Cathode and Photo Luminescence of Silicon Dioxide Layer Implanted with Ge Negative Ions at Multi-Energy

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Abstract. Ge\(^+\) ions were implanted into SiO\(_2\) layer three times by changing the energies of 50, 20 and 10 keV to form Germanium nanoparticles at a relatively wide-depth region. Then, the samples were annealed at 600-900°C for 1 h. Although Ge-nanoparticle formation was confirmed by cross-sectional TEM observation, XPS analysis showed about 30-60% of the Ge atoms in SiO\(_2\) on average were oxidized. In cathode and Photo luminescence measurements, the emissions of around 400 nm in wavelength from the samples were observed. The position of cathode luminescence peak was independent of Ge fluence in the implantation, and temperature in the measurement. These results suggest that the luminescence mechanism is not due to quantum confinement effect of Ge nanoparticles, it is due to the oxygen defect center of oxidized germanium. The luminescence intensity changed dramatically with varying Ge fluence in the implantation.

1. Introduction

Semiconductor nanoparticles embedded in dielectric materials are attractive materials for the development of electro-luminescent devices. Silicon dioxide including Ge nanoparticles is expected to apply to light emission source for communication in a LSI chip as well as to single electron devices, since 500-nm-thick SiO\(_2\) film including Ge nanoparticles was reported to show blue and violet electroluminescence by applying a voltage of 350 V [1]. However, it is required to decrease the operation voltage [2] for versatile application. In order to meet this requirement, we have tried to make Ge nanoparticles in a shallow depth region in SiO\(_2\) layer on Si substrate by using a negative ion implantation method with multi-energy. Moreover, we studied the cathode luminescence from the Ge-implanted SiO\(_2\) with varying conditions of the implantation to get guidance in strong blue and violet luminescence. Negative-ion implantation has an advantage of almost “charge-up free” feature for insulators and isolated electrode [3]. Therefore, the penetration depth of ions can be controlled correctly with a relatively low energy implantation into a thin insulator such as silicon dioxide. Moreover, the technique is suitable for careful examination about implanted atoms in the thin SiO\(_2\) film, because the charge up can make accidental dispersion of implanted atoms and the break down can make accidental defects.
2. Multi-Energy Implantation of Ge Negative Ions and Subsequence Annealing

Germanium negative-ions (Ge⁻) were implanted at room temperature into a thermally grown 100-nm-thick SiO₂ film on Si. We used a multi-energy implantation technique to make a relatively flat profile of Ge atomic density in some regions. In the multi-energy implantation, the Ge⁻ were implanted three times into the same sample by changing the energies of 50, 20 and 10 keV. For example, the calculated depth profile of Ge ions about 6 at.% at peak concentration is shown in Fig. 1(a). The calculation was executed by using the Transport of Ions in Matter (TRIM-DYN) program [4]. As seen from the total concentration curve, the implanted Ge layer with a concentration of about 6 at.% is expected to be formed from 10 nm to 40 nm in depth. The oxygen atom in the SiO₂ layer is expected to be scattered by the collision of Ge and be recoiled due to its lightweight comparing to Ge and Si. We calculated a lack or excess of O atoms from the stoichiometric value of the SiO₂. The O balance distribution in depth direction is also shown in Fig. 1(b). We expected O lacking in the surface region and O excess in the deep region around the end of range (EOR) of 40-100 nm. The gas pressure during the implantation was kept less than 1x10⁻⁴ Pa. We expected to obtain the layer of the implanted Ge with a thickness of about 30 nm by this multi-energy implantation. After implantation, the samples were annealed for 1 h by an electrical oven at various temperatures of 600, 800 and 900°C in a quartz tube in a N₂ gas flow (50 l/min) under low vacuum condition from a rotary pump (400 l/min).

3. Photo Luminescence

Photo luminescence (PL) of the Ge-implanted sample has been preliminary investigated by using 266 nm excitation light of triple harmonics from a Al₂O₃:Ti laser for the possibility of light emission. Fig. 2 shows PL spectrum obtained at room temperature from Ge-implanted sample at 6 at.% without subsequent heat treatment. The Ge-implanted sample showed PL peak around 410 nm (3.0 eV) in UV-blue region at room temperature. This PL peak is correspondent to the PL spectra reported by Rebohle et al [1]. Therefore, the peak around 410 nm is considered to be due to ODC attributing to two-fold-coordinate Ge atoms.

4. Oxidation of Implanted Ge Atoms

The depth distribution of fractions of metallic and oxidized Ge atoms were measured by X-ray induced photoelectron spectroscopy (XPS) with Ar ion etching, because the PL seems to relate with oxidized Ge. We measured survey spectra after etching by Ar⁺ irradiation at 4 keV. We obtained Ge atomic fractions in SiO₂ by the comparison of peak areas for detected photoelectrons of Ge 2p3/2, O 1s and Si 2p. As for fractions of metallic and oxidized Ge atoms, a chemical shift due to oxidation of Ge atoms was about 1.4 and 2.8 eV higher in binding energy for GeO and GeO₂, respectively. In the experiment, only chemical shift by GeO was distinguished. Therefore, we divided the detected Ge 2p3/2 peak into two Gaussian distributions from metallic (Ge-Ge) and mono-oxide (Ge-O) bondings by the peak fitting. Then, the ratio of metallic Ge atoms was calculated. Fig. 3 shows the percentage of
metallic Ge as a function of depth. After annealing at 900°C, Ge atoms in the surface region were oxidized. This was considered to be due to 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-annealed samples showed the higher oxidation degree of Ge atoms in the deep region of the SiO₂ than in the surface region. This oxidation at deep depth is considered to be due to the local excess of oxygen atoms as shown in Fig. 1(b). In Fig. 3(a), average oxidations of Ge in SiO₂ for the as-implanted, 600°C-annealed and 900°C-annealed samples were about 26, 30 and 60 %, respectively. After annealing at 800°C in N₂ and Air as shown in Fig. 3(b), the average oxidations were about 50 and 85 %, respectively.

5. Cathode Luminescence

Cathode luminescence (CL) of the Ge-implanted sample after annealing at 800°C in N₂ has been investigated with using an electron beam at 5 keV with 11µA. Strongly emitted luminescence was expected due to about 50% of the oxidized Ge. Fig. 4 shows CL spectra obtained from the Ge-implanted sample at 6 at.% after annealing at 800°C and from an unimplanted sample at room temperature. The unimplanted sample showed only broad luminescence peak at around 460 nm but the implanted sample showed large sharp luminescence peak at around 400 nm. This luminescence peak seems correspond to the above PL peak in Fig. 2 and is well agreed with the CL spectra reported by Rebohle et al [1] and H. J. Fitting et al [5]. Therefore, the peak around 400 nm is considered to be due to ODC attributing to two fold-coordinate Ge atoms. CL spectra of the sample made under other conditions were also measured to investigate dependency of the luminescence on implanted Ge concentration. The samples were prepared in the Ge concentration range of 0.05 - 6 at.% and annealed at 800°C. As shown in Fig. 5 (a) and (b), CL intensity increased with increasing in Ge concentration but decreased at the implanted Ge concentration more than 1.4 at.%. It is considered that these inverse proportions above 0.5 at.% were caused by lack of oxygen, density of large Ge nanoparticle and/or rich of defects in SiO₂. Although the lack of oxygen and excess of Ge were obtained, the number of luminescence source did not increase. High Ge concentration resulted in densely large size of Ge nanoparticles, and the nanoparticles in shallow of the SiO₂ intercepted luminescence from the source in a deep region. Many implanted Ge ions caused defects in the SiO₂ resulting in trapping of electrons for luminescence. For lower than 0.5 at.% of implanted Ge concentration, it is considered that Ge nanoparticles in the sample were enough small in size and in number so that they did not intercept the luminescence and could be oxidized to increase ODC of the luminescence sources. Therefore, the luminescence showed the maximum intensity at 0.5 at.% of implanted Ge concentration under the condition of sample preparation. These discussions may lead that the strong luminescence can be happened by tuning of condition of Ge implantation and subsequence annealing.
Fig. 6 shows CL spectra, which had been obtained by using an electron beam at 4 keV and 1 µA, at various temperatures. The intensity of luminescence was proportionate to the temperature, but their peak positions were independent of the temperature. These results also suggest that the luminescence is not due to quantum confinement effects of Ge nanoparticles. The dependency on temperature showed the possibility for application to light emission source at room temperature.

6. Conclusions

We were able to make a flat profile of Ge atomic density in some regions of SiO$_2$ on Si by using a multi-energy implantation technique. In the multi-energy implantation, Ge were implanted three times into the same SiO$_2$ layer by changing the energies of 50, 20 and 10 keV. XPS analysis revealed the implanted Ge atoms into the SiO$_2$ were oxidized not only after annealing at above 600°C but also just after implantation without subsequent annealing. The spectra of CL and PL for the Ge-implanted samples showed peaks around 400 nm in wavelength. The peak position was independent of Ge implantation fluence, annealing temperature and measurement temperature. These independencies suggest that the luminescence is not due to quantum confinement effects of Ge nanoparticles. It is considered that the luminescence is due to oxygen deficiency centers of GeO$_2$. The CL intensities were varied with Ge implantation fluence. These results suggest that size, density and oxidation degree of Ge nanoparticle affect the effective intensity of the luminescence. These results will provide guidance in light emission in UV-blue region from Ge-implanted SiO$_2$.

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References

[1] L. Rebohle, J. Von Borany, R.A. Yankov, W. Skorupa, I.E. Tyschenko, H. Froeb, and K. Leo, Appl. Phys. Lett. 71 [19] (1997) 2809-2811.
[2] J.M.J. Lopes, F.C. Zawislak, M. Behar, P.F.P. Fichtner, L. Rebohle, and W. Skarupa, J. Appl. Phys. 94 [9] (2003) 6059-6064.
[3] J. Ishikawa, H. Tsuji, Y. Toyota, Y. Gotoh, K. Matsuda, M. Tanho, and S. Sakai, Nucl. Instr. Methods, B96 (1995) 7-12.
[4] J.P. Biersack, Nucl. Instr. Meth. B 27 (1987) 21.
[5] H. J. Fitting, T. Barfels, A.N. Trukhin, B. Schmidt, A. Gulans, A. von Czarnowski, J. Non-Crystalline Solids, 303 (2002) 218-231.