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Specimen preparation methods for elemental characterisation of grain boundaries and isolated dislocations in multicrystalline silicon using atom probe tomography

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ABSTRACT

Multicrystalline silicon (mc-Si) is a cost effective feedstock for solar photovoltaic devices but is limited by the presence of defects and impurities. Imaging impurities segregated to nanometre-scale dislocations and grain boundaries is a challenge that few materials characterisation techniques can achieve. Atom Probe Tomography (APT) is a 3-dimensional time-of-flight microscopy technique that can image the distribution of elements at the atomic scale, however one of the most challenging factors when using APT is the complexity of specimen preparation for specific regions of interest. Atom probe specimen preparation methods have been developed in a dual FIB/SEM system that enable a specific extended defect such as an isolated dislocation or a section of a grain boundary to be selected for APT analysis. The methods were used to fabricate APT specimens from an isolated dislocation and a grain boundary in mc-Si samples. Complementary TEM images confirm the presence of the defects in both specimens, whilst APT analyses also reveal segregation of impurities to the defects.

1. Introduction

The photovoltaic industry has in recent years been dominated by the use of multicrystalline silicon (mc-Si) solar cells, which offer substantial cost reduction compared to monocrystalline silicon bulk material. However, the presence of high densities of defects such as dislocations, grain boundaries (GB) and stacking faults in multicrystalline silicon leads to more possible recombination centres for electron-hole pairs created during operation, reducing the efficiency of the solar cell, from a record efficiency of 25.6% for single crystal silicon to a maximum of 21.25% for mc-Si [1].

The decrease in efficiency of mc-Si solar cells has been linked to the density of dislocations and impurities, and the segregation of impurity atoms such as Fe, Cr, Ni and Cu to them [2]. New mc-Si growth methods have reduced the grain boundary density [3]and the dendrite casting method that induces ⟨110⟩ and ⟨112⟩ dendrite growth along the crucible bottom has also been demonstrated to grow large grains with a high number of electrically inactive Σ3 twin boundaries [4] that also reduce the dislocation density [5]. Nevertheless, recombination at dislocations and GBs still limits the efficiency of mc-Si solar cells. For many years, gettering has been used to remove transition metal impurities, in particular using phosphorus diffusion during high-temperature processing to draw the impurities to the phosphorus rich region forming metal rich precipitates at the surface. Whilst it has been demonstrated using bulk chemical characterisation techniques that increased metal content reduces cell efficiency [6,7], characterising the distribution of these impurities to atomic-scale defects pre- and post-gettering remains a challenge. Whilst synchrotron-based nanoprobe X-ray fluorescence mapping has been able to image larger defects [8], it can only obtain a resolution of 80 nm [9], insufficient to image the distribution of impurity atoms on individual defects in mc-Si.

In recent years atom probe tomography (APT) has become a valuable nanoscale characterisation tool for the development of new silicon-based semiconductor materials and devices, particularly as the scale of such devices shrink. For example, there are few techniques that can image the 3D chemical distribution across entire individual transistors [10]. The implementation of laser pulsing capabilities in atom probe instruments has been critical in opening up APT to a much wider range of semiconductor materials applications [11]. However, a concurrent advance in the development of site-specific Focused Ion Beam (FIB) based techniques [12], to prepare the very sharp needle-shaped specimens required by APT, was equally important.

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The development of FIB/SEM dual-beam systems enables the combination of milling with the ion beam, and imaging with the electron beam, in order to fabricate atom probe specimens with a much greater degree of control over the final tip shape and location. The standard preparation method is the FIB lift-out technique, where a small piece of the sample is removed from the bulk sample, transferred to a support structure and sharpened into a needle [12–14].

Numerous adaptations of the FIB lift-out process have been reported in the literature that allow APT specimens to be made from a specific region of interest (RoI). The characterisation of dopant and impurity segregation in silicon using APT has shown boron clusters at the intersection of grains [15,16], nickel segregation to dislocation loops in ion-implanted silicon wafers [17] and the segregation of P, As, C and O to grain boundaries in annealed multicrystalline silicon [18]. Recently an atom probe specimen preparation method developed by Stoffers and co-workers [19] was able to demonstrate the ability to extract grain boundaries from mc-Si samples in a reproducible manner. This was achieved by adapting a TEM-based preparation method developed by Felfer et al. [20], where the specimen containing a grain boundary is lifted and mounted onto a TEM grid and imaged using a TEM to identify the position of the defect. The specimen is then returned to the FIB for final polishing to precisely position the grain boundary at the tip apex for APT analysis. However, in addition to the time-intensity of the process, since the grain boundary is located perpendicular to the field evaporation direction in the APT analysis, specimens fabricated using this approach only contain a small section of the grain boundary. This limits the probability of precipitates and individual dislocations in the analysis, which may be distributed along grain boundaries within the bulk material.

Significantly, the Stoffers method is also only suitable for grain boundaries, rather than isolated dislocations. These defects are thought to play an important role in the segregation of undesirable impurities [21] however, dislocations are much more widely distributed and are generally thought to be a more important limiting factor in cell efficiency [5]. Hence it is critical to have a specimen preparation technique with the ability to identify, select and incorporate specific isolated dislocations for APT analysis. Using the traditional top-down liftout method to obtain an isolated dislocation in the analysis volume is extremely challenging. This is because the dislocation does not necessarily extend vertically down from the surface, and also the annular milling to create the needle specimen can result in etching away the desired feature.

This paper presents in detail two novel atom probe specimen preparation methods, based on a rotated form of the lift-out technique, for extracting isolated dislocations and grain boundaries from mc-Si subjected to different processing conditions. Complementary TEM was carried out to confirm the feature of interest was present in the fabricated specimen prior to APT analysis. Finally, the resulting APT reconstructions demonstrate the effectiveness of the techniques developed, to facilitate the characterisation of the mc-Si microstructure. The selective nature of this approach can also be combined with other characterisation such as electron beam induced current (EBIC) to link the structure and chemical segregation of a defect to its electrical activity. Although this paper demonstrates the method for the analysis of mc-Si, the specimen preparation methods described here could also be used to isolate and analyse individual selected dislocations and grain boundaries in other materials which have dislocations oriented roughly perpendicular to the sample surface.

2. Materials and Methods

This study examined p-type mc-Si wafers produced by REC Solar. Samples were taken from the top region of a commercial ingot produced by directional solidification, and subsequently diced into 5 mm square pieces.

For the purpose of proving that APT can successfully image dislocations at grain boundaries, a wafer of mc-Si was intentionally contaminated with gold. The sample was mechanically polished using 8, 1 and 0.25 μm polishing pads to remove saw damage regions, followed by chemo-mechanically polishing using a Chem-H polishing pad. Surface contaminants and oxide were removed using RCA and HF cleans respectively. A ~50 nm layer of gold was deposited on the surface, followed by annealing in argon gas at 1000 °C for one hour and oil quenching, which is predicted to produce a gold concentration near the wafer surface greater than ~50% of its solid solubility value of $\sim 10^{16}$ atoms/cm^3 [22].

In order to analyse the segregation of impurities to dislocations after gettering, Phosphorus Diffusion Gettering (PDG) was performed on another mc-Si specimen, which was annealed at 875 °C for 22 min in the presence of 650 sccm $POCl_3$, 500 sccm O_2 and 13.5 SLPM N_2. Subsequently the $POCl_3$ and O_2 flows were turned off and the specimen was cooled to 800 °C in an N_2 atmosphere at a rate of 10 °C/min, before removing the specimen from the furnace and cooling to room temperature. Prior to FIB analysis, the phosphorus silicate glass and phosphorus-rich region at the surface were removed by exposure to hot hydrochloric acid for 10 min followed by 2 h of chemo-mechanical polishing.

FIB liftouts were carried out in a Zeiss NVision 40 FIB-SEM system. Defects were lifted-out of the bulk sample using an in-situ Kleindiek nano-manipulator. A gas-injector was used in conjunction with SEM and FIB to deposit carbon and/or tungsten to protect the sample from Ga^+ damage and weld the liftout to the manipulator. An Omiprobe© lift-out grid containing five copper posts was used as a support structure for mounting the sample and mounted in a dedicated holder, as previously demonstrated by Felfer et al. [14]. FIB milling was undertaken using an accelerating voltage of 30 kV, with the exception of a final polishing step at 5 kV. The support structure during wedge attachment and preparation was positioned such that the copper posts are normal to the SEM column axis. During Specimen sharpening, the grid was held at 54^0 tilt such that the copper posts are parallel to the FIB column axis.

TEM images of the specimens were taken in bright field mode in a double-tilt holder Philips JEOL 2000FX microscope at an accelerating voltage of 200 kV. After characterisation in the TEM, APT analysis was carried out using a Cameca LEAP 3000X HR equipped with an energy-compensated reflectron, and an ultra-high frequency laser which operates at the wavelength of 532 nm. Experiments were performed in an ultra-high vacuum environment of better than 3×10^{-11} Torr, and cooled to a specimen temperature of 50 K. APT analyses were carried out using a 0.5 nJ laser beam energy, 0.3% evaporation rate and 160 kHz pulse frequency.

3. The Specimen Preparation Procedure

3.1. Defect Marking Techniques

Prior to FIB processing, preferential etching of the sample is required so that extended defects are observable via SEM. The bulk silicon sample is mechanically and chemo-mechanically polished to create a smooth surface, and surface contaminants removed using the standard RCA cleaning procedure [23]. In the final step, the sample is submerged in a Secco etch ((49%)HF:(0.05 M)$K_2Cr_2O_7$ at a ratio of 1:2) at 20 °C for 30 s, resulting in pits at the surface that highlight the position of dislocations and GBs. The size and geometry of the pits depends on the etch conditions used. These conditions were optimised to produce etched features with an approximate average width of 100 nm and depth of 170 nm. This leaves a GB or dislocation far enough below the material surface to reliably retain in the final APT specimen needle.

Fig. 1 shows a schematic of the overall liftout process. First, a dislocation pit is identified and marked with a tungsten dot and a layer of carbon to protect it from subsequent damage from the gallium beam. Then, the sample is cut into a wedge using the FIB and lifted out using a nanomanipulator, before mounting onto a TEM half-grid. The key