(Ni,Fe)Si$_2$ Precipitates in Silicon

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Cost-efficient mc-silicon solar material is usually contaminated with transition metals. Metal impurities either exist as interstitial atoms dissolved in Si or as precipitated silicides [1]. In both cases they cause carrier recombination and consequently a decrease in solar cell efficiency [2, 3]. Whether precipitation of the impurities is desired or not depends on the properties of the precipitates and the further processing planned for the material [4]. Hence, metal silicide precipitates have been widely determined and interactions between different metals during precipitation are in focus of nowadays research [5, 6].

The results presented here were ascertained at silicon grains simultaneously contaminated with Ni and Fe at 800-900°C. Detected precipitates either contain only Ni or both Ni and Fe. HRTEM and SAD images (Fig. 1) show, that all precipitates have NiSi$_2$ structure. Quantitative analysis of chemical composition of a ternary precipitate revealed Ni$_{0.84\pm0.07}$Fe$_{0.16\pm0.07}$Si$_2$.

NiSi$_2$ precipitates preferentially occur at dislocations and dislocation networks, but were also detected statistically distributed within the matrix (Fig. 2a). By contrast, (Ni,Fe)Si$_2$ precipitates were found merely at dislocations, dislocation networks and stacking faults (Fig. 2b).

All precipitates are confined by {111} planes. While precipitates statistically distributed in matrix are regular octahedra, at dislocations and stacking faults octahedra become distorted and subordinate {001} faces can occur. The extension of the precipitates generally ranges between 15 and 300 nm. Under equal initial conditions the precipitates at dislocations reach about the fourfold size of the statistically distributed precipitates (Fig. 2a).

Which interactions between metal impurities and dislocations can account for these observations? Accumulation of metal impurities at dislocations in Si due to elastic interactions is negligible unless metal clusters contribute to it [7]. Nevertheless, accumulation due to chemical interactions can be efficient. Furthermore, enhanced diffusion of impurities along dislocation cores ('pipe diffusion') was reported to be an important mechanism for Ni precipitation at dislocations [2]. Additionally, the precipitation energy barrier can be lowered by elastic and chemical interactions.

Consequently, the preferred occurrence of NiSi$_2$ precipitates at dislocations should be due to pipe diffusion, accumulation caused by chemical interactions and reduction of precipitation energy barrier by both chemical and elastic interactions. The same causes should be responsible for incorporation of Fe into the precipitates, except for the reduction of energy barrier by elastic interactions, which is - due to our estimations - influenced in an energetically unfavorable way by incorporation of Fe. The larger size of precipitates at dislocations must be caused by higher growing rates and/or Ostwald ripening, and consequently, by faster diffusion along the dislocation core. The reasons for the distorted octahedral shape might be the elongation of precipitates parallel to the dislocation core to reach higher elastic energy gain during early growth stages or enhanced diffusion along one direction, namely the dislocation line.

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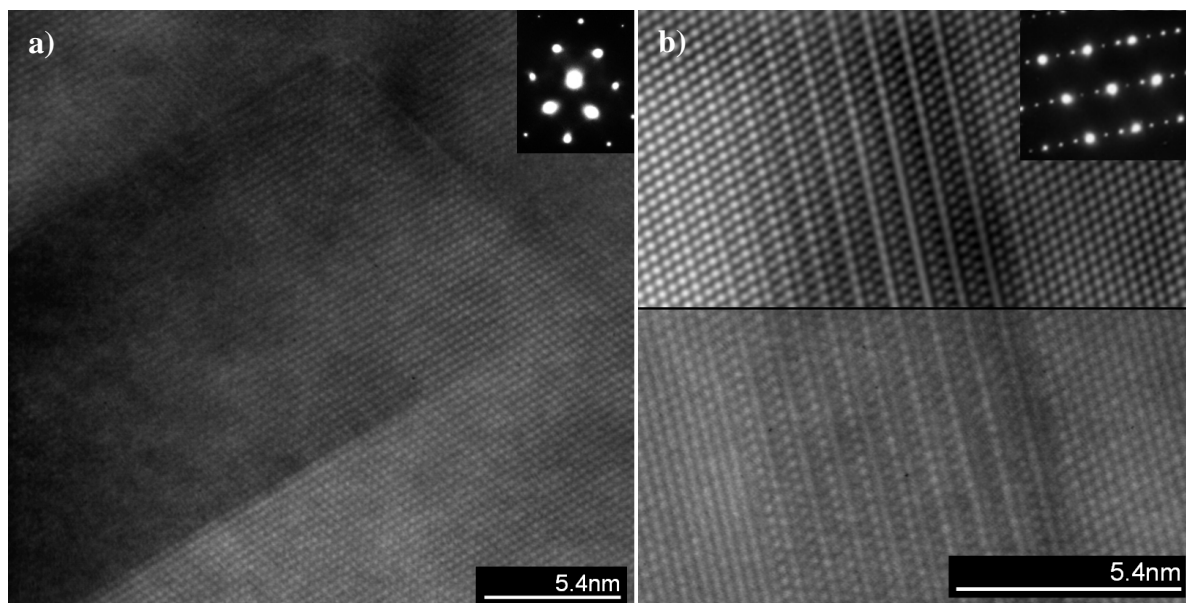7. K. Sumino, Microelec. Eng. **66** (2003) p268

Figure 1: HRTEM and SAD images of precipitates having NiSi$_2$ structure surrounded by Si matrix, B=[110] **a)** A-type orientation **b)** B-type orientation (upper part of HRTEM image is Bragg filtered)
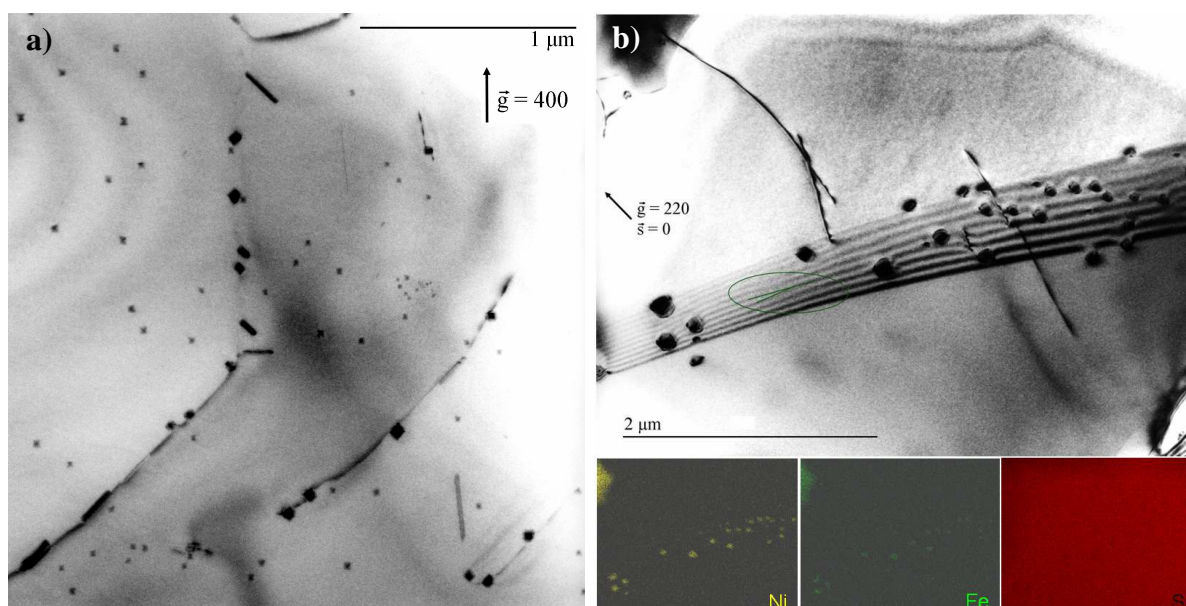

Figure 2: a) Precipitates at dislocations and statistically distributed in matrix **b)** Precipitates at a stacking fault, EDX mappings prove that they contain both Ni and Fe.