# A NOVEL PROCESS TO FORM EPITAXIAL SI STRUCTURES WITH BURIED SILICIDE

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## ABSTRACT

The interaction during low temperature thermal annealing of metal atoms from a Ni film evaporated on top of Si structures with a buried amorphous layer formed by ion implantation has been investigated. Rutherford Backscattering Spectrometry (RBS)/channeling, cross-sectional transmission electron microscopy (XTEM) and X-ray microanalysis were used to determine structures and compositions. It is shown that the combination of such silicon properties as the increased rate of silicidation reaction for amorphous silicon with respect to the crystalline one in combination with high metal atom diffusivity leads to formation of buried epitaxial Ni silicide islands at the interface between the amorphous and the top crystalline silicon layers. During thermal annealing at temperatures as low as 350° C, these islands move through the a-Si layer leaving behind epitaxially recrystallized Si.

## INTRODUCTION

Epitaxial Si structures with buried silicides are of growing interest because of their potential use in specific electronic devices and as interconnects in three dimensional integral circuits. Ion implantation of metal atoms and molecular beam epitaxy techniques are usually employed to form epitaxial silicon structures with buried cobalt or nickel silicides [1,2].

It is known that amorphous silicon has an excess of a free energy with respect to crystalline silicon ranging from 11 to 20 kJ/mol depending on the structural relaxation of amorphous silicon [3,4]. This means that free barrier and temperature of silicide nucleation should be lower on a metal/a-Si interface with respect to metal/c-Si interface because of the contribution of the crystallization heat of a-Si to the total heat of silicidation reaction. This was experimentally confirmed for Co disilicide formation [5] as well as for some other silicides.

Many metal atoms are known to be a fast diffusant in crystalline silicon. In many cases considerable diffusion transport of metal atoms takes place at a temperature lower then the temperature of solid phase recrystallization of amorphous silicon. This means that if the diffusion transport of metal atoms to the buried amorphous layer is high enough at some minimum temperature necessary for selected metal reaction with amorphous silicon, silicide growth on upper crystalline-amorphous silicon interface will be preferential with respect to silicidation at a metal-crystalline silicon interface.

The present work is devoted to investigating of buried silicide formation by metal atom diffusion from a surface metal film to a buried amorphous layer formed by ion implantation.

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## EXPERIMENTAL

Diffusion limited transport of different metal atoms was estimated by solving a one-dimensional diffusion equation taking into account diffusivity and solubility of the elements in the temperature range from 200° C to 500° C [6]. Transient diffusion due to radiation damage present in the surface crystalline film after ion implantation was not taken into account. Cu and Ni were selected for the experimental study of buried silicide formation, mainly because of the high diffusion transport of this species and low temperature of Ni silicide formation. The transport Ni atoms through 400 Å thick c-Si film was estimated to be appr. $5*10^{15}$ $cm^{-2}$ during heat treatment at 350° C for 40 hours. More than an order of magnitude greater value was found for copper under the same conditions.

The following procedure was used for sample preparation. N-type (100) silicon wafers with a resistivity of 7.5 Ω*cm were implanted with 100 keV $P^+$ ions to a dose of $10^{15}$ $cm^{-2}$ at room temperature. After ion implantation one half of each sample was preannealed at 450° C for one hour in flowing argon to form sharp interfaces between amorphous and crystalline silicon. Then all samples were subjected to chemical cleaning in 4% HF acid for few minutes to remove a native oxide followed by evaporation on the top of each sample of a ~100 Å thick Ni film. Metal evaporation was done under high vacuum conditions ($2*10^{-6}$ Pa).

After metal evaporation part of every sample subjected to preliminary annealing or not was annealed under vacuum ($10^{-4}$ Pa) at 200 to 500° C with a duration from 15 min to 159 hours.

## RESULTS AND DISCUSSIONS

All the samples were analyzed by RBS with the channeling technique. Table I lists the summary of RBS investigations of metal atoms in the surface regions of the structures after thermal annealing at all regimes used.

**Table I.** Metal atoms presence on the crystalline-amorphous silicon interface after thermal annealing at different regimes.

| Sample number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Metal | Ni | Ni | Ni | Ni | Ni | Ni | Ni | Ni | Ni | Ni |
| Preannealing | no | yes | no | yes | no | yes | no | yes | no | yes |
| Main anneal temperature (°C) | 200 | 200 | 250 | 250 | 350 | 350 | 350 | 350 | 250/43h + 500/1h | 250/43h + 500/1h |
| Duration (h) | 159 | 159 | 43 | 43 | 0.25 | 0.25 | 43 | 43 | --"-- | --"-- |
| -- Ambient | * | * | $N_2$ | $N_2$ | * | * | * | * | * | * |
| Metal atom accumulation on interface | no | no | no | no | no | no | yes | no | yes | yes |
| Metal atom position with respect to substrate | no | no | no | no | no | no | yes | no | no | no |

* - vacuum

As seen from table I metal atoms accumulation on the front interface between crystalline and amorphous silicon is observed in samples 7, 9 and 10 with Ni film on the top and only in sample 7 Ni atoms in the interface region located in regular manner with respect to Si substrate.

A RBS channeling spectrum of the structure after ion implantation followed by Ni film evaporation is shown on Figure 1. Figure 2 contains the channeling and random spectra of sample #7. This sample was not subjected to preliminary heat treatment after ion implantation prior to Ni film evaporation. The main anneal was performed at 350° C for 43 hours in

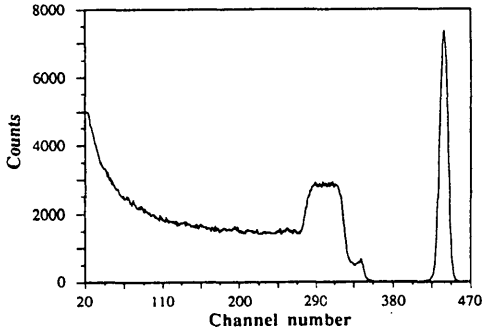


**Figure 1.** 1.4 MeV $^4He^+$ RBS channeling spectrum of the sample implanted with $P^+$ ions to a dose of $10^{15}$ $cm^{-2}$ after thermal treatment at 450° C for 1 hour followed by 100 Å Ni film deposition. Scattering angle 115°.

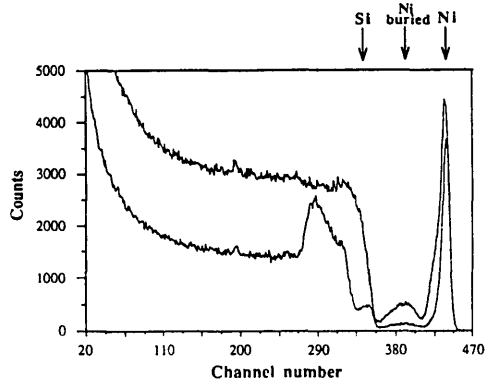


**Figure 2.** 1.4 $^4He^+$ MeV RBS random and channeling spectrum of sample #7: (100Å)Ni/c-Si/a-Si/Si(substrate.) structure annealed at 350° C for 43 hours. Scattering angle 115°.

vacuum after metal evaporation. Comparison of RBS spectra in Figures 1 and 2 shows that considerable changes occur in as deposited (100 Å) Ni/ c-Si / a-Si /Si (substrate) structure after thermal annealing. It is seen that accumulation of Ni atoms in a buried layer on c-Si/a-Si interface takes place in a regular (epitaxial) way with respect to the Si substrate with the maximum Ni concentration in the buried layer being located in the region of amorphous silicon. There is still approximately 400 Å thick layer of crystalline Si with relatively low Ni content remaining between the a-Si and the surface of the structure. To find out the detailed structure of this sample, it was studied with XTEM and X-ray microanalysis techniques. A bright field XTEM image of sample #7 is presented in Fig.3.

Fig.4 shows characteristic X-ray emission spectra from Si and Ni atoms of sample #7 measured on a buried silicide island, the crystalline silicon film above it and the interface region between crystalline silicon and metal film. This data proves that a silicon layer with relatively small Ni concentration exists between two Ni rich regions.

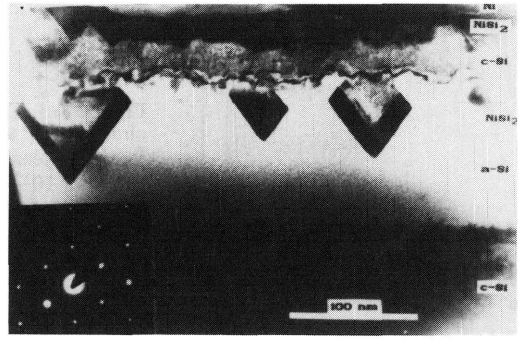


**Figure 3.** XTEM bright field image in orientation [110] and selected area diffraction patterns of the sample #7.

The following scheme may be proposed to take into account annealing induced changes in the structure of the sample examined. During thermal annealing at 350° C duffusion of Ni to the buried amorphous-crystalline interface occurs. The rate of silicide nucleation by metal atom interaction with amorphous silicon is higher than with the crystalline one. This lead to formation of buried silicide islands. Nucleation of buried silicide goes from crystalline surface silicon and their further growth proceeds epitaxially with respect to substrate. It is confirmed and by RBS spectra on Fig.2 and diffraction pattern on the inset of Fig.3. We may conclude that the silicide crystallizes in the $NiSi_2$ face-centered cubic structure which is isoperiodic (with misfit 0.4%) and almost isomorphic with silicon.

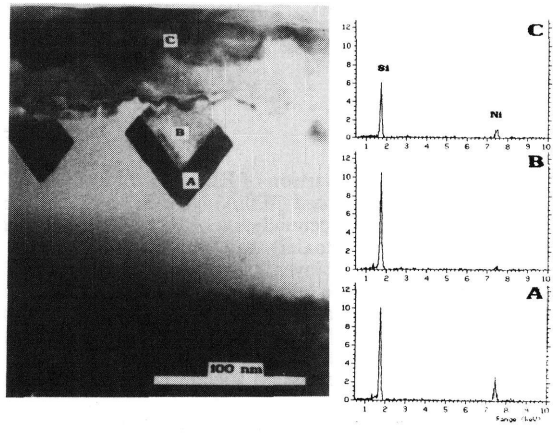


**Figure 4.** Ni and Si atoms characteristic X-ray emission intensity measured from different spots on the structure with buried silicide (sample #7).

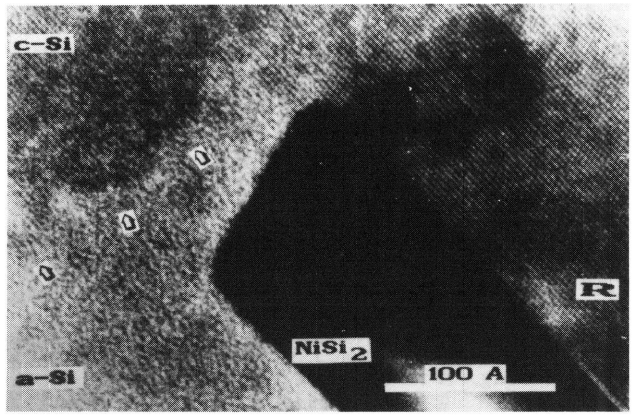


**Figure 5.** High resolution {110} image. Arrows indicate interface between c-Si and a-Si. 1 and 2 - recrystallization frontline, R-recrystallized silicon.

From Fig.5 it is seen that frontline of crystallization of nickel disilicide is proceeding parallel to <111> directions. It results in a shape of $NiSi_2$ islands as a set of prostrusions facetted with <111> planes with lowest free energy. Appearance of a back crystallization frontline is the main difference of diffusion-limited growth process in this experiment from those repeatedly observed in before [7].

Buried epitaxial silicide formation was observed on the sample #7 which was not subjected to preliminary annealing before Ni film evaporation. This may happen because of at least two reasons. First, radiation damage in crystalline surface region may enhance diffusion-limited Ni atoms transport from the surface metal film to buried amorphous layer. Second, the transition of buried amorphous layer from "as-implanted" to "well-relaxed" structural state with lower free energy induced by thermal treatment at a temperature lower then that of solid-phase epitaxy [8]. To investigate which of the two mechanisms dominate, we subjected a sample not heat treated after ion irradiation and with Ni film evaporated to a thermal annealing at 350° C for 15 min, the time when the most of transient processes of radiation defect rearrangement are almost completed [9]. Buried silicide growth was not observed in this sample. This means that damage accumulated in the surface region does not play by itself a key role in the process of silicide growth studied. The structural state of amorphous silicon is also important for buried silicide formation in the process investigated.

The last is additionally confirmed by accumulation of Ni atoms on a-Si/c-Si interface in samples no.9 and 10 (without and with preannealing, resp.) annealed at 500° C for 1 hour while at a rather smaller peak concentration than in sample #7.

## CONCLUSIONS

In the present work a novel process of epitaxial silicon structures with buries silicide is presented. Prolonged annealing at at 350° C of the structure with buried amorphous layer formed by ion implantation followed by Ni film evaporation leads to formation of epitaxial $NiSi_2$ islands buried within amorphous layer. Growing islands move through amorphous silicon layer leaving c-Si behind.

ACKNOWLEDGMENTS

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