Features of synthesis of Ti-Si-N coatings by condensation of vacuum arc plasma with a composite cathode

I.I.Aksenov, V.A.Belous, Yu.A.Zadneprovskiy, N.S.Lomino, O.V.Sobol*

National Science Center "Kharkiv Institute of Physics and Technology",

1 Akademicheskaya St., 61108 Kharkiv, Ukraine

*National Technical University "Kharkiv Polytechnic of Institute",

21 Frunze St., 61002 Kharkiv, Ukraine

Received November 25, 2010

The effects of nitrogen pressure on silicon content in Ti–Si–N coatings deposited by the vacuum-arc method using $Ti_{0.95}$ – $Si_{0.05}$ alloy as a consumable cathode material were investigated. It has been found that the silicon content in the coatings under any conditions of deposition is below its concentration in the cathode. In the pressure range from $5\cdot10^{-4}$ to 10^{-3} Torr the concentration of silicon in the coating is the lowest (~1.2 wt. %), and hardness of the condensate is the highest (35 GPa). The extremal character of dependences of the silicon concentration and hardness of the coatings on nitrogen pressure is a result of difference in structure-phase composition of the coatings obtained at different pressures.

Исследовано влияние давления азота на процентное содержание кремния в Ti-Si-N покрытиях, осаждаемых вакуумно-дуговым методом с использованием сплава $Ti_{0,95}$ -Si_{0,05} в качестве расходуемого катодного материала. Установлено, что концентрация кремния в покрытиях при всех условиях осаждения ниже его концентрации в материале катода. В диапазоне давлений от $5 \cdot 10^{-4}$ до $1 \cdot 10^{-3}$ Торр концентрация кремния в покрытии минимальна (~1,2 вес. %), а твёрдость конденсата максимальна (35 ГПа). В покрытиях, полученных в указанной области давлений, наблюдается наибольшая временная стабильность их микротвёрдости. Экстремальный характер зависимостей концентрации кремния в покрытиях и микротвёрдости конденсатов от давления азота является результатом различия структурно-фазового состава покрытий, получаемых при разных давлениях: с изменением плотности газовой мишени в конденсате помимо нитрида титана образуются нитриды кремния различной стехиометрии: SiN — в условиях низкого давления и Si₂N₄ — при повышенных давлениях азота.

I. Introduction

Multicomponent films based on nitrides of two and more metals differ from unicomponent films by their higher physico-mechanical characteristics and higher thermal stability. They find wide application as wearproof antifriction coatings in mechanical engineering, and as barrier layers — in microelectronics [1, 2]. Such coatings can be made by vacuum-arc method using a target

(cathode) made of a composite material of a specified structure. In this case the most uncertain is the question of the percentage of the cathode material components in the coating. Transfer of the material from the working surface of the cathode to the substrate in atmosphere of reaction gases is determined by a number of physical processes. On the cathode surface erosion-proof compounds (titanium nitrides in this case) are synthesized, in the drift space between

the cathode and substrate the erosion products are scattered on gas molecules, and the condensate on the substrate is subject to sputtering by condensed particles. All these factors can lead to substantial difference in the composition of the cathode material and the obtained coating composition.

In [3], taking composite cathodic materials (Ti-Si and Ti-Al) as an example, the transfer of components of these materials to coatings deposited by vacuum-arc method was experimentally studied at residual pressure in the vacuum chamber $2 \cdot 10^{-5}$ Torr. It was shown that the coating composition could considerably differ from the component ratio of the cathode. The effects of nitrogen on the transfer process of the deposited cathodic material components remained uncertain. Clearing of this question was an objective of the present work. Taking titanium-silicon composites as an example, we studied peculiar features of the transfer of cathode material components to the coating in the presence of nitrogen.

2. Experiment

In our experiments, we used a vacuumarc plasma source with magnetic stabilisation of a cathode spot and plasma flux focusing [3, 4]. The source contained a tubular anode with the focusing coil (Fig. 1). The distance from the end face of the cathode to the substrate holder was 350 mm. The coatings were deposited on stainless steel samples (substrates) of $20 \times 10 \times 1$ mm³ size, which were fixed on a substrate holder (a copper disc of 15 mm in thickness and 80 mm in diameter) placed opposite to the cathode. Ti-Si composites with 4 wt. % and 5 wt. % of silicon were used as cathode materials. The arc current for coating deposition was 90-100 A. A negative bias potential (-50 or -250 V) was applied to the substrate holder. The effects of the focusing magnetic field H_f on the silicon content in the condensates deposited on the substrates were studied, with the current in focusing coil $J_f = 0$ or 0.7 A. Pressure of residual gases p_0 in the vacuum chamber before each procedure of the coating deposition did not exceed $2 \cdot 10^{-5}$ torr. Concentration of silicon in the coatings $C_{\mathsf{S}_{\mathsf{i}}}$ was determined by the X-ray fluorescence method. (The value of $C_{\mathsf{S}|}$ and $C_{\mathsf{T}|}$ was defined considering $C_{\mathsf{S}|}$ + $C_{\text{Ti}} = 100 \%$, where C_{Ti} is titanium concentration in the coating, i.e. the nitrogen concentration was not taken into account). The deposition rate was measured by two methods: (i) an optical method $(V_s, \mu m/h)$ using

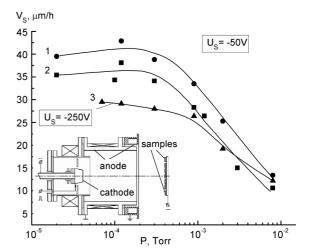


Fig. 1. Deposition rate of condensate as a function of nitrogen pressure; scheme of arrangement of samples-substrates. $U_s = -50 \text{ V}$ (1, 2), $U_s = -250 \text{ V}$ (3). The cathode made of Ti (1), Ti + 4 wt. % Si (2, 3).

an interference microscope MII-4 and (ii) a gravimetric method (V_p , $\mu g/mm^2 \cdot h$). Microhardness of the coatings was measured using a PMT-3 apparatus with Vickers pyramid at loading of 50 and 100 G and thickness of the condensate ~10 μm .

3. Results

In Fig. 1 the data on the coating deposition rate as function of nitrogen pressure V(p) are given. The curves were obtained at the substrate bias voltage -50 and -250 V. The curve for the Ti-cathode (for $U_{bias} = -50$) lay a little above the similar curve obtained with the cathode of titanium with addition of silicon. From Fig. 1 it follows also that at low pressures of nitrogen the condensate deposition rate remains practically at the same level and promptly decreases with pressure growth above $\sim 3.10^{-4}$ torr. (The deposition rate decrease on the disk-substrate holder edges in comparison with its centre did not exceed 5-10 % in all the explored range of nitrogen pressures). In the pressure range up to 10^{-3} Torr appreciable decrease in deposition rate was observed under higher substrate bias voltage $(U_{c} = -250 \text{ V})$, which can be attributed to self-sputtering of the condensate in the course of its deposition. At pressures above 10^{-3} Torr, this process becomes negligible owing to dispersion of the energy of impinging particles on a more dense gas target.

In the same range of pressures, dependences of concentration of silicon $C_{\rm Si}(p)$ in the coatings deposited at different poten-

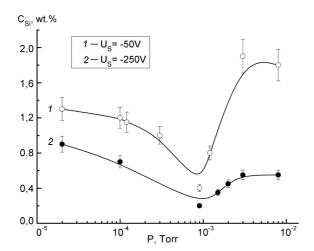


Fig. 2. Relative content of silicon in condensate depending on nitrogen pressure. Cathode made of Ti+4 wt. % Si.

tials on a substrate were obtained using a Ti-Si cathode (Fig. 2). With increase of pressure of the working gas (nitrogen) up to $p \cong 10^{-3}$ Torr there is a smooth decrease in concentration of the silicon. On one hand, according [5], it may be caused by higher medium kinetic energy of the titanium emitted from the cathode (122 eV) as compared with silicon ions (97 eV). Consequently, owing to collisions of ions with a gas target, the plasma stream was depleted by less violent particles. On the other hand, this process is promoted also by selective sputtering of silicon by the incident stream of particles [6]. At further rise of pressure, there is a rather abrupt increase in the Si content in the coating. The curve 2, obtained at higher bias potential on the substrate, illustrates the influence of the energy of condensed particles on C_{Si} : concentration of silicon in the condensate at $U_s = -250 \text{ V}$ decreases by several tens percent.

For the purpose of detection of possible correlations between behaviour of C_{Si} (p) and microhardness $H_{\mu}(p)$ curves, the corresponding diagrams were placed in one drawing (Fig. 3). It can be seen that in the range of pressures $10^{-5} \div 10^{-3}$ Torr, the dependences of the content of silicon in the condensate and the microhardness of these condensates are "in antiphase": H_{μ} is growing with reduction of C_{Si} and, on the contrary - growth of the silicon content leads to a decrease in microhardness. This deduction is valid both for the cathode with the additive of 4 % Si, and for the cathode with about 5 % of silicon. At more high pressures of nitrogen (approximately from

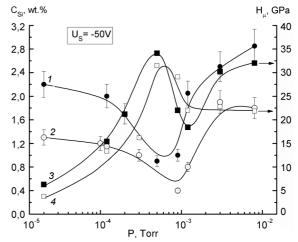


Fig. 3. Relative content of silicon in Ti-Si condensate (1, 2) and microhardness of coatings (3, 4) depending on nitrogen pressure. C_{Si} in the cathode is 5 wt. % (1, 3) and 4 wt. % (2, 4).

above 10^{-3} Torr) the behaviour of H_{μ} begins to correlate with the silicon content in the coating, and this correlation becomes stronger with higher content of silicon in the cathode.

To estimate a role of small additives of Si on $H_{\shortparallel}(p)$, two series of samples with the coatings deposited in identical technological conditions have been prepared: one with titanium cathode, and the other — with the cathode made of titanium with silicon additive (4 wt. %). The obtained $H_{\shortparallel}(p)$ dependences for two values of negative potential on the substrate are shown in Fig. 4. It can be seen that the values of microhardness of the coatings obtained with cathodes of both materials also increase with pressure increase up to 10^{-4} Torr, slightly differing from each other. In the range of pressures $10^{-4} \div 10^{-2}$ Torr, the dependence $H_{\parallel}(p)$ for the case of Ti-cathode is characterized by the presence of a wide plateau, and for the cathode with additional Si, a narrow maximum near 5.10^{-4} Torr is observed.

The roughness R_a , of the obtained TiN and Ti-Si-N coatings was studied in a wide range of pressures of the working gas $(10^{-5}-10^{-2}$ Torr), and the results are shown in Fig. 5. It can be seen that the arithmetical mean value of roughness for both types of condensates is in the range $0.3-0.6~\mu m$ at all pressures of gas, except a relatively narrow gap close to $p=10^{-3}$ Torr (at which an essential excess of the measured parameter is noted for coatings based on the Ti-Si-N). In this range of pressures flaking of fragments of coatings to depths up to several microns is observed (Fig. 6). The upper and

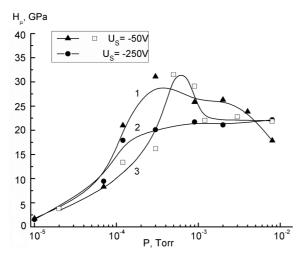


Fig. 4. Microhardness of coatings as function of nitrogen pressure. The cathode made of Ti (1, 2), and Ti + 4 wt. % Si (3).

lower rows of photos correspond to samples with coatings obtained at different pressures of nitrogen.

As follows from Fig. 3, the coatings deposited at pressures in the range of p = $(5\div8)\cdot10^{-4}$ Torr show peak values of microhardness, which under influence of interior stresses leads to large-scale (fractions of mm) surface erosion observed in experiments (Fig. 6a, b). It should be noted that such pattern of erosive destruction is observed on coatings 12 μm in thickness and it is absent on thinner condensates. Besides, the value of roughness R_a for coatings of 9 μm thickness is two times lower than for 12 µm coatings. The coatings obtained at higher pressures (in the range (5÷8)·10⁻³ Torr) are also characterised by high microhardness. But, because in the coatings composition the phase Si3N4 begins to prevail, they have roughness characteristic for the surfaces deposited from unfiltered stream (Fig. 6c,d), but without tracks of flaking.

It was of interest to consider temporal stability of properties of the obtained coatings. For this purpose, with that end in view, H_{μ} values for samples with coatings deposited at different pressures and different percentage of silicon in the cathode were repeatedly measured after 10 months. The results obtained are presented in Fig. 7. It can be seen that different segments of $H_{\mu}(p)$ curves are characterised by different temporal stability in hardness, with which other mechanical properties of coatings also correlate to a certain degree. The increased silicon content in the cathode material is

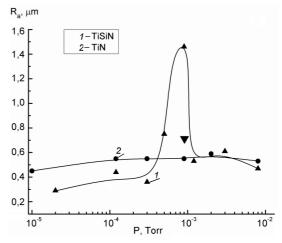


Fig. 5. Roughness of TiN and TiSiN coatings depending on nitrogen pressure of. 1– corresponds to TiSiN coating of 9 μm in thickness, and points 2 – to coatings of 12 μm in thickness. Thickness of TiN coatings is 10 μm .

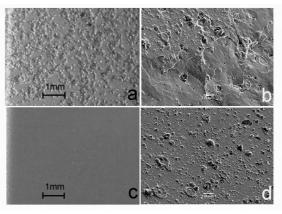


Fig. 6. Surface of the Ti–Si–N coatings deposited at nitrogen pressures $5\cdot 10^{-4}$ Torr (a, b), and $8\cdot 10^{-3}$ Torr (c, d). To the right, fragments of the pictures located to the left are shown, but at magnification $\times 1000$. (The cathode — Ti + 4 wt. % Si).

accompanied by the tendency to improvement of stability of the coatings.

In different experiments carried out using different X-ray installations (DRON-3 diffractometers), we obtained X-ray patterns of the coatings deposited at various pressures of nitrogen in similar experimental conditions (distance from the cathode and negative bias potential on the substrate) using Ti cathode and cathode made of titanium with 4 % silicon. For comparison, they are presented in Fig. 8. In both cases, in the conditions of low pressure of nitrogen (close to 10^{-4} Torr) X-ray spectra of the investigated coatings are characterized by the presence of a multiphase material.

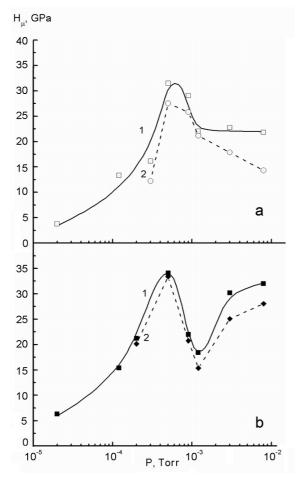


Fig. 7. Microhardness of coatings depending on nitrogen pressure. The cathode of Ti+4 wt. % Si (a), the cathode of Ti+5 wt. %

So, in system Ti-N at this pressure of gas, besides phase TiN, formation of phases with the smaller content of nitrogen occurs: Ti₂N with tetragonal lattice, and also TiN_{0.3}, with hexagonal lattice. In system Ti-Si-N the X-ray pattern at low pressure also testifies to heterophase character of the deposited material. And on the diffractogram of samples, alongside with the diffraction peaks of the basic phase, TiN, there is a wide curve with position of the nitride phase maximum characteristic for titanium nitride with tetragonal lattice and the nitrogen content lower than stoichiometric. With growth of nitrogen pressure, the coatings deposited from cathodes of different composition — both Ti, and Ti + 4 % Si — become single-phase and represent TiN with a cubic lattice of NaCl type. Characteristic feature for these coatings is the occurrence of texture [111]. No other phases, including silicon nitride, were revealed.

It is rather probable that at low concentration of silicon the (Ti, Si) N phase is formed, which represents solid solution of Si in TiN lattice. The lattice constant of the titanium nitride is 0.4275 nm, which exceeds a little the tabular value characteristic for massive TiN of stoichiometric composition (0.4243 nm). Such diversion can be caused by the influence of high compression residual stresses in the films, which is characteristic for ion-plasma condensates. At nitrogen pressure of 9.10⁻⁴ Torr a strong texture of axial type with the axis perpendicular to the substrate plane is revealed, i.e., crystallographic planes (111) are located preferentially parallel to the substrate plane. The size of coherent scattering region (CSR) in films is about 15 nm. On X-ray patterns of samples deposited at higher pressure (8.10⁻³ Torr), the lines of TiN phase are also well visible, though with different intensity ratio of reflexes indicating a texture change. In the condensate, the texture of axial type with [110] axis perpendicular to the substrate plane is formed, i.e. crystallographic planes (220) are preferentially located in parallel with the substrate plane. The reflex (220) is enhanced on the X-ray pattern in comparison with not textured samples. The lattice constant is 0.4271 nm, which is lower than at nitrogen pressure of $9 \cdot 10^{-4}$ Torr. It can be conditioned by a number of causes: increase in concentration of silicon, decrease residual stresses, deviations stoichiometric nitrogen content. The CSR in the film is 10-12 nm.

4. Discussion

For analyzing $C_{\mathsf{S}}(p)$ dependences presented in Fig. 3, we will estimate the number of metal atoms coming to the substrate $n_{\rm Me}$, accounting for the deposition rate and nitrogen molecular flow n_{N2} at different pressures of this gas. Such estimate shows that at 10^{-5} Torr $n_{\rm N2}/n_{\rm Me}\cong 0.1$, at 10^{-4} Torr $n_{\rm N2}/n_{\rm Me}\cong 1.0$, at 10^{-3} Torr $n_{\rm N2}/n_{\rm Me}\cong 12$, and at 10^{-2} Torr $n_{\rm N2}/n_{\rm Me}\cong 300$. It should be noted that at small pressures it is mainly the molecular nitrogen that comes to the substrate, while at increasing nitrogen pressure considerable amount will come to the substrate in the atomic state owing to higher frequency of collisions of gas molecules with ions in the gap between the cathode and the substrate. It simplifies process of formation of the nitride, since in the case of molecular nitrogen the molecule ad-

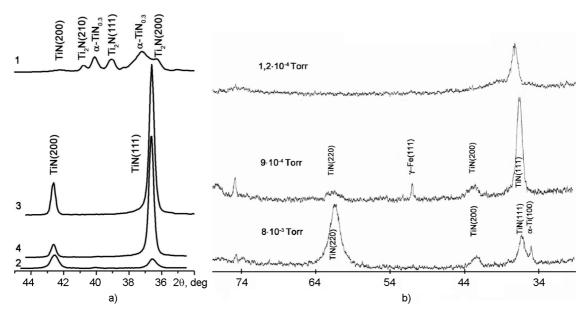


Fig. 8. X-ray patterns of the coatings deposited at different pressures of nitrogen. The upper block — for the cathode of Ti: $1.7 \cdot 10^{-4}$ Torr (1), $6 \cdot 10^{-4}$ Torr (2), $5 \cdot 10^{-3}$ Torr (3), $2 \cdot 10^{-3}$ Torr (4). The lower block — for the cathode of Ti + 4 wt. % Si.

sorbed on the surface should at first dissociate into atoms, and only after that the nitride formation can be realized by formation of two covalent bonds metal-nitrogen.

Such process thermodynamically is possible, since the change in Gibbs energy is negative as a result of this reaction. Really, the energy of dissociation of titanium nitride is equal to 807.33 kJ/mole. Apparently, these values exceed one-half of the nitrogen molecule dissociation energy, which is equal to 471.52 kJ/mole [9]. This testifies that the activation energy of formation of nitride on the condensate surface as a result of a dissociative chemosorption of the adsorbed molecular nitrogen will be equal to the energy of nitrogen dissociation. At the same time, for formation of nitride from atomic nitrogen such activation barrier is not present.

In the case of system Ti-Si-N, alongside with formation of titanium nitride, formation of silicon nitride is probable. Such process is also energetically favorable because the energy of such reaction is negative. However, depending on concentration of the arriving nitrogen, it can be realized by different trajectories. One trajectory is realized at rather low pressures, when $n_{\rm N2}/n_{\rm Me\leq 1}$. In this case, as shown[10, 11], there can be formation of phase SiN with cubic lattice of TiN matrix type. The gain of free energy is thus rather small and makes

 $-192~{\rm kJ/mole}$. Another trajectory is realized at strong flows of nitrogen onto the surface of growth, when, according to the thermodynamic approach based on minimization of Gibbs free energy, at sufficiently high activity of nitrogen the reaction $3{\rm SiN} + 0.5{\rm N}_2 = {\rm Si}_3{\rm N}_4$ can be realized, giving the gain $-168~{\rm kJ/mole \cdot atom}$ [10]. This indicates high thermodynamic gain in the system in formation of thermodynamically more stable ${\rm Si}_3{\rm N}_4$ (the free energy gain in formation of ${\rm Si}_3{\rm N}_4$ directly from atoms Si and N makes $-745.1~{\rm kJ/mole}$ in system ${\rm TiN-(SiN)Si}_3{\rm N}_4$).

Thus it can be assumed that changes in concentration $C_{\rm Si}$ observed in our experiments on increasing pressure (Figs. 2 and 3) can be related to formation of titanium nitride and two trajectories of synthesis of the silicon nitride. In particular, at pressures from above 10^{-3} Torr, the high gain of free energy in formation of ${\rm Si}_3{\rm N}_4$ phase is responsible, apparently, for increased relative content of silicon in the coating. Really, in this case formation of the bound complex of atoms with high net mass should lead to decrease in sputtering action of the titanium atoms in the course of condensation [12].

Finally, we will pay attention to currently available models of formation of a two-phase material in coatings of ternary system Ti-Si-N. Li et al. in their article [13] have supposed that considerable increase in

hardness found in Ti-Si-N coatings can be attributed to formation of nanocrystalline TiN particles surrounded with amorphous Si₃N₄ phase. However, when these effects were analysed in more detail and the sizes of crystal grains were determined [14], it became clear that this explanation was not correct, since such Si₃N₄ precipitates could not be generated within small crystal grains in the size of some nanometers. A new concept, based on strong thermodynamically governed and diffusion-controlled (spinodal) phase segregation leading to formation of stable nanostructural self-organisation, has been developed. Self-ordering in the binary systems, found out by Knotek and Barimani [15], and later by Andrievsky [16], is related to consecutive concentration oscillations at spinodal decomposition.

Let us remind that spinodal phase segregation is realized in a mixed binary system $A_{1-x}B_x$, for concentration interval in which the second differential coefficient of the free energy of the mixed phase is negative, and energy of interphasic strain is a quantity essentially smaller in comparison with the layering energy of this phase, and ultimate stable phases are coherent [17]. At low pressure of nitrogen this is applicable to fcc lattice of $\text{Ti}_{1-x}\text{Si}_x\text{N}_y$ system, where the layering energy is 6 kJ/mole atom [10], and the resulting state is represented by two lattices: fcc-TiN and fcc-SiN.

It should be noted that to account for the contribution of deformation energy in coherent spinodal curve it is necessary to know the interphase discrepancy. The calculated discrepancy between the volume per one atom in fcc-TiN and fcc-Ti $_{0.75} Si_{0.25} N$ is 0.14 %, and in fcc-SiN and fcc-Ti $_{0.75} Si_{0.25} N$ - 0.49 %, which is much less than the discrepancy of 9.4 % for β -Si₃N₄ and fcc-Ti_{0.75}Si_{0.25}N [11]. Hence, in conditions of stationary value of stoichiometry, the metastable fcc-Ti_{0.75}Si_{0.25}N should decompose in the beginning into fcc-TiN and fcc-SiN with small discrepancy of lattice, since transition in equilibrium β -Si₃N₄ state is connected with major volume changes and growth of the nitrogen content.

Thus, it is possible to conclude that formation of Si_3N_4 phase can be realized just in the course of Ti-Si-N coating deposition at high nitrogen pressure (>10⁻³ Torr). In this case just in the course of coating formation there is a possibility of layering of the solid solution by diffusion into two phases: phase TiN and energy-favourable,

though with more complex hexagonal lattice, phase Si_3N_4 .

If now to consider the structural state of the formed coating, it should be noted, that in the pressure range from 10^{-5} to 4.10^{-4} Torr, when the monotonous increase in hardness is observed, at low pressure of nitrogen the lowest titanium nitride Ti₂N is being formed, which, with the pressure rise in interval, transfers to stoichiometric composition with (111) texture. (The denoted structural transformations in the said interval of pressures practically coincides with structure evolution in the similar interval of pressures during titanium nitride preparation by sputtering of a pure titanium target). Any phases of silicon nitride are not revealed, and also silicon at rather low stream of nitrogen, characteristic for this interval of pressures, apparently, occurs in the solid solution (Ti, Si) N. It is possible to assume that, unlike pure TiN for which the texture does not change with rise of pressure, in the case of Ti-Si-N systems at pressure $8 \cdot 10^{-3}$ Torr the (110) texture is being formed.

Summarizing the obtained data, it should be noted that the increase in hardness with simultaneous relative reduction of Si component in coatings obtained in the pressure range of 10^{-5} – $7\cdot10^{-4}$ Torr correlates with evolution of phase composition from the lowest nitride phase Ti₂N to stable stoichiometric TiN phase with a cubic lattice. Owing to the high gain of energy in formation ofthe titanium (-807.33 kJ/mole - see above) in this interval of pressures, the silicon coming to the coating can form only mononitride of silicon with rather low energy of formation and mass. Such silicon can be intensively desorbed from the surface as a result of secondary sputtering by heavier atoms of titanium. It can be considered as the reason of depression of the relative content of Si in the coatings. High hardness is thus caused substantially by formation of preferentially oriented nanocrystals (10-12 nm) of the titanium nitride (with high binding energy, and thus — with high mechanical performance).

At higher nitrogen pressure, the high density of the stream of nitrogen atoms on the substrate in the course of coating growth allows formation of not only titanium nitride, but also the second phase with high energy of formation — Si₃N₄. Formation of such stable phase promotes containment of higher relative concentration of Si atoms in coatings to be formed.

5. Conclusions

Percentage of coating components differs from their concentration in the cathode and varies over a wide range depending on parameters of the deposition process — substrate bias voltage and pressure of working gas in the reactionary chamber. The concentration of silicon in the coating is always lower than in the Ti–Si cathode. In the conditions of our experiment it was from 10 to 50 % with respect to its content in the cathode.

Dependence of the silicon content in the coating on the gas pressure in the course of deposition is of nonmonotonic character with a minimum close to 10^{-3} Torr. In the same region there is a maximum on the dependence of hardness upon nitrogen pressure.

In the coatings obtained in the specified pressure region, the tendency to greater temporal stability of microhardness is observed.

The analysis of experimental data obtained gives the grounds to suppose that the mechanism of formation of coatings in conditions under consideration is based on formation of silicon nitrides of various stoichiometry, alongside with titanium nitride, in the condensate: SiN — in conditions of low pressure and Si_3N_4 — at higher nitrogen pressure.

References

- S.PalDey, S.S.Deevi, Mater. Sci. Engin., A342, 58 (2003).
- 2. I.I.Aksyonov, V.V.Vasilyev, A.A.Luchaninov et al., VANT, Ser. Vacuum, Pure Metals, Superconductors, No.1, 136 (2008).

- 3. I.I.Aksyonov, V.A.Bilous, S.K.Goltvyanytsya et al., VANT, Ser. Phys. of Radiat. Damage and Radiat. Mater. Scie., No.2, 184 (2009).
- I.I.Aksyonov, Vacuum Arc in Erosion Plasma Sources, NNTs KhFTI, Kharkov (2005) [in Russian].
- G. Yu. Yushkov, A. Anders, E.M. Oks, I.G. Brown, J. Appl. Phys., 88, 5618 (2000).
- 6. Sputtering of Solids by Ion Bombardment, ed. R.Berdysh. Mir, Moscow, 1984 [In Russian].
- 7. A.A.Andreev, L.P.Sablev, S.N.Grigoryev, Vacuum-arc Coatings, NNTs KhFTI, Kharkov (2010) [in Russian].
- 8. Dashman Scientific Foundations of Vacuum Technique, Wiley, NY (1962); S.Dashman, Scientific Foundations of Vacuum Techniques, Mir, Moscow, 1964 [In Russian].
- 9. V.A.Barvinok, Control of Stressed State and Properties of Plasma Coatings, Mashinostroenie, Moscow (1990) [in Russian].
- R.F.Zhang, A.S.Argon, S.Veprek, *Phys. Rev.* B, 79, 245426 (2009).
- R.F.Zhang, S.Veprek, Thin Solid Films, 516, 2264 (2008).
- J.Musil, S.Kadlec, V.Valvoda et al., Surf. Coat. Technol., 43-44, 259 (1990).
- S.U.Li, Y.Shi, H.Pen, *Plasma Chem. Plasma Process*, **12**, 287 (1992).
- 14. S. Veprek, S.Reiprich, S.Z.Li et al., Phys. Lett., 66, 2640 (1995).
- 15. O.Knotek, A.Barimani, *Thin Solid Films*, **174**, 51 (1989).
- R.A.Andrievski, I.A.Anisimova, A.P.Anisimov, Thin Solid Films, 205, 171 (1991).
- A.P.Shpak, O.V.Sobol, V.A.Tatarenko et al., *Metallofizika i Noveyshie Tekhnologii*, 30, 525 (2008).

Особливості синтезу Ti-Si-N покриттів, осаджених з плазми вакуумної дуги з композиційним катодом

I.І.Аксьонов, В.А.Білоус, Ю.О.Задніпровський, Н.С.Ломіно, О.В.Соболь

Досліджено вплив тиску азоту на відсотковий вміст кремнію у Ti-Si-N покриттях, осаджених вакуумно-дуговим методом з використанням сплаву $\text{Ti}_{0,95}-\text{Si}_{0,05}$ у якості катодного матеріалу що витрачається. Установлено, що концентрація кремнію у покриттях за всіх умов осадження нижча, ніж його концентрація у катодному матеріалі. У діапазоні тисків від $5 \cdot 10^{-4}$ до $1 \cdot 10^{-3}$ Торр концентрація кремнію у покритті мінімальна (~1,2 ваг. %), а твердість конденсату максимальна (35 ГПа). У покриттях, одержаних у зазначеній області тисків, спостерігається найвища часова стабільність їх мікротвердості. Екстремальний характер залежностей мікротвердості конденсату й концентрації кремнію у покриттях від тиску азоту є результатом різниці структурно-фазового складу покриттів, що одержуються при різних тисках. Із зміною щільності газової мішені у конденсаті окрім нітриду титану, утворюються нітриди кремнію різної стехіометрії: SiN — в умовах низького тиску та Si_3N_4 — при підвищених тисках азоту.