

ASSESSING THE ROLE OF TRANSITION METALS IN SHUNTING MECHANISMS USING SYNCHROTRON-BASED TECHNIQUES

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ABSTRACT

Shunts in RGS and BaySix materials have been analyzed using a powerful combination of techniques including lock-in thermography, x-ray beam induced current, and x-ray fluorescence microscopy. Transition metals have been identified at shunt locations in both materials. Titanium and silver were found at a shunt in BaySix material, suggesting a process-induced defect related to faulty metallization grid deposition. Iron and copper were found at inversion channels in RGS material, suggesting these extended defects are effective gettering sites for transition metals, which enhance the generation-recombination current in this extended space-charge region. The role of transition metals in certain shunting mechanisms in multicrystalline silicon (mc-Si) solar cells is assessed in light of these experimental data.

1. INTRODUCTION

Faster and cheaper silicon growth techniques employed by solar cell manufacturers control an increasing 54.3% of the total PV market [1]. While fast and cheap production makes economic sense, it has many disadvantages from a materials science perspective. Fast-growth sheet, ribbon, and multicrystalline ingot silicon contain typical metal impurity concentrations of 10^{14} - 10^{16} per cm^3 , several orders of magnitude higher than IC-grade Si [2], higher oxygen, nitrogen, and carbon concentrations, and a much higher density of structural defects.

Metal atoms that would otherwise be segregated from the crystal into the melt during a slow growth procedure become "frozen" into the fast-grown material and can form recombination-active clusters on the order of a few tens of nanometers in size, severely limiting solar cell performance [3]. In addition, rapid solar cell fabrication techniques can further jeopardize solar cell efficiencies. As a result, industrial mc-Si solar cell conversion efficiencies are typically ~12-16% (laboratory record 19.8% for a 1cm^2 cell area), compared to ~15-17% efficiencies for industrial solar cells made of high quality single-crystalline Czochralski or float-zone wafers (laboratory record 24.7% for a 4cm^2 FZ cell area) [4]. Understanding the nature of the defects that limit solar cell efficiencies is the first step for improving materials and processes.

One type of device defect that is particularly detrimental to solar cell efficiencies are shunts. Shunts may be caused by a variety of mechanisms (see Breitenstein et al., this conference [5]), but they all consist of localized regions of reduced pn junction barrier height that reduce the

open circuit voltage (V_{oc}) and fill factor (FF) of the solar cell by draining power from nearby regions. It has long been hypothesized that transition metals could be involved with certain shunting mechanisms, but few conclusive studies have been performed. Herein, we apply a unique combination of analytical techniques including lock-in thermography, x-ray beam induced current, and x-ray fluorescence microscopy to analyze two types of shunts in two different mc-Si solar cell materials: BaySix cast, and Ribbon Growth on Substrate (RGS). Metals have been located at shunts in both materials. We discuss the possible roles of the observed transition metals in each case.

2. EXPERIMENTAL APPROACH

The experimental approach employed to correlate transition metals with shunts is as follows: Fully-processed solar cells were measured with lock-in thermography to pinpoint precise shunt locations. The lock-in thermography technique applies a series of forward or reverse bias pulses to a solar cell in the dark, causing more current to flow through regions of reduced barrier height. This produces a periodic heating of shunting regions of the wafer, which can be viewed with an infrared focal plane array camera with a sensitivity of $100\ \mu\text{K}$ or better if a lock-in system operating at the voltage source frequency is used [6]. This makes it an ideal tool for locating shunts and leakage currents in solar cells and other solid state devices. The lock-in thermography measurements in this work were performed at Fraunhofer ISE (for cast mc-Si) and at MPI Halle (for RGS).

The fully-processed solar cells were then measured with Spectrally-Resolved Laser Beam Induced Current (SR-LBIC) to obtain a map of the variations in diffusion length. The SR-LBIC measurements in this work were performed at Fraunhofer ISE (for cast mc-Si) and at the University of Konstanz (for RGS). Because the Lock-In Thermography and the SR-LBIC measurements are taken over the entire solar cell, the two maps can be superimposed to obtain a correlation between shunting activity and diffusion length. The accuracy of such superposition depends on the precision of the alignment and the resolution of each measurement, and is typically ~300 μm for medium-resolution scans.

SR-LBIC scans can be easily correlated with the X-ray Beam Induced Current (XBIC [7]) scans performed in-situ at the x-ray fluorescence microprobe beamline of the Advanced Light Source (ALS), a 3rd-generation synchrotron at the Lawrence Berkeley National Laboratory. The principle of XBIC is similar to that of LBIC; the only differ-

ence is that the excitation radiation is not a laser, but a focused beam of x-rays produced by a synchrotron. These same x-rays, which are focused to a spot size adjustable between $1\text{-}25\ \mu\text{m}^2$ by a pair of 12.4 keV multilayer mirrors in Kirkpatrick-Baez formation, fluoresce impurities present in the solar cell. This fluorescence is detected by a silicon lithium-drifted detector. The depth of measurement of this technique is dependent upon the escape depth of the x-ray fluorescence of interest. For iron and copper, the attenuation length (distance after which I falls to $1/e$ of I_0) is 36 and 70 μm , respectively. Previous measurements on the sensitivity of this technique found the detection limit with the 12.4 keV mirrors to be $1 \times 10^{14}\ \text{cm}^{-2}$ for Fe at the surface of a sample after 45 sec. accumulation time. Although respectable, the strength of this technique lies in precipitate detection due to its small spot size. For a $1\ \mu\text{m}^2$ spot size, this detection limit equates into a single iron precipitate of radius 20 nm. Details can be found in Ref. [3] & [8]. Since both x-ray fluorescence microscopy (μ -XRF) and XBIC signals can be acquired simultaneously, one achieves a one-to-one correlation between transition metal impurity content and recombination activity with micron-scale resolution. Thus, the transition metal content at shunts can be mapped with a spatial resolution that is limited by the superposition of the lock-in thermography and SR-LBIC techniques.

3. EXPERIMENTAL RESULTS

3.1 Cast mc-Si

A shunt in a fully-processed, $45 \times 45\ \text{mm}^2$ cast multicrystalline silicon solar cell was analyzed using the sequence of techniques described above. At the shunt location, μ -XRF detected silver and titanium, both key constituents of the contact metallization. Furthermore, the ratio of their concentrations matched approximately their relative concentrations in the contact fingers, that is $\sim 300\text{-}1000\ \text{Ag} : 1\ \text{Ti}$. Palladium, if present, could not be detected due to the overlapping silver peaks.

This evidence, combined with the processing history of the solar cell, point to a process-induced defect occurring during the metallization. The front side metallization grid (titanium, palladium, silver) of this solar cell was evaporated and galvanically strengthened, and the emitter is shallow. With any processing error (e.g. hole in mask, mistake during mask liftoff) that deposits silver and palladium metals, both relatively fast diffusers in silicon, directly on the surface of the wafer, the ensuing heat treatment at 350°C for 30 min may be sufficient for these metals to diffuse through the thin emitter layer to the pn junction and cause the shunting behavior. Both silver and palladium have relatively large work functions, which according to simple Schottky theory creates a strong rectifying junction when contacting p-type silicon. The rectifying nature of this shunt as measured by lock-in thermography is consistent with this hypothesis.

3.2 Ribbon Growth on Substrate (RGS)

RGS silicon wafer technology is still in the R&D phase at the moment with a full-speed, continuously operating bench-scale machine under development. Under certain processing conditions, RGS material can exhibit the presence of so-called "current collecting channels", or channels of inverse conductivity type that extend from the emitter into the bulk of the solar cell. These current col-

lecting channels form under specific cooling conditions, when the high oxygen and carbon content of the wafers precipitates at structural defects such as grain boundaries or dislocations, creating a uniform coating and conductive path for minority carriers generated into the bulk to reach the emitter. These current collecting channels provide an obvious increase to the collected current of the solar cell, since they collect minority carriers generated deep within the bulk that otherwise would not have diffused to the emitter (minority carrier diffusion length is typically $\sim 20\text{-}40\ \mu\text{m}$ for fully processed material). The downside is that these channels tend to create a large leakage current, which consequently reduces V_{oc} and FF. With the help of lock-in thermography and μ -XRF analyses, we may be closer to understanding why this occurs.

3.2.1 Confirmation of Current Collecting Channels

Upon analysis of a $20 \times 20\ \text{mm}^2$ RGS cell with medium density of current collecting channels, both XBIC and long-wavelength LBIC (both techniques with incident radiation penetration depth $> 100\ \mu\text{m}$) detected localized regions of greatly enhanced current collection. To confirm that these features were indeed current collecting channels extending into the bulk of the sample, a tomographic-like rotation experiment was performed. At the ALS μ -XRF/XBIC beamline where these experiments were performed, a standard XBIC measurement holds the sample at a 45° angle relative to the incident xray beam. The apparent location of a feature within the bulk will move relative to a surface feature when the sample is rotated by 180° . This behavior is observed when a region of high current collection (a current collecting channel) is measured with XBIC, relative to a contact finger on the surface of the wafer measured by μ -XRF. This confirms that the observed regions of increased current collection are indeed current collection channels originating from deep within the bulk (at least $50\ \mu\text{m}$).

3.2.2 Correlation with Shunting Activity

Regions of enhanced current collection corresponded well with large localized shunts detected by lock-in-thermography. This provides a clear correlation between shunting activity and the presence of increased densities of current collecting channels. Further evidence was provided by two additional wafers analyzed with lock-in-thermography: a wafer with very low concentration of current collecting channels, and a wafer with a uniformly high concentration of current collecting channels. Most noticeably, the wafer with the lowest density of current collecting channels exhibited the smallest lock-in thermography signal, whereas the wafer with high density of current collecting channels exhibited the highest thermography signal, in agreement with previous results by *Hahn et al* [9].

A unique application of lock-in thermography is the ability to map the exponential factor (n-factor) of the dark IV curve over the surface of the solar cell [10]. Such an n-factor mapping was performed on the RGS cell with medium density of current collecting channels, shown in Fig 1. One can see that the n-factors $\sim 3\text{-}4$ at the shunt areas agree with a model suggested by *Breitenstein et al.* [11] to describe shunting current originating from current collecting channels. An additional interesting feature is the large and well-resolved thermography signal originating from the *phase*, indicating the presence of a heat source located below the surface of the wafer.

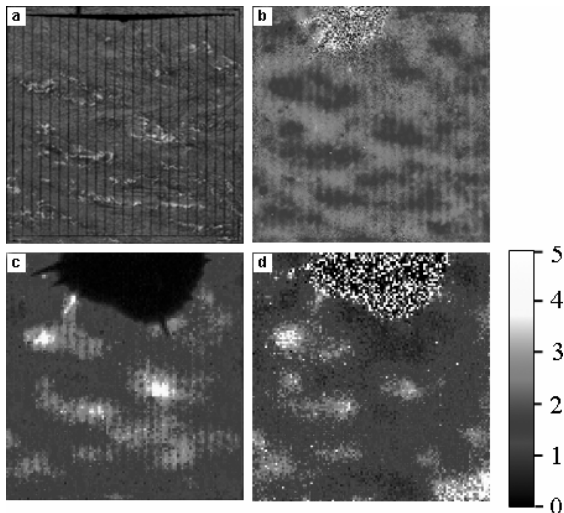


Fig. 1: 20x20 mm² RGS solar cell with medium density of current collecting channels (ccc's). (a) Long- λ LBIC, revealing ccc locations (bright spots = high collected current). (b) Phase image of 0.5 V forward bias, 24 Hz lock-in-thermography. Notice good correlation with LBIC. (c) 36 Hz Lock-in Thermography (from 0-3 mK) at 550 mV forward bias. Shunt locations correlate with ccc's. (d) n-factor mapping over the solar cell (0-5).

3.2.3 Presence of Transition Metals

After locating a current collecting channel with XBIC, a μ -XRF line scan with long accumulation time per point was performed across the channel. Both iron and copper were found in the vicinity of the current collecting channel (Fig. 2). Lower bounds for the peak metal concentrations were obtained with NIST standards by assuming the metals lie near to the wafer surface: Fe $\sim 1.7 \times 10^{14} \text{cm}^{-2}$, and Cu $\sim 1.5 \times 10^{14} \text{cm}^{-2}$. The iron signal was amassed in a single peak approximately the size of the beam, suggesting a single precipitate at the center of the current collecting channel (in this case, the current collecting channel was at a grain boundary). Copper, on the other hand, exhibited a much broader peak, suggesting a colony of microprecipitates in the vicinity of the current collecting channel. These results suggest that metals, known to be present in relatively large concentrations in the melt, have been gettered to the structural defects that form the current collecting channels. As such, one must critically examine what role, if any, the metals play in these shunts.

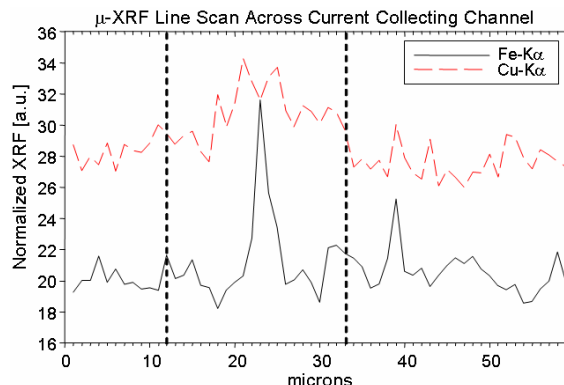


Fig. 2: A μ -XRF line scan across a current collecting channel (bounded between the dashed lines) reveals the presence of iron and copper.

3.2.4 The RGS Shunting Mechanism

The shunting observed in this prototype RGS material is most likely a combination of effects. Firstly, there is the possibility that certain networks of current collecting channels form an electrical contact between the emitter and the back surface, effectively shorting the solar cell. If this were the case, one would expect an ohmic behavior of the shunt, i.e., shunting behavior both in forward and reverse bias when measured by thermography. At 0.52 V forward bias 42.5 mA of current are passed, while in 0.52 V reverse bias only 5.2 mA are passed (edge shunts are negligible). This is indicative that ohmic shunts are not the primary effect.

The second plausible contribution to the shunting current entails space-charge effects in the extended space charge region surrounding the current collecting channels protruding from the emitter into the bulk. In a traditional pn junction, there are not many nucleation sites for metals to precipitate in the space-charge region. For the current collecting channel, the situation is different. Because the current collecting channel coincides with a structural defect, the possibility is high that metals may form single (i.e. Fe) or clusters (i.e. Cu) of recombination-active precipitates in the vicinity of the extended space charge region. How this affects the device properties of the solar cell is still under debate. One possibility is that metals present in high enough concentrations (i.e. clusters of precipitates) in the pn junction area adjacent to the current collecting channel might trap charges near the interface, pin the Fermi level near midgap, and contribute to lowering the potential barrier height. This may provide a complementary physical explanation to model proposed by Breitenstein *et al.* [11].

Another possibility that must be considered involves recombination-generation current. With the emitter in electrical contact to the current collecting channels, recombination centers along a current collecting channel may provide the easiest path for an electron to recombine with a hole in the bulk. In a steady-state system, the barrier height would be reduced. It has been noted, e.g., that an increase in the recombination-generation current can lead to ideality factors greater than 2 [12].

Both explanations above would lead to a rectifying shunt, because the pn junction, although altered, would not be bypassed. The key to reaping the J_{sc} benefit of current collecting channels without losing on V_{oc} and FF would be to mitigate the electrical activity of these centers.

3.2.5 Hydrogen Passivation

A viable means to improve RGS solar cell parameters is hydrogen passivation. The fully processed RGS solar cell was subjected to a 210-minute microwave-induced remote hydrogen plasma passivation at 350°C [13]. The solar cell was measured with lock-in thermography before and after hydrogen passivation to monitor changes in shunting activity. Since a perfect overlap of the two lock-in thermography measurements could not be ensured, each lock-in thermography measurement was divided into units of 10x10 pixels to average out the error due to misalignment (each lock-in thermography measurement contains a total of 288x288 pixels over the 20x20 mm² solar cell). This analysis was repeated for the samples with highest and lowest concentrations of current collecting channels. By comparing the average value within each 10x10 unit before and after hydrogen passivation, we see that, with few exceptions, every unit in each solar cell improved

more or less the same amount, as evidenced by the straight line in Fig. 3. (The only major exceptions were units within edge shunts observed in the lower-right corner of the solar cell, all of which demonstrated a higher-than-average improvement.) The fact that the current-collecting-channel-related shunts did not improve significantly more than the average background demonstrates that the hydrogen passivation, while effective in improving the overall pn junction quality, was not effective in removing these particular shunts. This could mean that the duration of the passivation anneal was not sufficient for hydrogen to diffuse deep into the bulk and passivate the metals gettered to the current collecting channels, given the slow diffusivity of hydrogen in RGS material. This hypothesis could be confirmed in future studies by, e.g., cross-sectional EBIC [14]. Alternative explanations include the possibility that hydrogen is ineffective in passivating these particular compounds formed by the precipitated transition metals at the current collecting channels. Additional investigations are required.

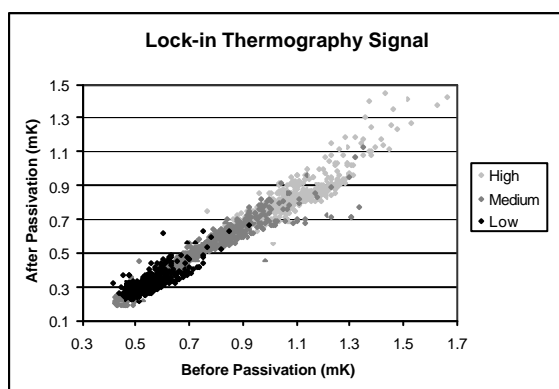


Fig. 3: A comparison of the thermography signal before and after H-passivation from different regions of 3 RGS solar cells containing High, Medium and Low densities of current collecting channels, respectively. All cells exhibit relatively homogeneous improvement after H-passivation.

4. CONCLUSIONS

Transition metals have been identified at shunting locations in two types of solar cell materials. High concentrations of silver and titanium were found at the first shunt, in a cast mc-Si solar cell, most probably a process-induced defect related to the contact metallization. Iron and copper precipitates were found at current collecting channels in RGS material, suggesting that these metals may be promoting shunting behavior by virtue of their location in the extended space-charge region. A hydrogen passivation anneal did not noticeably affect these shunts.

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REFERENCES

- [1] Ted Ciszek, private communication.
- [2] A.A. Istratov, T. Buonassisi, E.R. Weber, R.J. McDonald, A.R. Smith, R. Schindler, J.A. Rand, J. Kalejs, Publication Forthcoming.
- [3] S.A. McHugo, A.C. Thompson, I. Périchaud and S. Martinuzzi, "Direct correlation of transition metal impurities and minority carrier recombination in multicrystalline silicon", *Appl. Phys. Lett.* **72**, 3482 (1998).
- [4] M.A. Green, K. Emery, D.L. King, S. Igari, and W. Warta, "Solar Cell Efficiency Tables (Version 21)", *Prog. in Photovolt.: Res. and Appl.* **11**, 39 (2003).
- [5] O. Breitenstein, J.P. Rakotoniaina, S. Neve and M.H. Al Rifai, "Shunt Types in Multicrystalline Solar Cells", this conference.
- [6] O. Breitenstein, M. Langenkamp, O. Lang, and A. Schirmacher, "Shunts due to Laser Scribing of Solar Cells Evaluated by Highly Sensitive Lock-in Thermography", *Solar Energy Mat. & Solar Cells* **65**, 55 (2001)
- [7] O.F. Vyvenko, T. Buonassisi, A.A. Istratov, H. Hieslmair, A.C. Thompson, R. Schindler and E.R. Weber, "X-ray beam induced current: a synchrotron radiation based technique for the in-situ analysis of recombination properties and chemical nature of metal clusters in silicon." *J. Appl. Phys.* **91**, 3614 (2002).
- [8] S.A. McHugo, A.C. Thompson, C. Flink, E.R. Weber, G. Lamble, B. Gunion, A. MacDowell, R. Celestre, H.A. Padmore, Z. Hussain, "Synchrotron-based impurity mapping", *J. Cryst. Growth* **210**, 395 (2000).
- [9] G. Hahn, D. Sontag, C. Häbler, "Current collecting channels in RGS silicon solar cells - are they useful?" *Solar Energy Mat. & Solar Cells*, **72**, 453 (2002).
- [10] O. Breitenstein, M. Langenkamp, J.P. Rakotoniaina, J. Zettner, "The imaging of shunts in solar cells by infrared lock-in thermography", (WIP, Munich, 2001).
- [11] O. Breitenstein, M. Langenkamp, and J.P. Rakotoniaina, "EBIC investigation of a 3-dimensional network of inversion channels in solar cells on silicon ribbons." *Diff. and Defect Data B (Solid State Phenomena)*, **78-79**, 29 (2001).
- [12] J. Lindmayer, "Theoretical and practical fill factors in solar cells." *COMSAT Technical Rev.*, **2**, 105 (1972)
- [13] M. Spiegel, C. Zechner., B. Bitnar, G. Hahn, W. Jooss, P. Fath, G. Willeke, E. Bucher, H.-U. Höfs and C. Häbler, "Ribbon growth on substrate (RGS) silicon solar cells with microwave-induced remote hydrogen plasma passivation and efficiencies exceeding 11%", *Solar Energy Mat. & Solar Cells*, **55**, 331 (1998).
- [14] O. Krüger, W. Seifert., M. Kittler and O.F. Vyvenko, "Extension of Hydrogen Passivation of Intragrain Defects and Grain Boundaries in Cast Multicrystalline Silicon." *Phys. stat. sol. (b)*, **222**, 367 (2000).