SURFACE SEGREGATION AS A MEANS OF GETTERING Cu IN LIQUID-PHASE-EPITAXY SILICON THIN LAYERS GROWN FROM Al-Cu-Si SOLUTIONS

T.H. Wang, T.F. Cizek, R. Reedy, S. Asher, and D. King
National Renewable Energy Laboratory, Golden, CO 80401

ABSTRACT

We demonstrate that, by using the natural surface segregation phenomenon, Cu can be gettered to the surface from the bulk of silicon layers so that its concentrations in the liquid-phase-epitaxy (LPE) layers are much lower than its solubility at the layer growth temperature and the reported 10^{17} cm^{-3} degradation threshold for solar-cell performance. Secondary-ion mass spectroscopy (SIMS) analysis indicates that, within a micron-deep sub-surface region, Cu accumulates even in as-grown LPE samples. Slower cooling after growth to room temperature enhances this Cu enrichment. X-ray photoelectron spectroscopy (XPS) measurement shows as much as 3.2% Cu in a surface region of about 50 Å. More surface-sensitive, ion-scattering spectroscopy (ISS) analysis further reveals about 7% of Cu at the top surface. These results translate to an areal gettering capacity of about $1.0 \times 10^{16} \text{ cm}^{-2}$, which is higher than the available total-area density of Cu in the layer and substrate ($3.6 \times 10^{15} \text{ cm}^{-2}$ for a uniform $1.2 \times 10^{17} \text{ cm}^{-3}$ Cu throughout the layer and substrate with a total thickness of 300 μm).

INTRODUCTION

Cu-Al has been found to be a good solvent system to grow macroscopically smooth Si layers with thicknesses in tens of microns on cast metallurgical-grade (MG) Si substrates by liquid-phase epitaxy (LPE) 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, and it uses Cu to control Al-doping into the layers. Isotropic growth is achieved because of a high concentration of solute silicon in the solution and the resulting microscopically rough interface. The incorporation of Cu in the Si layers, however, was a concern because Cu is a major solution component and is generally regarded as a bad impurity for silicon devices due to its fast diffusivity and deep energy levels in the bandgap. One study[2] shows that Cu nonetheless will not degrade solar-cell performance until above a level of 10^{17} cm^{-3} . This threshold is expected to be even higher for thin-layer silicon solar cells owing to the less-stringent requirement on minority-carrier diffusion length. But to ensure long-term stability of solar cells,

lower Cu concentrations in the thin layers are still preferred.

When grown under near-equilibrium conditions from a Cu-Si melt, the silicon crystal is expected to be saturated with Cu to its solid solubility limit at the growth temperature ($1.2 \times 10^{17} \text{ cm}^{-3}$ for 900°C). More components in the melt will slightly change Cu incorporation about this level because of the change in free energy in the melt. Using Al-Cu-Si solutions, Cu incorporation will be a little less from experiments and calculation with the multi-component regular solution model. 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 Cu has lower surface energy than silicon. This indeed is the case: Cu aggregates to the surface during cool-down after layer growth. We may incorporate this surface segregation phenomenon to effectively getter fast-diffusing Cu from the bulk of silicon without using a dedicated gettering procedure.

LPE GROWTH OF SILICON

The liquid phase epitaxial growth setup and procedure is described elsewhere [1]. Thin silicon layers of 10-30- μm thickness were grown at temperatures around 900 °C on pure Czochralski(CZ) single crystal substrates in this study. The solution compositions were kept nearly constant at 23%Si-28%Al-49%Cu for the growth runs to minimize their effects on Cu incorporation in solid silicon. After a sample is withdrawn from the solution, a free silicon surface is exposed and the sample temperature is gradually reduced to room temperature. It is during this cool-down period that surface segregation occurs for various impurities in silicon crystals (both the layer and substrate) depending on their relative surface energy to silicon.

SURFACE SEGREGATION

Surface segregation is a redistribution of solute atoms (e.g., Cu) between the surface and bulk of a (Si)

crystal from the as-grown uniform distribution until the total energy of the crystal becomes a minimum. The equilibrium surface composition (mole fraction in the surface monolayer), x_{Cu}^s , of Cu as a function of temperature is described by the Bragg-Williams equation [3]. The equation predicts a full surface coverage at temperatures somewhere below the growth temperature,

$$\frac{x_{Cu}^s}{1-x_{Cu}^s} = \frac{x_{Cu}^B}{1-x_{Cu}^B} \exp \left[\frac{\Delta G + 2\Omega_{SiCu}^s(x_{Cu}^s - x_{Cu}^B)}{RT} \right],$$

where $\Delta G = (\mu_{Si}^{0s} - \mu_{Si}^{0B}) - (\mu_{Cu}^{0s} - \mu_{Cu}^{0B})$, μ 's are the surface and bulk chemical potential of pure Si and pure Cu, x_{Cu}^B is the bulk mole fraction of Cu, and Ω_{SiCu}^s is the interaction parameter between Si and Cu in the solid. For the grown Si crystal, a binary Si-Cu consideration (excluding Al) leads to $\Omega_{SiCu}^s = 12.81RT_0$, where T_0 is the growth temperature.

Due to the residual stress near the surface region even in as-grown layers, segregation to the surface is not limited to the top monolayer. Thus, combined with the fast diffusivity and relatively low solubility of Cu in silicon, this surface segregation effect may be used to effectively getter Cu from the bulk of the silicon thin layers and substrates.

Fig.1. SIMS depth profile of Cu with a total sample thickness $\approx 160 \mu\text{m}$.

The significance of surface segregation is evidenced by the depth profiling of Cu obtained with secondary-ion mass spectroscopy (SIMS) analysis in thin-layer silicon grown on high-purity single-crystal silicon substrates (Figs. 1 and 2). Because of the dynamic nature of SIMS measurements, the signal in the first 100 Å is not accurate, but both samples show Cu enrichment in the 0.3-0.4- μm surface region. 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 due to different substrate thicknesses. Both samples are expected to be saturated with Cu at the growth temperature of 900°C. The sample in Fig. 2 is thicker and would gather more Cu during growth from indiffusion of Cu than the sample in Fig. 1. 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.

Fig.2. SIMS depth profile of Cu with a total sample thickness $\approx 310 \mu\text{m}$.

GETTERING OF Cu

To fully use this Cu sink near the surface, a slower cooling after layer growth can be done to speed up the segregation process (Fig. 3). The same sample was analyzed with X-ray photoelectron spectroscopy (XPS), which shows as much as 3.2% of Cu in a surface region of about 50 Å. More surface-sensitive, ion-scattering spectroscopy (ISS) analysis reveals about 7% Cu at the top surface as shown in Fig. 4. Surface contaminants (e.g., O, C) prevented accurate measurement at the top monolayer, but this composition represents the minimum amount of Cu at the surface.

The slow diffusers (like B shown in Fig. 3) also exhibit surface segregation, yet the effects were limited to much smaller regions, indicating that surface segregation for slow-diffusing impurities is farther away from reaching the equilibrium state during the sample cooling period. Otherwise, one would expect it to extend to a depth and exhibit a profile similar to Cu.

According to the Bragg-Williams equation, the amount of Cu segregating to the surface would follow the curves in Fig. 5, where ΔG is the driving force arising from the difference between the chemical potential differentials (surface to bulk) of pure Si and Cu, and Ω is the interaction parameter (regular solution model) between Si and Cu in the solid silicon, which we determined

experimentally to be $12.81RT_e$. Therefore, it is straightforward to apply surface segregation as a gettering step following the LPE growth process.

Fig. 3. Slower post-growth cooling as compared to Fig. 2.

Fig. 4. Cu depth profile by ISS.

Taking the Cu depth profiles in Fig. 3 and Fig. 4 as nearly equilibrium, the gettering capacity is estimated to be about $1.0 \times 10^{16} \text{ cm}^{-2}$, higher than a monolayer of Cu, owing to the extensiveness of Cu enrichment in the sub-surface region.

The total areal density of Cu in the layer and substrate is estimated to be $3.5 \times 10^{15} \text{ cm}^{-2}$ at the uniform concentration of 1.2×10^{17} for the total thickness of 300 μm , for example.

After removing the top Cu-enriched surface region by wet chemical etch, bulk concentration of Cu is typically about $1 \times 10^{16} \text{ cm}^{-3}$, as seen in Fig. 6. Diagnostic solar cells made in such layers exhibit efficiencies as high as 15.3%, compared to 15.7% for Czochralski (CZ)-Si control cells.

Fig. 5. Equilibrium surface composition of Cu as a function of temperature. The upward and downward arrows are example paths for decreasing and increasing temperatures, respectively.

Fig. 6. Cu depth profile after a surface etch in 3:1:2 mixture of nitric, hydrofluoric, and acetic acids. The boron profile is shown as a reference to indicate no significant surface segregation between the time of the acid etch and SIMS measurement.

Note that this surface segregation will have the same effect in gettering other fast-diffusing impurities like Ni or Fe. Due to their overall lower solubility in silicon ($5 \times 10^{16} \text{ cm}^{-3}$ for Ni, $2.5 \times 10^{15} \text{ cm}^{-3}$ for Fe at 900°C), the bulk concentrations of these impurities after surface segregation should be low enough to not cause any device performance degradation, even if a low-purity metallurgical-grade-Si is used as LPE substrates. Slow diffusing impurities in a metallurgical-grade-Si substrate will not catch up the epitaxial growth front, thus they will not be of a 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 evidences are abundant, including SIMS analysis in which no significant impurity enrichment at grain boundaries was observed and the necessity of a thick sample in order to Cu-decorate defects in silicon [4]. Therefore, 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.

SUMMARY

Surface segregation can be used to effectively getter Cu and other fast-diffusing impurities (supposedly having lower surface energy than silicon) from bulk silicon when the impurity concentration exceeds its room-temperature solubility and when the silicon crystal is in thin (a few hundred microns) forms. When a free-silicon surface is available, this gettering process does not need special procedures, but only a prolonged cool-down step. The estimated total areal gettering capacity of $1.0 \times 10^{16} \text{ cm}^{-2}$ should be sufficient for Cu concentration up to $1.2 \times 10^{17} \text{ cm}^{-3}$ in a silicon wafer as thick as $800 \mu\text{m}$.

Silicon layers grown by LPE from Al-Cu solutions have shown below $1 \times 10^{16} \text{ cm}^{-3}$ in Cu concentration, and such a level of Cu impurity does not appear to degrade solar-cell performances.

This gettering procedure may be conveniently incorporated in many (sheet or ribbon) crystal growth and wafer processes, by using a slow cool-down and a surface-removal procedure. As a matter of fact, such a procedure may have already existed in many current processes naturally.

ACKNOWLEDGMENTS

We thank Dr. Y.S. Tsuo for diagnostic cell fabrications. Support for this work was provided by the U.S. Department of Energy under contract No. DE-AC36-83CH10093 to the National Renewable Energy Laboratory.

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