Structure and optical properties of a-C coatings doped with nitrogen and silicon

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Abstract
Using a pulsed arc discharge, carbon coatings binary-doped with silicon and nitrogen are deposited on quartz and silicon substrates. The structure and phase composition of the coatings are studied by atomic force microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. The optic band gap Eg and the refractive index of the coatings are determined depending on the alloying elements. The influence of nitrogen and silicon on the formation of the structure of the carbon matrix and the formation of chemical compounds in the coatings, leading to a change in the width optic band gap Eg, has been established. Changes in the roughness Ra and the size of the Csp^2 cluster are shown in the case of binary doping with nitrogen and silicon.

Introduction
The functional properties of coatings largely depend on their chemical, phase composition and morphology, and for carbon-based coatings they are determined by the sp^3/sp^2 ratio [1], the value of which can be changed both by regulating the deposition parameters and as a result of the formation of composite or multilayer coatings. Alloying with nitrogen leads to a change in the structure and properties of coatings (increase in wear resistance, decrease in internal stresses), which is recovered by the formation of chemical bonds between carbon and nitrogen atoms, and the incorporation of nitrogen into the structure of carbon chains [1]. Silicon alloying of a-C coatings causes a change in their structural-phase composition, optical and mechanical properties, and, which is especially important, electrophysical properties mainly due to the formation of chemical compounds [2]. With the joint introduction of nitrogen and silicon into the carbon coating, the formation of silicon nitrides, carbides and carbonitrides is possible, which affect the phase composition of the carbon matrix and change the properties. The aim of this work is to establish the effect of complex alloying of carbon coatings with nitrogen and silicon on their optical properties and to analyze the relationship between changes in properties and the phase composition of the carbon matrix.

Deposition technique
Using a pulsed vacuum arc discharge, carbon coatings doped with silicon, nitrogen, and binary doped with silicon and nitrogen are deposited on quartz and silicon substrates. The thickness

of the coatings was 86±5 nm. The deposition of a-C:Si:N coatings was due to the sputtering of a composite cathode at a nitrogen pressure in the chamber equal to 10^{-2} Pa. Carbon coatings were applied at a discharge voltage of 350 V and a pulse repetition rate of 15 Hz. The absorption spectrum of a-C coatings in the visible and UV regions was studied using a Cary-50 (Varian) spectrophotometer. The optical band gap was determined according to the Tauc method [3]. The refractive index was measured by laser ellipsometry. Surface morphology was studied using a Solver P47 PRO scanning probe microscope. The structure of the coatings was established by Raman spectroscopy and photoelectron spectroscopy.

The results obtained and their analysis

It was found by atomic force microscopy that for a-C:Si:N_2 coatings, in comparison with single-component carbon layers, the roughness (Ra) increases with a simultaneous increase in the grain size, which is associated with the interaction between carbon, silicon and nitrogen and the formation of the SiN phase, which characterized by higher growth rates than Csp^3 and Csp^2-N. A change in the ID/ G ratio and the width of the G-peak of the Raman spectrum of the-C: N_2 coating indicates an increase in the size of Csp^2 clusters and an increase in the concentration of carbon atoms in the state with sp^2 bond hybridization. High ID/IG values for the a-C:Si coating in combination with a decrease in the G-peak width indicate an increase in the size of Csp^2 clusters and the degree of their ordering.

For a-C:N_2 and a-C: Si:N_2 coatings, lower values of the ID/IG ratio, an increase in the width of the G-peak in comparison with coatings obtained with assisted nitrogen ions, as well as a shift in the position of the G-peak to a more high wavenumbers. The change in the phase composition of the carbon matrix was determined by the XPS. It is shown that the sp^3/sp^2 ratio is maximum for a-C coating. a-C:N_2 is characterized by an increase in the graphite component and the formation of C–N compounds, which determines an increase in absorption in the UV region (Fig. 1) and a decrease in the band gap Eg (Fig. 2), as well as a refractive index n=2.62. For the a-C:Si coating, at sufficiently large values of the sp^3/sp^2 ratio, the formation of bonds of the C-Si and Si-O is observed in the structure, which lead to an increase in Eg to 2.86 eV, while the value of n reaches 2.72.

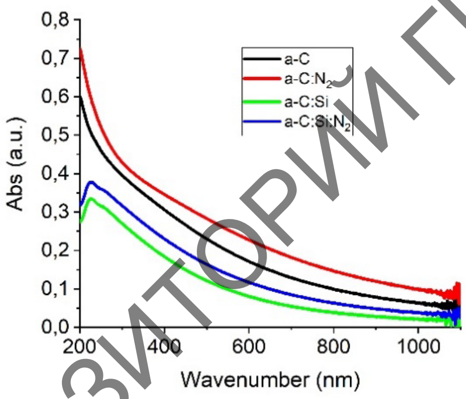

Fig. 1. Uv-Vis spectra for a-C films doped by Si and N

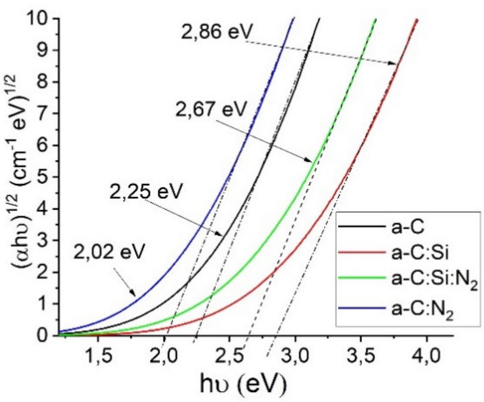

Fig. 2. Tauc plot of (αhν) versus photon energy hν for a-C films doped by Si and N

For a-C:Si:N_2 coatings, the formation of ternary SiN_xC_y compounds is possible, as well as an increase in C-N bonds due to the formation of pyridine-like compounds, which determines a decrease in the band gap (Fig. 2). It has been found that a change in Eg, which depends on the concentration of carbon atoms with an sp^2 bond, and an increase in the size of Csp^2 clusters, cause the formation of a broad absorption band in the UV region. Thus, a change in Eg and n is a sign of a change in their optical properties due to the formation of a cluster structure with different cluster sizes and sp^2/sp^3 bond ratios.

Conclusion

The regularities of the influence of complex alloying of carbon coatings with nitrogen and silicon on their optical properties have been determined. It was found that binary-doped carbon coatings have optical properties (Eg and n), the values of which are intermediate between the values characteristic of coatings doped with nitrogen and silicon. The decrease in the catalytic effect of silicon on the phase composition of the carbon matrix and, accordingly, the properties of the binary-alloyed coating is explained by its participation in the formation of chemical compounds with nitrogen.

References

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