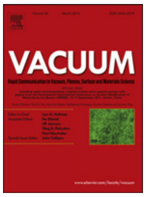
Vacuum 89 (2013) 118–121

Contents lists available at SciVerse ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum



Spectral analysis of nanosize forms of carbon synthesized by pulsed intense ion beams

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ARTICLE INFO

Article history:
Received 22 September 2011
Received in revised form
23 January 2012
Accepted 23 February 2012

Keywords:
Nanodiamonds
High intensity ion implantation
Carbon implantation
Silicon
Raman spectroscopy
Amorphization
SIMS depth profile analysis

ABSTRACT

The research results of nanodiamond formation in silicon during high intense ion implantation are presented. To produce a near-surface layer containing nanodiamond clusters a pulse ion implantation of carbon ions with different ion current densities (25–100cA/cm^2) and pulse numbers (10–500) was used. According to the Raman spectroscopy and electron paramagnetic resonance data the optimal parameters of ion implantation resulting in nanodiamond formation were found. Nanodiamonds are formed in the internal layer due to ion implantation with low pulse number (less than 100) and high ion current density (70–80 A/cm^2). An increase in pulse number results in amorphization of the implanted layer due to hydrogen atom accumulation that was revealed by the secondary ion mass-spectroscopy (SIMS) method.

1. Introduction

Nanocrystalline diamond (*nc*-diamond) is a novel material that has attracted theoretical and practical interest over the last years. Partly, this interest in studying *nc*-diamonds arises from the expectation that that its properties will differ from those of the bulk ones due in the main to the large surface to volume ratio [1–4]. Nanocrystalline diamonds are the small particles with an average dimension about up to 10 nm which are characterized by having a diamond crystal lattice. In [5] it was shown that diamond particles with such sizes may actually be more stable than graphite ones of the same size. The potential applications of the nanocrystalline diamonds include ultra-hard protective coatings, cutting tools,or, sliding parts [6,7]. In these cases *nc*-diamonds are used for enhancement of the materials microstructure. However, the latest research showed the possibility of *nc*-diamond (or other nanoscale carbon polymorph) usage in optics sensors and micro- and nano-electronics devices [8], as a material for field emission displays [9]. This requires incorporation of *nc*-diamond particles into the substrate to produce a heterogeneous structure. To use previously formed *nc*-diamonds particles for this is rather difficult.

Thus we suggest creation of a near-surface layer consisting of the *nc*-diamond clusters by a special type of ion implantation which is carried out in multi-pulse regime with high ion current density. Such type of ion implantation is realized by means of high intense pulse ion beams that result in high temperature and pressure in the surface layer [10,11]. This is necessary for diamond formation in the implanted area. The variation of implantation parameters will change the structure of the forming carbon clusters. On this account the problem of analytical investigation of the implanted layer and *nc*-diamond identification is an actual one. The most sensitive methods in this relation are the spectral methods that allow the structure features based on the interatomic bonds to be revealed [12].

The main purpose of this work is to reveal the different nano-scale forms of carbon forming in the near-surface layer of silicon substrate after treatment by high intense ion beams with a short-pulse regime and using different current densities and pulse numbers.

2. Experimental

Silicon single crystals (111) with size 1 × 1 cm and thickness 300 μm were used in the experiments to form *nc*-diamonds by high intense pulse ion beams. The ion beam generation was carried out

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doi:10.1016/j.vacuum.2012.02.037

in the TEMP-4 source at an accelerating voltage up to 250 kV. Two types of diodes with magnetic isolation were used for ion beam formation with current density more than 40–60 A/cm^2 and less than 20–30 A/cm^2 respectively. In the first case a focusing diode was used, in the second case a plane strip diode was used [13]. The pulse duration of accelerating voltage was 80 ns in both cases. The residual pressure in the chamber was $(2–4)\cdot 10^{-4}$ mbar which was reached due to pumping by a diffusion pump. This may cause some influence of the adsorbed atoms on the chemical composition of the surface layer. The silicon wafers were fixed on the surface of a collimated Faraday cylinder that was located at 130 mm from the ion diode and was in geometric focus of the plane strip diode. The density of ion current was changed from 20 to 100 A/cm^2. The ion beam consisted of 70–80% of carbon ions and 20–30% of hydrogen ions.

The implantation was carried out at 10, 100 and 500 pulses. The current pulse duration during implantation was 80 ns, pulse repetition frequency was 6 pulses/min. Samples were irradiated by pulse packets in 50 pulses in each with 20 min delay to exclude target overheating and damage. The implantation regimes are brought together in the Table 1.

To determine the structure of near-surface implanted layers containing carbon and hydrogen atoms Raman spectroscopy (RS) was used. RS spectra were registered at room temperature by Ramalog 4 Spex spectrometer in Ar$^+$-laser with power 0.10–0.15 W. The Raman spectra registration can often be accompanied by the appearance of luminescence lines. Therefore to exclude these lines on the registered spectra two wave-lengths of laser excitation (514 and 488 nm) were used. More complete information about the implanted layer structure was received by use of the electron paramagnetic resonance (EPR) method by a RadioPan SE/X-2543 spectrometer with H_{102} resonator in X-range at room temperature. The maximum power of super-high frequency electromagnetic radiation in the resonator was 70 mW. The modulation frequency of magnetic field was equal 100 kHz and the amplitude was 0.1 mT. The sensitivity of EPR spectrometer was $3\cdot 10^{12}$ spin/mT.

The presence of hydrogen atoms in the implanted layer was determined by secondary ion mass spectrometry (SIMS). The measurements were carried out with the use of the SIMS spectrometer SAJW-05 model [14]. The parameters during depth profile analyses were as follows: primary ion beam: 3 keV, Ar$^+$, primary beam raster: 0.028 cm^2, secondary ion detection area - 'electronic gate': 0.0042 cm^2. Prior to depth profile analysis, positive and negative secondary ion mass spectra were recorded using a 3 keV Ar$^+$ primary ion beam, with no beam raster. Sampling rate during secondary ion detection was 10 nm. Samples were sputtered up to the depths of 1 or 1.5 μm. The speed of sputtering was 0.25 nm/s that was calculated after profilometry measurement of the sputtered pit.

Morphology of the surface after ion implantation was investigated by atomic-force microscopy in the scanning equipment Solver P47 PRO.

3. Results and discussion

The influence of high intense ion beams on the silicon substrate causes shock wave formation and its spread into the implanted sample [15]. It mainly occurs due to the multi-pulsed regime of the implantation that allows high energy density to pass over a small time. In additional to that, the high values of ion current density provide sample heating. Thus, the pronounced type of ion implantation can produce the conditions for diamond formation.

Table 1
Regimes of ion implantation by high intense ion beams.

Regime	Ion current density, A/cm^2	Pulse number	Dose, cm^{-2}
# 1	70	10	3.5×10^{13}
# 2	80	10	4.0×10^{13}
# 3	100	10	5.0×10^{13}
# 4	25	100	1.25×10^{15}
# 5	25	500	6.25×10^{15}

Raman spectroscopy allowed the features of the implanted layer structure to be determined. There is a narrow peak at 1322 cm^{-1} in the RS spectra from the samples which were subjected to 10 pulses during pulsed ion implantation (Fig. 1). It is known that the corresponding peak from a bulk single crystal diamond is localized at 1332 cm^{-1}, but the observed shift of the spectral peak to the short-wave area accompanied by its broadening of more than 10 cm^{-1} is described by the phonon confinement model [16]. According to this model such transformation of diamond spectral line is caused by a decrease of the diamond crystallites size to 10–15 nm. The position of the peak does not change for ion current density rising from 70 to 100 A/cm^2, its intensity having fallen significantly at a current density of 100 A/cm^2. This allows a conclusion to be made about decrease of the diamond crystallite volume fraction in the analyzed layer at the latter regime of the implantation.

One more peculiarity of the RS spectra is a wide peak with weak intensity localized at 1100–1150 cm^{-1}. In [17] this peak is connected with nanocrystalline diamonds formed in CVD films and caused by the vibration of atoms in nanoclusters of *sp*^{3}-hybridized carbon atoms (size about 5 nm). There is a narrow peak at 1200 cm^{-1} in the RS spectra of all samples. The authors in [18] showed that this peak can be observed in single diamond crystals based on the theoretical calculation of vibration density states. However, it was found experimentally only in amorphous carbon. In our case it is difficult to correlate this peak with any of the given carbon structures since it is absent in the RS spectra registered with laser excitation at 488 nm wave length. It indicates a luminescence origin of the latter peak.

Increase of pulse number from 10 to 500 during the ion implantation results in the dose rising from 3.50×10^{13} cm^{-2} to 5.25×10^{15} cm^{-2}. At the corresponding RS spectra (Fig. 2) two wide spectral lines at 1350 cm^{-1} (D-peak) and 1580 cm^{-1} (G-peak) are observed. These lines are connected with different vibration modes of *sp*^{2}-hybridized carbon atoms. According to [19] such transformations of RS spectra occur in amorphous and diamond-like

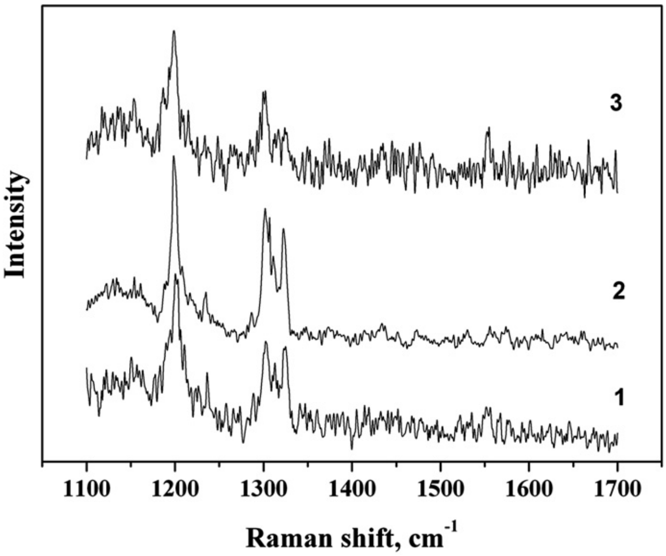

Fig. 1. RS spectra of the samples subjected the ion implantation with 10 pulses and ion current density 70 A/cm^2 (1), 80 A/cm^2 (2) and 100 A/cm^2 (3).