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Structural evolution of thermal annealed Si(0 0 1) surface layers fabricated by plasma immersion He^+ implantation

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ABSTRACT

Structural evolution in Si(0 0 1) surface layers after high-dose ($D = 5 \times 10^{17}$ cm^{-2}) low-energy (2 and 5 keV) plasma immersion He^+ ion implantation (He^+ PIII) and subsequent annealing at 853 and 1073 K was studied by complementary structural sensitive methods (TEM, XRR, RBS, and AFM). Formation of a three-layer structure (amorphous a-SiO_x sublayer at the surface, amorphous a-Si sublayer with large size helium-filled bubbles, and heavily damaged crystalline c-Si sublayer containing small-size bubbles and Si nanocrystallites) was observed for both implantation energies. This three-layer structure is retained after annealing. It was shown that the thickness of the oxide sublayer does not depend on implantation energy and does not change after annealing. This amorphous oxide sublayer together with dense top part of the a-Si sublayer forms a cap layer with a thickness of 15 nm that can be considered as a protective layer for the sublayers containing He-filled bubbles and Si nanocrystallites. The Si nanocrystallites were revealed at the boundary of the a-Si and the c-Si sublayers both in as-implanted at 5 keV and annealed samples.

1. Introduction

Treatment with high- and low-energy ions – ion engineering – is widely used to modify physical and chemical properties of silicon and other semiconductors [1]. One of the developed techniques is the modification of a crystalline substrate by implantation of dopants above the limits of their solubility [2]. Utilization of high-dose implantation with He^+ ions and protons results in the formation of a silicon layer containing bubbles with the noble gas in them [3]. In the last decades, this process was successfully used in the Smart-cut technology for SOI structures [4], for gettering of semiconductor substrates [5–7], and for monitoring of mechanical stresses [8,9]. The silicon heterostructures demonstrating photovoltaic properties were reported [10].

One of the modern trends in the electronics industry is the development of nanoscale semiconductor structures [11]. The implantation conditions and subsequent annealing determine the depth of the layer containing the gas-filled bubbles, amount, and size of the bubbles. A hidden "buried" layer is formed below the substrate surface with lower density compared to the matrix of the substrate. It gives an opportunity to fabricate nanocrystals from the matrix residues located between the bubbles [12]. Not only silicon but also other semiconductor substrates can be used as a matrix for the high-dose implantation.

Typical energies used for fabrication of silicon layers containing helium-filled bubbles are 10 keV and higher [3,13]. To produce shallow modified layers, though, a decrease of the bombarding particle energy down to 5 keV and below is necessary. However, at such a voltage standard beam implanters do not provide sufficient current density to obtain the required dose. High-dose doping of the substrates can be realized by the wide-aperture plasma immersion ion implantation (PIII) [14,15]. A distinctive feature of the PIII process is its productivity and simplicity. No ion mass selection or beam optics is needed, and the energy dispersion of ions is relatively high. The angular distribution of the implanted ions is controlled by the plasma pressure and the applied bias voltage pulse form and amplitude. The ion current can reach tens of mA/cm^2, and the process provides high implantation dose rate. As a consequence, for typical doses, the implantation time is reduced to several minutes and does not depend on the wafer size. A wide variety of applications of the layers with cavities (bubbles or voids) demands thorough studies of their fundamental properties. The knowledge of the evolution of the structural parameters of the layer at the early stage of bubble formation and during low-temperature annealing is especially important. At the same time, for all possible applications, the buried

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layer formed by dense bubbles should be well protected from the environment.

Thermal annealing is known to change the width of the helium depth distribution in the buried layer and the position of its maximum of the helium depth distribution in the buried layer due to the interaction between helium ions and vacancies [16,17]. However, the structural parameters of the subsurface layer (the phase of the material, the surface roughness, the thickness of the transition sublayers, the size, shape, and distribution of the cavities) have not been studied. In the case of nanoscale layers, the structural characteristics are of primary importance because of their influence on the electro-physical properties. The standard experimental techniques, applied for the studies of buried layers containing helium-filled bubbles and voids are transmission electron microscopy, Rutherford backscattering, thermal desorption spectrometry, and elastic recoil detection analysis. Among the X-ray techniques, only small-angle and grazing-incidence small-angle X-ray scattering were used [16,18–20]. At the same time, high-resolution X-ray reflectivity (HRXRR) gives a possibility to separate contributions from the specular and the off-specular (diffuse) scattering components and makes it possible to obtain valuable information on the structure of the subsurface layer [21]. The specular component possesses both high sensitivity to the changes in the electron density and high depth resolution. The diffuse one provides specific information on the features of the substrate surface, the size and the shape of cavities and particles. However, the main obstacle to the utilization of HRXRR is the difficulty in interpreting the diffuse scattering data due to the integral character of scattering from numerous different objects. This fact predetermines the complex use of complementary methods for diagnostics.

The aim of this work is an investigation of the microstructure of Si (0 0 1) subsurface layers after high-dose low-energy He^+ PIII treatment and annealing in the 850–1100 K range. The possibility of fabrication of a thin protective coating over the silicon layer with bubbles is also examined. The studies were performed using a combination of measurement techniques: cross-sectional transmission electron microscopy (X-TEM), energy filtered TEM (EF TEM) measurements, electron tomography (ET), Rutherford backscattering spectrometry (RBS), high-resolution X-ray reflectivity (HRXRR) and atomic force microscopy (AFM).

2. Experimental details

2.1. Materials and fabrication technique

The samples 20 × 20 mm^2 in size were cut from the conventional p-type (ρ = 12 Ω cm) commercial Cz-Si(1 0 0) wafer. Right before implantation, a layer of native oxide was removed after standard RCA-1 wet cleaning process including etching in a 5% solution of hydrofluoric acid at room temperature for 1 min. The implantation of He^+ ions was performed by plasma-immersion low-voltage ion implanter (developed in the Institute of Physics and Technology, Russian Academy of Sciences), equipped with an inductively coupled plasma (ICP) source. The helium plasma was excited at a frequency of 13.56 MHz at a discharge power of 500 W. The pressure in the working chamber was maintained at a level of 10 mTorr. Rectangular pulses (Fig. 1a) of a negative accelerating potential (duration 10 μs, repetition rate 1 kHz) were applied to the samples. Typical plasma parameters obtained by the Langmuir probe measurements are as following: the electron temperature T_e = 8.1 eV, the ion concentration $n_i^+ = 1.5 \times 10^{11}$ cm^{-3}. An application of the negative bias results in a current peak (Fig. 1b) with a duration of 0.3 μs due to the formation of the space charge layer. After the peak, the ion current to the substrate saturates to the value determined by the rate of injection of the ions into the space charge layer. The implantation dose (Fig. 1b) was determined by measuring the ion current through the sample during the bias pulse. The implantation of the He^+ ions was performed with high-dose ($D = 5 \times 10^{17}$ cm^{-2} for all samples, if not stated differently) at low energy (E = 2–5 keV). The

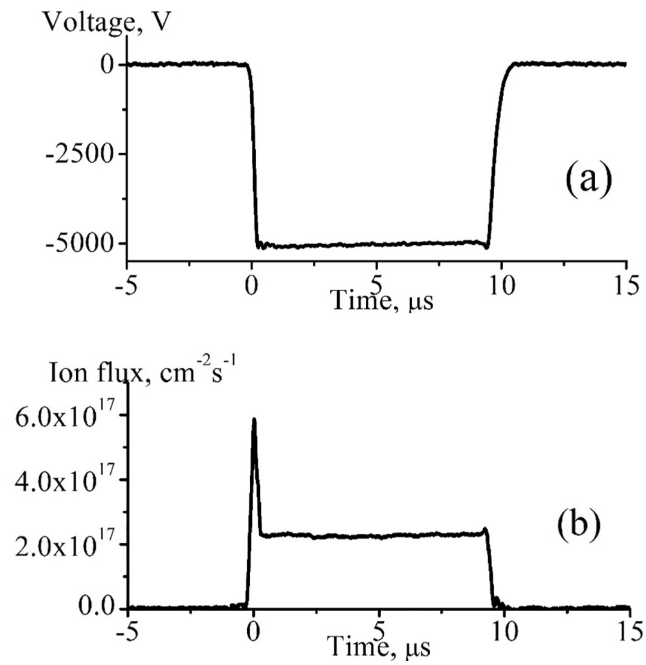

Fig. 1. Voltage (*a*) and flux (current) pulse (*b*) measured on the sample electrode. The average ion current density in the pulse is 13.8 mA/cm^2.

sample temperature during the PIII process did not exceed 323 K. The temperature was measured in situ by a thermal resistor on the sample of similar geometry in similar experimental conditions. Subsequent thermal annealing of the samples at 853 and 1073 K for 30 min was carried out in the vacuum of 8.8×10^{-6} mbar.

2.2. Measurement techniques

The cross-section samples for TEM were prepared by a focused ion beam (FIB) of Ga^+ in a scanning electron-ion microscope HeliosNanoLab™ 600i (FEI, USA). The specimens were studied in a Titan 80–300 TEM/STEM (FEI, USA) at an accelerating voltage of 300 kV. The microscope was equipped with a field emission cathode (Schottky), a SuperTwin objective lens and a high-resolution Gatan Imaging Filter (GIF), Tridiem energy-filter (Gatan, US). Digital Micrograph (Gatan, US) and TIA (FEI, US) software were used for the image processing.

The energy filtered TEM (EF TEM) measurements were performed in the low loss region of the electron energy loss spectrum with a 2 eV energy slit around the bulk Si plasmon loss peak (16.7 eV) and the SiO_2 plasmon loss peak (22.4 eV). High-resolution TEM (HR TEM) images were obtained at Scherzer defocus value.

The bright-field TEM tomography data sets were recorded at magnification 29,000 and a nominal underfocus of Δz = −0.5 μm. Tilt series were recorded between −60° and +60° with a tilt angle increment of 2°. The image alignment and tomogram reconstructions were performed by Inspect3D (FEI, Eindhoven) software. The volume was rendered and visualized using the UCSF Chimera software.

The RBS spectra of 1.7-MeV He^+ ions were obtained on an HVEE AN-2500 accelerator (Moscow State University). The backscattering angle of helium ions was 120°. Measurements were performed with ion beams with random orientation and aligned along the [0 0 1] crystallographic direction. The thicknesses of the disordered layer were determined using the single-collision energy-loss model [22].

The high-resolution X-ray reflectivity measurements were performed on a multipurpose SmartLab (Rigaku Corp.) diffractometer equipped with 9 kW copper rotating anode. The X-ray specular reflectivity curves were recorded in the ω/(2θ) scanning mode. The off-