Impact of metal silicide precipitate dissolution during rapid thermal processing of multicrystalline silicon solar cells

T. Buonassisi(a) and A. A. Istratov
Department of Materials Sciences and Engineering, University of California, Berkeley and Materials Science Divison, Lawrence Berkeley National Laboratory, Berkeley, California 94720

S. Peters, b) C. Ballif, c) J. Isenberg, d) S. Riepe, W. Warta, R. Schindler, and G. Willeke
Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany

Z. Cai and B. Lai
Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439

E. R. Weber
Department of Materials Science and Engineering, University of California, Berkeley and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

(Received 25 January 2005; accepted 24 July 2005; published online 16 September 2005)

Synchrotron-based analytical x-ray microprobe techniques were employed to study the dissolution of iron, copper, and nickel silicide precipitates at structural defects in cast multicrystalline silicon in response to rapid thermal processing (RTP). A direct correlation was observed between iron silicide precipitate dissolution, increased minority carrier recombination, and decreased device performance after high-temperature (1000 °C) RTP. In contrast, iron precipitates comparable in size to as-grown material remained after lower-temperature RTP (860 °C); in this case the material exhibited higher minority carrier diffusion length and better solar cell performance. RTP at both temperatures effectively dissolved nickel and copper silicide precipitates. It is concluded that iron dissolved from structural defect reservoirs detrimentally affects the cell performance, likely by forming distributed point defects and smaller precipitates. For cast multicrystalline silicon, higher performance can be expected by inhibiting the dissolution of these precipitates, i.e., by reducing the time and/or temperature of processing steps. © 2005 American Institute of Physics. [DOI: 10.1063/1.2048819]

Rapid thermal processing (RTP) of solar cells has long been considered a potentially attractive substitute for conventional emitter diffusion. Obvious advantages are the shorter annealing times and reduced floor space necessary for RTP equipment. However, it has been observed that some silicon materials respond poorly to RTP, resulting in lower solar cell devices efficiencies. Peters et al.1 reported that cast multicrystalline silicon (mc-Si) responds the poorest, edge-defined film fed growth (EFG) responds less poorly, and single-crystalline Czochralski material responds fairly well to rapid thermal processing. It was also observed that longer and higher-temperature anneals1,2,4 and faster cooling rates2,5 lead to poorer materials performance. It is typically proposed that these effects are due to the creation of pairs of interstitial iron and substitutional boron and other Fe-related defects.2,6 to hydrogen out-diffusion.4,6

To assess the role of metals and structural defects in decreasing cast mc-Si materials performance after RTP, we employed synchrotron-based analytical techniques7,8 to study the distribution and average sizes of metal-silicide nanoprecipitates along structural defects. These techniques, which include x-ray fluorescence microscopy (μ-XRF), x-ray absorption microspectroscopy (μ-XAS), and x-ray beam induced current (XBIC), are powerful techniques with submicron spatial resolution capable of characterizing the elemental composition, chemical state and recombination activity of an iron silicide precipitate as small as 16±3 nm in radius.9

Three sister wafers of cast mc-Si, i.e., adjacent vertical slices of the ingot, with virtually identical initial crystal structure, were selected for this analysis. The first wafer was left unprocessed and was used as a reference. The second and the third wafers were processed into solar cells using different temperatures for emitter diffusion from a phosphorus spin-on source. The second wafer was processed at 860 °C for 120 s, while the third wafer was processed at a higher temperature, 1000 °C for 20 s. Different annealing times were chosen to obtain comparable emitter depths. The average cooling rate at the end of RTP annealing was approximately 100 °C/s. While this study pertains specifically to emitter diffusion, the obtained conclusions are equally applicable to high-temperature processing during later stages of cell processing. No anti-reflection coating was deposited, as to minimize the effect of hydrogen passivation in these experiments. The solar cell fabricated using low-temperature (860 °C) RTP was found to be 20% (rel.) more efficient than the cell fabricated using high-temperature (1000 °C) RTP. Most of this change in efficiency was linked to an increase of the minority carrier diffusion length L_eff, as shown in the laser-beam induced current (LBIC) maps in Fig. 1.

A characteristic region of material was extracted for synchrotron-based analytical studies from the same location in all three sister wafers. Medium-resolution μ-XRF scans were performed over the same grain boundary in all three...
determined from standard-calibrated \( \mu \)-XRF measurements and estimates of the total grain boundary surface area per unit volume, in good agreement with neutron activation analysis data on similar samples.\(^9\),\(^10\),\(^11\) Iron content (in units of \( \mu \)-XRF counts per second) for different precipitates in the three samples was analyzed via high-resolution two-dimensional \( \mu \)-XRF scans over each precipitate with 50 nm steps and optimized focus conditions. In as-grown material, six iron precipitates were analyzed which had 523, 412, 508, 496, 464, and 302 counts after background subtraction, yielding an average of 451 with a standard deviation of 83 (equivalent to 60±4 nm diameter via standard reference material). In the low-temperature RTP sample (860 °C,120 s), the analyzed iron precipitates had 364 and 556 counts after background subtraction, yielding an average of 460 with standard deviation of 136 (equivalent to 60±6 nm diameter). Finally, in the high-temperature RTP (1000 °C,20 s) sample, the analyzed iron precipitates had 205, 271, 312, 114, 236, and 183 counts after background subtraction, yielding an average of 220 with standard deviation of 70 (equivalent to 46±6 nm diameter). Data for these three samples are plotted in Fig. 3. Comparison of these samples led us to the following observations:

1. In the as-grown material, multiple iron-rich clusters can be seen decorating the grain boundary. \( \mu \)-XAS analyses (not shown) revealed the chemical state of iron in these precipitates to be most similar to iron silicide. Some copper and nickel precipitates were also observed, although in lower spatial densities. The copper was determined by \( \mu \)-XAS to be in the form of copper silicide. Some similarly large clusters were observed in intragranular locations, probably coinciding with dislocations.

2. In the “low-temperature RTP” sample, some large FeSi\(_2\) precipitates remain, with the same count rate (i.e., number of metal atoms per precipitate) as in the as-grown material. However, while faint traces of Ni-rich precipitates can still be detected, the number of nickel atoms per precipitate is much reduced in amount relative to the as-grown sample. Cu\(_2\)Si precipitates are no longer detectable.

3. In the “high-temperature RTP” sample, FeSi\(_2\) precipitates are detected, but they contain on average 50% less iron atoms than as-grown material, giving evidence for iron silicide precipitate dissolution. No Cu- nor Ni-rich precipitates are above the detection limits.
These results indicate that low-temperature RTP effectively dissolves most Cu- and Ni-rich precipitates, while FeSi₂ precipitates are largely undisturbed. This effect is due to the orders of magnitude higher solubilities and diffusivities of Cu and Ni relative to Fe. On the other hand, high-temperature RTP not only completely dissolves the Cu- and Ni-rich precipitates, but it also partially dissolves the FeSi₂ precipitates. Higher temperatures greatly enhance the solubility and diffusivity of iron, allowing it to diffuse away from the precipitates at structural defects and contaminate the intragranular regions of the material. This effect can be seen by comparing XBIC images in Fig. 2: while the as-grown sample exhibits denuded zones around the grain boundaries and other structural defects, the high-temperature RTP sample shows exactly the opposite, i.e., grain boundary “bleeding” into the grains. The observation of material degradation due to high-temperature anneals, especially followed by fast cools, has been previously reported in the literature.1–6

One must conceive of iron precipitates at grain boundaries and intragranular structural defects as effective reservoirs of metals. When metal atoms accumulate at these reservoirs, the metal defect concentration elsewhere is reduced, improving the diffusion lengths in those regions. On the other hand, when metal silicide precipitates are partially dissolved during processing, metals can diffuse from these reservoirs and contaminate neighboring regions, effectively increasing the bulk minority carrier trap density and reducing the bulk diffusion lengths, as seen in Fig. 1. This effect is most pronounced for cast mc-Si, in which slow cooling during crystal growth promotes the formation of larger metal silicide precipitates (and a reduction in metal point defects) in as-grown material.

When processing mc-Si materials with such metal reservoirs, two effective strategies can be pursued to minimize the amount of dissolved metals distributed within the grains as the result of solar cell processing: (1) Fully dissolve these metal silicide nanoprecipitates and remove them from the active device region. This is complicated because of the limited capacity and segregation coefficient of gettering layers such as aluminum backside12 or phosphorus doped emitter,13 which results in a fraction of the metals remaining dissolved in the bulk. Additionally, it is known that cast mc-Si contains rather large (several 10’s of nm) metal silicide precipitates at grain boundaries,7 due to the slow cooling process that favors the formation of large precipitates.14 Thus, several hours are needed to fully dissolve iron silicide precipitates because of solubility and diffusivity limits,15 and the high total metal content (in the 10^14 cm^-3 range).

The alternative strategy is to (2) disturb Fe silicide clusters as little as possible by using lower-temperature treatments in the range of 800–900 °C. Low-temperature processing by Schultz et al.16 has recently led to a 20% record-efficient mc-Si device, suggesting that this process may be the most desirable given the current state of technology. By the same token, short H-passivation rapid thermal anneals are also preferred over long anneals, not only to limit hydrogen out-diffusion as suggested by Rohatgi et al.,4 but also to limit metal silicide precipitate dissolution.

To summarize the findings of this study, synchrotron radiation based x-ray microprobe techniques were used to demonstrate that short high-temperature RTP completely dissolves copper and nickel precipitates, but only partly dissolves iron silicide nanoprecipitates. When the rapid cooling occurs at the end of the RTP anneal, metals dissolved from the precipitates become “trapped in,” forming smaller and more distributed recombination centers (precipitates and point defects). This leads to a decrease in solar cell performance. To overcome this performance degradation, two strategies are to use shorter and preferably lower-temperature anneals to leave iron-silicide precipitates undisturbed, or use longer high-temperature treatments to completely dissolve iron-silicide precipitates and getter the dissolved iron. However, long high-temperature anneals may be incompatible with diffusion of shallow emitter layers.

The authors would like to thank E. Schäffer for LBIC measurements. This work was supported by NREL subcontract No. AAT-2-31605-03, with collaboration through the Fraunhofer Institute for Solar Energy Systems (ISE) supported by the AG-Solar project of the government of Northrhein-Westfalia (NRW). Use of the Advanced Photon Source and of the Advanced Light Source is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract Nos. W-31-109-ENG-38 and DE-AC02-05CH11231, respectively.