Nanometer-Sized Carbon Coatings on a Silicon Wafer: The Effect That Nitrogen Doping Level Has on Specific Conductivity and Morphology

A. Ya. Kolpakov, I. V. Sudzhanskaya, M. E. Galkina, I. Yu. Goncharov, A. I. Poplavskii, and S. S. Manokhin

Belgorod State University, ul. Pobedy 85, Belgorod, 308015 Russia
e-mail: sudzhanskaya@bsu.edu.ru

Abstract—Nitrogen-doped carbon coatings up to 100 nm thick are obtained on single-crystal silicon wafers with the use of the pulsed vacuum-arc technique with nitrogen gas puffing into a vacuum chamber. The dependence that the specific conductivity has on the nitrogen pressure is investigated. The nitrogen content of the coating and plasmon energy are obtained by the spectroscopy of electron-energy characteristic losses (EECLs). The coating morphology is investigated with scanning probe microscopy (SPM) and transmission electron microscopy (TEM). The dependences that the specific conductivity has on nitrogen pressure and thickness show nonlinear behavior; correlations between the coating morphology, specific conductivity, and plasmon energy are revealed. An explanation for the results is proposed.

INTRODUCTION

As was found previously [1], nanometer-sized carbon coatings produced on silicon wafers with pulsed vacuum-arc deposition improve such silicon-surface strength characteristics as microhardness and crack resistance. The nitrogen doping of the carbon coatings makes it possible to modify their energy-gap width; therefore, their application in nanotechnology and microelectronics has considerable promise. The carbon diamondlike coating properties depend on the method by which they are produced and the conditions of their formation, being defined by the relationships among phases with the sp^3-, sp^2-, and sp-hybridization of valence electrons. A considerable portion of the chemical bonds of valence electrons with sp^3-hybridization, ranging up to 80%, is specific to diamondlike coatings with an energy-gap width of up to 5.5 eV and high density of up to 3 g/cm^3 [2]. The coatings are of an amorphous structure, so describing them is very complicated. Electron-energy characteristic loss (EECL) spectroscopy makes it possible to find the percentage of the phases in a coating. The plasmon energy relates to the sp^3-hybridization of valence electrons. The larger the fraction of the phase with the sp^3-hybridization of valence electrons is, the higher the plasmon energy is [3]. The growth in a fraction of the phase with the sp^2-hybridization of valence electrons results in the formation of coatings with a lower density and narrower energy-gap width. As is known, electrical conduction is sensitive to the structure of the coating; this is of the utmost significance for hydrogen-free superhard diamondlike coatings, because, with a decrease in electrical conduction, the totality of their properties comes close to these of a natural diamond. Data on the correlation between the content of the phase with the sp^3-hybridization of valence electrons and the morphology of carbon coatings are published in a series of papers [4–6].

In this paper, the action of the nitrogen doping level on the specific conductance and morphology of nanometer-sized carbon coatings deposited on a silicon wafer is investigated.

EXPERIMENTAL

Nitrogen-doped carbon coatings up to 100 nm thick were produced on (100)-oriented KEF-4.5 single-crystal silicon substrates with the pulsed arc-vacuum technique [7]. The electrical conduction of the doped carbon coatings was measured with the four-point probe method. The determination of the thickness and an investigation into the doped carbon coatings with the use of a scanning probe microscope (SPM) operating in the mode of spreading-resistance imaging were conducted with the use of a Ntegra probe laboratory manufactured by NT-MDT. The plasmon energy and nitrogen content of the coatings were determined by EECL spectroscopy with the use of a Tecnai G2 F20 S-TWIN high-resolution transmission electron microscope (TEM) fitted with a Gatan 860 GIF 2001 postcolumn sector-type filter. To obtain TEM images of nanometer-sized carbon coatings, they were evaporated on a fresh cleavage of NaCl

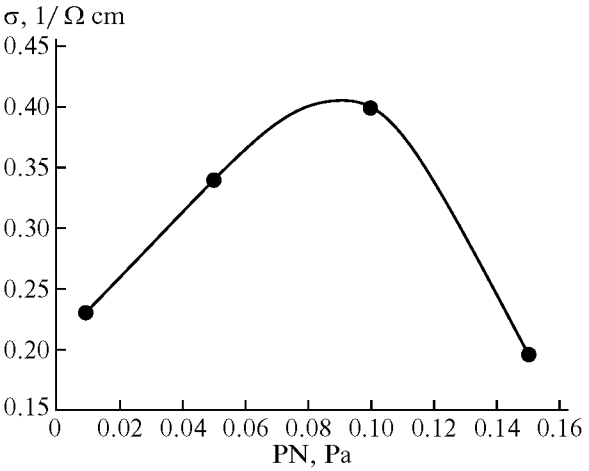

Fig. 1. Specific conductivity σ vs. nitrogen pressure PN for nitrogen-doped carbon coatings deposited on a silicon wafer; the thickness of the coatings was 100 nm.

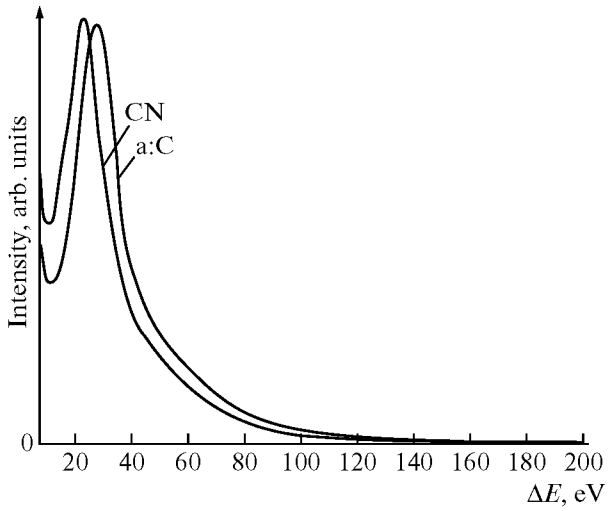

Fig. 2. Spectrograms of EECL ΔE for amorphous carbon (a-C) and nitrogen-doped carbon (C:N) coatings.

salt and subsequently separated with the use of the conventional procedure.

RESULTS AND DISCUSSION

The dependence that the specific conductivity σ has on the nitrogen pressure PN was found in the nitrogen-doped carbon coatings and presented in Fig. 1.

It is evident from the experimental dependence that, in the case of nitrogen-doped carbon coatings deposited on a wafer, electrical conduction increases with the nitrogen pressure up to 0.1 Pa. This phenomenon, which occurs upon an increase in pressure, is due to the growth in a fraction of the phase with the sp^2-hybridization of valence electrons as compared to that with the sp^3-hybridization [3].

A decline in electrical conduction in the range between 0.1 and 0.15 Pa is attributable to the gain in the content of a nonconducting phase; this assumption is supported by the results given in [8], where the authors state that the carbon nitride phase may come into existence as the nitrogen pressure increases. Moreover, so-called fullerene-like carbon nitride may occur as well; the results of investigations into its properties are published in [9]. The proposal for this structural formation is confirmed by the following:

(1) While colliding with gas, the effect of carbon plasma slowing is enhanced and the carbon ion energy decreases.

(2) The plasmon energy grows, as is revealed by the TEM patterns taken from a carbon coating obtained upon a rise in the nitrogen pressure to 0.4 Pa; these patterns are given below.

The spectroscopy of EECL ΔE made it possible to find the plasmon energy; in the case of a carbon coating, it was found to be equal to 29.1 eV; when the coating was produced with the use of the technique of puffing nitrogen gas into a vacuum chamber with a pressure of up to 0.1 Pa, this value was equal to 24.6 eV. The corresponding EECL spectra are presented in Fig. 2.

Under the nitrogen doping of a carbon coating, a decrease in the plasmon energy is related to an increase in the fraction of the phase with the sp^2-hybridization of valence electrons as compared to that with the sp^3-hybridization and to the lower density of the coating [3].

Thus, taking into account the investigation results on the electrical conduction and plasmon energy of the carbon coatings, one can reason that there is a correlation between these values.

The thickness dependence of the specific conductivity of a nitrogen-doped carbon coating is given in Fig. 3.

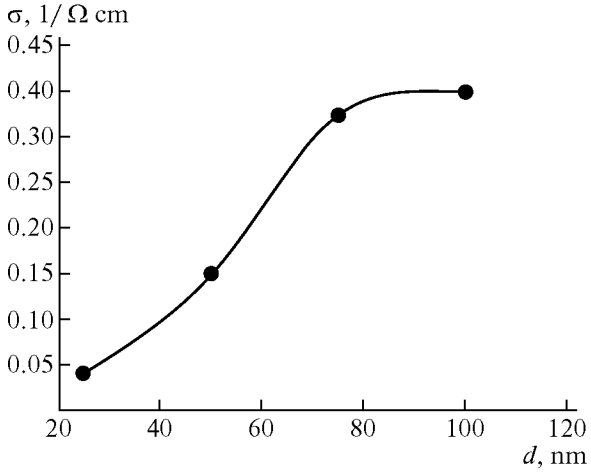

Fig. 3. Specific conductivity σ vs. thickness d for nitrogen-doped carbon coatings. The nitrogen pressure was 0.1 Pa.

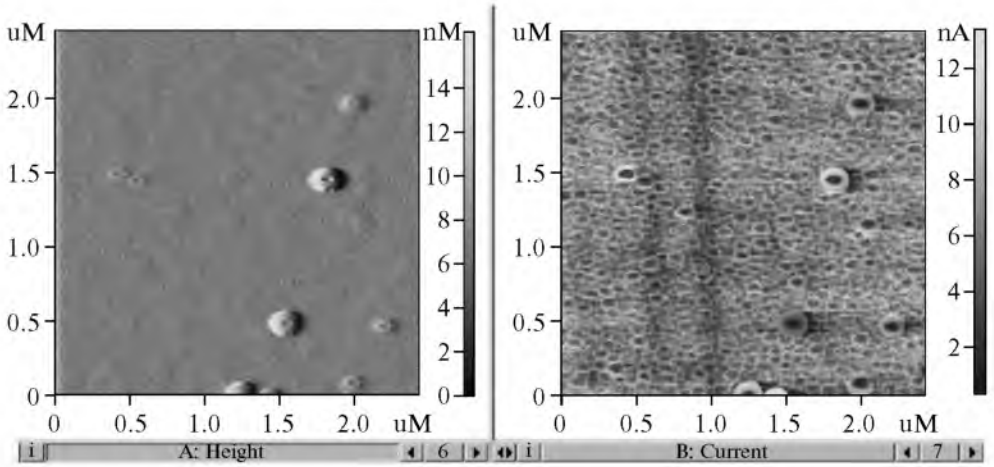

Fig. 4. Images of the 100-nm-thick nitrogen-doped carbon coating surface obtained with an SPM operating in the AFM mode (on the left) and in the mode of spreading resistance imaging (on the right).

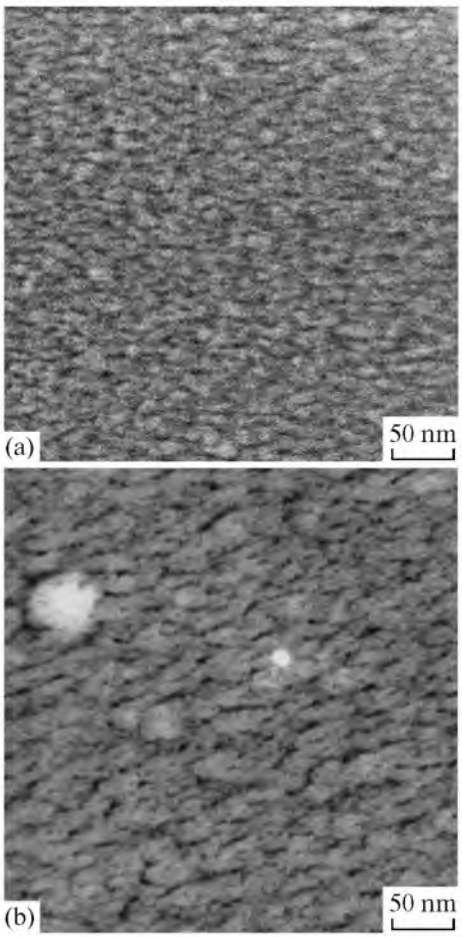

Fig. 5. TEM images of the surface of carbon coating doped with nitrogen under 0.01 Pa (a) and 0.4 Pa (b).

Analyzing the dependence shown in Fig. 3, we can state the following: the thinner the coating is, the lower the specific conductivity is.

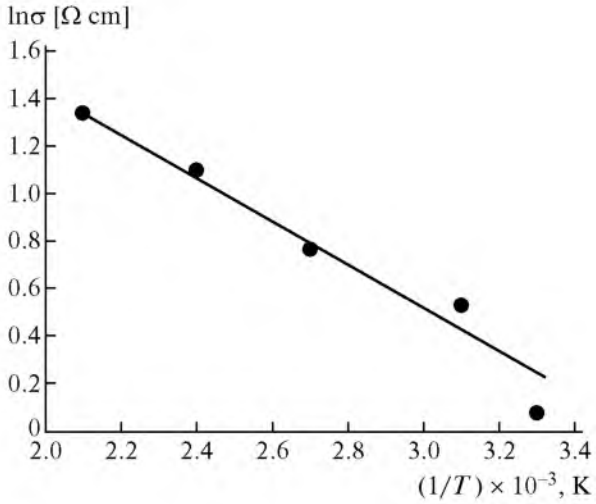

Fig. 6. Specific conductivity vs. temperature for carbon coating doped with nitrogen under 0.1 Pa.

We investigated a silicon surface coated with a doped carbon layer with the use of an SPM operating in the mode of spreading resistance imaging; the corresponding results are shown in Fig. 4. The thinner the coating is, the smaller the observed clusters are; clusters with a size in the range of about 100 and 10 nm and with an inhomogeneous distribution of electric conductance over their surface may be considered structural peculiarities that result in the occurrence of discrete quantizing levels.

The images of nitrogen-doped carbon coatings produced under 0.01 and 0.4 Pa were obtained with a TEM (Figs. 5a, 5b). The coating produced at 0.4 Pa has a fullerene-like structure. In this case, the plasmon energy grows up to 25 eV; this result coincides with that from [10].

The temperature dependence of the specific conductivity for a nitrogen-doped carbon coating is presented in Fig. 6.

Analyzing the obtained dependence, we can state that the doped carbon coating deposited on a silicon wafer shows semiconductor properties as its electrical conduction grows with temperature. In this case, the energy-gap width is 0.19 eV. For coating-free silicon, this characteristic is equal to 1.12 eV.

Thus, by varying the doping level of a nitrogen-doped carbon coating, we can modify the energy-gap width in the range from 1.12 eV (which corresponds to silicon) to 0.19 eV.

CONCLUSIONS

(1) The dependences that the specific conductivity has on the parameters of the formation process were found for nitrogen-doped carbon coatings. It was established that the specific conductivity of the carbon condensates peaks at a nitrogen pressure of 0.1 Pa, being a nonlinear function of a coating thickness; such behavior of the specific conductivity is common to nanometer-sized objects.

(2) The plasmon energy found with the EECLS technique appears to be equal to 29.1 eV for a carbon coating and 24.6 eV for a nitrogen-doped carbon coating with the greatest electrical conduction.

(3) In the case of a carbon coating produced in a vacuum chamber under an elevated nitrogen pressure of up to 0.4 Pa, a fullerene-like structure was revealed by high-resolution TEM. In doing so, it was found that the electrical conduction of the coating drops steeply and the plasmon energy rises to 25 eV.

(4) The obtained temperature dependence of the specific conductivity for the doped carbon coatings is common to semiconductor materials. It was found that the deposition of nitrogen-doped carbon coatings on a wafer makes it possible to modify its energy-gap width in the range from 1.12 to 0.19 eV.

ACKNOWLEDGMENTS

This work was supported by the Federal Program "Scientific and Pedagogical Personnel for an Innovative Russia" for 2009–2013 in the framework of the Nanotechnology and Nanomaterial Division (state contract no. P1223) with the use of equipment from the Diagnostics and Investigations of Nanostructured Materials Joint Research Center at Belgorod State University.

REFERENCES

1. I. V. Sudzhanskaya, M. E. Galkina, I. Yu. Goncharov, A. Ya. Kolpakov, and A. I. Poplavskii, "Microhardness of Silicon after Ion Irradiation and Deposition of the Carbon Coating," Deform. Razrushenie Mater., No. 10, 12–15 (2008).
2. P. Fallon, V. S. Veerasamy, C. A. Davis, and J. Robertson, "Properties of Filtered-Ion-Beam-Deposited Diamondlike Carbon as a Function of Ion Energy," Phys. Rev. B: Condens. Matter. **48** (7), 4777–4782 (1993).
3. V. S. Veerasamy, J. Yuan, and G. A. J. Amaratunga, "Nitrogen Doping of Highly Tetrahedral Amorphous Carbon," Phys. Rev. B: Condens. Matter **48** (24), 17954–17959 (1993).
4. J. Robertson, "Diamond-Like Amorphous Carbon," Mater. Sci. Eng., R **37**, 129–281 (2002).
5. Y. Lifshitz, G. D. Lempert, and E. Grossman, "Substantiation of Subplantation Model for Diamondlike Film Growth by Atomic Force Microscopy," Phys. Rev. Lett. **72** (17), 2753–2756 (1994).
6. M. Moseler, P. Gumbsch, C. Casiraghi, A. C. Ferrary, and J. Robertson, "The Ultrasmoothness of Diamond-Like Carbon Surfaces," Science (Washington) **309** (5740), 1545–1548 (2005).
7. M. E. Galkina, A. Ya. Kolpakov, O. V. Safronova, and I. V. Sudzhanskaya, "The Method for Forming a Superhard Doped Carbon Coating on Silicon in Vacuum," RF Patent No. 2 342 468, Byull. Izobret., No. 36 (December 27, 2008).
8. A. Wei, D. Chen, N. Ke, W. Y. Cheung, S. Peng, and S. P. Wong, "Effects of Nitrogen on the Structure and Properties of Highly Tetrahedral Amorphous Carbon Films," J. Phys. D: Appl. Phys. **31**, 1522–1526 (1998).
9. A. A. Voevodin, J. G. Jones, J. S. Zabinski, Zs. Czigany, and L. Hultman, "Growth and Structure of Fullerene-Like CN_x Thin Films Produced by Pulsed Laser Ablation of Graphite in Nitrogen," J. Appl. Phys. **92**, 4980–4988 (2002).
10. A. L. Shakhmin, A. M. Khodorkovskii, S. V. Murashov, T. O. Artamonova, and A. V. Golod, "Electron Structure of Thin Fullerene Films Deposited by Various Methods," Pis'ma Zh. Tekh. Fiz. **27** (3), 1–6 (2001). [Tech. Phys. Lett. **27** (2), 87–89 (2001)].