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Optical properties of Ti-Al-C-N films: effects of deposition parameters and carbon content

***Abstract**. Ti-Al-C-N films were obtained by reactive magnetron sputtering method under different deposition parameters (substrate temperature, bias voltage and relation between reactive gases partial pressure). Structure, elemental, phase and chemical compositiosn of the films were determined by scanning electron microscopy, energy dispersive X-ray analysis, X-ray diffraction and Raman scattering. It was found that the deposition parameters affect on the compositions and optical characteristics of Ti-Al-C-N coatings. The minimum absorptance and maximum reflectance correspond to Ti-Al-C-N film with carbon content of 36.44 at %.*

***Streszczenie**. Warstwy Ti-Al-C-N uzyskano za pomocą metody reaktywnego napylania magnetronowego dla różnych parametrów osadzania (temperatura podłoża, napięcie odchylenia i zależność między ciśnieniem cząstkowym reaktywnych gazów). Struktura, faza oraz skład chemiczny warstw zostały określone za pośrednictwem skaningowej mikroskopii elektronowej, analizy rentgenowskiej dyspersji energii, dyfraktometrii rentgenowskiej i rozproszenia Ramana. Odkryto, że parametry napylania mają wpływ na kompozycję i charakterystyki optyczne powłok Ti-Al-C-N. Minimalna absorpcja i maksymalny współczynnik odbicia uzyskane zostały dla warstw Ti-Al-C-N o zawartości węgla wynoszącej 36.44%. **(Właściwości optyczne warstw Ti-Al-C-N: wpływ parametrów osadzania i zawartości węgla)**.*

Keywords: Ti-Al-C-N films, reactive magnetron sputtering, X-ray diffraction, Raman spectroscopy, reflectance, transmittance, absorptance.
Słowa kluczowe: Warstwy Ti-Al-C-N, reaktywne rozpylanie magnetronowe, dyfrakcja promieniowa, spektroskopia ramanowska, współczynnik odbicia, przepuszczalność, absorpcja.

Introduction

Transition metal nitrides and carbides are attractive materials for technological applications such as hard and high corrosion resistance coatings in machining and cutting tools, diffusion barriers in microelectronics, layers of solar selective absorbers [1-3]. Transition metal carbonitrides Ti-Al-C-N can be considered as perspective materials with high termal stability, exellent oxidation resistance, enchanced mechanical performance and good optical properties.

The aim of this study is to investigate the influence of the carbon content and deposition parameters of reactive magnetron sputtering on Ti-Al-C-N films composition, morphology and optical properties.

Experimental details

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.

Ti-Al-C-N films have been deposited by a reactive magnetron sputtering of Ti-Al (Al doped with 4% Cu and 1% Si) mosaic target under an environment with a mixture of argon, nitrogen and acetylene gases at the pressure of 0.71 Pa and at the DC power of 450 W. Sublayers of TiAl and TiAlN were deposited onto substrates for the purpose to improve coatings adhesion. The deposition time was 30 min. Silicon and calcium-silicate glass were used as substrates.

In order to investigate the influence of deposition parameters on the structural and optical properties of Ti-Al-C-N films, deposition processes were conducted at four different technological regimes presented in Table 1.

The elemental composition and structure of the films were determined by energy dispersive X-ray analysis (EDX, X-ray detector manufactured by Princeton Gamma-Tech, Inc) and scanning electron microscopy (Hitachi S-4800), respectively.

The phase composition of the films was studied by X-ray diffraction (XRD) employing Cu-Kα radiation source.

The Raman measurements were performed at room temperature with a Raman confocal microscope Nanofinder High End (Lotis TII) using the excitation of polarized 532 nm solid state CW laser focused to the spot of ~1 μm in diameter on the surface. The excitation power was 2 mW and the exposition time 30 s.

The investigation of optical properties of Ti-Al-C-N films was carried out using spectrophotometric system with monochromator S-100.

Results and discussion

Table 1 demonstrates deposition parameters and elemental composition of Ti-Al-C-N films.

Table 1. Deposition parameters and elemental composition of Ti-Al-C-N coatings (the ratio N_2/C_2H_2 means relation between partial pressures of nitrogen and acetylene gases, T_s – substrate temperature, U_b – bias voltage)

Sample number		1	2	3	4
Deposition parameters	N_2/C_2H_2	1/2	1/2	1/2	1/4
	U_b, V	-	-200 V	-	-
	T_s, °C	-	-	380°C	-
Elements, at. %	C	19.87	26.26	31.63	36.44
	N	17.27	19.17	26.43	17.87
	O	9.93	3.11	3.92	3.99
	Mg	0.59	0.41	0.23	0.28
	Al	24.53	22.47	16.18	16.89
	Si	0.29	0.34	0.26	0.29
	Ti	26.90	27.10	20.88	23.75
	Cu	0.62	0.54	0.46	0.49
	Ar		0.61		
Relations between elements	Al/Ti	0.91	0.83	0.77	0.71
	(Al+Ti)/(N+C)	1.38	1.09	0.64	0.75

EDX analysis of the sample 1 indicated a large amount of oxygen (9.93 at.%) while other samples have a negligibly small oxygen amount (values from 3 to 4 at.%). The presence of oxygen can be attributed to contamination by oxygen, H_2O and oxidation of films surface under the air environment.

Substrate biasing, substrate heating, and reducing N_2/C_2H_2 ratio promote decreasing of relations (Al+Ti)/(N+C) and Al/Ti.

SEM images of Ti-Al-C-N films produced at different deposition parameters (see Table 1) are depicted in Fig. 1.

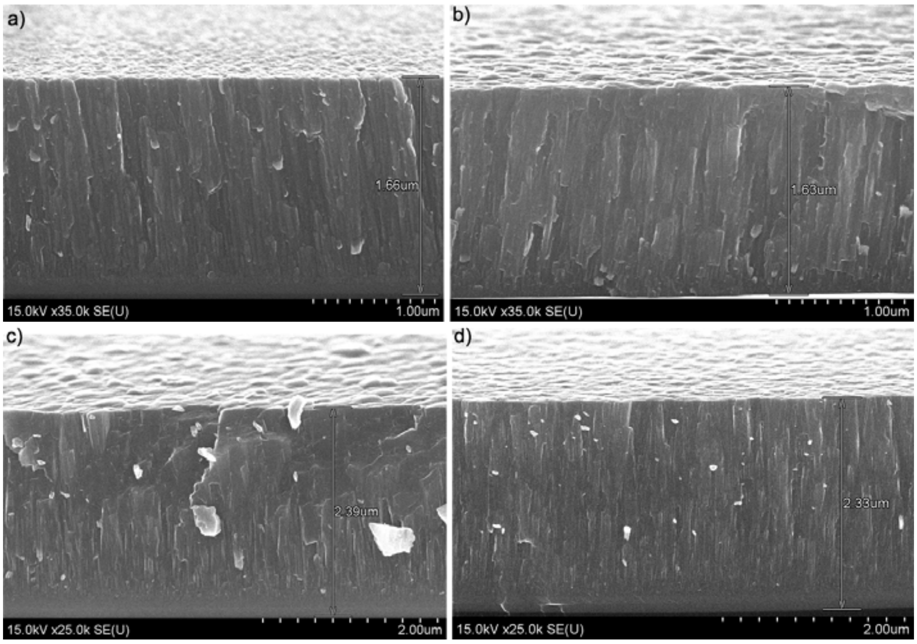

Fig. 1. SEM cross-sectional images of Ti-Al-C-N films deposited on the Si substrates at different deposition parameters: a) sample 1; b) sample 2; c) sample 3; d) sample 4

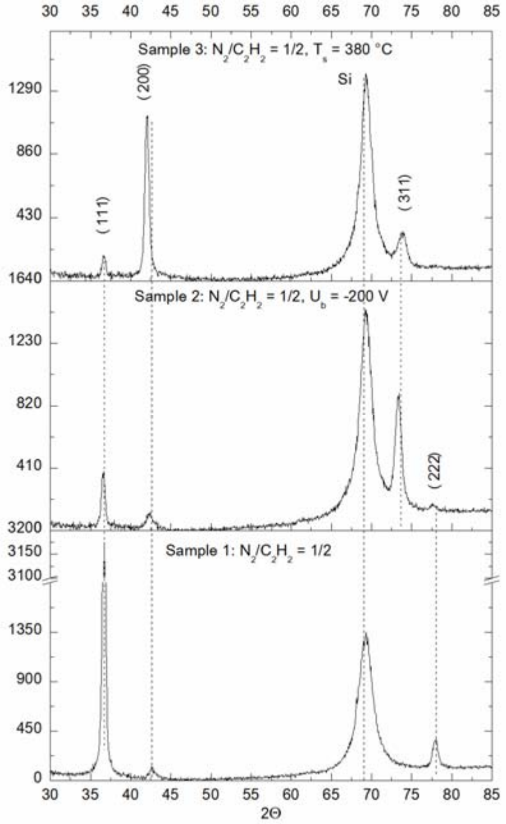

Fig. 2. XRD patterns of Ti-Al-C-N films produced at different deposition parameters

Each of Ti-Al-C-N films has smooth surface topography and columnar structure with the columns diameter widens as the films grow. It can be seen from the Fig 1 that the deposition parameters affect the surface morphology and the films roughness.

Substrate heating and reducing N_2/C_2H_2 ratio (i.e. increasing of carbon-containing gas) lead to a deposition rate increasing by 50%.

XRD patterns of Ti-Al-C-N coatings (sample 1, 2 and 3) are shown in Fig. 2. The identification of the peaks in the coatings reveals (Ti,Al)(C,N) phases with B1–NaCl structures. The phases associated with oxygen compounds were not detected.

The pattern related to sample 1 contains an intense (111) peak and two small peaks assigned to (200) and (222) planes. The (311) peak appears in the samples 2 and 3. When the substrate is heated (sample 3), the most intense peak, with the exception of the silicon substrate signal, becomes (200).

From Fig. 2 it can be seen that the peaks positions shift to a lower diffraction angle with increasing carbon content indicating an expansion in the d-spacing. The values of d_{111}, corresponding to the samples 1, 2 and 3, amounts to 0.2447, 0.2453 and 0.2456 nm, respectively. The observed expansion of the lattice may be caused by the substitution of carbon into the nitrogen lattice positions and the substitution of aluminum into the titanium lattice position, because of the very similar atomic radii of Ti and Al as well as of C and N atoms [4, 5].

Fig. 3 shows the Raman spectra of Ti-Al-C-N coatings with different elemental composition produced at various technological parameters.

Broad bands that correspond to the first-order transverse acoustic (TA) and longitudinal acoustic (LA) mode of fcc-TiAlCN can be observed in the region of 150-500 cm^{-1} [6, 7]. The peak at 450-470 cm^{-1} arises from the second-order acoustic (2A) mode [8, 9]. Transverse optical (TO) and longitudinal optical (LO) modes are in the range of 500-800 cm^{-1}.

Usually, the ratio of acoustical to optical scattering intensities is a measure of the Ti/N atomic ratio in fcc-TiN phase [10, 11]. In all samples, the intensity of the acoustical scattering peak (150-500 cm^{-1}) is higher than that of the optical scattering peak (500-800 cm^{-1}), indicating that the fcc-TiAlCN has a non-stoichiometric composition.

The broad band between 1200 and 1700 cm^{-1} is characteristic for C-C bondings of a highly disordered amorphous carbon phase of mixed sp^2 (graphite-like, G) and sp^3 (diamond-like, D) bonding states [4, 5, 12].

A spectrophotometric system was used for the measuring of reflectance and transmittance spectra in the range of 350-1000 nm. Absorptance spectra were calculated from the formula:

$$T+R+A = 1 \tag{1}$$

where T, R and A are transmittance, reflectance, and absorptance, respectively.

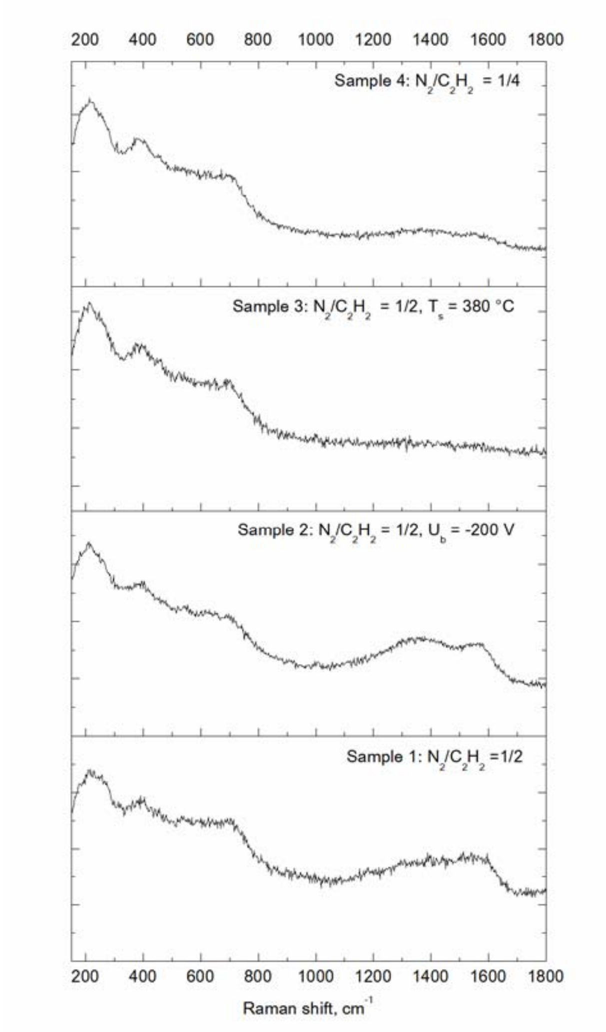

Fig. 3. Raman spectra of Ti-Al-C-N coatings obtained at various technological parameters

Reflectance (R), transmittance (T) and absorptance (A) spectra of deposited Ti-Al-C-N films onto glass substrates are shown in Fig. 4.

The value of reflection coefficient (Fig. 4a) gradually increases with the increase of wavelength for sample 1, which is typical for films with metallic conductivity type according to the Drude-Lorentz theory. Reflectance spectra of other samples (2, 3 and 4) remain almost unchanged in the whole measured range (changes by no more than 4 points). The sample 2 and sample 4 have the lowest and the largest reflectance, respectively.

Transmittance is low because of the high thickness of the films (see Fig. 1). The largest transmittance corresponds to the sample 2, which has a smallest thickness.

The sample 2 has the maximum absorption coefficient (77-81 %) in the whole investigated wavelength range. The sample 4 has the minimum absorptance among the all films under study.

It can be noted, that the optical properties of films depend on a number of factors, including its dielectric constants, thickness, element and phase compositions, surface topology etc. [13, 14].

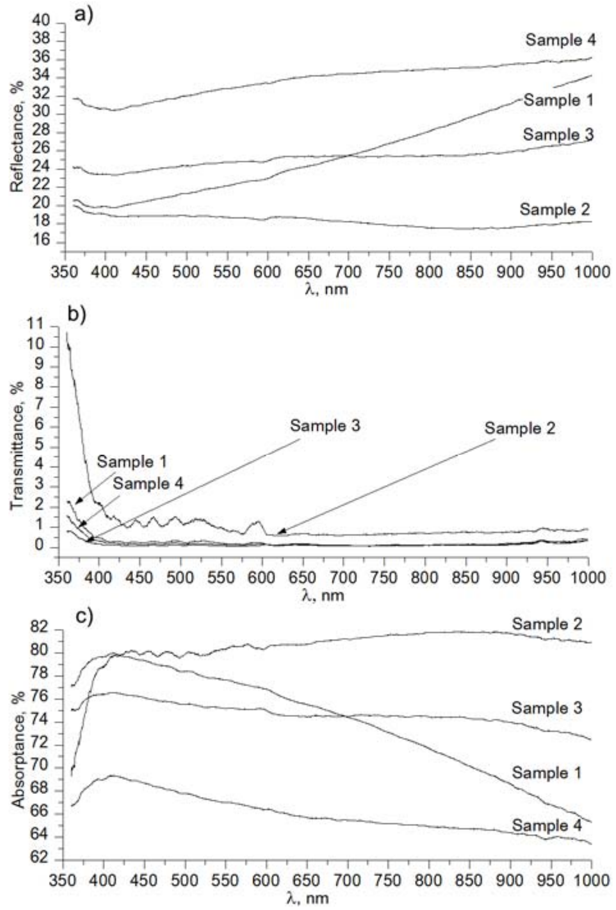

Fig. 4. Reflectance (a), transmittance (b), and absorptance (c) spectra of Ti-Al-C-N coatings produced at different deposition parameters

Conclusions

In the present study, Ti-Al-C-N films have been obtained by means of reactive magnetron sputtering at different deposition parameters.

Using EDX method, it has been found that substrate biasing, substrate heating, and reducing nitrogen/acetylene partial pressure ratio promote decreasing of relations (Al+Ti)/(N+C) and Al/Ti. Each of produced Ti-Al-C-N films has smooth surface topography and columnar structure.

Chemical composition was determined by XRD technique and Raman spectroscopy. Coatings under study consists of (Ti,Al)(C,N) phase with B1-NaCl structure and an amorphous carbon phase.

Carbon concentration, bias potential and substrate temperature has a signicant effect on the reflectance, transmittance and absorptance spectra in visible and near infrared regions. The minimum absorptance and maximum reflectance correspond to the Ti-Al-C-N film with the carbon content of 36.44 at.%.

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REFERENCES

[1] Barshilia H.C., Selvakumar N., Rajam K.S., Biswas A., Optical properties and thermal stability of TiAlN/AlON tandem absorber prepared by reactive magnetron sputtering. *Solar Energy Materials & Solar Cells*, 92 (2008), 1425-1433

[2] Lee Y.K., Latt K.M., Osipowicz T., Sher-Yi C., Study of diffusion barrier properties of ternary alloy ($Ti_xAl_yN_z$) in Cu/$Ti_xAl_yN_z$/SiO_2/Si thin film structure, *Materials Science in Semiconductor Processing*, 3 (2000), 191-194

[3] Jyothi J., Latha S., Bera Parthasarathi, Nagaraja H.S., Barshilia H.C., Optimization of process parameters to achieve spectrally selective TiAlC/TiAlCN/TiAlSiCN/TiAlSiCO/TiAlSiO high temperature solar absorber coating, *Solar Energy,* 139 (2016) 58-67

[4] Stueber M., Barna P.B., Simmonds M.C., Albers U., Leiste H., Ziebert C., Holleck H., Kovacs A., Hovsepian P., Gee I., Constitution and microstructure of magnetron sputtered nanocomposite coatings in the system Ti-Al-N-C, *Thin Solid Films,* 493 (2005), 104-112

[5] Lackner J.M., Waldhauser W., Ebner R., Bakker R.J., Chemistry and microstructure of PLD (Ti,Al)C_xN_{1-x} coatings deposited at room temperature, Appl. Phys. A 79 (2004), 1469-1471

[6] Choe H.J., Kwon S.-H., Lee J.-J., Tribological properties and thermal stability of TiAlCN coatings deposited by ICP-assisted sputtering, *Surface & Coatings Technology*, 228 (2013), 282-285

[7] Zhang X., Qiu Y., Tan Z., Lin J., Xu A., Zeng Y., Moore J.J., Jiang J., Effect of Al content on structure and properties of TiAlCN coatings prepared by magnetron sputtering, *Journal of Alloys and Compounds*, 617 (2014), 81-85

[8] Shum P.W., Li K.Y., Zhou Z.F., Shen Y.G., Structural and mechanical properties of titanium–aluminium–nitride films deposited by reactive close-field unbalanced magnetron sputtering, *Surface & Coatings Technology,* 185 (2004), 245-253

[9] Spengler W., Kaiser R., First and second order Raman scattering in transition metal compounds, *Solid State Communications*, 18 (1976), 881-884

[10] Spengler W., Kaiser R., Bilz H., Resonant Raman scattering in a superconducting transition metal compound –TiN, *Solid State Communications*, 17 (1975), 19-22

[11] Zhang X., Jiang J., Lin J., Moore J.J., Effect of N2 flow on low carbon TiAlNC coatings, *Surface & Coatings Technology,* 203 (2009), 3450-3453

[12] Zeng Y., Qiu Y., Mao X., Tan S., Tan Z., Zhang X., Chen J., Jiang J., Superhard TiAlCN coatings prepared by radio frequency magnetron sputtering, *Thin Solid Films*, 584 (2015), 283-288

[13] Gong D., Cheng X., Ye W., Zhang P., Luo G., The Effect of Annealing under Non-vacuum on the Optical Properties of TiAlN Non-vacuum Solar Selective Absorbing Coating Prepared by Cathodic Arc Evaporation, *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, 28 (2013), No 2, 256-260

[14] Bilokur M., Gentle A., Arnold M., Cortie M.B., Smith G.B., Optical properties of refractory TiN, AlN and (Ti,Al)N coatings, *SPIE Micro+ Nano Materials, Devices, and Applications*, 96685O-96685O-13