INFLUENCE OF DEPOSITION PARAMETERS ON STRUCTURE AND THERMAL STABILITY OF Ti-Al-N COATINGS PREPARED BY REACTIVE MAGNETRON SPUTTERING

Klimovich I.M.[1], Komarov F.F.[2], Ljudchik O.R.[1], Zaikov V.V.[1]

[1]Belarusian State University, Nezavisimosti ave. 4, 220030 Minsk, Belarus
[2]Institute of Applied Physics Problem, Kurchatov Str. 7, 220045 Minsk, Belarus
imklimovich@gmail.com

Ti-Al-N coatings were obtained by reactive magnetron sputtering method under different deposition parameters (substrate temperature, bias voltage and reactive gas flow). Structure and elemental composition of films were determined by scanning electron microscopy and energy dispersive X-ray analysis, respectively. Thermal stability of Ti-Al-N coatings was studied by Raman spectroscopy after annealing in air at various temperatures (550 °C, 650 °C and 700 °C). It was found that selection of appropriate deposition parameters allows to obtain Ti-Al-N coating with improved thermal stability.

Introduction

TiN is an important material for protective coatings, diffusion barriers and several other functional applications /1/. Addition of elements, such as aluminum leads to the formation of Ti-Al-N film with superior mechanical properties even at high temperatures /2/. The structure and physical properties of Ti-Al-N coatings strongly depend on the deposition parameters /3/, in particular, reactive and transport gases, substrate temperature, etc. The influence of deposition parameters on the structure and thermal stability of Ti-Al-N coatings is discussed in the work.

Experiment

The vacuum chamber was pumped down to a base pressure of $5 \cdot 10^{-4}$ Pa. Prior to deposition the substrates were cleaned by ion etching in argon plasma at $6.0 \cdot 10^{-2}$ Pa, wherein the discharge current was 20 mA, the discharge voltage was 2.4 kV, the cleaning time was 5 min.

The Ti-Al-N coating was deposited by reactive magnetron sputtering of a TiAl composite target in argon–nitrogen plasma at 0.71 Pa. The substrate in respect of the target was mounted at a distance of 80 mm. Pressure, deposition temperature and bias voltage were kept constant during the Ti-Al-N coating deposition. The deposition temperatures, T_s were 220 ∘C, 340 ∘C and 440 ∘C.

The bias voltages, U_b were - 90 V, - 150 V and - 200 V, and deposition time was 10 min.

Ti-Al-N films were deposited on silicon substrates at different values of reactivity α /4/. The value of reactivity of the process is the main parameter determining composition, and as a consequence the properties of coatings. The value of reactivity α is determined from the spectroscopic characteristics of the discharge by the formula /4/:

$$\alpha = \frac{I_0 - I}{I_0 - I^*},$$

where I_0 is the intensity of the atomic line for the metal target (in this study $\lambda = 506.5$ nm); I is the current intensity value of the titanium line while depositing; I^* is line intensity for a fully nitrated metal target.

The value of reactivity α = 1 corresponds to a fully nitrated or "poisoned" target (a fully nitrated deposition process) and the value of reactivity α = 0 corresponds to deposition process only in inert gas – argon. Three different values of reactivity were chosen α = 0.65 (nitrogen excess), α = 0.6 (stoichiometry) and α = 0.55 (nitrogen deficiency) in this study.

Results and discussion

The microstructure of the films was analyzed by the scanning electron microscopy (SEM) method. SEM photos (Fig. 1) were made using Hitachi S-4800 electron microscope. Energy dispersive X-ray spectra (EDS) were registered by Princeton Gamma-Tech, Inc X-ray detector. The results of EDS measurements, deposition rate v and thickness of coatings h are presented in Table 1.

Table 1. Element composition of Ti-Al-N coatings obtained at different deposition parameters

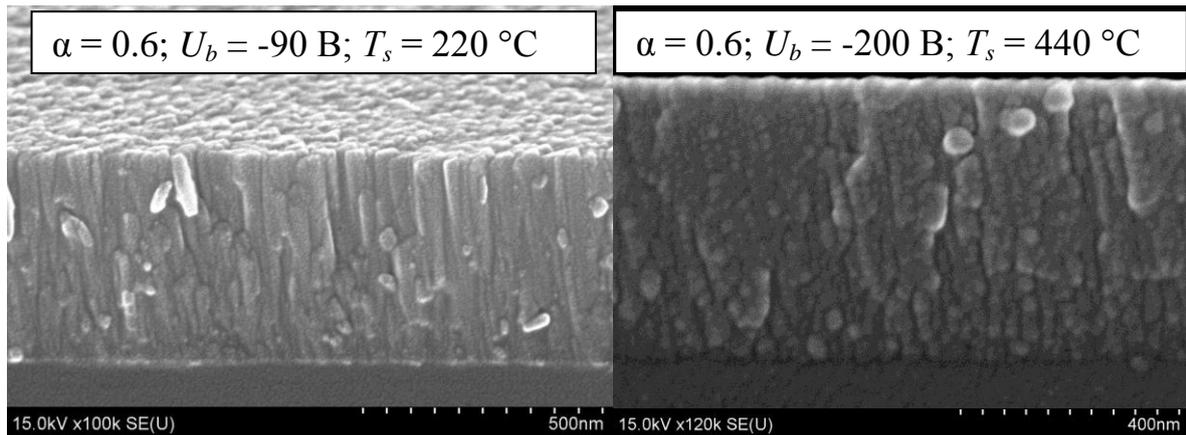| α	U_b	T_s, °C	h, nm	v, nm/min	Ti, at %	Al, at %	N, at %
0.55	-90	220	576	57,6	38	25.23	36.77
0.65	-90	220	443	44,3	34.66	23.10	42.24
0.6	-90	220	518	51,8	38.17	24.85	36.98
0,6	-90	440	379	37,9	36.69	23.61	39.70
	-150	220	498	49,8	40.36	23.36	36.28
	-150	340	389	38,9	37.08	21.78	41.14
	-150	440	419	41,9	35.12	24.08	40.80
	-200	220	477	47,7	38.82	23.96	37.22
	-200	340	442	44,2	37.06	22.39	40.55
	-200	440	509	50,9	35.57	24.77	39.66

Fig. 1. Cross-section morphology of Ti-Al-N films obtained at different deposition parameters

In the majority of cases, the coatings show columnar structure with an average columnar diameter of 45-65 nm. However, in the case of Ti-Al-N film obtained at $T_s = 440 °C$, $U_b = - 200$ V and $\alpha = 0.6$ microstructure is globular. This phenomenon can be connected with formation of fcc-TiN (111) and wurtzite AlN (100) phases /5/.

In order to test the thermal stability of Ti-Al-N coatings, they were annealed in air at various temperatures (550 °C, 650 °C and 700 °C) during 10 min and analyzed by Raman spectroscopy. The Raman measurements were performed at room temperature with a Raman confocal microscope Nanofinder High End (Lotis TII) using the excitation of polarized 473 and 532 nm solid state CW laser focused to the spot of ~ 1 μm in diameter on the surface. The excitation power was 200 mkW and the exposition time 120 s.

The Raman spectra of as-deposited and heat-treated Ti-Al-N coatings obtained at different deposition parameters are shown in Fig. 2 and Fig. 3.
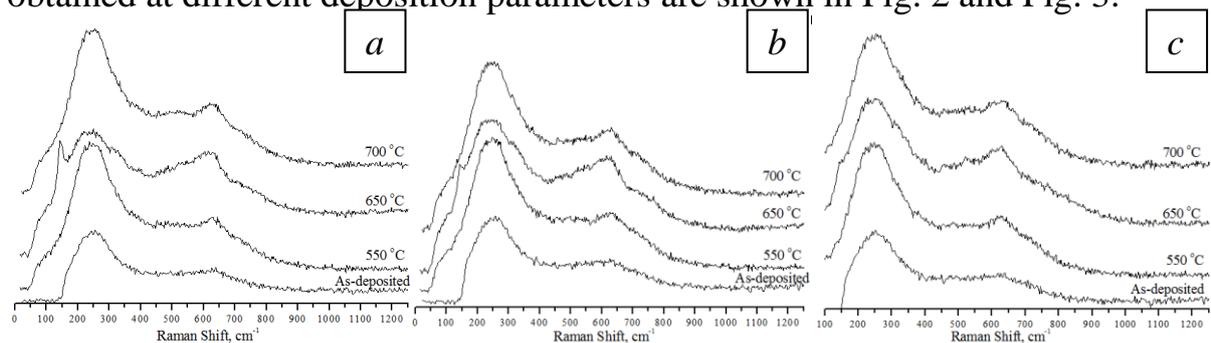

Fig. 2. Raman spectra of as-deposited and heat-treated Ti-Al-N coating obtained at $T_s = 220 °C$, $U_b = - 90$ V and different nitrogen flows: a - $\alpha = 0.55$, b - $\alpha = 0.6$, c - $\alpha = 0.65$
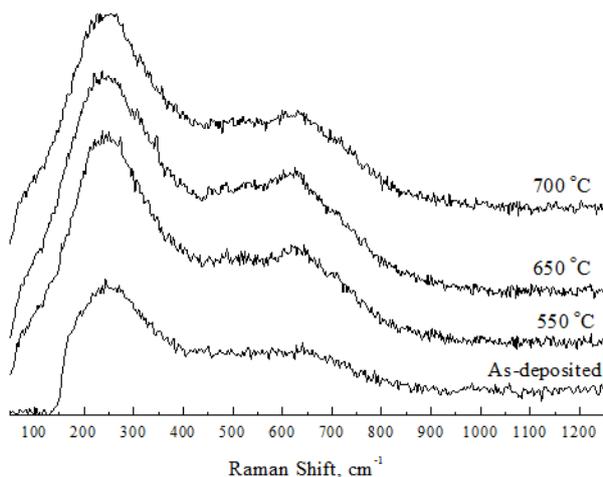
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Fig. 3. Raman spectra of as-deposited and heat-treated Ti-Al-N coating obtained at $T_s = 440\ °C$, $U_b = -200\ V$ and $\alpha = 0.6$

The spectrum of Ti-Al-N coatings shows two broad peaks centered at 243 and 626 cm^{-1}, which correspond to the longitudinal and transverse acoustic and optic phonon modes. The origin of these bands has been described in Ref. /6/. From Fig. 2 it's clearly seen that reactivity values (i.e. nitrogen flow) significantly influence on oxidation resistivity of Ti-Al-N films. In some cases at 650 °C (Figs 2*a* and 2*b*), a peak centered at 145 cm^{-1} emerged, which is due to the formation of TiO. The rutile structure TiO$_2$ appears in Ti-Al-N coatings with further increasing of the annealing temperature /7/, which leads to deteriorating mechanical properties of films. In the case of coating with globular structure (Fig. 3) no changes were observed in the spectra up to a temperature of 700 °C.

Conclusions

As a result of investigation, Ti-Al-N films with different stoichiometric composition and structure were formed. Method SEM found that the coatings reveal in preference columnar structure, but Ti-Al-N films obtained at $\alpha = 0.6$, $U_b = -200\ V$, $T_s = 440\ °C$ have a globular structure. It was found that Ti-Al-N coatings with stoichiometric composition and globular structure reveal the maximum oxidation resistance.

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