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Influence of Substrate Temperature on the Formation of Titanium Carbide Film

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Titanium carbide films have shown an extensive development during the last decades as coating materials. Titanium carbide shows excellent mechanical and chemical properties like a high melting point, hardness and great chemical and thermal stability. Titanium carbide films were deposited on glass and monocrystalline silicon substrates by direct current (DC) magnetron ion-plasma sputtering process from graphite/titanium combined target. Titanium carbide films with various C/Ti ratios can be deposited by DC magnetron sputtering using titanium sheets on the graphite target erosion area as a solid carbon source. The dependence of substrate temperature (150, 250, 350, and 450 °C) on the formation of titanium carbide phase was studied by X-ray diffraction analysis and Raman spectroscopy. The samples were studied by two different Raman spectrometers: AFM-Raman instrument Solver Spectrum (NT-MDT) with 473 nm laser and NTegra Spectra (NT-MDT) with 473 nm and 633 nm laser. The stoichiometry of deposited films was determined by energy-dispersive X-ray spectroscopy analysis.

Keywords: Magnetron sputtering, Titanium carbide, Thin films, Raman spectroscopy.

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1. INTRODUCTION

The use of titanium carbide as coating materials has shown an extensive development during the last decades [1]. Titanium carbide (TiC) presents excellent mechanical and chemical properties like a high melting point, hardness and great chemical and thermal stability [2-8]. TiC coatings produced by PVD methods have high hardness and wear resistance [9]. Deposition of titanium carbide films can be achieved by co-sputtering of carbon and titanium targets from mixed carbon and titanium plasma streams [10]. There is a report about deposition of TiC using reactive plasma sputtering system with titanium substrate and argon-acetylene gas mixtures [11]. Titanium carbide films with various C/Ti ratios can be deposited by DC magnetron sputtering using carbon sheets on the Ti target erosion area as a solid carbon source [12]. In this work, we report the deposition of TiC films by DC magnetron sputtering method with combined graphite/titanium target at different substrate temperatures.

2. EXPERIMENTAL

Titanium carbide films were deposited in magnetron sputtering system with DC power source. The target was pure graphite substrate 99.99 % with forty-millimeter diameter and the pure titanium round foil 99.999 % (40 mm diameter), which was cut into eight sectors and placed above the graphite target as a pie pieces. The graphite-titanium erosion area ratio was 50 %/50 %. The magnetron was continuously cooled by water flow. Special substrate holder with heating elements could increase the substrate temperature up to 450 ºC. The substrate and target distance was 120 mm. Titanium carbide film was deposited on glass and n-type monocrystalline silicon <100> substrate surfaces (with 1 cm^2 area). Experiments were conducted in vacuum system VUP-5. After loading the samples in the working chamber, vacuum was produced up to 10^{-4} Pa. Pure argon gas (99.999 %) was used as a working gas. Argon gas was introduced into the working chamber at constant flow. The working plasma discharge power was 90 W (600 V, 150 mA). The working pressure was ~ 1 Pa.

With 90 W power, we conducted experiment for one hour (60 min) without heating the substrate holder. All the subsequent experiments last the same time. Due to the plasma discharge influence, the sample was heated up to 150 °C at the end of the experiment. We did the same experiments with substrate holder temperatures: ~ 200 °C, ~ 315 °C and ~ 425 °C (which rose up to approximately 250 °C, 350 °C and 450 °C, respectively, due to the plasma discharge influence). Deposited films were analyzed by XRD, Raman spectroscopy and EDS analysis. XRD analysis was performed on DRON-7 X-ray diffractometer with CuK-alpha radiation with 1.5404 Å wavelength and 0.1-degree scanning steps. Raman spectra were obtained by AFM-Raman instrument Solver Spectrum (NT-MDT) and NTegra Spectra (NT-MDT). Energy dispersive X-ray spectroscopy analysis was performed on scanning electron microscope (FEI, Quanta 3D 200i).

3. RESULTS AND DISCUSSION

XRD patterns of titanium carbide films deposited on the surface of glass at temperature range from 150 °C to 450 °C are shown in Fig. 1a. XRD pattern shows a broad peak from 10 to 40 degrees, which belongs to glass substrate. There is a distinct peak at ~ 42.2 degrees, which is due to X-ray reflections from TiC (200) plane. Also, there is a very weak peak from TiC (220) plane at ~ 61 degrees. The results of X-ray diffraction from TiC film grown on the surface of monocrystalline silicon are shown in Fig. 1b. In this XRD pattern, one can observe the Si (111) peak at ~ 28.4 degrees and one more TiC

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peak from (111) plane at ~ 36 degrees, which could not be seen from samples grown on the glass surface, because of the broad and intensive signal from glass.

One can see that the intensity of TiC peaks increases with increasing substrate temperature. The increase of atomic mobility during the deposition may lead to the relaxation of the film structure to the lower energy state with the formation of (111) texture [13]. In our case, the increase of atomic mobility is caused by the increase of the substrate temperature. XRD results distinctly represent that increasing substrate temperature promotes the formation of TiC phase. According to the XRD data, we also can see that monocrystalline silicon is a more preferable substrate for deposition of TiC films.

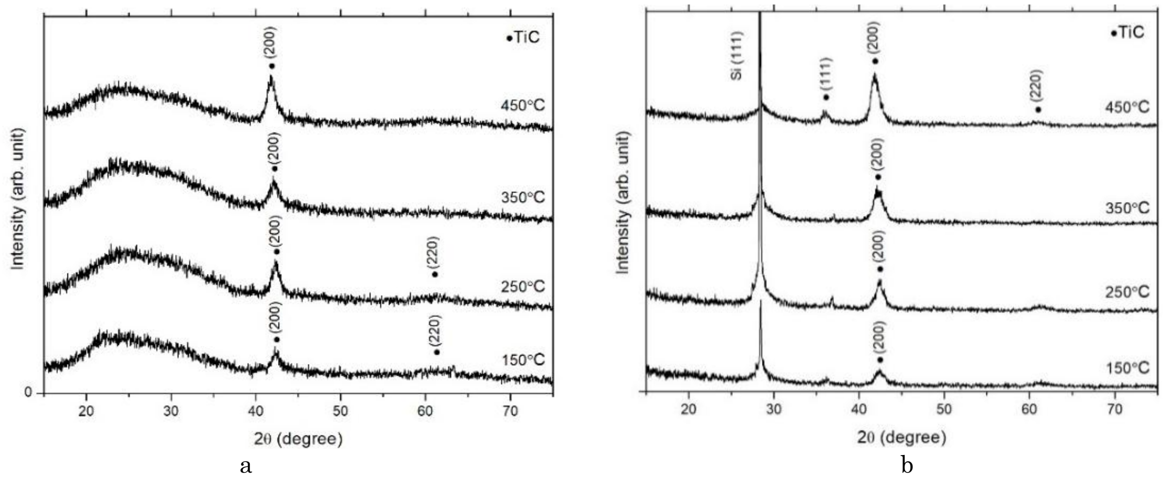

Fig. 1 – XRD pattern of TiC thin films: (a) TiC films deposited on glass surface; (b) TiC films deposited on silicon surface

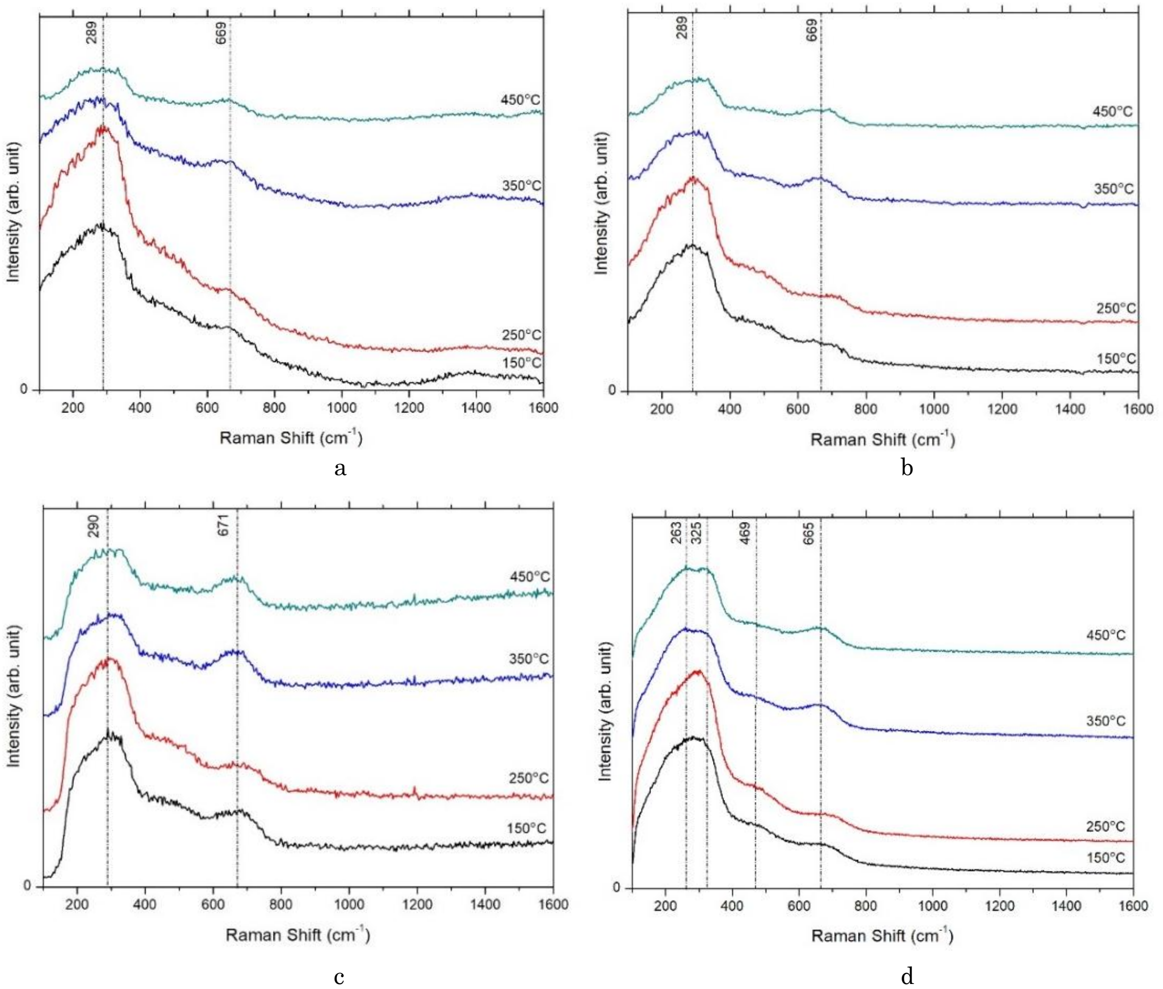

Fig. 2 – Results of Raman spectroscopy (Solver Spectrum), 473 nm laser: (a) TiC film deposited on glass surface; (b) TiC film deposited on silicon surface. Results of Raman spectroscopy (NTegra Spectra) of TiC film on monocrystalline silicon surface: (c) 473 nm laser; (d) 633 nm laser

Fig. 2a represents the Raman spectra of titanium carbide films on glass substrate registered by AFM-Raman instrument Solver Spectrum (NT-MDT) using 473 nm laser of 35 mW power. There are two regions observed in the Raman spectra of our films, from 100 to 800 cm^{-1} and from 1200 to 1600 cm^{-1}. The first region corresponds to titanium carbide and the second region occurs due to amorphous carbon phase. Raman spectra of titanium carbide films deposited on monocrystalline silicon wafer surface are shown in Fig. 2b. There is no peak corresponding to amorphous carbon phase on silicon substrate. Thus, we can conclude that the formation of titanium carbide phase depends on the crystalline structure of the substrate.

Titanium carbide films on silicon substrate were rescanned with another Raman spectrometer NTegra Spectra (NT-MDT) in order to confirm the results of the previous analysis with blue (473 nm) and red (633 nm) lasers. The results of the analysis with different lasers are shown in Fig. 2c and Fig. 2d, respectively. There are no significant differences occurred during the scanning with blue laser. While with red laser, we observe a good signal to noise ratio and splitting the broad peak from ~ 100 to ~ 400 cm^{-1} into two peaks with maxima at 263 cm^{-1} and 325 cm^{-1} for the samples obtained at 350-450 °C temperature range. The low-frequency peaks at 263 cm^{-1} and 325 cm^{-1} are associated with acoustical phonons of titanium carbide and/or nitride phase and the peak at ~ 665 cm^{-1} is due to titanium-carbon vibrations [14]. Increasing substrate temperature causes the rise of a peak at ~ 665 cm^{-1} and the decrease of the peak intensity in range from ~ 100 to ~ 400 cm^{-1}. The width, frequency and intensity of the Raman peaks strongly depend on defects, chemical composition, short-range order, crystalline structure and internal stresses in material. It is known that scattering in acoustic range (LA and TA modes) is determined by the vibrations of the Ti ions (typically 150-350 cm^{-1}), while peaks in the optical range (400-650 cm^{-1}) are generally attributed to the lightweight C ions (LO and TO modes) [15].

The Gaussian decomposition of Raman peaks is represented in Fig. 3 and vibrational modes with corresponding peak positions are shown in Table 1. I. Dreiling et al. found out that the acoustical phonons shift to higher frequencies due to changes in the lattice constant when carbon content in $Ti_xC_yN_z$ compound increases [16]. We observe the same tendency in our experiment, which was confirmed by the results of Raman spectroscopy represented in Table 1 and energy-dispersive X-ray spectroscopy (EDS) shown in Fig. 4. EDS analysis confirms that the stoichiometry of titanium carbide films synthesized at 450 °C is coincide with TiC. At lower tem-peratures, the percentage of titanium atoms is almost twice higher than that of carbon atoms. We presume that the small amount of carbon atoms at low temperatures is due to resputtering phenomena of lightweighted carbon atoms when hit by titanium atoms which have four-time bigger mass. During the increase of substrate temperature, the titanium and carbon atoms, which are deposited on substrate, can form chemical bond (covalent bond) so that the carbon atoms are not intensively re-sputtered from the surface of the film.

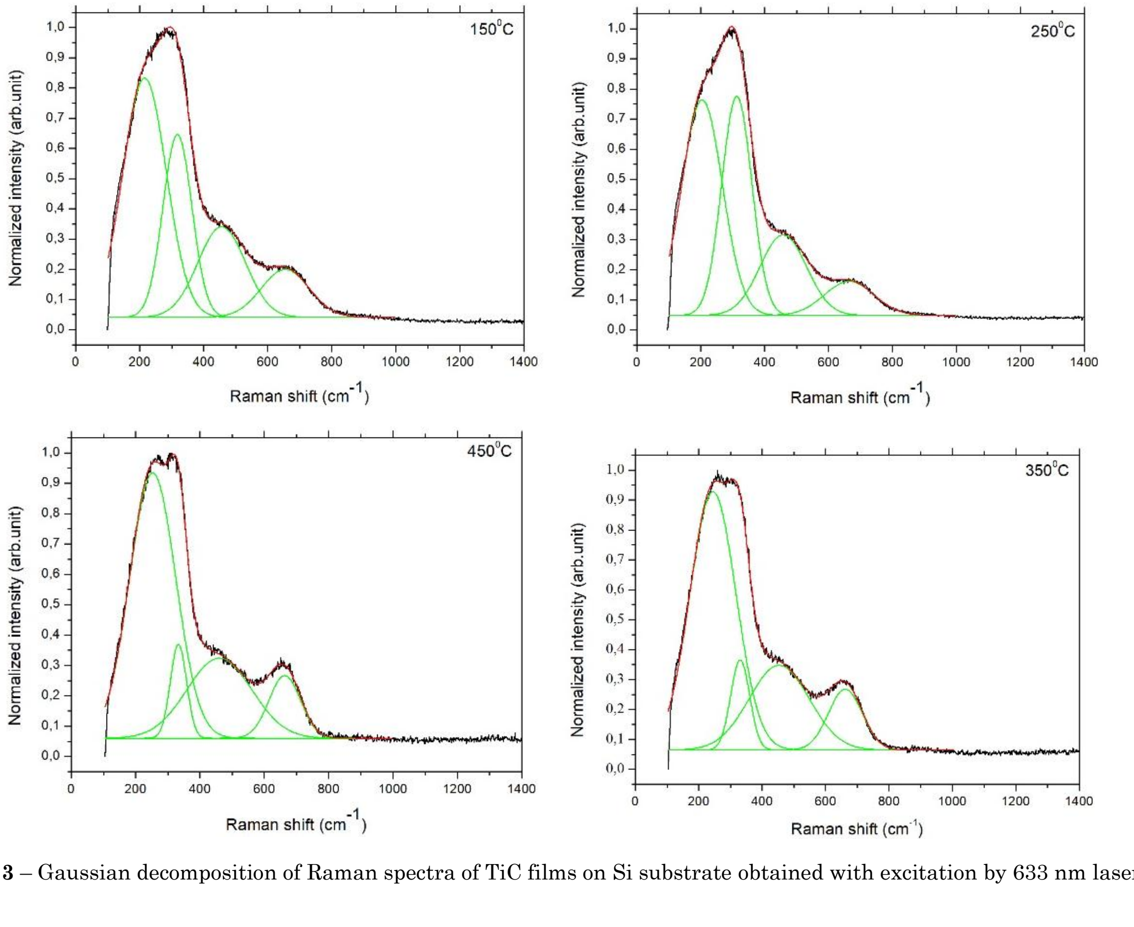

Fig. 3 – Gaussian decomposition of Raman spectra of TiC films on Si substrate obtained with excitation by 633 nm laser

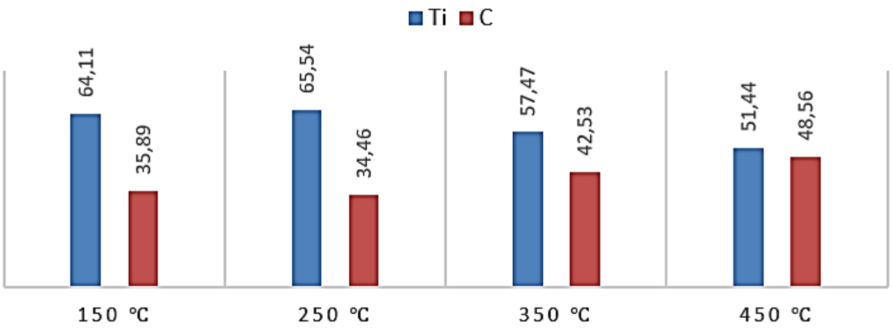

Fig. 4 – EDS analysis of TiC film on silicon substrate at different substrate temperatures

Table 1 – Peak positions after Gaussian decomposition

Substrate temperature (°C)	TA (cm^{-1})	LA (cm^{-1})	TO (cm^{-1})	LO (cm^{-1})
150	215	318	456	655
250	204	313	458	665
350	245	331	454	662
450	253	333	461	664

4. CONCLUSIONS

In this work, we studied the effect of synthesis conditions on the formation of titanium carbide phase on glass and monocrystalline silicon surfaces by DC magnetron ion-plasma sputtering of combined graphite/titanium target. The X-ray diffraction analysis and Raman spectroscopy showed that the structure of titanium carbide films depend on the substrate temperature. By the results of X-ray diffraction, we can conclude that the more preferable conditions for the formation of titanium carbide phase are the monocrystalline substrate surface and high temperatures. Gaussian decomposition of Raman spectra revealed the changes in vibrational modes presumably induced by changes in Ti_xC_y lattice parameters. According to EDS analysis it was found out that the Ti:C atomic ratio in synthesized films changes from ~ 2:1 at 150 °C to ~ 1:1 at 450 °C, which was explained by resputtering phenomena dominating at low synthesis temperatures. Thus, the increase of temperature up to 450 °C allows to synthesize films with stoichiometry that coincides with that of TiC.

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REFERENCES

1. Y. Benarioua, J. Lesage, E. Bemporad, D. Chicot, *Surf. Coat. Technol.* **200**, 5447 (2006).
2. Y.T. Pei, D. Galvan, J.T.M. De Hosson, A. Cavaleiro, *Surf. Coat. Technol.* **198**, 44 (2005).
3. T. Zehnder, J. Patscheider, *Surf. Coat. Technol.* **133-134**, 138 (2000).
4. T. Zehnder, P. Schwaller, F. Munnik, S. Mikhailov, J. Patscheider, *J. Appl. Phys.* **95**, 4327 (2004).
5. W. Gulbiński, S. Mathur, H. Shen, T. Suszko, A. Gilewicz, B. Warcholiński, *Appl. Surf. Sci.* **239**, 302 (2005).
6. R.S. Rawat, P. Lee, T. White, Li Ying, S. Lee, *Surf. Coat. Technol.* **138**, 159 (2001).
7. Y. Hu, L. Li, X. Cai, Q. Chen, P.K. Chu, *Diamond Relat. Mater.* **16**, **181** (2007).
8. S. Inoue, Y. Wada, K. Koterazawa, *Vacuum* **59**, 735 (2000).
9. A. Mani, P. Aubert, F. Mercier, H. Khodja, C. Berthier, P. Houdy, *Surf. Coat. Technol.* 194, **190** (2000).
10. Z. Fogarassy, N. Oláh, I. Cora, Z.E. Horváth, T. Csanádi, A. Sulyok, K. Balázsi, *J. Eur. Ceram. Soc.* **38**, 2886 (2018).
11. S. Zhang, X.L. Bui, J. Jiang, X. Li, *Surf. Coat. Technol.* **198**, 206 (2005).
12. E. Kusano, A. Satoh, M. Kitagawa, H. Nanto, A. Kinbara, *Thin Solid Films* **343-344**, 254 (1999).
13. A.Z. Ait Djafer, N. Saoula, N. Madaoui, A. Zerizer, *Appl. Surf. Sci.* **312**, 57 (2014).
14. L. Escobar-Alarcon, V. Medina, E. Camps, S. Romero, M. Fernandez, D.A. Solis-Casados, *Appl. Surf. Sci.* **257**, 9033 (2011).
15. B.H. Lohse, A. Calka, D. Wexler, *J. Appl. Phys.* **97**, 114912 (2005).
16. I. Dreiling, D. Stiens, T. Chassé, *Surf. Coat. Technol.* **205**, 1339 (2010).

Вплив температури підкладки на формування плівок карбіду титану

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Протягом останніх десятиліть, плівки карбіду титану використовуються як матеріали для покриттів. Карбід титану проявляє чудові механічні та хімічні властивості, такі як висока температура плавлення, твердість і гарна хімічна та термічна стабільність. Плівки карбіду титану наносилися на скляні та монокристалічні кремнієві підкладки методом іонно-плазмового магнетронного розпилення при постійному струмі з об'єднаної мішені графіт/титан. Плівки карбіду титану з різними співвідношеннями C/Ti можуть бути нанесені методом магнетронного розпилення при постійному струмі з використанням титанових листів в області ерозії графітової мішені як джерела твердого вуглецю. Залежність температури підкладки (150, 250, 350, та 450 °C) від утворення фази карбіду титану вивчалася методом рентгеноструктурного аналізу та раманівської спектроскопії. Зразки досліджувалися двома різними раманівськими спектрометрами: AFM-Raman instrument Solver Spectrum (NT-MDT) з 473 нм лазером і NTegra Spectra (NT-MDT) з 473 нм і 633 нм лазерами. Стехіометрія осаджених плівок визначалася за допомогою енергодисперсійного рентгенівського спектроскопічного аналізу.

Ключові слова: Магнетронне розпилення, Карбід титану, Тонкі плівки, Раманівська спектроскопія.