Scanning X-ray fluorescence microspectroscopy of metallic impurities in solar-grade silicon

Daniel Macdonald*1, Fiacre Rougieux1, Yves Mansoulie1, Jason Tan1, David Paterson2, Daryl L. Howard2, Martin D. de Jonge2, and Chris G. Ryan3

1 School of Engineering, College of Engineering and Computer Science, The Australian National University, Canberra, Australian Capital Territory 0200, Australia
2 Australian Synchrotron, 800 Blackburn Rd, Clayton, Victoria 3168, Australia
3 CSIRO Earth Science and Resource Engineering, Clayton Victoria 3168, Australia

Received 24 February 2010, revised 18 March 2010, accepted 24 March 2010
Published online 23 April 2010

Keywords impurities, precipitates, silicon, X-ray fluorescence

*A corresponding author: e-mail daniel.macdonald@anu.edu.au, Phone: +61 2 6125 2973, Fax: +61 2 6125 0506

A rapid scanning synchrotron-based X-ray fluorescence microprobe technique is applied to relatively impure crystalline silicon feedstock for solar cells. The results reveal the distributions of metallic impurities in the material over regions several millimetres in size, allowing scans across several grains. Relatively high concentrations of Fe, Cu and Zn were observed, with traces of Mn and Ni. The metals were mostly present as discrete particles up to 60 μm in size, while Cu was more uniformly distributed. More than 50% of the detected Fe was present as large particles at the grain boundaries, probably due to diffusion and precipitation during cooling. In contrast, less than 5% of the Cu resided in such large particles. The particles contained multiple metallic elements, with strongly varying proportions of their metal constituents.

1 Introduction With the prospect of using low-cost ‘solar-grade’ silicon for solar cells, it is necessary to determine impurity concentrations and distributions in silicon feedstocks. The spatial distributions of impurities in metallurgical-grade silicon (MG-Si) have previously been studied, for example, by electron microprobe techniques [1, 2]. However, these techniques are unlikely to be sensitive enough for more refined solar-grade silicon, such as upgraded metallurgical-grade silicon (UMG-Si). At the other end of the purity spectrum, very sensitive spatially resolved techniques such as synchrotron-based X-ray fluorescence (SXRF) have been applied to ingot-grown multicrystalline silicon wafers [3–5]. These SXRF techniques reveal the nanoprecipitates which are predominant in these wafers, but have low scan speeds, and are thus limited to studying small areas, usually near grain boundaries. Here we apply a recently developed detector system for SXRF imaging, allowing rapid scans over entire grains, while still producing high definition maps. We demonstrate that this system is well suited to studying impurities occurring both at the grain boundaries, and within the grains, in moderately contaminated solar-grade silicon such as UMG-Si. The results give insight into the formation mechanisms of metallic particles in this material.

2 Experimental details UMG-Si samples were obtained from a commercial supplier. Large chunks (~10 cm in size) were carefully cracked to create smaller flakes (~5–10 mm wide and 1–2 mm thick) with previously unexposed, and hence very clean, planar surfaces. These flakes were analysed using the X-ray fluorescence microscop-phy (XFM) beamline at the Australian Synchrotron [6]. An X-ray beam with photon energy of 18.5 keV, a spot size of 3 μm and an intensity of approximately 1010 photons/s/μm² was produced by a Kirkpatrick–Baez mirror microprobe. The sample was scanned at a constant speed of 0.1 mm/s. The X-ray fluorescence was detected ‘on-the-fly’ with a novel multielement detector and integrated spectroscopic imaging system, dubbed the ‘Maia’ detector [7, 8]. The prototype detector contains 96 parallel detector elements, collects photons over a wide solid angle, and has real-time processing, allowing fast scan speeds. With a pixel size of
1.25 μm, a scan over a 1 mm × 1 mm square took 2.2 h. Data were subsequently processed using spectral deconvolution, background subtraction and projection of separated elemental images [9, 10]. Deconvolution of the SXRF data used the dynamic analysis (DA) method [11, 12] and the GeoPIXE [10] software suite. The metallic impurities most commonly detected were Fe (Kα emission at 6.4 keV), Cu (8.0 keV), Mn (5.9 keV), Zn (8.6 keV) and Ni (7.5 keV). Examples of XRF spectra are shown in Fig. 1 for Region B containing an Fe-rich particle with trace amounts of Cu and Zn, and Region A not containing any large particles, but with detectable amounts of Cu.

3 Results and discussion

The material exhibits clearly defined grains which are approximately 1–5 mm wide and elongated, running in parallel. Figure 2 shows a band-to-band photoluminescence image [13] of a separate flake of the material, revealing the typical grain structure. Figure 3a–e shows the distributions of Fe, Cu, Zn, Mn and Ni, respectively, determined by SXRF, in a region of UMG-Si approximately 1.5 mm × 1.7 mm in size. Figure 3f depicts Regions A and B from Fig. 1, Scans 1–4 from Figs. 4 and 5, and the positions of grain boundaries.

The SXRF images in Fig. 3 show that Fe, Zn, Mn and Ni occur largely as discrete particles ranging in size from 5 to 60 μm. Cu also occurs almost uniformly across the sample, with higher concentrations in large ‘hazes’ that are not aligned to grain boundaries, as shown in Fig. 3b, and as discussed in more detail below. In general, however, the metal particles tend to aggregate near the grain boundaries. The grain boundaries are not perpendicular to the surface, but run at an angle to it. As the metal particles are located at various depths along the grain boundaries, and the X-ray emission from the particles is absorbed by the silicon matrix, the result is an apparent fading in intensity away from the line where the boundary intersects the surface. The X-ray attenuation lengths vary from 28 μm for Mn Kα emission (5.9 keV) to 86 μm for Zn Kα emission (8.6 keV) (http://www.cxro.lbl.gov). These lengths are indicative of the depth resolution, and are consistent with the scale of the graded regions, with Zn exhibiting a larger graded region than Mn.

Figures 3a and d show that a small fraction of the Fe-rich particles also contain large quantities of Mn, while most contain no detectable Mn. This serves to illustrate the...
effectiveness of the decomposition of the SXRF spectra into peaks attributable to the individual elements. Since the Fe and Mn lines are the closest in terms of energy, inadequate decomposition of the spectra would lead to a degree of cross attribution for these two elements, in turn leading to qualitatively similar distributions, which is not observed.

The aggregation of metal particles near grain boundaries indicates that the cooling of the UMG-Si after manufacture is sufficiently slow to allow fast diffusing metals to migrate to the grain boundaries, where they can precipitate. This effect has been documented in directionally solidified multicrystalline wafers [5]. The greater concentrations of metallic particles near the grain boundaries, especially Fe, suggest that crushing and acid leaching [1, 2, 14] may be an effective method for further purifying this material.

The particles contained a mixture of metallic elements, as revealed by the line scans shown in Figs. 4 and 5, the locations of which are shown in Fig. 3f. Scan 1 in Fig. 4 shows an Fe-rich particle on the left, which also contains significant amounts of Mn, and lesser amounts of Cu, Ni and Zn. The scans in Fig. 5 show other particles of varying size and composition, some with distinct features within them. It should be noted that the different attenuation lengths of the emitted X-rays for each metal would cause some variation in the detected spectra for particles at different depths in the sample. However, this effect alone is not sufficient to explain the observed spectra, revealing significant variations in the chemical composition of the particles. Such multielement metal particles are thought to reduce the physical mismatch with the host lattice [15].

Figures 4 and 5 also serve to indicate the background noise levels for each of the elements, which lie between 10 and 50 counts per pixel. The intensities within the large particles are significantly above these limits, while the signal for Cu lies above this limit also between the large particles.

As mentioned above, an almost uniform background level of Cu with additional large Cu hazes were observed, possibly comprised of small particles that cannot be individually resolved in this study. This is not a measurement artefact, as evidenced by the small but clear Cu peak in the spectrum in Fig. 1 for Region A, which contains no large particles, and is outside the heavier Cu haze, showing that the Cu signal everywhere is significantly above the detection limit. This more uniform distribution is surprising, since Cu is the most rapid diffuser of the metals observed, and might be expected to accumulate heavily at the boundaries during cooling. However, less than 5% of the total Cu counts were attributable to large particles greater than 10 μm in diameter, compared to more than 50% of the Fe signal. The more uniform distribution of Cu may indicate that the material contains intra-grain defects which act as effective precipitation sites for Cu, competing with the grain boundaries. This is in contrast to previous studies on directionally solidified multicrystalline silicon wafers, in which very rapid diffusers like Cu and Ni were precipitated entirely at grain boundaries [5]. The apparent Zn haze in Fig. 3c is close to the detection limit, as can be seen by the very small Zn peak in Fig. 1, which barely rises above the background noise, and the low intensities for Zn between the particles in Figs. 4 and 5, in contrast to Cu.

4 Conclusions The synchrotron-based XRF Maia detection system allows rapid, high definition and accurate mapping of impurity concentrations in relatively impure solar-grade silicon. In the UMG-Si studied here, most metal impurities were found to occur as discrete particles at grain boundaries, with varying elemental compositions. In addition, a more uniformly distributed haze of Cu was detected that was not aligned to the grain boundaries. The large area scans enabled by the Maia detector allow the clear detection of such intra-grain features.

Acknowledgements This research was undertaken on the X-ray fluorescence microscopy (XFM) beamline at the Australian Synchrotron, Victoria, Australia. The authors are grateful to A. Cuevas for providing the UMG-Si samples.
References