The Effect that Nitrogen Ion Irradiation and the Deposition of a Nanosize-Thick Carbon Coating Have on Microhardness and Crack-Growth Resistance in Silicon

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Abstract—The behavior of silicon wafers in the starting state (after both irradiation with nitrogen ions and after nitrogen ion irradiation and the deposition of an 80-nm-thick carbon coating) has been investigated. Processing with nitrogen ions and the coating deposition result in both a significant shrinkage of the crack length around the indentations and their utter absence under low indenter loads. This phenomenon is due to the high level of compression stresses in the carbon coating; these stresses compensate for the tensile ones that show up through indentation. Combining nitrogen ion irradiation and the deposition of the coating makes a considerable increase in the microhardness and crack-growth resistance in silicon possible.

INTRODUCTION

The ion-plasma surface-processing procedures and vacuum coating technology (with the use of low-temperature plasma) open up new possibilities for modifying the surface of different articles in order to upgrade their characteristics: microhardness, coefficient of friction, thermal stability, etc.; these properties define the service life of the articles [1–4].

Superhard carbon coatings obtained on a substrate by the condensation of accelerated particles of carbon have attracted the considerable interest of researchers, because they are similar to natural diamonds in their physicomechanical properties; among all types of coatings, carbon holds the greatest promise for nanotechnologies. In recent years, interest in the vacuum-arc deposition methods of obtaining the ultrafine carbon coatings on microelectromechanical systems (MEMS) has accelerated throughout the world because these coatings are among the hardest [5].

The low-energy ion etching of materials has found wide use in refining the coating adhesion to a substrate [5]. As is known, the accelerated ion irradiation of a surface results not only in its sputtering, but also in the accumulation of radiation-induced point defects in the near-surface layer [6]. At definite doses, amorphization of the target material (that is, the substrate), as well as clustering of defects and their coalescence into larger ones, occurs; these phenomena may affect the mechanical properties of the material. The picture becomes significantly more complicated in the case of conceivable phase transitions in a modified material; this is observed in silicon in the same way it is in the course of accelerated particle irradiation, as well as in the process of its indentation, which is used to study the mechanical characteristics of materials [7, 8].

We have previously revealed the effect of an increase in the crack-growth resistance of silicon in the course of indentation due to the deposition of nanosized nitrogen-doped carbon coating onto its surface [9]. However, in [9], the irradiation was used to enhance the carbon-coating–substrate-adhesion strength, and the investigation into the effect of ion irradiation on the microhardness and crack-growth resistance in silicon received inadequate attention. For this reason, we have studied the behavior of silicon in the course of indentation (i) in the initial state of silicon wafer, (ii) after nitrogen ion irradiation, and (iii) after nitrogen ion irradiation combined with the deposition of an 80-nm-thick carbon coating. This coating thickness was determined by the peculiarities of its application to MEMS and, among other things, to the kantilevers of scanning probe microscopes.

EXPERIMENTAL

The investigation was concerned with KEF-4.5 silicon wafers. The nitrogen ion irradiation of the specimens and carbon coating deposition were performed with a UVNIPA-1-001 unit equipped with an II-4-0.15 ion gas source and a pulsed carbon plasma source.

Silicon specimens were etched with nitrogen ions at a discharge voltage of 2.5 kV, a discharge current of 80 mA, and an ion current density of 0.15 mA/cm^2. As this took place, the mean energy of the nitrogen ions was about 1.0 keV. Starting from the results of the previous investigations, we took an ion irradiation dose equal to 90 J/cm^2 [9].

The coating was deposited with the use of carbon plasma at a capacitive energy storage voltage of 300 V; the storage capacitance was equal to 1000 μF. The pulse repetition frequency of a discharge was 2.5 Hz. The carbon coating deposition rate was 0.1 nm/pulse.

The coating thickness was found with the step method using a SMENA-A scanning probe microscope. The microhardness of the specimen surface was measured with the Vickers's method using a DM8 microhardness gage at indentation loads of 10, 25, and 50 g. The persistence time under load was 15 s. The mean of 20 measurements was found.

The subsequent analysis of indentations and the measurement of the crack length were done with an Olympus GX-51 optical microscope and special software.

After the nitrogen ion etching, the specimens were investigated with electron probe microanalysis using a Quanta 200 3D scanning X-ray microanalyzer.

Table 1. Measurement data on microhardness

Object under microindentation	Microhardness, GPa		
	$HV_{0.01}$	$HV_{0.025}$	$HV_{0.05}$
Starting silicon	14.4	9.12	9.49
Irradiated silicon	19.14	15.44	12.51
Silicon irradiated with ions and covered with a coating	22.58	16.1	13.4

Table 2. Measurement data on crack length

Object under microindentation	Crack length range, μm		
	load of 10 g	load of 25 g	load of 50 g
Starting silicon	1.87–3.05	4.06–5.97	2.98–11.1
Irradiated silicon	1.22–2.51	2.2–5.77	3.25–10.4
Silicon irradiated with ions and covered with a coating	–	1.36–2.36	2.12–4.78

RESULTS AND DISCUSSION

The measurement results on the microhardness of silicon specimens (i) in the initial state, (ii) after nitrogen ion etching, and (iii) after the nitrogen ion etching, combined with the deposition of a 80-nm-thick carbon coating, are presented in Table 1. The images of microhardness indentation obtained at an indentation load equal to 50, 25, and 10 g are shown in Fig. 1. The maximum and minimum values of crack lengths obtained in a set of indentations with different loads are presented in Table 2; the indentations are shown in Fig. 2.

The indentations of an indenter with applied loads of 50 and 25 g are displayed in Fig. 1a, where one can notice heaps pointed out by arrows; such heaps are common in plastic deformation. The process of crack growth is scarcely affected by the nitrogen ion irradiation (Fig. 1b). At the same time, in silicon specimens irradiated by nitrogen ions and having carbon coating

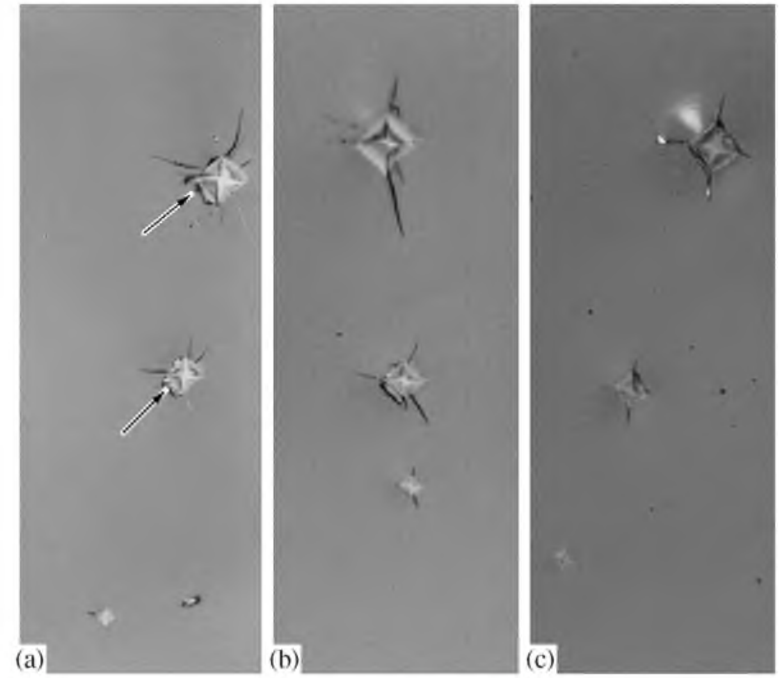

Fig. 1. Images of microhardness indentations on a surface of (a) starting silicon, (b) nitrogen ion irradiated silicon, and (c) silicon irradiated by nitrogen ions and covered by carbon coating 80 nm thick. Magnification ×1000.

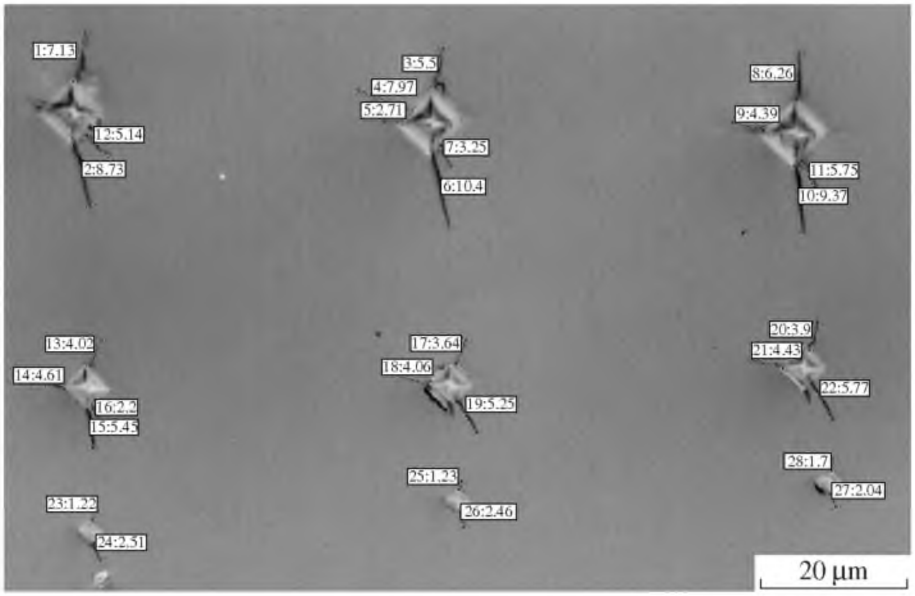

Fig. 2. Measurement of crack length with optical microscope with the use of a software program.

deposition, the crack lengths significantly go down (Fig. 1c and Table 2); at an applied load of 10 g, cracks are entirely absent.

The measurement data on microhardness presented in Table 1 make it possible to conclude that the silicon microhardness essentially depends on the ion irradiation. Notice that, in this case, the long-range interaction observed in a number of experiments [11] appears. We simulated atomic collisions with the use of a TRIM code [11] and found that the mean-free path for 1-keV nitrogen ions in silicon was about 5.0 nm; as is readily seen, this value is too small to significantly change the silicon microhardness. In our case, the thickness of a silicon coating exhibiting elevated microhardness due to nitrogen ion irradiation substantially exceeds the rated value of an ion-free path.

To exclude the assumption that silicon nitride may come about from ion irradiation, the investigation was performed with X-ray microanalysis using a Quanta 200 3D scanning X-ray microanalyzer. After cleaning the silicon surface with nitrogen atoms, these atoms escaped detection in the process of the investigation of the surface. Therefore, the rise of the silicon microhardness related to nitrogen ion irradiation is attributable to the effect of this material's point-defect saturation. This is the phenomenon that defines the strengthening brought on by the locking of dislocations; this proposal is supported by the fact that a silicon surface irradiated by nitrogen atoms and deposited with an ultrafine carbon coating does not contain heaps in the vicinity of indentations of an indenter (Fig. 1b).

The rise in the microhardness and the crack-growth resistance appear due to the deposition of ultrafine carbon coatings; these phenomena are attributable to the high level of compressional stresses (on the order of 10 GPa) in the carbon coating; the compressional stresses compensate for the tensile ones caused by indentation.

CONCLUSIONS

(1) It has been found that, at the given values of nitrogen ion irradiation and carbon coating thickness, the nitrogen ion-plasma surface treatment is the most important factor affecting the rise of silicon microhardness.

(2) The carbon coating is the deciding factor favorable to the crack-growth resistance in silicon.

(3) The joint action of the nitrogen ion irradiation and carbon coating deposition makes it possible to increase the microhardness and crack-growth resistance in silicon.

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REFERENCES

1. I. I. Aksenov, V. G. Padalka, V. G. Strel'nitskii, et al., "Some Properties of Diamond-Like Coatings and Possible Fields of Their Applications," Sverkhtverd. Mater., No. 1, 25–28 (1979).

2. Kwang-Ryeol Lee, Kwang Yong Eun, and Keum-Mo Kim, "Application Carbon Films for Anti-Abrasion and Low Friction Properties of VCR Head Drums," Surf. Coat. Technol. **76–77**, 786–790 (1995).
3. S. M. Rotner and V. A. Mokritskii, "Diamond-Like Films in Microelectronics: Diamond-Like and Carbon Films" in *Proceedings of the 12th International Symposium on Thin Film Epitaxy (ISTFE-12), Kharkov, Ukraine, 2001* (Kharkov, 2001), pp. 114–115.
4. Simone Anders, C. Sing Bhatia, et al., "Application of Cathodic Arc Deposited Amorphous Hard Carbon Films to the Head/Disk Tribology," in *Spring Meeting of the Materials Research Society, San Francisco, CA, United States, April 13–17, 1998* (San Francisco, 1998).
5. G. F. Ivanovskii, *Ion–Plasma Processing of Materials* (Radio i Svyaz', Moscow, 1986) [in Russian].
6. G. H. Kinchin and R. S. Pease, "The Displacement of Atoms in Solids by Radiation," Rep. Prog. Phys. **18**, 1–51 (1995).
7. Yu. I. Golovin and A. I. Tyurin, "Microcontact and Nanocontact Interactions of Solids," Priroda (Moscow), No. 4 (2003).
8. V. Domnich and Y. Gogotsi, "Phase Transformation in Silicon under Contact Loading," Rev. Adv. Mater. Sci. **3**, 1–36 (2002).
9. A. Ya. Kolpakov, M. E. Galkina, I. V. Sudzhanskaya, et al., "Modification of Silicon Surfaces by Doped Carbon Coatings of Nanometer-Scale Thickness," Uprochnyayushchie Tekhnol. Pokrytiya, No. 10, 53–56 (2006).
10. N. A. Bert, I. P. Soshnikov, and M. G. Stepanova, "Long-Range Structural Interaction Effect in Gallium Arsenide during Ion Bombardment," Fiz. Tverd. Tela (St. Petersburg) **40** (3), 438–440 (1998) [Phys. Solid State **40** (3), 401–403 (1998)].
11. J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon, New York, 1996).