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# Thermal Reaction of NixSi1-x (x=0.18~0.28) Thin Films

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We have investigated thermal reaction of amorphous thin Ni-Si films, which have larger Si compositions than stoichiometric $NiSi_2$, by Rutherford backscattering spectrometry, glancing angle x-ray diffraction and resistivity measurements. In the composition range of the present study the formation of $NiSi_2$ phase were observed after the annealing between 300 and 700℃. No other crystalline phases such as $Ni_2Si$ and NiSi, which are formed in the interfacial reactions between Ni films and crystalline Si substrates, were detected. A low value of resistivity, 70μΩcm at room temperature, has been obtained for initial 30 at.% Ni film by 700℃ annealing. Also the resistivity of the film with initial 20 at.% Ni decreased to less than 200μΩcm by the annealing, although it showed high resistivity, 4900μΩcm, at as-deposited.

## 1.INTRODUCTION

Thin metal silicide films have been the subject of broad interest to the electronic industry because of their low electrical resistivity and high-temperature stability. Many experimental studies of silicide formation in thin films have involved interfacial reactions between metal films and silicon films or substrates.[1] Also codeposition of alloy metal-silicon films with suitable compositions can be the first step to form thin metal silicide films. In such a case a heat treatment is required after the preparation of the alloy film to obtain the desired electrical and structural properties.[2,3] However it is usually somewhat difficult to assure a desired composition of metal and silicon atoms in the alloy film because it is not so easy to maintain fixed evaporation rates throughout the deposition. Therefore some deviations from expected compositions can not be avoided. Recently crystallizations of amorphous silicide thin films, which do not have stoichiometric compositions, have been studied.[4,5]

Silicides of Ni have been the object of extensive studies because $NiSi_2$ as well as $CoSi_2$ can be epitaxially grown on Si crystals. However little studies on crystallization of amorphous Ni-Si alloy film, which has greater Si composition than that of $NiSi_2$, have been reported. In this study we have prepared amorphous Ni-Si alloy films, whose Ni composition is smaller than 0.33, and investigated thermal reaction of these Si-rich Ni-Si alloy films.

## 2.EXPERIMENTAL

Amorphous $Ni_xSi_{1-x}$ alloy films were prepared by codeposition of Ni and Si onto degreased $SiO_2$ substrates with the use of Ar-RF sputtering at room temperature. The base pressure of the sputtering chamber was $1 \times 10^{-7}$ Torr, and during the deposition the pressure of Ar gas was $2.0 \times 10^{-2}$ Torr. The sputtering targets were specially made by putting fan-shaped Ni plates on circular Si target. The substrates were continuously rotated in the sputtering chamber during the deposition to obtain uniform thicknesses and compositions. The composition and its uniformity of these films in depth were measured by Rutherford backscattering spectrometry (RBS) with the use of 2MeV He ions. The compositions of Ni atoms, x, of the alloy films were 0.20, 0.24, 0.30, respectively. The uniformity of the composition in depth was good as shown in Fig.1. Also the areal densities of these films were measured by RBS. They were 5.5, 5.6, $5.7 \times 10^{17}$ atoms/cm$^2$ for x=0.20, 0.24, 0.30, respectively. We could not know the precise film thicknesses because we need the value of the volume density of the alloy films to gauge the thickness from RBS measurements. Therefore we have estimated the

thicknesses on the assumption that the volume densities of these alloy films do not so much differ from that of NiSi2, $7.59 \times 10^{22}$ atoms/cm$^3$. The estimated film thicknesses were 72, 73, 75nm for the film of x=0.20, 0.24, 0.30, respectively.

The heat treatments of the samples were performed by a tube furnace with an atmosphere of continuously flowing Ar. The samples were heated up at the rate about 14℃/min, annealed for 2 hours at 300, 500, 700 ℃, respectively, then cooled to room temperature.

Structure and resistivity measurements of the as-deposited and the annealed samples were performed at room temperature. The crystalline phase formed by the annealing was identified with the use of glancing angle X-ray diffraction. RBS was used for depth composition analysis. The SSB detector was set at 105° with respect to the incident ion beam direction in order to enhance the depth resolution. The depth resolution was about 12nm for the near surface region of the sample. The sheet resistance of the samples were measured with the use of van der Pauw method at room temperature after the annealing. The electrodes of 1mmϕ for the sheet resistance measurement were bonded on the corner of 8mm × 8mm sample surface with the use of the supersonic bonder.

## 3.RESULTS AND DISCUSSION

Fig.1 shows the RBS spectra of as-deposited and 300, 700 ℃ annealed Ni-Si films. The Ni composition of the as-deposited film was 0.20. The compositional uniformity in depth of the as-deposited film was good as shown in the figure. However, RBS spectra for the annealed films shows that the compositional redistribution has occurred by the heat treatment. As the annealing temperature increased Ni atoms gathered into narrower region, which induced the formation of the layer with greater Ni composition. The Ni composition x has reached to 0.27 locally in the film by 700 ℃ heat treatment. The surface of the films became Si-rich. This indicates that the diffusion of Ni and/or Si atoms have occurred

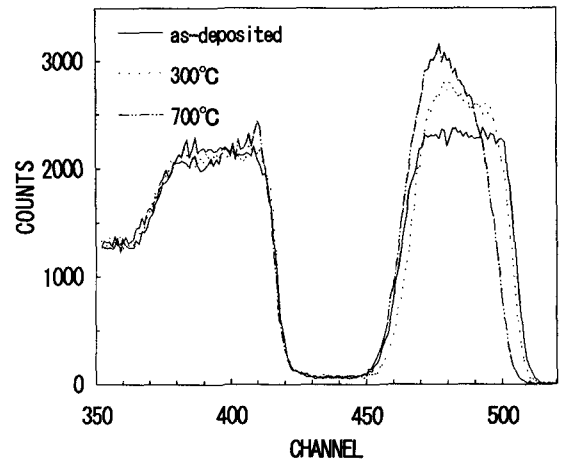


Figure 1. RBS spectra of as-deposited and annealed $Ni_{0.20}Si_{0.80}$ films.

during the annealing process. Such concentration of Ni atoms also occurred for x=0.24 and 0.30 films. However the amount of the change in the Ni composition decreased as the initial Ni composition increased. The maximum Ni composition was 0.26 for $Ni_{0.24}Si_{0.76}$, and 0.31 for $Ni_{0.30}Si_{0.70}$ after 700℃ annealings.

Figure 2 presents glancing angle X-ray diffraction (XRD) spectra taken from samples annealed at 300, 500, 700 ℃ for two hours in Ar atmosphere, and then cooled to room temperature. The spectrum (A) in the figure is of the as-deposited film whose Ni composition was 0.20. The absence of any peaks indicates that the as-deposited $Ni_{0.20}Si_{0.80}$ alloy film was amorphous. The spectrum from the sample annealed at to 300℃ (B) shows some peaks which are attributed to the reflection from crystalline NiSi2. These peaks can also be attributed to crystalline Si phase. We can hardly distinguish between NiSi2 and Si phases by XRD because the crystal structure of NiSi2 and Si is fluorite type and diamond type, respectively, and the lattice constant NiSi2 is nearly equal to that of Si. The intensity of these peaks for 700℃ annealed sample is much larger than that of 300 and 500℃

annealed one. No other crystalline phases, such as Ni metal or other Ni silicides were detected. The features of the XRD spectra for other samples, which had Ni composition x=0.24 and 0.30 at as-deposited, were similar to that of x=0.20 film.

Figure 3 shows the change in the electrical resistivity of Ni-Si films by the annealing. We have converted the sheet resistance, which was obtained by van der Pauw measurement, to the resistivity by multiplying it by the film thickness on the assumption that no changes in the film thickness have occurred during the annealing process. All the measurements were performed at room temperature after the annealing. For the samples of Ni composition x=0.20, 0.24 and 0.30 at as-deposited, the resistivity decreased as the annealing temperature increased. After 700℃ annealing the

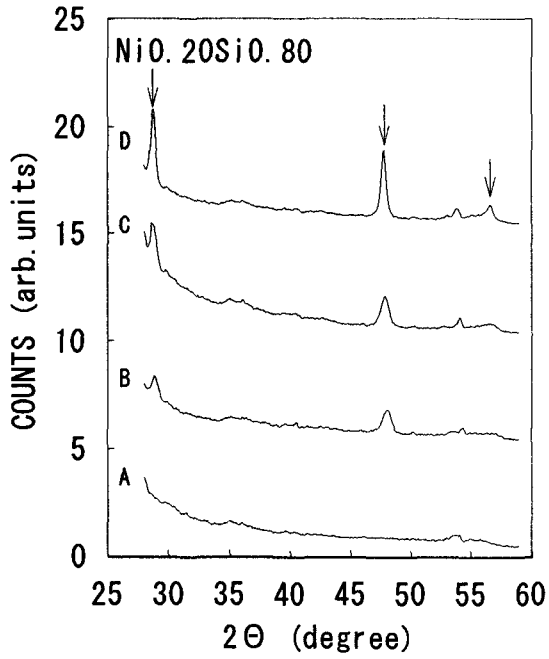


Figure 2. The glancing angle X-ray diffraction spectra of as-deposited (A) and annealed (B,C,D) $Ni_{0.20}Si_{0.80}$ films. The annealing temperatures were 300℃ (B), 500℃ (C) and 700℃ (D). The peaks indicated by arrows are attributed to the reflections from crystalline $NiSi_2$ and/or Si.

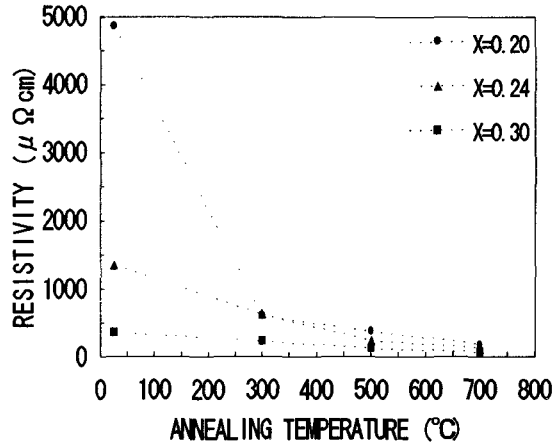


Figure 3. The resistivity of $Ni_xSi_{1-x}$ films before and after the annealings. The measurements were performed at room temperature.

sample of x=0.30, which is close to stoichiometric $NiSi_2$ composition, has shown very low resistivity, 70μΩcm. Also the resistivity of the x=0.20 film, which was 4900μΩcm at as-deposited, has decreased to 600μΩcm by 300℃, and to 180μΩcm by 700℃ annealing.

We have detected crystalline $NiSi_2$ and/or crystalline Si phase after the annealing of Si-rich amorphous alloy films. Although we could not distinguish these two phase only by XRD measurements, it is certain that the $NiSi_2$ phase have appeared because the resistivity decreased as the crystallization proceeded by the annealing. Thus $NiSi_2$ is the first and only phase of silicide to appear in the silicidation process of Si-rich amorphous Ni-Si alloy. Furthermore it has appeared by the annealing down to 300℃. This is in contrast with the case of interfacial reactions between Ni films and crystalline Si, where metal-rich $Ni_2Si$ is observed as the first phase at about 250 ℃, then NiSi is formed, and finally $NiSi_2$ appears abruptly at about 750 ℃ as the end phase.[1]

The high transformation temperature of NiSi to $NiSi_2$ on crystalline Si have been attributed to a

nucleation-controlled growth process, whereas the formation of $Ni_2Si$ and NiSi is a diffusion-controlled process, in which the dominant moving species is Ni.[1,7] The results in the present study is similar to the observation by Cammarata et al., who found the formation of $NiSi_2$ precipitates during 400 ℃ annealing in amorphous Si, which was amorphized by the implantation of $4 \times 10^{20}/cm^3$ Ni impurities.[6] Lien et al. have observed a low temperature formation of $NiSi_2$ at 350 ℃ in the interfacial reaction of NiSi and amorphous Si.[7] They have reported that in the case of the interfacial reaction of NiSi and amorphous Si the growth of $NiSi_2$ is a diffusion-controlled process. Also only the disilicide phase was detected after the annealing between 300 and 600 ℃ in the case of amorphous $Co_{0.20}Si_{0.80}$ alloy film.[5] In the present study the formation of $NiSi_2$ in Si-rich Ni-Si alloy films might be a kind of diffusion-controlled process because the redistributions of atoms were observed after the annealings by RBS measurements. It is very difficult to comment on why $NiSi_2$ only appears at such a low temperature by the annealing of Si-rich Ni-Si alloy films, because this phenomenon is controlled by many factors such as thermodynamic factor and surface energies. However, it is suggested that $NiSi_2$ formation or exclusive $NiSi_2$ formation at low temperatures will occur when Si atoms, which are required for silicidation, are supplied from ambient amorphous alloy or amorphous Si film.

## 4.SUMMARY

We have investigated thermal reaction of amorphous thin Ni-Si films, which have larger Si compositions than stoichiometric $NiSi_2$. In the Ni composition range between 20 and 30 at.% only the formation of $NiSi_2$ phase were observed after the annealing between 300 and 700 ℃. This is in contrast to the interfacial reactions between Ni films and crystalline Si substrates, in which $Ni_2Si$ and NiSi are formed at below about 750℃. A low value of resistivity, 70μΩcm at room temperature, has been obtained for $Ni_{0.30}Si_{0.70}$ film by 700 ℃ annealing. Also the resistivity of $Ni_{0.20}Si_{0.80}$ film has decreased to 180μΩcm by the annealing, although it showed high resistivity, 4900μΩcm, at as-deposited.

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