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Three-dimensional minority-carrier collection channels at shunt locations in silicon solar cells

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ABSTRACT

In this contribution, we demonstrate the value of using a multiscale multi-technique characterization approach to study the performance-limiting defects in multi-crystalline silicon (mc-Si) photovoltaic devices. The combination of dark lock-in thermography (DLIT) imaging, electron beam induced current imaging, and both transmission and scanning transmission electron microscopy (TEM/STEM) on the same location revealed the nanoscale origin of the optoelectronic properties of shunts visible at the device scale. Our site-specific correlative approach identified the shunt behavior to be a result of three-dimensional inversion channels around structural defects decorated with oxide precipitates. These inversion channels facilitate enhanced minority-carrier transport that results in the increased heating observed through DLIT imaging. The definitive connection between the nanoscale structure and chemistry of the type of shunt investigated here allows photovoltaic device manufacturers to immediately address the oxygen content of their mc-Si absorber material when such features are present, instead of engaging in costly characterization.

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1. Introduction

The dominant photovoltaic (PV) market share is still held by cells based on crystalline silicon absorbers despite recent advances in CdTe and Cu($In_{1-x}Ga_x$)Se_2 solar cells. Although crystalline silicon solar cells have approached the theoretical efficiency limit (Shockley and Queisser, 1961; Tiedje et al., 1984), these devices are made from high-purity Si material with low dislocation densities and few or no grain boundaries. Exploring different processing methods and materials has led to reduced manufacturing cost, but not without sacrificing the ability to produce champion-efficiency devices. Grain boundaries and dislocations are present in most solar cells based on crystalline silicon absorbers, and the interaction of these structural features with impurities can profoundly influence device efficiencies (Davis et al., 1980; Hofstetter et al., 2009; McHugo et al., 1997; Riedel et al., 2002; Seifert et al., 1993; Stutzler and Queisser, 1986). Enhanced non-radiative recombination and reduced diffusion length result from impurity decoration of grain boundaries and dislocations. In addition, impurity precipitates are also known to cause diode breakdown in reverse-bias conditions (Kwapil et al., 2009a, 2009b), but the mechanisms by which this occurs is not fully understood for all cases. Significant effort has been made by the silicon PV community to understand the nature of shunts, or regions that exhibit abnormal current flow under different bias conditions (Breitenstein et al., 2008, 2009, 2007; Lausch et al., 2011; Schubert et al., 2010). Emerging from previous research using correlative characterization techniques is a better knowledge of shunts that includes: a classification of different types of shunts (Breitenstein et al., 2004) and theories of how dislocations, grain boundaries, and impurities interact to result in the shunting behavior observed though thermographic imaging techniques.

Several classifications exist (Breitenstein et al., 2004; Langenkamp and Breitenstein, 2002) of shunts in multicrystalline silicon (mc-Si) solar cells, and they are based on the origin of each type of shunt. In this work, we consider shunt types that do not originate from gross disturbances (e.g., cracks, holes, metallization side effects) resulting from cell processing, but rather, the types associated with structural defects and impurities in the bulk of the absorber. The presence of these types of shunts is a more difficult issue to address than those associated with processing and handling of devices. Understanding the nature of shunts in a

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particular device is important for mitigating the presence and effects on performance for devices processed in the future. Here, we investigate shunts that exhibit an increase in current flow (heating) under forward- and reverse-bias conditions and reduced collection in plan-view electron beam induced current (EBIC) imaging.

1.1. Inversion channels at structural defects

Previously, the cause of certain types of shunts has been connected to what are thought to be inversion channels around structural defects in various types of silicon PV devices. Inversion channels have been shown to exist around both dislocations (Breitenstein et al., 2001) and grain boundaries (Breitenstein et al., 2008, 2007, 2004) in ribbon-grown and cast mc-Si. In the grain-boundary studies, the inversion type around grain boundaries was connected to the presence of SiC precipitates decorating the grain boundaries acting as n-type conductors. In this case, type inversion is the result of the band offset between the SiC and the p-type silicon absorber, not the trapping of positive charges. Transmission electron microscopy (TEM) investigations of one of the boundaries found micron-sized SiC precipitates at some boundaries and long SiC filaments at others. These authors expressed some doubt regarding the ability of widely spaced precipitates to cause continuous networks of type inversion in this case. However, the small volume associated with the TEM sample may have excluded the features responsible for the observed type inversion. In another work, inversion channels were observed around dislocations and a model was constructed based on the oxygen content typical of ribbon-growth-on-substrate (RGS) silicon (Breitenstein et al., 2001). However, there was no direct observation of oxygen at the dislocations because there was no nanoscale analysis. It should be mentioned that the inversion channels were observed in all the previously mentioned studies via the backside EBIC technique. In backside EBIC, the back contact is partially removed; therefore, any collection of minority carriers generated at the back of the absorber (far from the junction) is due to the presence of conduction pathways for minority carriers. In the present work, a similar analysis is performed by looking at cross sections prepared by the focused ion beam (FIB) method, where carriers generated away from the depletion region should show significantly decreased EBIC collection unless there is a minority-carrier conduction path near the excitation. In this investigation, we demonstrate both the methodology and results of a multiscale, multi-technique correlative study of shunts in mc-Si photovoltaic devices.

2. Material and methods

A mc-Si solar cell about 80 μm thick was investigated in this study. The device parameters for this solar cell are: open-circuit voltage (V_{oc}) = 535 mV, short-circuit current density (J_{sc}) = 26.94 mA/cm^2, series resistance (R_s) = 3.089 Ω cm^2, shunt resistance (R_{SH}) = 78.79 Ω cm^2, and efficiency measured as 7.78%. Specific conditions were used to process this device and thus these parameters are not representative of typical devices produced by this manufacturer. Dark lock-in thermography (DLIT) images were acquired with 12.6 Hz pulses at 0.9 V forward bias and 4 V reverse bias that allowed qualitative identification of the local current density–voltage (*J*–*V*) behavior of the shunts. EBIC imaging and TEM sample preparation were performed in-situ in a FEI Nova NanoLab 200 dual beam FIB. Using the EBIC stage in the FIB allows for site-specific preparation of defects, as well as serial sectioning of the entire defective regions (Yoshida et al., 2005). EBIC images in the plan-view orientation were acquired at accelerating voltage of 15 kV and beam current of ~1 nA. In cross section, the EBIC images were acquired with 5 kV to enable imaging with higher spatial resolution. One shunt identified with DLIT imaging was sectioned at 90° angles to highlight the three-dimensional nature of the defect. Scanning transmission electron microscopy (STEM)/TEM imaging and energy-dispersive spectroscopy (EDS) analysis were done on an FEI Tecnai F20 field emission TEM operating at 200 kV.

3. Results

DLIT imaging was performed on the entire Si device to identify the locations of shunts, and the results are shown in Fig. 1. Several positions, labeled I through V, exhibited heating due to the 4-V reverse-bias pulses, as indicated in the image by the accompanying scale in arbitrary units. After DLIT imaging, marks were placed around shunt locations with a pulsed laser so that they could be easily identified for subsequent investigations. These marks are clearly visible in several of the EBIC images in Fig. 1.

To locate the position of the shunt with greater precision than afforded by DLIT imaging, EBIC imaging was first done in the plan-view orientation inside the FIB. Images acquired from several of the shunt locations—with the locations of the shunts corresponding to the labels in the DLIT image—are shown in Fig. 1. The red circles in the EBIC images indicate where heating was observed, and it is interesting that all these regions occur at the intersection of three structural defects and exhibit dark EBIC contrast. It is well known that structural defects in silicon are preferential locations for impurity precipitation. Shunts in mc-Si have been associated with a variety of impurities, including C, N, O, and various transition metals (Breitenstein et al., 2004; Buonassisi et al., 2004; Kwapil et al., 2009a, 2009b). The point of intersection of multiple structural defects is likely to be decorated by impurities and impurity precipitates. Higher-magnification EBIC images revealed that the dark regions were not well defined in the shunt locations. This may be due to the electron-beam accelerating voltage used (15 kV) or perhaps the current-splitting effect described previously (Breitenstein et al., 2007; Kaminski et al., 2004). Additionally, small precipitates (<100 nm) have been associated with shunts and pre-breakdown sites in mc-Si; because the EBIC images were diffuse in the shunt locations, we needed a systematic approach to cross-sectional EBIC analysis to identify all the features in the region that may result in the shunt behavior. It should be noted that there are other dark spots and regions where multiple defects intersect in the EBIC images, but the features within the circles appear to be unique with respect to the DLIT signal.

All five marked positions contain features that heat in reverse-bias conditions, but only the shunt in position I exhibits heating in both forward and reverse bias, as indicated in Fig. 2. The linearity of the *J*–*V* characteristics of the shunt could not be definitively confirmed because of the different magnitude of the voltage pulse used for the forward (0.9 V) and reverse (4 V) DLIT imaging. The *J*–*V* response of shunts can reveal the possible atomic-scale origin, as has been suggested in previous work (Breitenstein et al., 2004).

After identifying the location of the shunted regions within several microns via EBIC imaging in-situ in the FIB, the sample was tilted so that a trench could be cut on one side of the dark feature. A final low-energy clean (5 kV) was used to reduce the effects of ion-milling damage and surface recombination on the exposed surface. After an EBIC image was acquired on tilted cross sections, additional 0.5–1 μm cuts were made, removing material in a serial fashion; after each cut, an EBIC image was acquired from the newly exposed surface. Several precipitates became visible in the SEM image near the expected center of the shunt, as shown in Fig. 3. The EBIC image on the right side of Fig. 3 was acquired at this