Formation of Nano Diamonds in Surface Layer of Materials during Short Pulse Ion Beam Implantation

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The research results of the cubic carbon nanosized particle synthesis during short pulse ion beam implantation to silicon target are presented. The experiments are carried out using the high power ion beam accelerator “TEMP”. The beam parameters are as follows: the ion energy is 250-300 keV, the pulse duration is 80 ns, the elemental composition of beam is carbon ions and protons, and the ion current density is 20-25 A/cm². The formation of SiC nanosized particles and nanodiamonds in the surface layer of silicon is found out under sequential action of more than 100-500 pulses.

Key words: high power ion beams, pulse implantation, magnetically insulated diode, silicon, nanodiamonds.

INTRODUCTION

To obtain nanosized diamonds as well as SiC compositions in the silicon surface layer is an urgent problem in semiconductor electronics [1]. Nanodiamonds in the surface layer of silicon and the other materials can be used as “nuclei” for further epitaxial growth of the diamond films [2, 3]. Detonation diamonds spread onto the surface obtained in a considerable amount from explosives are used, as a rule, as a nucleation centers [4-6]. Nanodiamond synthesis directly in the surface layer of the material is of interest. The formation of SiC compositions is obtained by the ion implantation of carbon into silicon [7]. The synthesis conditions are improved due to further pulse heating using a pulse laser emission or a pulse powerful ion beam [8]. The first results of SiC nanosized particles synthesis in the silicon surface layer were obtained during the implantation of carbon ions by short pulses of high power ion beams [9]. The given work is the research of nanodiamond synthesis capability in silicon surface layer under the action of pulse powerful ion beam with advanced relative content of carbon ions at “self-annealing” mode [10, 11], when heating to high temperatures is provided during the pulse and forming pressure waves in the surface layer of the material. Absorbed dose alternation in the target surface layer is provided by variation of the pulse number.

EXPERIMENTAL

The high power ion beam accelerator TEMP-4 based on planar diode with magnet self-isolation is used in experiments, Fig.1.

Fig. 1. The working chamber of the high power ion beam accelerator TEMP-4: 1 – the vacuum chamber, 2 – the diode with magnet self-isolation, 3 – the sample holder.

An accelerating voltage of the magnet-isolated diode (MID) was 250-300 kV, the current pulse duration was 80 ns, the pulse repetition frequency was 15-20 pulses/min. A potential electrode is made from graphite. The samples were irradiated by pulse packets in 50-100 pulses with 20-min. delay to avoid target overheating. The current density was lower than ablation threshold of the target material, it was 20-25 A/cm², Fig. 2. The distance from the diode to a treated target was 14 cm. A delay time of signals appearing from collimated Faraday cup, Fig. 2, corresponded to ions travel time of this distance. The ion beam included carbon ions 86% and protons 14%. The accuracy of the beam composition measurement in the sample of 500 pulses did not exceed +/- 8%. A number of current pulses per target

varied from 100 up to 500. The energy spectrum of the ion beam for carbon is presented in Fig. 3, c). A low-energy part of the ion spectrum complied with the beam formation in MID at rising and descending edge of the accelerating voltage, Fig. 2. The working pressure of a residual gas in the chamber varied from $\sim 10^{-4}$ mm of mercury at the beginning of irradiation up to $\sim 10^{-3}$ mm of mercury at pulse repetition rate 20 min^{-1} . The chamber pumping was performed with a diffusion oil-vapor pump.

The plates made of single-crystalline silicon {100} were used as a target. We used X-ray diffraction, transmission electron microscopy, Raman spectroscopy, Auger spectroscopy to analyze the target.

Fig. 2. The oscillograms of the accelerating voltage (1), total current (2) and ion current density (3) of a planar diode with self-isolation, 8 mm gap.

The methods of scanning electron microscopy (SEM JCM-7500FA of Tomsk Polytechnic University Nano-center) and atomic-force microscopy (AFM "Solver-HV" of NT_MDT production) were applied to the research surface morphology of the implanted silicon. A portion of irradiated samples was purified with the use of ozone and 50% nitric acid solution at a temperature 190°C [12] to remove a carbon amorphous phase from the surface. The measurements with the use of AFM microscopy were carried out in air under standard conditions. The measurement of the surface potential distribution was carried out by the Kelvin probe method using Si-cantilevers of NSG10/W₂C series with round-off radius of the probe being 30-35 nm.

The phase composition was determined by the X-ray structure analysis method in Bragg-Brentano geometry with Shimadzu XRD – 600 diffractometer with radiation CuK(α).

A study of the structure and phase powder composition prepared from the surface of a silicon target irradiated by 500 pulses was carried out by the methods of electron diffraction microscopy. The samples for electron microscopic analysis were prepared as follows: a surface layer was removed mechanically from the irradiated silicon surface, the obtained powder was deposited by a thin film onto the slide and a graphite layer was deposited onto it using VUP-2k equipment. Then extractive coal replicas, which were analyzed with the electron microscope EM 125, were prepared.

The elemental target composition test by the Auger electron spectroscopy method

In Fig. 3 the measured distributions of the implanted ions by the Auger electron spectroscopy method are

presented. Curves 1 and 2, Fig. 3, a) being extreme values of the carbon concentration differ in irradiation modes (the pressure in the working chamber, the pulse ratio). Curve 2 corresponds to the irradiation mode with a high pulse frequency, 20 min^{-1} and a higher residual gas pressure in the working chamber (less than $\sim 5 \cdot 10^{-4}$ mm of mercury). Curve 1 corresponds to that with a lower pulse repetition rate and a lower pressure of the residual gas in the working chamber ($< 10^{-4}$ mm of mercury). But even in the second case (curve 2, Fig. 3, a) concentration of carbon in the surface layer significantly exceeds the calculated concentration of the carbon implanted only by the pulse beam, Fig. 3, b).

Fig. 3. The distribution of the carbon concentration in the surface layer of silicon measured by a) Auger-spectroscopy method (500 pulses) and b) calculated concentration of carbon implanted by the beam (500 pulses)

The concentration of carbon significantly exceeds the concentration, which provides implantation of carbon ions transmitted by the beam. The concentration rises with the increase in pressure in the working chamber.

Analysis of silicon target surface by SEM and AFM methods

Some irradiated samples were purified using ozone and 50% nitric acid solution at temperature 190°C [12] to remove the amorphous phase of carbon from the surface. Targets with precoating of the sample surface with a thin conducting silver layer were used for analysis. Fig. 4 demonstrates micropictures of the same part in the standard SEM photography mode (a) and mode "compo" (b), when reflected electrons are fixed from the surface layer of 100 nm thickness.

Fig. 4. a) SEM-image of irradiated silicon, b) Compo mode

The comparison of two photos in Fig. 4 allows to conclude that particles of the other phase sized from 5-10 up to 100 nm were projected beyond the surface partially, but they are located under the surface silicon layer with a greater concentration.

Measurements using AFM microscopy were carried out in air under standard conditions. AFM image of the silicon target after etching in nitric acid is given in Fig. 5, *a*. The main element of the relief is grains sized 20-120 nm in diameter and of 5-50 nm height. Since as a result of etching implanted silicon samples and powerful pulse ion beam action, matrix itself – silicon – obtains grain structure of the surface, the measurement of the surface potential distribution (Fig. 5, *b*) was carried out at the same surface area. The main task was to find out what silicon surfaces correspond: if these are silicon crystals or particles of the other phase composition: SiC or cubic carbon. It was found out that there are regions with abrupt differentials of work function ~ 60 mV at the sample surface. Their spatial arrangement coincides with the spatial arrangement of particles salient onto the surface. In terms of the sharp potential difference, these formations can be connected with the formations on the basis of carbon: SiC and crystal carbon forms.

X-ray diffraction

A complete-profile analysis was carried out in Bragg-Brentano geometry using Shimadzu XRD – 600 diffractometer with $\text{CuK}(\alpha)$ radiation. A number of current pulses being over 100, surface layer of the silicon target passes from the monocrystalline phase into polycrystalline one. Increase in number of pulses up to 500 results in rise of SiC proportion and crystalline carbon with cubic lattice in the surface layer of the target. In Fig. 6 the spectrogram of silicon target processed in 500 beam current pulses mode is shown.

Fig. 6. X-ray spectra of silicon processed at short pulse implantation mode.

SiC – moissanite composition is formed in the surface layer of the target, the lattice parameter of 0.2981 nm and cubic carbon form with different value of the in-

teratomic distance: the synthetic nanodiamond with the lattice parameter of 0.35672 nm and orthocarbon of 0.42206 nm. The size of a coherent-scattering region of peaks broadening for the given sample for SiC is 5 nm, coherent-scattering region size varied from 8 up to 40 nm depending on the cubic forms of carbon and on different modes of irradiation. Percentage of crystal phases in the surface layer of the silicon target in experiments with above-mentioned beam parameters was within the range 24 – 80 % for SiC and 14-26% for carbon cubic forms.

Transmission electron microscopy

Investigations showed the following results: the phase composition of powder is SiC, graphite of hexagonal close-packed (HCP) modification and graphite of cubic modification ($a = 0.5545$ nm). The relative content of HCP graphite and cubic modification is nearly the same and makes $\sim 20\%$ of researched powder volume. Carbon particles of cubic modification are ellipsoids and have distinguished boundaries (Fig. 7, *c, d*). In electron-microscopic images of the largest particles there is a diffraction contrast in the form of dark strips of various shapes and length, which can indicate the elastic stresses of the carbon lattice, different thickness of particle areas (Fig. 7, *c*). Moreover, the microelectron diffraction pattern obtained from such a particle is monocrystalline and does not contain diffraction features (Fig. 7, *d*). HCP graphite particles, as a rule, do not have faceting modification (Fig. 7, *e, f*).

Thus, the transmission electron microscope registers the presence of the modified silicon, SiC compound and cubic form of carbon in the surface layer.

Fig. 7. a, b, e – the electron-microscopic images of powder particles; b, d, f – microelectron diffraction patterns of the given particles, respectively.

Raman spectroscopy

The method of Raman scattering was applied for silicon irradiated by 500 sequential pulses of the beam current, Fig. 8. It is obvious from spectra of Raman scattering that a number of pulses being 500 during silicon processing by the powerful pulse ion beam, G shift to high wave region 1600 cm^{-1} is observed, that indicates nanocrystalline carbon forming [13]. It is known that fluctuations of the hexatomic rings with tension and compression of sp^2 -bonds account for G line, corresponding to 1581 cm^{-1} in the graphite spectrum. G line drifts towards high frequencies up to 1600 cm^{-1} in the nanocrystalline carbon due to the size quantization of background in nanocrystals. D peak location

in the spectrum corresponds to 1350 cm^{-1} value. D strip can be an indication of the aromatic rings clusters with sp^2 -bonds in the structure of the disordered carbon. During mathematical spectra treatment by 500 pulses, 2 strips of 1240 and 1480 cm^{-1} are observed, which are not connected directly with standard D and G strips of the amorphous carbon. The similar strips are observed in the paper [14] and the authors of this work interpreted these strips as belonging to diamond nanocrystallite.

Fig. 8. The spectra of Raman scattering of the silicon samples treated at 500 pulses mode. The peaks corresponding to nano crystal diamonds are marked with arrows.

When a number of pulses is 100, characteristic lines are not detected in the sample.

DISCUSSION OF RESULTS

The capability to form the silicon carbide polycrystals and cubic carbon in a monocrystal silicon target during the pulse ion implantation of carbon ions in the surface layer and concomitant carbonization of the surface layer from the residual gas of the working chamber is shown in the paper.

The averaged carbon concentration in the surface layer formed only by carbon ions transmitted by ion beam makes $\sim 1\text{--}2 \cdot 10^{20}\text{ ion/cm}^3$. Also the results of direct measurement of carbon concentration by Auger spectroscopy, and observed SEM, transmission electron microscope, X-ray diffraction of forming compositions on the basis of carbon (SiC) and crystal formations of the carbon indicate considerably higher concentration of carbon in the surface layer. The surface layer carbonization mechanism attributes, to our mind, to the adsorption of the carbon particles in the gap between the pulses from carbon-containing residual gas by further radiation-induced diffusion during repetition pulses of beam current in conditions of temperature and voltage gradients generated under the action of the pulse ion beam onto the surface.

With the help of the methods of X-ray diffraction, transmission electron microscopy, by Raman spectroscopy formation of nanosized particles SiC and carbon with cubic and hexagonal lattice in silicon is shown. The average size of the coherent scattering region of particles of cubic carbon is up to 40 nm in silicon.

CONCLUSIONS

Use of short pulse powerful ion beams with increased (80 - 90 %) relative content of carbon ions enables to form nanosized particles (8-40 nm) of crystal carbon (synthetic nanodiamond and ortocarbon) and silicon carbide in the surface layer of silicon.

The formation of nanoparticles is provided by the increased surface concentration supplied with carbon adsorption from the residual atmosphere and its further radiation-enhanced diffusion under the action of gradients of temperature and pressure.

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