Incorporation of Fe into NiSi\textsubscript{2} precipitates

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1016/j.egypro.2011.01.005">http://dx.doi.org/10.1016/j.egypro.2011.01.005</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>Elsevier</td>
</tr>
<tr>
<td>Version</td>
<td>Final published version</td>
</tr>
<tr>
<td>Citable link</td>
<td><a href="http://hdl.handle.net/1721.1/92557">http://hdl.handle.net/1721.1/92557</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>Creative Commons Attribution</td>
</tr>
<tr>
<td>Detailed Terms</td>
<td><a href="http://creativecommons.org/licenses/by-nc-nd/3.0/">http://creativecommons.org/licenses/by-nc-nd/3.0/</a></td>
</tr>
</tbody>
</table>
EMRS Fall Meeting 2010

Incorporation of Fe into NiSi₂ Precipitates

S. Langkaua, G. Wagnera, M.I. Bertoni², T. Buonassisi², G. Kloessa

¹Institute of Mineralogy, Crystallography and Materials Science, Leipzig University, Scharnhorststr. 20, D-04275 Leipzig, Germany
²Massachusetts Institute of Technology, 77 Massachusetts Avenue 35-213, Cambridge, MA 02139, USA

Abstract

The present paper provides evidence that Fe can be incorporated into NiSi₂ precipitates by solid-state diffusion. Furthermore, analysis of Si crystals contaminated with Ni and Fe at 1100°C and post annealed at 600°C and 800°C for 20 – 240 min revealed a strong indication that this incorporation is limited by bulk diffusion rather than incorporation kinetics.

© 2011 Published by Elsevier B.V.

Keywords: precipitates, silicides, silicon, solid state diffusion, time dependence, transmission electron microscopy

1. Introduction

Electrical properties of solar-grade silicon can be improved by systematic precipitation of detrimental metal contaminants [1]. The observation of multi-metal silicide precipitates in silicon solar material [2 – 4] raises the question, whether atoms of metal species that tend not to precipitate readily (e.g., Fe) can be incorporated into silicide precipitates of other metals (e.g., NiSi₂). Herein, we show that Fe can be incorporated into NiSi₂ precipitates by solid-state diffusion and analyse the temperature and time dependency of this incorporation.
2. Proof of Fe incorporation into NiSi$_2$ precipitates

2.1 Experimental

Samples were weighted in from powders of elements (Si 67at. %, Ni 13at. %, Fe 20at. %) and annealed at 900°C for two days. Subsequently, they were grindded for homogenization and then annealed again at 800°C for 7 days. This procedure resulted in a mixture of silicon and silicide grains.

Afterwards, samples were prepared for transmission electron microscopy (TEM) analysis, i.e., polished and bonded on Cu rings for stabilization before they were etched with Ar$^+$ ions until perforation.

TEM measurements were carried out at a Philips CM-200 microscope equipped with a LaB$_6$ cathode and a super-twin lens. The chemical composition of precipitates was determined by TEM–EDX measurements carried out in nanoprobe mode with a beam diameter of 5–7 nm. The EDX system (EDAX) was calibrated and hence allowed for a quantitative analysis with uncertainties <1 at. %.

2.2 Results

Ternary silicide precipitates containing Ni and Fe simultaneously were detected in the silicon grains. The maximum Fe content was measured to be Fe/(Fe+Ni) = 30 at. %, which agrees with the solubility reported for bulk phases [5,6]. These precipitates exhibit {111} interfaces to the silicon matrix and have an irregular octahedral shape with platelet-like habit. The precipitates have an NiSi$_2$ structure in A- or B-type orientation to the matrix and form at structural defects. A more detailed description of their properties is given in [7].

2.3 Discussion

Precipitates were detected only in few of the silicon grains, but then in surprisingly high densities. Assuming that these particles formed by precipitation during cooling, all metal atoms contained in them must have been dissolved in the surrounding matrix during annealing. This corresponds to concentrations of $10^{19} – 10^{20}$ atoms/cm$^2$ in the Si matrix. These values exceed the solubility of Ni and Fe in Si at the highest temperature applied (900°C) by 3 to 6 orders of magnitude ($c_0$(Ni)=$7 \cdot 10^{16}$cm$^3$, $c_0$(Fe)=$4 \cdot 10^{15}$cm$^3$ [8]). Therefore, it is very unlikely that precipitates formed during cooling from annealing temperatures. Concentrations of $10^{19} – 10^{20}$ metal atoms/cm$^2$ could be introduced into the material by ion milling for TEM sample preparation, which is explained in detail in [7].

3. Time and Temperature Dependency of Fe Incorporation

3.1 Experimental

High purity silicon crystals (5x5x10mm$^3$) were intentionally contaminated with Ni and Fe by depositing layers of the metals onto the surface and subsequently annealing the samples at 1100°C. After 5 hours, samples were quenched to room temperature to freeze in the equilibrium solubility concentration of Ni and Fe at 1100°C ($c_0$(Ni)=$8 \cdot 10^{17}$cm$^3$, $c_0$(Fe)=$3 \cdot 10^{15}$cm$^3$ [8]). Thereafter, samples were polished and etched with a HF(50%):HNO$_3$(65%)=1:12.5 mixture to remove residual metal silicides from the surface. Afterwards, post-annealing at different temperatures for different times was conducted to investigate the dependence of precipitate ripening and Fe incorporation on these parameters. The following conditions were considered: a) 600°C, 20 min, b) 600°C, 240 min, c) 800°C, 20 min, d) 800°C, 240 min.
Fig. 1: TEM BF images, SAD patterns and EDX mappings of precipitates after annealing at 600°C, a) 20 min, b) 20 min, c) 240 min

In order to avoid surface effects, slices in approximately 1 mm distance from the surface were cut out of the crystals for TEM preparation (for further details, cf. Sec. 2.1).

3.2 Results

Precipitates after post-annealing at 600°C for 20 min and 240 min

Fig. 1 shows typical defects observed after post-annealing at 600°C. NiSi₂ precipitates formed as thin platelets, which, at the same time, are stacking faults in the surrounding Si matrix. Evidence for this is provided by two observations: Firstly, accumulated Ni was usually observed by EDX across the entire precipitate/stacking fault (see EDX mappings in Fig. 1). Secondly, the SAD pattern of the precipitate in Fig. 1a is characteristic for NiSi₂ in [001] orientation and differs from the SAD pattern of Si in [001] orientation by the presence of 200 reflection spots
(encircled in Fig. 1a). Furthermore, the diameter of these precipitates agrees roughly with that observed for pure NiSi₂ precipitates after annealing at 600°C for 20 min (1.1 μm [9]).

Surprisingly, Cu was accumulated in small particles accompanying these defects (see mappings in Fig. 1). Corresponding SAD patterns showed double diffraction spots (Fig. 1b) and diffraction contrast images revealed Moiré fringes (Fig. 1b). Both are typically observed for Cu₅Si precipitates in Si, caused by superposition of the two very different structures [10]. In addition, colonies of many tiny precipitates (Fig. 1a, c) are characteristic for Cu₅Si precipitation [11].

There is no indication of mixing of the Ni and Cu silicide precipitates in these samples, although miscibility was observed at bulk phases [6] and precipitates [12] before.

In samples annealed for 20 and 240 min at 600°C, TEM-EDX analysis revealed no accumulation of Fe in NiSi₂ precipitates.

Precipitates after post-annealing at 800°C for 20 min

Fig. 2 shows some NiSi₂ precipitates found in samples annealed for 20 minutes at 800°C. They show the same habit as reported in Sec. 2.2: distorted octahedra with platelet-like habit (cf. sketch in Fig. 2b, [7]). In some cases, these NiSi₂ precipitates are accompanied by colonies of smaller particles (Fig. 2a). Usually observed Moiré fringes indicate that these particles are Cu₅Si precipitates [10].

EDX analysis revealed a clear increment of the Fe signal at these precipitates with respect to the background signal detected in the Si matrix (~0.1%). The measured ratios of at. % Fe/(Fe+Ni) are given in Fig. 2c. Note that EDX measurements are always a superposition of the small precipitates and the surrounding matrix. Hence, the total metal content measured was usually 1 to 5 at. %. Consequently, the determined Fe/(Fe+Ni) ratio might be affected by considerable errors. However, the total number of 13 measurements detected at 6 different precipitates serves a fair statistic and mitigates the error of the determined average Fe/(Fe+Ni)=2.1% (standard deviation 0.8%).

Precipitates after post-annealing at 800°C for 240 min

NiSi₂ precipitates found after annealing for 240 min at 800°C (Fig. 3) were always accompanied by colonies of small Cu₅Si precipitates and dislocations. Furthermore, they often occurred together with stacking faults.

The EDX mapping in Fig. 3 shows that Fe was enriched in NiSi₂ precipitates, rather than in Cu₅Si precipitates or at the stacking fault. Results of quantitative EDX point measurements are given in Fig. 4. The average Fe/(Fe+Ni) ratio measured at the NiSi₂ precipitates after 240 minutes at 800°C was 24.5% (standard deviation 5%).

Fig. 2: a, b) TEM BF images of typical precipitates after annealing at 800°C, 20 min, c) Fe/(Fe+Ni) ratio in all measured precipitates
3.3 Discussion

Cu contamination

There are three possibilities, how the unintentional Cu contamination might have taken place. Firstly, Cu might have been accidentally introduced during metal deposition and annealing for sample preparation. Secondly, in-diffusion from the furnace tube or silica ampoule during annealing might have caused Cu contamination. Thirdly, during TEM specimen preparation, Cu from the stabilization ring could have been introduced into the samples by ion milling.

Ripening

NiSi₂ precipitates are known to form as thin platelets (thickness of only 2 \{111\} planes) with large diameters (0.86µm) upon quenching of Ni-contaminated Si crystals [9]. During post annealing, these precipitates are expected
to approach an energetically more favourable shape, i.e., a smaller surface/volume ratio. Hence, their diameter decreases, while their thickness increases [9].

The shape of precipitates did not change significantly between 20 min and 240 min, neither in the samples annealed at 600°C, nor in those annealed at 800°C (cf., Fig. 1 – 3). However, precipitates annealed at 800°C are observed to have a smaller diameter, which is due to faster ripening at the higher temperature.

Fe incorporation

The ratio of solubilities of Fe and Ni in Si at the in-diffusion temperature (1100°C) \( c_S(\text{Fe})/c_S(\text{Fe}+\text{Ni})\) = 0.4% is much smaller than the detected ratios Fe/(Fe+Ni) in the precipitates (2.1% after 20 min, 800°C, 24.5% after 240 min, 800°C). Consequently, even if all Fe atoms contained in the samples after in-diffusion were incorporated into the NiSi2 precipitates, they would be insufficient to cause concentrations as high as detected.

The observed Fe/(Fe+Ni) ratios might arise from in-diffusion of Fe from an external source. Driving forces for such a process are entropy and the high solubility of Fe in NiSi2 (Fe/(Fe+Ni)=34%, [6]).

The corresponding atom flux \( I \) can be calculated from the solubility \( S \), diffusivity \( D \) and travelled distance \( d \) by

\[
I = \frac{S \cdot D}{d}
\]

The resulting areal density \( N_{\text{area}}(\text{Fe}) \) can hence be estimated by

\[
N_{\text{area}} = I \cdot t
\]

Transforming \( N_{\text{area}} \) into the atomic volume density \( N \)

\[
N = (N_{\text{area}})^{3/2}
\]

allows for an estimation of the resulting Fe/(Fe+Ni) ratio, assuming that the Ni atoms contained in the samples correspond to the solubility of Ni in Si at the in-diffusion temperature (1100°C). Presuming that all Ni atoms are precipitated and the incorporation of Fe atoms into the NiSi2 precipitates is fast in comparison to their transport, the increase of Fe/(Fe+Ni) in the NiSi2 precipitates under different conditions is given by Fig. 5. The distance between surface and precipitates was approximately 1 mm (see Sec. 3.1). The theoretical estimation agrees well with the experimental observations, which strongly supports the presented hypothesis.

However, it remains unclear from what external source Fe was incorporated. Residua of the deposited metal layers could serve as a source, if their removal by polishing and etching was insufficient (see Sec. 3.1). Fe could also originate from the surrounding silica ampoule or the alumina furnace tube.

4. Conclusion

Fe atoms can be accumulated in NiSi2 precipitates by solid-state diffusion. Encouraging this mechanism during processing might improve solar cell efficiency, since Fe atoms in p-type Si have a large nucleation energy barrier and tend not to precipitate readily [13, 14].

The incorporation velocity of Fe into the NiSi2 seems to be determined by bulk iron diffusion rather than by the incorporation kinetics. More work needs to be done to verify

![Fig. 4: Fe/(Fe+Ni) ratio in NiSi2 precipitates after annealing at 800°C, 240min](image-url)
this conclusion, e.g., the time dependent diffusion experiments should be repeated with a well defined Fe source and a precisely defined distance between surface and precipitates.

In addition, it remains open how Cu was introduced into the present samples. It would be interesting to clarify this question to conclude how Cu, Ni and the stacking faults interacted in the present samples to form the complex defects observed.

![Graph](image_url)

**Fig. 5:** Estimated increase of the ratio Fe/(Fe+Ni) in NiSi₂ precipitates (green lines), assuming that Ni diffused into the samples at 1100°C and precipitated completely upon quenching, while additional Fe atoms diffused in from an external source during post-annealing. The diffusion of Fe atoms is presumed to determine the rate of incorporation. Different conditions (temperature, distance \( d \) between surface and precipitates) are given for each graph. Experimental observations (black dots) agree well with this estimation.
5. Acknowledgment

The authors are grateful to the electron microscopy facility at CMSE, MIT. We would also like to thank David P. Fenning, Sandra Lobe, Sven Gerhardt, Jan Lorbeer, Ronny Kaden and Michael Bratsch for enlightening discussions. Support for this research was partially provided by the U.S. Department of Energy, under contract numbers DE-FG36-09GO19001 and through the generous support of Doug Spreng and the Chesonis Family Foundation. One author (S.L.) wishes to thank the Fellowship Foundation (Stiftung Stipendien-Fonds) of the German Chemical Industry Association (VCI) and the German Academic Exchange Service (DAAD) for providing graduation fellowships.

6. References


