Germanium nanoparticles formed in silicon dioxide layer by multi-energy implantation and oxidation state of Ge atoms

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Abstract. Ge nanoparticles (NPs) embedded silicon oxide is expected to be promising light emission source, especially, UV – blue light region. We have tried to form Ge NPs in a 100-nm-thick SiO$_2$ layer on Si substrate by multi-energy implantation of Ge negative ions with energies of 50, 20 and 10 keV and doses of $1.4 \times 10^{16}$, $3.2 \times 10^{15}$ and $2.2 \times 10^{15}$ ions/cm$^2$, respectively. Samples were annealed for 1 h at a temperature less than 900°C. By this implantation, formations of Ge nanoparticles in a surface 50-nm depth region were expected. The depth distribution of implanted Ge atoms in the oxide was measured by XPS (Ge 2p, O 1s, Si 2p) with monochromatic Al K$_{\alpha}$ and Ar etching at 4 keV. The depth profiles were well agreed with the cross-sectional TEM image. But some extent of Ge atoms diffused to the SiO$_2$/Si interface at 900°C. The chemical shifted spectra of Ge 2p$_{3/2}$ showed about 60% of the oxidation of Ge atom around the end of the range (EOR) even in the as-implanted sample. This oxidation was considered to be due to the excess oxygen atoms near EOR by forward of sputtered oxygen atoms from SiO$_2$ layer. Raman spectra supported this oxidation. In a preliminary investigation of cathode luminescence, the Ge-implanted sample with annealing at 600°C showed CL peak at 3.12 eV (397 nm in wavelength) in UV-blue region at room temperature. This means the Ge-implanted sample has a possibility for light emission in the UV-blue region.

1. Introduction

Ge nanoparticles (NPs) embedded silicon oxide is expected to be promising light emission source, especially, UV – blue light region. Although 500-nm-thick SiO$_2$ film including Ge NPs was reported to show blue and violet electroluminescence by applying a voltage of 350 V [1], the decrease of the operation voltage is demanded for application to light emission source for communication in a LSI chip and other versatile applications [2]. Ge nanoparticles should be formed in a considerably thin SiO$_2$ layer to fulfill this requirement. Therefore, we have tried to make Ge nanoparticles in a shallow depth region of a thin SiO$_2$ layer on Si substrate by using a negative-ion implantation method with multi-energy. Since, the negative-ion implantation has an advantage of almost “charge-up free” feature for insulators and isolated electrode [3-5], the penetration depth of ions can be precisely controlled with a relatively low energy implantation even into an insulator such as silicon dioxide.

2. Experimental

Germanium negative-ion implantation was performed by a negative-ion implanter (Nissin Electric Corp., Japan) [6] equipped with an RF (radio frequency) plasma-sputtering type heavy negative ion source [7, 8]. Ge- ions extracted from the source at 10 keV were mass separated by a sector magnet and then accelerated up to desired implantation energy. After eliminating fast neutrals from the beam by bending beam line with deflection electrodes, the $^{72}$Ge negative-ion beam was introduced into a collector cup with a limiting aperture of diameter 8 mm in an implantation chamber of the negative-ion implanter. In the collector cup, Ge negative ions were implanted at room temperature into a
thermally grown silicon dioxide layer with a thickness of 100 nm on silicon substrate (15 mm x 15 mm). In the multi-energy implantation, Ge ions were implanted three times into the same SiO\textsubscript{2} layer by changing the energy of 50, 20 and 10 keV in this order. The dose amounts of these energies are 1.4 x 10\textsuperscript{16}, 3.2 x 10\textsuperscript{15}, and 3.2 x 10\textsuperscript{15} ions/cm\textsuperscript{2}, respectively. The current density was about 1 \( \mu \text{A/cm}^2 \), and the gas pressure during the implantation was kept less than 1 x 10\textsuperscript{-4} Pa (background pressure was 3 x 10\textsuperscript{-5} Pa). We expected to obtain Ge implanted layer with a thickness of about 50 nm by this multi-energy implantation. After implantation, the samples were annealed by an electrical oven at various temperatures of 600, 700, 800 and 900°C for 1 h in a quartz tube under vacuum condition by a rotary pump (400 l/min).

The depth distribution of implanted Ge atoms and the fractions of metallic and oxidized Ge atoms were measured by X-ray photoelectron spectroscopy (XPS, AXIS-165S, Shimadzu/Kratos, Japan) with Ar ion etching. We measured the survey spectra in a binding energy range up to 1300 eV and the narrow spectra in a range of 1205 – 1235 eV by irradiation of a monochromatic Al K\( \alpha \) ray (1486.6 eV) after every Ar ion etching at 4 keV for 300 s. The etching speed was about 0.017 nm/s (5.1 nm for 300 s). We obtained Ge atomic fractions in SiO\textsubscript{2} from the comparison of peak areas of Ge 2p, O 1s and Si 2p in the survey from detected photoelectrons with correction by sensitivity of the apparatus for these photoelectrons. For the fractions of metallic and oxidized Ge atoms, there are generally two chemical shifts of about 2.7 and 3.6 eV in Ge 2p\textsubscript{3/2} (1217.4 eV) due to oxidation for GeO and GeO\textsubscript{2}, respectively. In the experiment, we detected only the chemical shift due to GeO, and divided the detected Ge 2p\textsubscript{3/2} spectra into two Gaussian distributions of metallic (Ge-Ge) and mono-oxide (Ge-O) by the curve fitting. Then, the ratio of metallic Ge atoms was calculated.

Ge nanoparticles in the samples were observed by a cross-sectional transmission electron microscope (XTEM). The specimen was fabricated by a focus ion beam (FIB) of Ga\textsuperscript{+} with 30 keV (FB-2000A, Hitachi) and observed its cross-sectional image by TEM apparatus with 200 keV (JEM2100F, JEOL).

Raman spectra of the annealed samples with an average Ge fraction of 12 at.\% were measured for confirming the formation of Ge-Ge bonds in the sample. Ar ion laser at wavelength of 458 nm was used for a prove source, and the Raman shift from 152 to 503 cm\textsuperscript{-1} was measured at room temperature. Ge-Ge bond shows Raman shift in a range of 250 – 300 cm\textsuperscript{-1}, depending on this particle size [9]. Since penetration length of the source laser light is about 250 nm, a small satellite signal due to Si-Si bond also appeared in a range of 220 – 304 cm\textsuperscript{-1} for the 100-nm-SiO\textsubscript{2} layer on Si substrate. Therefore, we subtracted the disturbing signal due to Si-Si bonds from the detected spectra as to eliminate the step increase in the spectra near 220 cm\textsuperscript{-1}.

A preliminary measurement of cathode luminescence for the multi-energy Ge implanted sample with 6 at.\% after annealing at 600°C was also executed with an electron beam at 4 keV with 1\mu A. The electron beam was irradiated in a size of 1 mm in diameter for 40 s per one measurement. The spectrum analysis was in a range of 1 – 6 eV in photon energy (210 – 1240 nm in wavelength) at various temperatures of 14, 100, 200 and 295 K.

3. Results and Discussion

3.1. Calculated depth distribution of multi-energy implanted Ge atoms in SiO\textsubscript{2}.

The calculated depth profile of Ge atoms in the multi-energy implantation (50 keV, 1.4 x 10\textsuperscript{16} ions/cm\textsuperscript{2}: 20 keV, 3.2 x 10\textsuperscript{15} ions/cm\textsuperscript{2}; and 10 keV, 2.2 x 10\textsuperscript{15} ions/cm\textsuperscript{2}) is shown in Fig. 1(a). The calculation was executed by using a PC version program of DYNAMIC MONTE-CARLO PROGRAM TRIM-DYN (dynamic ion transport in matter incl. recoil cascades, (c)Biersack, Berlin 1983 & 89) [10] with including dose effect. From the total concentration curve, the formation of Ge implanted layer with a concentration of about 6 at.\% from 10 nm to 50 nm in depth is expected as shown in the figure. The oxygen atom in the SiO\textsubscript{2} layer is much lighter than Ge atom, so that the oxygen atom is likely scattered by the collision of Ge and by recoil of Si. Then, deficit of oxygen atoms from the stoichiometric value of SiO\textsubscript{2} is expected to result after implantation into the SiO\textsubscript{2} layer.
This deficit was also calculated at the same time and shown in Fig. 1(b). O atoms in the shallow region are scattered out from the layer to the vacuum and to the deeper direction. Then some excess of O atoms in the deeper region of 40 – 100 nm was expected.

Figure 1 Calculated depth profile of Ge atoms by multi-energy implantation (a) and oxygen deficit in the SiO₂ layer (b).

3.2. Depth distribution by XPS measurement

The Ge atoms of the multi-energy implanted samples after annealing at various temperatures were analyzed by XPS with Ar etching with every 300 s for detecting Ge depth profile. Fig. 2 shows XPS survey spectra of a sample after annealing at 900°C as a parameter of Ar etching time by every 1500 s. In the spectra, the relatively strong Ge 2p (1210-1250 eV), week Ge 3p (129-122 eV), small 3d (29.4 eV), strong O 1s (around 530 eV), and fairly strong Si 2s and 2p peaks appeared before etching of 4530 s. After etching for 6030 s, only Si was detected except Ar peak. The small Ge 3p peak appeared between Si 1s and Si 2p. Therefore, it is better to use Ge 2p peak rather than Ge 3p and 3d peak for obtaining Ge concentration. Based on areas of Ge 2p, O 1s and Si 2p peaks in the survey spectra, depth profiles of Ge atoms in SiO₂ for samples before annealing and after annealing at 600°C and 900°C layer were obtained as shown in Fig. 3. The maximum fraction of Ge atoms in SiO₂ layer was about 4.2 at.% for the as-implanted sample. From the RBS measurement, the area density of Ge atoms was agreed with the initial total dose amount of 1.94 x 10¹⁶ ions/cm². Besides, it was found in the comparison between Ge 2p and Ge 3d by using a reference sample of GeO₂ plate that the photoelectron yield of XPS Ge 2p was affected to decrease to about 0.68 due to presence of oxygen atoms. Therefore, the deficit in Ge fraction between XPS measurement and the calculation is expected due to matrix effect, and the maximum Ge fraction in SiO₂ is considered to be about 6 at.% for the as-implanted sample. After annealing at 600°C, the Ge fraction slightly decreased due to diffusion. At 900°C-annealing, Ge atoms diffused more and reached the interface of SiO₂/Si. The Ge atoms accumulated there and a peak of Ge fraction was seen in Fig. 3.

Fig. 2. XPS survey spectra of the multi-energy implanted Ge sample after annealing at 900°C and Ar etching.
3.3. Oxidation of implanted Ge atoms

The oxidation state of Ge atoms can be evaluated by observation of chemical shift. We measured the narrow spectra for Ge 2p3/2 peak after Ar etching for various time. Fig. 4 shows the narrow spectra of Ge 2p 3/2, where the depth value was calculated from the etching time. Two peaks in the Ge 2p3/2 photoelectrons were observed in the etched sample. The peaks at 1217.5 eV and 1220 eV were corresponded to Ge 2p3/2 peaks from metallic Ge-Ge and Ge oxide of Ge-O, respectively.

By fitting with two Gaussian-type distributions of Ge 2p3/2 peaks, we can calculate the ratio of metallic Ge. Fig. 5 shows the percentage of metallic Ge as a function of depth. After annealing at 900°C, Ge atoms in the surface region was oxidized. This was considered to be due to the penetration of oxygen from the residual gas to the sample surface during the annealing. On the contrary, the both of the as-implanted and 600°C-annealing samples showed oxidation of Ge atoms in the deep-depth region more than those in the surface region. In these samples, this oxidation at deep depth is not expected by the oxygen invasion from the residual gas. It was considered to be due to the excess of oxygen atoms resulted by implantation as shown in Fig. 1(b).

3.4. TEM observation of Ge nanoparticles

The cross-sectional TEM image of the sample after annealing at 600°C for 1 h was studied as shown in Fig. 6, where (b) is enlarged one corresponding to the rectangular area in Fig. 6 (a). The image is a little opaque, but the Ge nanoparticles were observed in the region from the surface to 70 nm in depth. The Ge NPs dense but small in size less than 4 nm.

3.5. Raman spectroscopy for Ge-Ge bonding

The XPS analysis in subsection of 3.3 showed the oxidation of implanted Ge atoms at a deep depth. Raman spectra were investigated to confirm that the Ge NPs have Ge-Ge bonds in 12 at.%-Ge samples. Fig. 7 shows Raman spectra obtained for the Ge-implanted samples after annealing at various temperatures. Si-Si bonding resulted in the satellite peak near Raman shift of 304.1 cm⁻¹. The each curve of Raman spectra were already eliminated the Si-Si effect. After annealing at the temperature more than 600°C, each Raman spectra showed a peak around 270 - 300 cm⁻¹. These peaks corresponded to the Ge-Ge bonding, depending on the size of Ge NPs [9].
The sample after annealing at 800°C for 1h showed strong peak at 300 cm⁻¹. The largest Ge NPs are expected to form in the layer. However, there is no peak in the sample after annealing at 900°C. This was well corresponded to the XPS result of Ge oxidation as shown in Fig. 5.

3.6. Cathode luminescence
Cathode luminescence of the Ge-implanted sample has been preliminary investigated for the possibility of light emission. Fig. 8 shows cathode luminescence spectra obtained at room temperature from the multi-energy Ge-implanted sample at 6 at.% after annealing at 600°C for 1 h and from the unimplanted SiO₂/Si sample. The unimplanted sample showed well known two luminescence peaks at around 1.9 eV and 2.7 eV. These luminescence peaks are due to oxygen defect center (ODC), and they each are attributed to the non-bridged oxygen hole center (NBOHC, 1.8 – 1.9 eV) and two fold-coordinated Si atoms, respectively. [11, 12]. On the contrary, the Ge-implanted sample showed CL peak at 3.12 eV (397 nm in wavelength) in UV-blue region at room temperature. This CL peak is well agreed with the CL spectra reported by Rebohle et al. [1, 13] and H.-J. Fitting et al. [11]. Therefore, the peak at 397 nm is also considered to be due to ODC and attributed to two fold-coordinate Ge atoms. This result showed the Ge-implanted sample has a possibility for light emission in the UV-blue region.

4. Conclusion
We have investigated the multi-energy implantation of Ge negative ions into 100-nm-SiO₂ layer on Si with respects of depth profile and oxidation fraction of implanted Ge atoms, Raman spectra and cathode luminescence. The relatively shallow Ge-implanted layer with a thickness of 40 nm with an average concentration of 4 at.% was obtained by three multi-energy implantation of 50 keV (1.4 x 10¹⁶ ions/cm²), 20
keV (3.2\times 10^{15} \text{ ions/cm}^2) and 10 \text{ keV (2.2 \times 10^{15} \text{ ions/cm}^2)}. The strongest Ge-Ge bonding was found after annealing at 800^\circ\text{C for 1 h}. This is considered to be the best condition for forming Ge nanoparticles. In the cathode luminescence study with 4 \text{ keV electron beam for the Ge-implanted sample after annealing at 600^\circ\text{C for 1h}}, CL peak was obtained at 3.12 \text{ eV (394 nm in wavelength)}. This showed the multi-energy Ge-implanted sample has a possibility of light emission in UV-blue region.

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6. References

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