JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 8 No 4, 04023(4pp) (2016)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 8 № 4, 04023(4сс) (2016)

Effect of Nitrogen Atmosphere Pressure During Vacuum Arc Deposition of Multiperiod (Ti, Si)N/MoN Coatings on their Structure and Properties

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(Received 30 June 2016; revised manuscript received 23 November 2016; published online 29 November 2016)

Using complex structural engineering methods including elemental analysis, X-ray diffraction studies and microhardness tests, the influence of the operating pressure of nitrogen atmosphere during the deposition (P_N) on the formation of phase, structural state, and mechanical properties of multiperiod vacuum arc coatings of the (Ti, Si)N/MoN system has been studied. It is shown that in the range of used pressures of $P_N = 0.05...0.67$ Pa, the changes at the element level occur with increasing pressure: Si content decreases, N and Mo/Ti ratios increase. At the phase level, the changes mainly take place in the molybdenum-based layers, where the transition Mo → γ-Mo_2N → MoN occurs with increasing pressure. Maximum hardness (37.5 GPa) in this case is achieved during the formation of TiN/γ-Mo_2N layers with isostructural crystal lattice. The use of high-temperature annealing (1023 K) allows to increase the hardness of the coatings produced at a relatively low $P_N = 0.09$ Pa, when, due to the low content of nitrogen, the formation of additional Ti_5Si_3 solid phase is possible.

Keywords: Multilayer coating, (Ti, Si)N/MoN, Pressure, Nitrogen pressure, High temperature annealing, Structure, Hardness.

DOI: 10.21272/jnep.8(4(1)).04023 PACS numbers: 61.46. – w, 62.20.Qp, 62-65. – g

1. INTRODUCTION

A heightened interest in nanostructured materials has been observed in recent years. The so-called nanocomposite coatings, which possess unique mechanical, physicochemical and tribological properties and consist of nanocrystallites of the interstitial phases of transition metals and amorphous phase obtained by stratification according to the spinodal mechanism are currently the most promising [1, 2]. The basis for increasing the functional properties of such materials is the impermeable boundary of nanocrystalline grains, which prevents the dislocation slip and propagation [3]. The highest mechanical properties for the first development stage in such nanocomposites were obtained for the TiN/a-Si_3N_4 system [4-8]. The promise of using nitrides based on zirconium [9], Cr, Mo, as well as multi-element high-entropy alloys [10] as the components has been recently shown.

The possibilities of structural engineering in multiperiod systems combining (Ti, Si)N and MoN layers have been studied in the paper. The pressure of the working (nitrogen) atmosphere in the deposition process, which varied in the range of $P_N = 0.05 ... 0.67$ Pa, was used as the main influence parameter.

2. EXPERIMENTAL

The samples were obtained by vacuum arc method on the modified facility Bulat-6 [11]. The pressure of the working (nitrogen) atmosphere during deposition was $P_N = 0.05 ... 0.67$ Pa. The coating deposition was carried out from two sources (Ti, Si and Mo) with a continuous rotation of the substrate-holder at a speed of 8 rpm that allowed to obtain a layer of a thickness of about 7-8 nm at a total coating thickness of 9-11 μm.

Silicon was introduced into the titanium target and from there in an amount of 1.8-1.2 wt. % – into the coating for enhancing nitride formation in TiN layers and producing the (Ti, Si)N composition.

During the deposition process, a constant negative potential of a value of $U_{CP} = -110$ V was applied to the substrates. High-temperature annealing was performed at 1023 K for 1 hour in a vacuum furnace VHT 8/22-GR Nabertherm GmbH.

The phase and structural analysis was conducted by X-ray diffractometry in Cu-K_α radiation on the facility DRON-4. Separation of the profiles into components was carried out by applying the "New Profile" software package (development result of NTU "KhPI").

The coating hardness was measured with a hardness tester DM-8 by the micro-Vickers method at an indenter load of 50 g.

The elemental composition of the coatings was studied by analyzing the spectra of the characteristic X-ray radiation generated by an electron beam in a FEI Nova NanoSEM 450 scanning electron microscope. The spectra were taken with an EDAX energy-dispersive X-ray spectrometer installed in the microscope.

3. RESULTS AND DISCUSSION

Analysis of the lateral cross-sections morphology of the coatings obtained throughout the studied P_N interval showed sufficiently high uniformity and low defectiveness in thickness (Fig. 1). At that, with decreasing pressure during deposition (Fig. 1a), the average value of the coating thickness decreases, apparently because of more intense secondary sputtering processes.

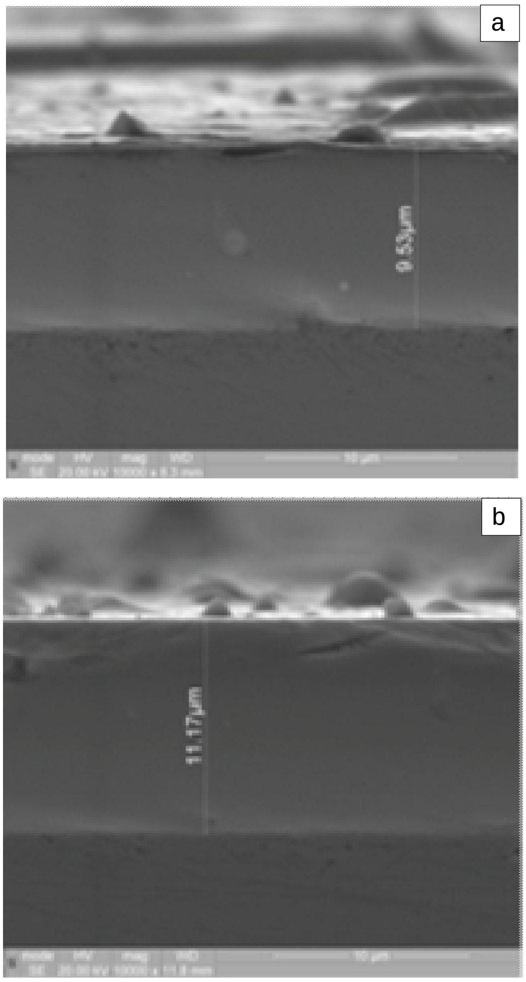

Fig. 1 – The lateral cross-section morphology of the coatings obtained at $U_{CP} = – 110$ V; $P_N = 0.05$ Pa (a), $P_N = 0.67$ Pa (b)

These processes also cause changes in the elemental composition. As shown by the analysis of the energy-dispersive spectra (Fig. 2), as well as their generalization given for the silicon content in the coatings (Fig. 3a) and the Mo/Ti atomic ratio (Fig. 3b), with increasing pressure of the working (nitrogen) atmosphere, the relative silicon content decreases and the Mo/Ti ratio increases.

Here, the nitrogen content, as expected, is minimal when producing coatings at the lowest $P_N = 0.05$ Pa and is about 38 wt. % and is maximal at $P_N = 0.39...0.67$ Pa and reaches 49 wt. %.

In addition to the above discussed secondary selective sputtering, which decreases with increasing pressure and thus enhancing tightly-bound nitride phase (in this case, the specific content of the heaviest and highly self-sputtering constituent in the formed layers – Mo, which also has the lowest heat of formation of stable nitride complexes, should increase), a “contamination” of the evaporated target by nitrides, resulting in a decrease in the vaporization efficiency, can also lead to a relative decrease of the specific component of strong nitride-forming elements (Ti, Si) at high pressure.

In this context, the phase composition is the second important component besides the elemental one. XRD phase analysis was used to study it.

An analysis of the obtained diffraction spectra showed that in the coatings produced at the lowest pressure of

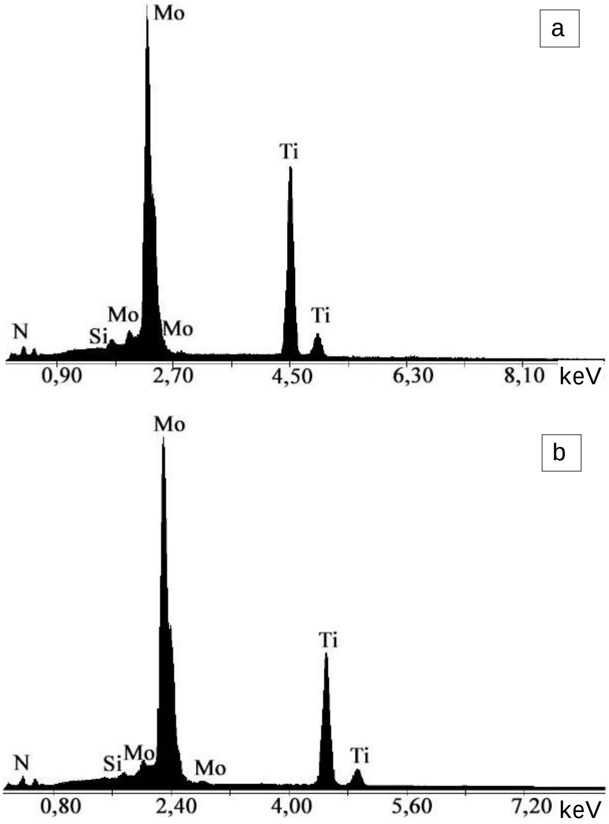

Fig. 2 – Energy-dispersive spectra of the coatings obtained at $P_N = 0.05$ Pa (a) and $P_N = 0.67$ Pa (b)

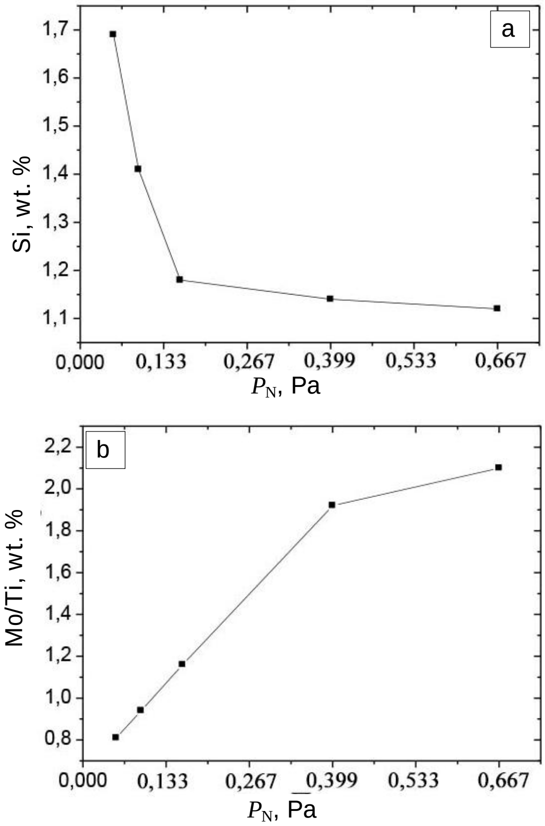

Fig. 3 – Dependences of the change in the atomic content of Si (a) and Mo/Ti atomic ratio (b) in the coatings on the pressure of the working (nitrogen) atmosphere during deposition

0.053 Pa (Fig. 4a), the nitrogen deficiency is mainly manifested in the Mo-based layers, where the formation of metallic molybdenum (bcc crystal lattice) is observed. As a result of annealing, the effect of the formation of metallic molybdenum is enhanced (spectrum 2, Fig. 4a). An increase in P_N to 0.093 Pa leads to the formation of nitrides with the isostructural cubic crystal lattice in the layers based on titanium and molybdenum. In the latter case, this is the γ-Mo_2N phase (Fig. 4b). Formation of the Ti_5Si_3 phase (PDF 29-1362) is detected in the coatings apart from the nitride phases after high-temperature annealing.

The nitride TiN and γ-Mo_2N phases with the isostructural crystal lattice of the NaCl type and appearance of a weak texture of the crystallites with the [100] axis are detected in the coatings before and after annealing with increasing P_N to 0.159 Pa. An increase in P_N to the value of 0.399 Pa leads to an increase in the degree of texture (see Fig. 4d).

The formation of the molybdenum mononitride phase with the hexagonal crystal lattice (PDF 25-1367) in the Mo-based layers is the feature of the diffraction spectra of the coatings obtained at the highest $P_N = 0.667$ Pa (see Fig. 4e). The diffraction reflexes of this phase are enhanced after high-temperature annealing (spectrum 2 in Fig. 4e).

The revealed effect of P_N on the elemental and phase compositions has a decisive influence on such a universal mechanical characteristic as the coating hardness. In Fig. 5 we illustrate the dependences of hardness on P_N for the coatings after their production (dependence 1) and high-temperature annealing (dependence 2).

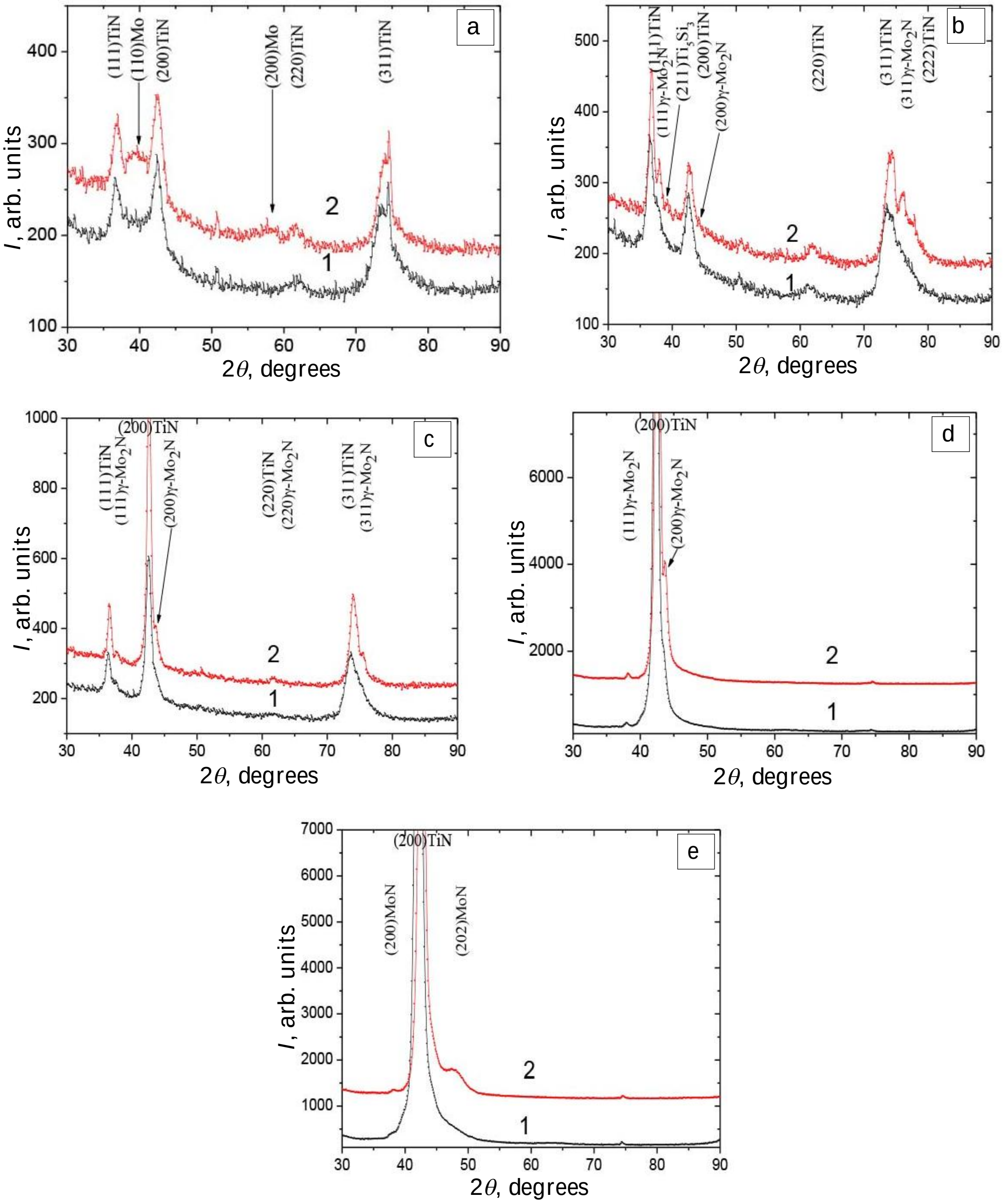

Fig. 4 – Diffraction spectral regions of the coatings deposited at different P_N: a – 0.053 Pa, b – 0.093 Pa, c – 0.159 Pa, d – 0.399 Pa, e – 0.667 Pa. 1 – after annealing; 2 – after high-temperature annealing at 1023 K

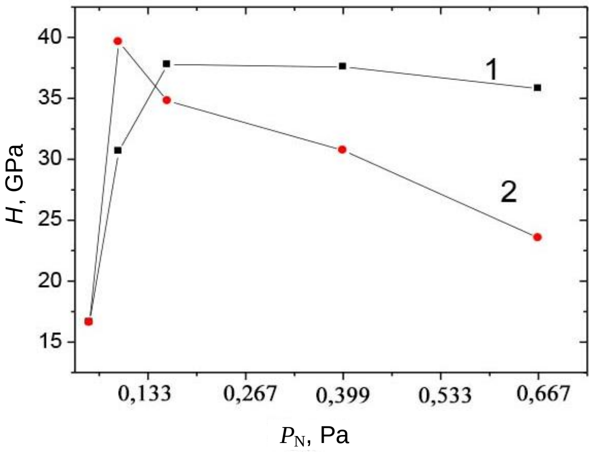

Fig. 5 – Dependences of the coating hardness (*H*) on the pressure of the working (nitrogen) atmosphere ($P_{\rm N}$) before (1) and after (2) high-temperature annealing

It is seen that the dependence of hardness on $P_{\rm N}$ in the deposited coatings reaches the maximum values of about 37.5 GPa in the pressure range of 0.159...0.399 Pa (Fig. 5, dependence 1). From the positions of structural engineering, this state corresponds to the presence of the TiN and γ-Mo_2N nitride phases with the isostructural crystal lattice of the NaCl type in both layers (Fig. 4c, d). Annealing is accompanied by a decrease in hardness of the coatings obtained in the pressure range of 0.159... 0.667 Pa that is associated with the typical growth of crystallites of the constituent phases. This is especially true for a pressure of 0.667 Pa, when, according to the phase analysis, the formation of the MoN phase with the hexagonal crystal lattice (Fig. 4e, spectrum 2) occurs in the Mo-based layers. At the same time, annealing of the coatings obtained at $P_{\rm N}$ = 0.093 Pa leads to a significant increase in hardness by more than 30 % (up to 40 GPa). The comparison with the phase analysis data shows that the appearance of an additional silicide phase (Ti_5Si_3) in the titanium-based layers with the nitrogen deficiency can be the reason for increasing hardness for this type of coatings.

4. CONCLUSIONS

1. Surface morphology of multilayer coatings of the (Ti, Si)N/MoN system is characterized by a sufficiently high homogeneity and planarity at all technological deposition parameters.

2. It is shown that a relative decrease in the silicon content in the coatings and an increase in the molybdenum component occur with increasing $P_{\rm N}$.

3. With increasing $P_{\rm N}$, the phase composition varies from the TiN/Mo composition at the lowest pressure to the TiN/MoN composition at the highest pressure.

4. High-temperature annealing stimulates the crystallite growth that determines their better detectability on the diffraction spectra. At that, the formation of an additional Ti_5Si_3 silicide phase occurs for the coatings obtained at a relatively low vacuum $P_{\rm N}$ = 0.093 Pa.

5. The highest hardness (up to 37.5 GPa) is achieved in the coatings obtained in the pressure range of 0.159 ... 0.399 Pa that corresponds to the presence of nitride TiN and γ-Mo_2N phases with the isostructural crystal lattice of the NaCl type in both layers.

6. High-temperature annealing at 1023 K allows to increase hardness (up to 40 GPa) of the coatings obtained at a relatively low vacuum $P_{\rm N}$ = 0.093 Pa that is explained by the formation in this case of an additional solid silicide Ti_5Si_3 phase.

REFERENCES

1. S. Veprek, *Thin Solid Films* 317, 449 (1998).
2. O.V. Sobol′, O.N. Grigorjev, Yu.A. Kunitsky, S.N. Dub, A.A. Podtelezhnikov, A.N. Stetsenko, *Sci. Sintering* 38, 63 (2006).
3. O.V. Sobol′, *J. Nano-Electron. Phys.* 8 No 2, 02024 (2016).
4. W.J. Meng, X.D. Zhang, B. Shi, R.C. Tittsworth, L.E. Rehn, P.M. Baldo, *J. Mater. Res.* 17, 2628 (2002).
5. M. Nose, W.A. Chiou, M. Zhou, T. Mae, M. Meshii, *J. Vac. Sci. Technol. A* 20, 823 (2002).
6. X. Hu, Z. Han, G. Li, M. Gu, *J. Vac. Sci. Technol. A* 20, 1921 (2002).
7. M. Kong, W. Zhao, L. Wei, G. Li, *J. Phys. D: Appl. Phys.* 40, 2858 (2007).
8. H.D. Mannling, D.S. Patil, K. Moto, M. Jilek, S. Veprek, *Surf. Coat. Technol.* 146-147, 263 (2001).
9. U.S. Nyemchenko, V.Ju. Novikov, O.V. Sobol′, S.S. Grankin, E.M. Tulibiyev, A. Radko, *J. Nano- Electron. Phys.* 7 No 1, 01041 (2015).
10. N.A. Azarenkov, O.V. Sobol, V.M. Beresnev, A.D. Pogrebnjak, D.A. Kolesnikov, P.V. Turbin, I.N. Toryanik, *Metallofiz. Novei-shie Technol.* 35 No 8, 1061 (2013).
11. O.V. Sobol′, A.A. Andreev, S.N. Grigoriev, V.F. Gorban′, M.N. Volosova, S.V. Aleshin, V.A. Stolbovoy, *Problem. Atomic Sci. Technol.* 4(74), 174 (2011).