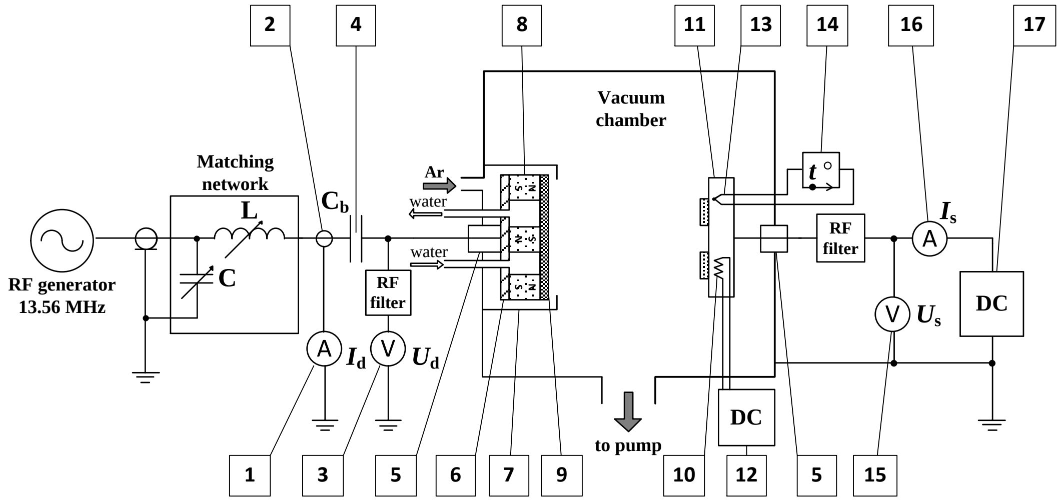

Fig. 1 – Scheme of magnetron sputtering system: 1 – discharge current indicator; 2 – Rogowski coil; 3 – negative self–bias potential on target indicator; 4 – blocking capacitor; 5 – insulator; 6 – unbalanced magnetron; 7 – anode; 8 – permanent magnet; 9 – target; 10 – substrate holder heater; 11 – substrate holder; 12 – substrate holder heater`s power supply; 13 – thermocouple; 14 – temperature sensor; 15 – indicator of the substrate bias; 16 – ion current indicator through the substrate holder; 17 – DC power supply for the substrate bias application

Sputtering of a hot-sintered target HfB_2 was carried out in a plasma of Ar^+. Hafnium diboride coatings were deposited on stainless steel substrates 12X18H10T (20 × 10 × 3 mm) pre-polished to roughness R_a = 0.25 μm. The pressure of the residual gases in the chamber before deposition was $2 \div 3 \times 10^{-3}$ Pa. During spraying the working gas pressure was 0.87 Pa; RF–generator power was 500 W. The bias potential applied to the substrate was varied from +50 to – 50 V relatively to the ground in 25 V increments. Distance between the target and the substrate was $d_{S\text{-}T}$ = 60 mm. The substrate temperature was maintained at ~400 °C. The deposition time was 60 min for all modes. Under these conditions, HfB_2 coatings having an average thickness ~ 1 μm.

X-ray diffraction researches of the material structure were carried out on an automated diffractometer DRON-3. The CuKα radiation (wavelength 0.154 nm) and the Bragg-Brentano focusing method θ-2θ (2θ – Bragg angle) were used in the shooting. The values of current and voltage on the X-ray tube were 20 mA and 40 kV. Shooting of specimens was carried out with horizontal slits of 4 mm on the tube and of 1 mm on the detector in continuous registration mode with a rate of 1°/min in a 2θ angle range from 25° to 60°. Calculation of the nanocrystallites size D and microdeformation $<\varepsilon>$ was performed by Sherrer method.

3. RESULTS AND DISCUSSION

In the earlier analysis [8] of the physical processes in formation of nanocrystalline transition metals diboride films was shown, that optimal parameters in DC-magnetron sputtering were the bias potential of – 50 V and the substrate temperature 550 °C. There was formation of strongly textured superstoichiometric films $TiB_{2.4}$ with the best physico-mechanical characteristics: nanohardness 48.5 GPa, modulus of elasticity 430 GPa and elastic recovery 80% [9]. As shown in [10], the strongest texture of TiB_x films formed at substrate bias of –100 V, and substrate temperature of 175°C. Strongly textured superstoichiometric films with composition B/Ti ~ 2.3-2.4 had nanohardness 48.6 ± 3.1 GPa and elastic modulus of 562 ± 18 GPa, that correlates with previously obtained results. However, in the work [11], in DC-magnetron sputtering of TiB_2 target when substrate bias was varied – 100 V to +100 V nanocrystalline non-textured films were obtained, that is eventually determined their physical and mechanical properties: nanohardness was varied from 13 ± 2 GPa (+100 V) to 23 ± 3 GPa (– 100 V), the elastic modulus from 120 ± 18 GPa (+100 V) to 200 ± 20 GPa (– 100 V). Even more, these features are manifested in RF-magnetron sputtering.

It was found that nanocrystalline tantalum and hafnium diboride films deposited by RF-magnetron sputtering method had the best physico-mechanical characteristics: nanohardness 43.9 GPa and 44 GPa, elastic modulus 348 GPa and 396 GPa, elastic recovery 88% and 87% respectively.

Effect of substrate bias and temperature and the substrate structure on the properties and characteristics of tantalum and hafnium diboride films was studied in [5]. It was shown that without substrate heating the sign and magnitude of the susbstrate bias significantly effect on the formation of the coating structure. According to X-ray diffraction analysis, at zero and positive substrate biases, textured films with preferential growth normally to the plane (0.01) were formed, the presence of a negative potential led to the formation of non-textured films close to the amorphous state. In this case, tantalum and hafnium diboride films with the best physico-mechanical characteristics (H = 44.6 GPa and E = 348.6 GPa for TaB_2; H = 44.0 GPa and E = 469 GPa for HfB_2) were obtained at a positive substrate bias (+50 V).

Comparing the results obtained, it can be noted that the energy conditions leading to the formation of nanocrystalline films depend on the features of the specific experiment.

In magnetron sputtering systems, the value of the energy density $\mathcal{E}_{bi}$ depends on the substrate bias U_s and ion current density j_s on substrate. Dependence j_s on U_s is determined by the current-voltage characteristic, which character is determined by a type (RF or DC) and configuration of the magnetron system. I.e. energy density $\mathcal{E}_{bi}$, delivered to the growing surface is a function of U_s ($\mathcal{E}_{bi} = f(U_s)$). Depending on a value of $\mathcal{E}_{bi}$ the formation of coatings having a different structure from amorphous-like to nanocrystalline is occurred.

The current-voltage characteristics measured on substrates in DC, RF and pulsed magnetron sputtering qualitatively coincide, which is confirmed by the results obtained in DC magnetron sputtering of TiB_2 [12-14] and TiN [15], in RF-magnetron sputtering of Ti [16] and TaB_x [17], as well as for various kinds of DC and pulsed magnetron sputtering systems [7, 18-20]. Should be noted that the properties of the pulsed discharge are identical to the properties of the RF discharge [21], since there are also negative and positive periods in it.

The quantitative difference between the characteristics of DC and RF (pulsed) discharges is that the plasma potential U_p in RF (pulsed) discharge is higher than the plasma potential in the DC discharge. For example, in the work [7] $U_p = +28$ V for pulsed discharge and $U_p = +5$ V for DC discharge. Similar results are presented in the paper [22]: $U_p = +15$ V for RF discharge and $U_p = +3$ V for DC discharge. A characteristic feature is also that the floating potential on the substrate U_{fl} in DC discharge is negative [7, 15], but in RF [23] and Pulsed [7] – positive.

These differences can explain why the formation of nanocrystalline films of transition metal diborides occurs at different substrate biases. Therefore, dependence of I_s on U_s for the magnetron sputtering system shown in Fig. 1. was measured in present work.

Current-voltage characteristics – dependences of the ion (electron) current on the substrate I_s from the substrate bias U_s applied to the substrate at different pressures Ar^+ are shown in Fig. 2. As can be seen from Fig. 2 dependencies I_s from U_s taken at different pressures were practically coicided, so for this experiment the pressure was 0.87 Pa.

The obtained characteristics make it possible to estimate the value of the energy density $\mathcal{E}_{bi}$, delivered to the growing surface by bombarding ions.

Figure 3 exhibits the diffraction patterns of hafnium diboride films which I-V characteristics are shown in Fig. 2.

It was shown by X-ray diffraction studies (Fig. 3 a-f) that depending on the applied substrate bias U_s and ion current density j_s hafnium diboride films (structural type AlB_2) are formed with different structural perfection and nanocrystallites size varied from 2.3 to 20 nm. Table 1 shows the structural characteristics of the HfB_2 films depending on the deposition modes (symbol "–"in the values of current density indicates an ionic component of given quantity).

At the application the positive substrate bias of +25 B and +50 B values of electron current were 70 мA and 160 мA respectively. Due to ion bombardment, the grain size was reduced from 4 to 2.3 nm and nanocluster films were formed.

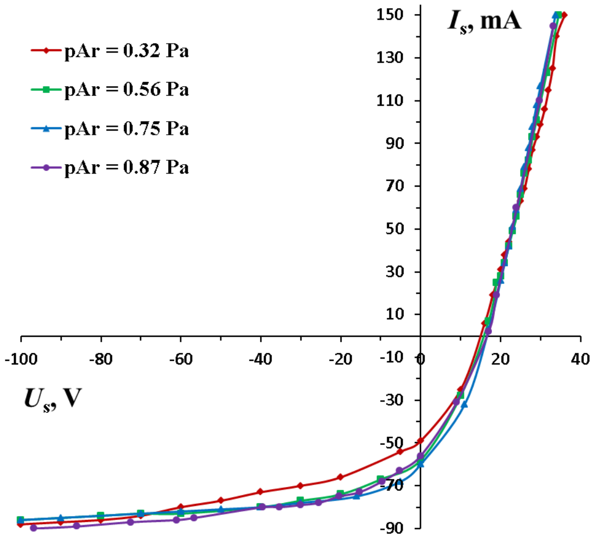

Fig. 2 – Current-voltage characteristics measured on the substrate at different pressures of the working gas. Negative semiaxis I_s corresponds to the ion current on the substrate, and the positive one to the electron

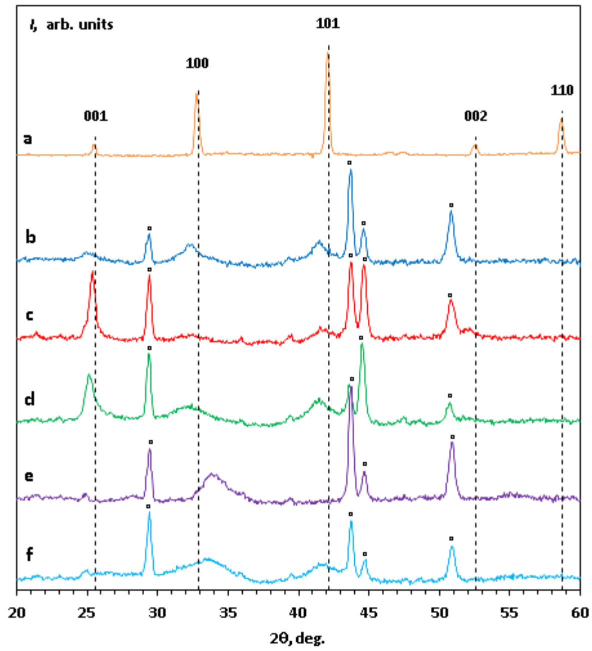

Fig. 3 – Diffraction patterns of hafnium diboride films obtained at different values of the substrate bias: a) target; b) – 50 V; c) – 25 V; d) 0 V (ground); e) +25 V; f) +50 V. The symbol "▪" indicate the reflexes of the substrate

Nanocrystalline films with a weak growth texture normally to the plane (0.01) were formed on the grounded substrates. The lattice parameters were close to tabulated, the nanocrystallines size was 10 nm.

Appling a negative bias potential – 25 B to the substrate adducts to an is resulted in increase of degree texture of hafnium diboride films, which is probably associated with increase in the ion current on the substrate. In this case, the size of the nanocrystallites increases to 20 nm.

Table 1 – Structural characteristics of HfB_2 films

№	Mode		Lattice parameters, Å			D, nm	$<\varepsilon>$
	U_s, V	j_s, mA/cm²	a	c	c/a		
			3.1425*	3.4760*	1.11		
1	– 50	– 1.5	3.1849	3.5315	1.11	8	0.0246
2	– 25	– 1.4	3.1776	3.5110	1.10	20	0.0094
3	0	– 1.0	3.1990	3.5244	1.10	10	0.0071
4	+25	1.1	d_{001} = 2.6291 (2.7212*)			4	–
5	+50	3	3.1689	3.5460	1.12	2.3	0.0277

* – Database of JCPDS

The effect of plasma on the growing surface becomes significant with an increase in the negative substrate bias up to – 50 V. Formation of nanocrystalline non-textured films with strongly blurred diffraction peaks (001), (100) и (101) occurs, and size of the nanocrystallites decreases to 8 nm.

The presented changes in the grain size depending on the deformation and thermal impacts were shown in [24, 25].

4. CONCLUSIONS

The results of carried out study have shown that the total energy contribution to the growing film essentially effects on the formation of its structure in the magnetron sputtering.

Plasma potentials determined by the deposition parameters and the geometry of the magnetron sputtering system, as well as substrate bias, make it possible to vary the energy delivered to the surface, which mainly depends on the current-voltage characteristics measured on the substrate.

Hafnium diboride films with various structural perfection from nanoclustered to nanocrystalline with a growth texture in plane (0.01) and nanocrystallites size varied from 2.3 to 20 nm were obtained.

This work was performed within the framework of a budget themes No 0116U002621 "Physical bases of the formation of the structure and properties of nanostructured transition metal borides, nitrides and boridonitrides films for application in mechanical engineering" and No 0117U002247 "Technological bases of the synthesis of nanostructured, nanocomposite and multilayer coatings of refractory compounds for application in mechanical engineering".

Влияния параметров ВЧ-магнетронного распыления на структуру пленок диборида гафния

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Исследовано влияние энергетического фактора на формирование структуры нанокристаллических пленок диборида гафния. Показано, что при магнетронном распылении, изменение плотности энергии $\mathcal{E}_{bi}$, доставляемой растущей пленке бомбардирующими ионами, за счет изменения потенциала смещения U_s и плотности ионного тока j_s, на подложке приводит к формированию пленок диборида гафния различного структурного состояния от нанокластерного до нанокристаллического с текстурой роста нормалью к плоскости (0.01) и размером нанокристаллитов от 2,3 до 20 нм соответственно.

Ключевые слова: Магнетронное распыление, Диборид гафния, Потенциал смещения, Структура, Ионный ток.

Вплив параметрів ВЧ-магнетронного розпилення на структуру плівок дибориду гафнію

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Досліджено вплив енергетичного фактора на формування структури нанокристалічних плівок дибориду гафнію. Показано, що при магнетронному розпиленні, зміна густини енергії $\mathcal{E}_{bi,}$ що постачається зростаючій плівці бомбардуючими іонами, за рахунок зміни потенціалу зміщення U_s, та щільності іонного струму j_s, призводить до формування плівок дибориду гафнію різного структурного стану від нанокластерного до нанокристалічного із текстурою зростання нормаллю до площини (0.01) та розміром нанокристалітів від 2,3 до 20 нм відповідно.

Ключові слова: Магнетронне розпилення, Диборид гафнія, Потенціал зміщення, Структура, Іонний струм.

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