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Effect of the Magnetron Sputtering Parameters on the Structure and Substructural Characteristics of Tantalum Diboride Films

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The effect of the RF- and DC-magnetron sputtering parameters on the structure and substructural characteristics of protective coatings based on tantalum diboride thin films was studied in this work.The results of the studies showed that the sign and magnitude of the applied bias potential at the use of both types of magnetron sputtering (RF and DC) have a crucial effect on the structure and substructural properties of tantalum diboride films. It was established that nanocrystalline tantalum diboride films of the overstoichiometric composition ($C_B/C_{Ta} \approx 2.2$-2.6) and having strong growth texture in plane (00.1) were obtained at the bias potential of + 50 V and – 50 V in the RF- and DC-magnetron sputtering respectively. Thus obtained films had the best physico-mechanical properties and general substructural characteristic quantities: nanocristallites size of ~ 30 nm, and increased value of «*c*» parameter compared with the tabulated.

Keywords: Magnetron sputtering, Tantalum diboride, Bias potential, Structure, Nanohardness, Elastic modulus.

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1. INTRODUCTION

The problem of obtaining thin films and coatings with predetermined properties and structure refers to one of the most important tasks of modern solid-state physics. This is due to the growing practical use of thin films and coatings primarily in solid-state microelectronics and mechanical engineering [1-3].

The film coatings of transition metal diborides (TiB_2, CrB_2, TaB_2, HfB_2, et al.) are actively investigated owing to their high physical and mechanical characteristics. [4]. Compounds of this type have a high melting temperature, therefore their synthesis in the film state is performed by magnetron sputtering (RF and DC). Titanium boride and boridenitride films are most studied in this class of compounds [5-8], at the same time tantalum borides and boridenitrides are least studied [9, 10]. Methods of control of electro-physical properties of tantalum boride and boridenitride films (~ 300 nm) obtained by reactive and non-reactive RF-magnetron sputtering were studied in these works. Physical and mechanical properties were not studied due to the specifics of these works.

Our preliminary studies [11, 12] showed that the formation process of the film nanostructures in RF-magnetron sputtering is dependent on the parameters of sputtering such as: the structure and temperature of substrate, the power of sputtering, the bias potential applied to the substrate holder.

Therefore, the study of the effect of RF- and DC-magnetron sputtering parameters on the structural and substructural properties of tantalum diboride films is the aim of this work.

2. SPECIMENS, METHODS OF OBTAINING AND RESEARCH OF STRUCTURE

2.1 Specimens

Unbalanced planar round magnetron equipped with a disc target of diameter 100 mm and thickness of 10 mm made of sintered TaB_2 powder was used in the RF- and DC-magnetron sputtering systems. The tantalum diboride coatings were deposited on a substrate 20 × 5 × 5 mm in size made of AISI 302 stainless steel. Substrates were polished to the roughness of $R_a = 0.25$ μm before deposition. Prior to deposition, the substrates were ultrasonically precleaned in acetone and then sputter cleaned in an argon DC discharge. The substrate was fixed in a holder with a clamp and the temperature was measured by a thermocouple at the holder-specimen interface.

2.2 Method of RF-magnetron Sputtering

A horizontal RF-sputtering system based on a planar magnetron was used in this work for the deposition of TaB_2 films.

The upgraded setting UVN-75r-3 was used as a vacuum post. The magnetic field of the magnetron with an intensity about 4×10^3 A/m on the surface of the target is 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.

Schematic diagram of the sputtering assembly is shown in Fig. 1. Sputtering of the target was carried out in Ar^+ plasma. The pressure of the residual gases in the chamber before deposition was $2 \div 3 \times 10^{-3}$ Pa.

The following parameters and conditions were varied during the deposition: working gas pressure from 0.32 to 0.65 Pa; power of RF generator of 500 W; the bias potential applied to the substrate from + 50 to – 50 V relatively to the ground.

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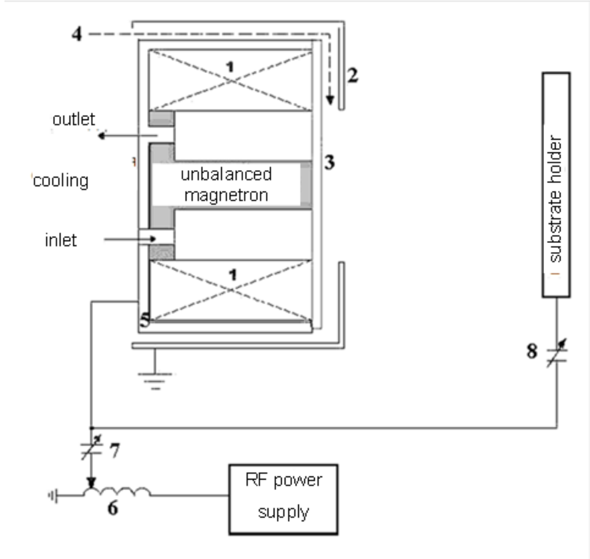

Fig. 1 – Schematic diagram of the RF-magnetron sputtering system. 1 – toroidal magnet; 2 – anode; 3 – target; 4 – inlet of working gas; 5 – the housing of cathode assembly; 6 – the matching coil of variable inductance; 7,8 – the variable matching capacitors

2.3 Method of DC-magnetron Sputtering

Ion-plasma system for the deposition of coatings was assembled on the basis of a vacuum processing unit of the URM3 type (Fig. 2).

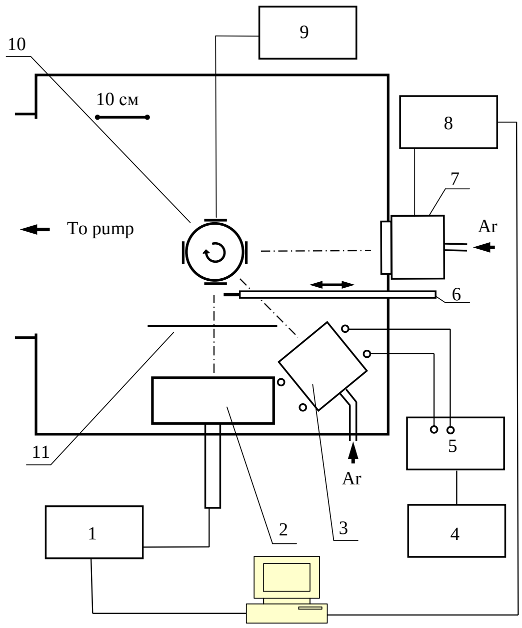

Fig. 2 – The ion-plasma system for the reactive synthesis of coatings based on planar magnetron, RF-inductive couple plasma source and ion source. 1 – DC magnetron power supply; 2 – magnetron; 3 – RF ICP source; 4 – RF generator; 5 – RF matchbox; 6 – probe; 7 – ion source; 8 – DC power supply; 9 – power supply for specimens polarization; 10 – specimens rotation system; 11 – shutter [13]

The composition of the ion-plasma system includes: the low-pressure magnetron located at the end face of the chamber, the RF-inductive couple plasma source located within the chamber, the ion source located on the side flange of the chamber.

The working pressure in the chamber of the sputtering system was ~ 0,1 Pa. The discharge power was 2500-2800 W. The substrate temperature was varied from 200 to 300 °C. The deposition was carried out both at a grounded metal substrate holder and at the application of a positive or negative bias potential. The specimens were placed at a distance of 20 cm from the target, the time of deposition was 30 min. Ion purification was performed directly before deposition by argon ions within 3 min.

2.4 X-ray Diffraction Researches

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 was performed by approximation method.

3. RESULTS AND DISCUSSION

The effect of various substrates on the orientation and structure of the films as well as the effect of the deposition modes on the film growth were studied in previous works [11, 12]. These studies show that the process of formation of the film nanostructures depends on several factors: the structure and temperature of the substrate, the power of sputtering and the bias potential supplied to the substrate.

3.1 RF-magnetron Sputtering

The results of X-ray diffraction researches have shown a significant effect of the bias potential on the structure of the obtained films. The textured films with predominant growth by normal to the plane (00.1) were formed at zero and + 50 V bias potentials supplied to the substrate holder. The supplying of a negative bias potential (– 25 V) led to the formation of untextured amorphous-like nanocrystalline coatings (Fig. 3).

The growth of textured nanocrystalline TaB_2 films occurred in the case of a grounded substrate holder (the bias potential is zero) (in addition to the peaks (00.1) and (00.2), the peaks (10.1), (10.0), (11.1), (10.2) are seen in the X-ray diffraction pattern)) (Fig. 3 a).

The degree of texture of the films increased (Fig. 3 b) at the bias potential of +50 V supplied the substrate holder. The shift in the position of the lines (00.1) and (00.2) occurred in this case.

The supply of a negative substrate bias (– 25 V) most significantly affected on the mechanism of coating formation – an amorphous phase TaB_x was formed (Fig. 3 c).

The lattice parameters were significantly different from the tabulated values (a = 0.30981 nm, c = 0.32266 nm), the parameter a was varied within

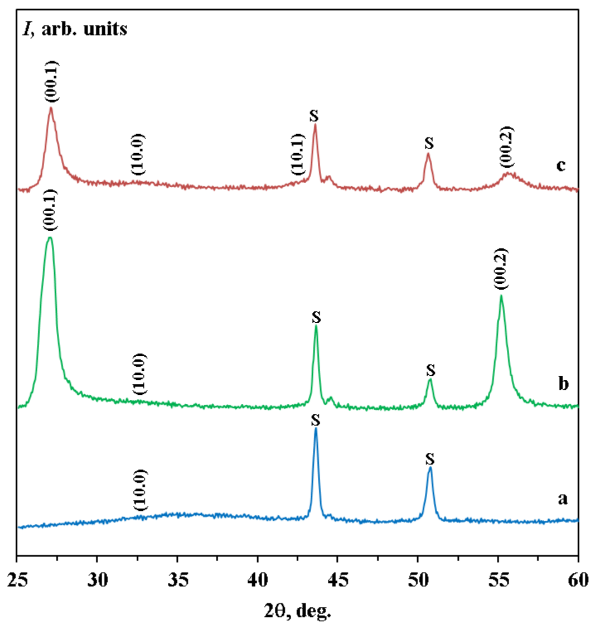

Fig. 3 – X-ray diffraction patterns of tantalum diboride films deposited by RF-magnetron sputtering at different substrate biases: a) –25 V; b) +50 V; c) 0 V. S – the substrate reflections.

0.3157-0.3244 nm, the parameter c = 0.3271-0.3333 nm, which probably reveals on the increased concentration of dissolved boron atoms in the lattice TaB_2. The size of nanocrystallites was varied from 24 to 42 nm. The texture perfection of the formed coatings grew with the increase in the size of nanocrystallites. The level of microdeformation of the lattice was 0.2-0.3 %. The study of physico-mechanical properties showed a significant difference in the characteristics of films obtained at different bias potentials and having different structures. The obtained textured coatings with a columnar structure exhibited an increase in the value of nanohardness and the elastic modulus from 35 and 266 GPa (grounded substrate) to 44 and 348 GPa (substrate bias of + 50 V) respectively. The amorphous-cluster coatings obtained at negative substrate bias are different in their physico-mechanical characteristics from the coatings described above. The hardness of coatings of 11.5 GPa (at a bias potential of – 25 V) is smaller in comparison with hardness of the solid tantalum diboride of stoichiometric composition (25 GPa). The elastic modulus of the films is lower – 232 GPa and 262 GPa, respectively.

3.2 DC-magnetron Sputtering

X-ray diffraction studies show (Fig. 4 a-d) that textured films with preferential texture growth in plane (00.1) and composition close to the stoichiometric phase of TaB_2 (AlB_2 structural type, P6/mmm space symmetry group) were formed at a grounded substrate, a floating potential and a positive or negative bias potential.

The peaks corresponding to the TaB_2 phase – (00.1), (10.1), (00.2) (11.1), (10.2) are shown in the X-ray diffraction patterns (Fig. 4), however, the intensity of the lines is violated: the strongest line (10.1) has an intensity less than line (00.2). This reveals that films were formed nanostructural, i.e. were growing preferentially in plane (00.1). In addition, there was a weak asymmetry of the lines (00.1) and (00.2), which could be due to the absence of the phase stoichiometry or the presence of a stacking faults.

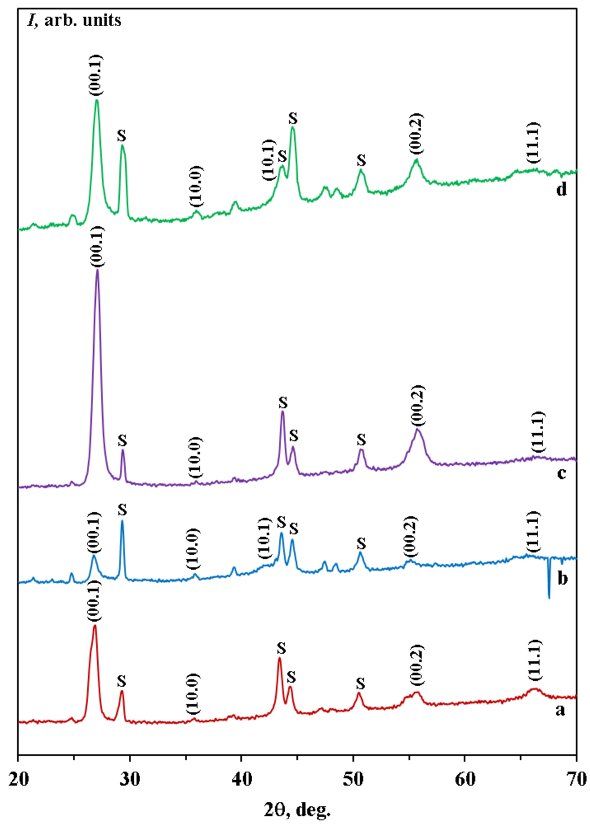

Fig. 4 – X-ray diffraction patterns of tantalum diboride films deposited by DC-magnetron sputtering at different substrate biases: a) ground, gap (specimen 1); b) floating potential (specimen 2) c) – 50 V (specimen 3); d) + 50 V (specimen 4). S – the substrate reflections

The films with a growth texture in plane (00.1) were formed at grounded substrate; a weak asymmetry of peaks (00.1) and (00.2), and peaks of weak intensity (10.0), (10.1), (11.1), (10.2) were observed (Fig. 4 a).

The supply of a negative bias potential of – 50 V (Fig. 4 c) leads to an increase in the degree of texture in plane (00.1). There were only peaks (00.1) and (00.2). The degree of texture decreases substantially at floating potential (Fig. 4 b) unlike the negative one. A diffraction peak corresponding to the plane (10.1) is appeared. This peak has a blurred shape characterizing the nanostructured state of the film. An appeared diffraction peaks (10.0), (00.2) and (11.1) are more intensive. The degree of asymmetry (00.1) and (00.2) is amplified. The supply of a positive bias potential also leads to a significant increase in the degree of texture, there is a significant asymmetry of the peaks (00.1) and (002), which reveals to stacking faults.

Highly textured films obtained at a negative and positive bias potentials (Table 3.1) had lattice parameters: a = 0,3114-0,3117 nm, c = 3,3317 nm, which were substantially larger than tabulated (a = 0,30981 nm,

c = 0,32266 nm).

The parameters decreased in the films obtained at a grounded substrate. The parameter a almost coincides with the tabulated, and the parameter c is decreased in comparison with the previous specimens, but is large relatively to the tabulated.

The values of the lattice parameters (a and c) at a floating potential are differed insignificantly from the tabulated – within the limits of the error.

Table 1 – The structural characteristics of TaB_2 films

Mode	Substrate current, mA	Lattice parameters, nm			Size of nano-crystallite, nm	<ε>
		a	c	a/c		
Ground	–	0,3096	0,33041	1,07	32,668	0,4
Gap	280-320	0,3089	0,32452	1,05	32,293	0,42
– 50 B	20-25	0,3114	0,33317	1,07	32,293	0,42
+ 50 B	650	0,3117	0,33317	1,07	27,798	0,47
		0,30981*	0,3226*	1,04*		

* – Database of JCPDS

The process of formation of tantalum diboride films with a high degree of texture occurs similar to the process of formation of textured titanium diboride and boridenitride films, which have been subjected to the most detailed investigation by C. Mitterer, P.H. Mayrhofer et al. in the works [5-8]. The effect of the sputtering parameters (bias potential, working gas pressure, substrate temperature) on the structure of titanium diboride and boridenitride films was studied in these works.

The formation of titanium diboride films with a column structure and growth texture in plane (00.1) obtained by non-reactive DC-magnetron sputtering of the TiB_2 target at bias potential of – 80 V and without preliminary substrate heating was noted by C. Mitterer with co-workers in one of the first papers [5].

All Ti-B films obtained at the negative bias range of – 50 ÷ – 150 V independently on the change in the other parameters were composed of the hexagonal phase of TiB_2 with the predominant growth orientation in plane (00.1) parallel to surface. Thus the change of parameter c from c = 0.3225 nm to c = 0.32587 nm at substrate temperature T_S = 550°C occurred within the change in applied bias potential from – 50 V to – 150 V, i.e. there was an increase in the parameter «c» for films with a growth texture (00.1) compared to the value calculated for the TiB_2 powder standard (c = 0.3229 nm). Measurement of the chemical composition by the EPMA method showed that all textured films were overstoichiometric with ratio B/Ti ≈ 2.4.

The formation of nanostructured transition metals diboride films without pronounced orientation was noted in the number of works [14, 15].

As was noted in paper [14] the energy supplied to the growing film at substrate bias of – 30 V was insufficient to stimulate the crystallization of film and formation of a growth texture (00.1) even at substrate temperature T_S = 550°C. It was noted that the parameter c = 0.32158 nm decreases compared with the standard (c = 0.32295 nm).

Similarly the titanium diboride films were obtained R.A. Andrievskii and co-workers [15] in DC-magnetron sputtering at substrate bias of – 30 V (U = 1.5 kV). The formation of nanostructured TiB_2 films with a small crystallite size (4-8 nm) occurs in this case. The transition to RF-magnetron sputtering mode at zero bias potential with the conservation of all other parameters leads to a small increase in the crystallite size to 5-10 nm.

The value of the lattice parameters is significantly different from the tabulated values for TiB_2 (a = 0.3025 nm and c = 0.3228 nm). It is noteworthy that the parameter a increases to 0.3048 nm and the parameter c decreases to 0.318 nm.

4. CONCLUSIONS

The results of the studies showed that the sign and magnitude of the applied bias potential have a crucial effect on the formation of structure and substructure of tantalum diboride films at the use of the RF- and DC-magnetron sputtering, that ultimately determines physico-mechanical and electro-physical properties of these films.

It was established that nanocrystalline tantalum diboride films of the overstoichiometric composition (C_B/C_{Ta} ≈ 2.2–2.6) and having strong growth texture in plane (00.1) were obtained at the bias potential of + 50 V and – 50 V in the RF- and DC-magnetron sputtering respectively. It should be noted that obtained films had the best physico-mechanical properties and general substructural characteristic parameters: nanocristallites size of ~ 30 nm, and increased value of «c» parameter compared with the tabulated.

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Влияние параметров магнетронного распыления на структуру и субструктурные харак-теристики пленок диборида тантала

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В работе проводились исследования влияния параметров магнетронного (ВЧ и ПТ) распыления на формирование структуры и субструктурных характеристик защитных покрытий на основе тонких пленок диборида тантала. Результаты проведенных исследований показали, что знак и величина приложенного потенциала смещения при использовании обоих типов магнетронного распыления (ВЧ и ПС) имеет определяющее влияние на формирование их структуры и субструктурных свойств. Установлено, что нанокристаллические пленки диборида тантала сверхстехиометрического состава (СВ/СТа ≈ 2,2-2,6), обладающие сильной текстурой роста плоскостью (00.1) были получены при потенциале смещения + 50 В и – 50 В при ВЧ- и ПТ-магнетронном распылениях соответственно. При этом полученные пленки имели наилучшие физико-механические свойства и общие характерные субструктурные величины: размер нанокристаллитов ~ 30 нм, и увеличенное значение параметра «*c*» по сравнению с табличным.

Ключевые слова: Магнетронное распыление, Диборид тантала, Потенциал смещения, Структура, Нанотвердость, Модуль упругости.

Вплив параметрів магнетронного розпилення на структуру і субструктурні характеристики плівок дибориду танталу

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У роботі проводились дослідження впливу параметрів магнетронного (ВЧ та ПС) розпилення на формування структури і субструктурних характеристик захисних покриттів на основі тонких плівок дибориду танталу. Результати проведених досліджень показали, що знак і величина прикладеного потенціалу зміщення при використанні обох типів магнетронного розпилення (ВЧ та ПС) має визначальний вплив на формування структури, складу і фізико-механічних властивостей плівок дибориду танталу. Встановлено, що нанокристалічні плівки дибориду танталу надстехіометричного складу ($C_B/C_{Ta} \approx 2{,}2$-$2{,}6$), які мають сильну текстуру росту площиною (00.1) були отримані при потенціалах зміщення + 50 В та – 50 В при ВЧ- та ПС-магнетронному розпиленнях відповідно. При цьому отримані плівки мали найкращі фізико-механічні властивості і загальні характерні субструктурні величини: розмір нанокристалітів ~ 30 нм, і збільшене значення параметра «*c*» у порівнянні з табличним.

Ключові слова: Магнетронне розпилення, Диборид танталу, Потенціал зміщення, Структура, Нанотвердість, Модуль пружності.

СПИСОК ЛИТЕРАТУРЫ

1. R.A. Andrievskii, *Ros. Khim. Zh.* **XLVI** No 5, 50 (2002).
2. A.D. Korotaev, D.P Borisov, V.Yu. Moshkov, S.V. Ovchinnikov, Yu.P. Pinzhin, V.M. Savostikov, A.N. Tyumentsev, *Phys. Mesomech.* **8** No5-6, 93 (2005).
3. A.D. Pogrebnjak, A.P. Shpak, N.A. Azarenkov, V.M. Beresnev, *Phys. Usp.* **52**, 29 (2009).
4. R.A. Andrievski, *Russ. Chem. Rev.* **84** No 5, 540 (2015).
5. F. Kunc, J. Musil, P.H. Mayrhofer, C. Mitterer, *Surf. Coat. Technol.* **174-175**, 744 (2003).
6. P.H. Mayrhofer, C. Mitterer, J.G. Wen, J.E. Greene, I. Petrov, *Appl. Phys. Lett.* **86**, 131909 (2005).
7. P.H. Mayrhofer, C. Mitterer, J.G. Wen, I. Petrov, J.E. Greene, *Appl. Phys.* **100**, 044301 (2006).
8. P.H. Mayrhofer, C. Mitterer, L. Hultman, H. Clements, *Prog. Mater. Sci.* 51 No8, 1032 (2006).
9. L. Shun-Tang, L. Chiapyng, *J. Electrochem. Soc.* **150** No 10, 607 (2003).
10. L. Shun-Tang, L. Chiapyng, *Mater. Chem. Phys.* **82**, 691 (2003).
11. A.A. Goncharov, G.K. Volkova, V.A. Konovalov, V.V. Petukhov, *Phys. Met. Adv. Technol.* **28** No 12, 1621 (2006).
12. A.A. Goncharov, V.A. Konovalov, S.N. Dub, V.A. Stupak, V.V. Petukhov, *Phys. Met. Metall.* **107** No 3, 285 (2009).
13. S. Yakovin, A. Zykov, S. Dudin, V. Farenik, A. Goncharov, I. Shelest, V. Kuznetsov, *Probl. At. Sci. Tech.* **107** No 1, 187 (2017).
14. R.A. Andrievskii, G.V. Kalinnikov, N.P. Kobelev, Ya.M. Soifer, D.V. Shtanskii, *Phys. Solid State* **39** No 10, 1661 (1997).
15. R.A. Andrievskii, G.V. Kalinnikov, D.V. Shtanskii, *Phys. Solid State* **42** No4, 760 (2000).