# COMPETING REACTIONS OF EXISTING Ni SILICIDE AND Ni OR Si INDUCED BY THERMAL ANNEALING AND MeV Si ION BEAM MIXING

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## ABSTRACT

The competing reactions between existing Ni silicides surrounded by Si and Ni were investigated by thermal annealing and MeV Si ion beam mixing. With high energy irradiation, the energy deposition at both interfaces, Ni/Ni silicide and Ni silicide/Si, is equal. Two MeV $He^+$ RBS and TEM were used to obtain the reacted layer composition and epitaxial orientation, respectively. Also glancing angle Co $K_\alpha$ X-ray diffraction was utilized to identify phase formation. The main results indicate that the existing silicides preferentially react with Ni layer, and that there are pronounced differences of Ni silicide phase transition between thermal annealing and MeV Si ion beam mixing, even though the mixing was performed in radiation enhanced diffusion regime. The results can be explained in term of the heat of silicide formation and surface energy change.

**Keywords:** Chemical reaction kinetics Ni silicides MeV Si ion beam mixing Annealing RBS TEM

## 1 INTRODUCTION

Nickel silicides are one of the most common silicides, which are used to a considerable extent in application of silicon IC devices, and of which formation mechanism induced by thermal reaction and ion beam mixing is also extensively investigated. Normally for bilayer Ni/Si system, a Ni layer on Si single crystal substrate, the first phase formed is $Ni_2Si$, then the second phase NiSi is formed when the Ni layer is consulmed if increaseing annealing temperature or prolonging

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annealing time, finally $NiSi_2$ is formed when $Ni_2Si$ is totally transisted to NiSi at annealing temperature of 750 ℃. The same phase formation sequence for ion beam mixing is observed[1]. Due to small difference of free energy between Ni silicides, the sequence of Ni silicide phase formation could be changed by different reaction conditions. For nickel-crystalline silicon construction, the first reaction layer at interface is $Ni_2Si$, while for nickel-amorphous Si, some ones found that $Ni_2Si$ had been observed as the first phase to form[2], but the other reported the simultaneous formation of layers of $Ni_2Si$ and NiSi at the interface[3]. R. C. Camrrata *et al* indicated that precipitates of $NiSi_2$ phase were found firstly in nickel-implanted amorphous silicon thin films because of surface energy, and recently Rao's experimental results[5] show that $Ni_2Si$ phase is formed in Si implanted crystal nickel. These results suggest that there is a heavy competition in Ni silicide formation.

In this paper Ni silicide samples with sandwich type, Si<111>/NiSi/Ni (sample A) and Si<111>/$NiSi_2$/Ni (sample B) are prepared, and competing reactions of existing Ni silicides with Si or Ni induced by thermal annealing and MeV Si ion beam mixing, which deposited the same energy at both interfaces and eliminated impurity influence, are investigated by 2 MeV $He^+$ RBS, TEM and Co $K_\alpha$ glancing angle X-ray diffraction. The mechanism of Ni silicide phase transition is also discussed by heat of silicide formation and surface energy.

## 2 EXPERIMENTAL PROCEDURES AND RESULTS

### 2.1 Sample preparation

Si<111> wafers, n type, received the usual cleaning procedure and were etched in buffered HF to remove any residual layer of $SiO_2$ as much as possible, then were put into deposited chamber immediatly, which was pumped by cryopump in a background vacuum of 1.33 μ Pa range. The Ni layers with thicknesses of 25—50 nm were deposited on the Si wafers in a working vacuum of 1.33 μ Pa range. Ni silicides were formed in a furnace with flux $N_2$ or Ar. NiSi phase formation is at 500 ℃ for 20 min and $NiSi_2$ phase formation with a good epitaxil (channeling $\chi_{min}$ 7—9 %) is at 800 ℃ for 10 min[6]. After silicide formation, the second Ni depositions were performed in the same condition as the first.

### 2.2 Thermal reactions and MeV Si ion beam mixing

Thermal reactions were performed in a common furnace with Ar or $N_2$ flux at the temperatures from 200 to 500 ℃ for 20 min. During annealing samples were covered by a pure silicon wafer to protect oxidation. 1.5 MeV Si ion beam (Rp is far away from interfaces) was used to penetrate both interfaces, Ni silicide/Ni and Si<111>/Ni silicide, and to deposite the same energy at the both interfaces, which was confirmed by TRIM simulation. Implantation dose is from $1\times 10^{15}$ at./cm$^2$ to $1\times 10^{17}$ at./cm$^2$.

Samples were mounted by clamps and vacuum grease on a copper block, which were heated in temperature range from room temperature to 300 ℃.

**2.3 $NiSi_2$ competing reactions**

The existing $NiSi_2$ layer in sample B maintained stably after thermal annealing at temperature up to 400 ℃ for 20 min. However, the $NiSi_2$ layer returned to an uniform NiSi layer by 500 ℃, 20 min annealing. Fig.1a shows 2 MeV $He^+$ RBS spectra for sample B with thermal annealing. The solid line with a step (-$NiSi_2$) represents as-deposited sample, while the dashed line with a step (-NiSi) is for 500 ℃, 20 min annealed sample. The $NiSi_2$ layer in as-deposited sample was totally reacted with Ni layer to form NiSi phase.

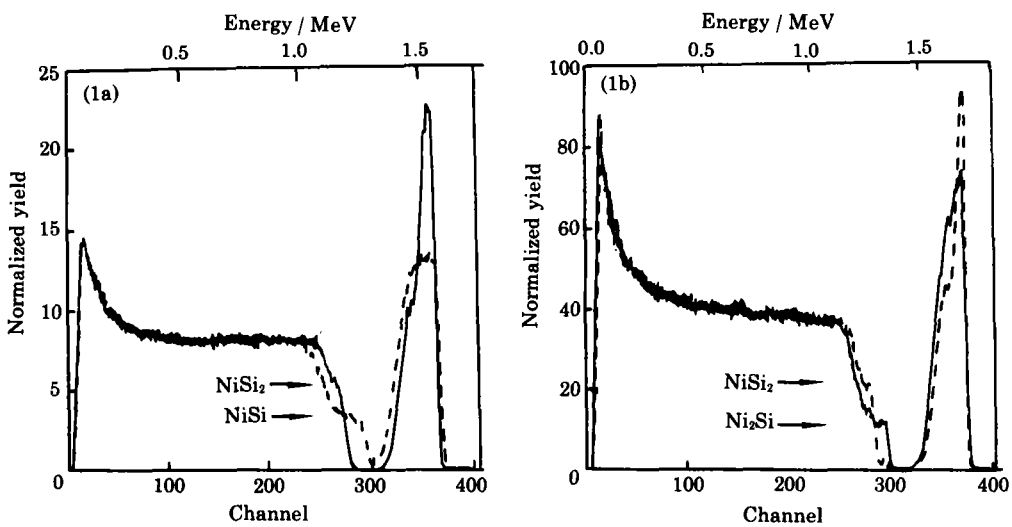


**Fig.1 2 MeV $He^+$ RBS spectra for sample B with 500°C 20 min thermal annealing (a) and with 1.5 MeV $5\times10^{16}$ Si/cm$^2$ ion beam mixing at 250°C (b)**

The solid line and the dashed represent before and after reaction, respectively

In ion beam mixing case, the $NiSi_2$ layer was mixed with Ni layer by 1.5 MeV Si ion beam at room temperature to form an ununiform reacted layer. However, an uniform reacted layer was formed by 250 ℃ Si ion beam mixing with $5\times10^{16}$ Si/cm$^2$, of which the 2 MeV $He^+$ RBS spectra were shown in Fig.1b. In experimental resolution the $NiSi_2$ layer only reacted with Ni layer and Si substrate remained no change. But the composition of the reacted layer is $Ni_2Si$ which is completely different from that formed by thermal annealing (-NiSi). We also used C-RBS to examine the orientation of reacted layers. Fig.2 shows the channeling spectra of the sample. There is a 25 % yield reduction at Ni high energy edge of aligned spectrum for ion beam mixing. The results suggest that the $Ni_2Si$ reacted layer is constructed with <111> preferential orientation. But no channeling effect could be found in sample B with 500 ℃, 20 min

thermal annealing.

In order to identify phase formation and construction of reacted layers some samples were examined by transmission electron microscopy. The TEM image, together with the corresponding diffraction pattern, for sample B with $1\times10^{17}$ Si/cm$^2$ at 250°C is shown in Fig.3. The interplanar spacings of $Ni_2Si$ and NiSi were taken from Ref.[7]. Two Ni silicide phases $Ni_2Si$ and NiSi co-existed in the sample B were proved by the diffraction rings. And some grain epitaxil were also found in the image. Those results were also confirmed by Co $K_\alpha$ glancing angle X-ray diffraction.

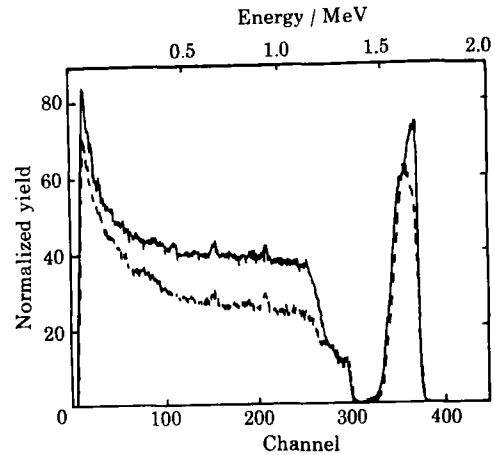


**Fig.2 2 MeV $He^+$ C–RBC spectra for sample B with 1.5 MeV $5\times10^{16}$Si/cm$^2$ at 250°C**

**Fig.3 Transmission electron microscope results from sample B (1.5MeV $1\times10^{16}$ Si/cm$^2$ at 250°C)**

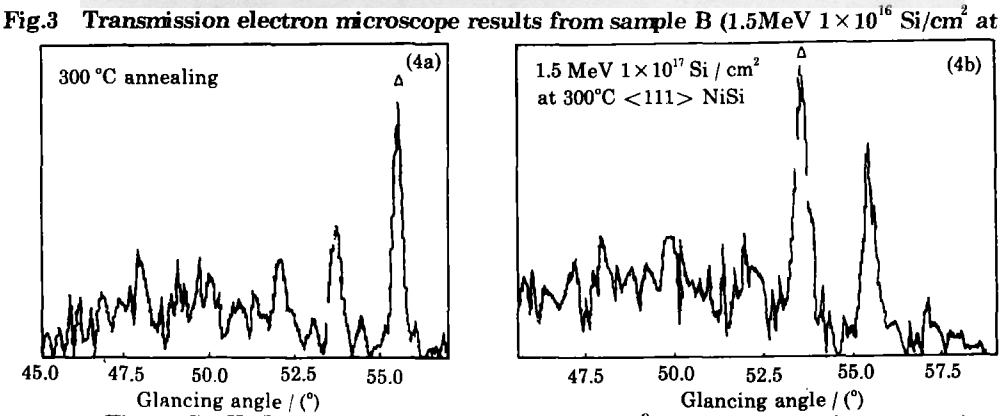


**Fig.4 Co $K_\alpha$ X-ray diffraction patterns with 1° glancing angle for sample A**

## 2.4 NiSi competing reactions

Similar conditions were found in sample A. The existing NiSi layer did not react with Ni or Si by annealing at temperature lower than 350℃. The thickness of NiSi layer was increased after 400℃ annealing. However, 1.5 MeV Si ion beam bombardment at room temperature to 300℃ induced NiSi layer reacting with Ni layer to form $Ni_2Si$. The diffraction patterns of Co $K_\alpha$ X-ray with I° glancing angle for the reactions are shown in Fig.4. The Ref.[7] indicated that the strongest and the second strongest lines of NiSi phase are 55.61° and 53.81°, respectively, while the strongest line of $Ni_2Si$ phase is 53.66°. In Fig.4a the diffraction peak at 55.61° is higher than that at 53.81°, while the intensity of the two peaks is reversed in Fig.4b. It means that the existing NiSi layer reacted with Ni layer to form $Ni_2Si$ phase after 1.5MeV Si bombardment. The TEM image with corresponding diffraction pattern for the reaction is shown in Fig.5.

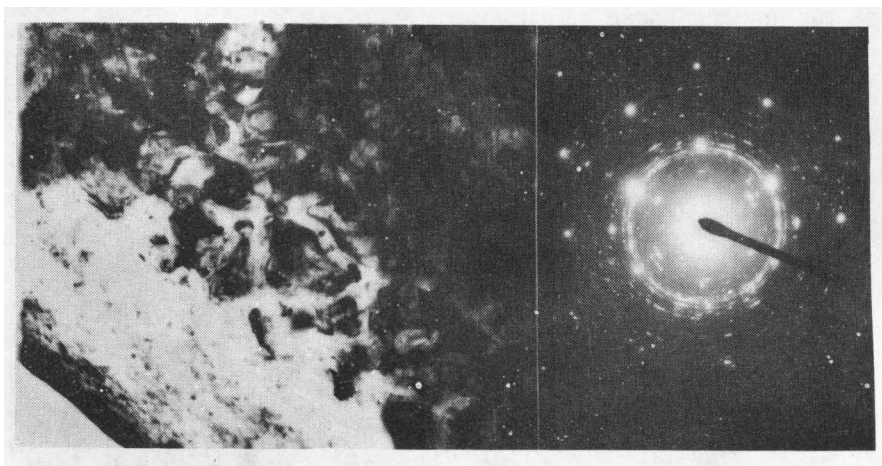

**Fig.5 Transmission electron microscope results from sample A (1.5 MeV $1\times10^{17}$ Si/cm$^2$, 300°C)**

## 3 DISCUSSION

In layer structure samples the sequence of phase formation for Ni silicide is well known. $NiSi_2$ is a stable phase. Normally ion beam mixing for silicide formation at appropriate temperature which is lower than thermal formation temperature leads to the same phase sequence as that by thermal annealing, and provides the possibility of forming metastable crystal phase because of raising the energy level of the system[3]. Our previous work[6] reported that part of

**Table 1**

**The heat of formation for some reactions of interest (calculation)**

| Reactants | Products | Heat of formation/ 4184J |
|---|---|---|
| Ni+Si | $Ni_2Si$ | -31.5* |
| | $Ni_2Si$ | -20.4 |
| | $NiSi_2$ | -20.7 |
| NiSi+Si | $NiSi_2$ | -0.3 |
| NiSi+Ni | $Ni_2Si$ | -11.1* |
| $NiSi_2$+Ni | NiSi | -20.3 |
| | $Ni_2Si$ | -42.3* |

* Represents the predicted reactions

amorphized $NiSi_2$ layer was also recrystallined easily by thermal and ion beam. The present results indicate that $NiSi_2$ is not stable if the $NiSi_2$ layer is sandwiched between Ni and Si, and that the phase transition induced by thermal and ion beam mixing in radiation enhanced diffusion regime is also different.

If we assume that in solid-state reactions the system free energy is equal to the enthalpy change $\Delta H$, the heat of silicide formation for some reactions of interest here could be calculated. The results are summarized in Table 1. The predicted reactions completely coincided with our results of ion beam induced reactions. For the reactions induced by thermal annealing the temperature threshold of reaction. NiSi+Ni and $NiSi_2$+Ni, are higher than 350℃ and 400℃, respectively, at which products $Ni_2Si$ has been reacted with Si to form NiSi phase. So the thermal reactions will drive the system to NiSi phase directly.

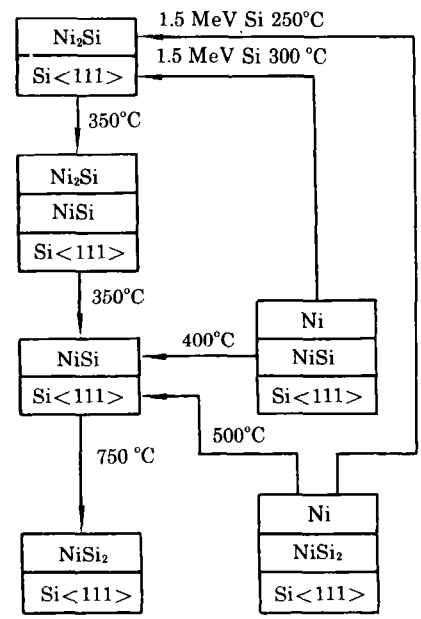


**Fig.6 Schematic diagrams showing the sequence of phase formation in the Ni silicide competing reaction with Ni and Si, induced by thermal annealing and MeV Si ion beam mixing**

R.C.Cammarata *et al*[4] indicated that Ni silicide formation is also influenced by surface energy in layered samples. We deduce from Ni silicide formation of layered system that the surface energy between $Ni_2Si$/Ni is less than that between $NiSi_2$/Ni. It means that reaction of $NiSi_2$/Ni to form $Ni_2Si$ will reduce surface energy.

As a summary the competing reactions of existing Ni silicides with Si or Ni induced by thermal and MeV ion beam mixing are shown schematically in Fig.6.

## REFERENCES

1 Nicolet M A, Lau S S. VLSI electronics: microstructure science. New York: Academic Press, 1983; Vol.6
2 Hung L S, Mayer J W. Thin solid Films, 1983; 199:85
3 Olowolfe J O, Nicolet M A, Mayer J W. Thin Solid Films, 1975; 38:143
4 Cammarata R C, Thempson C V, Tu K N. Appl Phys Lett, 1987; 51:1106
5 Rao Ziqiang, Sood D, Williams J S. to be published
6 Ridgway M C, Elliman R G, Williams J S. Appl Phys Lett, 1990; 56:2117
7 d'Heurle F, Petersson C S, Baglin J E E *et al.* J Appl Phys, 1984; 55:4208
8 Hung L S, Hong Q Z, Mayer J W. Nucl Instr Meth, 1989; B37/38:414