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Germanium nanoparticles formation in silicon dioxide layer by multi-energy implantation of Ge negative ions and their photo-luminescence

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Abstract

Ge^- ions were implanted into SiO_2 layer three times by changing the energy of 50, 20 and 10 keV in this order to form germanium nanoparticles at a relatively wide-depth region. Then, the sample was annealed at 600–900 °C for 1 h. Although Ge nanoparticles 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 measurement, the emissions of around 400 nm in wavelength from the samples were observed. The photo-luminescence peak position was independent of implanting Ge fluence, annealing temperature intensity and intensity of excitation light. These results suggest that the luminescence mechanism is not quantum confinement effect of Ge nanoparticles but oxygen defect center of oxidized germanium. The luminescence intensity changed dramatically with varying implanting Ge fluence.

Keywords: Ion implantation; Heat treatment; Germanium; Photo-luminescence

1. Introduction

Semiconductor nanoparticles embedded in dielectric materials are attractive materials for the development of electroluminescent 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 photo-luminescence from the Ge^--implanted SiO_2 with varying condition of the implanting and subsequence annealing 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 were implanted into SiO_2 on Si by a negative-ion implanter (Nissin Electric Corp., Japan) [4] with

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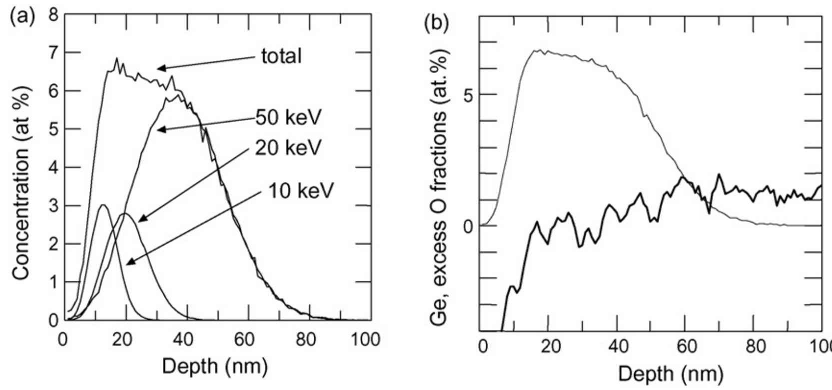

Fig. 1. Calculated depth profile of (a) Ge atoms by multi-energy implantation and (b) oxygen deficit (excess and shortage) in the SiO_2 layer.

an RF (radio frequency) plasma-sputtering type heavy negative-ion source [5]. Ge^- were implanted at room temperature into a thermally grown silicon dioxide layer with a thickness of 100 nm on silicon substrate (15 mm × 15 mm). We used a multi-energy implantation technique to make a relatively flat profile of Ge atomic density in some region. In the multi-energy implantation, the Ge^- were implanted three times into the same SiO_2 layer by changing the energy of 50, 20 and 10 keV in this order. Each fluencies for these energies is 1.5×10^{16}, 2.6×10^{15}, and 2.0×10^{15} ions/cm^2, respectively, or 3.0×10^{15}, 9.0×10^{14}, and 4.5×10^{14} ions/cm^2, respectively, or 1.1×10^{15}, 3.0×10^{14}, and 2.0×10^{14} ions/cm^2, respectively. Calculative Ge atomic concentrations in maximum were about 6, 1.4 and 0.5 at.%, respectively. 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 [6] with including dose effect. As seen from the total concentration curve, Ge-implanted layer with a concentration of about 6 at.% is expected to be formed from 10 to 50 nm in depth. The oxygen atom in the SiO_2 layer is expected to be scattered by the collision of Ge and recoils due to its lightweight comparing to Ge and Si. We calculated a shortage or excess of O atoms from the stoichiometric value of the Ge-implanted SiO_2. The O balance distribution in depth direction is also shown in Fig. 1(b). 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. The gas pressure during the implantation was kept less than 1×10^{-4} Pa (background pressure was 3×10^{-5} Pa). We expected to obtain Ge-implanted layer with a thickness of about 40 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 N_2 gas flow (50 l/min) under low vacuum condition by a rotary pump (400 l/min).

The cross-sectional TEM image of the sample after annealing at 600 °C was studied as shown in Fig. 2, where (b) is enlarged one corresponding to the rectangular area in Fig. 2(a). The image is a little opaque, but the Ge nanoparticles were observed in the region from the surface to middle of the SiO_2 in depth. The Ge nanoparticles were dense but small in size less than 4 nm. The wider distribution of Ge nanoparticles than the calculated profile of Ge atoms can be due to thermal diffusion of Ge atoms in the 600 °C-annealing.

3. Cathode luminescence

Cathode luminescence (CL) of the Ge-implanted sample has been preliminary investigated for the possibility of light emission. Fig. 3 shows cathode luminescence spectra obtained at room temperature from Ge-implanted sample at 6 at.% and unimplanted SiO_2/Si sample. The unimplanted sample showed luminescence peaks at around 470 nm (2.7 eV in photon energy).

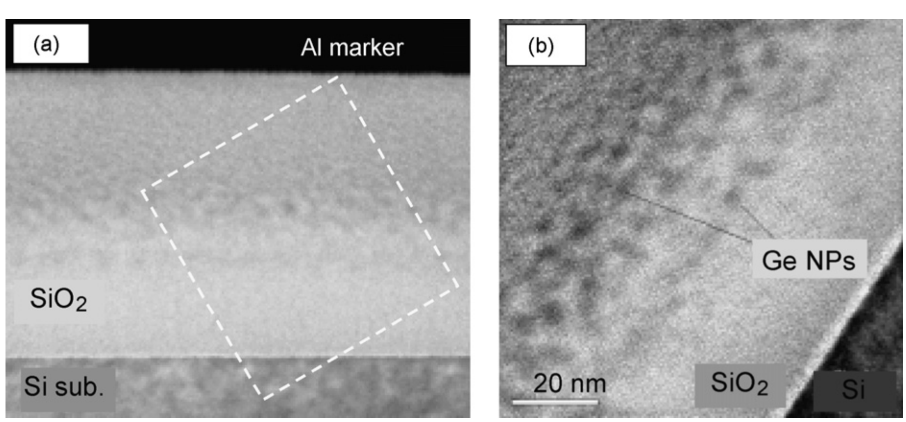

Fig. 2. Cross-sectional TEM image of the multi-energy Ge-implanted sample after annealing at 600 °C for 1 h (b) is enlarged one corresponding to the rectangular area of (a).