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Homogeneous Hetero-Epitaxial $NiSi_2$ Formation on (100)Si

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The substrate impurity effects on the interface formation kinetics of $NiSi_2$ were examined. All of NiSi transformed to $NiSi_2$ on both BF_2 doped Si and As doped Si at above 850 ^oC . Good epitaxial growth of $NiSi_2$ on (100)Si was confirmed. The interface roughness between $NiSi_2$ and Si strongly depended on the substrate impurities. Smooth interface was formed on As doped Si, however, on BF_2 doped Si the interface was highly faceted on {111} plane with the average roughness of about 80–110 nm. The mechanism of the interface formation would be related to the covalent radius of the impurity atoms relative to that of Si, so that the interface roughness could be controlled by choosing the substrate impurity species.

1. Introduction

A self–aligned silicide (salicide) technology has been widely investigated to reduce the sheet resistance of the diffused layers.[1] Recent investigations have been focused on the applicability of $TiSi_2$[2] or $CoSi_2$[3] for salicide technology because of their low electrical resistivity and thermal stability. However, as the design rule shrinks to the quartermicron range, the contact resistance becomes a dominant contributor to the parasitic series resistance around the shallow junction regions.[4] This problem is more stringent for contacts to boron doped Si, because boron is more difficult to be electrically activated than arsenic. Therefore, a lower Schottky–barrier height to p–type Si is better for the contact material in the future deep submicron regime.

Ni silicide has a low Schottky–barrier height to p–type Si with the lowest lattice mismatch to Si among metal silicides, and shows a good epitaxial growth on Si.[5] However, because of the large {111} facets formed at the $NiSi_2$/(100)Si interface,[6] the application of $NiSi_2$ to ULSI devices was difficult. It has not yet been reported about the control and improvement of the $NiSi_2$/Si interface morphology.

In this study, the authors have examined the substrate impurity effects on the interface formation kinetics, and discussed the controllability of the interface morphology, showing the potential of $NiSi_2$ as a new candidate for the salicide materials.

2. Experimental Procedure

Five–inch–diameter, phosphorus doped, 5–11 Ω cm (100)Si wafers were used. As^+ (40 keV, $2x10^{15}cm^{-2}$) and BF_2^+ (65keV, $2x10^{15}cm^{-2}$) ions were implanted, and 0.3 μm CVD–SiO_2 films were deposited on the ion implanted Si followed by annealing at 900 ^oC for 60 min in a N_2 ambient to form n^+ and p^+ diffused layers. Phosphorus doped n^+ diffused layers were also prepared by annealing in a $POCl_3$ ambient at 1000 ^oC for 30 min. After removing SiO_2 films, the well–known RCA cleaning,[7] diluted HF dip, deionized water rinse and spin–drying in a N_2 stream were done. 70 nm thick Ni films were deposited on the substrates at room temperature by e–gun evaporation using a load–lock type ultra–high–vacuum (UHV) system with a base pressure of $2.7x10^{-8}$ Pa. Annealing for silicidation was carried out in an Ar ambient for 1 h at temperatures between 600 and 900 ^oC using a lamp furnace, which was evacuated to a pressure of $5.0x10^{-5}$ Pa before introducing the purified Ar. Residual oxygen concentration in the annealing ambient was

controlled within a few ppb. After silicidation, the samples were cut into pieces and analyzed by X–ray diffraction (XRD), Rutherford backscattering spectrometry (RBS), high–resolution transmission electron microscopy (HRTEM).

3. Results and discussion

Figures 1(a) and 1(b) show the high resolution XRD spectra near the (400) reflections of Si and $NiSi_2$ on BF_2^+ implanted p^+–Si ($Si(BF_2)$) and As^+ implanted n^+–Si (Si(As)), respectively. Fig.1(a) shows that the strong (400) reflections of $NiSi_2$ appeared at above 800 ^oC. This indicates that the phase transition from NiSi (orthorhombic, MnP structure[8]) to $NiSi_2$ (cubic CaF_2 structure) started at about 800 ^oC on $Si(BF_2)$, and $NiSi_2$ was epitaxially grown on (100) Si. These results were similar to the case of un–implanted Si. Fig.1(b) shows that the (400) reflections of $NiSi_2$ appeared at above 700 ^oC on Si(As), which implies that the presence of As lowers the phase transition temperature from NiSi to $NiSi_2$. After 850 ^oC annealing, complete transformation from NiSi to epitaxial $NiSi_2$ on (100) Si was confirmed on both types of substrates.

In Figures 2(a) and 2(b), RBS spectra are shown for $Si(BF_2)$ and Si(As), respectively. The phase transition behavior from NiSi to $NiSi_2$ observed by the XRD analysis were also confirmed from the RBS analysis. The average atomic ratio of Si to Ni in the silicide layers calculated from the scattering yields of the Ni and Si signals reached to 2 at 850 ^oC on $Si(BF_2)$ and at 800 ^oC on Si(As), indicating the complete transformation to $NiSi_2$ from NiSi.

On the other hand, the roughness of each silicide film can also be discussed from the RBS spectra shown in Figures 2(a) and 2(b). The roughness of the silicide films strongly depended on both the phase of silicide and the kind of substrate impurities. In the case of NiSi, the film thickness was uniform both on $Si(BF_2)$ and on Si(As), because the slope at the tailing edge of the Ni spectrum is steep. However, as for $NiSi_2$, substrate impurity strongly affected the film uniformity. Although only a little roughening was observed on Si(As), much more roughening occurred

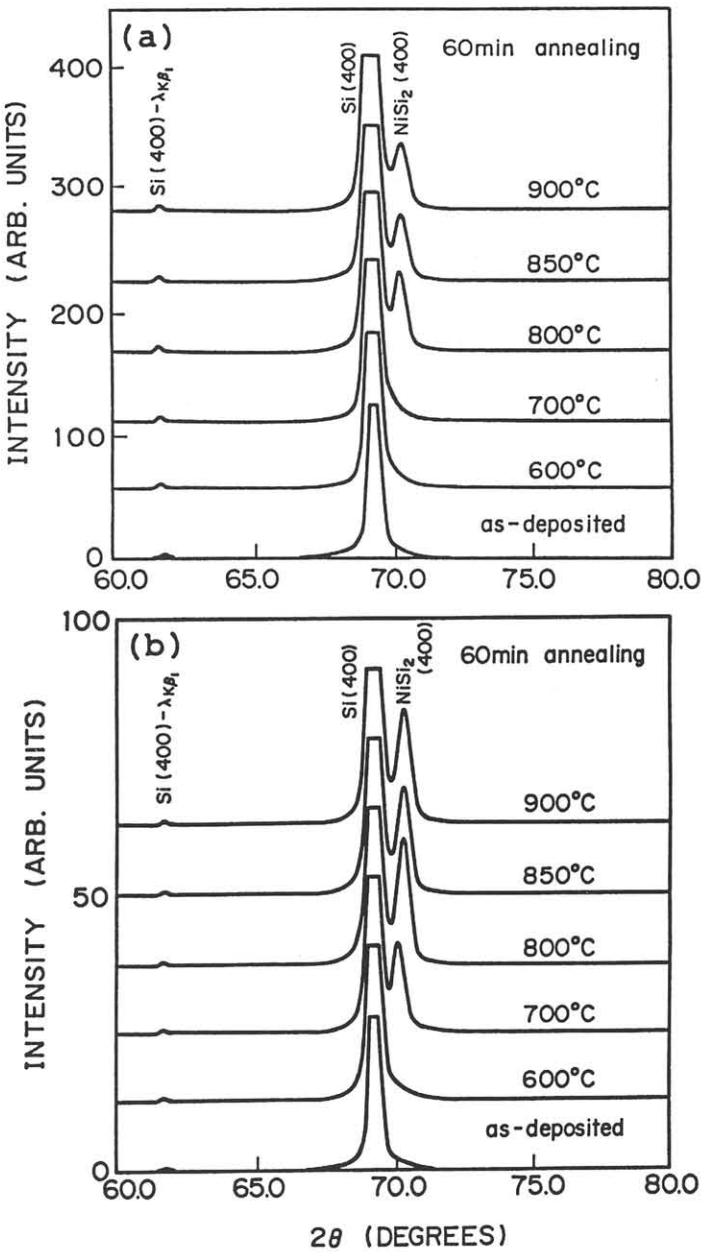

Fig.1. High resolution XRD spectra around the (400) reflections of Si and $NiSi_2$ after annealing at 600, 700, 800, 850, 900 ^oC for 1h (a) on $Si(BF_2)$ and (b) on Si(As).

on $Si(BF_2)$. To evaluate the roughness quantitatively, the increase in roughness relative to the as–deposited Ni film was obtained by comparing the Ni spectrum width between the 16% and 84% level of the spectrum height, which corresponds to twice the energy standard deviation as described by Chu et al.[9] From this analysis the degree of film roughness can be estimated to about 10–20 nm for 170 nm NiSi on both types of substrates and about 80–110 nm and 30–40 nm for average thickness of 240 nm $NiSi_2$ on $Si(BF_2)$ and Si(As), respectively. The surface roughness of each

film was almost the same independent of the silicide phase and the substrate impurity by the surface profile measurement. Therefore, the broadening in the RBS spectrum at the interface region for $NiSi_2$ on $Si(BF_2)$ indicates silicide/Si interface roughening. Another RBS observations were made on phosphorus doped n^+–Si (Si(P)) and un–implanted Si (Si(UI)). Table 1 summarizes the estimated interface roughness at 850 ^oC on each substrate with the covalent radius of impurity atom. The suppression of the interface roughening was clearly observed only on Si(As).

A detailed interface observation was made by cross–sectional transmission electron microscopy (TEM). Figures 3(a) and 3(b) show the TEM photographs of $NiSi_2$ on $Si(BF_2)$ and on Si(As), respectively. From Fig. 3(a) large interface roughening was observed on $Si(BF_2)$. It is clearly shown that the roughening

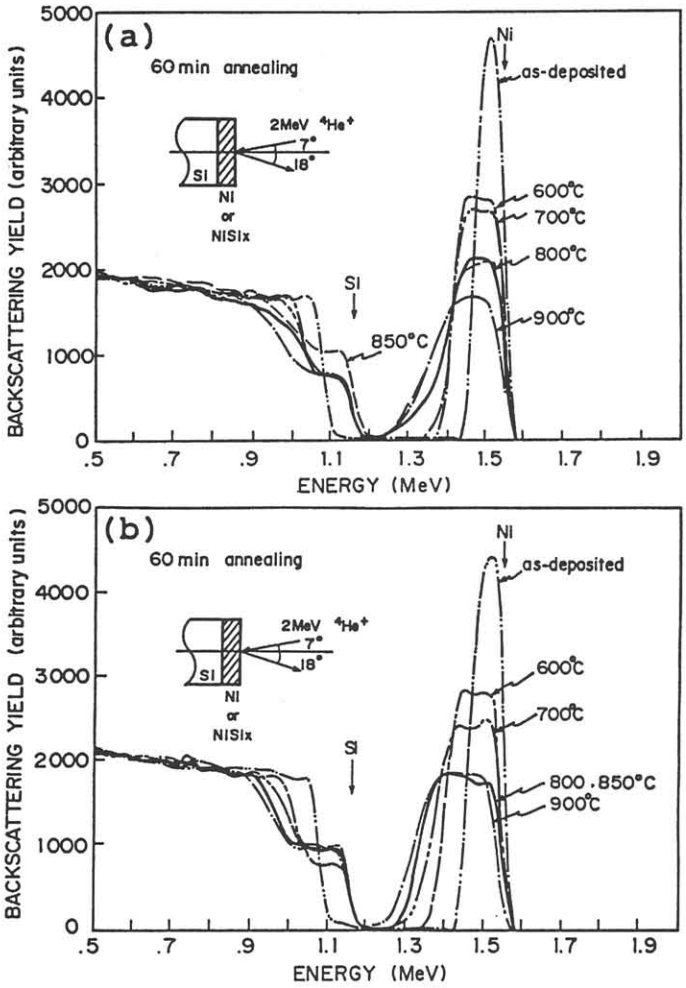

Fig.2. RBS spectra for 70 nm thick Ni film evaporated on (100)Si before and after annealing at 600, 700, 800, 850, 900 ^oC for 1h (a) on $Si(BF_2)$ and (b) on Si(As).

Table 1 : Normarized interface roughness on various substrates

Substrate	Normarized interface roughness	Covalent Radius of impurity atom(Å)
Si(UI)(*)	1. 0	1. 11 (Si)
Si(BF_2)	0. 9	0. 82 (B)
Si(As)	0. 3	1. 20 (As)
Si(P)	1. 0	1. 06 (P)

(*) un-implanted Si

occurred by {111} facet formation at the $NiSi_2$/Si interface. On the other hand, Fig. 3(b) shows that the {111} facet formation was suppressed and smooth interface was formed on Si(As). On both substrates, the surface of $NiSi_2$ was fairly smooth independent of the large difference of the interface roughness. These results agreed with the RBS observations mentioned above.

To obtain further information, high resolution TEM (HRTEM) observation was made. Figures 4(a) and 4(b) show the lattice images at the $NiSi_2$/Si interface on $Si(BF_2)$ and Si(As), respectively. Both figures show that the epitaxial interfaces were well defined and atomically abrupt. However, an about 1 nm crystalline distorted layer was clearly observed only at the $NiSi_2$/Si(As) interface. This distorted interfacial layer was able to relax the interface strain due to the lattice mismatch of 0.4% between $NiSi_2$ and Si. Therefore, the interface free energy would be lowered and the stable {100} interface can be formed to a long distance on Si(As). On $Si(BF_2)$, no such a distorted layer was observed, so that the {100} interface energy is considered to be higher than that on Si(As). Since the interface energy between (100) $NiSi_2$ and (100) Si is higher than (111)$NiSi_2$/(111)Si interface, {111} facets would be easily formed at such a simple epitaxial interface as on $NiSi_2/Si(BF_2)$.

4.Conclusion

The authors have studied the substrate impurity effects on the interface formation kinetics of $NiSi_2$. All of NiSi transformed to $NiSi_2$ on both $Si(BF_2)$ and Si(As) at above 850 ^oC, and good epitaxial growth of $NiSi_2$ on (100)Si was confirmed. The interface roughness between $NiSi_2$ and Si strongly depended on the substrate impurities. Smooth interface was formed

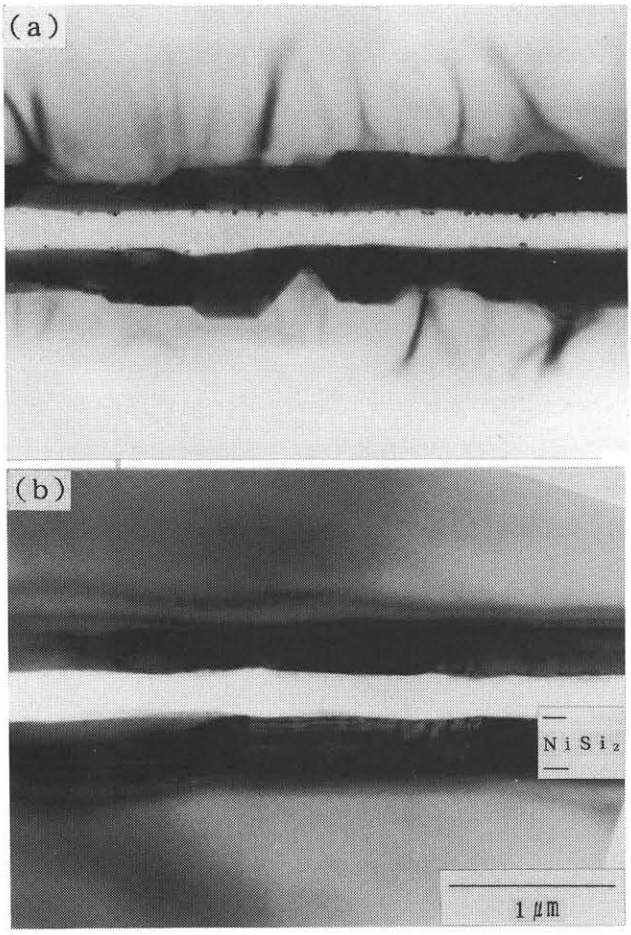

Fig.3. Cross–sectional TEM photographs of $NiSi_2$ (a) on $Si(BF_2)$ and (b) on Si(As).

on Si(As), however the interface was highly faceted on the {111} plane with the average roughness of about 80–110 nm on $Si(BF_2)$. On Si(P), the interface roughness was comparable with that on $Si(BF_2)$. The mechanism of the interface formation would be related to the covalent radius of the impurity atoms relative to that of Si, not to the carrier type or crystalline defects. So that the interface roughness could be controlled by choosing the substrate impurity species with appropriate covalent radius.

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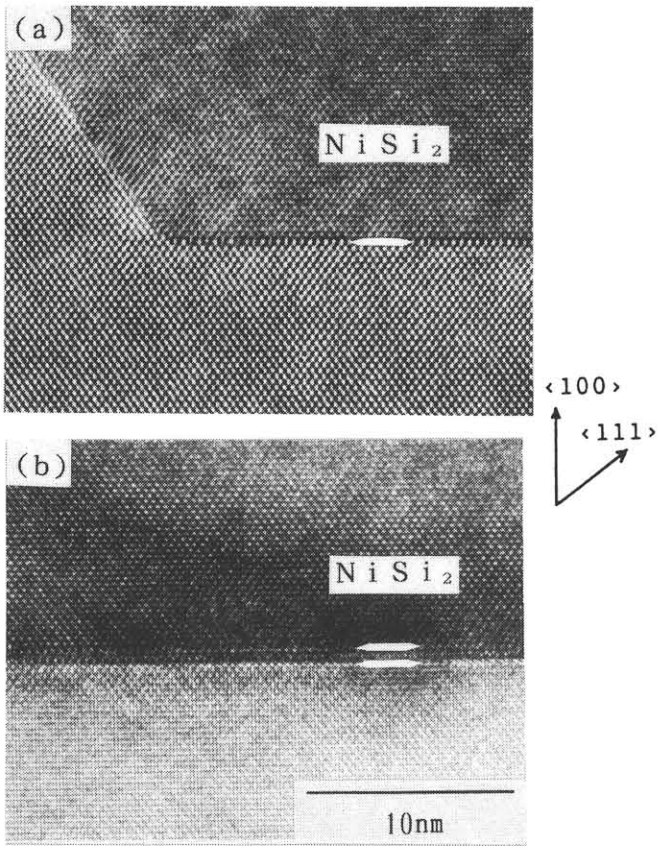

Fig.4. (110) lattice image of the $NiSi_2$/Si interface by HRTEM (a) on $Si(BF_2)$ and (b) on Si(As). White allows indicate the interface position and the interfacial layer.

References

1) Shyam P. Murarka; J. Vac. Sci. Technol. B4(1986)1325.
2) C. Y. Ting, F. M. d'Heurle, S. S. Lyer, and P. M. Fryer; J. Electrochem. Soc. 133(1986)2621.
3) L. Van den hove, R. Wolters, K. Maex, R. De Keersmaecker, and G. Declerck; J. Vac. Sci. Technol. B4(1986)1358.
4) Kwok K. Ng, and William T. Lynch; IEEE Trans. Electron Devices, ED–34(1987)503.
5) R. T. Tung, and J. M. Gibson; J. Vac. Sci. Technol. A3(1985)987.
6) H. Foll, P. S. Ho, and K. N. Tu; Phil. Mag. A45(1982)31.
7) W. Kern, and D. Puotinen; RCA Rev. 31(1970)187.
8) F. d'Heurle, C. S. Petersson, J. E. E. Baglin, S. J. La Pzlaca, and C. Y. Wong; J. Appl. Phys. 55(1984)4208.
9) W. K. Chu, J. W. Mayer, and M. A. Nicolet; Backscattering Spectrometry (Academic,New York, 1978), p.328.