Research Performance Progress Report (RPPR) for DOE/EERE

Project Title: “Defect Engineering, Cell Processing, and Modeling for High-Performance, Low-Cost Crystalline Silicon Photovoltaics”

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Project Objective: The objective of this project is to close the efficiency gap between industrial multicrystalline silicon (mc-Si) and monocrystalline silicon solar cells, while conserving the economic advantage of low-cost, high-volume substrates inherent to mc-Si.

Task 1: Develop and apply characterization techniques to identify and decouple the influences of performance-limiting defects in mc-Si solar cells

Mc-Si is a highly inhomogeneous material; minority carrier lifetime can vary widely from one area of a wafer to the next. In this task, we defined these as “good regions” and “bad regions” of the material in terms of microstructural composition.

Of primary interest are “bad regions,” which limit solar cell device performance. Bad regions can be observed in the minority carrier lifetime map in Fig. 1 (left), as yellow/red regions of the sample. We have identified dislocations as the primary performance-limiting defect in these regions of material. Fig. 1 illustrates the strong correlation between

regions of low minority carrier lifetime (left) and regions of high dislocation density (right). Because these regions cover a large area fraction of the wafer, dislocations are concluded to be among the most deleterious bulk defect for *standard* mc-Si materials.

Our prevailing hypothesis, is that a combination of dislocations and metallic impurities causes low minority-carrier lifetimes in these so-called “bad” regions. We employed X-ray fluorescence microscopy (μ -XRF) to map the distribution of metal-rich clusters in mc-Si materials — pushing the spatial resolution of this technique to better than 80 nm, in collaboration with the Advanced Photon Source Beamline 26-ID-C. The most recombination-active extended defects (grain boundaries and dislocations) were identified as those containing the highest concentration of transition-metal silicide precipitates (Fig. 2 & 3). These results were repeated for grain boundaries, with consistent results. Further details can be found in M.I. Bertoni *et al.* “Nanoprobe X-ray fluorescence characterization of defects in large-area solar cells,” *Energy & Environmental Science* **4**, 4252 (2011).

Figure 1: Left: Microwave photoconductivity decay (μ -PCD) measurement of minority carrier lifetime of a wafer extracted from near the middle of an ingot. Adjacent regions of high (blue/purple) and low (red/yellow) minority carrier lifetime are evident. Right: Measurement of dislocation density (black = high, white = low).

Figure 2. Two populations of dislocations are distinguished by quantum efficiency mapping (conducted by Markus Rinio, Fraunhofer ISE): Deleterious and more benign. (a) A medium-resolution IQE map, highlighting (b) two regions of interest. (c) Dislocation etch pit maps indicate that underperforming regions correspond to regions of high dislocation density. (d) Quantitative pixel-by-pixel correlation between IQE and dislocation density in (b) indicates that Region A contains strongly recombination-active dislocations (deleterious), while Region B contains dislocations with an order of magnitude lower recombination activity (comparatively benign). The red squares in (c) indicate regions selected for nano-XRF analysis.

Figure 3. Nano-XRF detects metals at recombination-active dislocations. (a) Four dislocation etch pits from Region A, which contains recombination-active dislocations. In nano-XRF maps, three out of the four etch pits exhibit metal contamination, namely copper and iron. (b) Four representative etch pits from Region B, which contains benign dislocations. Eleven etch pits were analyzed in total, and not one exhibited significant metal contamination.

In addition to the nano-XRF mentioned above, we refined and applied a series of characterization techniques to non-destructively detect and characterize dislocations in multicrystalline silicon:

- Infrared birefringence imaging: Images dislocations non-destructively in multicrystalline silicon. V. Ganapati et al., "Infrared birefringence imaging of

residual stress and bulk defects in multicrystalline silicon,” *Journal of Applied Physics* **108**, 063528 (2010).

- *In-situ* X-ray fluorescence microscopy (Fig. 4): Measures metal-impurity precipitates at high temperatures under controlled ambient gas. S. Hudelson et al., “Retrograde Melting and Internal Liquid Gettering in Silicon,” *Advanced Materials* **22**, 3948 (2010).

Figure 4: Solidification of a nickel-silicon liquid droplet. (a) At high temperature, the nickel-silicon droplet is centered within a single large particle. The Ni K-edge XANES spectrum of the particle (solid black) is found to resemble the liquid state standard (dotted red). (b,c) As the liquid droplet cools, the large central particle shrinks as the surrounding particles grow, indicating a net movement of nickel to the outer particles. XANES spectra of the particle indicate that the particles are still liquid in nature. (d) Upon dropping below the Ni-Si eutectic temperature, the liquid droplet solidifies, as indicated by the black Ni-XANES spectrum matching the solid NiSi_2 spectrum (dashed blue).

Task 2: Engineer defects for enhanced bulk minority carrier lifetime.

Having identified dislocations and metallic impurities as two principal performance-limiting defects, we focused on developing the means to reduce their densities.

Part 1: Metallic impurities: Observing the fact that metal impurities enhance defect recombination activity, we developed a simulation tool to predict the evolution of impurities during solar-cell processing in collaboration with the research group of Carlos del Cañizo, Institute for Solar Energy (Madrid, Spain). This tool, which we called “Impurities to Efficiency” simulator, ranks among our most impactful developments:

- This tool predicts the evolution of iron impurities during phosphorus diffusion, permitting one to rapidly (few min / simulation) explore a wide parameter space, identifying the optimum trade-off between performance and quality [J. Hofstetter *et al.*, *Progress in Photovoltaics* **19**, 487–497, 2011; and citing articles].
- We applied this tool to co-develop junction-annealing steps for novel *pn*-junction fabrication technologies, with significant industrial impact [D.M. Powell *et al.*, *Photovoltaics International*, February 2012, p. 91].
- We demonstrated how precipitated iron usually dictates the final dissolved iron concentration [D.P. Fenning *et al.*, *Journal of Applied Physics* **133**, 044521, 2013].
- An online version of this tool (<http://pv-i2e.mit.edu>) performed over 3,000 simulations (outside MIT) since its launch in Summer 2011.
- We developed a series of “design rules” to aid junction formation (including ramp rates, plateau times & temperatures, and cooling conditions) [D.P. Fenning *et al.*, under preparation].

Fig. 5. Graphical description of the “Impurities to Efficiency” process simulation tool, which predicts the efficiency impact of a given material quality and time-temperature processing profile.

Part 2: Dislocation-density reduction: Like metallic impurities, dislocations are mobile in silicon at high temperatures, and are commonly engineered in other materials (e.g., “hardening” or “softening” of metals). Leveraging this knowledge, we explored the effect of high-temperature annealing on dislocations in multicrystalline silicon. Our preliminary results indicated a reduction of dislocation density at temperatures approaching the melting temperature of silicon (Fig. 6, from M.I. Bertoni *et al.*, *Solid State Phenomena* **156-158**, 11-18, 2010; and K. Hartman *et al.*, *Applied Physics Letters* **93**, 122108, 2008). As seen in the aforementioned references (and *via* the “Fit” curves in Fig. 6), dislocation-density reduction can be well described by an empirical expression proposed for FCC metals. The activation energy for this process was determined to be 2.1 ± 0.2 eV, on par with glide of 60° dislocations in silicon.

We noticed that these preliminary results, while exciting, varied from material to material and from furnace to furnace. We explored several hypotheses for driving forces, eventually settling on “stress” as a key differentiator. When stress was applied during annealing — either by mechanical loading, or other means — dislocation velocity is increased. (M.I. Bertoni *et al.*, *Physica Status Solidi Rapid Research Letters* **5**, 28-30, 2011.)

Fig. 6. Influence of annealing temperature and time on dislocation-density reduction in the absence of applied stress.

Fig. 7. Dislocation-density reduction demonstrated for various temperatures: Optical microscope images of dislocation-etched ribbon silicon materials, unannealed control samples (above) and annealed (below) specimens, the latter of which are used to generate raw data for Fig. 6.

Our work highlighting the impact of dislocations on multicrystalline silicon contributed to an increased awareness of the dislocation issue in minority-carrier lifetime reduction. The industry eventually developed a solution to avoid the formation of dislocations during growth: By growing small-grained multicrystalline silicon, thermal stress is absorbed in grain boundary deformation (slip), thus avoiding the creation of high dislocation densities.

Part 3: Defect Passivation: We examined the effectiveness of hydrogen passivation as a function of defect type and microstructure at grain boundaries in multicrystalline silicon. In collaboration with IMEC and the University of Konstanz, we analyzed a solar cell with alternating mm-wide bare and SiN_x -coated stripes using laser beam-induced current, electron backscatter diffraction, X-ray fluorescence microscopy, and defect etching to correlate pre- and post-hydrogenation recombination activity with grain boundary character, density of iron-silicide nanoprecipitates and dislocations. A strong correlation was found between grain boundary recombination activity and the nature / density of etch pits along the boundaries, while iron silicide precipitates above detection limits were found to play a less significant role. These results suggest that the lifetime impact of impurities at extended defects may depend on the fraction of dissolved (vs. precipitated) impurities, a function of the extended defect microstructure.

Figure 8 (above). *LBIC Contrast of Long Grain Boundaries.* LBIC contrast before and after passivation is compared for individual GBs. The dotted diagonal line represents zero passivation improvement. Data points falling well below this line correspond to grain boundaries that are effectively passivated. Conversely, GBs falling nearby this line do not passivate. Scanning electron micrographs of typical passivating and non-passivating grain boundaries are illustrated to the right; labels A, B, C, and D refer to regions designated in Figs. 1 and 2. Note the 160° faceting angle characteristic of non-passivating GBs.

Figure 9 (right). *Recombination Activity of Grain Boundaries by Type and Dislocation Density.* LBIC contrast is plotted versus dislocation etch pit density (EPD) for GBs exhibiting little to no improvement after hydrogenation (Fig. 2). Note a strong proportional dependence of GB recombination activity on EPD both before and after hydrogenation.

Task 3: Develop defect-tolerant device processes and architectures.

Through a combination of modeling and experimental validation, we developed computer models to predict the impact of defects on device performance (including the “I2E simulator” mentioned in Task 2). We worked closely with industrial partners, increasing the efficiency and throughput of solar-cell processes. In our most successful partnerships, throughput was increased by up to 5x, and cell efficiency improved by several percent absolute. These advances highlight the necessity for our community to develop accurate process simulation tools to augment a veritable cornucopia of device simulators.

As a publishable example of this work, we demonstrate how post-gettering lifetime enhancements are possible after phosphorus diffusion, by implementing a modified cooling profile. Observed is not only a lifetime enhancement over the entire ingot, but also an increase of fraction usable material (yield) by recovery of “red-zone” material.

Fig. 10. Minority carrier lifetime of wafers after P-diffusion, illustrating the improvement in minority carrier lifetime possible by adding a low-temperature anneal. Experiment conducted at industrial partner; data courtesy of Nathan Stoddard and Rubin Sidhu.

Among the interesting learnings:

- Customized phosphorus diffusion processing should be applied to different regions of the ingot. Because of higher impurity contents in the “red zone,” higher temperature plateaus and longer cools to room temperature are needed to enhance material performance.
- It is necessary to model the **entire** solar cell process, including metallization firing, if precipitates remain in the bulk after phosphorus diffusion.
- This process-modeling approach may be generalized to thin film materials, perhaps resulting in similar performance increases.

Summary: The objective of this project is to close the efficiency gap between industrial multicrystalline silicon (mc-Si) and monocrystalline silicon solar cells, while conserving the economic advantage of low-cost, high-volume substrates inherent to mc-Si.

Over the course of this project, we made significant progress toward this goal, as evidenced by the evolution in solar-cell efficiencies. While most of the benefits of university projects are diffuse in nature, several unique contributions can be traced to this project, including the development of novel characterization methods, defect-simulation tools, and novel solar-cell processing approaches mitigate the effects of iron impurities and dislocations. In collaboration with our industrial partners, this project contributed to the development of cell processing recipes, specialty materials, and equipment that increased cell efficiencies overall (not just multicrystalline silicon).

Additionally, several students and postdocs who were either partially or fully engaged in this project (as evidenced by the publication record) are currently in the PV industry, most notably Steve Hudelson (1366 Technologies), Prof. Mariana Bertoni (Arizona State University; formerly 1366 Technologies), and Dr. Bonna Newman (formerly Twin Creeks), with others hopefully to follow.