Properties of ta-C coatings prepared by pulsed cathodic arc source at various distances

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Abstract. Tetrahedral amorphous carbon (ta-C) coatings have been prepared on silicon substrates by the pulsed cathodic arc source. For the limitation of the heat flux of the carbon plasma to the sample, the diaphragm of 27 mm diameter has been used. The deposition process has been carried out at three different distances between the arc source and the substrate: 150, 215 and 265 mm. The properties of ta-C coatings have been studied by Raman spectroscopy and dynamic nanoindentation techniques. The analysis of Raman spectra parameters has revealed that the concentration of ordered aromatic rings in Csp² cluster decreases with distance between the arc source and the substrate while the concentration of chain groups increases. Nanoindentation has shown the decrease in nanohardness and Young’s modulus with the distance. Nanohardness value falls from 21 GPa to 16 GPa and Young’s modulus value goes down from 197 GPa to 177 GPa. So, it’s possible to control the formation of ta-C coatings structure by changing distance between the pulsed cathodic arc source and the substrate.

1. Introduction

Tetrahedral amorphous carbon (ta-C) coatings prepared by the pulsed cathodic arc deposition have a high hardness and Young’s modulus, low coefficient of friction, high wear resistance, high chemical inertness and biocompatibility. Such coatings are applied in automotive industry [1] and medicine [2].

The deposition distance is an important parameter of the deposition process. The plasma intensity (especially the pulsed one) and the distribution of ion energies depend on the distance between the arc source and the substrate due to the divergence of the plasma flux with distance [3]. It causes the different spatial energy density of the flux from the distance between the arc source and the substrate. This fact leads to the properties changes of the films. Therefore it’s necessary to study the effect of the deposition distance on the properties of ta-C films. In the case of ta-C films, an important properties are the mechanical properties. The structure of ta-C films is important too.

The purpose of this research is to establish the dependence of the structure and the mechanical properties of ta-C coatings on the distance between the pulsed cathodic arc source and the substrate.
2. **Experimental part**

The ta-C films have been deposited on substrates made of polished single crystal of silicon with orientation of crystal line planes (111) and thickness 0.3 mm at the starting pulsed voltage of 350 V, the pulse frequency of 10 Hz, and the pulse number of 3000 (according to the previous studies [4]). The deposition process is illustrated in figure 1.

![Figure 1. Scheme of deposition of ta-C coatings by pulsed cathodic arc source.](image)

The deposition has been conducted at three different distances between the pulsed cathodic arc source and the sample: 150, 215 and 265 mm. The 27 mm aluminum diaphragm has been located in front of the substrate at the distance of 115 mm for the limitation of the heat flux of the carbon plasma to the substrate. The silicon substrates have been purified with ethanol and after that washed in distilled water. When the residual pressure in the vacuum chamber has reached $3 \times 10^{-3}$ Pa, argon (chemical purity 99.995%) has been introduced into the chamber to the pressure of $5 \times 10^{-2}$ Pa and the substrates have been cleaned with argon plasma excited by the ion source of the End-Hall type. The purification has been carried out for 20 minutes at the discharge voltage of 100 V and the ion current density of 25 A/m$^2$. After purification, the substrate has been cooled in the vacuum chamber at the base pressure of $3 \times 10^{-3}$ Pa for 30 minutes. After cooling, the coatings were deposited on the substrates.

Raman spectroscopy (T64000, Horiba-Jobin Yvone) with laser beam wavelength of 514.5 nm and 3 mW power has been used for studying of the structure of ta-C films. The Raman spectra have been recorded in the range of wave numbers from 800 to 2000 cm$^{-1}$. Scanning electron microscopy (SEM) (Hitachi S-4800) has been used for the determination of the thickness of the coatings. The more accurately the thickness of the films is measured, the less are the errors that arise in the determination of mechanical properties by the method of nanoindentation. The mechanical properties of ta-C coatings, such as nanohardness and Young's modulus, have been determined by the dynamic nanoindentation techniques, according to the recommendations in [5]. It made possible to obtain the quasi-continuous dependence of the mechanical properties on the penetration depth of the indenter in one experiment.

3. **Results and discussion**

3.1. **Structure**

Raman spectra of ta-C films prepared by the pulsed cathodic arc source at different distances are shown in figure 2. The shape of the spectra is characteristic of the Raman spectra of carbon coatings
produced by the arc method and is characterized by the presence of an asymmetric peak in the range 1000–1800 cm\(^{-1}\) with a maximum localized at 1560 cm\(^{-1}\).

\[\text{Figure 2. Raman spectra of ta-C coatings deposited at different distances between the pulsed cathode-arc source and the sample: 150 mm (a); 215 mm (b); 265 mm (c).}\]

According to [6], this spectrum can be represented as a superposition of two peaks with the maxima localized at 1360 and 1560 cm\(^{-1}\). The produced spectra with the purpose of their further precise and reliable analysis and the parameters necessary for further analysis, such as the full width at half height (FWHM) of G peak, the ratio of \(I_D/I_G\) intensities and the position of D peak were adjusted by Gaussian curves. Inside the peak, vibrational states of amorphous carbon, bands G and D are hidden. G band which is responsible for the vibrations of carbon atoms with sp\(^2\) state of hybridization of bonds in aromatic rings and, as a rule, correlated with graphite, lies in the range 1530–1580 cm\(^{-1}\). The band D, responsible for the disordering of the structure, behind the clusterization of the coating and determining the change in the dimensions of the Csp\(^2\) clusters and their orientation lies in the region of 1350–1400 cm\(^{-1}\). It is stated [6] that the broadening of D peak is determined by the increase in the orientation degree of Csp\(^2\) clusters of carbon. The Raman parameters of the spectrum related to the D and G peaks are determined only by the vibrations and organization of sp\(^2\)-bound carbon atoms. The peak in the area of 950–1000 cm\(^{-1}\) belongs to second-order scattering from the silicon substrate.

The results of mathematical treatment of Raman spectra are introduced in figure 3. The main parameters of the Raman spectrum shows the dependence of the change in the structure of the carbon matrix from the change in the distance between the source and the substrate. The \(I_D/I_G\) ratio is related with the degree of structural disordering.

\[\text{Figure 3. The } I_D/I_G \text{ ratio (a), FWHM}_G \text{ (b) and D-peak position (c) as a functions of the distance between the pulsed cathodic arc source and the sample.}\]

The decrease in the \(I_D/I_G\) ratio (figure 3a) means the decrease in the concentration of aromatic rings per Csp\(^2\) cluster and the increase in the concentration of chain groups [6]. Also, according to \(I_D/I_G = \text{sp}^2/\text{sp}^3\) ratio, it is possible to make the assumption of the increase in the fraction of sp\(^3\)
hybridized atoms in coatings or according to the ratio \( \frac{I_D}{I_G} \sim c(\lambda)/L_a \) the size of the Csp\(^2\) cluster grows in the coating. The index \( a \) in the parameter \( L_a \) means that the dimensions are calculated in the basal plane, i.e. along the crystal direction \( a \) for the ideal graphite lattice and the \( L_a \) dimension corresponds to the ordered cluster width. Direction \( a \) in the crystal lattice of graphite corresponds to the line (110), the intensity of which for coatings based on amorphous carbon is very small, and therefore the calculation error is high. Therefore, the values of \( L_a \) calculated from the Raman spectroscopy data are very approximate and do not correspond to the data obtained by X-ray diffraction analysis (XRD), since they characterize the change only in one direction in the graphite cluster. It is also believed that the use of the term "crystallite" for coatings based on amorphous carbon is not correct. As it is stated in [6] that the change (increase) in the intensity of the D-band can be associated both with the deformation of aromatic rings and with the increase in the number of conjugated chains of –C–C– type or –C=C–, which leads to the reduction in the ratio of \( \frac{I_D}{I_G} \). If a polyconjugated polymer system is formed from the chains, the Raman spectra will be characterized by a rather large degree of ordering. Consequently, the decrease in \( \frac{I_D}{I_G} \) value (figure 3a) and the increase in G-peak width (figure 3b) with the increasing distance between the arc source and the substrate are associated with two simultaneous processes: the disordering in the polymer matrix (disorientation of conjugated chains) and the increase in the degree of ordering in the graphite-like Csp\(^2\) cluster [7, 8]. The position of D peak (figure 3c) can shift towards low wavelengths due to the decrease in the number of the ordered aromatic rings [9].

3.2. Mechanical properties

The properties of ta-C coatings have been determined mechanically by the dynamic nanoindentation techniques. As the result, the nanohardness and the Young's modulus have been measured. In the case of measurements by the method of nanoindentation, the rule based on the estimates of the influence zone under the indenter is used [10]. It states that for the thin films the true hardness of the coating can be measured at indentation depth of 1/10 of the film thickness. Therefore, before carrying out the tests of mechanical properties, it is necessary to determine the thickness of the coatings. Thus, before carrying out the measurements by the method of nanoindentation, it is necessary to determine the thickness of the coatings. Figure 4 shows the images of the scanning electron microscope of the cross section of samples coated with platinum

![Figure 4. SEM images of cross-section of ta-C films deposited at different distances between the pulsed cathodic arc source and the sample: 150 mm (a); 215 mm (b); 265 mm (c).](image)

As seen, the thickest sample, with the thickness of 138 nm, has been prepared at 150 mm from the arc source. We can say that the evaporation process goes to the steady-state regime with the steady-state spatio-temporal distribution of the plasma flow at the distance greater than 200 mm. Hence, the distance does not affect the growth rate of the coatings. Taking into account the peculiarities of the deposition of coatings, namely the substrate fastening on the tool making planetary rotation with the change in the distance from the source from 60 mm to 280 mm, the optimum deposition parameters appear at a distance of 60–150 mm.
After determining the thickness of the coatings, the nanohardness and the Young's modulus have been defined. The dependences of these values on the distance between the pulsed cathodic arc source and the substrate are presented in figure 5.

**Figure 5.** The nanohardness (a) and the Young's modulus (b) as the functions of the distance between the pulsed cathodic arc source and the substrate.

As it can be seen, the nanohardness for all coatings decreases significantly with the increase in distance. It means that the change in the structure of the carbon matrix occurs. It can be concluded that the carbon atoms/ions produced from the pulsed cathodic arc discharge at the distance of 150 mm with high flux density and high energy, have sufficient energy to form ordered structures and Csp² clusters of smaller size. It leads to the formation of more closely packed structures and, accordingly, determines the higher nanohardness of the coating. The ion flux density determines the temperature of the substrate and the appearance of so-called thermoelastic peaks that affect the formation of the coating structure and is determined by the decompression effect of the carbon condensate caused by the diffusion flux of vacancies from the surface to the depth of the coating.

The important characteristic of the material in indentation is the hardness ratio of the material to the Young's modulus. This value gives information on the structural state of the coating, namely, the grain size. In our case, the ratio $H/E$ varied from 0.11 to 0.09 (figure 6), which determines the decrease in the grain size with the increasing distance between the source and the substrate which coincides with the Raman spectroscopy data.

**Figure 6.** Ratio $H/E$ as the function of the distance between the pulsed cathodic arc source and the substrate.

4. **Conclusion**

The study of the structure and the mechanical properties of the ta-C coatings has shown that the concentration of ordered aromatic rings in Csp² cluster decreases with distance between the arc source
and the substrate while the concentration of chain groups increases. The disordering in the polymer matrix and the increase in the degree of ordering in the graphite-like Csp² cluster occur. The nanohardness and the Young's modulus decrease with the distance. In general, we can say that the process of structure formation is determined by the energy and spatial parameters of the pulsed plasma flow and it is possible to control the structure formation processes in the coating by changing the deposition distance.

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