Effect of Internal Stress on the Surface Morphology of Hard Nanoscale Carbon Coatings

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Abstract—The influence of ion energy on the magnitude of internal stress, electric conductivity, and surface morphology of nitrogenated carbon coatings on silicon produced by the pulsed vacuum-arc technique has been studied by scanning electron microscopy and scanning probe microscopy. It has been found that an increase in the ion energy with variation in applied acceleration voltage substantially increases the internal compression stress in the forming coating. The ion irradiation results (1) in a considerable inhomogeneity of the internal stress distribution over the coating and (2) in the formation of 15- to 50-nm-high nanoscale islands. Inhomogeneity of the coating conductivity with a minimum on the peaks of the islands has been observed, which indicates the prevalence of tetrahedral bonds between carbon atoms in these regions with sp^3 hybridization of atomic electron orbitals (sp^3 phases). An explanation of the results has been proposed based on the existing model of the formation of internal stress in coatings prepared under ion irradiation.

INTRODUCTION

The formation of hard diamond-like carbon coatings in vacuum requires surface bombardment by accelerated ions. Applications of such coatings are determined by their high microhardness, low friction, bio and chemical inertness, transparency in the infrared range, unique emission characteristics, etc. [1].

However, ion irradiation not only results in the formation of coatings with the prevalent sp^3 phase, but also leads to a high internal compression stress, which, in the opinion of some authors, is required for producing coatings with the highest density and microhardness [2].

One of the most promising fields for the application of thin carbon coatings is nanotechnology, but the high level of internal stress in the coatings may lead to catastrophic deformation of micromechanical parts, such as the microprobes (cantilevers) of scanning probe microscopes.

Further investigation is clearly necessary to develop methods for measuring the internal stress in nanoscale carbon coatings, as well as studies aimed to extending our knowledge on how stress forms because, internal stress plays the leading role in self-organization of nanoscale carbon coatings [3] that made promisingly lead to various nanostructures.

To explain the emergence of internal stress in coatings formed under ion bombardment, various models have been proposed. The majority of them are subimplantation and thermal peak models [4] that consider the carbon ion energy as one of the main parameters.

This work is aimed at studying the influence of the ion energy on the magnitude of internal stress and surface morphology of 30- to 70-nm-thick hard carbon coatings.

EXPERIMENTAL TECHNIQUES

To measure the internal stress, 30-nm nitrogenated carbon coatings were deposited onto NT-MDT CSG01 silicon cantilever beams with a thickness of 2.0 μm and a length of 350 μm. To study the surface morphology, KEF-4.5 single-crystal silicon substrates with 70-nm coatings were used. The coatings were produced by deposition of carbon plasma generated in cathode spots of a pulsed vacuum-arc discharge [5] with a consumable MPG-6 graphite cathode. The vacuum chamber was preliminarily pumped down to a pressure of no more than 10^{-3} Pa. The coating deposition rate was 0.1 nm per pulse with the pulse rate of 2.5 Hz. The substrate temperature was no higher that 50°C. To increase the electric conductivity of the carbon coatings, nitrogen at a pressure of 0.01 Pa was let into the chamber. Three ways of producing the carbon coating were studied: without acceleration voltage (floating substrate potential) and with a negative accelerating voltage of 800 and 1200 V.

The cantilever beam bending was determined with the use of a QUANTA 200 3D scanning ion electron microscope. The surface of silicon with the carbon coating was investigated by means of an NT-MDT Smena-A scanning probe microscope in the atomic-force and spreading resistance modes. In both modes,

Table

No.	Carbon coating deposition mode	Internal stress σ_f, GPa	Surface roughness S_a, nm
1	Without accelerating voltage	7.0	0.8
2	Accelerating voltage of 800 V	17.0	3.7
3	Accelerating voltage of 1200 V	18.0	4.6

the DCP20 cantilevers with a 70-nm nitrogen-doped diamond-like carbon coating were used. The coating thickness was determined by measuring the height of an artificial step between the coating and substrate using the same microscope in the atomic-force microscopy mode.

The magnitude of the internal stress was determined from the cantilever beam deflection according to Stoney's formula [6]:

$$\sigma_f = \frac{E_{Si} t_c^2}{6(1 - \nu_{Si}) R_c h_f}, \quad (1)$$

where E_{Si} is the coefficient of elasticity of Si, t_c is the cantilever thickness, ν_{Si} is the Poisson ratio for Si, $R_c \approx l_c^2/(8 f_c)$ is the curvature radius of the bent cantilever beam, l_c is the beam length, f_c is the cantilever beam deflection, and h_f is the coating thickness.

RESULTS AND DISCUSSION

The table presents the values of internals stress in the carbon coating obtained in different regimes together with the surface characteristics determined with the use of atomic-force microscopy.

Analyzing the data in the table and the results of atomic force microscopy shown in Fig. 1, one can see a high internal stress in the carbon coatings produced with the accelerating voltage and a change in the surface morphology with an increase in the ion energy, which may be associated with the generation of radiation defects under ion bombardment.

Let us prove this point with the use of the basic ideas of models that describe the emergence of internal stress in the coatings produced under ion irradiation [7].

The magnitude of internal stress σ is determined by the change in the coating volume during its formation and is generally written as

$$\sigma = \frac{E}{2(1+\nu)} \frac{\Delta V}{V}, \quad (2)$$

where E is the coefficient of elasticity of the coating and ν is the Poisson ratio.

The expression that couples the change in the coating volume with the steady-state relative density of radiation defects has the form

$$\frac{\Delta V}{V} = \frac{k_i \rho_i - k_v \rho_v}{\rho}, \quad (3)$$

where ρ_i and ρ_v are the relative density of interstitial atoms and partial vacancies, respectively; ρ is the relative density of the developed coating; and k_i and k_v are the coefficients of the volume change associated with the presence of the respective radiation defects.

Application of the acceleration voltage leads to an increase in the fraction of the displaced atoms that occupy the positions of partially interstitial atoms. According to the Kinchin–Pease theory, the number of the displaced atoms is $N_d = E_i/E_d$, where E_i is the ion energy and E_d is the lowest atom displacement energy (on the order of 25 eV for the carbon coating). This leads to an increase in the relative density of the partially interstitial atoms in the coating with the ion energy and, according to Eq. (3), to an increase in the internal stress.

A decrease in the coating thickness, on the other hand, increases the probability of the vacancy diffusion towards the surface, which decreases their concentration in the bulk of the coating and, in turn, leads to an additional increase in the internal compression strength. It should be taken into account that the diffusion is stimulated by not only by temperature, but to a greater extent by inhomogeneous fields of internal stress in the coating.

The formation of nanosized islands on the surface of the carbon coating is caused by relaxation of the internal compression stress, whereas the ion irradiation results in a considerable spatial inhomogeneity of the internal stress. This is confirmed by computer simulation of atomic collisions induced by carbon atoms performed in the SRIM-2006 software environment [8].

Figure 2 shows the profiles of ion occurrence in the positions of partially interstitial atoms in carbon coatings of various density produced by computer simulation of atomic collisions induced by 100-eV carbon atoms.

The results of computer simulation and surface scans of the carbon coating imply that the ion irradiation creates regions with the different internal stresses owing to different concentrations of point radiation defects. This results in the formation of islands due to the relaxation of the internal stress. The maximum height of the islands increases from 13 to 51 nm with the accelerating voltage.

It should be emphasized that the size of an island's base is almost the same in both cases, on the order of

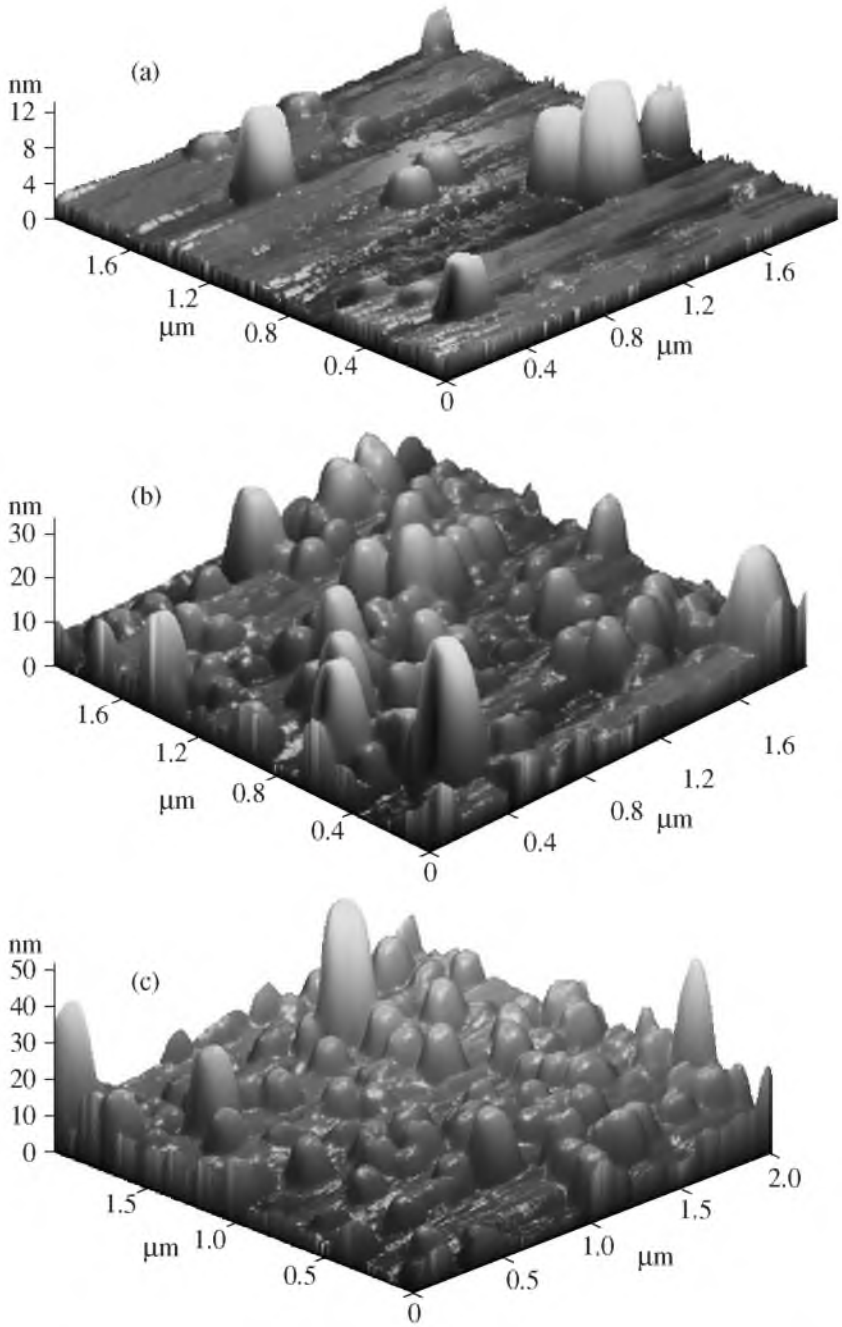

Fig. 1. 2×2 μm surface scans of the nitrogenated carbon coating produced (a) without the accelerating voltage and with an accelerating voltage of (b) 800 and (c) 1200 V.

250 nm, as confirmed by the scans of separate islands presented in Fig. 3.

This allows us to make an important conclusion that the island summit is the surface of the preferential coating formation, by analogy with whiskering according to a "vapor–liquid droplet–solid" scheme. In our case, the island summit is saturated by radiation defects and broken bonds, and application of the accelerating voltage results in an increased intensity of electric field at the summit followed by the retraction of plasma ions from the Debye layer.

The two-stage formation of islands may be supposed: the initial nucleation due to the internal compression strength and the second stage of the preferential deposition of plasma ions at the island summit due to the accelerating potential applied to the substrate.

Scanning in the spreading resistance mode allowed us to estimate the electric properties of the nitrogenated

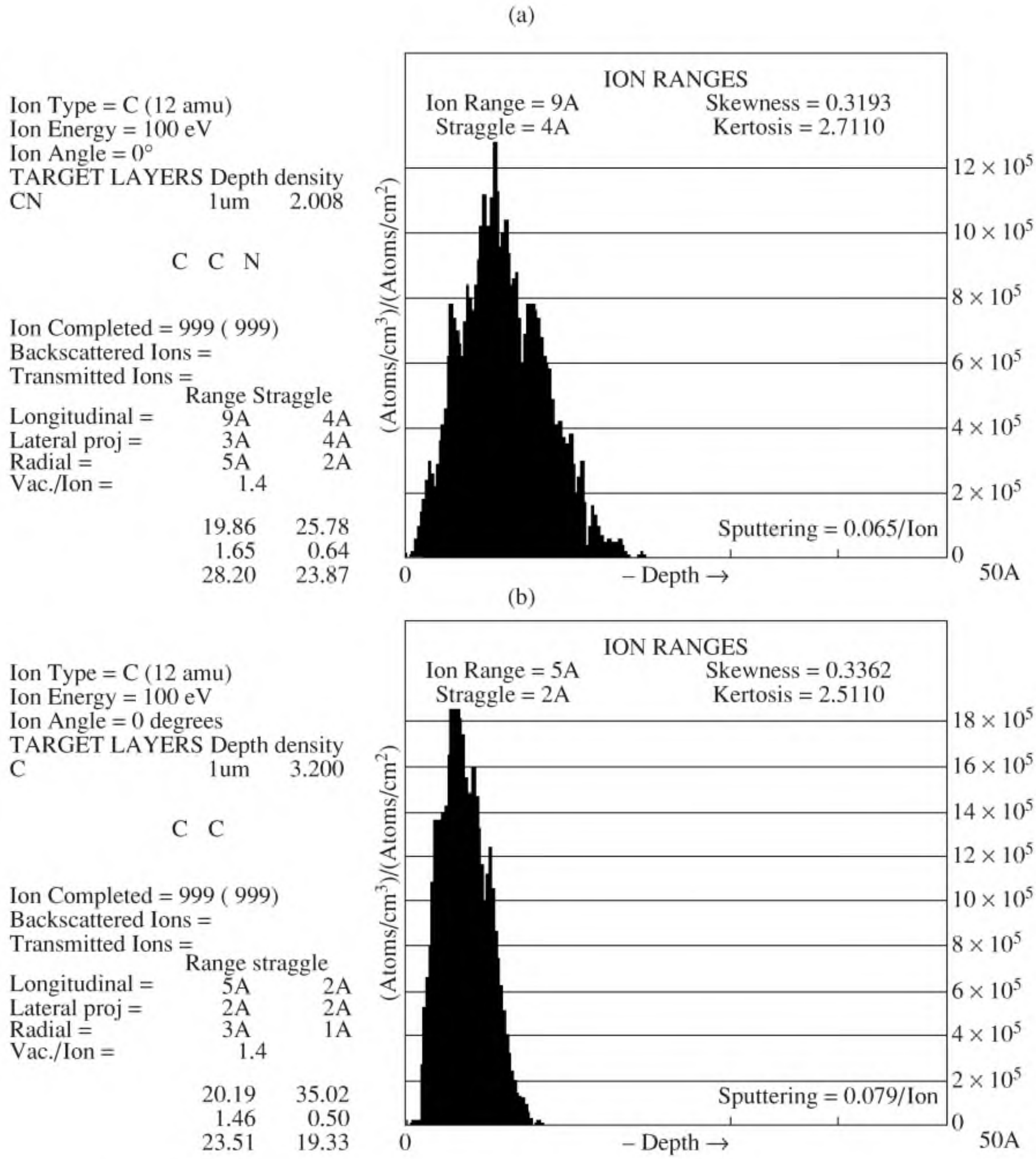

Fig. 2. Profiles of ion occurrence in the positions of partially interstitial atoms in the carbon coating of a density of (a) 2.2 and (b) 3.2 g/cm^3 produced by computer simulation of atomic collisions induced by a 100-eV ion.

carbon coating, which correlate with the fraction of the sp^2 phase as compared to that of the sp^3 phase. Figure 4 shows the scan of a separate island on the surface of the nitrogenated carbon coating produced under an accelerating voltage of 1200 V.

Analyzing the variation of the current over the island's surface, it should be mentioned that the lowest current and, respectively, the highest resistance were observed at the island summits, indicating the prevalence of the sp^3 phase in these regions, which is associated with a strong ion compression effect. Thus, the results of the computer experiment are confirmed.

CONCLUSIONS

1. Application of m accelerating voltage to a substrate during the formation of a nitrogenated carbon coating substantially increases the internal compression stress in the coating and the surface roughness as a result of the increased height of islands.

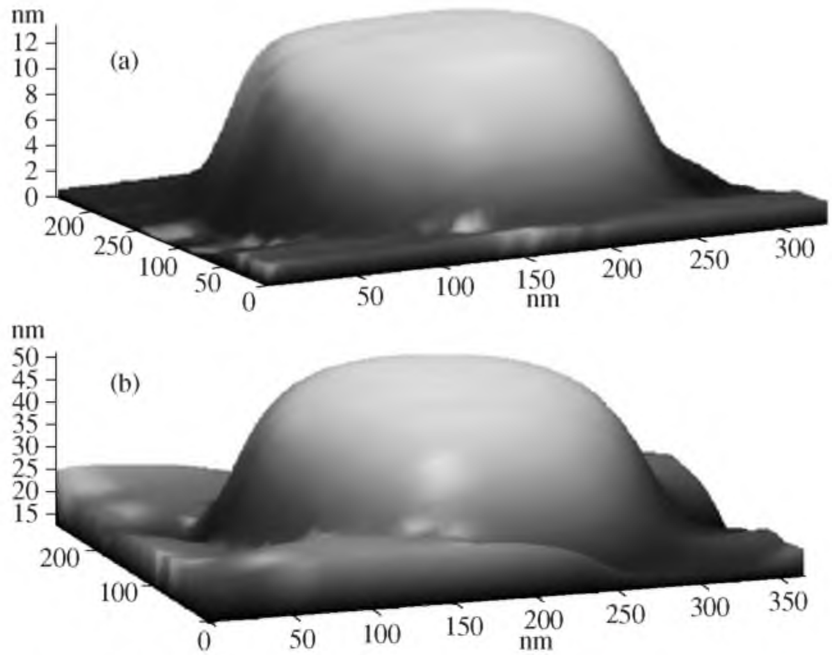

Fig. 3. Scans of separate islands on the surface of the carbon coating produced (a) without the accelerating voltage and (b) with an accelerating voltage of 1200 V.

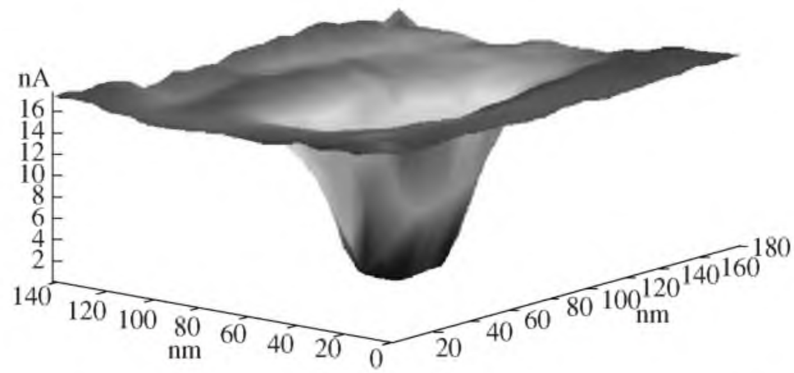

Fig. 4. Scan of a separate island on the surface of the nitrogenated carbon coating obtained in the spreading resistance mode.

2. The ion irradiation creates regions of the carbon coating with different internal stresses, which is associated with different concentrations of point radiation defects. This results in the formation of islands due to the relaxation of the internal stress.

3. The maximum island height increases from 13 to 51 nm with the accelerating voltage, whereas the size of the island's base is almost the same, on the order of 250 nm, for the three carbon coating formation modes under investigation.

4. The lowest current and, respectively, the highest resistance were observed at the island summits, indicating the prevalence of the sp^3 phase in these regions.

ACKNOWLEDGMENTS

We are grateful to the Shared Center of the Center of Nanostructural Materials and Nanotechnologies of the Belgorod State University for assistance in performing the measurements on the QUANTA 200 3D raster ion electron microscope.

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