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Irradiation sequence dependence on the state of Ag-Co metal nanocomplex synthesized by ion implantation into amorphous SiO_2

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1 Introduction

Nano size metal nanoparticles are known to exhibit unique properties such as photonic, magnetic and chemical properties due to quantum effects caused by discrete energy levels resulting from low crystal periodicity. In addition, their properties also depend on their size, shape, lattice structure, morphology, alloy composition and their atomic mixing state. Therefore, it is necessary to control these parameters to effectively utilize their properties. Ion irradiation into solids is one of useful methods to synthesis of nanoparticles with control such parameters. It is known that some kind of ions implanted into SiO2 move and form clusters during irradiation. So far, we have successfully synthesized new functional nanoparticles in glassy solid by using this method [1,2]. We found that it is possible to form Ag-Ni nanocomposite by this method [3]. Also, Co-Ag system is known as bulk-immiscible at room temperature. Some research has been carried out to synthesize Co-Ag composite nanoparticles, and they have been reported as materials that exhibit properties such as catalytic activity [4]. In our previous work, we have successfully synthesis of core-shell like Ag-Co nanocomposites in SiO_2 by Ag ion implantation after Co ion implantation. In this report, we would discuss the Co and Ag ions sequential irradiation dependence on the formation of nanocomposites into SiO_2 glass.

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 Co ions at room temperature by using ion implanter at TIARA, National Institutes for Quantum and Radiological Science and Technology (QST-Takasaki). The SiO_2 glass was first irradiated with Co ion, followed by Ag ion, and also in the reverse order. The implantation energies 200 keV for Co ions and 380 keV for Ag ions were determined as the same projected range of Ag and Co. The irradiation fluence of Ag and Co io n are both 6×10^{16} /cm^2. To estimate the structure of synthesized nanocomposites in SiO_2, these samples were examined by XAFS using X-ray at KEK-PF BL27, grazing incidence X-ray Diffraction (GIXD). Also, the characteristic feature of these samples was measured by scanning TEM with energy dispersive X-ray spectroscopy (EDS) and UV-vis spectroscopy.

3 Results and Discussion

Figure 1 shows STEM-EDS image of fabricated metal nanoparticles in SiO_2 with Co and Ag ions implantation with different irradiation order. We found that Ag-based nanoclusters were formed in both irradiation orders, but clear differences in the size and state of the particles were observed depending on the irradiation order. As shown in figure 2, it is also clear from XRD results that a structure is formed in the glass as with an FCC structure has been confirmed in both irradiations. In particular, the Bragg peaks of pure Co in the hcp structure, which is the stable structure of pure Co metal at room temperature, were not observed even in the irradiation sequence of Co and Ag. This suggests that the Co aggregates are assembled in the FCC configuration rather than the hcp configuration. In other words, this is thought to be the result of the diffusion

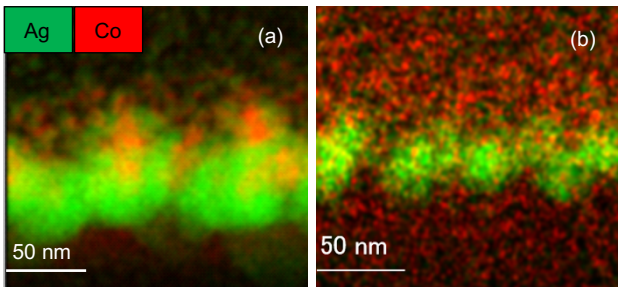

Fig. 1 STEM-EDS images for the samples (a) Co-Ag implantation order and Ag-Co implantation order in SiO_2.

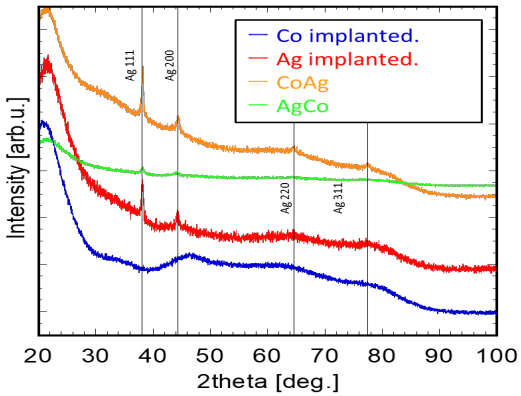

Fig. 2 XRD profiles for the Ag, the Co, Ag-Co and the Co-Ag implantation sample.

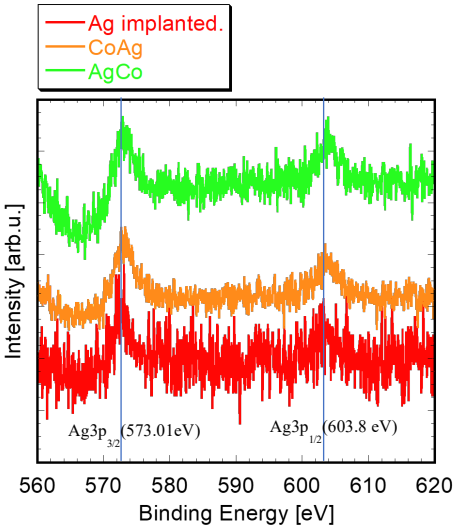

Fig. 3 XPS spectra of Co-Ag implanted SiO_2 focused on the core level of Ag-3$p_{3/2}$ and Ag-3$p_{1/2}$.

assembly of Co atoms being induced during the assembly process of the Ag atoms irradiated later.

Figure 3 shows the comparison of XPS spectra for different irradiation sequence of Ag-Co and Co-Ag. In both irradiation sequences, Ag-3p3/2 and Ag-3p1/2 peaks appeared, which indicates that Ag-Ag metallic bonds were formed in the particles produced in both cases, and there was almost no bonding of Ag atoms to oxygen or Co atoms. This result is in good agreement with the results of the previous study [5]. In addition, in the previous report, a chemical shift of the Co-2p3/2 core level of the Co-Co bond energy was observed in the case of Co-Ag ion implantation, and it was shown that some Co atoms did not form bonds with atoms other than Co. However, since we were unable to obtain a spectrum for the Ag-Co case in this experiment, the chemical bond state of the Co atom in the reverse irradiation order is still unclear.

Figure 4 shows that the EXAFS spectra of Ag-Co and Co-Ag irradiated SiO_2. In this figure, Co-Co bond peaks can be confirmed for both irradiations, but their intensity is higher for Co-Ag and lower for Ag-Co. This indicates that the aggregates formed after irradiation with the two ions have more Co atoms in the case of Co irradiation first.

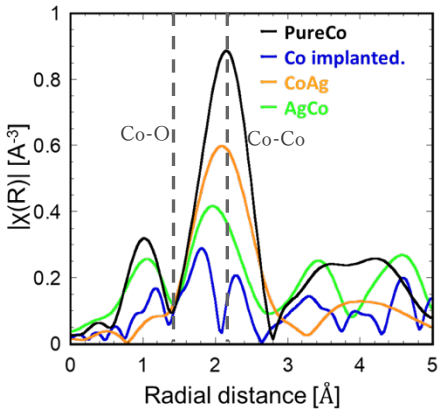

Fig. 4 XAFS-FT spectra of the Co-*K* absorption edge of the SiO_2 implanted Ag, Co-Ag, and Ag-Co.

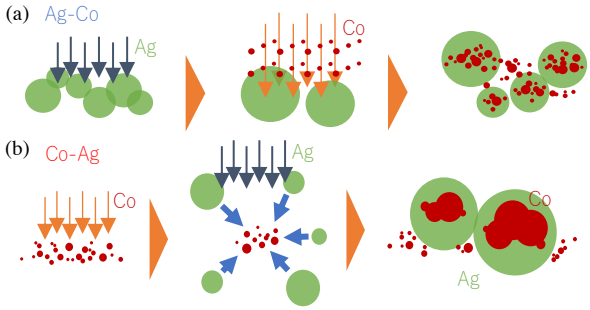

Fig. 5 Schematic illustration of the formation process of Ag-Co nano-composites by implanting Ag and Co ions into SiO_2 with different irradiation order considered based on the experimental results.

Furthermore, when only Co ions are irradiated, almost no Co-Co bonds are formed, and it is clear that the Ag irradiation promotes Co-Co bonds, i.e., the diffusion of Co atoms. Furthermore, since the Co atom diffusion increases when Ag is irradiated after Co irradiation, it can be said that it is further promoted by the diffusion of Ag.

Figure 5 (a) and (b) show the diffusion and assembly process of the atoms implanted when irradiated in the order Ag-Co and Co-Ag, respectively, and Ag diffuses during irradiation and can be assembled in either order, but Co cannot self-diffuse during irradiation. However, when Ag is irradiated later, Co diffuses along with the diffusion of Ag, and it is thought that Co is also incorporated into the Ag aggregates. In this way, when atoms with different diffusivities affect diffusion, it was found that the order of irradiation has a large effect on the state of the particles generated.

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