

Engineering metal-impurity nanodefects for low-cost solar cells

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Published online: 14 August 2005; doi:10.1038/nmat1457

As the demand for high-quality solar-cell feedstock exceeds supply and drives prices upwards, cheaper but dirtier alternative feedstock materials are being developed^{1–3}. Successful use of these alternative feedstocks requires that one rigorously control the deleterious effects of the more abundant metallic impurities. In this study, we demonstrate how metal nanodefekt engineering can be used to reduce the electrical activity of metallic impurities, resulting in dramatic enhancements of performance even in heavily contaminated solar-cell material. Highly sensitive synchrotron-based measurements^{4,5} directly confirm that the spatial and size distributions of metal nanodefects regulate the minority-carrier diffusion length, a key parameter for determining the actual performance of solar-cell devices. By engineering the distributions of metal-impurity nanodefects in a controlled fashion, the minority-carrier diffusion length can be increased by up to a factor of four, indicating that the use of lower-quality feedstocks with proper controls may be a viable alternative to producing cost-effective solar cells.

The photovoltaic industry has been growing at a steady annual rate of 25–30% over the past several years. This progress was driven chiefly by silicon-based solar cells, which now constitute nearly 90% of the global market. Although silicon is the second most abundant element in the crust of the Earth, it is typically found in an oxidized complex in nature. The refined and highly purified polysilicon feedstock used to fabricate commercial solar cells and integrated circuits is a much rarer commodity, with an annual production of approximately 30,000 tons. With continued growth in the photovoltaic industry, demand for silicon feedstock finally exceeded supply in 2004, provoking a drastic price increase for silicon feedstock and jeopardizing the continued growth of the photovoltaic industry.

To eliminate dependence on high-quality silicon feedstock, the development of low-cost ‘solar-grade silicon’ (SoG-Si, refs 1–3) has been proposed, which contains much higher concentrations of

deleterious transition metal impurities. Many studies^{6–8} have shown that transition metals can decrease the minority carrier diffusion length—a key parameter for determining the efficiency of solar-cell devices. Attempts have been made to use lower-quality feedstock, but with little commercial success. An entirely new approach is needed to make cost-effective solar cells from low-cost, abundant, but impurity-rich feedstocks.

This need is exacerbated by the fundamental limitations of removing metals during the processing of solar-cell devices^{9–13}, which contribute to the relatively lower efficiencies¹⁴ of multicrystalline silicon (mc-Si) solar cells compared with single crystalline cells. Related work¹⁵ has proved that phosphorus diffusion gettering is rather limited in removing metals (phosphorus diffusion is a processing step used to create the pn-junction of the solar cell, which has an important secondary effect of gettering a fraction of metals from the bulk): between 10–40% of interstitial diffusing metals (Cu, Fe, Co, Cr, Ag and so on) and nearly 100% of substitutional diffusing metals (Zn, As, Sb, Sn and so on) remain in the material after gettering. Although gettering has proved an efficient means to increase the cell efficiency to acceptable levels when applied to the currently used materials, in the future SoG-Si materials a standard phosphorus gettering step would not be sufficient for reducing the metal concentration to acceptable levels. In order to effectively use dirty but readily available and economically competitive feedstocks to manufacture high-efficiency solar cells, a completely new approach to mitigate the deleterious effects of metals is needed to complement the existing gettering and passivation treatments.

In this study, we suggest an approach to dealing with metals that can be used in conjunction with existing solar-cell processing techniques, and which we expect to become instrumental in the future technologies. Instead of removing all metals from mc-Si—a prospect that is frustrated by physical limitations and cost restrictions—we suggest that large amounts of metals inside the material are acceptable, as long as their size and spatial

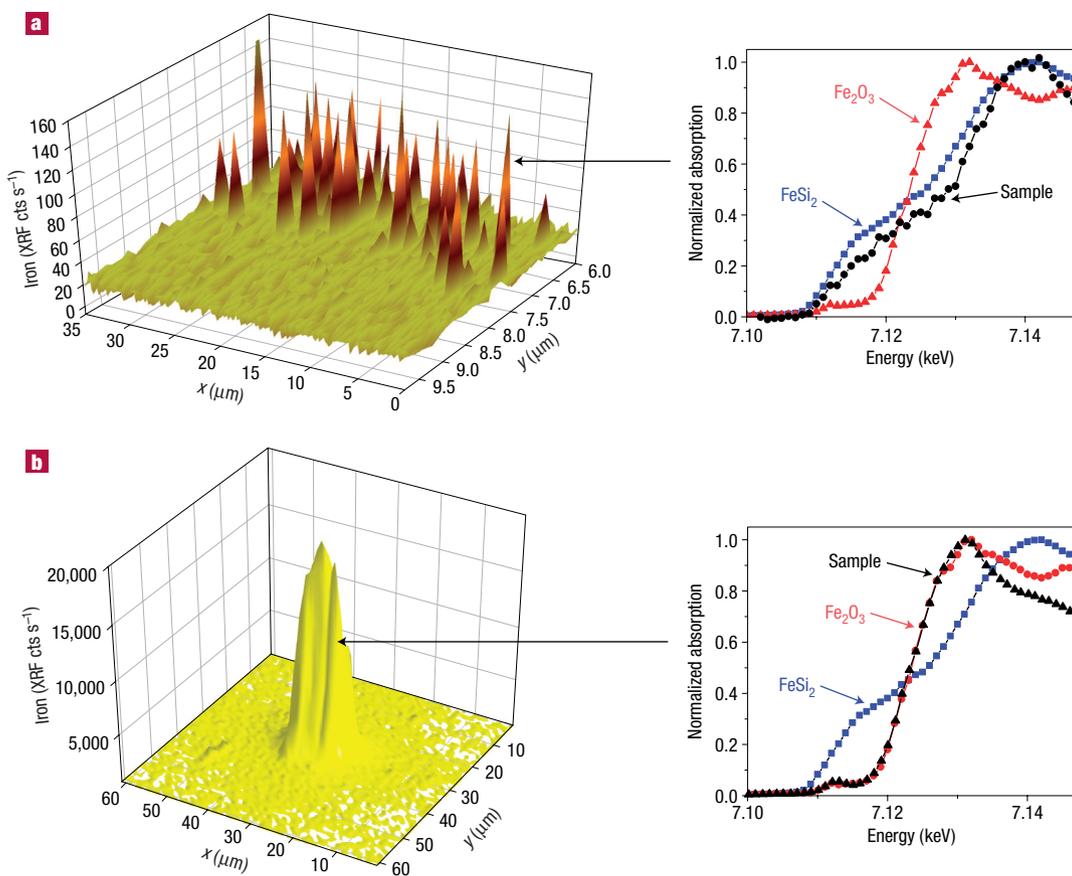


Figure 1 The different types of metal defect in commercial solar-cell material. **a**, Iron silicide nanoprecipitates, with radii $\sim 20\text{--}30$ nm. **b**, Iron oxide inclusion, several micrometres in diameter. X-ray fluorescence (left) maps the iron nano- and microdefects, whereas X-ray absorption spectra (right) determine their chemical states. The vertical scale in μ -XRF maps is in counts per second.

distributions are properly engineered. Furthermore, we provide experimental evidence of how metal nanodefekt engineering can be used to recover minority carrier diffusion lengths even in heavily contaminated materials.

In the past, metal nanodefekt clusters embedded in a semiconductor matrix have been difficult to study because of their small size (typically tens of nanometres) and comparably large separating distances (up to tens of micrometres). However, recent advances in synchrotron-based X-ray fluorescence microscopy (μ -XRF; refs 4,5, also see Supplementary Information) permit the detection of a single iron silicide impurity precipitate with a radius of 16 nm or greater within 1 s, which makes it possible to map the distribution of metal impurity nanoclusters over several thousands of cubic micrometres of semiconductor material per hour, ensuring statistically meaningful data within reasonable amounts of time. X-ray absorption microspectroscopy characterizes the chemical states of impurity clusters, elucidating the chemical origins and stability^{16,17}. Finally, a newly developed technique—spectrally resolved X-ray-beam-induced current—generates a map of the minority-carrier diffusion length, which reveals the precise impacts of metal impurity clusters on local material performance¹⁸. These powerful techniques can be combined and performed *in situ* at suitable synchrotron microprobe beamlines, allowing one to detect, characterize and assess the impacts of individual metal clusters on solar-cell performance.

This suite of techniques is applied herein to study the nature, distribution and impact of metals on the electrical properties of

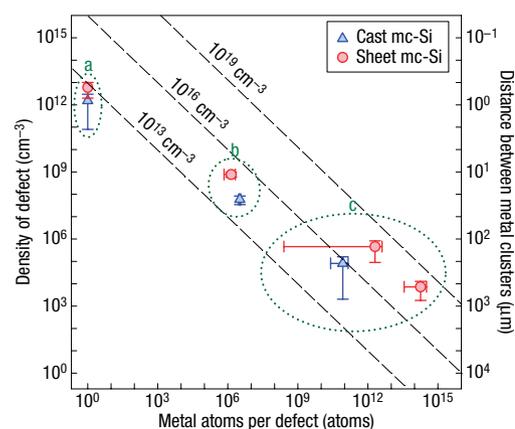


Figure 2 Metal defect distributions in commercial and next-generation solar-cell materials. The spatial density (cm⁻³) of these defects is related to their average size (number of atoms) for solar-cell materials of the current generation ('cast' mc-Si) and future generation ('sheet' mc-Si). Dashed diagonal lines indicate constant metal concentrations. Different defect types are labelled by letters and circles. **a**, Dissolved metal point defects. **b**, Metal silicide nanoprecipitates. **c**, Micrometre-sized inclusions of foreign particles. The error bars represent the range of precipitate sizes and their densities observed in a large set of samples. The symbols represent the arithmetical average of all data. The error bars appear asymmetric because of the logarithmic scale of the plot.

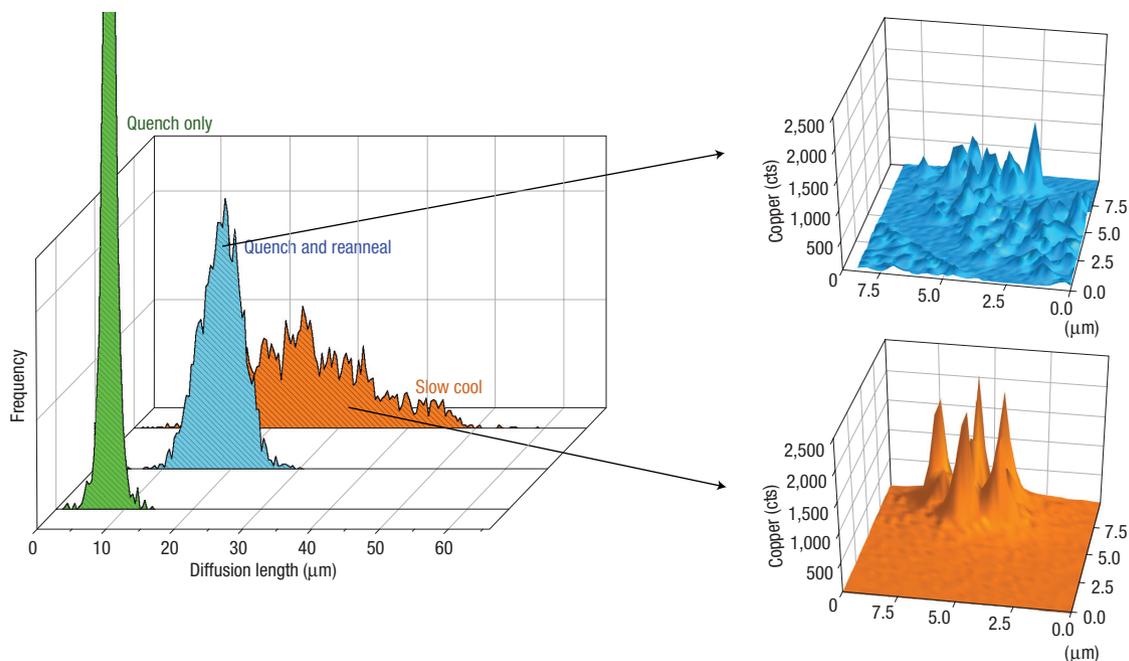


Figure 3 Effect of the distribution of metal defects on material performance. Material performance (minority-carrier diffusion length histograms, left) in three differently cooled samples (quench, quench and re-anneal, slow cool) is compared with size and spatial distributions of metal defects (high-resolution μ -XRF maps (right), XRF copper counts per second plotted against x and y coordinates in μm). The material with microdefects in lower spatial densities clearly outperforms materials with smaller nanodefects in higher spatial densities, despite the fact that all materials contain the same total amount of metals.

two different mc-Si solar-cell materials: traditional directionally solidified ‘cast’ mc-Si (ref. 19) and a next-generation material known as SiliconFilm ‘sheet’ mc-Si (ref. 20).

The predominant type of metal nanodefect detected in these materials is the metal silicide nanoprecipitate (radius ~ 20 – 30 nm) (Fig. 1a). These nanoprecipitates are found both at grain boundaries and at structural defects in the grains. The association of impurities with structural defects has been observed in a variety of other systems^{21–23}. Both strain fields around these defects and the high degree of disorder in the crystal lattice are believed to be responsible for lowering the nucleation barrier for precipitates²⁴ that are formed from dissolved, supersaturated metals.

Another type of metal-rich particle is detected in very low spatial densities, averaging several micrometres in size, and is generally composed of metal oxide (Fig. 1b). Interestingly, most transition-metal-oxide species are not predicted to form in a silicon matrix because the silicon–oxygen bond is stronger than most metal–oxygen bonds²⁵. In addition, these micrometre-sized particles are too large to have formed from precipitated impurities, especially given the rapid growth speed of sheet material. However, many metal-oxide species have melting temperatures significantly above that of silicon. This enables them to survive for a certain time in liquid silicon during crystal growth, before dissolving. Thus, it is most probable that these observed particles are trapped inclusions of foreign material. The varied compositions of these particles often resemble stainless steel, pure iron oxide or titanium oxide, which could originate from furnace parts or impurities in the feedstock and growth surfaces. Partial dissolution of such particles in the molten silicon during crystal growth is the probable origin of the majority of metal contamination found in mc-Si solar-cell materials. Some of these dissolved metals could precipitate to form metal silicide nanoprecipitates, whereas the remainder can be found in the atomically dissolved^{26,27} state.

We analysed the average sizes and spatial densities for three different types of metal-related defect: micrometre-sized inclusions, metal silicide nanoprecipitates and atomically dissolved metals (Fig. 2). The total amount of metals contained in each type of cluster is represented by the dotted lines, indicating total metal content.

Although we show that the majority of metals are contained in micrometre-sized inclusions, the average distances between these particles is very large, so they cannot have a significant direct impact on minority-carrier diffusion length. Unlike these large inclusions, smaller metal clusters and interstitial metals (represented on the left-hand side of Fig. 2) are present in significantly higher spatial densities and are much more dangerous to solar-cell device performance. These observations led us to the conclusion that to maximize solar-cell efficiency without changing the total metal concentration, all metals must be completely contained in large, micrometre-sized clusters separated by several hundreds of micrometres, thus minimizing the interaction between metal atoms and charge-carrying electrons.

To test this hypothesis, we purposely engineered different metal distributions in heavily contaminated mc-Si material and compared these directly to the minority-carrier diffusion length. We found that metal-impurity distributions can be predictably engineered, for example, by controlling the sample cooling rate from high temperatures. Three samples of high-purity mc-Si grown by float-zone technique at the National Renewable Energy Laboratory were heavily contaminated with copper, nickel and iron at $1,200$ °C (the concentration of the metals was determined by their solubility at the diffusion temperature) to mimic the high metal content that is probably to be found in future SoG-Si material, and were subjected to different cooling rates: quench (200 °C s^{-1} cooling rate), slow cool (3 – 8 °C s^{-1}) and quench to room temperature followed by a re-anneal at 655 °C

terminated by slow cool. The metal nanod defect distributions in these three samples were mapped using μ -XRF and the minority-carrier diffusion lengths were determined by spectrally resolved X-ray-beam-induced current.

Very fast cooling rates result in a homogeneous distribution of predominantly dissolved metals and their complexes. The histogram labelled 'quench' in Fig. 3 shows a narrow distribution of minority-carrier diffusion lengths under 10 μm , unacceptable for solar-cell devices. The sample quenched and subsequently re-annealed shows a fine distribution of nanod defect clusters, tens of nanometres in size, with lower spatial densities than in the quenched sample. Simultaneously, the minority-carrier diffusion length increases almost twofold (Fig. 3). Finally, a low density of micrometre-sized defect clusters was observed in the slowly cooled sample, which has a maximum minority-carrier diffusion length a factor of four higher than the quenched sample. These results provide direct evidence for the correlation between changes in the distribution of metal defects and enhancement of material performance.

The concept proposed in this study opens a new and exciting opportunity to recover low-quality silicon for commercially viable solar-cell material. This concept is not necessarily limited to annealing sequences used in this article as examples. For instance, it could also be extended to appropriate engineering during crystal growth. As material performance is shown to be limited primarily by the distribution of the interstitial metals, metal clusters and metal precipitates, and not only by total metal concentrations, even heavily contaminated materials can show dramatic enhancements through nanod defect engineering. The defect engineering could be complemented by the existing solar-cell processing techniques such as gettering or hydrogen passivation, which can be expected to improve the material performance even further. Our results demonstrate how metal-rich SoG-Si, which would be much cheaper and far more abundant than current silicon feedstock material, has the real potential to produce cost-effective solar cells, provided metal nanod defects are engineered correctly.

Received 14 March 2005; accepted 30 June 2005; published 14 August 2005.

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Acknowledgements

Collaboration with M. Heuer, S. Fakra, M. D. Pickett, R. Jonczyk, T. F. Ciszek, K. O. Dijon, J. Isenberg, W. Warta, R. Schindler and G. Willeke is gratefully appreciated. This work was funded by National Renewable Energy Laboratory subcontract AAT-2-31605-03. Use of the Advanced Photon Source and of the Advanced Light Source is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract Numbers W-31-109-ENG-38 and DEAC03-76SF00098, respectively. Correspondence and requests for materials should be addressed to A.A.I. Supplementary Information accompanies this paper on www.nature.com/naturematerials.

Competing financial interests

The authors declare that they have no competing financial interests.