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Electrical Characteristics of Thin SiO_2 Film Including Ge Nanoparticles formed by Negative Ion Implantation

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The electrical characteristics of nanoparticles in a thin insulator film are important properties to develop very low power-consumption electron devices using nanoparticles. We have investigated electrical characteristics of 25-nm-SiO_2/Si films including Ge nanoparticles by Capacitance-Voltage (CV) method. Ge nanoparticles were formed by negative ion implantation and subsequent annealing. Ge atoms in the SiO_2 were evaluated with a high-resolution RBS and cross-sectional TEM. Ge atoms were implanted at 10 keV with total doses of 1 x 10^{15} and 5 x 10^{15} ions/cm^2. The annealing were conducted at 300, 500, 700 and 900°C for 1 h. After 900°C-annealing, Ge atoms diffused to SiO_2/Si interface. After 300°C-annealing, a CV curve showed so small hysteresis that could not be used as memory devices. After 500°C-annealing, both samples with 1 x 10^{15} ions/cm^2 and with 5 x 10^{15} ions/cm^2 had clear hysteresis curves. Calculations of charge and nanoparticle intensity from the flat band shift and the implanted Ge dose show that there is one electron in each nanoparticle of 3-nm diameter. These results suggest that thin SiO_2 films including Ge nanoparticles formed by negative ion implantation can be utilized as memory devices.

Key words: Nanoparticles, Ion implantation, Oxide film, Germanium Negative ion

1. INTRODUCTION

Conductor nanoparticles embedded in dielectric materials have so small capacitance that they can show Coulomb blockade phenomena at room temperature [1, 2]. Therefore, metal nanoparticles in SiO_2 are attractive materials for the development of single electron memories with nanoparticles embedded in gate insulators of MOSFETs. As MOSFET devices shrink, nanoparticles have to be embedded in a very thin SiO_2 film on Si substrate. Formations of nanoparticles in thin SiO_2 films with implantation technique have been already reported [3-7]. These nanoparticles should be chargeable and dischargeable to be used as memory devices. Si nanoparticles with CVD method were applied to floating gate type memory with about 0.25 V of threshold voltage shift [8]. We think that spherical nanoparticles in high-quality thermally oxidized silicon created by negative ion implantation are better to store electrical charge. So we used negative ion of Ge, which fit semiconductor processing. Thermally grown SiO_2 was implanted by Ge ion implantation and annealed to form nanoparticles. Electrical characteristics of the Ge implanted SiO_2 were investigated with Capacitance-Voltage (CV) method. The results showed that the Ge implanted SiO_2 charged and discharged electrical charge.

2. EXPERIMENTAL

Germanium negative ions were generated in an RF (radio frequency) plasma-sputtered type heavy negative ion source and extracted at 10 keV [9, 10]. After mass-separation by a sector magnet, the Ge ion beam was introduced into a collector cup with a limiting aperture of 8-mm diameter in an implantation chamber of the negative ion implanter (Nissin Electric Corp., Japan) [11]. In the collector cup, Ge negative ions were implanted into a silicon dioxide film with thickness of 25 nm thermally grown on silicon substrate (15 mm x 15 mm) at ion energy of 10 keV with doses of 1 x 10^{15} and 5 x 10^{15} ions/cm^2 at a room temperature. Figure 1 shows the depth profiles of implanted Ge atoms calculated by using the transport of ion in matter (TRIM-DYN)

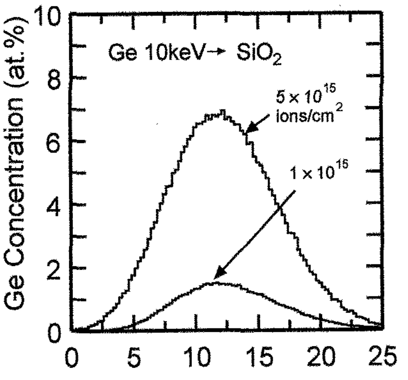

Fig. 1. Depth profile of Ge atoms implanted into SiO_2 medium calculated by using TRIM-DYN program under conditions at 10 keV with 1 x 10^{15} and 5 x 10^{15} ions/cm^2

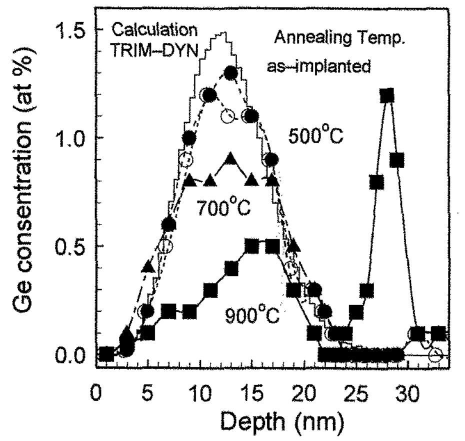

Fig. 2. Depth profiles of Ge atoms obtained from HR-RBS for Ge-implanted 25-nm-SiO_2/Si samples at 10 keV with 1 x 10^{15} ions/cm^2 after annealing at various temperatures.

program [12].

The Ge profiles show almost Gaussian distributions with a peak concentration of 1.5 and 7.0 at.% at the depth of 12 nm, where is approximately a half of the thickness of the SiO_2 film.

The implanted samples were annealed at temperature of 300, 500, 700, and 900°C for 1 h in an vacuum quartz tube of an electrical oven. Al electrodes were formed on the samples with vacuum evaporation.

Capacitance-Voltage (CV) characteristics of the samples were measured by sweeping voltage of the Al electrode with ground state of Si substrate. The voltage was swept from positive to negative and return from negative to positive voltage.

The real depth profiles of Ge atoms implanted into the 25-nm thick SiO_2 on Si before and after the heat treatment were measured by the high-resolution Rutherford backscattering spectrometry (HR-RBS), an apparatus of HRBS500 (KOBELCO, Japan).

Cross-sectional images of the samples were observed by scanning-type transmission electron microscope (STEM) of EM-002B (Topcon Techno, Japan) by 200 keV of electron beam energy, after cutting the samples with focus ion beam (FIB) of Ga^+ with 30 keV.

3. RESULTS AND DISCUSSION

The results of the HR-RBS measurements are shown in Fig. 2. The implanted depth-profiles of Ge atoms considerably agreed with the predicted profile for annealing below 700°C although Ge atoms were depleted by about 10% of the initial dose. After annealing at 900°C, the other Ge concentration peaks of 1.2 at.% that appeared around the interface of SiO_2/Si is higher than the peak is in the SiO_2 film. Besides, a peak position in the SiO_2 film shifted about 4 nm to the interface side from the peak position for the as-implanted sample.

The cross-sectional TEM (XTEM) images are shown in Fig. 3 for each sample implanted with 1 x 10^{15} ions/cm^2 and annealed at (a) 500°C, (b) 700°C, (c) 900°C and in Fig. 4 for a sample implanted with 5 x 10^{15} ions/cm^2 and annealed at 700°C. Results show thin black shadows that are we think Ge nanoparticles with about several-nm diameter were appeared around the middle of the SiO_2 film for the samples annealed at temperatures less than 700°C. The Ge concentration of about 1 at.% in the conditions and the size of Ge nanoparticles of about several-nm diameter agree with the relations between the results of nanoparticle size and atomic concentration from our previous studies of Ag nanoparticles formation [13].

Although, we could not identify any nanoparticles after annealing at 900°C in the XTEM image of Fig. 3(c), the RBS results suggest that 900°C annealing makes many Ge atoms diffuse and disappear from the SiO_2 film. After annealing at high temperature of 900°C, remaining of Ge atoms was not enough to form nanoparticles, or the remained Ge concentration of 0.5 at.% might form so small nanoparticles that can not be observed by our XTEM apparatus. In Fig. 4 with 5 x 10^{15} ions/cm^2, nanoparticles with a diameter of around 3-nm are observed.

The CV characteristics of samples implanted by Ge negative ions and annealed under various conditions are shown in Fig. 5. Hysteresis curves with a range of about 0.6 V appeared for dose of 1 x 10^{15} ions/cm^2 with 500°C annealing, as shown in Fig. 5(a). At larger doses of 5 x 10^{15} ions/cm^2, the range of hysteresis was about 6.6 V, as shown in Fig. 5(b). The reason for the large hysteresis is considered to be formation of large nanoparticles to store more electrical charges. Size of the large nanoparticles is about 3-nm on a basis of a XTEM image of Fig. 4 with 700°C-annealing.

Figure 5(c) shows a result of CV measurement for the sample implanted with 1 x 10^{15} ions/cm^2 and annealed at 900°C. Figure 5(c) clearly indicates that the sample cannot be evaluated with CV method. The reason for

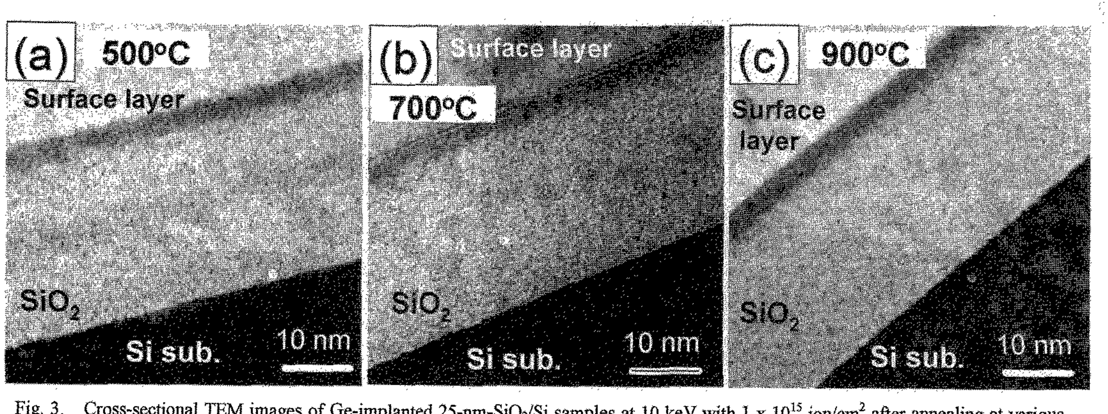

Fig. 3. Cross-sectional TEM images of Ge-implanted 25-nm-SiO_2/Si samples at 10 keV with 1 x 10^{15} ion/cm^2 after annealing at various temperatures of : (a) 500°C; (b) 700°C and (c) 900°C.

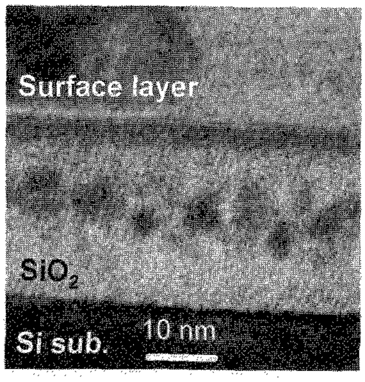

Fig. 4. Cross-sectional TEM images of Ge-implanted 25-nm-SiO_2/Si samples at 10 keV with 5 x 10^{15} ion/cm^2 after annealing at 700°C.

this abnormal CV curves is considered as the Ge accumulation around the interface of SiO_2/Si due to thermal diffusion obtained by the RBS. At 300°C, only small hysteresis appeared although the implanted doses were as high as 5 x 10^{15} ions/cm^2. This result was considered to be caused by too low annealing temperature to form enough many large nanoparticles to store many electrical charges.

An electrical hysteresis characteristic is a important requirement of memory film for application for semiconductor memory device. Memory film with larger hysteresis in CV characteristics is better because the range of the hysteresis, flat band shift (ΔV_{FB}) moves to threshold voltage shift (ΔV_{th}) of MOS memory transistor which include the film as the gate oxide.

The ΔV_{FB} is obtained by

$$\Delta V_{FB} = - (x_c / T_{ox}) (Q_s / C_{ox}),$$

where x_c is the average distance of the stored charge from interface of the gate electrode, Q_s is the surface density of the stored charge, C_{ox} is the capacitance per unit area of the gate insulator, and T_{ox} is the thickness of the gate insulator.

The stored charge surface density, Q_s, can be

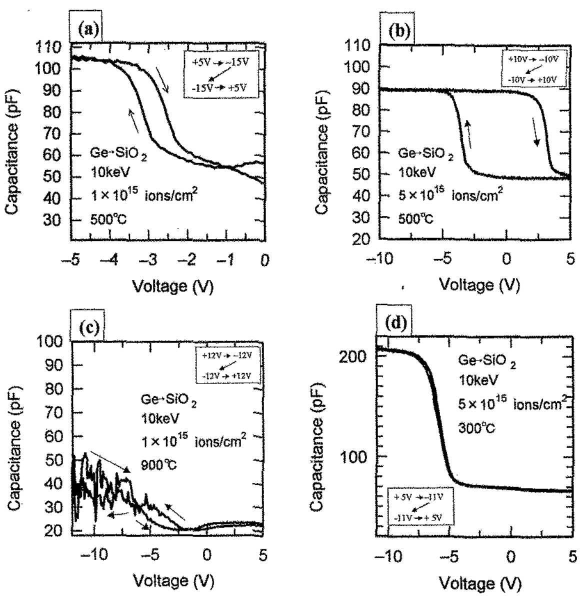

Fig. 5. CV characteristics of Ge-implanted 25-nm-SiO_2/Si samples at 10 keV with (a) 1 x 10^{15} ion/cm^2 after annealing at 500°C, (b) 5 x 10^{15} ion/cm^2 after annealing at 500°C, (c) 1 x 10^{15} ion/cm^2 after annealing at 900°C and (d) 5 x 10^{15} ion/cm^2 after annealing at 300°C.

calculated with the equation and the ΔV_{FB} of 6.6 V. The x_c is 12.5 nm on the assumption that Ge nanoparticles are at middle depth of the 25nm-SiO_2 film by consideration of the XTEM images. If relative dielectric constant of SiO_2 is 3.9, Q_s calculated is 1.8 x 10^{-2} C/m^2, so, changing to numbers of electron is 1.1 x 10^{17} e/m^2, or 1.1 x 10^{13} e/cm^2.

Next, surface density of Ge nanoparticles is calculated. The implanted Ge atoms of 5 x 10^{15} ions/cm^2 form Ge nanoparticles of 7 x 10^{12} /cm^2, if all implanted Ge atoms form particles of 3-nm diameter and Ge density is 5.4 g/cm^3. The above calculations lead to 1.4 electrons per particle on average (e/p).

For the sample implanted with 1 x 10^{15} ions/cm^2 and annealed at 500°C, the ΔV_{FB} of 0.6 V leads to 0.8 electrons per particle on average.

These results of about one stored electron per particle suggest that Ge nanoparticles formed by negative ion implantation can charge and discharge and be used as memory devices.

Although we assume that the size of all nanoparticles is roughly 3-nm diameter, and that all implanted Ge atoms are used to form the nanoparticles with 3-nm diameter, some implanted Ge atoms actually are not used to form nanoparticles and still keep atomic state. The Ge atoms with atomic state do not contribute to charging electrons.

In case of low dose implantation, the Ge atom should require more long distance than that in case of high dose implantation to combine with other Ge atoms to form a nanoparticle. Comparison of the nanoparticles formation of Ge atoms at the same annealing conditions, the percentage of formation at high dose is much more than that of the formation at low dose.

Therefore it is possible for actual stored electrons per particle to be larger than that of our estimations, and for the difference of stored electrons per particle between in the sample of 1 x 10^{15} ions/cm^2 and in the sample of 5 x 10^{15} ions/cm^2 to be smaller than that in our estimations.

4. CONCLUSION

We have measured electrical characteristics of the samples with CV method. The samples of thermally grown SiO_2 on Si substrate were implanted with Ge negative ions and annealed at various temperatures. The implanted Ge atoms were evaluated by RBS and XTEM. For the sample annealed at 900°C, Ge atoms diffused and accumulated around the SiO_2/Si interface. For 300°C, the hysteresis was too small to be used for memory devices. For 500°C, the hysteresises of the samples implanted with both 1 x 10^{15} and 5 x 10^{15} ions/cm^2 are 0.6 and 6.6 V, respectively. The evaluations of stored charge densities and Ge particle densities from the hysteresis width and the implanted doses indicated one or several stored electrons per particle on average. These results suggest that the thermally grown SiO_2 including Ge nanoparticles formed with negative ion implantation can be used to memory devices.

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