

Cathode Luminescence from SiO₂ Layer Including Ge Nanoparticles Formed by Negative-Ion Implantation

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We implanted germanium negative ions into a 100-nm-thick SiO₂ layer on Silicon substrate and have investigated about oxidation of implanted Ge atoms and cathode luminescence for the possibility of blue light emission. The ions were implanted into the same SiO₂ layer with three times at different energies of 50, 20, and 10 keV (multi-energy implantation). The dose amounts were 1.4×10^{16} , 3.2×10^{15} and 2.2×10^{15} ions/cm², respectively. Samples were annealed for 1 h at a temperature less than 900°C. The depth distribution and oxidation of implanted Ge atoms in the oxide were measured by XPS analysis with Ar etching. The depth profiles were well agreed with the cross-sectional TEM image. But some extent of Ge atoms diffused to the SiO₂/Si interface at 900 °C. The chemical sifted 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 SiO₂ layer. In cathode luminescence measurement, the Ge-implanted sample after annealing at 800°C showed strongest 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.

Key words: Ion implantation, Negative ions, Nanoparticle, Germanium, Cathode luminescence,

1. INTRODUCTION

Silicon oxide including Ge nanoparticles has gathered much attention for light emission source in UV-blue region, since Rebohle, L. et al [1] showed blue and violet electroluminescence (EL) from 500-nm-thick SiO₂ film including Ge NPs by applying a voltage of 350 V. The decrease of the operation voltage is still required for its application to light source in data communication in a LSI chip and other versatile applications [2]. The simply way to achieve low operation voltage is to form Ge NPs in a considerably thin SiO₂ layer. We tried to make Ge NPs in 100-nm-thick SiO₂ layer by multi-energy negative ion implantation, which has a “charge up free” property [3-5] for isolated electrodes and insulators without any compensator.

2. GERMANIUM NEGATIVE-ION IMPLANTATION

Germanium negative ions were produced by RF (radio frequency) plasma-sputtering type heavy negative ion source [6, 7], and after mass-separation the ⁷⁴Ge negative ions were implanted into a thermally grown silicon dioxide layer with a thickness of 100 nm on silicon substrate by using a negative-ion implanter (Nissin Electric Corp., Japan) [8]. In the multi-energy implantation, the ions were implanted three times into the same SiO₂ layer at different energies of 50, 20 and 10 keV in this order under a residual gas pressure less than 1×10^{-4} Pa. The dose amounts of these energies are 1.4×10^{16} , 3.2×10^{15} , and 3.2×10^{15} ions/cm², respectively, with a current density of about 1 μA/cm². 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 in a N₂ gas flow (50 l/min) under low vacuum condition.

3. SAMPLE EVALUATION

Photoelectron spectroscopy with Ar ion etching (XPS, AXIS-165S, Shimadzu/Kratos, Japan) was used for measurements of Ge depth distribution in the SiO₂. The X-ray source was a monochromatic Al Kα ray (1486.6 eV). The etching speed at 4 keV was about 0.017 nm/s (5.1 nm for 300 s). The compositions of Ge implanted samples were obtained from spectra of Ge 2p, O 1s, and Si 2p. We corrected Ge 2p intensity by a factor of 1.47 since Ge 2p electrons were absorbed by oxygen atoms. The correction factor was measured by using a pure (99.999%) GeO₂. As for oxidation state of Ge atoms in the Ge-implanted samples, it was obtained from chemical shifts of 2.7 and 3.6 eV from Ge 2p_{3/2} (1217.4 eV) for GeO and GeO₂ bonds, respectively. Since only chemical shift of GeO was detected in the measurement, we used two peaks of Ge and GeO for curve fitting to obtain metallic and oxidized Ge fraction.

Nanoparticles was observed by a cross-sectional transmission electron microscope (XTEM) with 200 keV (JEM2100F, JEOL) after fabricating by a focus ion beam (FIB) of Ga⁺ with 30 keV (FB-2000A, Hitachi).

Cathode luminescence (CL) of the multi-energy Ge implanted sample with 6 at.% after annealing at 600°C was measured by using an electron beam at 4 keV with 1 μA for 40 s per one measurement. The size of electron beam was 1 mm in diameter. The spectrum analysis was in a range of 1 – 6 eV in photon energy (1240 – 207 nm

in wavelength) at various temperatures of 14, 100, 200 and 295 K.

4. RESULTS AND DISCUSSION

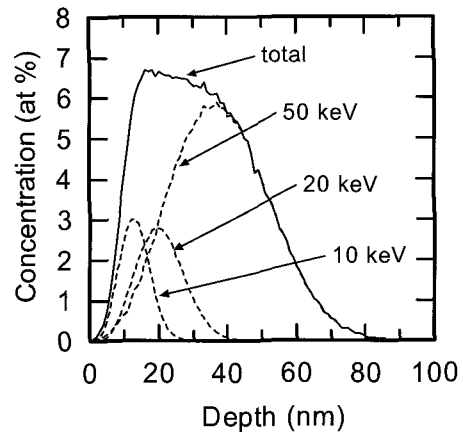
4.1 Depth Distribution of Implanted Ge Atoms

Fig. 1 shows calculated depth profile of Ge atoms in the multi-energy implantation (50 keV, 1.4×10^{16} ions/cm²; 20 keV, 3.2×10^{15} ions/cm²; and 10 keV, 2.2×10^{15} ions/cm²) by using TRIM-DYN program [9] with including dose effect. In the multi-energy implantation, Ge implanted layer with a concentration of about 6 at.% forms in a depth region from 10 to 50 nm. The oxygen atom in the SiO₂ layer is expected to be likely scattered by the collision of Ge and recoils due to its light weight comparing to Ge and Si. We calculated a shortage or excess of O atoms from the stoichiometric value of the multi-energy Ge-implanted SiO₂. The O balance distribution in depth direction is also shown in Fig. 1. We expected O shortage in the surface region and O excess in the deep region around the end of range (EOR) of 40–100 nm.

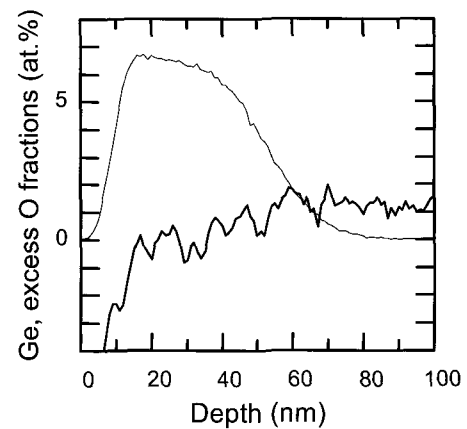
As for real distribution of Ge, we measured XPS spectra every after 300 s Ar etching for multi-energy implanted samples after annealing at various temperatures. The Ge distribution calculated from three peak areas of Ge 2p, O 1s and Si 2p peaks is shown in Fig. 2. The maximum fraction of Ge atoms in 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 1.94×10^{16} ions/cm². Besides, it was found in the comparison between Ge 2p and Ge 3d by using a reference sample of GeO₂ pellet that the photoelectron yield of XPS Ge 2p was affected to decrease to about 0.68 due to presence of Oxygen atoms. Therefore, we corrected Ge 2p intensity by multiplying a factor of 1.47. The corrected Ge concentration is shown in Fig. 3. The maximum Ge fraction in SiO₂ of about 6 at.% for the as-implanted sample well agreed to the calculated value. 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 Figs. 2 and 3.

4.2 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 2p_{3/2} 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 2p_{3/2} photoelectrons were observed in the etched sample. The peaks at 1217.5 eV and 1220 eV were corresponded to Ge 2p_{3/2} peaks from metallic Ge-Ge and Ge oxide of Ge-O, respectively. By fitting with two Gaussian-type distributions of Ge 2p_{3/2} 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-



(a) Calculated Ge depth profiles



(b) Excess and shortage of O atoms

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

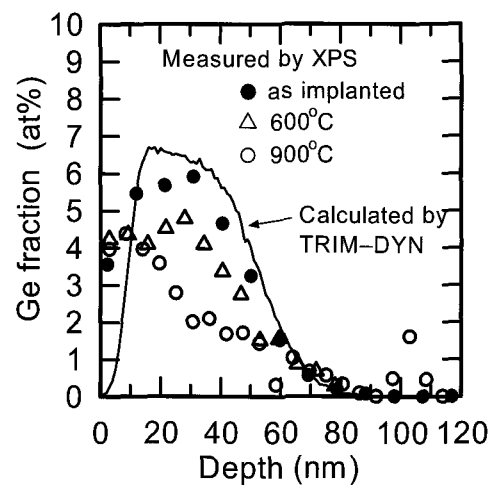


Fig. 3. Corrected depth profiles of Ge atoms in SiO₂ layer on Si from Ge 2p, O 1s and Si 2p peaks in the XPS survey spectra of the multi-energy implanted Ge samples. The correction factor of 1.47 was used for Ge 2p signal.

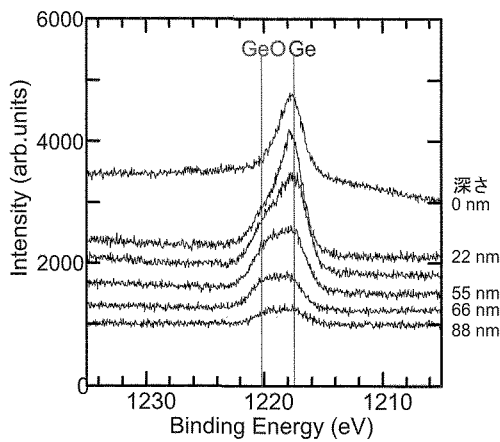


Fig. 4. XPS Narrow spectra of Ge 2p 3/2 for various depths of the as-implanted sample.

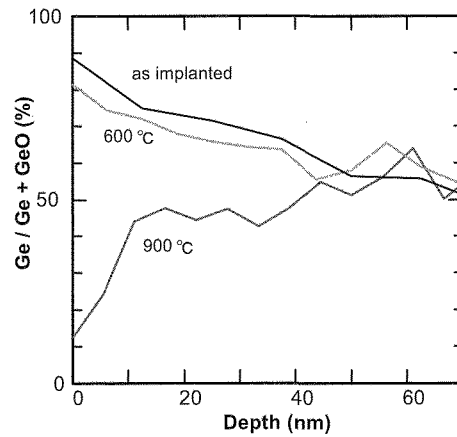


Fig. 5. Ratio of metallic Ge atoms as a function of depth for various annealing samples.

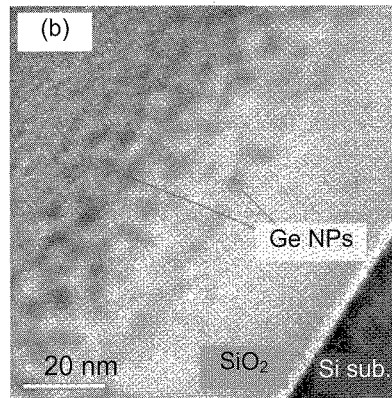
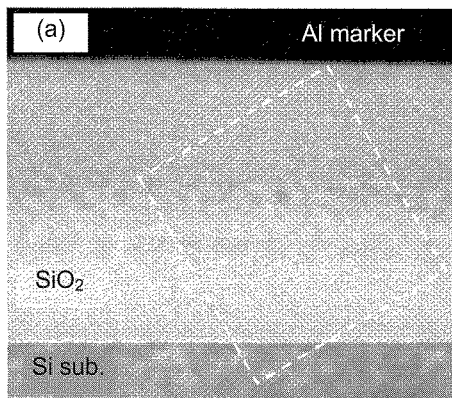


Fig. 6 Cross-sectional TEM image of the multi-energy Ge-implanted sample after annealing at 600°C for 1 h. (b) is enlarged one corresponding to the rectangular area of (a).

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).

4.3 Nanoparticle observation by TEM

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.

4.4 Cathode luminescence

Cathode luminescence of the Ge-implanted sample has been preliminary investigated for the possibility of light emission. Fig. 7 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

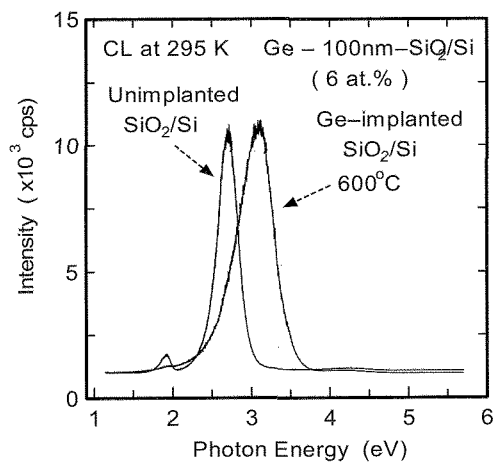


Fig. 7. Cathode luminescence spectra for the multi-energy implanted samples after annealing at 600°C.

non-bridged oxygen hole center (NBOHC, 1.8 – 1.9 eV) and two fold-coordinated Si atoms, respectively. [10, 11]. 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, 12]

and H.-J. Fitting *et al.* [10]. 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. Single space and 9 point all text, unless super- and subscripts cause the text to be hard to read. In the case of crowded text, allow 1.5 spaces between lines. SI (modified) units must be used in all text, tables, and figures.

4. CONCLUDING REMARKS

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 (1.4×10^{16} ions/cm²), 20 keV (3.2×10^{15} ions/cm²) and 10 keV (2.2×10^{15} ions/cm²). The strongest Ge-Ge bonding was found after annealing at 800°C for 1 h. This is considered to be the best condition for forming Ge nanoparticles. In the cathode luminescence study with 4 keV electron beam for the Ge-implanted sample after annealing at 600°C for 1h, CL peak was obtained at 3.12 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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