Effect of dual implantation with Ag and Ni ions on the optical absorption of silica glass

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Effects of dual implantation with Ag and Ni ions on the optical absorption of silica glass were investigated. The surface plasmon absorption spectrum after the dual implantation does not correspond to the sum of the spectrum for only Ag ion implantation and that for only Ni ion implantation. The experimental result suggests that morphology and/or the composition of Ag nanoparticles were changed by the subsequent Ni ion implantation. Furthermore, the result of positron annihilation coincidence Doppler broadening profile of Ag and Ni ion implanted sample also shows that the synthesized Ag nanoparticles is affected by the Ni implantation.

Key words: metal nanoparticles, ion implantation, amorphous glass, optical absorption

1. INTRODUCTION

Metal nanoparticles show specific electronic-states such as the nano-size periodicity of crystal unlike bulk metal. They are expected as new function materials due to their properties, such as catalysts [1], optical devices [2] and antibacterial agent [3]. The characteristic features of nanoparticles depend on the size, morphological shape, crystal structure and alloy components, but their correlations have never been clarified yet. Moreover, it is difficult to control them in the process of nanoparticle production in solids. Ion implantation is a candidate as one of the methods to synthesize the nanoparticles in solids. Hori *et al.* have reported that nanometer sized copper precipitates produced in a bulk iron material by copper ion implantation cause the increase in hardness [4, 5]. It has been reported that metal nanoparticles are produced in transparent SiO₂ glass by metal ion implantation [6-8]. It is well known that colloidal nanoparticles sometimes show characteristic optical absorption called the surface plasmon resonance (SPR). There are a lot of reports that observe the SPR peaks of synthesized nanoparticles by the single ion implantation. A lot of experiments using dual beam implantation have also been performed so far [9-12]. To synthesize composite nanoparticles, Shen *et al.* performed the dual beam implantation with low energy (60-70 keV) Ni and Ag ions and the subsequent annealing at elevated temperature [13]. The mechanism of the synthesis of the composite nanoparticles has, however, never been fully understood. In the present experiment, we have used the dual beam implantation with higher energy (200-380keV) Ag and Ni ions and tried to synthesize Ag and Ni composite nanoparticles without the subsequent annealing.

The reason why we focus on the production of Ag and Ni composite nanoparticles is that they have highly active catalyst and unique light absorption property, which have been reported by Kumar *et al.* [14].

2. EXPERIMENTAL PROCEDURE

High-purity amorphous silica glass (SiO₂) sheets (5 × 5 × 1 mm³) were prepared as an implantation target material. The SiO₂ targets were implanted firstly with 380 keV Ag ions and then 200 keV Ni ions at room temperature by using an ion implanter at Takasaki Advanced Accelerator Research Institute, Institutes for Quantum and Radiological Science and Technology (QST-Takasaki). The implantation fluence of Ag ions was 3 × 10¹⁶ ions/cm² and that of Ni ions was 6 × 10¹⁶ ions/cm². For comparison, the implantation only with Ag ions and that only with Ni ions were also performed. After the ion implantation, the optical absorption spectra were examined by using a UV-VIS [SHIMADZU 3100] scanning spectrophotometer with the wavelength of 200-800 nm. To characterize the local electron momentum distribution, the positron annihilation coincidence Doppler broadening (CDB) measurement was performed. ²²Na (200 kBq) was used as a positron source and the CDB spectra were measured with two Ge detectors in coincidence with total counts of more than 10⁸. The CDB ratio spectrum was obtained by normalizing the electron momentum distribution of each spectrum to that of the SiO₂ bulk before the implantation.

3. RESULTS & DISCUSSIONS

3.1 Single implantation with Ag or Ni

Fig. 1 shows the UV-vis absorption spectrum of the sample implanted with Ag ions. An absorption peak around 420 nm is clearly observed, confirming that Ag nanoparticles are definitely synthesized by Ag ion implantation without annealing.

Fig. 2 shows the UV-vis absorption spectrum of SiO₂ sample implanted only with Ni ions. In Fig. 2, we can not find any clear absorption peaks. Amekura *et al.* and Yeschenko *et al.* have reported that Ni nanoparticles have two SPR peaks [15, 16].

Fig. 1 UV-vis absorption spectrum of SiO₂ after 380 keV Ag ion implantation with the fluence of 3×10^{16} ions/cm².

Fig. 2 UV-vis absorption spectrum of SiO₂ after 200 keV Ni ion implantation with the fluence of 6×10^{16} ions/cm².

Amekura *et al.* have also reported that for the synthesis of Ni nanoparticles in SiO₂, the thermal annealing at elevated temperatures after the ion implantation is indispensable. According to their experimental result, the two broad peaks appear around 214 nm and 387 nm after the thermal annealing, and the mean diameter of Ni nanoparticles was 2.9 nm [15]. The result in Fig. 2 implies that without the thermal annealing, Ni nanoparticles are not produced in SiO₂ because Ni ions cannot sufficiently diffuse in the sample at room temperature, and if any, their size of Ni nanoparticles is smaller than 2.9 nm. On the other hand, for the Ag ion implantation, as can be seen in Fig. 1, the SPR peak of Ag can be observed even for the half fluence (3×10^{16} ions/cm²) and the synthesis of Ag nanoparticles is confirmed.

3.2 Dual implantation with Ag and Ni ions

Fig. 3 shows the depth profiles of 380 keV Ag and 200

keV Ni ions which were calculated by SRIM code 2008 [17]. 200 keV Ni and 380 keV Ag ions are accumulated almost at same depth in SiO₂.

Fig. 4 shows the schematic drawing of the process of Ag and subsequent Ni ion implantation in SiO₂. Firstly, the SiO₂ sample was implanted with Ag ions, and we observed that Ag nanoparticles were synthesized in the sample. After the Ag ion implantation, the sample was implanted with Ni ions at almost the same implantation depth.

Fig. 3 Depth profiles of 380 keV Ag and 200 keV Ni ions in amorphous SiO₂ which are calculated by SRIM code.

Fig. 4 Schematic illustration of the process of Ag and subsequent Ni ion implantation into SiO₂.

Fig. 5 Sample photos of SiO₂ after Ag and Ni ions implantation. (a) Ni ion implantation with the fluence of 6×10^{16} ion/cm² (b) Ag ion implantation with the fluence of 3×10^{16} ions/cm², and (c) Ni ion implantation of 6×10^{16} ions/cm² after Ag ion implantation of 3×10^{16} ions/cm².

Fig. 5 shows the color change of the samples by the three kinds of the implantations. At least, to the naked eye, the effect of subsequent Ni ion implantation on the color of the sample can not be recognized.

Fig. 6 UV-vis absorption spectra for (a) implantation only with 380 keV Ag to the fluence of $3 \times 10^{16}/\text{cm}^2$, (b) implantation only with Ni ions to the fluence of 6×10^{16} ions/ cm^2 , and (c) implantation with Ag ions and Ni ions. In the figure, the sum of the spectrum for Ag implantation and that for Ni implantation (indicated by (d)) is also shown.

Fig. 6 shows the optical absorption spectrum for the SiO_2 sample implanted with Ag and Ni ions. For comparison, the spectra for only Ag ion implantation and only Ni ion implantation are shown in the figure. If the Ag ion implantation and the Ni ion implantation independently contributed to the optical absorption for the dual ion implanted sample, the spectrum for the dual ion implantations would be the same as the sum of the two spectra for only Ag ion implantation and only Ni ion implantation, which is also plotted in Fig. 6. To compare clearly the shape of the spectrum for the dual beam implantation and that of the sum of two spectra, the intensities of both spectra are normalized as the areas of the both spectra become unity. As can be seen in Fig. 5, the color of the sample implanted with only Ag ions is orange, since the SPR peak is around 400nm. The color of sample implanted only with Ni ions is gray, because the optical absorption occurs over the wide wavelength range. Although the shape of the spectrum for the dual implantation is different from that for only Ag ion implantation, the effect of the Ni ion implantation on the sample color is hardly observed.

The experimental result for the dual implantation with Ag and Ni ions (spectrum (c) in Fig. 6) is quite different from the sum of the two spectra for only Ag and only Ni ion implantation (spectrum (d) in Fig. 6). The present result shows that the Ag ion implantation and the subsequent Ni ion implantation do not independently contribute to the optical absorption, but the Ni ion implantation affects the Ag nanoparticles. The effects of Ni ion implantation on the SPR absorption peak for Ag nanoparticles are, (1) a small blue-shift of the Ag

SPR peak, and (2) an appearance of absorption shoulder at the longer wavelength of the Ag SPR peak.

Fig. 7 The graph is ratio curve of Ag-Ni alloy in glass and pure Ag and Ni bulk.

Possible reasons for the change in the SPR peak for the Ag nanoparticles are, (1) synthesis of composite nanoparticles with Ag and Ni atoms [9], (2) change in the morphology of Ag nanoparticles by the Ni implantation, [18], and (3) change in refractive index of SiO_2 matrix due to lattice defects induced by the Ni ion implantation

[10].

Positron annihilation spectroscopy characterizes the electronic structure of defects in solids. The CDB shows the elemental variations and their electron distribution around a defect and some elemental nanoparticles embedded in bulk materials [19-21]. Fig. 7 shows the CDB ratio curves of the silica glass implanted with Ag and Ni ions, and pure silver and nickel bulk. The horizontal line of unity corresponds to the silica glass without ion implantation. In the low electron momentum region, all of the CDB ratio are less than unity, meaning that positrons are annihilated in the region in which the electron density is higher than that of the bulk SiO₂ matrix. As the electron density is higher in metal nanoparticles than in SiO₂ matrix, the present result suggests that positrons are mainly annihilated in the metal nanoparticles. If the metal nanoparticles consisted of only Ag atoms, the CDB curve for the silica glass implanted with Ag and Ni ions would be the same as that for pure Ag. According to the experimental result in Fig. 7, however, the both CDB curves are not consistent with each other. Therefore, the nanoparticles synthesized by the dual implantation with Ag and Ni ions are possibly composite nanoparticles which include not only Ag atoms but also Ni atoms.

5. SUMMARY

The silica glass samples were implanted with Ag ions of 380 keV and subsequently Ni ions of 200 keV. The result of UV-vis absorption spectrum measurements shows that the optical absorption spectrum of Ag nanoparticles was affected by the Ni ion implantation. The CDB results show that in the sample with dual ion implantation, Ag nanoparticles have interaction with Ni atoms. One of the possible reasons for the change in SPR peak for Ag nanoparticles by the Ni ion implantation is the synthesis of Ag-Ni composite nanoparticles. To clarify the effect of Ni ion implantation on the Ag nanoparticles, we will characterize the microstructures and chemical binding of the nanoparticles synthesized by the dual implantation with Ag and Ni ions.

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