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Improving the mechanical property of amorphous carbon films by silicon doping

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ABSTRACT

The aim of the present work was to optimise the deposition process of a-C:Si films and to establish the relationships between the structure, surface morphology, elementary and phase composition and the mechanical and tribological properties with respect to the C/Si ratio in the films. The a-C:Si films were formed via sputtering a composite silicon-graphite target by pulse arc discharge. The C/Si atomic concentration ratio was changed varying the C/Si mass concentration ratio of the cathode. Raman spectrometry showed that Si doping leads to a reduction in size of Csp^2 clusters and to an increase of degree of disorder in the film structure with increasing the Si concentration. XPS analysis revealed the presence of the C-Si bonds in the films, which are typical for silicon carbide, with Csp^2/Csp^3 reducing at the increase of Si concentration in the film. It has been shown that the doping of the a-C films with Si results in decreased both the residual stresses and the surface energy, and influences the films friction kinetics, primarily friction coefficient. In general, the a-C:Si films properties depend on the silicone concentration and the certain Si concentration threshold value can provide the surface micro-structure stabilisation, which is dealt with the graphitisation temperature increase, presumably due to Si_xO_y formation at the film surface that leads to the improved tribological properties of the a-C:Si films.

1. Introduction

The films based on amorphous carbon (a-C) possess a unique combination of mechanical properties and have been widely studied over the past decades. However, high internal stresses, low adhesion to some types of substrates, and low temperature stability limit their industrial use.

To eliminate the above-mentioned drawbacks and improve properties of the a-C films, atoms of both non-metallic (N, Si, B, F) [1,2] and metallic (Ti, W, Ni, Cu, etc.) elements are used to modify their structure during deposition [3–6]. In particular, recently published works [7–9] prove that the incorporation of silicon results in the structural changes of amorphous diamond-like matrix, which positively influence certain mechanical properties of the films. Nevertheless, further an understanding of the doping effect of silicon on the structure formation during deposition is extremely important for two main reasons: (i) silicon and carbon are able to interact chemically forming a new solid phase – silicon carbide; (ii) silicon doped a-C: Si films are known to have enhanced properties including tribological ones. For example, it was shown in [10, 11], that compared with pure a-C films, a-C: Si films

have lower values of internal stresses as well as reduced friction coefficient in dry and wet environments.

However, in most works devoted to the study of silicon-carbon films, carbon or silicon containing gases were used to form these films that led to the presence of hydrogen and so-called polymer-like C-H bonds in the structure of the films, which, in turn, deteriorated the microhardness and wear resistance of the films [12–14]. After all, the doping effect of silicon on the structure formation, when the pulsed silicon carbon plasma of a cathode-arc discharge is used, is assumed to be different compared with that of chemical vapour deposition (CVD) methods, as evaporation in these methods occurs in high vacuum, without the presence of reactive gases. The aim of the present work was to optimise the deposition process of a-C:Si films and to establish the relationships between the structure, surface morphology, elementary and phase composition and the mechanical and tribological properties with respect to the C/Si ratio in the films.

2. Experimental

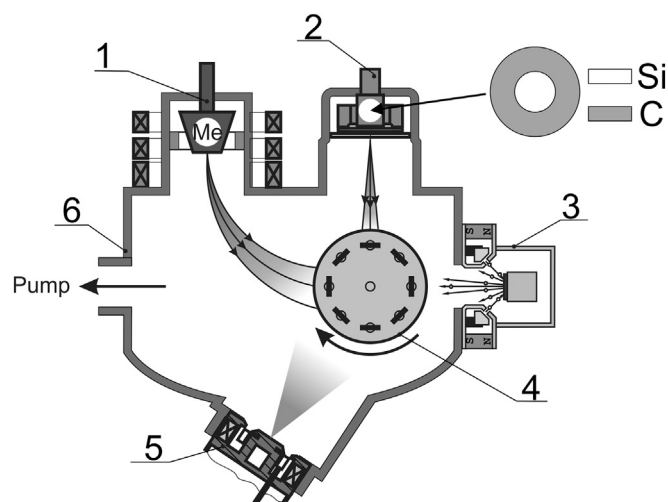a-C:Si films have been produced by evaporation of a composite

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Fig. 1. Schematic diagram of the process: 1 – DC arc with a metal cathode; 2 – plasma source of pulse cathode-arc discharge with a composite silicon-graphite cathode; 3 – sputtering ion source (was not used for the experiment); 4 – rotating table with the substrates; 5 – assisting ion source used for heating and cleaning of the substrate surface; 6 – vacuum chamber.

silicon-graphite target by the pulse arc discharge with the following parameters: pulse current $I_{pulse} = 3000$ A, pulse duration $\tau_{pulse} = 150\,\mu s$, pulse-repetition frequency $f = 5\,Hz$, and discharge voltage $U_{pulse} = 350$ V. Schematic diagram of the deposition process is introduced in Fig. 1.

The polished plates of silicon single crystal (type 100) were used as substrates. Before deposition, the substrates were cleaned in an ultrasonic bath in acetone and then in alcohol. The substrates were placed into the vacuum chamber, which was pumped out up to the residual pressure 10^{-3} Pa, after that argon was introduced into the chamber to a pressure of 10^{-2} Pa and cleaned with a low-energy ion source for 15 min at an ion current density of $25\,A/m^2$. After cleaning, the chamber was evacuated to a pressure of 10^{-3} Pa. To reduce the temperature effects, the films were deposited at room temperature. The thickness of the films was determined after cleavage using a scanning electron microscope (Hitachi S-4800). The films with the same thickness of 278 ± 10 nm were analysed.

The atomic concentration of the elements in the film was determined using a scanning electron microscope equipped with Energy Dispersive X-ray Spectroscopy (EDS) – AN 10000 (Link Analytical, England) in conjunction with SEM Stereoscan-360 (Cambridge Instruments, England). The determined concentration accuracy was 0.1 at.%. The spectra were obtained from the area of $5 \times 5\,\mu m$ in seven different random locations for each sample.

The ratio of atomic concentrations of C/Si in the film was varied via the change in the ratio of the C/Si concentration in the cathode, notably, by changing the surface area of the cathode occupied by graphite and silicon. The spraying speed of graphite and carbon were taken into consideration while choosing the ratio of areas occupied by graphite and silicon in the cathode, as shown in Table 1.

The structure of the composite films was studied by Raman spectroscopy. Raman spectra were excited by laser radiation having the

wavelength of 532 nm and the power of 10 mW (Senterra, Bruker) focused on a 1 µm spot on the film's surface. Visual examination with the aid of an optical microscope proved that under the effect of the power density of the Raman laser radiation, the surface of the film was not damaged. The Raman spectra were obtained using 10×10 mm samples in five spots located at 2 mm from the edges and in the centre. The spectra were analysed by OPUS (Bruker) software. The deconvolution of the peaks was executed by curve fitting using Gaussian–Lorentz function. To evaluate the coatings microstructure, the parameters obtained from the Raman spectra were analysed, namely, the ratio of the areas of D and G peaks, i.e. I_D/I_G ratio. The change in the I_D/I_G ratio, as well as in the position and width of G peak, allows assessing the effect of alloying elements on the microstructure of the carbon matrix, namely, the size and degree of the disorder of Csp^2 clusters.

The composition of the chemical bonds in the film was studied by X-ray photoelectron spectroscopy using PHI Quanta (Japan). The resulting spectrum was calibrated using the C1s line with 284.6 eV binding energy. The mathematical fitting of the spectra was performed using XPSPEAK software. The effect of the alloying element on the change in a relative content of carbide SiC and carbon $C-Csp^3$ bonds in the film was determined using a ratio of the appropriate peak areas in the XPS spectrum of C1s state of the carbon atoms, i.e. $N (C-Si)/N (C-Csp^3)$.

The microhardness of the films was determined by the Knoop method in 15 different places on the surface of the film, the average value was determined from the results obtained. The load and duration of the test were 245 mN and 10 s, respectively. As the thickness of the analysed films was less than 1 µm, microhardness measured was the superposition of microhardnesses for the system "film-substrate". The hardness of the silicon substrate measured in this mode was 9.56 ± 0.32 GPa.

Surface morphology and roughness (Ra) were studied by the Dimension Icon (Bruker) atomic force microscope (AFM) in tapping mode with a scanning scope of $4 \times 4\,\mu m$ and a scan rate of 1.0 µm/s. Residual stresses were determined from the change in the radius of curvature of the silicon substrate before and after the deposition of the film according to the procedure given in [15].

Tribological tests of a-C and a-C:Si films were carried out using a "sphere-plane" method at 23 °C and 70% relative humidity. The friction parameters and the procedure for calculating the wear resistance are given in [3].

3. Results and discussion

Table 1 shows the concentration of elements in the films after deposition and Fig. 2 presents the results of Raman spectroscopy. It is known that for the spectrum of amorphous carbon films, a broad asymmetric peak in the range 1000–1800 cm^{-1} is characteristic. This peak is formed by changing the size, orientation of carbon clusters consisting of carbon atoms with sp^2 bond states. This peak can be represented as a superposition of two peaks, the so-called D and G peaks with vertices, with an ideal film structure located at 1350 and 1580 cm^{-1}, respectively. G-peak is the result of stretching vibrations from sp^2-bonded carbon atoms in aromatic rings and –C=C– chains. D-peak is formed due to the deformation vibrations of carbon atoms in the aromatic rings of Csp^2 clusters of carbon and cannot be determined by

Table 1
Parameters of the a-C and a-C:Si films structure.

Sample	Area		Raman			XPS		AFM	SEM + EDS		
	C, mm^2	Si, mm^2	ID/IG ratio	G peak position, cm^{-1}	G peak width, cm^{-1}	Csp^2/Csp^3	N(C-Si)/N(C-Csp^3)	Ra, nm	C, at.%	Si, at.%	O, at.%
a-C	615	0	0.68	1584,6	156.3	0.31	–	18.6	83.7	0	16.3
a-C:Si$_{7,2\%}$	123	492	0.63	1684.3	161.3	0.19	0.075	19.2	73.6	7.2	19.2
a-C:Si$_{15,8\%}$	68	547	0.61	1692.4	168.9	0.15	0.21	35.6	70.3	15.9	13.8