

Dependence of Precipitation Behavior of Cu and Ni in CZ Multicrystalline Silicon on Cooling Conditions

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Dependence of precipitation behavior of Cu and Ni in CZ and multicrystalline silicon on cooling conditions

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The objective of this study was to investigate the size, chemical state, and spatial distribution of metal clusters formed in substantially different cooling conditions of the samples. All samples were scratched on the back with Fe, Cu, and Ni wires and annealed at 1200°C for 2.5 hours in forming gas (N₂+5% H₂ ambient). “Slowly cooled” samples were cooled to room temperature inside of the furnace. The cooling took 12 hours, the cooling rate was 25-30 K/min in the beginning of the cool, dropping down to 3-8 K/min in the medium temperature range, and to even lower cooling rates by the end of the cool. “Quenched/reannealed” samples were quenched in silicone oil, cleaned in hot acetone to remove oil residues, etched in HF:HNO₃ mixture to remove surface metal-silicides, inserted into a preheated furnace running at 655°C, annealed for 2.5 hours, and then slowly cooled in the furnace within approximately 12 hours. These two annealing conditions were combined with two types of samples: CZ samples with approximately 1.5×10⁶ cm⁻³ of oxygen precipitates, obtained from MEMC (courtesy of R.Falster), and multicrystalline Si samples grown at NREL using float zone technique by Ted Ciszek. Multicrystalline growth was achieved using heavily dislocated seed. The following four samples were analyzed: (1) a “slowly cooled” CZ sample; (2) a “slowly cooled” mc-FZ-Si sample; (3) A “quenched / reannealed” CZ sample; (4) A “quenched / reannealed” mc-FZ-Si sample.

Although all of these samples were intentionally contaminated with Cu, Ni, and Fe, very low density of iron clusters was found in XRF maps. Therefore, the majority of data presented below are confined to Cu and Ni only. It is known that iron rarely forms precipitates detectable by traditional analytical techniques such as transmission electron microscopy (TEM); the only experimental condition under which large iron-silicide precipitates were observed by TEM in the bulk of silicon samples were experiments with implantation of large doses of iron into silicon with a subsequent anneal (see [1] and references therein). It appears that iron prefers to homogeneously decorate extended defects rather than to form large metal precipitates. In addition, the relatively low solubility of Fe in single-crystalline silicon at 1200°C, which is at least two orders of magnitude less than Cu or Ni, can be a limiting factor for precipitate size.

In the slowly cooled CZ sample, very few decorated oxygen precipitates were visible in XBIC and Ni/Cu μ-XRF map (Fig. 1). In the slowly cooled mc-FZ-Si samples (Fig. 2), a clear image of grain boundaries was observed in the XBIC map. μ-XRF map of nickel revealed that Ni has very selectively precipitated at some of the grain boundaries. Copper precipitated in much lower concentrations, and copper-related contrasts were barely visible in μ-XRF maps. Even though copper has a higher solubility at the diffusion temperature than nickel, we see a much stronger signal from nickel than from copper. This observation lead us to the following two conclusions:

First, surface metal silicide, which serves as a source of metals during the high-temperature anneal, acts as a highly efficient sink during cooling. Lets estimate how the surface

area of a CZ sample with 10^6 cm^{-3} of oxide precipitates compares with the surface area of the sample. Let's say we have a 1 by 1 cm sample, 0.5 mm thick. Its surface area is 2 cm^2 , and its volume is 0.05 cm^3 . Assuming that $N=10^6 \text{ cm}^{-3}$ of oxide precipitates are formed by precipitation of $\Delta O_i=10^{18} \text{ cm}^{-3}$ of interstitial oxygen and using the standard value for density of silicon dioxide, the average radius of a precipitate is given by

$$r(\text{nm}) = \sqrt[3]{\frac{\Delta O_i(\text{cm}^{-3})}{N(\text{cm}^{-3})}} \times 0.174 = \sqrt[3]{\frac{10^{18} \text{ cm}^{-3}}{10^6 \text{ cm}^{-2}}} \times 0.174 = 1.74 \mu\text{m}$$

The total surface area of all oxygen precipitates in our sample with $V=0.05 \text{ cm}^3$:

$$S = 4\pi r^2 \times N \times V = 4\pi \times (1.74 \times 10^{-4} \text{ cm})^2 \times 10^6 \text{ cm}^{-3} \times 0.05 \text{ cm}^3 = 0.019 \text{ cm}^2$$

Hence, the total surface area of oxygen precipitates in the CZ sample is 100 times less than the surface area of the sample! It is not surprising that near-surface metal silicides are more efficient gettering sites for the dissolved metals than oxygen precipitates, which under the conditions of slow cooling gather the majority of dissolved metals from the wafer bulk.

In mc-FZ-Si samples the density of structural defects is higher than in CZ-Si (a rough estimate gives a value of 100 cm of GBs visible on each cm^2 of the wafer surface, or 5 cm^2 of GB area per cm^2 of the sample surface area), and therefore a larger fraction of the total metal concentration is found precipitated in the bulk for the same cooling conditions.

The second conclusion is that our observations confirm that precipitation of copper is associated with a greater precipitation/nucleation barrier than precipitation of nickel. This higher barrier is consistent with a large lattice expansion of copper silicide as compared to nickel silicide [2-5] and electrostatic repulsion between interstitial copper and nuclei of copper precipitates in p-type Si [6]. A larger barrier makes copper more selective in choosing where to precipitate, which leads to a lower density of copper-decorated sites than density of nickel-decorated sites despite a higher solubility of Cu.

About ten metal precipitates found in the slowly cooled mc-Si sample were analyzed in detail. It was found that the majority of the precipitates contain both Cu and Ni. Statistical correlational analysis between Cu and Ni using all data points in the map revealed that a large fraction of the particles were Ni-rich, with the ratio of Ni to Cu of approximately 3.4. A smaller fraction of the particles were Cu-rich, with the ratio of Cu to Ni of approximately 1.45. Absorption spectra of Cu were found to be similar to Cu_3Si only in the particles where Cu dominates. In particles in which Ni dominates, the phase of Cu did not agree with any of our standards. Our current model is that it could be a mixed copper-nickel silicide, e.g., $\text{Cu}_3\text{Ni}_{10}\text{Si}_7$. A work is in progress to synthesize a mixed copper-nickel-silicide for a comparative study. Several iron-containing particles were found and analyzed as well; the position of the absorption edge and shape of the absorption spectra were closer to iron silicide than to anything else, but the details did not fully agree neither with FeSi_2 nor with FeSi . An attempt to fit the observed absorption spectra by addition of a spectrum of iron oxide to that of iron silicide did not explain the shape of the experimental spectra either.

The precipitation behavior of Cu and Ni in “quenched /reannealed” samples was found to be completely different, see Figs. 3 and 4. In the CZ sample (Fig. 3) it appears that both Cu and Ni have decorated the same oxide precipitates. The density of decorated oxide particles matched the density of oxide precipitates. For instance, we counted 15 particles in the area of $470 \mu\text{m}$ by

410 μm . Assuming a 70 microns $\mu\text{-XRF}$ probing depth, we obtain the density of metal precipitates of $1.1 \times 10^6 \text{ cm}^{-3}$, which matches the density of the oxide precipitates. Hence, we conclude that all SiO_2 precipitates are metal-decorated. The ratio of Ni counts to Cu counts in this sample was in the range of 0.23 to 0.26, which reasonably matches the ratio of Ni and Cu solubilities. In the mc-Si sample (Fig. 4) all structural defects were beautifully decorated. Ni has strongly decorated all grain boundaries and weakly decorated intragranular dislocations. Copper was found on both grain boundaries and dislocations.

The observed strong decoration behavior can be explained as follows. Rapid quench from the annealing temperature prevents metals from diffusion towards the surface silicides. Once the surface silicides are removed by chemical etching and samples are inserted back into preheated furnace running at 655°C , quenched-in metals get mobile and at the same time remain highly supersaturated. Supersaturation of metals determines the energy gained by a metal when it precipitates and therefore the height of potential barrier for precipitation which it can overcome. In such conditions metals can precipitate at sites which would be very unfavorable if the sample were cooled slowly.

In summary, “quenched / reannealed” samples feature much higher density of decorated defects and overall much higher concentrations of Cu and Ni precipitated at structural defects than in the samples which were slowly cooled from 1200°C . In quenched/reannealed samples the detected concentrations of precipitated Cu is greater than that of Ni (which agrees with a higher Cu solubility), whereas in slowly cooled samples the Ni concentration is generally higher than the Cu concentration. We think that this difference is explained by the efficiency of surface silicides as a sink for the dissolved metals. Since Cu is a faster diffuser than nickel and since the barrier for nucleation of Cu precipitates is higher than that for Ni, a higher fraction of Cu diffuses out in slowly cooled samples, leaving a relatively high Ni concentration in the bulk. In contrast, in quenched/reannealed samples, where surface silicides are removed and supersaturation ratio (i.e., the ratio of the interstitially dissolved metal concentration to its equilibrium solubility) is sufficient for easy nucleation of Cu precipitates, both Cu and Ni precipitate in the bulk and the ratio of their measured concentrations better reflects the ratio of their solubilities.

Copper has been extensively used for delineation of defects in silicon; the technique is known as copper decoration (see, e.g., [7, 8]). Our results provide a direct evidence that the efficiency of this process greatly depends on the cooling regime of the wafer.

The findings of this study contribute to the understanding of the behavior of metal impurities during crystal growth. Faster cooling of ribbon/sheet/ingot is likely to lead to a higher density of small metal precipitates. Slow cooling would stimulate formation of a lower density of larger metal precipitates, which are likely to affect the minority carrier diffusion length to a lesser extent than high density of small precipitates. The range of temperatures where the cooling rate gets important includes temperatures where dissolved metals get supersaturated but remain highly mobile, i.e., may include temperatures from 1000°C down to 500°C , depending on the metal. Most cooling regimes used for ingot growth are actually close to what we used in the “slow” cool. Our results suggest that distribution of metals in an mc-Si wafer may be engineered by a heat treatment with a properly designed cooling profile.

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FIGURES

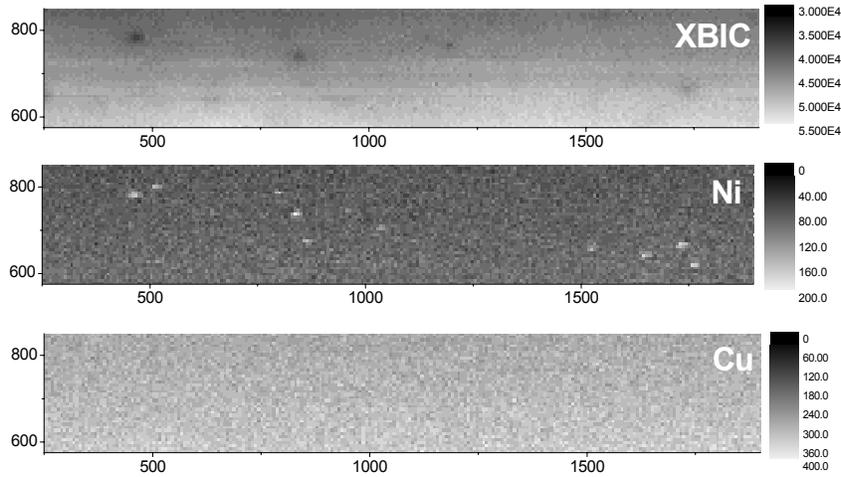


Fig. 1. Maps obtained on slowly cooled CZ samples. Ni and Cu μ -XRF maps were measured with a much larger step size than the beam size. Nearly every Ni precipitate had a small amount of copper in it, and vice versa. The scale on the maps is in microns.

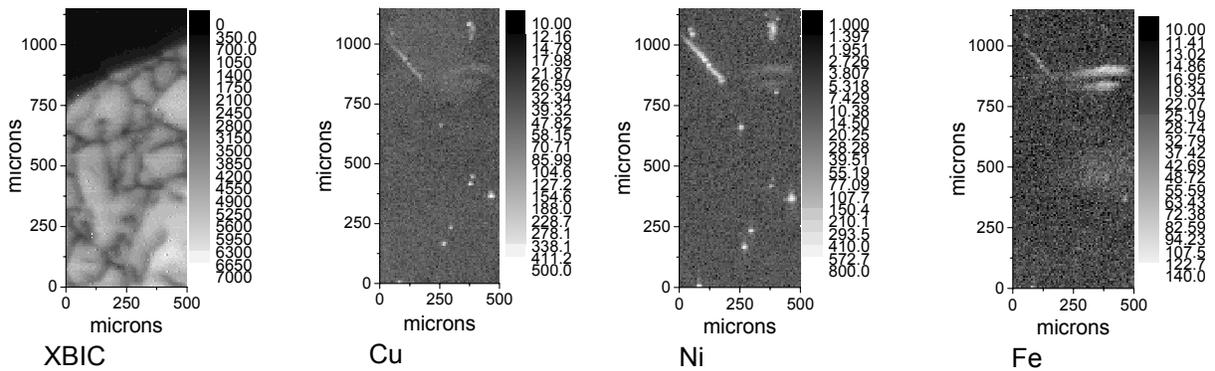


Fig. 2. Maps obtained on slowly cooled mc-FZ-Si samples: Ni μ -XRF map (top left), Cu μ -XRF map (top right), and XBIC (bottom left). The intensity scale is in arbitrary units (counts).

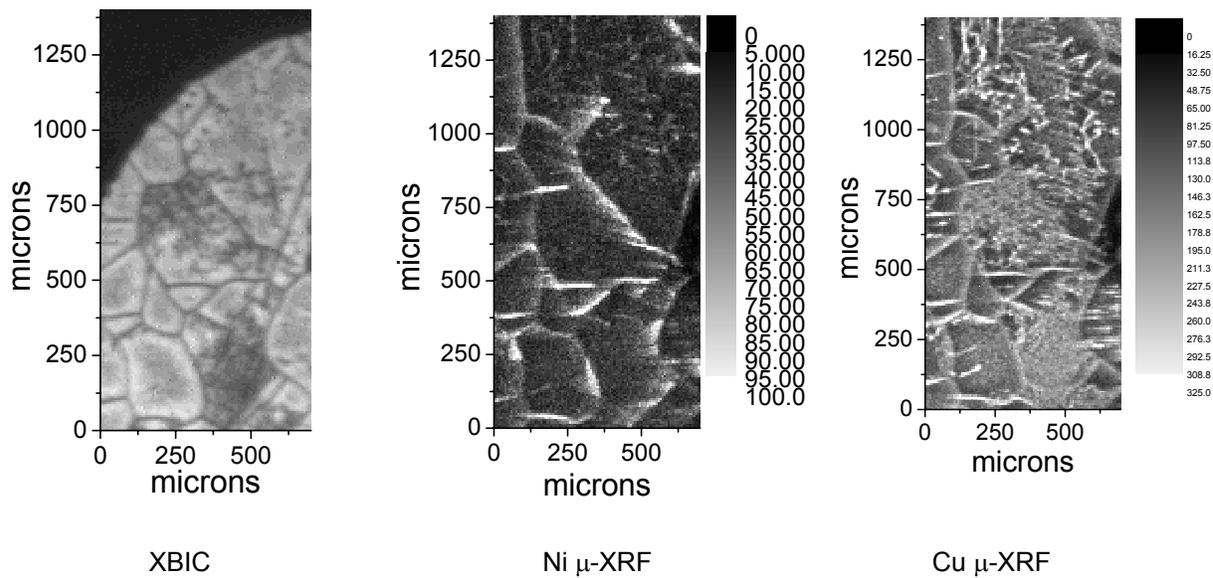
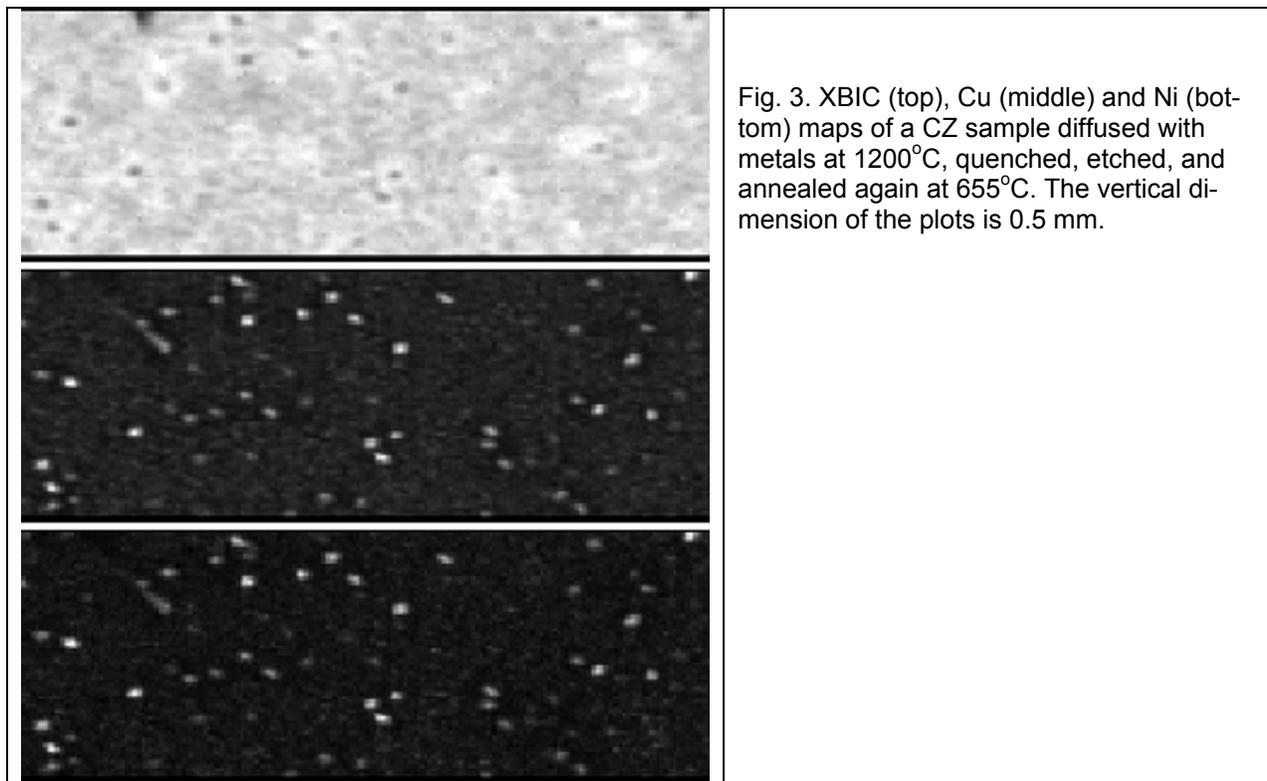


Fig. 4. XBIC, nickel μ -XRF, and copper μ -XRF maps of multicrystalline FZ samples which were intentionally contaminated at 1200°C, quenched and re-annealed at 655°C.

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