Nanocrystal Formation of Metals in Thermally Grown Thin Silicon Dioxide Layer by Ion Implantation and Thermal Diffusion of Implanted Atoms in Heat Treatment

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Abstract. Ion implantation technique is useful method to dope atoms in a thin layer to make nanoparticles. However, the thermal annealing is required for recovering ion-induced damages and growing NPs. Therefore, the redistribution of implanted atoms in the layer is very important in the formation process of nanoparticles in size and position. We have investigated the redistribution of Ag atoms implanted in a thermally grown 25-nm-thick SiO$_2$ layer on silicon substrate. Ag negative ions were implanted at 10 keV in the thin oxide layer, where the projected ranges are calculated 12 nm. Samples were annealed at a temperature of 800 degrees or less for 1 h in vacuum with Ar gas flow (50 ml/m). Depth profiles of implanted atoms were investigated by high-resolution Rutherford backscattering spectrometry (HRBS). The formed nanoparticles in the layer were studied by high-resolution cross-sectional transmission electron microscope (XTEM). The samples implanted with Ag negative ions at 10 keV with $5 \times 10^{15}$ ions/cm$^2$ were measured by HRBS at scattering angle of 80 degree with He ions at 400 keV. Ag atoms distributed at the surface and at a depth corresponded to the calculated profile after annealing at a temperature below 500 °C. It is expected that the surface accumulation of Ag atoms resulted from thermal diffusion of implanted atoms during implantation. At 500 degree C, the very small peak in concentration was observed at a depth of 22 nm. This means that a diffusion barrier for Ag atoms exits in this depth. At 700 degree C, the main peak of concentration was appeared at 20 nm in depth, in which FWHM was 7 nm. The XTEM observation showed that the Ag NPs aligned at the same depth of 20 nm along the interface of SiO$_2$/Si, and that they were nanocrystals (NCs). This mono-layered Ag NCs well corresponded to the HRBS spectra. Thus, we have formed almost mono-layered nanocrystals for Ag implantation in thin silicon dioxide layer.

1. Introduction
Electrarily conductive nanoparticles (NPs) embedded in an oxide insulator are desired to apply for development of single electron memories because of their ability to show Coulomb blockade phenomenon at room temperature [1,2]. In case of nanoparticles in a thin gate oxide layer in MOSFET, the formation of mono-layered nanoparticles, i.e., particles align at a certain depth in the oxide, is required for the thinner layers in the future. Several methods to form nanoparticles and to
reply this requirement were reported by using ion implantation technique: Nakajima, A. et al [3] for Sn NPs at deep depth; Takeda, Y. et al [4] for Cu NPs at a shallow depth; Heinig, K.H. et al [5] for Si NPs both at shallow and deep depths; Tsuji, H. et al [6, 7] for Au NPs at a shallow depth and Ag NPs at a deep depth. In formation methods of the above Sn and Ag NPs, implanted atoms were redistributed by heat treatment after ion implantation. The depth positions of nanoparticles for the both cases were at the same distance of 2 nm from the interface of SiO₂/Si. Although a diffusion barrier can be expected in a low-energy implantation of 10 keV, there is no report for such diffusion barrier for Sn and Ag atoms. For a high-energy implantation at about several hundreds keV, at which ions can pass through a SiO₂ layer, an excess Si atoms sputtered from Si substrate into the SiO₂ could act as nucleation center [5]. In the low-energy implantation, however, the formation mechanism of nanoparticles aligned along the interface between SiO₂ and Si substrate is still unknown. In this paper, we implanted Ag negative ions into a thermally grown thin silicon dioxide layer on silicon substrate. The samples were annealed at various temperatures to obtain mono-layered Ag NPs. In this process, redistribution profile of implanted Ag atoms in the very thin SiO₂ on Si was investigated by using a high-resolution Rutherford backscattering spectrometry (HRBS) in order to detect the diffusion barrier.

2. Experimental

Silver negative ions were generated in an RF plasma-sputtered type heavy negative ion source and extracted at 10 keV [8, 9]. After mass-separation by a sector magnet, the ¹⁰⁷Ag⁺ beam was introduced into a collector cup with a limiting aperture of 8 mm in diameter in an implantation chamber of the negative ion implanter (Nissin Electric Corp., Japan). In the collector cup, the negative ions were implanted into a thermally grown silicon dioxide layer with thickness of 25 nm on silicon substrate (15 mm x 15 mm) at ion energy of 10 keV with dose of 5 x 10¹⁵ ions/cm² at a room temperature. The projected range of Ag atoms is calculated to be about 12 nm in amorphous SiO₂ with 2.20 g/cm³ by the transport of ion in matter (TRIM-DYN) program [10]. This range corresponds to about a half depth of the SiO₂ thickness. After implantation, these implanted samples were annealed at various temperatures of 500, 700 and 800°C for 1 h under Ar flow (50 ml/min) condition in an evacuated quartz tube of an electric oven. We applied negative ions in the ion implantation since the negative ion implantation has almost “charge-up free” feature [11] for insulators.

The depth distribution of implanted Ag atoms in the 25-nm thick SiO₂ layer on Si before annealing and the redistribution after the heat treatment were measured by HRBS in an ultra high vacuum condition of 10⁻⁶ Pa by using relatively low-energy He ion beam as a probe primary. The beam energy and current intensity of the probe beam (2 x 2 mm²) were 400 keV and 30 nA, respectively. The energy of reflected ions at 100 degrees were analyzed by a magnetic energy analyzer in a range from

![Figure 1](image1.png)  **Figure 1.** Estimated concentration of Ag atoms implanted into SiO₂ medium at 10 keV with 5 x 10¹⁵ ions/cm² calculated by TRIM-DYN program.

![Figure 2](image2.png)  **Figure 2.** Depth profiles of Ag atoms implanted SiO₂ layer before and after annealing at various temperature of 500°C, 700°C and 800°C by HRBS.
230 to 410 keV, and the reflected ions were counted at an energy step of 0.388 keV. Although this energy step, in principle, simply corresponds to the depth resolution of 0.1 nm, the depth resolution under the above total conditions is considered to be 0.5 nm at the surface region in a silicon dioxide. Random spectrum was searched by rotating the sample surface and recorded. The depth profile of Ag atoms in the SiO$_2$ layer was obtained by backscattering cross-section and scattering yield ratio of Ag and Si atoms in amorphous SiO$_2$. The typical error in RBS measurement is considered to be ±5%. On the other hand, the images of the samples annealed at each temperature were observed by cross-sectional transmission electron microscope (XTEM) by 200 keV electron beam. The XTEM specimens were prepared by FIB (Ga$,^+$, 30 keV).

3. Result

3.1. Depth Profiles by Calculation and HRBS Measurement

The calculated depth profile of implanted Ag atoms in amorphous SiO$_2$ is shown in Fig. 1 under the conditions of 10 keV and 5 x $10^{15}$ ions/cm$^2$. The peak is appeared at a depth of 12 nm with a Ag concentration of about 9 at.%. The total sputtering yield was 1.8. But, the surface recession due to sputtering was about 0.65 nm as assuming expansion by implanted Ag atoms. The Ag ions passed through the layer were only 0.018%.

Figure 2 shows Ag concentrations for the samples annealed at various temperatures. The accumulation of Ag atoms at the surface for two samples of as-implanted and after 500°C-annealing was observed. These two samples also showed concentration peak of Ag atoms at the depth of 12 nm. In the sample annealed at 500°C, there are other two small peaks around 6 nm and 22 nm, where they indicate two small segregations of Ag atoms owing to the annealing. The remained Ag atoms in samples were 5 x $10^{15}$ and 3.3 x $10^{15}$ atoms/cm$^2$ for the as-implanted and after annealing at 500°C.

After annealing at 700°C and 800°C, Ag atoms were redistributed and the Ag-main-concentration peak initially at 12 nm moved to the depths of 20 nm and 25 nm, respectively. There is no any segregation of Ag atoms in the surface side from each main peak. The Ag segregations at 22 nm for 500°C-annealing and 20 nm for 700°C suggested an existence of a certain diffusion barrier of Ag atoms in the SiO$_2$ layer near the interface of SiO$_2$/Si. The Ag atoms remained in the samples after annealing at 700°C and 800°C are both 1.4 x $10^{15}$ atoms/cm$^2$, which is about 28 % of implanted Ag atoms.

3.2. Ag Nanoparticles

Figure 3 shows cross-sectional TEM images for Ag implanted samples after annealing at various temperatures of (a) 500°C, (b) 700°C and (c) 800°C. In Fig. 3(a), Ag NPs of 3 - 4 nm in diameter were formed in the SiO$_2$ layer. The depth distribution of 47 Ag NPs obtained from counting Ag NPs every 2-nm depth of Fig. 3(a) is shown in Fig. 4. This histogram shows two main peaks in Ag NP number at depths of 13 nm and 21 nm. No Ag NP at the surface was obtained. The surface layer of Ag observed by HRBS was probably removed during preparation of TEM samples. After annealing at 700°C (Fig. 3(b)), all the Ag NPs were obtained at the same depth of 20 nm, with the minimum distance of 2 nm from the interface. The particle size was almost 7 nm in diameter. The position of formed Ag NPs well
agreed with the peak depth of remained Ag atoms in the HRBS at 700°C. After annealing at 800°C, no particle was observed inside the SiO₂ layer as shown in Fig. 3(c). However, some wedge-like things were observed in the interface region of SiO₂/Si. This was reactant of Ag and Si after diffusion of Ag atoms to the interface.

4. Discussion

4.1. Ag Thermal Diffusion

The surface segregation of Ag for the as-implanted sample and after annealing at 500°C was not predicted from the TRIM-DYN calculation. This segregation is considered to be due to thermal diffusion during implantation procedure. The local temperature near the ion-penetrating path increased due to nuclear collision by primary ion and recoil atoms. Then, it might enhance thermal diffusion of Ag atoms to the surface, resulting the surface layer of Ag. Comparison with two depth profiles of the as-implanted and after annealing at 500°C suggested that the effective temperature for Ag diffusion is estimated to increase up to near 500°C.

4.2. Diffusion Barrier

After annealing at 500°C, three segregations of Ag atoms, excepting the Ag layer at the surface, obtained by HRBS are at depths of 6, 12 and 22 nm. In the energy loss process in ion implantation at 10 keV in SiO₂, the depth distribution of displacement energy of target atoms is calculated to have a peak at a depth of 6.5 nm by TRIM-DYN. Such displacement energy might result many damages such as oxygen deficit or voids even in the amorphous SiO₂. Therefore, the segregation of Ag at 6 nm is considered to be contributed by ion-induced effect. The large segregation of Ag atoms at 12 nm in HRBS well agreed with the calculated projected range of Rp and also with the peak depth (13 nm) of the Ag NPs in TEM image of Fig. 3(a) and its histogram of Fig. 4. The small segregation of Ag atoms at 22 nm in depth in HRBS was not predicted by the TRIM-DYN calculation. However, this depth of 22 nm is well corresponded to the second peak depth (21 nm) of Ag NPs in Fig. 4. These deepest Ag NPs are considered to mostly align at the depth. This alignment suggests a certain diffusion barrier near the depth of 22 nm. After annealing at 700°C, the segregation of Ag atoms in HRBS (Fig. 2) at the depth of 20 nm well agreed with the position of mono-layered Ag NPs in TEM (Fig. 3(c)) at 20 nm in depth. It is considered that the Ag atoms diffused toward the deeper side from the implanted depth were trapped at the depth of 22 nm and then accumulated here. As a result, the diffusion barrier exists at a vicinity distance from the interface of SiO₂/Si. However, the barrier lost its effect to the thermal diffusion of Ag atoms at 800°C.

Although the reason for the barrier is not understood, the followings are considered for resulting density change in SiO₂. The thermally grown silicon dioxide on Si substrate is generally amorphous. On the other hand, Si substrate is a single crystal with a periodic regularity. In the oxidation process, oxygen atoms at first bind the surface Si atoms. Then, O atoms gradually invade between Si-Si bonding to grow the SiO₂. Therefore, the regularity of Si crystal is expected to affect SiO₂ formation in
configuration in a vicinity region at the interface SiO₂/Si. The transition region in SiO₂ facing to Si substrate was stressed to increase the density a little in compassion to the normal amorphous SiO₂. This is considered to act as a diffusion barrier of Ag atoms. Owing to this diffusion barrier, monolayered Ag NPs were formed at a bottom region of the oxide layer.

4.3. Atomic Concentration and NP Size
Particle size is related to the density and diffusion length of implanted atoms at the annealing temperature. Particle density depends on the diffusion length. In simple case where the diffusion length at a temperature is comparable with distance between particles, the particles with the same size uniformly formed after annealing. The diameter is proportional to the cubic root of the average atomic density. From results of HRBS after annealing at 500°C, an average Ag concentration in 3 – 23 nm depth range is calculated to be about 0.53 at.% as assuming the surface Ag segregation was excluded. The diameter of Ag NPs at 500°C was 4 nm from Fig. 3(a). Then, in the estimation with the above relation between the diameter and the concentration, the Ag concentration of 1.7 – 2.8 at.% is required for Ag NPs with diameters of 6 – 7 nm as seen in Fig. 3 (b) after annealing at 700°C. On the other hand, the Ag distribution obtained by HRBS at 700°C has a peak concentration of 2.89 at.% and FWHM of 6.3 nm, i.e. the average Ag concentration is 1.5 at.%. Thus, the above relationship between particle size and the atomic concentration is roughly acceptable to estimate sizes of Ag NPs in SiO₂.

5. Conclusion
We have investigated depth profile of Ag atoms implanted in thermally grown SiO₂ layer on silicon substrate by the HRBS method for as-implanted and after annealing at various temperatures. The surface layer of Ag atoms of samples as-implanted and after annealing at 500°C is considered to be due to local heating during implantation. After annealing at 500°C, one large and two small segregations of Ag were detected inside the layer. The large one is placed at the depth corresponding to the mean projected range. Others were at 6 nm in depth near the surface and at 22 nm in the oxide layer near the interface of SiO₂/Si. The deep segregation is expected to be due to density change of SiO₂ in the transition layer in the vicinity of the interface. This transition layer worked at a diffusion barrier up to a temperature of 700°C. Owing to this barrier, we obtained mono-layered Ag NPs along the interface, from which the minimum distance of 2 nm. The aligned Ag NPs were confirmed by cross-sectional TEM.

References
[1] K. Yano, T. Ishii, T. Hashimoto, T. Kobayashi, F. Murai, and K. Seki, *IEEE Trans.*, ED 41, 1628-1638 (1994).
[2] H. Tsuji, N. Arai, T. Matsumoto, K. Ueno, Y. Gotoh, K. Adachi, H. Kotaki, and J. Ishikawa, Appl. Surf. Sci., 238, 132-137 (2004).
[3] A. Nakajima, T. Futatsugi, N. Horiguchi, and N. Yokoyama: *Apple. Phys. Lett.* 71, 3652-3654 (1997).
[4] Y. Takeda, C.G. Lee, N. Kishimoto, *Nucl. Instr. and Meth.*, B 191, 422-427 (2002).
[5] K. H. Heinig, T. Mueller, B. Schmidt, M. Strobel, and W. Moeller, *Appl. Phys.*, A 77, 17-25 (2003).
[6] H. Tsuji, N. Arai, T. Matsumoto, K. Ueno, K. Adachi, H. Kotaki, Y. Gotoh, and J. Ishikawa, Surf. Coat. Tech., 196, 39-43 (2005).
[7] J. Ishikawa, H. Tsuji, N. Arai, T. Matsumoto, K. Ueno, K. Adachi, H. Kotaki, and Y. Gotoh, *Nucl. Instr. Meth.*, B 237, 422-427 (2005).
[8] H. Tsuji and J. Ishikawa, Rev. Sci. Instrum., 63, 2488-2490 (1992).
[9] H. Tsuji, J. Ishikawa, Y. Gotoh, and Y. Okada, AIP Conf. Proc., 287, 530-536 (1994).
[10] J.P. Biersack, Nucl. Instr. Meth., B 27, 21-36 (1987).
[11] H. Tsuji, Y. Gotoh, J. Ishikawa, Nucl. Instr. and Meth., B 141, 645-651 (1998).