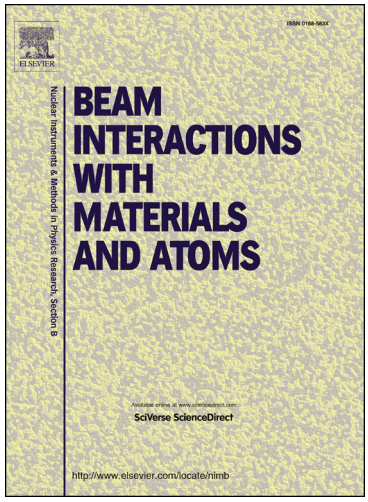

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Contribution to Nuclear Instrument and Methods B

Analysis of depth redistribution of implanted Fe near SiO_2/Si interface

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Abstract

We have studied diffusion and clustering processes of room-temperature (RT)-implanted Fe ions in a SiO_2/Si structure during annealing at 600 and 800 ˚C temperatures. The depth profile of implanted Fe was analyzed by Rutherford backscattering spectroscopy (RBS). In the previous study, we found that the hot-implanted Fe ions near the SiO_2/Si interface at high substrate temperatures of 600 and 800 ˚C were distributed significantly different from the result predicted in the TRIM simulation. We think that the diffusion phenomena during the ion implantation at such elevated temperatures are recognized to be strongly enhanced by ion-beam-irradiation effect. In this study, to simplify the diffusion phenomenon, we particularly treat thermal diffusion process of RT-Fe implantation around the SiO_2/Si interface in the post annealing at high temperatures. It is clearly seen that Fe atoms post-annealed at 800 ˚C are preferably gathered at a definitive depth in the SiO_2 layer around 15 nm distance from the interface. We finally compare the Fe depth distribution for hot-implanted samples to that for the post-annealed ones by RBS analysis quantitatively.

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1. Introduction

We have developed a noble synthesis method of single-walled carbon nanotubes (SWCNTs) from metal clusters formed in SiO_2/Si substrates by hot-ion implantation technique so far [1,2]. Now, one is concerned with how to control the diameter and chirality of CNTs, since they define the electronic properties of band gap and electric conductivity [3]. In general, the diameter of CNTs is definitively responsible for that of metal clusters which behave as a catalytic seed of CNT synthesis. In order to fabricate CNTs with desired diameters, therefore, it is required to form uniform metal nanoparticles on/in the substrate. It is commonly known that most of metal ions implanted in oxides, such as SiO_2, MgO, and Al_2O_3, form clusters with a uniform size with several nm in diameter [4-6].

We have so far shown that the hot-implanted Fe ions in a SiO_2 layer had a significantly uniform size, and succeeded in synthesizing SWCNTs from the catalytic clusters using microwave-plasma-enhanced chemical vapor deposition (MPCVD), though we could not control the chirality of the SWCNTs. One believes that SWCNTs growth with a single chirality is generally responsible for the crystal orientation of the catalytic clusters. We then tried to form highly-oriented Fe clusters by Fe^+ hot-implantation just around the SiO_2/Si interface, because we expect both effects of clustering in the SiO_2 layer and epitaxial growth of Fe clusters on the single crystalline Si(001) substrate reflecting the orientation of the substrate.

We have recently studied growth of Fe clusters formed around a SiO_2/Si interface by hot-ion implantation at substrate temperatures of 300, 600, and 800 ˚C [2]. We characterized the implanted Fe using Rutherford backscattering spectroscopy (RBS) and transmission electron microscope (TEM). It was found in a TEM image for the 300 ˚C-implanted sample that tiny clusters with a mean diameter of 2.4 nm were formed in the SiO_2 layer. Besides, some of the clusters were found to be aligned near the SiO_2/Si interface. The depth profile of Fe obtained from the RBS analysis was not significantly different from the prediction from a Monte Carlo simulation by TRIM code. On the other hand, we observe nanoclusters with a mean diameter of 3.2 nm in the SiO_2 layer at a certain depth of ~ 10 nm apart from the interface for the 600 ˚C-implanted sample. We found significantly larger crystalline precipitations with size of 5 – 10 nm in diameter at the interface, which were assigned to be -$FeSi_2$ nanoparticles by TEM analysis. Most of the implanted Fe atoms in the SiO_2 layer were segregated either on the SiO_2 surface or the SiO_2/Si interface when the implantation was performed at the substrate temperature of 800 ˚C.

It should be noted that the diffusion process during ion implantation at elevated temperatures is recognized to be significantly enhanced by ion-beam-irradiation effect. In the present study, we thus simply focus on the thermal diffusion process of RT-implanted Fe around the SiO_2/Si interface during post implantation annealing.

2. Experiment

A SiO_2 layer was formed by dry thermal oxidation of Si(001) substrates at 900 ˚C for 2 h. The oxide thickness of the grown SiO_2 film was estimated to be about 40 - 45 nm by ellipsometry. We then optimized the incident energy of Fe ions by TRIM code in the SRIM2010 package [7], in order to implant the Fe ions as distributing around the SiO_2/Si interface. In this simulation, we assumed 2.21 g/cm^3 as the volume density of the SiO_2 layer [8]. As a result of the simulation, the optimized implantation energy was estimated to be 43 keV.

The ion implantation was performed using a medium-current ion implanter at Shonan-Hiratsuka Campus at Kanagawa University (SHC-KU). The implanter allows us to implant at wide substrate temperatures range from liquid nitrogen temperature to 1000 ˚C in a whole wafer with a 6-in. diameter uniformly by scanning accelerated ion beam with ~20×20 mm^2 size. The Fe ions are generated by sputtering a pure Fe repeller plate by Ar plasma ignited in an arc chamber. The maximum terminal voltage of the accelerator is 200 kV and the current density for the Fe ion with the energy of 43 keV typically is several hundred nA/cm^2. In the present study, the direct beam with 20×20 mm^2 size was irradiated on the sample of 8×8 mm^2 without beam scanning in order to reduce the time in the implantation. The Fe was implanted at room temperature (RT) in order to reduce the excess thermal diffusion enhanced by ion irradiation effect during the implantation. The Fe-implanted samples were annealed at 600 and 800 ˚C for 10, 30, and 60 min by an infrared radiation heater in vacuum of 10^{-5} Pa.

The depth profile of implanted Fe was analyzed by RBS using a pelletron accelerator placed at SHC-KU. In the present study, 1.8 MeV He^{++} ions were incident on the samples at a slightly tilted angle with respect to surface normal. The scattered primary ions with a grazing angle of 10˚ from the surface plain were detected by a Si surface barrier solid state detector. In order to obtain accurate random spectra, the sample was rotated around the surface normal during the measurements.

The observed spectra were analyzed by RBS simulation code by means of best-fitting the simulated spectrum to experimentally observed one by adjusting the fitting parameters defining the sample structures of elemental composition and layer thickness. The details of the simulation method can be found in some earlier papers [9-11].

3. Results and discussion

Fig. 1 shows a schematic image of the implantation along with the ion distribution simulated by the TRIM code assumed the parameters of the incident energy of 43 keV and the SiO_2 thickness of 40 - 45 nm, which corresponds to the actual thickness measured by ellipsometer in advance. Here, the atomic fraction of Fe at the interface is about 5 % for ion dose of 1×10^{16} ions/cm^2.

Fig. 2 shows a RBS spectrum observed for an as-implanted sample at RT with ion dose of 1×10^{16} ions/cm^2. Circles and a solid curve indicate experimentally observed spectrum and the best-fitted one, respectively. A dotted curve corresponds to the spectrum assumed the depth profile obtained from the TRIM simulation. The arrow indicates the SiO_2/Si surface and interface positions, which are evaluated from the kinematic factor and the energy-width corresponding to the SiO_2 thickness derived from the stopping power of SiO_2 in the RBS spectrum, respectively. It is clearly seen that the depth distribution of the as-implanted Fe at RT is roughly similar to the depth profile shown in the TRIM calculation, though some broadening is observed in the actual profile. This indicates the fact that the excess diffusion during the implantation at RT is not negligibly small.

Fig. 3 shows a RBS spectrum observed for the samples post-annealed at 600 ˚C for 60 min. The arrows indicate the positions of the surface and interface. It is found that the scattering yield near the interface at the SiO_2 film side is slightly decreased. However, the depth profile of Fe is not changed for annealing for 10 – 60 min.

Fig. 4 shows a RBS spectrum observed for the sample post-annealed at 800 ˚C for 60 min. The depth profile of the implanted Fe is not also changed for 10 – 60 min annealing. It is seen that two peaks are clearly separated in the spectrum. The interface position deduced from energy loss in the SiO_2 layer is found to be the valley between two peaks; therefore, these peaks observed at higher and lower energies correspond to the Fe atoms in the SiO_2 layer and in the Si substrate, respectively. It is found that the areal density of Fe near the interface is significantly low.

We then compare the above results to the previous study on the Fe distribution for the Fe-clusters-formed samples around the SiO_2/Si interface by hot-ion implantation at high substrate temperatures of 300, 600, and 800 ˚C [2]. In that study, we found Fe nanoclusters with a mean diameter of 3.2 nm in the SiO_2 layer at a certain depth of ~ 10 nm apart from the SiO_2/Si interface for the 600 ˚C-implanted sample. On the other hand, almost all implanted Fe atoms in the SiO_2 layer were segregated either on the SiO_2 surface of the SiO_2/Si interface for the 800 ˚C-annealed sample. We could not observe

such surface segregation in the sample Fe-implanted at RT followed by annealing at 800 ˚C as shown in Fig. 4. It should be noted here that the diffusion during the ion implantation at elevated temperatures is recognized to be significantly enhanced by ion-beam-irradiation or local heating in the beam spot. Such external factors are responsible for the enhanced diffusion appearing in the hot-implanted samples. We have clearly observed the ion-beam enhanced diffusion even at relatively low energy region of about 700 eV/u in an amorphous SiO_2 layer. Numerically studied diffusion process of Fe in a SiO_2 layer by solving a Langevin equation will be shown in the near future.

4. Conclusions

We have studied diffusion and clustering processes of RT-implanted Fe ions around the SiO_2/Si interface during post annealing at elevated substrate temperatures. The Fe depth profile after post-annealing at 600 and 800 ˚C for 10 - 60 min was quantitatively analyzed by RBS method. As a result, the depth profile of the sample post-annealed at 600 ˚C does not show drastic changes from that of the as-implanted one. On the other hand, Fe atoms post-annealed at the 800 °C are preferably gathered at a definitive depth around 10 – 20 nm in the SiO_2 layer from the interface. The depth profiles of Fe are not changed by sequential annealing for below 60 min. Compared with the previous results which were obtained from the RBS analysis of the samples formed by hot-ion implantation at 600 and 800 ˚C, the diffusion length in the post-annealed samples seems to be smaller. It is clearly indicated that diffusion of Fe in SiO_2 layer is significantly enhanced by ion-beam-irradiation even in the amorphous SiO_2 structure and at low ion energy of several tens of keV.

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Figure captions

Fig. 1 :
A schematic image of the implantation along with the ion distribution simulated by the TRIM code assumed the parameters of the incident energy of 43 keV and the SiO_2 thickness of 40 - 45 nm,

Fig. 2 :
Whole RBS spectrum (a) and magnified spectrum (b) observed for the as-implanted sample at RT with ion dose of 1×10^{16} ions/cm^2. Circles and a solid curve indicate experimentally observed spectrum and the best-fitted one, respectively. A dotted curve corresponds to the spectrum assumed the depth profile obtained from the TRIM simulation.

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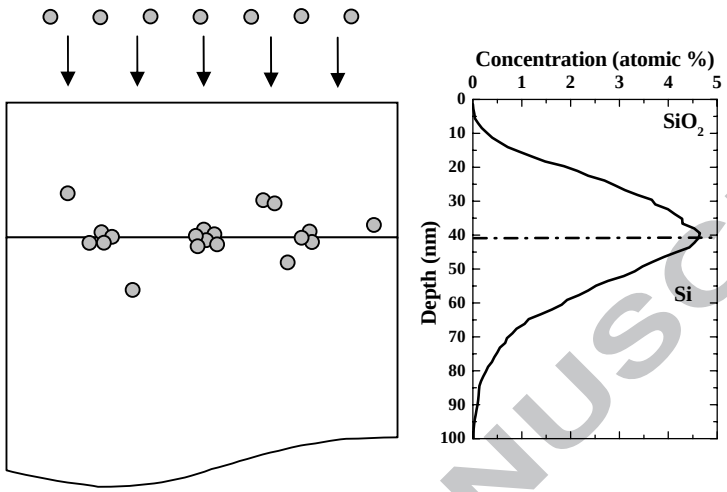

Fig. 1

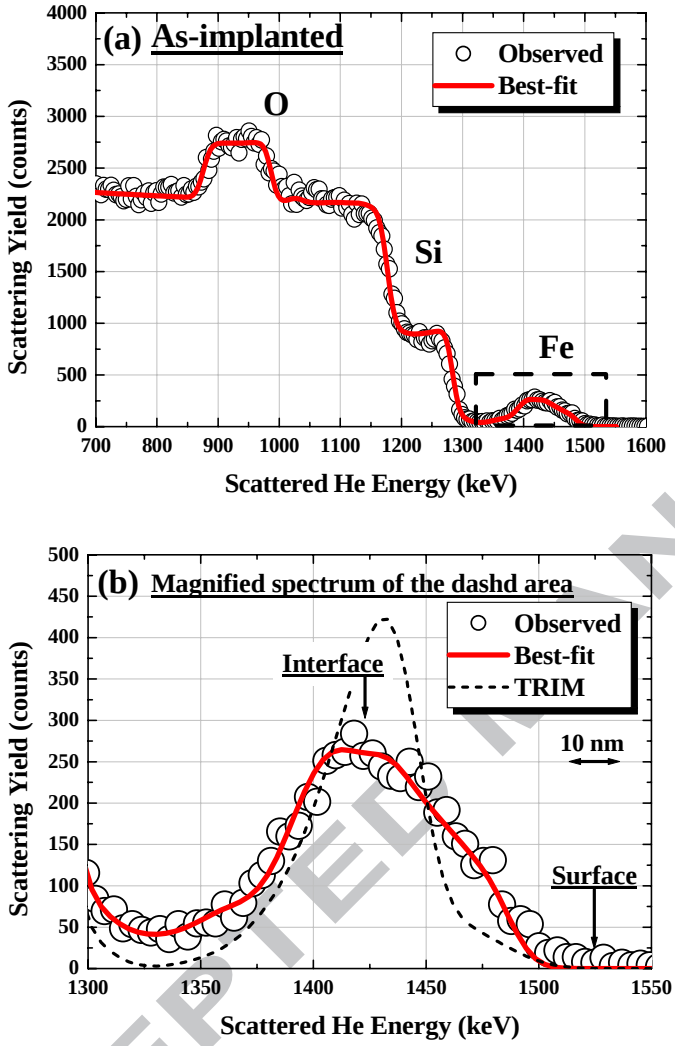

Fig. 2

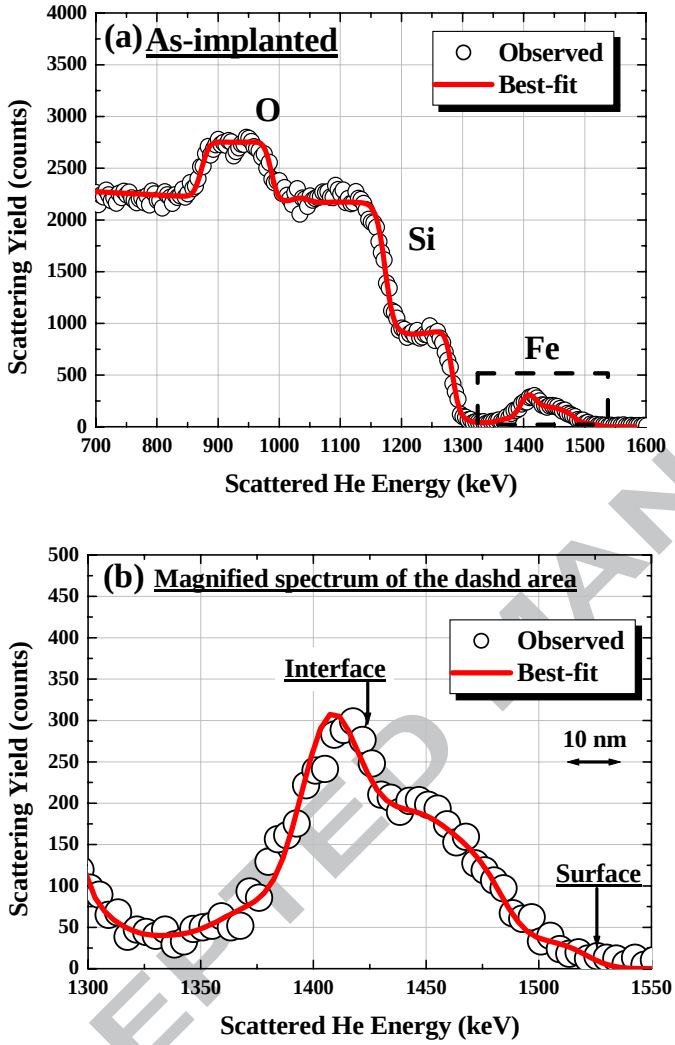

Fig. 3

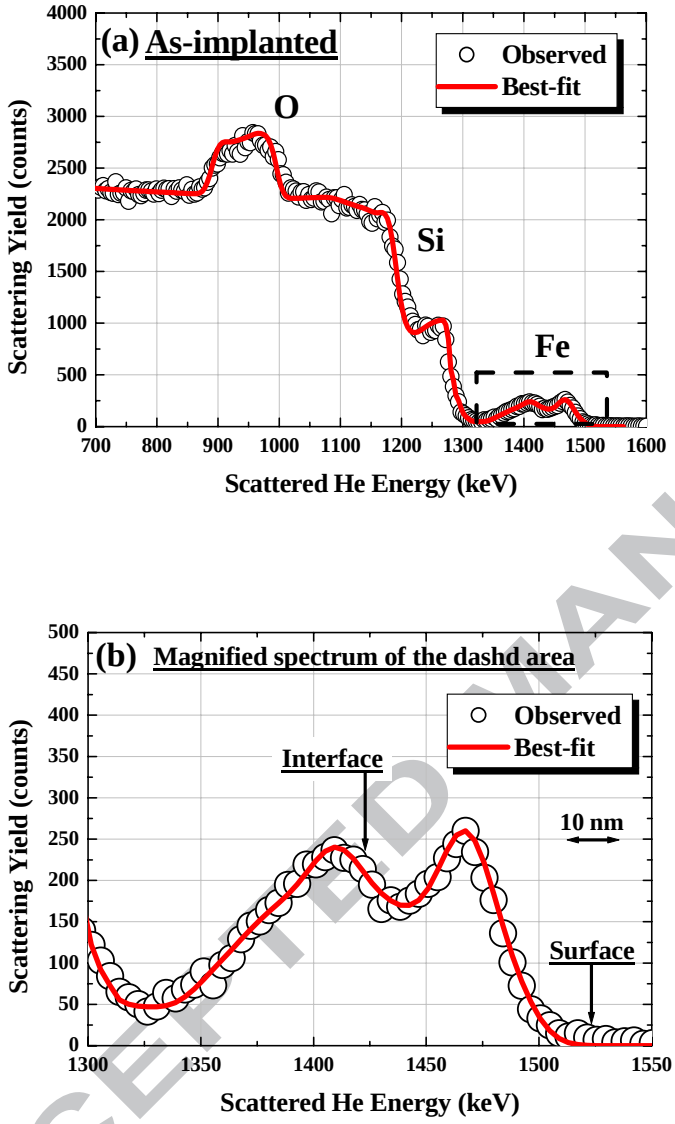

Fig. 4