Electrical and morphological change of Ag-Ni films by annealing in vacuum

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Abstract

Ag and Ag-Ni films (Ni: 0.6, 2.0 and 4.8 at.%) with a thickness of 95 nm were deposited on SiO_2/Si substrates and the thermal stability of the films was evaluated. The films were annealed at temperatures from 400 to 700^{o}C for 1 hour in vacuum. The as-deposited Ag and Ag-Ni films had a smooth surface. The Ag-Ni films had an electrical resistivity higher than that of the Ag film because of the impurity scattering effect. However, the resistivity of Ag-Ni films decreased until 600^{o}C by annealing. As the morphological change after annealing, void formation was observed for the Ag film at 500^{o}C. Then after the annealing at 600^{o}C, agglomeration with a partly uncovered substrate was clearly observed for the Ag film. On the other hand, void formation was also observed for the Ag-Ni films at 600^{o}C. Further annealing at 650^{o}C caused agglomeration of the Ag-Ni films with an increase in their resistivity. Due to the insolubility of Ni into Ag, small islands of Ni appeared at this temperature. Consequently, Ag-Ni films are useful for suppressing agglomeration up to the annealing temperature of 600^{o}C. The resistivity of the Ag-Ni (0.6 at.%) film was 2.1-2.4 μΩcm after annealing from 400^{o}C to 550^{o}C comparable with that of the Ag film (1.9–2.2 μΩcm) and it remained low, though that of the pure Ag film increased significantly at 600 ^{o}C.

Introduction

For the future downscaling of electronic devices, silver is believed to be a potential and probable candidate as an interconnect material. Having features such as the lowest electrical resistivity and a high electromigration resistance [1-3], silver films have been intensively studied and many reports have focused on the suppression of their agglomeration behavior, which is a drawback of silver films making them unreliable interconnects [4-6]. One of the solutions is considered to be alloying silver with other metals [7-9]. An improvement in the use of Ag(Al) films has recently been reportedly [8,9]. As an explanation of the agglomeration, it is pointed out that crystal grains tend to be <111>-oriented to minimize the surface energy of the film when the films are heated. Ag atoms in other textured grains migrate and merge into growing {111} grains and the substrate becomes partly uncovered. It is reported that the migration is retarded in Ag(Al) films as compared with that in Ag films, which results in the suppression of agglomeration.

Previously we investigated the continuous-discontinuous transition thickness of Ag and sputter-deposited Ag-Ni films at the initial growth stage. The transition thickness increased with increasing substrate temperature, and the transition thickness of Ag-Ni films was thinner than that of Ag films, indicating a pseudo-two-dimensional growth mode. Namely, the transition thickness of Ag-Ni film was 30 nm and that of Ag film was 77 nm at 300^{o}C. This result suggests that the Ag-Ni films are more heat-resistant than Ag films and can be candidate silver

metallization materials. Unlike the Ag-Al system, Ag-Ni is a representative insoluble binary alloy system as shown by the phase diagram in ref. 10. It is interesting to examine whether the Ag-Ni films can suppress the agglomeration despite its insoluble feature. In the present study, we investigate the changes in the electrical resistivity, morphology and crystal structure of Ag-Ni films after annealing in vacuum for the purpose of clarifying the thermal stability of the films. The suppression mechanism of agglomeration is also discussed for the present system by comparing it with a reported case.

Experimental

The deposition of Ag film was carried out by sputtering a 60-mm-diameter Ag target (99.99% purity) in Ar gas using an rf sputtering system. For Ag-Ni film deposition, Ni chips (99.99% purity) with areas of 5mm x 5mm, 10mm x 10mm and 10mm x 20mm were placed on the Ag target. The system was evacuated to below 3.7×10^{-5} Pa, and then sputtering gas was introduced, with the gas flow controlled at 3.5 cm^3/min. The gas pressure was fixed at 1.1 Pa during sputtering. The rf power was 100 W, and the distance between the substrate and the target was fixed at 45 mm. A (100)Si wafer with a 100-nm-thick thermally grown SiO_2 layer was used as the substrate without heating for the deposition. Annealing treatment at temperatures ranging from 400°C to 700°C in vacuum for 1 hour was also carried out after evacuating below 1.0×10^{-4} Pa in a lamp heating furnace.

Film thickness was estimated by multibeam interferometry. The crystal structure of the obtained films was investigated by X-ray diffraction (XRD) analysis with Cu-Kα radiation. Crystallite size was calculated using Scherrer's equation on the basis of the full width at half maximum (FWHM) values of the diffraction peaks at normal θ–2θ scans. The surface morphology of the films was observed using a scanning electron microscope with a detector of energy dispersive X-ray spectrometry (EDS) and an atomic force microscope. Ni content in the films was determined by X-ray fluorescent spectroscopy (XRF). Electrical resistivity was measured by the four-point probe method.

Results and Discussion

The properties of the as-deposited Ag and Ag-Ni films are summarized in Table 1. The Ni contents in the Ag-Ni films with chip areas of 5x5, 10x10 and 10x20 mm^2 were 0.6, 2.0 and 4.8 at.%, respectively. The Ag film had a slightly higher resistivity than the bulk (1.6 μΩcm). With the increase in Ni content, resistivity increases due to the impurity scattering effect. The grain sizes estimated from Ag(111) peaks in the XRD analysis decreased particularly for Ag-Ni(4.8 at.%) probably because the Ni atoms distributed around Ag grains disturb the growth of Ag grains.

Figure 1 shows surface morphology after annealing observed by scanning electron microscopy (SEM). No noticeable difference was observed among the films before and after annealing at 400°C (not shown here). By atomic force microscopy (AFM), the root mean square roughness (RMS) values of these films were found to be in the range from 1.5 to 1.9 nm in the as-deposited films and increased to the range from 3.2 to 4.5 nm after annealing at 400°C. After annealing at 500°C, void formation is observed only for Ag films (Fig.1a). For Ag-Ni films (Fig.1b-d), void formation is not recognized yet. At this temperature, the RMS value of the Ag film also increased to 9.4 nm. On the other hand, the Ag-Ni films maintained a low RMS value of 4.5 nm. At 600°C, voids formed in the Ag-Ni films too (Fig.1f-h). For the Ag film the substrate was partly uncovered (Fig.1e). Among the Ag-Ni films (Fig.1f-h), those with a low Ni content

had less voids. Further annealing promotes the agglomeration of the films and the uncovered area increases for the Ag film (Fig.1i). Even for the Ag-Ni films, the substrate is markedly uncovered and the uncovered area for the films with a high Ni content is large (Fig. 1j-l). Thus, we found that agglomeration cannot be suppressed at 650^{o}C. Finally, at 700^{o}C, all the films transformed into agglomerated grains and were not in the film state thereafter (not shown here).

In the images of the Ag-Ni films above 650^{o}C, a lot of very small islands, the number of which increases with Ni content, are observed. It is speculated that Ni atoms that exist around Ag grains also agglomerate to form small Ni islands. As shown in Figure 2, point analysis by EDS revealed that the film part consists of Ag and the small islands contain Ni but no Ag. Consequently, we confirmed that Ni in the Ag-Ni films segregate after annealing at a high temperature. This is considered to be the characteristic point in the present insoluble binary system.

Thus, the agglomeration suppression effect caused by the addition of Ni is observed. However, it has been reported that SEM images show no evidence of any significant agglomeration for the case of Ag(Al) films even after annealing at 600^{o}C [9]. Because void formation is observed for Ag-Ni films at this temperature, Ag(Al) (Al:5 at.%) is considered to have a superior suppression effect. For the case of Ag(Al) films, the result after annealing at 650^{o}C is not shown in the literature, so we cannot compare between the two systems. In addition, the agglomeration of Ag film at 600^{o}C which is shown in the literature and that in the present study are also very different. Namely, for the former, the area of uncovered substrate was significantly large. The superior point of the present system is that a very small amount (0.6 at.%) of addition is effective because added Ni atoms exist between Ag grains and not inside them. For cases in which a soluble metal is added, a larger amount of addition might be required to have an effective suppression result.

Figure 3 shows the change in the electrical resistivity of each film as a function of annealing temperature. After the annealing at 400^{o}C, all the films show decreased resistivities, which are almost the same except for the Ag-Ni (4.8at.%) film with the highest Ni content. Namely, the resistivities of Ag, Ag-Ni (0.6 at.%), (2.0 at.%) and (4.8 at.%) are 1.9, 2.5, 2.7 and 5.3 μΩcm, respectively. Then at 500^{o}C, both the Ag and Ag-Ni (0.6at.%) films have a resistivity of 2.1 μΩcm. At 600^{o}C, resistivity of the Ag film begins to increase, though that of Ag-Ni films remains low (2.0 μΩcm for 0.6 at.% Ni film). In Fig.1, it can be seen that the agglomeration level differs significantly between the Ag and Ag-Ni films. The change in resistivity is accordant with that in morphology. At 650^{o}C where agglomeration proceeded even for the Ag-Ni films, the resistivity of all the films became higher than that of the as-deposited films. After the annealing at 700^{o}C the films became too resistive to be measured by the present method. It was observed that the Ag-Ni films with adequate Ni content ($\leq$ 2.0%) have the same or lower resistivities above 400^{o}C of annealing, though they have higher values than the Ag films in the as-deposited state.

When the Ag film is agglomerated, it is considered that atoms within randomly orientated grains move toward {111} grains because the {111} planes have the lowest surface energy in the order of {111}<{100}<{110}. By the XRD analysis, the as-deposited Ag and Ag-Ni films showed (111) preferential orientation with a small peak at (200). We investigated the change in the XRD peak intensities of (111) and (200) with increasing annealing temperature, and the results for the Ag and Ag-Ni(0.6 at.%) films are shown in Figure 4. Here we selected the Ag-Ni(0.6 at.%) film, as a counterpart of the Ag film, to minimize the error caused by the small Ni peak appearing in high-temperature annealing, because the peak positions of Ag(200) and Ni(111) are very close to each other. The (111) peak of both films became markedly enhanced after annealing at 400^{o}C compared with that of the as-deposited films. The (111) intensity of the

Ag film increases with annealing temperature up to 600°C, then it begins to decrease. It is considered that the peak intensity at 700°C decreased significantly due to partial evaporation of the film. The increase continues up to 650°C for Ag-Ni (0.6 at.%) films. The two other Ag-Ni films showed the same result. The enhancement of the peak is considered to be the grain growth of {111} to which other textured grains also change. The present result suggests that grain migration, which accompanies agglomeration and results in an uncovered substrate, is retarded in the Ag-Ni films. This has been confirmed by SEM observation. The (200) peak, on the other hand, increases up to 500°C, then at 600°C intensity decreases for both the Ag film and Ag-Ni films. It is considered by the annealing at a moderate temperature of up to 500°C, that most of the first randomly oriented grains transform to <111> and that some transform to <100>, then at more than 500°C, the <100> texture also changes to <111>. In the Ag-Ni films, the Ni atoms distributed around the Ag grains disturb the migration of Ag grains.

Consequently, we found that Ag-Ni films could suppress agglomeration compared with pure Ag films. By selecting an adequate Ni content, Ag-Ni films are hard to agglomerate maintaining a lower resistivity than Ag films. The lowest Ni content film in the present study showed the best result. Compared with the reported cases of Ag(Al) films, the mechanism for the suppression is different; unlike Al dissolved into Ag crystallite, Ni does not, and exits mostly at grain boundaries. The Ni atoms disturb the migration of Ag atoms toward <111> and retard agglomeration. However, by annealing at a high temperature of 650°C, Ni atoms also agglomerate and form isolated small islands, resulting in the dissipation of the suppression effect on Ag-Ni films. For films with a high Ni content, the formation was promoted.

Although the mechanism of suppression is different from Ag(Al), the usefulness of Ni addition is confirmed in this study. The addition of 0.6 at.% Ni can contribute to the improvement in the thermal stability of Ag films and attain a lower resistivity. However, further Ni addition (4.8 at.%) leads to earlier void formation of the films and makes it difficult to achieve a resistivity lower than that of Ag film. In the future, it will be possible to attempt the improvement of Ag film thermal stability by alloying with other low-resistivity metals instead of Al or Ni.

Conclusion

Compared with Ag films, the agglomeration of Ag-Ni films was found to be suppressed from the result of SEM observation and resistivity measurement. The film with a Ni content of 0.6 at.% was most effective, exhibiting the lowest level of agglomeration. The resistivity of the Ag-Ni film was also comparable to that of the Ag film in the range of 400°C to 550 °C, and it remained low (2.1 μΩcm) at 600°C though that of Ag increased to 9.2 μΩcm, significantly. Because Ag and Ni are not soluble, Ni formed isolated islands by annealing at 650°C, resulting in the dissipation of the suppression effect on Ag-Ni films.

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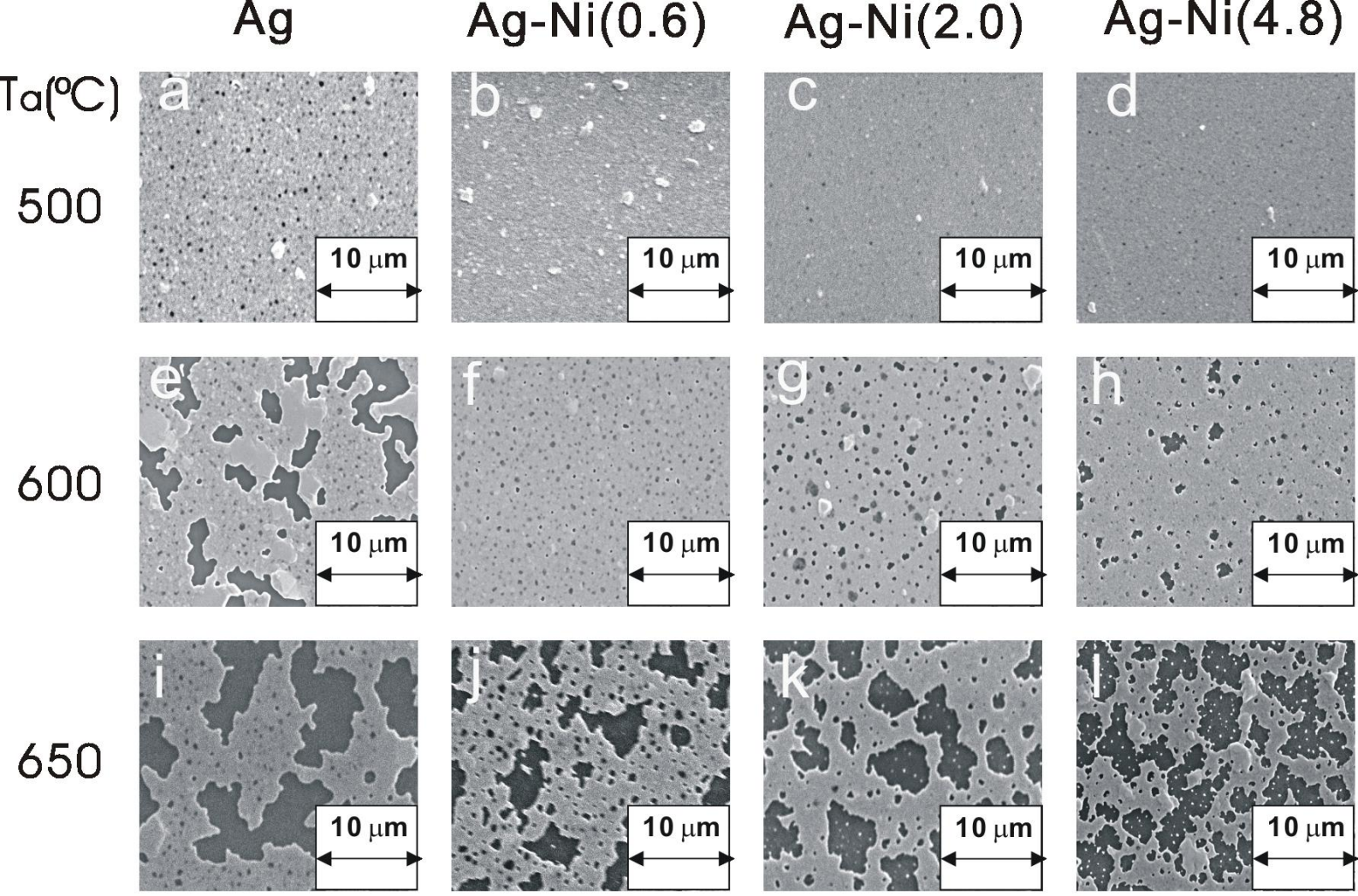
Table 1 Characterization of as-deposited Ag film and Ag-Ni films

	Ag film	Ag-Ni films		
Area of Ni chip(mm^2)	0	5 x 5	10 x 10	10 x 20
Ni content (at.%)	0	0.6	2.0	4.8
Resistivity ($\mu\Omega cm$)	3.0	4.5	8.1	12
Grain size (nm)	30	29	27	25

Figure captions

Fig. 1 SEM images of films after annealing at 500, 600 and 650^{o}C.
Fig. 2 EDS spectra for Ag-Ni(4.8 at.%) film after annealing at 650^{o}C.
Fig. 3 Resistivity change of films before and after annealing treatment.
Fig. 4 XRD intensity change of Ag and Ag-Ni(0.6 at.%) films. (a) (111) peak and (b) (200) peak.



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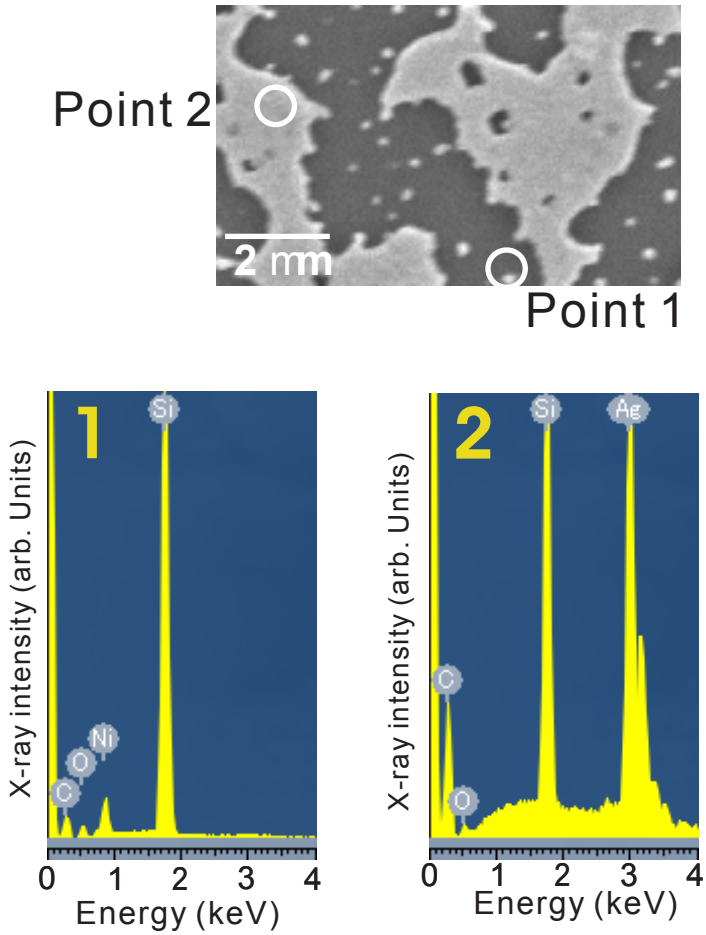

Fig. 2 EDS spectra for Ag-Ni(4.8 at.%) film after annealing at 650°C.

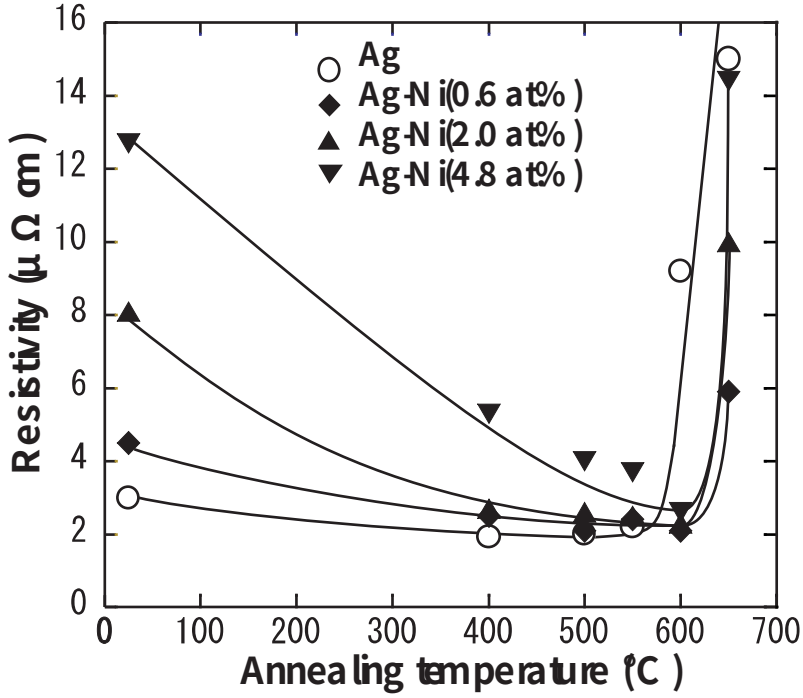

Fig.3 Resistivity change of films before and after annealing treatment.

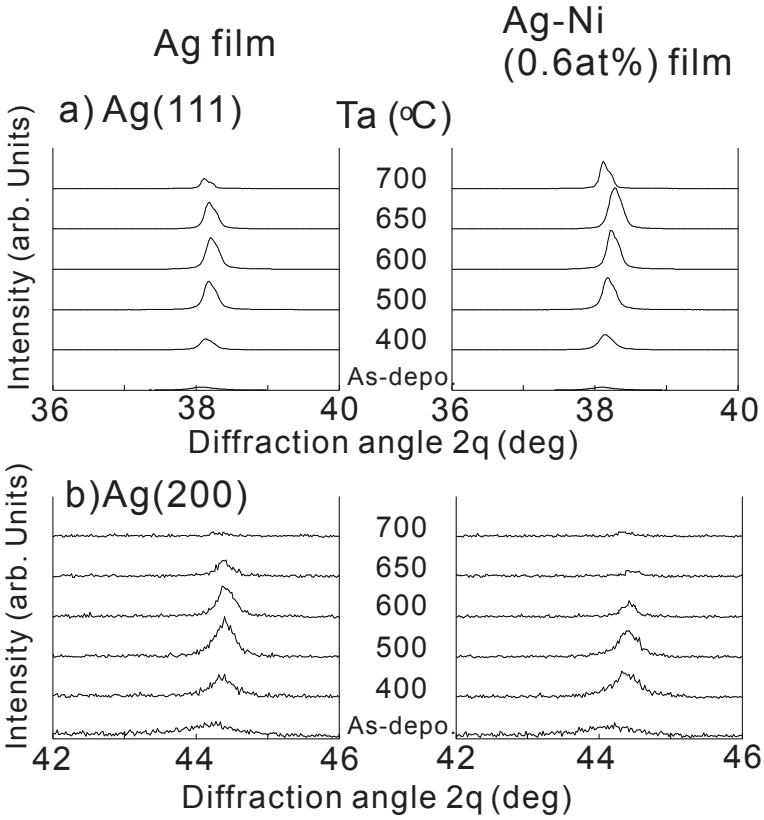

Fig. 4 XRD intensity change of Ag and Ag-Ni(0.6 at.%) films. (a) (111) peak and (b) (200) peak.