BL-27A, BL-27B/2022G039

Characterization of metal nanocomposite synthesized by ion implantation into amorphous SiO_2

F. Hori[1*], T. Yamada[1], S. Matsuo[1], A. Iwase[1], T. Matsui[1], N. Taguchi[2], S. Tanaka[2], S. Semboshi[3]
[1] Osaka Metropolitan University, Sakai, Osaka, 599-8570, Japan
[2] National Institutes of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Ikeda, Osaka, 563-0026, Japan.
[3]Tohoku University, Sendai, Miyagi, 980-8577, Japan

1 Introduction

Nano size materials have attracted tremendous attention due to their unique properties, such as luminescence, absorption, magnetic property, catalytic activity and hydrogen absorption. These properties come from their size, shape, alloy system and complex electronic state which is not appear in bulk materials. Metal ions implantation into solid is one of a method to synthesis of nanostructured material this is highly controlled impurity injection with high density of energy into solid. In some cases, metal nanoparticles are formed in silica glass without annealing by ion implantation. We suppose this method is useful to synthesize the new functional nanomaterials with control of alloy structures and phases. So far, we have successfully synthesized new functional nanoparticles in glassy solid by using this method [1,2]. In this study, amorphous SiO_2 was alternately irradiated with Ni and Ag ions at room temperature to investigate the effects of multi-ion irradiation and changing their irradiation order on the formation of nanoparticles in solid. We found that it is possible to form metal nano-composite and also the irradiation sequence affects the formation of Ag-Ni metal nano-composite. In this report, we will discuss the structure of nanoparticles synthesized by Ag and Ni ions irradiation in SiO_2.

2 Experimental

Amorphous silica glass (SiO_2: 5 × 5 × 1 mm^3) was used as an implantation target. The target was irradiated with 380 keV Ag ions and 200 keV Ni ions at room temperature by using ion implanter at TIARA, National Institutes for Quantum and Radiological Science and Technology (QST-Takasaki). Dual irradiation with Ag and Ni ions has done by changing irradiation order (AN: is irradiated firstly with Ag ions and followed by Ni ions, NA: is vice versa). The irradiation fluence of Ag ion is 5×10^{15} to 7×10^{16} /cm^2 and that of Ni ions was 1×10^{15} to 1×10^{17} /cm^2. In order to estimate the structure of synthesized nanocomposites in SiO_2, these samples were examined by XPS and EXAFS using X-ray at KEK BL27A and B, Grazing Incidence X-ray Diffraction (GIXD) and Scanning TEM with Energy dispersive X-ray spectroscopy (EDX) analysis. Also, the characteristic feature of these samples was measured by scanning TEM with energy dispersive X-ray spectroscopy (EDS) and UV-vis spectroscopy. Fig.1 shows the depth profiles of implanted ions of 380 keV Ag and 200 keV Ni calculated by TRIM, as compared with the result different energy of ions irradiated. By adjusting the ion energy, it is possible to deposit different ions to the same depth.

3 Results and Discussion

Figure 1 shows the UV-vis absorption spectra of Ag-Ni and Ni-Ag irradiation ordered samples. In general, it is known that some metal nanoparticles exhibit absorption peaks in the visible light band due to surface plasmon resonance (SPR) of electrons. In this figure, it can be seen absorption profile for each sample showing that formation of metal nanoparticle. However, SPR profile of synthesized nanoparticles by Ag-Ni and Ni-Ag irradiation are clearly different, despite implanting the same doses of

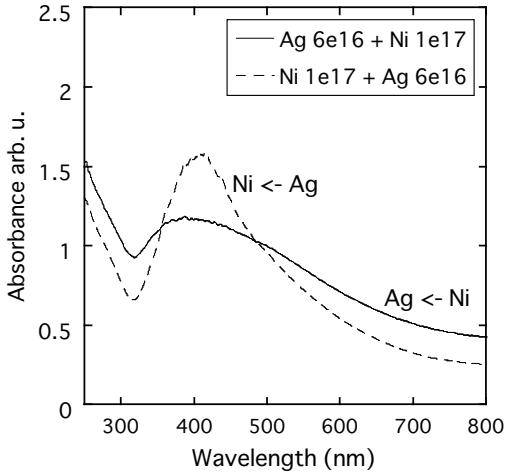

Fig. 1 UV-vis spectra of Ag and Ni ions irradiated SiO_2 glass samples.

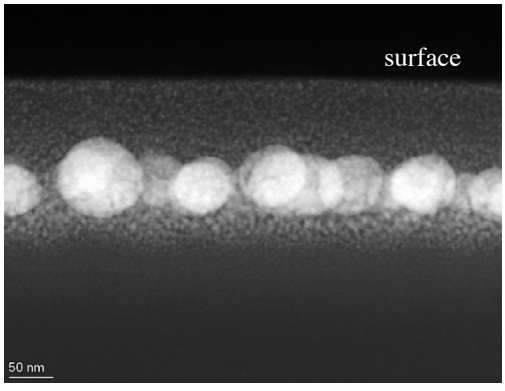

Fig. 2 STEM image of metal nanoparticles in SiO_2 fabricated by Ni-Ag irradiation sequence.

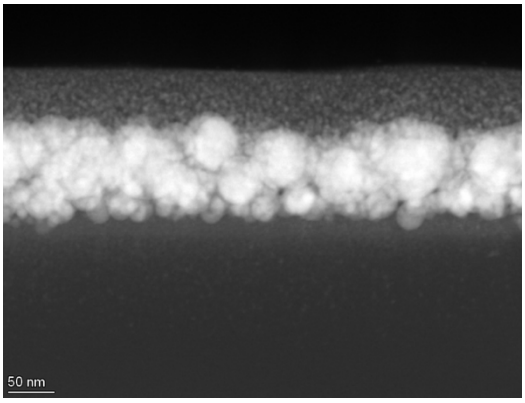

Fig. 3 STEM image of metal nanoparticles in SiO_2 fabricated by Ag-Ni irradiation sequence.

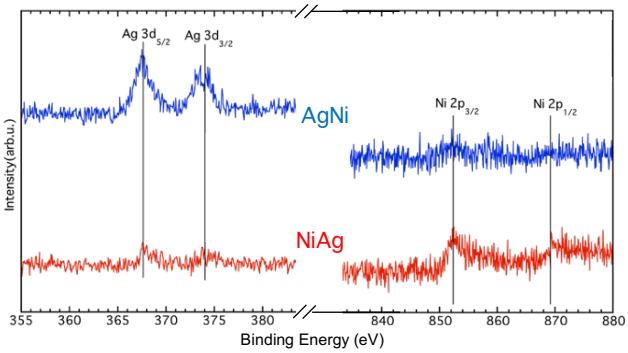

Fig. 4 XPS spectra of nanoparticles with respect to binding energies of Ag and Ni atoms of nano-composites in SiO_2 formed by Ag and Ni ions irradiation.

Ag and Ni. This indicates that the structure and electronic states of the formed nanostructures are different. It is clear from XRD results that a structure is formed in the glass, and a structure with an fcc structure has been confirmed in both irradiation sequence.

Figs. 2 and 3 show STEM images of fabricated metal nanoparticles in SiO_2 with different irradiation order. In both cases, the mean depth of fabricated nanoparticles almost the same, about 170 nm from the surface. This value well agrees with the result of the maximum depth of ion deposition calculated by TRIM code. However, the Ni-Ag distribution has a more localized formation depth of nanoparticles than the Ag-Ni distribution. Moreover, although the average diameters of nanoparticles under Ag-Ni irradiation is slightly smaller than that of Ni-Ag, the size distribution is also distinctly different. Therefore, it can be seen that the order of irradiation has an effect on the diffusion of implanted atoms.

Figs. 4 shows the XPS spectra of fabricated nanoparticles by Ag-Ni and Ni-Ag irradiation. The peaks corresponding to Ag and Ni can be observed in the XPS spectrum, respectively. This result suggests that atoms of either element of Ag and Ni contribute to the formation of these nanostructures with metallic bonds. However, the intensity is different, and the atom implanted by irradiation first shows a stronger intensity. This result also shows the alloy structure is not same for these nanoparticles. Formed

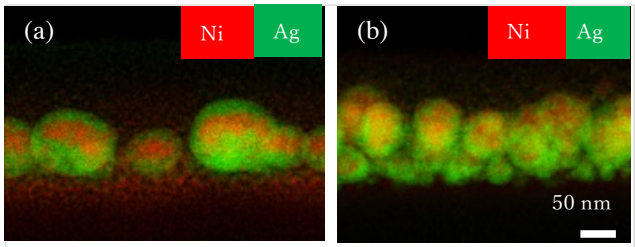

Fig. 5 STEM-EDX elemental analysis images of nanoparticle formed in SiO_2 by (a) Ni-Ag and (b) Ag-Ni irradiation sequence.

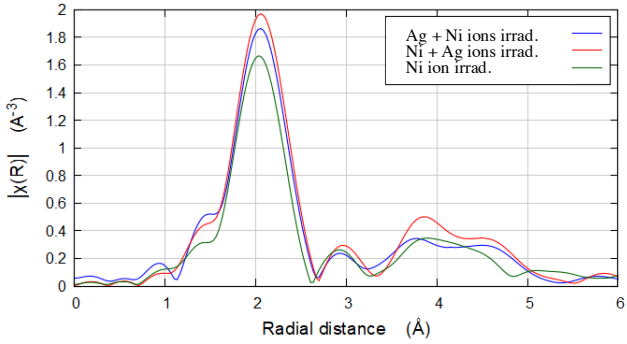

Fig. 6 EXAFS-FT spectra of the Ni absorption edge of SiO_2 irradiated with Ag and Ni ions in reverse order, and that of SiO_2 irradiated only with Ni ions for comparison.

nanoparticles were elemental analyzed by STEM-EDX mapping imaged depicted as in figure 5. As shown in these figures, Ni-Ag irradiation forms composite nanoparticles with core-shell-like discrete structure, while Ag-Ni irradiation forms mixed alloys or composites of homogeneously assembled small pure metal clusters. Fig. 6 shows that the EXAFS spectra of Ag-Ni and Ni-Ag irradiated SiO_2. In this figure, it can be seen that the Ni-Ni bond peak does not change, but their intensities are slightly different. This indicates that although the crystal structure is the same, there is a difference in the ratio of bonding species of Ni atoms in the particles, that is the solubility of Ni and Ag atoms. Thus, it was found that the order of irradiation has a great influence on the formation of nanostructures consist of implanted ions by irradiation of multiple metal ions into a glass solid. One of the reasons for the formation of different aggregates is thought to be the difference in the diffusion coefficient of each ion species within the glass solid.

Acknowledgements

The authors thank the technical staff of TIARA facility at QST-Takasaki. They also thank Drs. N. Usami, Y. Okamoto and Y. Baba for their kind help.

References

[1] T. Yamada *et al.*, Nanotechnology **31**, 455706 (2020).
[2] T. Yamada *et al.*, Trans. Mater. Res. Soc. Jpn. **45**, 127 (2020).

* horif@omu.ac.jp