

COMPOSITE TiC-aC:H COATINGS SYNTHESIZED BY CO-DEPOSITION FROM THE PLASMA OF VACUUM ARC SOURCE WITH TITANIUM CATHODE AND PLASMA OF HIGH-FREQUENCY DISCHARGE IN BENZENE VAPOURS

A.A. Luchaninov, A.O. Omarov, V.E. Strel'nitskij, R.L. Vasilenko

National Science Center "Kharkov Institute of Physics and Technology", Kharkov, Ukraine;

Iu.N. Nasieka, V.N. Naseka, N.I. Boiko

V.E. Lashkaryov Institute of Semiconductor Physics NAS of Ukraine, Kiev, Ukraine

E-mail: strelnitskij@kipt.kharkov.ua

Composite TiC-aC:H coatings had been synthesized by co-deposition from the plasma of vacuum arc source with titanium cathode and plasma of high-frequency discharge in benzene vapours. Raman spectra of coatings contain TiC carbide peaks, as well as D and G peaks of diamond-like aC:H-phase. SEM studies have shown that surface of the coatings is cellular or look like "cauliflower", the dimensions of structural elements vary from tens to hundreds nanometers. At the benzene vapor pressure $6 \cdot 10^{-3}$ Torr and RF-potential 200...500 V the coatings deposited have the best mechanical properties – hardness 32...37 GPa and Young modulus 350...400 GPa.

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1. INTRODUCTION

Composite TiC-aC:H coatings consisting of solid TiC nanocrystals embedded in a relatively more flexible aC:H matrix, have increased strength, while retaining the inherent to the constituent their phases hardness and abrasive resistance. According to the published data, depending on the relative amount of these two phases, the properties of nc-TiC-aC:H can vary from very hard coatings with a hardness more than 40 GPa, and the Young's modulus above 300 GPa, to films with a friction coefficient less than 0.1 and a speed wear less than $2 \cdot 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ [1]. Varying process parameters, this type of coatings is usually obtained by magnetron deposition in a high-frequency discharge in a mixture of argon with gaseous hydrocarbons, in particular acetylene [2].

In this paper, TiC-aC:H coatings were synthesized by deposition from a vacuum-arc source with titanium cathode and plasma of high-frequency discharge in benzene vapours. The increased coating growth rate deposited with the vacuum-arc method in comparison with the magnetron method allows to significantly increasing the productivity of the process. TiC-aC:H coatings synthesized at various vapor pressure of benzene in the working chamber and different values of the RF-potential on the substrate have been studied by the Raman spectroscopy method, the results of which confirm the composite composition of the coatings. Elemental analysis of deposited coatings was carried out, hardness and modulus of elasticity were measured, the values of which, depending on process parameters, vary widely, which expands the possible applications of TiC-aC:H coatings.

2. TECHNIQUE OF EXPERIMENTS

The deposition of TiC-aC:H coatings was carried out by the joint operation of a vacuum-arc plasma source with a titanium cathode and a high-frequency discharge in benzene vapor. The apparatus scheme is shown in Fig. 1.

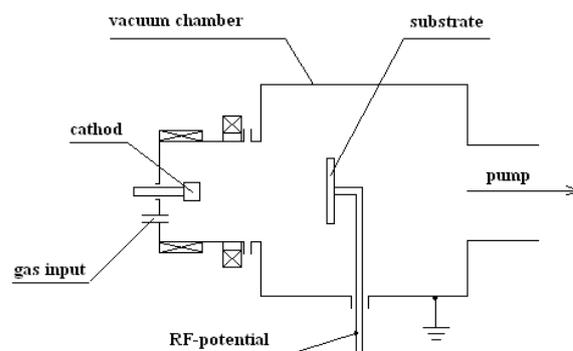


Fig. 1. The scheme of the experimental apparatus

Samples from stainless steel 12Cr18Ni10T and single-crystal silicon wafer were fixed on a water-cooled rotating substrate holder with a diameter of 180 mm. Before the deposition of TiC-aC:H coatings, surfaces of samples were cleaned in an argon atmosphere at an RF-potential of $U = 1200 \text{ V}$ for 10 min. After the arc discharge parameters were adjusted, the RF-generator was tuned to the required potential. The arc discharge current during the deposition of TiC-aC:H coatings was of 100 A. The vapor pressure of benzene $P_{\text{C}_6\text{H}_6}$ in various series of processes was of $2 \cdot 10^{-3}$; $4 \cdot 10^{-3}$ or $6 \cdot 10^{-3}$ Torr. RF-potential with a frequency of 7 MHz was applied from a generator to the substrate via a separating capacitor. In process of deposition, the RF-potential of the substrate was of 200, 500, and 1000 V at each of the three vapor pressure values of benzene in the working chamber. The thickness of the coatings was from 1 up to $3.2 \mu\text{m}$ during the deposition time 15...20 min.

The thickness of the coatings was measured by the interference microscope MII-4. The hardness and Young's modulus were measured by the G200 nanoindenter in the continuous stiffness measurement (CSM) mode. Raman measurements were carried out on the HORIBA Jobin-Yvon T64000 spectrometer equipped with a UV-Visible-NIR Olympus BX4 confocal microscope and a TE-1024x256 Andor CCD

detector with thermoelectric cooling. To excite the vibrational spectra, we used a gas Ar-Kr laser $\lambda_{\text{ex}} = 488 \text{ nm}$, an integrated output power was of 100 mW. The surface morphology and coating composition were examined using a scanning electron microscope JSM 7001F equipped with an INCA ENERGY 350 X-ray spectrometer.

3. RESULTS OF THE RESEARCH

Experiments have shown that the characteristics of the TiC aC:H coatings deposited in the investigated ranges of process parameters are significantly different. The deposition growth rate of coatings in different modes is given in Tabl. 1.

Table 1

The deposition growth rate of TiC-aC:H coatings as a function of the vapor pressure of benzene and the RF-potential of the substrate

RF-potential, V	Vapor pressure of benzen, $\times 10^{-3}$ Torr		
	2	4	6
	Deposition rate, $\mu\text{m/h}$		
200	7.6	9.6	9.8
500	5.6	8.6	9
1000	4.2	6	6.5

As can be seen from the values given in Table 1, the deposition growth rate of coatings is quite high, much higher than in the magnetron method (up to 1 $\mu\text{m/h}$), it depends both on the pressure of benzene and on the substrate bias potential. The coating growth rate increases with increasing benzene pressure at a fixed potential; similarly, the coating growth rate increases with decreasing RF-potential from 1000 to 200 V at a fixed benzene pressure.

The Raman spectroscopy method was used to study samples of various series of processes with a fixed vapor pressure of benzene. In Fig. 2 presented the vibrational spectra (and their decomposition into elementary components, Gaussians) of coatings deposited at a vapor pressure of $6 \cdot 10^{-3}$ Torr and 200, 500, and 1000 V RF-potentials, characterized by the highest deposition rates (and correspondingly the largest thickness). The blue curves are experimental spectra, the shaded areas are the components of the decomposition and the points are the sum of the decomposition components.

The analysis shows that in the spectrum of coatings deposited at an RF-potential of 200 V there are peaks of 354 and of 635 cm^{-1} , characteristic for nanocrystalline (or non-stoichiometric) TiC, and D and G peaks of the diamond-like aC:H-phase (1400 and 1600 cm^{-1}) [5], which indicates that these coatings are composite. The Raman band at 900 cm^{-1} was not reliably identified.

When processing the EDX analysis of the elemental coating composition, the SEM JEOL JSM7001F database was used (with the initial calibration by the Ti standard). According to the results of the EDX analysis, the C:Ti ratio was of 0.6 for $U = 500 \text{ V}$ and of 0.2 for $U = 1000 \text{ V}$, i. e. less than one in all synthesized coatings. And, it is possible also a systematic error

associated with the deposition of carbon on the investigated sample surface from the working environment of the microscope due to steam-oil pumping. Based on the Raman spectroscopy data, in some samples this ratio is greater than 1. For this reason, we believe that the EDX measurements are lower and should be considered as estimates, indicating only the tendency of the C:Ti ratio to change with the parameters of the coating synthesis process.

Consideration of the thermodynamically equilibrium phase diagram [4] shows that at a carbon concentration of less than 1...2% (solubility limit) in the Ti-C-system, a monophasic solid solution of carbon in titanium can form. With an increase in carbon concentration up to 40%, the system is two-phase and consists of α -titanium and titanium carbide. In the range of 40...97%, monophasic titanium carbide – exists. With a further increase % C, the system is two-phase and consists of titanium carbide and carbon.

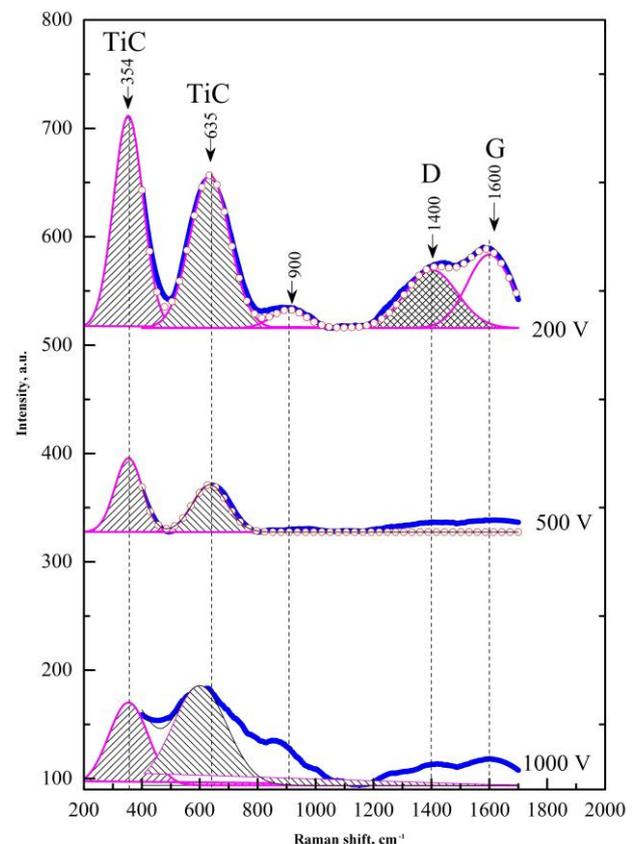


Fig. 2. Raman spectra of coatings deposited at $P_{\text{C}_6\text{H}_6} = 6 \cdot 10^{-3} \text{ Torr}$

It is known that titanium doping with carbon (in the solubility range, i.e. the existence of a solid solution) leads to an increase in hardness from 1 to 2 GPa. The measured hardness values (above 30 GPa) in coatings deposited at RF-potentials of 200 and of 500 V indicate the presence of a large amount of titanium carbide solid phase (with the formula from $\text{TiC}_{0.4}$ up to $\text{TiC}_{0.97}$ [4]) along with the another phase, which has a lower hardness. Indirectly, the type of this second phase is indicated by the Raman spectra of the samples. In the coating deposited at bias potential 200 V, there is a diamond-like aC:H-phase (which is characterized by

peaks of 1400 and 1600 cm^{-1}). In coatings deposited at a bias potentials of 500 and 1000 V, these peaks are practically not detected, which suggests that the carbon content in these coatings is less or equal to stoichiometric, and the second phase is α -titanium.

Such changes in the phase composition of the coatings as a function of the RF bias potential can be explained in term of the known experimental fact of a decrease in the content of light atoms (in this case, carbon) in the coating as the energy of the deposited ions increases due to their preferential sputtering. The deposition rate decreases, which was observed experimentally.

The morphology of the coatings surface deposited in various regimes is shown in Fig. 3.

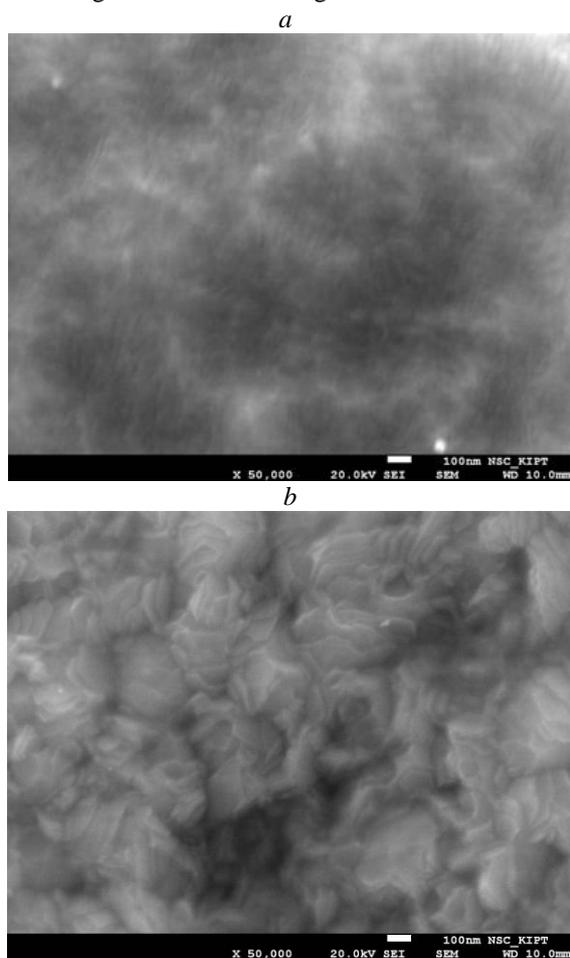


Fig. 3. SEM image of the surface of TiC-aC:H coatings deposited at $P_{\text{C}_6\text{H}_6} = 2 \cdot 10^{-3}$ Torr, $U = 200$ V (a), $P_{\text{C}_6\text{H}_6} = 6 \cdot 10^{-3}$ Torr, $U = 1000$ V (b)

The surface of coatings synthesized at a low working gas pressure $P_{\text{C}_6\text{H}_6} = 2 \cdot 10^{-3}$ Torr and a low substrate potential of $U = 200$ V (see Fig. 3,a) has a fine-cellular structure characteristic for crystalline materials deposited by PVD methods under columnar growth conditions, in particular nitrides [6].

Coating deposited at high pressure $P_{\text{C}_6\text{H}_6} = 6 \cdot 10^{-3}$ Torr and an increased potential of $U = 1000$ V (see Fig. 3,b) have a developed surface with structural elements size ranging from tens to hundreds nanometers. Similar changes in the surface pattern of TiC-aC:H coatings with an increase in the ratio of

atomic concentrations of C:Ti elements were observed in [1]. At small C:Ti (less than 1), the surface is faceted, which was interpreted by the authors as evidence of the columnar structure of the coating, and for large values of this parameter (6 or more) resembles cauliflower.

The mechanical properties of coatings were measured by the method of nanoindentation. The hardness of the coatings synthesized at a pressure of $6 \cdot 10^{-3}$ Torr and different values of the RF bias potential was of 8...37 GPa, the modulus of elasticity was of 220...400 GPa (Tabl. 2). Such a wide range of mechanical properties indicates the decisive role of the deposited ions energy during the coating synthesis, which was noted also by the authors of [1, 3].

Table 2
Mechanical characteristics of TiC-aC:H coatings deposited at $P_{\text{C}_6\text{H}_6} = 6 \cdot 10^{-3}$ Torr

RF-potential, V	Hardness, GPa	Young's modulus, GPa
100	22	250
200	37	400
500	32	350
1000	8	220

From the correlation of the results of nanoindentation and measurements of the Raman spectra, it follows that composite coatings with an elevated titanium carbide phase content have the highest mechanical properties.

CONCLUSIONS

The possibility of composite TiC-aC:H coatings synthesis was experimentally shown when co-deposition from the plasma of vacuum arc source with titanium cathode and plasma of high-frequency discharge in benzene vapours. Depending on the mode of deposition the one of the phases of the composite, is nanocrystalline titanium carbide and the second one is diamond-like carbon or α -titanium.

The most significant effect on the structure and phase composition of TiC-aC:H coatings (as well as on their properties) is rendered the value of the RF bias potential upon deposition.

The best mechanical characteristics have the coatings deposited at the RF substrate bias potential in the range of 200...500 V. A more detailed study of deposition regimes, when varying the RF-potential within this range, will allow us to refine the process parameters under which the synthesized TiC-aC:H coatings have the greatest hardness.

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КОМПОЗИТНЫЕ TiC-aC:H-ПОКРЫТИЯ, СИНТЕЗИРОВАННЫЕ ПРИ СОВМЕСТНОМ ОСАЖДЕНИИ ИЗ ВАКУУМНО-ДУГОВОГО ИСТОЧНИКА ТИТАНОВОЙ ПЛАЗМЫ И ПЛАЗМЫ ВЧ-РАЗРЯДА В ПАРАХ БЕНЗОЛА

А.А. Лучанинов, А.О. Омаров, В.Е. Стрельницкий, Р.Л. Василенко, Ю.Н. Насека, В.Н. Насека, Н.И. Бойко

Разработан процесс синтеза композитных TiC-aC:H-покрытий методом совместного осаждения из плазмы вакуумно-дугового источника с титановым катодом и плазмы ВЧ-разряда в парах бензола. В рамановских спектрах покрытий присутствуют пики, соответствующие карбиду титана TiC, а также пики D- и G-алмазоподобной aC:H-фазы. SEM-исследования показали, что морфология поверхности TiC-aC:H-покрытий либо ячеистая, либо напоминает «цветную капусту», размеры структурных элементов варьируются от десятков до сотен нанометров в зависимости от режима осаждения. Покрытия, осажденные при давлении паров бензола в рабочей камере $6 \cdot 10^{-3}$ Торр и ВЧ-потенциале на подложке 200...500 В, обладают наилучшими механическими свойствами – твердостью 32...37 ГПа и модулем упругости 350...400 ГПа.

КОМПОЗИТНІ TiC-aC:H-ПОКРИТТЯ, СИНТЕЗОВАНІ ЗА УМОВ СУМІСНОГО ОСАДЖЕННЯ З ВАКУУМНО-ДУГОВОГО ДЖЕРЕЛА ТИТАНОВОЇ ПЛАЗМИ ТА ПЛАЗМИ ВЧ-РОЗРЯДУ В ПАРАХ БЕНЗОЛУ

О.А. Лучанинов, А.О. Омаров, В.Е. Стрельницкий, Р.Л. Василенко, Ю.М. Насека, В.М. Насека, М.І. Бойко

Розроблено процес синтезу композитних TiC-aC:H-покривтів методом спільного осадження з плазми вакуумно-дугового джерела з титановим катодом та плазми ВЧ-розряду в парах бензолу. У раманівських спектрах TiC-aC:H-покривтів присутні піки карбіді титану та піки D- і G-алмазоподібної aC:H-фази. SEM-дослідження морфології поверхні покривтів виявили структури у вигляді комірок або «кольорової капусти», розміри структурних елементів варіюються від десятків до сотень нанометрів залежно від режиму осадження. Покривтя, осаджені при тиску парів бензолу $6 \cdot 10^{-3}$ Торр і ВЧ-потенціалі на підкладці 200...500 В, мають найкращі механічні властивості – твердість 32...37 ГПа і модуль пружності 350...400 ГПа.