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ON THE PERFORMANCE LIMITING BEHAVIOR OF DEFECT CLUSTERS IN COMMERCIAL SILICON SOLAR CELLS

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ABSTRACT: We report the observation of defect clusters in high-quality, commercial silicon solar cell substrates. The nature of the defect clusters, their mechanism of formation, and precipitation of metallic impurities at the defect clusters are discussed. This defect configuration influences the device performance in a unique way – by primarily degrading the voltage-related parameters. Network modeling is used to show that, in an N/P junction device, these regions act as shunts that dissipate power generated within the cell.

Keywords: Multicrystalline Silicon - 1: Defect Clusters - 2: Impurity Precipitation - 3

1. INTRODUCTION

The low-cost substrates used for commercial Si solar cell fabrication have high concentrations of impurities and defects. A variety of measures such as higher quality feedstock and better crucible quality have resulted in reduced metallic impurity content to the levels approaching 10^{14} cm^{-3} . Likewise, improvements in the thermal conditions during the crystal growth processes have yielded substrates with very low average defect density – typically $<10^5/\text{cm}^2$. However, this reduction in the defect density is accompanied by an agglomeration of defects to form local defect clusters. These defect clusters can have a strong influence on the device characteristics by primarily lowering the voltage-related cell parameters without significantly lowering the photocurrent [1]. These characteristics of defect clusters appear to control performance of the high-efficiency, large-area solar cells. This paper briefly describes the nature of the defect clusters in the photovoltaic (PV) silicon substrates and explains the mechanism(s) by which these defects control the device performance.

2. NATURE OF DEFECT CLUSTERS

Defect clusters consist of agglomerations of extended defects like dislocations, stacking faults, and (in some cases) grain boundaries, in otherwise very low defect density wafer. Figure 1 is a map showing the distribution of defects in a 5-cm x 5-cm section of a commercial, multicrystalline silicon (mc-Si) wafer. The darker regions indicate higher defect densities. This figure shows that a majority of the wafer has a low or zero dislocation density, while other regions have high concentrations of defects that are clustered together. The average value of the dislocation density in the entire wafer is about $10^5/\text{cm}^2$. The structure of a defect cluster can be seen in Figure 2. The defects were delineated by etching the sample in Sopori etch [2]. Detailed analyses show that a defect cluster involves a series of long, intertwined dislocation loops. Because these loops and networks are high-energy defect configurations, they are thermally unstable and can change during device processing. Furthermore, the defect clusters can be efficient nucleation sites that can

become decorated with impurity precipitates during crystal growth. This propensity for impurity decoration of a defect cluster has a strong bearing on how it affects the device performance.

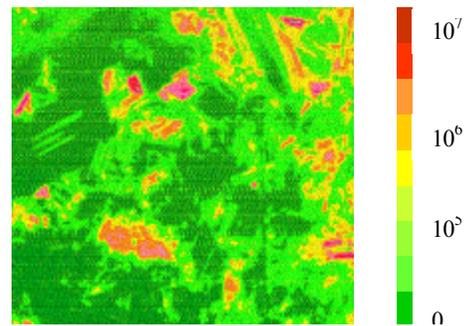


Figure 1. A defect map of a 5-cm x 5-cm section of a commercial mc-Si wafer. The scale is in defects/cm²

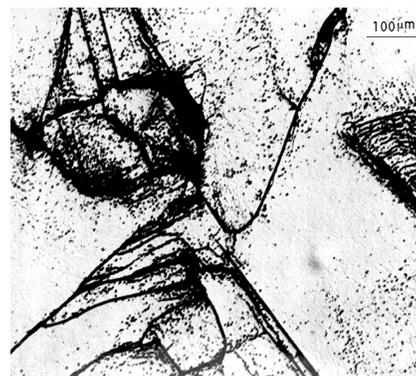


Figure 2. Photograph showing chemically delineated structure of a defect cluster.

3. FORMATION OF DEFECT CLUSTERS

Accumulation of point defects to form either vacancy or interstitial defects is well known in silicon technology. The local temperature gradients and the point-defect supersaturation drive such a process. Defect clusters are formed during the cool-down

portion of an ingot. The following explanation appears to be the most likely reason for the formation of defect clusters. During the crystal growth, the defects are formed in the regions of the ingot where the stress levels exceed the plastic yield stress. Because the yield stress depends on the crystal orientation, a given stress can exceed the yield stress of some grains. This stress can lead to the generation of extended defects, like dislocations and stacking faults, in a selective manner. Thus, during the growth of a multicrystalline ingot (or a ribbon) a few “easy” grains can effectively relieve the stress by becoming heavily decorated with defects. If the magnitude of the stress is only slightly larger than the minimum yield stress, the generation of defects will be limited to the grains of such preferred orientations. However, a large thermal stress would result in the generation of defects in all grains. Consequently, the clustering would occur only when the material quality is quite high. Thus, one can expect a high-quality, multicrystalline silicon wafer to have localized regions of heavy dislocations.

4. PRECIPITATION OF METALS AT DEFECT CLUSTERS

Because a defect cluster is an agglomeration of extended defects, its behavior will be similar in many ways to that of a grain boundary. Thus, one may expect defect clusters to act as internal gettering sites and trap impurities. A decoration of these defects by the metallic impurities can further increase their carrier recombination and lead to profound effects on the cell performance. In addition, precipitates can begin to dissolve at temperatures required for solar cell processing, creating internal sources for impurities. This behavior is further discussed in the conclusion section of this paper.

An indirect evidence of impurity precipitation came from earlier work on mapping of metallic impurities (like Fe and Cr), defects, and minority carrier diffusion length (MCDL) in commercial PV-Si wafers [3]. It was observed that the regions having low values of the MCDL corresponded to lower concentrations of the metals, as well as to higher concentrations of defects. Because Fe and Cr are fast diffusers, they are expected to be uniformly distributed in the entire sample. These apparent inconsistencies can be reconciled by assuming impurity precipitation occurs in the defected regions, which causes the dissolved impurity concentration to go down in that region. Thus, previous analysis concluded, on an indirect basis, that heavily defected regions would have precipitated impurities. Extensions of similar analyses that show high recombination associated with the defect clusters can be observed directly by methods such as the photoluminescence and the minority carrier diffusion length (MCDL) mapping. Figure 3 illustrates these results. Figure 3a is a map of the room temperature photoluminescence (PL) of a 5-cm x 5-cm sample showing strong local variations in the PL signal (in arbitrary units). Figure 3a was done with a beam size of about 20 μm ; the dark regions correspond to higher PL signal. The defect map of the region, corresponding to the PL map in Figure 3a, is shown in

Figure 3b. This figure was made by PVSCAN5000 with a beam size of about 300 μm ; here the darker regions have lower defect density. An excellent correlation is observed between the two images. Figure 3c shows a MCDL map of the same sample, measured by the SPV technique, using a beam size of 3 mm. A correlation between the PL emission and the MCDL is seen. In addition, one can observe the inverse correlation of PL and MCDL with the defect clusters.

A direct evidence of precipitation comes from the

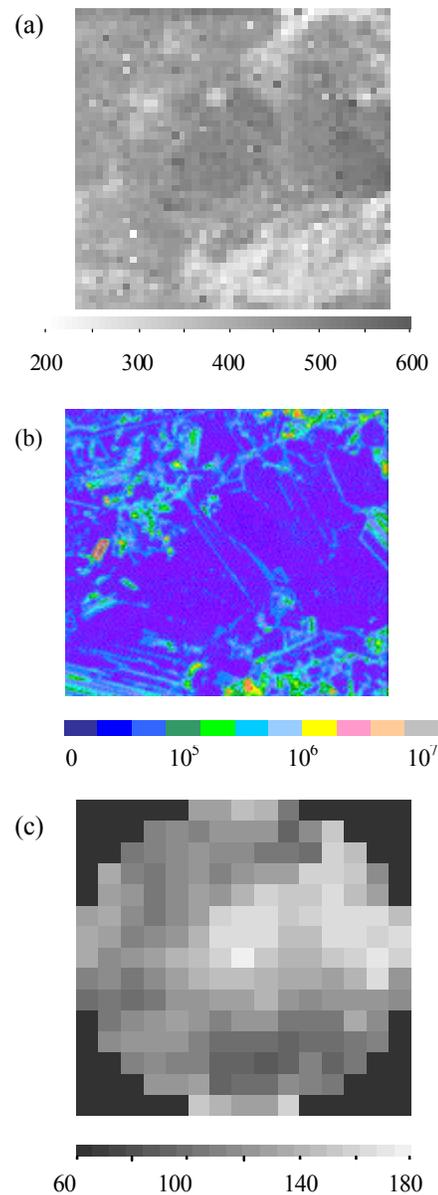


Figure 3: (a) PL in arbitrary units, (b) defect density in defects/cm², and (c) MCDL in μm maps of a 2-in x 2-in silicon sample showing correlation between them {the circular shape of the map in (c) is because the instrument is designed for the measurement of circular wafers}.

TEM analyses made on different regions of mc-Si samples. Figure 4 is a micrograph of the precipitates observed in a region of a defect cluster. It was also determined that such precipitates occur only within the defect clusters.

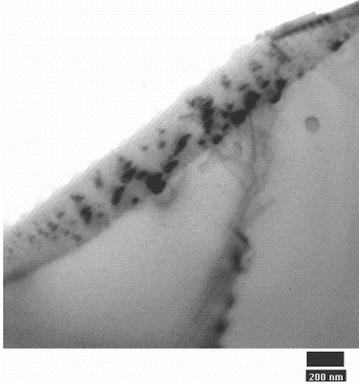


Figure 4. A TEM photo of a defect cluster showing direct evidence of impurity precipitation

5. INFLUENCE OF THE DEFECT CLUSTERS ON THE DEVICE PERFORMANCE

Defect clusters are localized regions of high carrier recombination in the as-grown substrate. This behavior is seen from Figure 3 as lower local values of the MCDL associated with the defected regions in an as-grown substrate. However, in spite of this reduction, the MCDL of the defected regions is above $50 \mu\text{m}$ – a value that can lead to a significant generation of photocurrent. It is because of this reason that the photogenerated current of a cell is not greatly impacted by defect clusters.

Defect clusters can affect the device performance in a number of other ways. A quantitative investigation of the effect of defect clusters on the performance of a large-area cell can be performed using a phenomenological approach that involves determination of:

1. The characteristics of the cell in the regions with no defect clusters
2. The characteristics of the defected region in the cell, and
3. A method of combining 1 and 2 to determine the effect of distributed defects on the device.

Item 1 above is well known – it can be expressed in terms of the J_{ph} and two exponential components of the dark current in a standard form as:

$$J_{\text{dark}}(V) = J_{01} \cdot \exp\left\{\frac{-eV}{kT} - 1\right\} + J_{02} \cdot \left\{\exp\left(\frac{-eV}{2kT} - 1\right)\right\}. \quad (1)$$

The saturation currents J_{01} and J_{02} can be written in standard forms of a P/N junction.

$$J = J_{\text{ph}} - J_{\text{dark}}(V). \quad (2)$$

where J_{ph} and $J_{\text{dark}}(V)$ are the photogenerated and the dark current densities, respectively.

A similar formalism can be applied to the cell corresponding to the defected region [4]. We have shown that the defected region can also be represented by equations similar to eq. (1) and (2) above. However, in this case, the values of various parameters will be different.

We have developed a computer model for an N/P junction device that calculates these parameters and uses a distributed network model to combine various regions of the device.

6. NETWORK MODEL FOR TOTAL CELL CHARACTERISTICS

The device is divided into an array of diodes, with each diode is small enough to assume a uniform distribution of defects. Each node in the matrix depicts a local cell, connected to other cells by a resistor representing the series resistance. The series resistance arises from a number of sources that include the sheet resistivity of the junction in an N/P device. Each local region, having a known defect density, is described by dark current given by:

$$I_{\text{dark}} = I_{01} \left\{ \exp\left(\frac{eV}{kT} - 1\right) \right\} + I_{02} \left\{ \exp\left(\frac{eV}{2kT} - 1\right) \right\} + I_{01} \left\{ \exp(eVn) - 1 \right\}.$$

(The last term in the above equation is added to represent tunneling current that occur in heavily defected regions due to hopping mechanism.) Hence, a local cell element (n,m) in the matrix is represented by a current source comprised of I_{01nm} and I_{02nm} , and a corresponding light-induced current density $J_{\text{ph},nm}$. One can represent

$$J_{01nm} = I_{01} \times F_{nm} \times \exp\left(\frac{eV}{kT} - 1\right), \text{ and}$$

$$J_{02nm} = I_{02} \times F'_{nm} \times \exp\left(\frac{eV}{2kT} - 1\right),$$

where I_{01} and I_{02} represent dark saturation currents in the “defect-free” device element. F_{nm} and F'_{nm} are the factors representing the ratio of dark current normalized by the “defect-free” current, for each component. A finite-element computer code, written in Microsoft Excel, is used to analyze the network.

Our network modeling results show that:

1. Defect clusters in a large-area cell act as shunts that preferentially lower V_{oc} and FF without significantly lowering J_{sc} .
2. Such shunts act as “internal sinks” by dissipating the power within the cell.
3. Cell performance is sensitive to the spatial distribution of the defects.
4. Clustering of defects can cause significantly more degradation in the device performance compared to a situation where the total number of defects are uniformly distributed over the entire device.

We consider an example of a cell in which 20% of the device area is covered by defect clusters, and 80% of the area is defect-free. The parameters for the defect-free region are:

$J_{ph} = 0.035 \text{ A/cm}^2$, $J_{01} = 3.6 \times 10^{-9} \text{ A/cm}^2$, $J_{02} = 4.5 \times 10^{-13} \text{ A/cm}^2$.

From the experimental data, the parameters for the “defected” cell are:

$J_{ph} = 0.0245 \text{ A/cm}^2$, $J_{01} = 3.6 \times 10^{-8} \text{ A/cm}^2$, $J_{02} = 4.5 \times 10^{-11} \text{ A/cm}^2$.

Figure 5 shows the calculated I-V characteristics of these two cells. Their cell parameters are: $V_{oc} = 650 \text{ mV}$, $J_{sc} = 34.45 \text{ mA/cm}^2$, $FF = 81.01$, and the efficiency = 18.4 for defect-free; and $V_{oc} = 62 \text{ mV}$, $J_{sc} = 32.7 \text{ mA/cm}^2$, $FF = 75.76$ and $Eff = 16.7$ for defected cells, respectively. It is seen that all the parameters of the “defected” cell are lower than for the “defect-free” cell. However, the major reduction is in the V_{oc} and the FF. It should be pointed out that in an “undefected” cell, a reduction of 30 mV would be accompanied by a large reduction in J_{sc} in accordance with the cell equation; shunting produces a disproportionate reduction in the voltage.

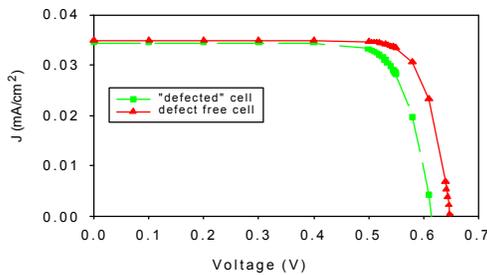


Figure 5. Calculated I-V characteristics showing a significant decrease in V_{oc} by introducing defect clusters in a solar cell.

7. EFFECT ON SOLAR CELL PROCESSING

Because defect clusters are decorated with impurities, they are likely to make device performance very sensitive to the process conditions. This effect can happen via two mechanisms: (i) the inability to getter precipitated impurities, and (ii) processing mc-Si wafers at high temperature ($>900^\circ\text{C}$) can cause partial dissolution of the precipitated impurities leading to increased impurity concentrations in the device.

8. CONCLUSION

We have shown that the clustering of defects can occur in high-quality, multicrystalline Si solar cell substrates. A mechanism for the formation of such defects is proposed. Defect clusters can contain precipitated impurities; as a result, impurity gettering cannot work well in such regions [5]. If device fabrication is done at high temperatures, typically exceeding 900°C , some of the precipitates can start dissolving which, in turn, can increase the concentration

of soluble impurities in the bulk of the device. This behavior can make cell performance very sensitive to the processing conditions. Defect clusters act as shunts, degrading primarily the voltage-related parameters of the device. By introducing device-processing conditions that can rapidly dissolve the precipitates and allow them to be gettered, one can ameliorate the effect of defect clusters by processes such as phosphorus diffusion and Al alloying. Such a high-temperature process may also unpin the defects to acquire a lower energy configuration and a lower density.

Detailed analyses have shown that the net reduction in the photogenerated current is much smaller than the fractional area of the defect clusters. This is because the photocurrent can be quite high even for short MCDL values. Consequently, the dominant effect of the defect clusters is not via the reduction in the photocurrent, but by affecting the voltage-related parameters.

In addition, as described in this paper, because defect cluster propagates through the entire thickness of the substrate, it is a “filamentary” junction shunt. The shunting effect is further enhanced by the impurity decoration during the crystal growth.

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