

INCORPORATION OF Cu AND Al IN THIN LAYER SILICON GROWN FROM Cu-Al-Si

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ABSTRACT

Cu and Al concentrations in silicon thin layers grown from Cu-Al-Si are determined by segregation at the solid-liquid interface, and for the fast diffusing Cu, also at the free silicon surface. Using the multicomponent regular solution model and experimental results, we found that Si-Al and Si-Cu interactions in the liquid solution are repulsive, and Al-Cu interaction is attractive. As a result, Al incorporation as a function of Cu and Al compositions in the growth solution is determined at about 900°C. Up to 0.2 $\Omega\cdot\text{cm}$ P-type resistivities caused by Al doping are achieved because of suppression of Al incorporation by Cu, yet with a substantial amount of Al still present in the liquid for substrate surface-oxide removal. On the other hand, Cu concentration in the grown layers is reduced by Al in the liquid during growth and by surface segregation after growth. The surface segregation phenomenon can be conveniently used to getter Cu from the bulk of silicon layers so that its concentration ($\sim 10^{16} \text{ cm}^{-3}$) is much lower than its solubility ($2.5 \times 10^{17} \text{ cm}^{-3}$) at the layer growth temperature and the reported 10^{17} cm^{-3} degradation onset for solar-cell performance.

INTRODUCTION

Growing silicon thin layers on metallurgical-grade silicon substrates by liquid-phase epitaxy offers the advantages of excellent crystallinity, high growth rate, perfect lattice match, and practicality over other current thin-silicon techniques for making low-cost silicon solar cells. Cu-Al has been found to be a good solvent system to grow macroscopically smooth Si layers with thicknesses in tens of microns at temperatures near 900°C [1]. This solvent system uses Al to ensure good wetting between the solution and substrate by removing silicon native oxides. Isotropic growth is achieved because of a high concentration of solute silicon in Cu-Al and the resulting microscopically rough interface. The incorporation of Al and Cu in the Si layers, however, needs to be controlled to obtain the desired electrical doping and to minimize the detrimental effect of Cu.

The solid solubility of Al and Cu in silicon (Al or Cu concentration in equilibrium with the liquid phase of Al-Si or Cu-Si) at 900°C is reported at $1.5 \times 10^{19} \text{ cm}^{-3}$ and $2 \times 10^{17} \text{ cm}^{-3}$, respectively [2]. Therefore, if grown from a binary

solution of Al-Si or Cu-Si, silicon crystals would have too low an electrical resistivity or too much Cu contamination for solar cells, although one study [3] shows that Cu nonetheless will not degrade solar-cell performance until above a level of 10^{17} cm^{-3} .

With ternary solutions of Al-Cu-Si at a near-constant growth temperature of 900°C , Al and Cu concentrations in grown silicon layers may be quite different from the binary case because of changes in free energy (by the third component, Cu or Al) in the liquid phase. We will simply treat the ternary solution with the multicomponent, regular solution model [4] and combine it with experimental results to determine the Al doping level with respect to liquid compositions and growth temperature. Because of its low diffusivity ($\sim 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ [5]), Al redistribution after growth is negligible. However, segregation at the solid-liquid interface and at the free-silicon surface are both important for Cu concentration because of the high diffusivity of Cu ($\sim 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ [5]), as we will see later. The driving force for the surface segregation of Cu arises from the difference between the chemical potential differentials (surface to bulk) of pure Si and Cu [6]. We will demonstrate the extent of the effect and use it as a mechanism to getter Cu from grown silicon layers.

INTERACTION PARAMETERS FOR THE LIQUID

To use the regular solution model, we need to first determine the interactions between the elements. The activity coefficient for Si in a ternary system of Cu-Al-Si may be derived as

$$\gamma_{Si}^l = \exp \left\{ \frac{1}{RT_e} \left[\Omega_{SiAl}^l (x_{Al}^l)^2 + \Omega_{SiCu}^l (x_{Cu}^l)^2 + (\Omega_{SiAl}^l + \Omega_{SiCu}^l - \Omega_{AlCu}^l) x_{Al}^l x_{Cu}^l \right] \right\}, \quad (1)$$

where Ω 's are interaction parameters between the components denoted by subscripts, R is the gas constant, and T_e is the equilibrium temperature. Similar results are readily obtained for Cu and Al by permutation as all Ω 's are symmetric.

Because the chemical potentials of respective elements in the liquid phase are equal to those in the solid phase at equilibrium, the activity of a given element in the solid phase must be equal to its counterpart in the liquid phase, which can be written as the product of its activity coefficient and composition. Because the silicon crystal is almost pure (to 99.9%), the Si activity is approximately unity and so is its activity coefficient. Therefore, the relationship between the compositions in the liquid when the mixture is at equilibrium (temperature T_e) with the solid phase may now be written as:

$$\frac{1}{x_{Si}^l} = \exp \left\{ \frac{1}{RT_e} \left[\Omega_{SiAl}^l (x_{Al}^l)^2 + \Omega_{SiCu}^l (x_{Cu}^l)^2 + (\Omega_{SiAl}^l + \Omega_{SiCu}^l - \Omega_{AlCu}^l) x_{Al}^l x_{Cu}^l \right] \right\}. \quad (2)$$

From this equation, the interaction parameters can be determined by trying three mixtures of different compositions at the same growth temperature. A best

set of solutions to equation (2), representing an average of four groups of experiments (each group has three different mixtures), is obtained as (at a common melting point of $T_e \approx 1173\text{K}$),

$$\Omega_{SiAl}^l = 2.430RT_e,$$

$$\Omega_{SiCu}^l = 2.469RT_e,$$

$$\Omega_{AlCu}^l = -0.103RT_e.$$

Both Ω_{SiAl}^l and Ω_{SiCu}^l are large positive numbers, so Si-Al and Si-Cu interactions are of a repulsive nature. Ω_{AlCu}^l is negative, however, implying an attractive interaction between Al and Cu. Therefore, Cu in the growth solution will not only dilute Al, but will also retain Al in the liquid, thus providing greater control for Al doping.

A binary Al-Si mixture of $x_{Al}^l/x_{Cu}^l/x_{Si}^l = 0.65/0.00/0.35$ that gives $\Omega_{SiAl}^l = 2.485RT_e$ does not fit into the above best set of solutions for interaction parameters. This indicates that the regular solution model is limited to the low-Al region (probably $x_{Al}^l < 0.4$), which is all we need in actual layer growth for enhancing wetting between the growth solution and substrate surface.

SEGREGATION OF AL AT THE SOLID LIQUID INTERFACE

If it is grown out of an Al-Si binary solution at 900°C , a silicon crystal is expected to have $1.5 \times 10^{19} \text{ cm}^{-3}$ of Al, or a segregation coefficient of 8.6×10^{-4} . To find the new value when Cu is present, we first write the Al activity coefficient as:

$$\begin{aligned} \gamma_{Al}^l &= \exp \left\{ \frac{1}{RT_e} \left[\Omega_{SiAl}^l (x_{Si}^l)^2 + \Omega_{AlCu}^l (x_{Cu}^l)^2 + (\Omega_{SiAl}^l + \Omega_{AlCu}^l - \Omega_{SiCu}^l) x_{Si}^l x_{Cu}^l \right] \right\} \\ &= \exp \left\{ 2.43 (x_{Si}^l)^2 - 0.103 (x_{Cu}^l)^2 - 0.142 x_{Si}^l x_{Cu}^l \right\}. \end{aligned} \quad (3)$$

Because aluminum is always very dilute ($< 0.04\%$) in the crystalline silicon matrix, the activity coefficient of Al in solid silicon can be treated as constant for all Al concentrations in silicon; this is known as Henry's law.

The solution $x_{Al}^l/x_{Cu}^l/x_{Si}^l = 0.28/0.49/0.23$ resulted in a silicon layer with $1.7 \times 10^{18} \text{ cm}^{-3}$ of Al, i.e., $x_{Al}^s = 0.34 \times 10^{-4}$; the constant Al activity coefficient γ_{Al}^s in solid silicon at $T_e \approx 1173\text{K}$ is thus calculated:

$$\gamma_{Al}^s = \frac{x_{Al}^l \gamma_{Al}^l}{x_{Al}^s} = \frac{x_{Al}^l}{x_{Al}^s} \exp \left[2.43 (x_{Si}^l)^2 - 0.103 (x_{Cu}^l)^2 - 0.142 x_{Si}^l x_{Cu}^l \right] = 8991. \quad (4)$$

We thus get the segregation coefficient of Al for growth of silicon from the Al-Cu-Si mixtures at $T_e \approx 1173\text{K}$:

$$K_{Al} = \frac{1}{8991} \exp \left[2.43 (x_{Si}^l)^2 - 0.103 (x_{Cu}^l)^2 - 0.142 x_{Si}^l x_{Cu}^l \right]. \quad (5)$$

The concentration of Al as a function of liquid compositions at $T_e \approx 1173\text{K}$ is plotted in Fig.1, together with experimental results measured by secondary-ion mass spectroscopy (SIMS). This shows that the Al concentration in solid silicon is

not only controlled by Al composition in the liquid, but by Cu as well. As a result, by adjusting both Cu and Al compositions to allow growth at about 900°C, resistivity of the thin-layer silicon can be easily controlled in a range of 0.01-0.2 $\Omega\cdot\text{cm}$, with a substantial amount of Al present in the liquid solution for substrate surface-oxide removal.

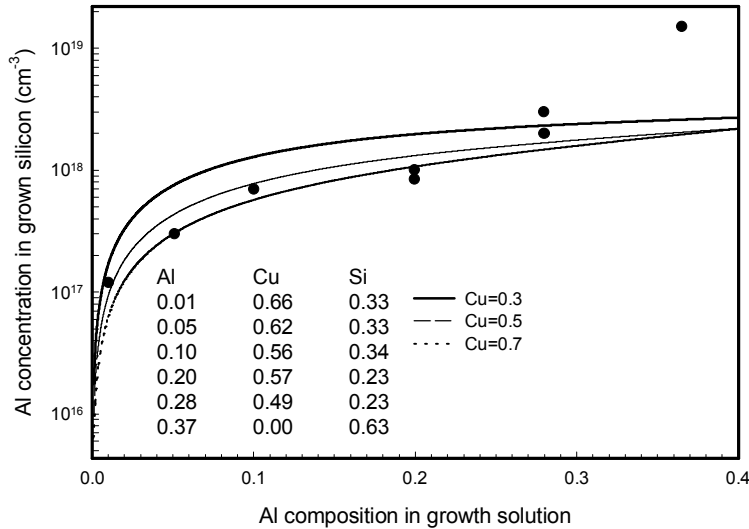


FIGURE 1. Multi-component regular solution model (lines) and experimental (dots) results of Al segregation at 900°C.

Cu INCORPORATION

Segregation at the solid-liquid interface is considered first. When it is grown under a near-equilibrium condition from a Cu-Si melt, a silicon crystal is expected to be saturated with Cu to its solid solubility limit at the growth temperature, just like the case for Al. To verify that the reported solid solubility of Cu was not affected by its fast diffusion, a 2-cm-diameter ingot of single-crystal silicon was submerged in a Cu-Si melt equalized at 920°C for 8 hours (resulting in a Cu diffusion depth of ~ 1.7 cm from the ingot surface) to allow Cu to fully diffuse into the ingot. A 2-mm-thick slice was then cut and polished at room temperature shortly before SIMS measurement. Figure 2 is a SIMS map, taken after sputtering away the top surface, showing non-uniform Cu distribution with aggregations at swirl-defect sites. By averaging over 6 areas of $150\ \mu\text{m} \times 150\ \mu\text{m}$, the bulk concentration of Cu is calculated to be about $2.5 \times 10^{17}\ \text{cm}^{-3}$, which is slightly higher than reported in the literature [7]. This concentration is dictated by segregation at the solid silicon and Cu-Si liquid interface.

When an Al-Cu-Si solution is used, the Cu segregation will be less than with Cu-Si solutions, similar to the case of Al,

$$K_{Cu} = \frac{1}{1.12 \times 10^5} \exp\left[2.469(x_{Si}^l)^2 - 0.103(x_{Al}^l)^2 - 0.064x_{Si}^l x_{Al}^l\right], \quad (6)$$

where Cu activity coefficient in solid silicon, $\gamma_{Cu}^s = 1.12 \times 10^5$, has been determined from experiments as we did in section 3 for Al.

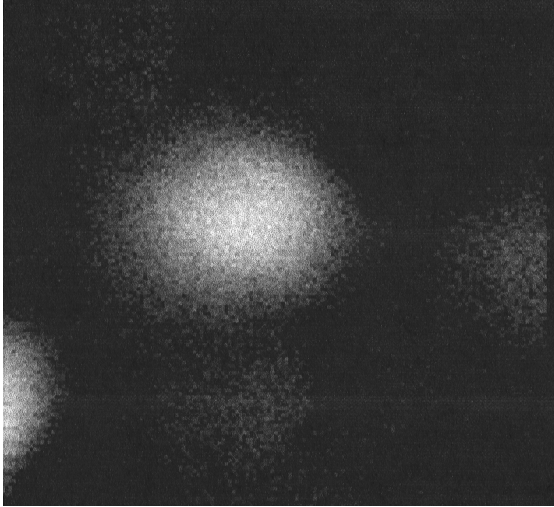


FIGURE 2. SIMS map of Cu distribution in an area of $250 \times 250 \mu\text{m}^2$ in Cu-diffused single crystal Si.

During post-growth cool-down, the Cu will become supersaturated and segregate to the surface or precipitate at the defect sites. The free-silicon surface is the preferred escape site for the supersaturated Cu atoms because the high free energy in the bulk will be spent on creating a new Cu-terminated surface if the Cu has lower surface energy than silicon. This indeed is the case: Cu segregates to the surface during cool-down after layer growth (see Fig. 3). We may incorporate this surface segregation phenomenon to effectively getter fast-diffusing Cu from the bulk of silicon without using a dedicated gettering procedure.

Fig. 4 is the Cu depth profile in a thicker sample grown at otherwise similar conditions as the one in Fig. 3. Because of the dynamic nature of SIMS measurements, the signals in the first 100 \AA of the two samples are not accurate, but both of them show Cu enrichment in the $0.3\text{-}0.4\text{-}\mu\text{m}$ surface region. More surface-sensitive, ion-scattering spectroscopy (ISS) analysis reveals about 7% Cu at the top surface (about 50 \AA deep) of a sample slowly cooled after growth. One can easily notice the difference in the bulk Cu concentrations between the two samples. A logical explanation is the difference in total Cu content caused by different substrate thicknesses. Both samples are expected to be saturated with Cu at the growth temperature of 900°C . The sample in Fig. 4 is thicker and would gather more Cu during growth from the in-diffusion of Cu than the sample in Fig.

3. During the sample cool-down period after growth, Cu out-diffuses to the surface and results in different levels of reduction in bulk Cu concentrations.

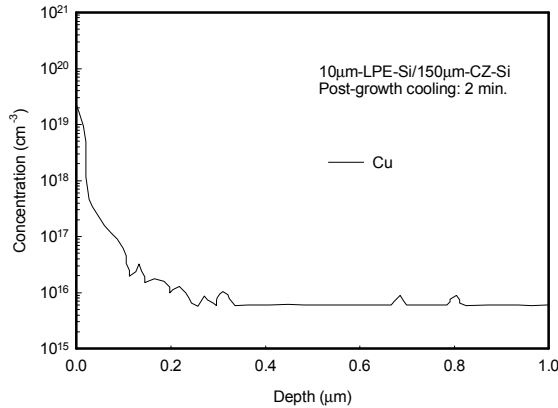


FIGURE 3. SIMS depth profile of Cu with a total sample thickness $\approx 160 \mu\text{m}$.

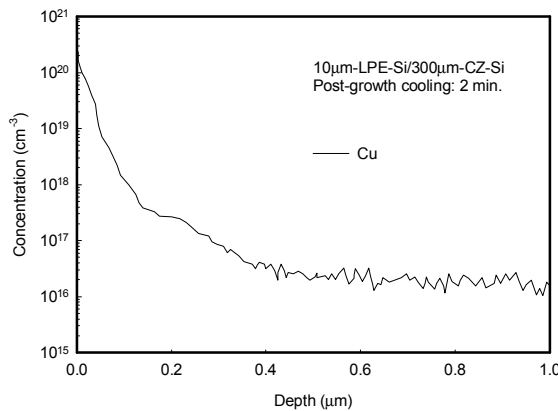


FIGURE 4. SIMS depth profile of Cu with a total sample thickness $\approx 310 \mu\text{m}$.

After removing the top Cu-enriched surface region of about $0.5 \mu\text{m}$ by wet chemical etch, the bulk concentration of Cu is typically about $1 \times 10^{16} \text{ cm}^{-3}$, as seen in Fig. 5. Such a level of Cu in silicon is not expected to cause degradation effects for solar cells. This has a strong implication for using metallurgical-grade silicon as substrates for liquid phase epitaxial growth of high-quality silicon thin layers for solar cells, because the surface segregation will have a similar effect in gettering other fast-diffusing impurities like Ni or Fe. Slow-diffusing impurities in a

low-purity substrate will not catch up to the epitaxial growth front, thus they will be of no concern.

For grain boundaries, the relative (to the bulk) chemical potentials of Si and Cu atoms at these locations are very likely to be lower than that of a free surface. This implies that the difference between the relative grain-boundary energy of Si and that of Cu is smaller than the difference between the relative surface energy of Si and Cu. The same argument may be made for other defects in silicon. Experimental evidence is abundant [8], including SIMS analysis in which no significant impurity enrichment at grain boundaries was observed, and, also, the necessity of a thick sample to Cu-decorate defects in silicon. Therefore, the free silicon surface is the preferred escape site for fast-diffusing impurities even for defected materials, provided a small silicon thickness and sufficient time are given.

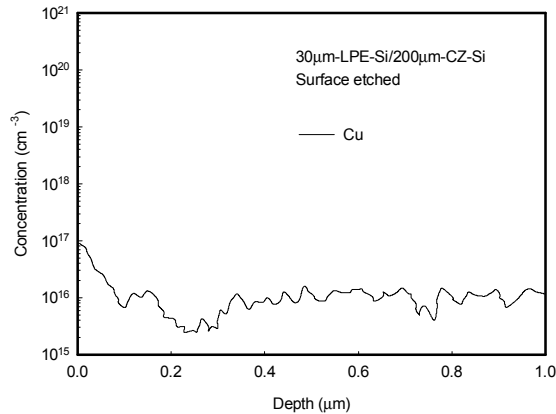


FIGURE 5. Cu depth profile after the original surface was removed by etching.

CONCLUSIONS

The segregation of Al and Cu at the solid-liquid interface during growth and of Cu at the free silicon surface after growth in liquid-phase epitaxy of silicon at about 900°C has been studied. We found, by using the multicomponent regular solution model and experimental results, that Si-Al and Si-Cu interactions in the liquid solution are of a repulsive nature and Al-Cu interaction is of an attractive nature. Al concentration in solid silicon is controlled by both Al and Cu in the liquid. Consequently, resistivity of the thin-layer silicon can be easily controlled in a range of 0.01-0.2 Ω·cm, with a substantial amount of Al present in the liquid solution for substrate surface-oxide removal.

Surface segregation can be used to effectively getter Cu and other fast-diffusing impurities (assuming a lower surface energy than silicon) from bulk silicon when the impurity concentration exceeds its room-temperature solubility

and when the silicon crystal is thin (a few hundred microns). When a free-silicon surface is available, this gettering process does not need special procedures, but only a prolonged cool-down step.

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