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Diffusion Barrier for Silver Atoms in Thermally Grown Oxide Layer on Silicon and Mono-Layered Ag Nanocrystals Formed by Negative-Ion Implantation and Subsequent Annealing

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Thermal diffusion behavior of implanted silver atoms has been investigated by using a high-resolution RBS measurement during formation process of mono-layered Ag nanoparticles in a thermally grown thin oxide layer on silicon. Ag atoms were implanted by negative ion implantation at 10 keV with $5x10^{15}$ ions/cm^2 into the 25 nm-thick SiO_2/Si. Samples were annealed at 500 - 800°C for 1 h under Ar gas flow. At annealing temperature of 500°C, implanted Ag atoms distributed at the surface and at a depth corresponded to the calculated profile. It is expected that the surface accumulation of Ag atoms resulted from thermal diffusion of implanted atoms during implantation. At 500°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. The diffused atoms accumulated at this depth. At 700°C, the main peak of concentration was appeared at 20 nm in depth, where FWHM was 7 nm. These results well corresponded to the mono-layered Ag nanocrystals observed by HR-TEM.

Key words: Thermal diffusion, Silver nanocrystal, Negative-ion implantation, Annealing, Diffusion barrier

1. INTRODUCTION

Electrically 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 SiO_2/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 SiO_2 layer, an excess Si atoms sputtered from Si substrate into the SiO_2 could act as nucleation center [5]. In the low-energy implantation, however, the formation mechanism of nanoparticles aligned along the interface between SiO_2 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 SiO_2 on Si was investigated by using a high-resolution Rutherford backscattering spectrometry (HRBS) in order to detect the diffusion barrier.

2. EXPERIMENT

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 $^{107}Ag^-$ 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 5×10^{15} ions/cm^2 at a room temperature. The projected range of Ag atoms is calculated to be about 12 nm in amorphous SiO_2 with 2.20 g/cm^3 by the transport of ion in matter (TRIM-DYN) program [10]. This range corresponds to about a half depth of the SiO_2 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 SiO_2 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. Figure 1 shows the configuration of HRBS measurement system. The beam energy and current intensity of the probe beam (2 x 2 mm^2) 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 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. RESULTS

3.1 Calculated Distribution of Implanted Ag Atoms

The calculated depth profile of implanted Ag atoms in amorphous SiO_2 is shown in Fig. 2 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%.

3.2 Distribution of Implanted Ag Atoms by HRBS

We obtained HRBS spectra near the surface region as shown in Fig. 3, where arrows at 364 and 284 keV indicate the Ag and Si (in SiO_2) surface edges. The spectra of as-implanted and after 500°C-annealing sample show two Ag peaks and many small ones. The main peaks near 364 eV indicate surface layer of Ag atoms. Other peaks in a range of 320 – 360 keV indicate Ag accumulation inside the SiO_2 layer. HRBS yields at energy range less than 255 keV were contributed by Si atoms in Si substrate.

Figure 4 shows Ag concentrations for the samples annealed at various temperatures. As a standard density for obtaining Ag concentration in the SiO_2 layer in the quantitative analysis, Si yield around 280 keV from the SiO_2 layer after correction by the total fluence of He ions was used. Since the SiO_2 layer is amorphous, it was then applied as a standard even when channeling in Si substrate was happened. 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

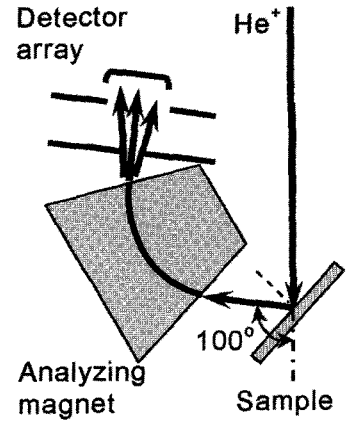

Fig. 1. Schematic configuration of a measurement system for high-resolution Rutherford back- scattering spectrometry (HRBS).

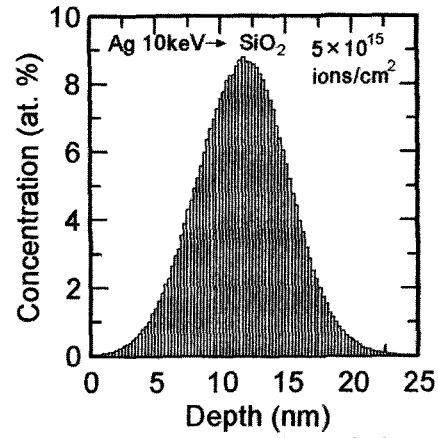

Fig. 2. Estimated concentration of Ag atoms implanted into SiO_2 medium at 10 keV with 5 x 10^{15} ions/cm^2 calculated by TRIM-DYN program.

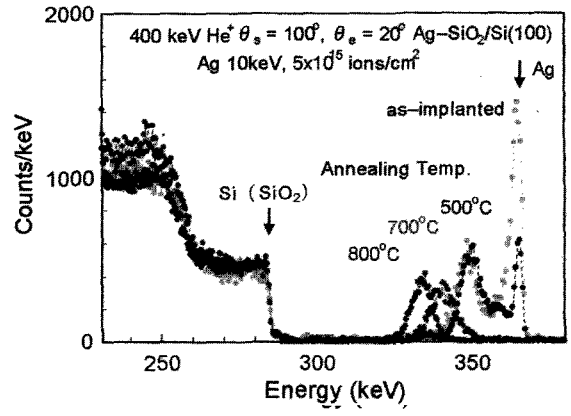

Fig. 3. HRBS yields of Ag-implanted SiO_2/Si samples before and after annealing at various temperatures of 500°C, 700°C and 800°C.

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.

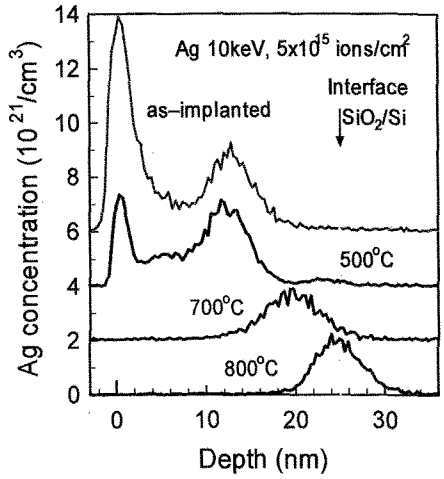

Fig. 4. Depth profiles of Ag atoms implanted SiO_2 layer before and after annealing at various temperature of 500°C, 700°C and 800°C by HRBS data (from Fig. 3).

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.

3.3 Ag Nanoparticles

Figure 5 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. 5(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. 5(a) is shown in Fig. 6. 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. 5(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 SiO_2 layer as shown in Fig. 5(c). However, some wedge-like things were observed in the interface region of SiO_2/Si. This was reactant of Ag and Si after diffusion of Ag atoms to the interface.

4. DISCUSSION

4.1 Ag Thermal Diffusion During Implantation

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

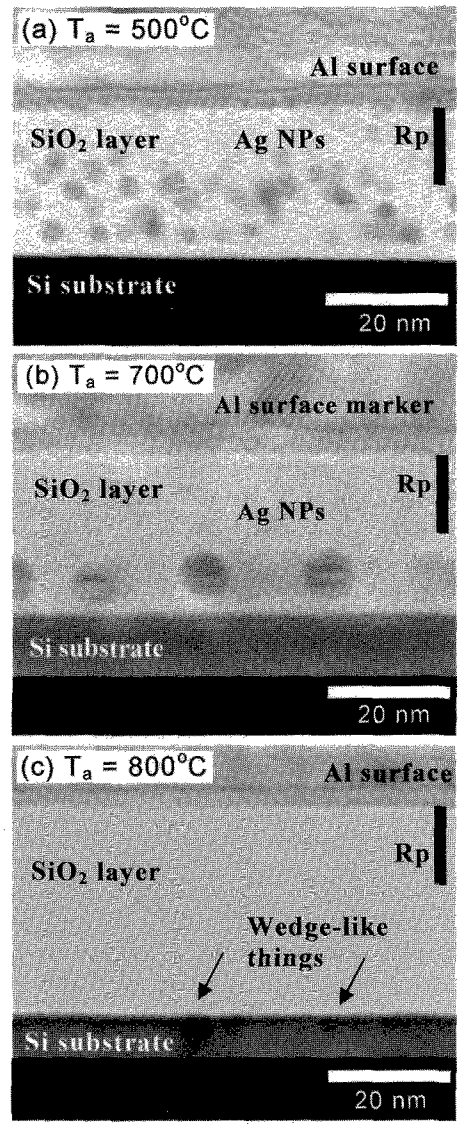

Fig. 5. Cross-sectional TEM images of Ag-implanted 25-nm-SiO_2 layers on Si samples at 10 keV with 5 x 10^{15} ion/cm^2 after annealing at various temperatures of (a) 500°C, (b) 700°C and (c) 800°C.

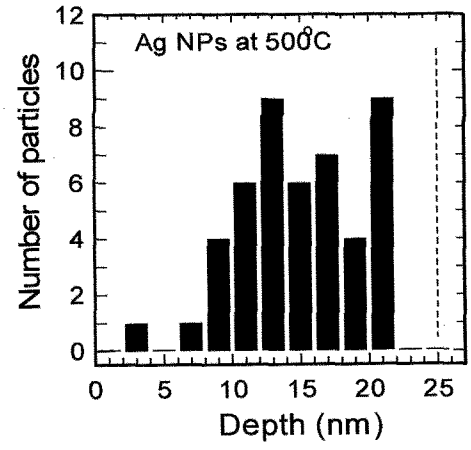

Fig. 6. Histogram of Ag NPs formed in 25-nm-SiO_2 layers after annealing at 500°C (from Fig. 5(a)).

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 Ag Thermal Diffusion and 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 SiO_2, 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 SiO_2. 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. 5(a) and its histogram of Fig. 6. 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. 6. 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. 4) at the depth of 20 nm well agreed with the position of monolayered of Ag NPs in TEM (Fig. 5(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 SiO_2/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 SiO_2. 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 SiO_2. Therefore, the regularity of Si crystal is expected to affect SiO_2 formation in configuration in a vicinity region at the interface SiO_2/Si. The transition region in SiO_2 facing to Si substrate was stressed to increase the density a little in compassion to the normal amorphous SiO_2. This is considered to act as a diffusion barrier of Ag atoms. Owing to this diffusion barrier, mono-layered Ag NPs were formed at a bottom region of the oxide layer.

4.3 Atomic Concentration and Nanoparticle 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. 5(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. 5 (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 SiO_2.

5. CONCLUSION

We have investigated depth profile of Ag atoms implanted in thermally grown SiO_2 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 SiO_2/Si. The deep segregation is expected to be due to density change of SiO_2 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.

5. REFERENCES

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