

## MECHANISMS FOR HARDENING FILM MATERIALS: W – Ti – N AND TiN – Cu SYSTEMS AS EXAMPLES

L. R. Shaginyan and A. V. Kurdyumov

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*We have studied the mechanism for increasing the hardness of nanocomposite (W, Ti)N film materials (reactive magnetron sputtering of the alloy W – 30 at.% Ti) and TiN – Cu (reactive vacuum arc vaporization of Ti with simultaneous magnetron sputtering of copper). By studying the composition, structure, and microhardness of condensates obtained under different deposition conditions, we have established a correlation between film microhardness and structure. We have shown that the microhardness of a material based on (W, Ti)N is inversely proportional to the grain size. Limitation of the mobility of film-forming species and their access to the growing grains present on the surface by molecules of the nitrides WN and TiN is the mechanism limiting grain growth. A similar mechanism is also operative in formation of a composite coating based on hard (TiN) and soft (Cu) metallic phases. In this case, copper atoms are a grain growth inhibitor. They do not react with the titanium nitride and are sorbed on the nitride grain boundaries, preventing their growth.*

**Keywords:** nanocomposite film material, structure, film-forming species, microhardness.

### INTRODUCTION

The mechanical properties of a material are determined by its two fundamental characteristics: interatomic interaction and structure. The stronger the binding between atoms and the lower the probability of movement of dislocations, the higher the strength properties of the material. A change in the interatomic interaction energy is achieved by mixing chemically different atoms in different ratios, which makes it possible to create a broad range of alloys and compounds with considerably different properties.

A change in the structure of the material, with the aim of improving its strength properties, is achieved by various methods. Thus we know [1, 2] that the mechanical properties of structurally inhomogeneous (heterogeneous) systems are considerably better than for homogeneous materials. The major physical reason for this is the additional resistance to movement of dislocations provided by structural inhomogeneities. In a one-phase polycrystalline material, grain boundaries act as such inhomogeneities; in multiphase systems (composite materials), in addition to grain boundaries the inhomogeneities can also be interphase boundaries, serving as sites for stress relaxation.

Bulk materials with a heterogeneous structure and small grain size are prepared by various methods: strain hardening and solid solution hardening, hardening by dispersed phases. A fundamentally different method for improving the mechanical properties of bulk materials is deposition of layers on them that have appreciably better mechanical properties. The physical factors providing strength and hardness for the coatings remain the same as for the bulk materials, but the methods for forming a heterogeneous structure with highly dispersed grains should be different.

We especially note that when a coating (or film) is formed from the vapor phase, the grain size in it is *a fortiori* smaller than in the bulk material obtained from the melt. This is due to the fact that the vapor phase – condensed phase temperature differential is much greater than in the liquid – solid case, and as a result the “quench” rate for the material during its formation from the vapor is considerably higher than when it is obtained from the melt. The grain size in the

coating is smaller when there is a greater difference between the temperature of the condensation surface (substrate) and the melting point of the coating material.

A further decrease in grain size in the coating or film deposited from the vapor phase (and accordingly hardening of the film) may be achieved by increasing the density of the nuclei, suppressing their growth, and reducing the mobility of film-forming species on the condensation surface. We note that the density of the nuclei is a function of the mobility of the film-forming species (the mobility of the adsorbed atoms, or adatoms) on the condensation surface. The mobility of the adatoms in turn depends in a complicated fashion on the energy of the species (and not only film-forming species) arriving at the growth surface, the surface temperature and the surface concentration of atoms or molecules that are foreign to the given material.

In reviews [3, 4] devoted to consideration of the principles, methods, and technological means for creating superhard coatings and films, an important role is played by ion bombardment of the growing condensate. The ions sputter atoms and adatoms, weakly bound to the film and migrating through the growth surface [5, 6], create local thermal spikes on the surface which rapidly dissipate, and produce a quenching effect [4]. These phenomena result (for a certain ion energy) in formation of condensates with a small grain size. Another approach to obtaining superhard coatings and films is to combine ion bombardment and creation of nanocomposite film materials [3, 4]. The latter may be either materials consisting of two hard phases (for example, MeN/Si<sub>3</sub>N<sub>4</sub>, MeN/BN, where Me are transition metals Ti, W, Zr etc. [3]), or materials containing one hard phase and one soft phase (for example, ZrN/Cu, TiN/Al [4]). However, neither these reviews nor other modern papers devoted to topics in the physics and technology of films and coatings consider the effect of the form of the film-forming species (atoms, molecules, atomic clusters) on formation of the condensate substructure.

Moreover, in isolated earlier papers it has been shown that the presence of molecules in film-forming species can have a considerable effect on formation of highly dispersed or even amorphous condensates of covalent semiconductors [7, 8]. In the review [9], evidence is also given in favor of the idea that molecules participating in formation of laser condensates of different compounds promote a decrease in grain size. We also note that so far there has been no convincing explanation for the effect of increased hardness of composite film materials formed by a hard phase (nitrides, borides, carbides) and a soft phase (metallic), although it has been hypothesized that a metallic phase hinders grain growth in the matrix phase.

Accordingly, we conducted two series of experiments. In the first series, we studied the correlation between the composition of film-forming species, the structure, and the microhardness of films obtained by magnetron sputtering of a target of composition W – 30 at.% Ti in a mixture of gases Ar – N<sub>2</sub>. We note that film material based on (W, Ti)N is of interest as a diffusion barrier in integrated circuits [10, 11], and also as a nanocomposite material for creating superhard wear-resistant coatings [12]. In the second series of experiments, we studied the interconnection between the structure of the composite film material based on TiN/Cu, the copper content in the material, and its hardness.

## EXPERIMENTAL PROCEDURE

Films of composition (Ti, W)N were deposited by reactive magnetron sputtering of a W – 30 at.% Ti target of diameter 100 mm in a mixture of Ar and N<sub>2</sub> gases. The films were deposited simultaneously on the substrate of steel disks and on polished wafers of silicon single crystals. The total pressure of the working gas was  $P_{\text{tot}} = 0.5$  Pa; the nitrogen content in the gas was varied from 0 to 60%. The bias voltage on the substrate holder during deposition was  $U_{\text{bias}} = -100$  V. The substrate temperature during deposition did not exceed 350°C. The film thickness was 3.5 μm on the average. The technology for deposition of such films is described in more detail in [13].

Films of composition TiN/Cu with variable copper content were obtained on an apparatus where a device for vacuum arc vaporization of a titanium target and a magnetron unit with copper target were mounted diametrically opposite each other in the cap [14]. Both discharges (vacuum arc and magnetron) were maintained in a nitrogen atmosphere. The substrate, clamped in a special carousel rotating in a circle, was alternately turned toward the vacuum arc and magnetron sources of film-forming species. Bias voltage on the substrate  $U_{\text{bias}} = -150$  V, nitrogen pressure  $P_{\text{N}_2} = 0.4$  Pa; substrate temperature in these experiments did not exceed 300°C; average film thickness was 1.5 μm.

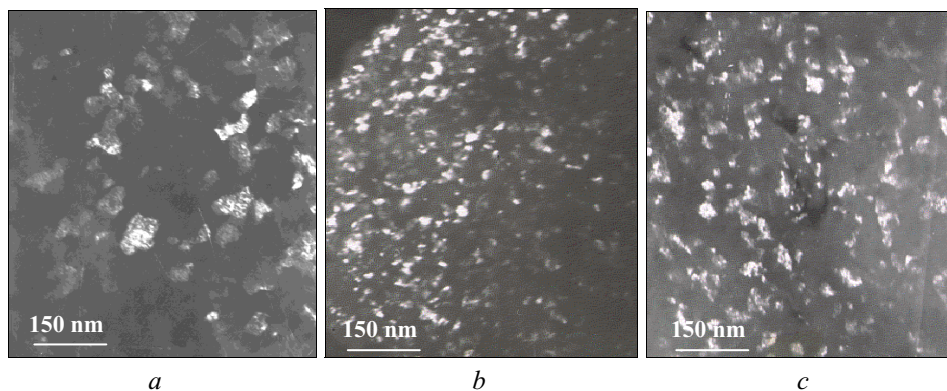


Fig. 1. Dark-field images (slice of the film parallel to the substrate) for (W, Ti)N films deposited at different nitrogen partial pressures: a) in the absence of nitrogen; b)  $P_{N_2} = 0.07$  Pa; c)  $P_{N_2} = 0.3$  Pa

The film thickness was measured with a Tencor Alpha-Step 500 profilometer. The film structure was studied by transmission electron microscopy, electron microdiffraction using a PÉM-U electron microscope, and also wide field electron diffraction using an ÉMR-100 electron diffraction instrument. The chemical composition of the films was studied by electron probe microanalysis on a JEOL JXA733. The microhardness was measured using a Fischerscope H-100 nanohardness tester with a 20 mN load on the indenter and an indentation depth no greater than 10% of the film thickness.

The composition of the species arriving at the condensation surface (during deposition of films in the (W, Ti)N system) was determined by mass spectrometric analysis using a Hiden Analytical EQP/EQS Analyzer-1000 with a detector entrance aperture (diameter 0.2 mm) located in the substrate region [15]. The analyzer included ion optics elements, a quadrupole mass filter (up to 500 amu), and a photoelectron multiplier for secondary electrons.

## RESULTS AND DISCUSSION

*The role of molecules in formation of film composite materials with elevated hardness.* Table 1 and the dark-field electron micrographs (Fig. 1) give the results of a study of the composition, microstructure, and microhardness of (W, Ti)N films deposited with different nitrogen contents in the Ar and  $N_2$  gas mixture.

We note that in the structural study of W – Ti and (W, Ti)N films, we did not detect a titanium or titanium nitride phase in the films despite the presence of titanium within their composition (Table 1). Most likely this is due to the high dispersity of these phases in the films, which reduces the sensitivity of the diffraction studies. The problem is exacerbated by the following factors. First of all, the titanium content in the films is low (about 12-15 at.%); secondly, the bcc lattice parameter of Ti is not very different from the bcc lattice parameter for W ( $a_{Ti} = 0.328$  nm,  $a_W = 0.317$  nm); thirdly, the electron atomic scattering factor for titanium is half as much as the value for tungsten. This is also the case for the TiN phase, since the lattice type is the same for  $W_2N$  and  $\delta$ -TiN and their parameters are close ( $a_{TiN} = 0.424$  nm,  $a_{W_2N} = 0.412$  nm). In [16], the absence of titanium and titanium nitride phases is also noted in W – Ti and (W, Ti)N films.

Films deposited by sputtering the alloy W – 30 at.% Ti in pure argon ( $P_{N_2} = 0$ ) are practically pore-free and are formed from relatively large (about 50-100 nm) crystallites of  $\beta$ -W phase (Fig. 1a). When very small amounts of nitrogen ( $P_{N_2} = 0.03$  Pa) are added to the argon, the size of the crystallites decreases slightly (to about 20-40 nm), and along with the  $\beta$ -W phase we see traces of the phase  $W_2N$ .

A substantial decrease in the size of the crystallites (down to 10 nm) was observed for a nitrogen partial pressure  $P_{N_2} = 0.07$  Pa (Fig. 1b). Such films consisted of two phases: the matrix phase  $W_2N$  and  $\beta$ -W, i.e., a nanocrystalline two-phase material was formed under such conditions. It was precisely these films that had the maximum

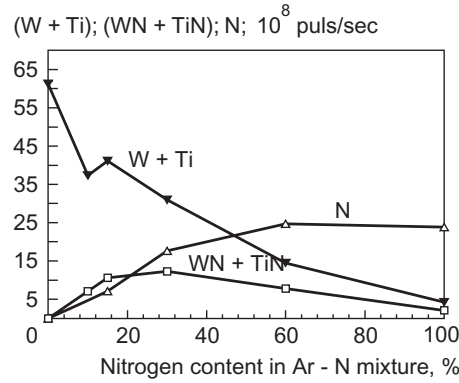


Fig. 2. Dependence of the composition of the flux of film-forming species on the nitrogen content in the argon/nitrogen mixture

hardness (approximately 62 GPa). A further increase in the nitrogen content in the working gas ( $P_{N_2} = 0.3$  Pa) led to formation of one-phase  $W_2N$  condensates with crystallite size 2-4 times larger (about 20-40 nm, Fig. 1c) than for films deposited with lower nitrogen concentrations. Such films had lower microhardness (about 45 GPa, Table 1).

What is the reason for such a nonmonotonic change in the crystallite size and microhardness of the condensates as the nitrogen concentration increases in the working gas? As already mentioned, the most important physical factor affecting the microstructure and crystallite size is the mobility of the film-forming species on the condensation surface. The parameters affecting the mobility of the film-forming species, such as the substrate temperature, the energy of the species arriving at the growth surface, and the gas pressure, were kept unchanged in all the experiments. The only technological parameter varied in these experiments was the partial pressure of nitrogen.

In the “empirical” real structure zone model as developed by Barna and Adamik [16], it was shown that codeposition of a chemically active impurity with the matrix material has a considerable effect on the microstructure and grain size of the condensate. According to this model, the grain size in the film is inversely proportional to the concentration of the impurity element on the growth surface. At low concentrations, the species of the impurity phase are distributed preferentially along the grain boundaries, which limits the mobility of the film-forming species along these boundaries and decreases their flux to the growing grains, preventing normal grain growth. However, at such impurity concentrations, the process of grain coalescence (which determines their enlargement) is not very restricted. For moderate concentrations of the impurity species, there are already enough of them to block the coalescence process, which leads to formation of a film with reduced grain size. When the concentration of impurity species is high, growth of grains of the matrix phase is limited by growth of crystallites of new phase, and their sizes prove to be even smaller.

The presented model can be used to explain the changes in the microstructure of (W, Ti)N films as the partial pressure of nitrogen increases in the working gas, if we consider the nitrogen atoms as the impurity species. However, in this case, contrary to the prediction of the model concerning a monotonic decrease in grain sizes as the nitrogen

TABLE 1. Properties of (W, Ti)N Films Deposited at Different Nitrogen Partial Pressures in the Working Gas

$P_{N_2}$ , Pa	Microhardness, GPa	Composition, at.%			Phase composition	Grain size, nm
		W	Ti	N		
0	22	88	12	0	$\beta$ -W	50-100
0.07	62	52	20	28	$W_2N + \beta$ -W	About 10
0.3	45	48	12	43	$W_2N$	About 40-60

concentration increases, in the films we observed their unexpected growth as  $P_{N_2}$  increased to 0.3 Pa and higher (Table 1; Fig. 1c).

In order to understand the reasons for this phenomenon, we used gas phase mass spectrometry in the substrate region to study the composition of the species arriving at the condensation surface as a function of the partial pressure of nitrogen in the chamber (Fig. 2). We established that along with tungsten, titanium, and nitrogen atoms, the film-forming species also include WN and TiN molecules, the relative content of which increases up to 35% and then slowly falls off as the nitrogen concentration in the chamber increases. As the partial pressure of nitrogen increases in the chamber, the number of nitrogen atoms gradually increases while the number of metal atoms drops. However, in the low partial pressure region for nitrogen ( $0 < P_{N_2} < 0.1$  Pa), the total number of nitride molecules arriving at the condensation surface proves to be higher than the number of nitrogen atoms. From this it follows that when  $P_{N_2} < 0.1$  Pa, the main species (in addition to the indicated atoms) on the growth surface are WN and TiN molecules. If we consider them as impurities relative to the W, Ti, and N atoms, then according to the Barna and Adamik model [16], they will play the decisive role in formation of a highly dispersed structure for films deposited with  $P_{N_2} < 0.1$  Pa (Fig. 1b). It is also important to note that the nitride phase in these films is preferentially formed by WN and TiN molecules sputtered from the target surface, and not from those appearing as a result of the reaction  $Me + N = MeN$  ( $Me = W, Ti$ ) on the condensation surface.

In the region  $P_{N_2} > 0.1$  Pa, the number of nitrogen atoms already exceeds the total number of MeN molecules and continues to increase with further increase in the partial pressure of nitrogen, while the total number of MeN nitride molecules in this case gradually decreases (Fig. 2). Consequently, the structure of (W, Ti)N films deposited for  $P_{N_2} = 0.3$  Pa (Fig. 1c) is preferentially formed from W, Ti, and N atoms rather than from WN and TiN molecules as occurs for  $P_{N_2} < 0.1$  Pa.

From comparison of the microstructure for films formed preferentially from MeN molecules (Fig. 1b) with the microstructure formed mainly by W, Ti, and N atoms (Fig. 1c), we see that the larger molecular WN and TiN species have a stronger effect on the structure than atomic nitrogen. This may be due to the following reasons. When film-forming species are predominantly metal atoms and nitride molecules, the low mobility of the latter and their relatively large sizes more effectively (compared with nitrogen atoms) limit the mobility of adatoms on the condensation surface, which leads to formation of a highly dispersed film structure. If the major film-forming species are only metal and nitrogen atoms, then as a result of synthesis of the nitride film  $Me + N = MeN$  on the condensation surface, heat is evolved that raises the temperature of the condensation surface. As a result, the grain size in the film increases. This hypothesis is confirmed by the rise in temperature of the massive substrate holder from 300°C to 330-350°C observed when  $P_{N_2} = 0.3$  Pa during deposition of a (W, Ti)N film.

The data obtained on the film microstructure allows us to explain the way their mechanical properties change. We know that the ultimate strength  $\sigma_s$  (and also the hardness) of bulk material depends on the grain size  $d$ , and specifically these parameters are inversely proportional according to the Hall-Petch relation:

$$\sigma_s = \sigma_0 + K \cdot d^{-1/2},$$

where  $\sigma_0$ ,  $K$  are constants. We also know that the mechanical properties of bulk composite material are higher than for one-phase material, and are determined by the concentration of the second phase, the ratio of the crystallite sizes for the different phases, and their morphology [2]. Similarly, film composite materials also acquire elevated mechanical properties for a certain combination of these parameters [3].

(W, Ti)N films deposited under optimal conditions ( $P_{N_2} = 0.07$  Pa,  $U_{bias} = -100$  V) are a two-phase composite material  $W_2N + \beta$ -W with maximum microhardness, which results from the strong interatomic binding in the nitride phase and also the high dispersity of both phases, hindering slip and cracking processes. Furthermore, the presence of a metallic phase as highly dispersed and uniformly distributed crystals reduces the probability of grains of the nitride phase coming into contact with each other. So the local stress concentration at the boundary of these grains may be easily

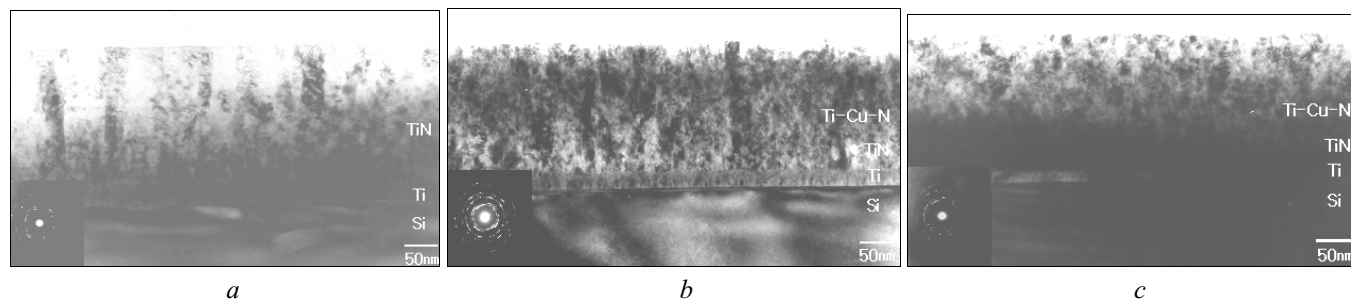


Fig. 3. Micrographs and electron microdiffraction patterns obtained from transverse cross sections of films in the TiN – Cu system with copper content 0 (a), 1.5 (b), and 2.3 at.% (c)

compensated by a plastic metallic phase [1]. Films of composition (W, Ti)N deposited for  $P_{N_2} > 0.1$  Pa are first of all one-phase, which increases the probability of brittle fracture for such material; secondly, they consist of coarser grains. Both these factors are responsible for their lower hardness.

*The role of metallic impurity in formation of nanocomposite film materials with elevated hardness.* From the data considered above, it follows that the hardness of film material can be increased by introducing an impurity in fairly small amounts which will play the same role as nitride molecules in growth of (W, Ti)N films. In this case, the impurity material can be softer than the matrix phase, but its concentration should not exceed a certain value [1].

In order to test this hypothesis, we conducted experiments to obtain film nanocomposite material containing titanium nitride as the hard matrix and copper as the impurity phase. In studying the correlation between structure and microhardness for this composite material as we varied the copper concentration in the nitride matrix, we obtained the results shown in Figs. 3 and 4.

The copper-free films were textured with preferred orientation of the (111) and (220) planes parallel to the substrate, and had a columnar structure with average grain size of about 20–30 nm (Fig. 3a). Such a structure is typical for films of refractory compounds deposited by reactive ion plasma methods [18]. When copper was added to their composition, they became less textured, the grain size decreased, and their shape became more equiaxed (electron microdiffraction patterns (in the insert) and micrographs in Fig. 3b, c). It is important to note that despite the presence of copper in the condensates, it is not observed by the diffraction methods, which suggests either a very small size for the copper crystallites or else that it is present as adsorbed monatomic layers along the grain boundaries of the titanium nitride. We were unable to determine the reasons for the formation of a thin layer of titanium on the boundary with the substrate in these films. We note that such an effect of composition inhomogeneity (and accordingly film structure inhomogeneity) through its thickness was also observed in [13, 19] in films of the W – Ti – N system, but so far no explanations have been found.

The microhardness of the films initially increases as the copper concentration in the films increases, reaching a maximum at 1.5 at.% Cu, and then the microhardness decreases even down to smaller values than in a pure TiN film (Fig. 4). The evolution of the structure of the TiN film as copper is added to its composition may be explained using the Barna-Adamik model [16]. According to this model, impurity atoms (in this case, copper) arriving at the growth surface are located on the boundaries of the growing nitride grains, reducing the mobility of the titanium and nitrogen atoms and reducing the flux of the latter into the grains, thus preventing their growth and shape development. The higher the concentration of copper impurity atoms, the more grain development is blocked in the matrix phase (TiN), which we also observed in the experiment (Fig. 3).

The dependence of the microhardness of the film of nanocomposite material on the copper concentration in the film is explained as follows. First of all, we note that substitution of titanium or nitrogen atoms by copper in the TiN lattice is virtually ruled out because the interaction between titanium and nitrogen atoms is stronger than the interaction between these atoms and copper. On the other hand, the radius of the copper atom is sufficiently large so that copper proved to be an interstitial impurity in TiN. Therefore addition of small amounts of copper to TiN does not affect its

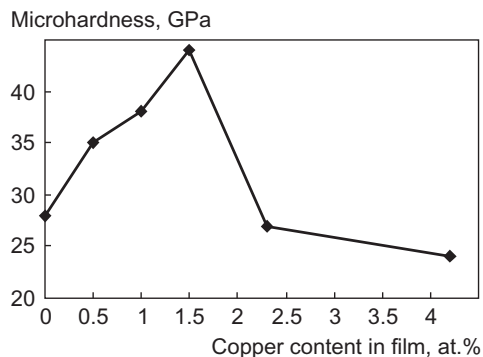


Fig. 4. Dependence of the microhardness of films in the TiN – Cu system on the copper content in the films

initial hardness but, starting from some copper concentration in the composite, leads to a decrease in its hardness due to segregation of copper into a separate phase. For low copper concentrations, during formation of the composite material the copper atoms were located on the nitride grain boundaries and inhibited grain growth, which according to the Hall-Petch relation has a positive effect on the strength of the composite. When some concentration limit is exceeded (in our case, this is 1.5 at.%), when there is sufficient copper to form interlayers between nitride grains and (or) to segregate into an independent (even if highly dispersed) phase, we will observe a decrease in strength and hardness of this material. It is precisely for this reason that the decrease in strength characteristics occurs for the composite material even with further decrease in grain size for the matrix phase, which we also observed experimentally.

### CONCLUSION

An increase in strength properties of coatings and films, as for the bulk materials, can be achieved by reducing the sizes of their structural elements. However, the methods and mechanisms for such hardening are different for the studied materials.

In the example of a film nanocomposite material (W, Ti)N, we have shown that a decrease in grain size in films deposited by reactive magnetron sputtering occurs due to the presence within the composition of the film-forming species of (in addition to tungsten and titanium atoms) larger nitride molecules WN and TiN. Under conditions when the concentration of molecules on the growth surface is higher than the concentration of atomic nitrogen, they prevent grain growth, and as a result a highly dispersed two-phase material is formed ( $W_2N + \beta-W$ ) with maximum hardness. When the concentration of atomic nitrogen on the growth surface exceeds the concentration of the molecules, first of all a one-phase material  $W_2N$  is formed and secondly, due to the exothermicity of the reaction between nitrogen and the metal atoms, the temperature of the condensation surface rises, promoting growth of the material with a coarser grains. For these reasons, the hardness of such a material is lower than the hardness of a two-phase highly dispersed material.

The mechanism for the increase in hardness for coatings based on nanocomposite materials containing a hard phase (for example, nitrides, carbides, borides of transition metals Ti, W, Zr, etc.) and a soft phase (metals Cu, Ni, Y, Ag, etc., weakly interacting with nitrogen) is analogous to the mechanism considered for the (W, Ti)N system. However, it is not nitride molecules but rather metal atoms of the soft component that act as a grain growth inhibitor in these materials, which we have shown for the example of the effect of small copper impurities on the structure and microhardness of a film composite material based on TiN.

### REFERENCES

1. V. I. Trefilov, Yu. V. Mil'man, and S. A. Firstov, "The physics of the strength of refractory materials," in: *Physical Materials Science in the USSR* [in Russian], Nauk. Dumka, Kiev (1986), pp. 222-251.
2. D. M. Karpinos and L. I. Tuchinskii, "Dispersion-hardened composite materials," in: *Physical Materials Science in the USSR* [in Russian], Nauk. Dumka, Kiev (1986), pp. 312-334.

3. S. Veprek, "The search for novel superhard material," *J. Vac. Sci. Technol.*, **A17**, No. 5, 2401-2420 (1999).
4. J. Musil, "Hard and superhard nanocomposite coatings," *Surf. Coat. Technol.*, No. 125, 322-330 (2000).
5. A. N. Pilyankevich, V. Y. Kulykovski, and L. R. Shaginyan, "The influence of ion bombardment on the structure of ion-plated indium films," *Thin Solid Films*, **137**, No. 2, 215-224 (1986).
6. L. R. Shaginyan, M. Misina M., S. Kadlec, et al., "Mechanism of the film composition formation during magnetron sputtering of WTi," *J. Vac. Sci. Technol.*, **A19**, No. 5, 2554-2566 (2001).
7. V. P. Zakharov and I. M. Protas, "Mass spectrometric study of the conditions for amorphous film formation by condensation from the vapor phase," *Dokl. Akad. Nauk SSSR*, **215**, No. 3, 562-564 (1974).
8. Yu. G. Poltavtsev, N. M. Zakharov, V. M. Pozdnyakova, and I. M. Protas, "Effect of the vapor phase composition on short-range order in the structure of gallium arsenide films," *Kristallografiya*, **17**, No. 1, 203-206 (1972).
9. L. R. Shaginyan, "Pulsed laser deposition of thin films: expectations and reality," in: *Handbook of Thin Film Materials*, H. S. Nalwa (ed.), Academic Press, San Diego (2002), Vol. 1, pp. 627-674.
10. A. G. Dirks, R. A. Wolters, and A. J. Nelissen, "On the microstructure property relationship of (W, Ti)N diffusion barriers," *Thin Solid Films*, No. 193/194, 201-210 (1990).
11. H. Ramarotafika and G. Lemperiere, "Influence of DC substrate bias on the composition, crystalline size and microstrain of WTi and WTi – N films," *Thin Solid Films*, No. 266, 267-273 (1995).
12. J. Musil, "Superhard nanocomposite coatings," in: *Proceedings, 14th International Symposium on Plasma Chemistry* (August 1999, Prague), Prague (1999), Vol. 1, p. 17.
13. L. R. Shaginyan, M. Mishina, J. Zemek, et al. "Composition, structure, microhardness and residual stress of W – Ti – N films deposited by reactive magnetron sputtering," *Thin Solid Films*, No. 408, 136-147 (2002).
14. S. Myung Hyun, M. Lee Hyuk, G. Han Jeon, and L. R. Shaginyan, "Microstructure and mechanical properties of Cu doped TiN superhard nanocomposite coatings," *Surf. Coat. Technol.*, No. 163-164, 591-596 (2003).
15. M. Mishina, L. R. Shaginyan, M. Macek, and P. Panjan "Energy resolved ion mass spectroscopy of the plasma during reactive magnetron sputtering," *Surf. Coat. Technol.*, No. 142-144, 348-354 (2001).
16. J. M. Oparowski, R. D. Sisson, and R. R. Biederman, "Effects of processing parameters on the microstructure and properties of TiW thin film diffusion barriers," *Thin Solid Films*, No. 153, 313-328 (1987).
17. P. B. Barna and M. Adamik, "Real structure zone models," *Thin Solid Films*, No. 317, 27-31 (1998).
18. M. Ohring, *Materials Science of Thin Films*, Academic Press, San Diego (1992).
19. D. B. Bergstrom, F. Tian, I. Petrov, et al., "Origin of compositional variations in sputtered Ti – W barriers," *Appl. Phys. Lett.*, **67**, No. 21, 3102-3104 (1995).