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SYNTHESIS OF Ti-Si AND Ti-Si-N COATINGS BY CONDENSATION OF FILTERED VACUUM-ARC PLASMA

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Synthesis of Ti-Si and Ti-Si-N coatings using a filtered vacuum-arc plasma source with consumable titanium-silicon cathode was investigated. The thickness of films and their elemental composition were defined by means of the X-ray fluorescent analysis. It has been established, that the silicon concentration in coating can be changed over a wide range, from zero to the maximum value defined by silicon content in the cathode, by adjustment deposition process parameters – working gas pressure, substrate negative bias voltage, magnetic field intensity and its spatial distribution.

INTRODUCTION

The synthesis of the Ti-Si-N composite films with hardness above 40 GPa is one of the most significant achievements in the field of functional thin coatings production. The remarkable properties of coatings made of this material can be attributed to peculiarities of their structure: nanodimensional crystallites of titanium nitride are embedded in the amorphous silicon nitride matrix. These coatings have high mechanical and tribotechnical characteristics that are retained at high temperatures. In some cases, this quality makes them irreplaceable when used on cutting tools.

One of the promising methods of said composite material synthesis is the vacuum-arc one. Since the sputtering of silicon by vacuum-arc is rather problematical, the following technique is used. Cathode is made of electrically conductive material which consists of titanium and silicon in the needed proportion. Cathode sputtering products in the form of plasma flux are directed onto the substrate. If they are being condensed in vacuum or argon presence, a Ti-Si film is being formed, if in nitrogen medium – a Ti-Si-N film is being deposited. However, there are no currently published data related to the formation of filtered (without macroparticles – droplets or/and solid fragments of the cathode material) plasma fluxes generated by vacuum-arc discharge with titanium-silicon cathode and to the Ti-Si and Ti-Si-N films synthesis by condensation of those fluxes.

This work studies some features of the said films deposition using a dual vacuum-arc plasma source whith a T-shaped two-channel magnetic filter.

1. EXPERIMENTAL DETAILS

Deposition of Ti-Si and Ti-Si-N films was performed in a laboratory apparatus which contain a two-channel vacuum-arc plasma flux formation system having a T-shaped plasma filter. Structure and operation principle of this system in detail was described previously [1]. In this research we used its single-cathode variant schematically shown in Fig. 1. Only one input channel of the filter was currently active (right in Fig. 1). Other channel had no plasma source: its anode was closed by a flange having a current lead with a collector 6 instead of cathode. The distance z_1 between the substrate holder 7 and the plasma duct outlet in most

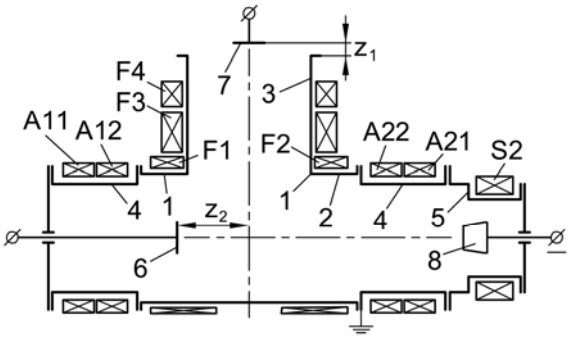

Fig. 1. Filtered vacuum-arc plasma source: 1,2 and 3 − input and output sections of the T-shaped plasma duct respectively; 4 – anode; 5 − cathode unit case; 6 – collector; 7 − substrate holder; 8 – cathode; S2 − stabilizing coil, A21, A22, A11, A12, F1 − F4 − plasma guiding coils

experiments was + 25 mm until explicitly noted. Substrate position inside plasma duct is marked with a minus sign. The distance z_2 between the collector and the plasma duct outlet 3 axis was 140 mm. Magnetic coils of the passive channel (left) in all experiments were turned off (except specified in the text), so this channel was used only as a trap for macroparticles.. The values and directions of currents in the coils for three operating modes (a, b and c) are given in Table. Coil currents generating magnetic field opposite to other coils, were marked with a minus sign.

Current modes of system coils

Mode	Current, A					
	I_S	I_{A21}	I_{A22}	I_{F2}	I_{F3}	I_{F4}
a	1,5	− 0,4	0,5	2,0	4,0	3,0
b	1,5	− 0,4	0,5	2,0	4,0	− 3,0
c	1,5	0,4	0,5	2,0	4,0	3,0

A titanium-silicon alloy was used as a cathode material; silicon content in it was 5 wt.%. The coatings were deposited on polished molybdenum samples 20×17×0.3 mm in size. Two such samples were placed on the substrate holder 7 with a 5 mm gap. Data obtained from these two samples were averaged. In some experiments a third sample was placed on the

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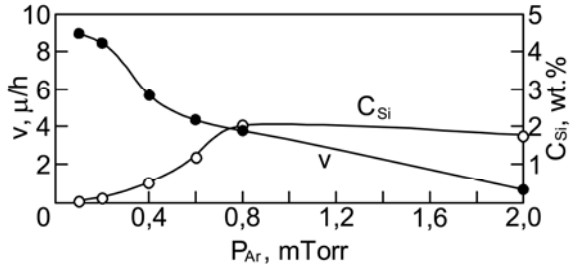

Fig. 2. Deposition rate and silicon concentration against argon pressure. Additive polarity of the coil F4 (mode "a")

collector 6. Film deposition rate and composition radial distributions investigation was carried out using the substrate holder having 9 samples. The samples were arranged in one horizontal row with a 20 mm pitch.

The chamber was evacuated to the residual pressure of $2 \cdot 10^{-5}$ Torr before introducing working gas (Ar, N_2) in it. The nitrogen pressure P_N was maintained at the assigned level with the aid of an automatic inlet valve. Film deposition was performed using a floating potential on the substrates. For a qualitative evaluation of higher negative bias U_s effect on the film deposition rate and its elemental composition, deposition was made at $U_s = -100$ V. The arc current I_a in all experiments was 100 A.

Thickness of coatings and their silicon content were determined by X-ray fluorescent analysis using SPRUT spectrometer, manufactured by "UkrRentgen" company.

2. RESULTS AND DISCUSSION

Fig. 2 and 3 show relationship between film deposition rate v and its silicon content C_{Si} versus argon P_{Ar} and nitrogen P_N pressures in the working chamber. These curves were obtained with coils power supply in mode "a" (see Table). From these figures one can observe similarity in nature between the relations $v(P_{Ar})$ and $C_{Si}(P_{Ar})$ and the relations $v(P_N)$ and $C_{Si}(P_N)$ at floating substrate potential. The deposition rate in both cases declines monotonously with increasing pressure. Silicon concentration in the condensate deposited at low pressure (less then 10^{-4} Torr) is fractions of one percent. But it rises rapidly with pressure increase and after reaching its maximum value has no significant changes with further pressure growth. This nature of relationships can be interpreted as follows. Low content of silicon in the coatings, which is characteristic of the left-hand branch of the curves $C_{Si}(P_{Ar})$ and $C_{Si}(P_N)$, may be a result of the sputtering processes taking place during the deposition of Ti-Si condensate. It is expected that in case of the titanium-silicon vacuum arc plasmas the sputtering process should be relatively intense, even at such substrate bias potentials that are close to the floating one, what is deduced from the following. The energy E_{iZ} of ion interacting with the substrate is determined, mainly, by three terms:

$$E_{iZ} = E_{iZ,0} + ZeU_s + E_{iZ,p},$$

where $E_{iZ,0}$ – ion energy when it leaves zone of its origin (near the cathode spot); Z – multiplicity of ionization; e – elementary charge; U_s – substrate potential (in this case it is floating); $E_{iZ,p}$ – the potential energy (energy consumed for Z-fold ionization of

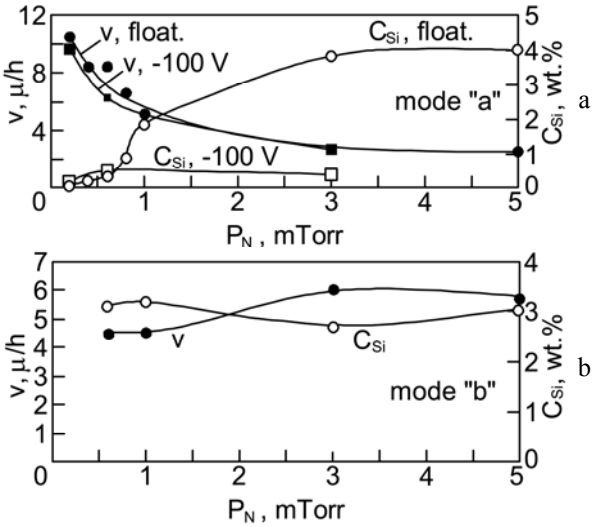

Fig. 3. Deposition rate and silicon concentration against nitrogen pressure at substrate bias of − 100 V, and at floating potential for additive (a) and subtractive (b) polarity of the coil F4

atom). By substituting the values of the right hand of the said equality which are characteristic of single-, double- and triple-charged ions of titanium [2], we obtain the following values of energies: $E_{i1} = 114$ eV, $E_{i2} = 190$ eV and $E_{i3} = 260$ eV for substrate-incident ions of Ti^{1+}, Ti^{2+} and Ti^{3+}, respectively. Those kinds of energy values highly exceed the condensate sputtering threshold (for metals this threshold is about 20 … 30 eV [3]).

Assuming that silicon sputtering coefficient induced by titanium (and other) ions, is higher than the coefficient of titanium self-sputtering, it is expected that the silicon concentration in the condensate should be much lower as compared to its value for the cathode material, what is observable in the left-hand branch of the curves $C_{Si}(P_{Ar})$ and $C_{Si}(P_N)$ in Fig. 2 and 3,a. It can also be assumed that the interaction cross-section of silicon ions with gas particles is lower than titanium ions one. Titanium ions are heavier and have a higher mean charge than silicon ones, which means that silicon flux component is less dissipated. In this case one can expect increase of silicon content in the coating with gas pressure growth. This happens due to decrease in titanium/silicon ions ratio, which have came to substrate. Moreover it should lead to noticeable deposition rate drop. The assumption is confirmed by the appropriate curves in Fig. 2 and 3,a. It also follows from these figures that the coating concentration of silicon attains higher values during its deposition in nitrogen than in argon. This may be explained by preferential silicon sputtering which in case of argon

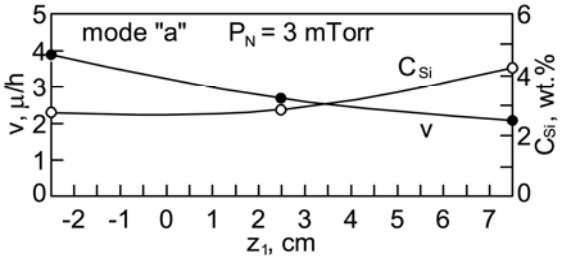

Fig. 4. Deposition rate and silicon concentration against distance between substrate and the plasma duct output

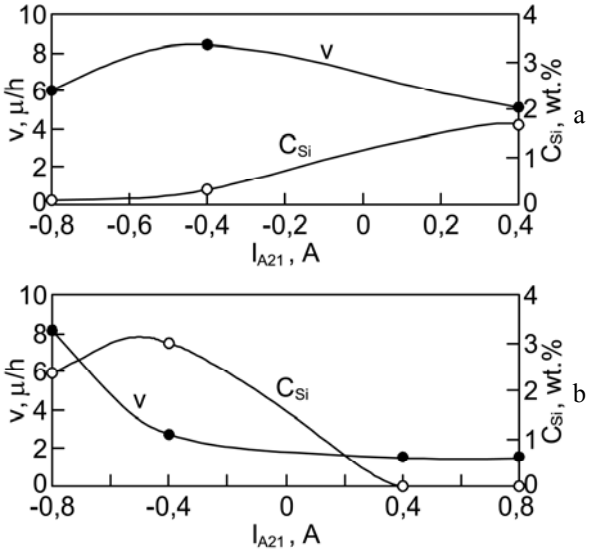

Fig. 5. Deposition rate and silicon concentration against anode coil A21 current at nitrogen pressure 0,6 mTorr (a), and 3 mTorr (b); mode "a"

presence is more intensive owing to a high sputtering ability of argon ions [3].

At $U_s = -100$ V coating silicon content did not exceed 1% in entire nitrogen pressure range. However, the curve $v(P_N)$ for this case coincides with the one obtained at the floating potential of the substrate (Fig. 3,a). A steep decrease in C_{Si} with the increasing negative substrate potential can be attributed to enhanced role of titanium ions in the preferential silicon sputtering.

The nature of $v(P_{Ar})$ and $v(P_N)$ dependencies, as shown in Fig. 2 and 3,a, is typical for plasma sources with magnetic guiding of plasma fluxes: the deposition rate decreases with increasing gas pressure due to plasma flux particles scattering on gas target [4].

Fig. 3,b demonstrates change in $v(P_N)$ induced by current polarity change in the output plasma guide coil (mode "b"). The opposite current in the output coil causes creation of cusp-shaped magnetic field [1]. It follows from this figure that with such field geometry at the system output, deposition rate and silicon content

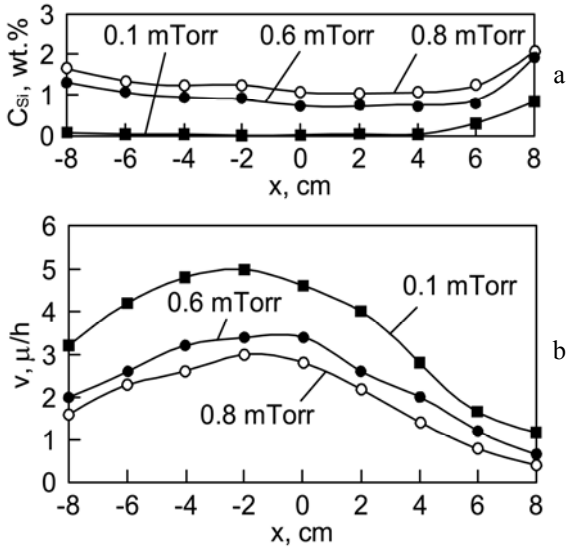

Fig. 6. Radial distribution of silicon concentration (a) and deposition rate (b) for argon; mode "a"

are nitrogen pressure independent. In field of this shape the energy of ions, that sputter the film, decreases [4]. Moreover, the film re-sputtering from the plasma duct walls in the vicinity of the magnetic gap can be feasible. Silicon, being preferentially sputtered (see above), moves toward the substrate in form of neutral vapour, insensitive to electromagnetic fields. This is indicated by the weak dependence of C_{Si} on z_1 found in the vicinity of the plasma guide output section (Fig. 4). An observable tendency toward silicon concentration enhancement away from the system output can be attributed to decreasing density of titanium flow arriving to the substrate which, being completely ionized, follows the divergent bundle of the magnetic force lines [4].

It should be noted, that silicon content in coating deposited on collector substrate varies from 3 to 4 wt.% within the said nitrogen pressure range. Neutral vapour and macroparticles emitted by the cathode can freely reach the collector. And since they make the main part of the film total mass and have the same composition as a cathode, it leads to such weak dependency of C_{Si} on P_N.

Fig. 5 shows the relationships of deposition rate and film silicon contamination versus magnitude and direction of anode coil (A21) current. Negative current values correspond to the contrary direction of the currents as compared to the rest coils currents. The plot indicates a strong influence of magnetic field topography in the anode region on deposition rate and silicon content. In particular, at $P_N = 3$ mTorr, with the variations of the current I_{A21} ranging from $-0{,}4$ to $+0{,}4$ A, the coating silicon concentration falls off monotonously from its maximum value ~ 3 wt.% to zero. Mechanisms responsible for the nature of the above relationships are not yet clear.

Fig. 6 shows radial distribution curves of silicon concentration and deposition rate at the plasma guide output against argon pressure. It follows from the Figure that film silicon concentration grows along with gas pressure, while deposition rate becomes lower. This agrees well with above data (Fig. 2). Additive coil F4

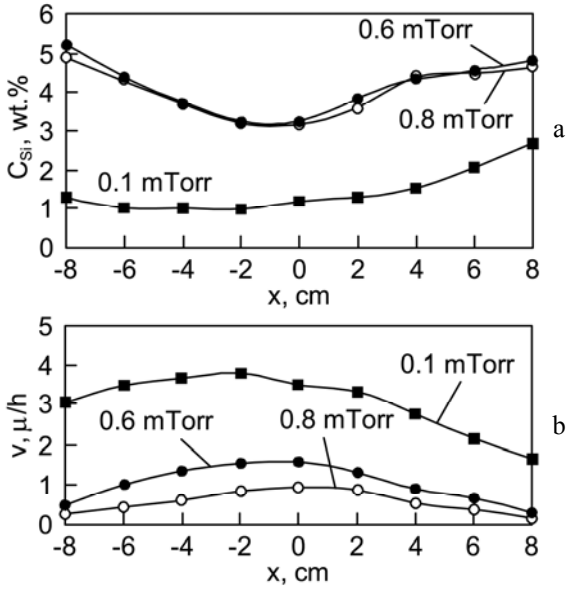

Fig. 7. Radial distribution of silicon concentration (a) and deposition rate (b) for argon; mode "b"

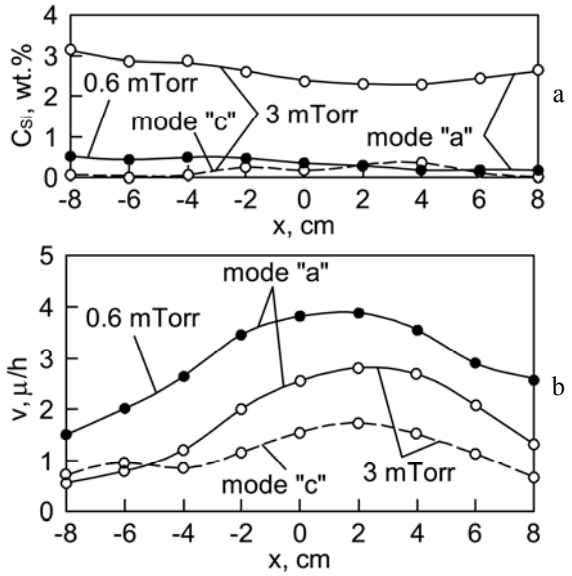

Fig. 8. Radial distribution of silicon concentration (a) and deposition rate (b) for nitrogen

polarity leads to focusing both, silicon and titanium ion fluxes. Their spatial distributions have similar form – humped form. So component ratio remains nearly unchanged, that leads to good silicon homogeneity. Deposition rate, on the contrary, has said humped profile due to ions flux focusing. Energizing of the output coil F4 according to the mode "b" (Fig. 7) changes components ion fluxes distributions. However, it affects components in a different way due to component ion mass and charge state differences. Titanium ion flux remains more humped then silicon one. And, as we can see from Fig. 7,a, silicon content has lower values near the substrate center. Silicon concentration lowering may be also the result of its preferential sputtering by titanium ions which flux intensity is much higher near the substrate center (see above). The nature of deposition rate curves in Fig. 7,b remains the same as in Fig. 6,b. The only sufficient difference is mean deposition rate drop due to loses in cusp-shaped magnetic field.

Radial distribution curves of silicon concentration and coating deposition rate in nitrogen are shown in Fig.8 and 9. The behavior of the curves is actually the same as for argon, although there are certain variations in the absolute values of the measured parameters. Measurement results of $C_{Si}(P_N)$ and $v(P_N)$ made for mode "c" are shown in Fig. 8 as dashed lines. Deposition rate under those conditions was approximately two times lower with the silicon concentration drop almost to zero.

Returning to Fig. 6, note that condensate maximum deposition rate is shifted to the left, unlike other Figures. The shift took place when coil F1 was turned on (with 0.4 A current). It was done to clarify the possibility of correcting flux radial displacement., which was found to be successful.

The results of the measurements indicate that the nature of C_{Si} and v dependences on gas pressure at the system axis in all cases do not contradict the assumptions made while discussing the results shown in Fig. 2 through 5. It is hard to do any unambiguous

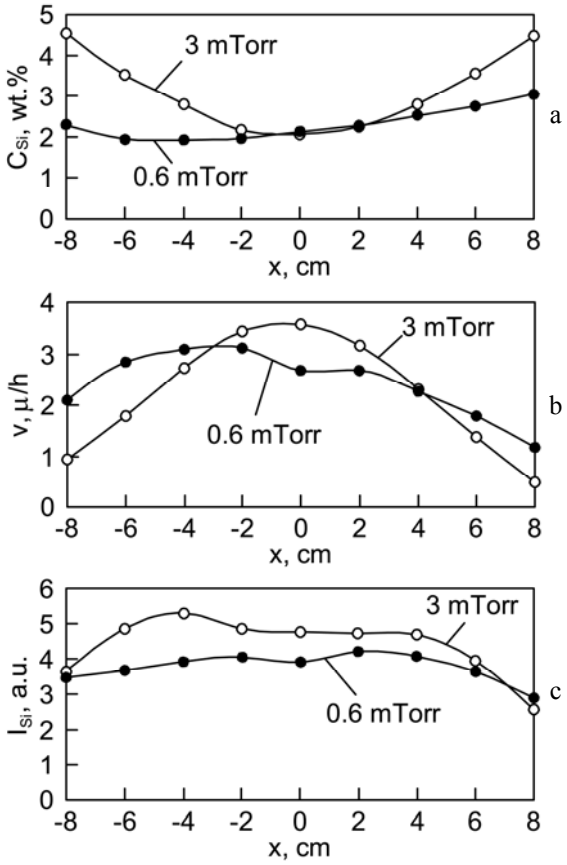

Fig. 9. Radial distribution of silicon concentration (a), deposition rate (b), and silicon line intensity (c) for nitrogen; mode "b"

conclusion about C_{Si} and v radial distributions formation mechanisms due to large quantity of interrelated factors affecting final result. It can be gas type, its density and ionization level, ion charge and energy spatial distributions, film sputtering intensity. The influence degree of majority of those factors on film formation process for vacuum-arc technological systems that are less complicated than described here is still unknown. Further, more detailed studies are required in order to establish the nature of the mechanisms that responsible for the relationships obtained and to confirm (or refute) the assumptions and suppositions made when interpreting the results of the experiments.

3. CONCLUSIONS

The results presented in this work point out the feasibility of using the vacuum-arc technique to deposit composite coatings based on Ti and Si by condensing the filtered plasma of the vacuum-arc discharge from the titanium-silicon cathode. It has been demonstrated that the coating deposition rate and components ratio in the condensate can be adjusted within wide range by changing of gas medium density (pressure), substrate bias, intensity and distribution geometry of magnetic field in the system.

It has been found that further study of deposition process parameters are needed in order to determine their influence on physical and functional properties of the coatings.

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СИНТЕЗ Ti-Si- и Ti-Si-N-ПОКРЫТИЙ КОНДЕНСАЦИЕЙ ФИЛЬТРОВАННОЙ ВАКУУМНО-ДУГОВОЙ ПЛАЗМЫ

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Исследован процесс синтеза Ti-Si- и Ti-Si-N–покрытий с использованием источника фильтрованной вакуумно-дуговой плазмы с титан-кремниевым катодом. Толщина плёнок и их элементный состав определялись рентгенофлуоресцентным методом. Установлено, что концентрация кремния в покрытии может быть изменена в широких пределах, от нуля до максимальной величины, определяемому содержанием кремния в катоде, путём регулировки параметров процесса осаждения – давления рабочего газа, отрицательного напряжения смещения на подложке, напряжённости и пространственного распределения магнитных полей.

СИНТЕЗ Ti-Si- ТА Ti-Si-N–ПОКРИТТІВ КОНДЕНСАЦІЄЮ ФІЛЬТРОВАНОЇ ВАКУУМНО-ДУГОВОЇ ПЛАЗМИ

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Досліджено процес синтезу Ti-Si- та Ti-Si-N–покриттів з використанням джерела фільтрованої вакуумно-дугової плазми з титан-силіцієвим катодом, що витрачається. Товщина плівок та їх елементний склад визначались рентгенофлуоресцентним методом. Установлено, що концентрація силіцію в покритті може змінюватись в широкому діапазоні, від нуля до максимальної величини, що визначається вмістом силіцію в катоді, шляхом регулювання параметрів процесу – тиску робочого газу, негативної напруги зміщення на підкладці, напруженості та просторового розподілу магнітних полів.