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Silver Nanoparticle Formation in SiO_2 Film by Negative-Ion Implantation for Single Electron Device

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Formation of silver nanoparticles in a thin SiO_2 films by silver negative-ion implantation was investigated for single electron memory device. Silver negative ions were implanted into 50-nm-thick SiO_2 film on Si substrate at 30 keV with dose in a range from 1×10^{15} to 1×10^{17} ions/cm^2. After implantation, the samples were subsequently annealed in Ar gas flow for 1 h at temperature in a range from 150 to 900 °C. The projected range at 30 keV is 25 nm and peak concentration of Ag atoms is estimated to be 0.8 at. % for 1×10^{15} ions/cm^2 in TRIM-DYN. Cross-sectional TEM observation showed that the nanoparticles with 2-3 nm in diameter were formed in the samples after annealing at temperature below 800°C and even in as-implanted one. The size of such nanoparticle is considered to be sufficiently small to obtain Coulomb blockade at room temperature. In the I-V characteristics measured with Au electrode with 2 mm in diameter, current steps were appeared with a voltage interval of about 0.12 V. These steps are considered to be Coulomb stairs by small nanoparticles with about 3 nm in diameter. The size well agreed with the result of the cross-sectional TEM observation.
Key words: Ion implantation; Nanoparticle; Coulomb blockade; Single electron memory

1. INTRODUCTION

Nanoparticles embedded in oxide materials have gathered much attention because of their capability to exhibit unique electrical properties due to quantum effect [1, 2], and their large nonlinear and fast response optical properties [3, 4]. Especially the electronic property such as coulomb blockade and coulomb stair due to metal nanoparticles in oxide film on Si is expected for development of single electron devices. Their properties deeply depend on nanoparticle state in the film such as particle size, depth distribution, density, and distance from the electrode. Ion implantation technique is expected as an attractive method for doping metal atoms at certain depth in the film and forming nanoparticles with a certain size by a subsequent heat treatment [5]. The negative ion implantation can avoid an uncertainty of implantation by its "charge-up free" property due to using negative ions as implant particle [6-8]. Therefore, the negative ion implantation is suitable to create metal nanoparticles with well-controlled size and distribution profile in a thin oxide film.

2. SIZE OF NANOPARTICLE FOR COULOMB BLOCKADE.

The required size of nanoparticles for coulomb blockade at room temperature is considered in a simple case where one metal nanosphere in a oxide film with a distance d from Si substrate. When an electron entered the metal nanosphere in the oxide film from the Si electrode through a tunneling junction, the electrostatic energy of the nanosphere increased by $e^2/2C$, where the nanosphere has a capacitance of C in the system. Therefore, this energy should be sufficiently more than the thermal energy of free electrons, k_BT, to suppress the thermal tunneling. This requirement is given by

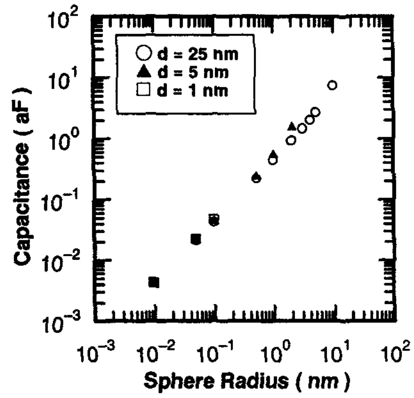


Figure 1. Capacitance of a nanosphere in SiO_2 on an electrode as a function of the radius.

$$e^2/2C \gg k_BT \tag{1}$$

$$\text{then, } C \ll 3.1\ [\mathrm{aF}] \quad (\text{at } 300\mathrm{K}), \tag{2}$$

The capacitance of the nanosphere in the above simple system is calculated and given by

$$C = 2\pi\varepsilon_0\varepsilon_r\sqrt{d^2-4r^2}\sum_{j=0}^{\infty}\left[\coth\left\{\left(j+\frac{1}{2}\right)\mathrm{arccosh}\left(\frac{d}{2r}\right)\right\}-1\right] \tag{3}$$

$$C \approx 4\pi\varepsilon_0\varepsilon_r r\left(1+{r}/{2d}\right) \quad (r << 2d) \tag{4}$$

where ε_0 and $\varepsilon_0\varepsilon_r$ are dielectric constants of vacuum and the insulator, respectively, and r is the sphere radius, d is distance of tunneling junction between the sphere and the electrode. The calculated capacitance of sphere with radius of r in SiO_2 is shown in Fig. 1 for various tunneling distances of d = 1, 5, and 25 nm. The capacitance is almost proportional to the sphere radius and hardly dependents on the distance. Taking account of high-energy tail of free electrons, the required particle radius should be less than 2 nm for the capacitance less than 1aF.

3. EXPERIMENTAL

Silver negative ions were implanted at 30 keV to a thermally grown 50-nm-thick SiO_2 film on a n-type Si substrate with various doses of $1x10^{15}$, $1x10^{16}$ and $1x10^{17}$ ions/cm^2 by a negative ion implanter [9]. The silver negative ions were produced by an RF plasma sputtered heavy negative ion source [10,11] and after mass-separated the Ag negative ion beam was transported to the implantation chamber. During the implantation, the current density and residual gas pressure were about 2μA/cm^2 and less than $1x10^{-4}$ Pa, respectively. The projected range of Ag atoms for the implantation energy of 30keV is calculated to be 25 nm in SiO_2 (amorphous, 2.2 g/cm^2) by TRIM and it corresponds to a half of thickness of the SiO_2 film. Subsequent thermal annealing was carried out in Ar gas flow at temperature in range 100 - 900 °C for 1 h in a fused quartz tube by an electrical oven. As references, silver negative ions were also implanted into silica glass (T-4040, fused quart glass, 0.5 mm in thickness, Toshiba Ceramics) at the same condition.

Ag-implanted SiO_2 film on Si was measured its optical reflectivity spectra by a spectrometer (MPS-2000, Shimadzu) in range from 200 to 1100 nm. For reference, Ag-implanted silica glass was measured its transmittance and reflectivity spectra. For obtaining real size of created Ag nanoparticles in SiO_2 film, cross-sectional transmission electron microscopic (TEM) images were observed by a scanning TEM (HD-2000, 200keV, Hitachi).

For the electronic property, I-V characteristics of the Ag-implanted SiO_2 film on Si were measured.

4. DEPTH PROFILE OF Ag BY TRIM-DYN

Effects of sputtering and scattering by implanted atoms are considered to be not negligible for low energy and high dose such as 30keV and $1x10^{17}$ ions/cm^2. We calculated depth profile of implanted Ag atoms in amorphous SiO_2 (2.2 g/cm^3) by a dynamic Monte Carlo simulation program of TRIM-DYN which includes sputtering effects [12]. The calculated profiles of Ag atoms are shown in Fig. 2. The projected range for relatively low dose cases is almost the same as the value calculated by the simple TRIM and the depth profiles showed a Gauss distribution. At 30 keV with dose of $1x10^{15}$ and $1x10^{16}$ ions/cm^2, Ag concentrations at the peak are 0.8 at.% and 8 at.% in SiO_2, respectively. For $1x10^{17}$ ions/cm^2, the implanted Ag atoms were almost uniformly distributed with 20 - 30 at.% from the surface to over 20 nm, and the profile was far from the Gauss distribution due to sputtering and scattering by already doped Ag atoms.

5. OPTCAL PROPERTIES

5.1 Optical Reflection properties of Ag-implanted SiO_2

The optical properties of transmittance and reflectance for Ag-implanted sample with $1x10^{16}$ ions/cm^2 are shown in Fig. 3 after various heat treatments; (a) for silica glass and (b) 50-nm SiO_2 film on Si. In the silica sample of Fig. 3(a), clear absorption peaks were observed at near 400 nm in the transmittance spectra. From the Mie theory, the absorption peak due to surface plasmon resonance (SPR) of Ag nanospheres is calculated to appear at wavelength of 400 nm [13]. This means that Ag nanoparticle were formed in the silica glass. The average diameter of formed nanoparticles is roughly estimated to be several nm in comparison of FWHM of calculated and measured SPR absorption spectra. In the reflectance spectra, the minimum points appeared at different wavelength from those of the absorption peak in corresponded transmittance spectra. This is due to interference of reflection waves except only the sample annealed at 800°C. As for SiO_2 film on Si of Fig. 3(b), the minimum peak in reflectance spectra appeared at 450 nm and disagreed with the wavelength of the theoretical absorption. This result means that the nanoparticles were formed in a local layer within the implanted region and that reflectance was resulted by the interference among each reflection from boundaries.

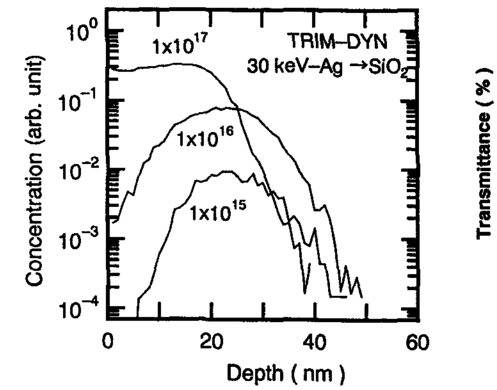


Figure 2. Depth profile of implanted Ag atoms in amorphous SiO_2 simulated by TRIM-DYN.

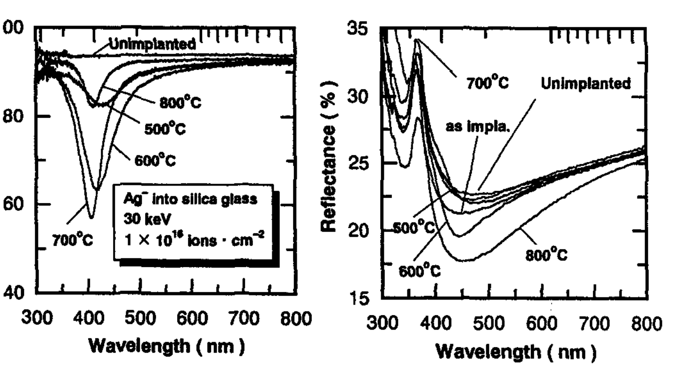


Figure 3. Optical transmittance spectra of (a) the Ag-implanted silica glass and (b) reflectance spectra of the Ag-implanted 50-nm SiO_2 film on Si.

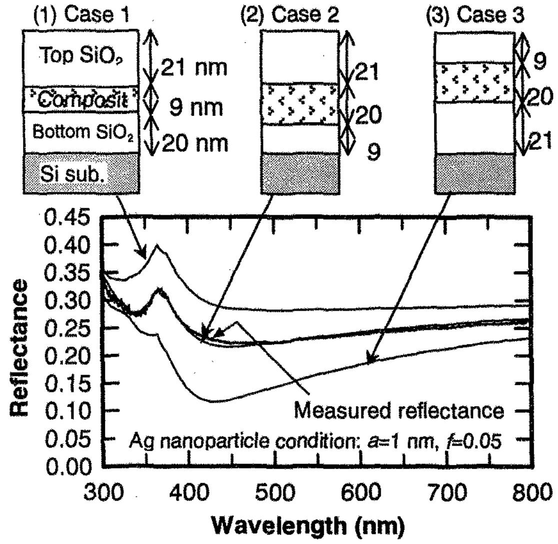


Figure 4. Fitting of reflectivity spectra for Ag-implanted 50-nm-thick SiO_2 film on Si with 1×10^{16} ions/cm^2 after annealing at 500°C.

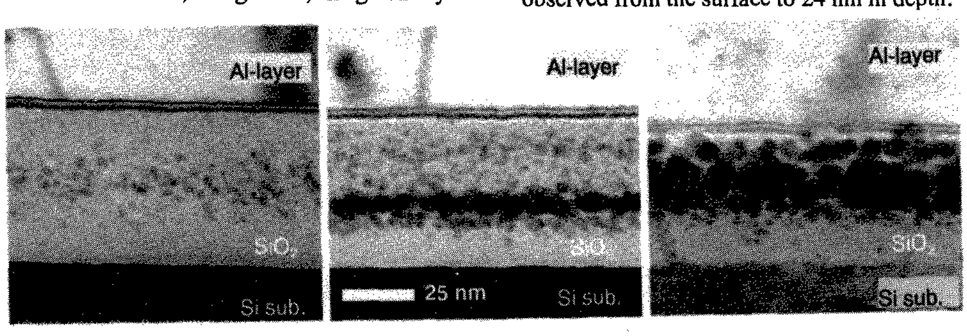
5.2 Calculation of Reflection from Three Layers on Si

As the simplest case, a composite layer uniformly including uniformly nanoparticles is considered to be formed in a position almost corresponded to implanted layer in the oxide film on Si substrate as a schematic diagram of this three layers on Si are shown in Fig. 4. The total reflection is calculated with all complex optical constants for each layer and Si substrate [14]. The complex optical constants or complex dielectric constants for amorphous SiO_2 and Si substrate are appeared in the data book and well known. For the composite layer including Ag nanoparticles, the complex dielectric constant is depended on the size and density of Ag nanoparticles. The effective dielectric constant of the composite medium is given by Maxwell-Garnett theory [15] with medium and metal nanoparticle dielectric constants including the size dependent corrections and the volume fraction, i.e. the occupied volume by metal nanoparticles in medium. The complex dielectric constant of metal, in general, is given by summation of Drude term due to free electrons in a conduction band and the interband term due to transition from a valence band to the Fermi level. We calculated the dielectric constant of Ag nanosphere by summation of theoretically calculated Drude term with the effective plasma extinction coefficient including size correction in the relaxation time [15] and measured interband term of bulk silver.

The calculated reflection for the three layers structure on Si was obtained as a function of the wavelength with assumption of Ag nanosphere size, the volume fraction, thickness of each layer in 50 nm thick SiO_2 on Si substrate. The calculated reflection spectra can be fitted to the measured spectra by choosing optimum values in range. For an example, the calculated spectra fitting to the reflection data for Ag-implanted oxide film with 1×10^{16} ions/cm^2 after 500°C are shown in Fig. 4. The fitting conditions in the figure are as follows; radius of Ag nanoparticle is 1 nm, volume fraction 0.05, the thickness of the top SiO_2 layer, the composite layer and the bottom SiO_2 layer are d_1 = 21 nm, d_2 = 20 nm, and d_3 = 9 nm, respectively. Although there is still difference between two reflectance, these two curves are considerably well corresponded. Therefore, the estimated average diameter of Ag nanoparticle is about 2 nm. In the sample of 1×10^{17}, the average diameter was estimated to be about 8 nm in the region from 10 to 20 nm in depth. The fitting is difficult for the sample of 1×10^{15} ions/cm^2, because that the sample showed very small change in reflectivity from the unimplanted sample.

6. TEM OBSERVATION

Fig. 5 shows cross-sectional TEM images of Ag-implanted 50-nm-thick SiO_2 film on Si with various doses after annealing at 500°C. In Fig.5(a) of 1×10^{15}, the Ag nanoparticles with diameter of 2 - 3 nm appeared in the center region of 15 - 35 nm in depth, and the film thickness is 52nm. For the sample of 1×10^{16} in Fig. 5(b), the film thickness decreased to 49 nm due to sputtering effect. It was found that the almost Ag nanoparticles with various size in 2 - 6 nm in diameter located at region from 24 to 37 nm in depth. In Fig. 5(c) for 1×10^{17}, Ag nanoparticles with various size in 4 - 10 nm were observed from the surface to 24 nm in depth.



(a) Ag^+: 1×10^{15} ions/cm^2 (b) Ag^+: 1×10^{16} ions/cm^2 (c) Ag^+: 1×10^{17} ions/cm^2

Figure 5. Cross-sectional TEM images of Ag-implanted 50-nm-thick SiO_2 film on Si after annealing at 500°C.

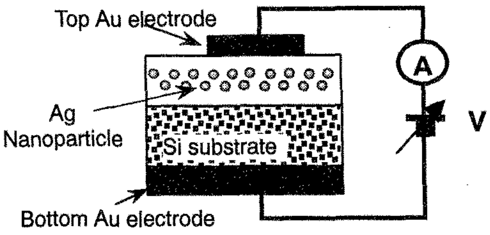


Figure 6. Schematic configuration of the measurement system for *I-V* characteristics of Ag-implanted SiO_2 film on Si substrate.

The above estimation of Ag nanoparticle formation from the reflection spectra for the sample of $1x10^{16}$ has a considerably good agreement with the TEM observation, although the difference between measured and calculated reflectivity existed due to assumption with simple one composite layer with uniform size in the calculation. When the finer layer structure with two or more composite layer including different size and volume fraction of Ag nanoparticles is assumed, the better fitting will be obtained.

7. I-V CHRACRTERISTICS

Fig. 6 shows a schematic configuration of the *I-V* measurement system. Top circle Au electrode with diameter of 2 mm was deposited on the SiO_2 film and also the bottom Au electrode on the rear Si substrate without Shottky-diode contact. By changing voltage applied to the top and bottom electrode, the *I-V* characteristics were measured at room temperature.

The obtained *I-V* curves are shown in Fig.7, where the sample was the $1x10^{15}$-Ag-implanted SiO_2 film on after annealing at 700 °C. The steps in the current are clearly observed in the *I-V* curve for both case of increasing and decreasing applied voltage even in the measurement at room temperature. The step width in voltage is in 0.10 - 0.14 V. These voltage shielding were considered to be caused by Coulomb blockade of Ag nanoparticle created in the SiO_2 film. In this case, the nanoparticle is to have small capacitance of 0.6 - 0.8 aF. Then, the radius of the nanoparticle is considered to be 1.1 -1.5 nm (2 - 3 nm in diameter) from the Eq. (4) as seen in Fig.1. This result is in good agreement with the size of Ag nanoparticles obtained by TEM observation.

8. CONCLUTION

Ag nanoparticles with diameter of 3 nm were formed in the center region of the 50-nm-thinck SiO_2 film on Si by silver negative-ion implantation. The Ag-implanted SiO_2 film showed clear steps in *I-V* curves measured at room temperature. The implantation conditions were Ag negative ion, 30 keV, $1x10^{15}$ ions/cm^2 and annealing at 700°C. These steps are considered to be due to Coulomb blockade by Ag nanoparticles. As a result, negative ion implantation was found to be applicable to form metal nanoparticle with sufficiently small size for obtaining Coulomb blockade phenomena at room temperature.

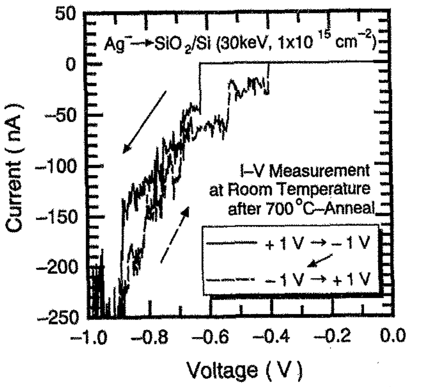


Figure 7. *I-V* characteristics of the Ag-implanted SiO_2 film on Si at 30 keV, $1x10^{15}$ ions/cm^2 after annealing at 700°C.

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