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Direct Correlation of Transition Metal Impurities and Minority Carrier Recombination in Multicrystalline Silicon

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DIRECT CORRELATION OF TRANSITION METAL IMPURITIES AND MINORITY CARRIER RECOMBINATION IN MULTICRYSTALLINE SILICON

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Impurity and minority carrier lifetime distributions were studied in as-grown multicrystalline silicon used for terrestrial-based solar cells. Synchrotron-based x-ray fluorescence and the Light Beam Induced Current technique were used to measure impurity and lifetime distributions, respectively. The purpose of this work was to determine the spatial relation between transition metal impurities and minority carrier recombination in multicrystalline silicon solar cells. Our results reveal a direct correlation between agglomerations of chromium, iron and nickel impurities with regions of high minority carrier recombination. Additionally, based on the results we estimate the maximum possible size of the agglomerates present in the high recombination regions. These results provide the first direct evidence that transition metal agglomerates play a significant role in solar cell performance.

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Multicrystalline silicon can be used to fabricate solar cells with moderate solar conversion efficiency and low fabrication costs. These cells are presently manufactured for terrestrial-based applications; however, an improvement in the efficiency of these cells would greatly increase their commercial viability. In theory, multicrystalline silicon or mc-silicon solar cells could perform as well as expensive, single crystalline silicon solar cells which have cell efficiencies typically in the range of 17-20% [1] and even up to 24% [2]. Although small solar cells ($1 \times 1 \text{ cm}^2$) have been made with mc-silicon with efficiencies of up to 18.6% [3], standard mc-silicon solar cells ($10 \times 10 \text{ cm}^2$) possess efficiencies of 13-15%. The primary cause for lowered efficiencies is localized regions of high minority carrier recombination. These regions possess high concentrations of dislocations [4-6]. It is known that minority carrier recombination at dislocations themselves is relatively weak but greatly increases by decoration or precipitation of transition metal impurities [7-10]. This suggests that dislocations in high recombination regions of mc-silicon are decorated with transition metals, however, past research has not presented direct evidence showing the source for carrier recombination at these dislocations. Jastrzebski, et al., [11], have presented results which indirectly suggest that metal impurities could be precipitated in regions of high carrier recombination of mc-silicon. Other work has revealed that metal impurity agglomerations are present at dislocations in mc-silicon [12], however, no correlation was established to carrier recombination. This research seeks to determine whether a correlation between metal impurity distributions and regions of high minority carrier recombination exists in mc-silicon solar cells.

Boron doped mc-silicon with an oxygen concentration of $2\text{-}3\times 10^{17}$ atoms/cm³ and a carbon concentration of $5\text{-}6\times 10^{17}$ atoms/cm³ was used. The wafers were formed by an electromagnetic casting method [13], followed by sawing and chemical etching to remove saw damage. Minority carrier recombination was mapped across the as-grown material with the light beam induced current (LBIC) method. The wavelength of the light used for carrier excitation during LBIC measurements was 880nm. Al layers of 95Å and 2500Å were evaporated onto the frontside and backside of the sample, respectively, in order to provide electrical contacts for LBIC measurements. Prior to evaporations, the material was cleaned with a RCA cleaning process and silicon etching. The backside contact was formed with a 450°C - 30 minute anneal to create an ohmic contact. The evaporation for the frontside contact, which created a MIS structure with a thin, native oxide layer present, was performed after annealing the backside-contact. The frontside of the samples were analyzed using synchrotron-based XRF mapping in order to determine metal impurity content and distribution. Prior to XRF measurements, the Al layers were removed with a VLSI grade HCl and HNO₃ chemical etch and the surface of the material was cleaned with VLSI grade piranha (H₂SO₄:H₂O₂) etch and HF dips. The XRF equipment is located at the Center for X-ray Optics microprobe beamline in the Advanced Light Source Center. It uses 12.5keV monochromatic radiation to excite elements in the sample with a spatial resolution of 1µm² and a Si-Li detector to measure fluorescence x-rays from the sample, all in atmospheric conditions. The XRF microprobe sensitivity is impurity and matrix specific but, for example, the system can detect a single Ni precipitate/agglomerate in silicon greater than 10-20nm in diameter. The sampling depth for 3d transition metal impurities in silicon is approximately 50µm. It should be

noted that the sensitivity of the microprobe drops considerably for elements with an atomic number < 16 . Impurity concentrations are quantified with the use of standard samples of known impurity levels. Etch features on the sample surface, caused by slight preferential etching of grain boundaries during the silicon etch prior to Al contact formation, were used as reference points to locate regions of interest.

LBIC mapping of minority carrier recombination across the mc-silicon sample revealed localized regions of high carrier recombination. A typical LBIC map in a portion of the material is shown in Figure 1 where dark regions indicate areas of high carrier recombination. Of particular interest is the band of high carrier recombination located approximately in the center of the scan area.

X-ray Fluorescence (XRF) spectra were taken at $1\mu\text{m}^2$ points in the region of Figure 1 as denoted by the black box. Typical spectra are shown in Figure 2. No x-ray fluorescent radiation associated with impurities was measured in regions of the mc-silicon with low minority carrier recombination. However, x-ray fluorescent radiation associated with the 3d transition metals was found in regions of the material with high carrier recombination. As seen in Figure 2, the Fe $K\alpha$ and Fe $K\beta$ fluorescence radiation at 6.4 keV and 7.06 keV, respectively, are clearly discernable above background noise. The ratio of these spectral peak heights is approximately 4:1 for $K\alpha$ to $K\beta$. This ratio is in accordance with the expected intensity ratio of $K\alpha$ to $K\beta$ radiation defined by the electron transition probability between the Fe atom L and K shells which generates $K\alpha$ fluorescence radiation and the Fe atom M and K shells which generates $K\beta$ fluorescence radiation. The presence of both Fe $K\alpha$ and Fe $K\beta$ radiation, with the expected intensity ratios, acts as fingerprint for the presence of Fe and provides direct evidence that Fe is

present in this region of the material. Fluorescent radiation at 5.4 keV and 7.47 keV is also clearly distinguished above background noise while small spectral peaks at 5.95 keV and 8.26 keV are only slightly above background. The intense peaks at 5.4 and 7.47 keV concur with the energies of Cr K α and Ni K α fluorescent radiation, respectively, while the presence of weaker peaks at 5.95 and 8.26 keV correspond with Cr K β and Ni K β fluorescent radiation, respectively. Considering the expected intensity ratio of K α to K β for both Cr and Ni is 4:1, and the peak intensity of the presumed Cr K α and Ni K α spectral peaks at 5.4 keV and 7.47 keV is only 10 counts, the expected peak intensity of Cr K β and Ni K β coincides with the approximate intensity of the weaker peaks. This provides strong evidence that Cr and Ni impurities are present in this region of the material.

Concentrations of impurities at each 1 μm^2 spot were calculated by analysis of the collected spectra in comparison to standard samples with known concentrations of impurities. Impurity maps were produced in the region denoted by the black box in Figure 1. Figures 3a,b and c are impurity maps of Cr, Fe and Ni in this region. Clearly there is a correlation between metal impurity distributions and minority carrier recombination. This is the first direct proof that metal impurity agglomerates play a significant role in mc-silicon solar cell performance.

The XRF microprobe sensitivity limit for dissolved 3d transition metals is approximately 10^{17} atoms/cm³. Considering the maximum dissolved concentration of Fe and Cr is $<10^{17}$ atoms/cm³ [14], the distributions of Fe and Cr in Figure 3 are impurity precipitates/agglomerates. The Ni is also likely precipitated since the Ni diffusion coefficient is extremely high, which allows for rapid precipitation. At each measured

1 μm^2 spot a single precipitate or a number of precipitates may reside. If only one precipitate is assumed present, the precipitate diameter can be calculated from the measured impurity concentrations. Further assuming the precipitate is located at or near the surface, the precipitate diameter, d , is given by:

$$d_{@surface} = 2 * \left[\left(\frac{3}{4\pi} \right) * \frac{dose * area}{density} \right]^{1/3} \quad (1)$$

where dose is the measured concentration (atoms/cm²), area is the sampled area, i.e. the x-ray spot size, and density is the atomic density of the impurity in the precipitate. For instance, the measured concentration of 5x10¹⁶ atoms/cm² for Fe, shown in Figure 3b, would suggest one precipitate with a diameter of 0.288 μm is present in that area. This is calculated with 1 μm^2 x-ray spot and a Fe atomic density of 4x10²² atoms/cm³ in FeSi₂. It should be noted that equation (1) assumes no absorption of the outgoing fluorescent x-rays by the silicon matrix, i.e., the impurities are assumed to be at the surface. This assumption only allows for calculation of a lower limit to the concentration of impurities in each 1 μm^2 region of the material. A more accurate calculation of the diameter of the impurity precipitate can be made using equation (2) if the depth of the Fe precipitates/agglomerates is known.

$$d_{@depth,Q} = d_{@surface} * [\exp(-\mu * Q)]^{1/3} \quad (2)$$

Here Q is the depth of the precipitate and μ is the linear absorption coefficient for the matrix material, e.g. silicon, for the x-ray fluorescence radiation emitted by the impurity, e.g. $\text{FeK}\alpha$.

A critical assumption of the calculation of impurity precipitate size in equation (1) is the assumption that only one precipitate exists in the $1\mu\text{m}^2$ measured area. Contrary to this presumption is past work, [12], which has shown Cu and Ni precipitates in mc-silicon exist in nm-scale precipitates/agglomerates, which are dispersed over μm -scale regions. Furthermore, work of Shen et al., [15], has indicated that Fe forms a fine dispersion along dislocation lines as opposed to solitary clusters or precipitates. These past works would suggest a fine dispersion of impurity precipitates exist in the XRF maps of Figure 3 as opposed to a single large precipitate.

In conclusion, Cr, Fe and Ni metal impurities were found in electromagnetically cast multicrystalline silicon used for solar cells. The distribution of impurities correlated directly with regions of high minority carrier recombination. The impurities are in the form of precipitates/agglomerates with a maximum diameter estimated at $0.3\mu\text{m}$, although a fine dispersion of smaller precipitates/agglomerates is expected. The work presented here is the first direct proof that metal impurity agglomerates significantly affect the performance of multicrystalline silicon solar cells.

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REFERENCES

1. J. M. Gee, R. R. King and K. W. Mitchell, *Proceeding of the 25th IEEE Photovoltaic Specialists Conference*, Washington D.C., pg. 409, (1996)
2. J. Zhao, A. Wang, P. Altermatt and M. A. Green, *Appl. Phys. Lett.* **66**, pg. 3636, (1995)
3. A. Rohatgi and S. Narasimha, *Solar Energy Materials and Solar Cells*, **48**, pg. 187, (1997)
4. S. Pizzini, A. Sandrinelli, M. Beghi, D. Narducci, F. Allegretti, S. Torchio, G. Fabbri, G. P. Ottaviani, F. Demartin and A. Fusi, *J. Electrochem. Soc.* **135**, pg. 155, (1988)
5. B. L. Sopori, L. Jastrzebski, T. Tan and S. Narayanan, *Proceedings of the 12th European Photovoltaic Solar Energy Conference*, Netherlands, pg. 1003, (1994)
6. S. A. McHugo, H. Hieslmair and E. R. Weber, *Appl. Phys. A.* **64**, pg. 127, (1997)
7. C. Cabanel and J. Y. Laval, *J. Appl. Phys.* **67**, pg. 1425, (1990)
8. T. S. Fell, P. R. Wilshaw and M. D. d. Coteau, *Phys. Stat. Sol. (a)*, **138**, pg. 695, (1993)
9. V. Higgs and M. Kittler, *Appl. Phys. Lett.* **63**, pg. 2085, (1993)
10. M. Kittler, W. Seifert and V. Higgs, *Phys. Stat. Sol. (a)*, **137**, pg. 327, (1993)
11. L. Jastrzebski, W. Henley, D. Schielein and J. Lagowski, *J. Elec. Chem. Soc.* **142**, pg. 3869, (1994)
12. S. A. McHugo, *Appl. Phys. Lett.* **71**, pg. 1984, (1997)
13. I. Périchaud, G. Dour, B. Pillin, F. Durand, D. Sarti and S. Martinuzzi, *Sol. State Phen.* **51-52**, pg. 473, (1996)
14. E.R. Weber, *Appl. Phys. A*, **30**, 1, (1983)
15. B. Shen, T. Sekiguchi, R. Zhang, Y. Shi, H. Shi, K. Yang, Y. Zheng and K. Sumino, *Jpn. J. Appl. Phys.* **35**, pg. 3301, (1996)

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Figure 1: Light Beam Induced Current map of carrier recombination across a portion of multicrystalline silicon. An impinging radiation of 880nm was used to generate minority carriers. Dark regions indicate high carrier recombination. The black box denotes the area analyzed with x-ray fluorescence.

Figure 2: X-ray fluorescence spectra taken in high and low minority carrier recombination regions of multicrystalline silicon. Data was taken at points in the region denoted by the black box of Figure 1. Note the fluorescence signal of Cr, Fe and Ni in the high recombination region.

Figure 3a,b&c: a) Cr, b) Fe and c) Ni distributions in multicrystalline silicon. The mapped area directly corresponds to the area in the black box of Figure 1. Note the correlation between metal impurity distributions and carrier recombination.

Figures 1 of 3, S.A. McHugo, "Direct correlation of transition metal impurities and minority carrier recombination in multicrystalline silicon"

Figure 2 of 3, S.A. McHugo, "Direct correlation of transition metal impurities and minority carrier recombination in multicrystalline silicon"

Figures 3a,b&c of 3, S.A. McHugo, "Direct correlation of transition metal impurities and minority carrier recombination in multicrystalline silicon"

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