Light-induced degradation in multicrystalline silicon solar cells made of metallurgical grade silicon

Xianpei REN[1, a], Chao CHEN[1, b], Haoran CHENG[1], Falin HE[2]

[1]School of Energy Research Xiamen University, 361005 Xiamen, P R China,
[2]College of Physics and Mechanics and Electrics Xiamen University, 361005 Xiamen, P R China
[a]e-mail： renxianpei@163.com; [b]e-mail：cchen@xmu.edu.cn，Corresponding author

***Abstract*—This study focuses on the evolution under illumination of the efficiency of multicrystalline silicon solar cells made of metallurgical grade silicon. First, we calculated the activation energy of BO_{i2} defect generation and annihilation from efficiency measurements and compared with previous values deteremined by Minority carrier lifetime and open-circuit voltage measurements, the results are much consistent. Then we shown via external quantum efficiency measurements that this material is sensitive to light-induced degradation effects due to the formation of BO_{i2} defects and the dissociation of iron-boron pairs, and the former is the major fator. Finally, we discussed how to reduce the light-induced degradation.**

Keywords- light-induced degradation；boron-oxygen defect；iron-boron pairs；, external quantum efficiency

Ⅰ. INTRODUCTION

Since light-induced degradation(LID) in B-doped wafers was first observed by Fischer and Pschunder in 1973[1], much attention has been paid to the research of LID of crystalline silicon material and solar cells. In the past, the investigation of LID mainly focused on high-purity boron-doped silicon (EG-Si) and solar cells by the Siemens purification.

In recent years, solar-grade silicon purified by metallurgical route (SoGM-Si) appears as a cost-effective way to sustain the tremendous growth of the photovoltaic industry. Such material typically contains elevated levels of transition metal impurities (such as Cr, Fe, Ti, Cu), and large amount of both boron and phosphous, means that the material is compensated. So more and more groups start to investigate LID in compensated silicon and metal impurities contaminated silicon and solar cells. Most of these studies, boron and phosphorus were intentionally added to the EG-Si melt in order to study the impact of dopant compensation on the LID[2,3]; As for the investigation of other degradation effects except from the well known boron-oxygen (BO_{2i}) defects correlated degradation, they used transition metal impurities contaminated EG-Si material intentionally[4,5]. These methods have the advantage of controlling the doping concentration and metal impurities quantitatively, but these materials are not the real SoGM-Si.

On the other hand, For the activation energy of generation and annihilation of BO_{2i} defect, most of the values are determined on silicon wafers lifetime measurements[6,7], some are from open-circuit voltage(V_{oc}) measurements[8,9]. Rarely reported from the cell efficiency measurements.

In this paper, we calculate the activation energy from efficiency of SoGM-Si cell aimed at comparing the values with previous values deterimined by Minority carrier lifetimes and voc measurements. In addition, we test the external quantum efficiency (EQE) of the SoGM-Si cell at the different degradation states to compare iron-boron pairs(FeB) and BO_{2i} defect impact on the EQE.

Ⅱ. EXPERIMENTAL DETAILS

An $n^+/p/p^+$ SoGM-Si solar cell with a size of 156×156 mm^2 was used in this investigation, we cut the cell into nine pieces with size of 52×52 mm^2 by a laser slicing machine. For doping concentration measurements, the metal contacts and the silicon nitride coating were removed from a processed wafer, the wafer was etched in an acid solution to remove a total of at least 20 um to remove the emitter, the [B] and [P] concentration determined by second ion mass spectroscopy (SIMS) were $6.4\times10^{16}cm^{-3}$ and $2.1\times10^{16}cm^{-3}$, so the net doping concentration $p0\approx4.3\times10^{16}cm^{-3}$.

Efficiency and EQE measurements are performed at 25 °C using Abet Sun 2000 Solar Simulator and Spectral Response Measurement System Model QEX7 respectively. Illumination at room temperature was performed under a halogen lamp, the light intensity of 70 mw/cm^2 was adjusted using a calibrated solar cell.

III. RESULTS AND DISCUSSION

A. Defect generation

It is well knowned that two main causes of LID have been identified in silicon materials and cells, both of them are related to the most common acceptor element, boron, in silicon: (i) the dissociation of iron-boron pairs(FeB) and (ii) the formation of recombination-active BO_{2i} defects. While the first mechanism is particularly relevant in metal-contaminated SoGM-Si materials, the latter process is important in EG-Si materials rich in oxygen[10].

In order to start from a defined state, the SoGM-Si solar cell is annealed in the dark for 20 min at 200 °C before we begin to monitor the efficiency, thus most of the BO_{2i} defects and FeB pairs are expected to be completely dissociated. So the degradation of efficiency only due to the generation of BO_{2i} defects, not the dissociation of the iron-boron pairs. Figure 1 shows the evolution of the efficiency under illumination for SoGM-Si solar cell at room temperature. It is clearly seen that the decay curve was very steep in the the first few seconds, this is due to the formation of the fast-forming center of BO_{2i} defect. Furthermore, the stable efficiency after illumination is shown to be limited by the slowly forming center alone. So the curve becomes flat with the increasing illumination time and a stable level is reached after ～30 h.

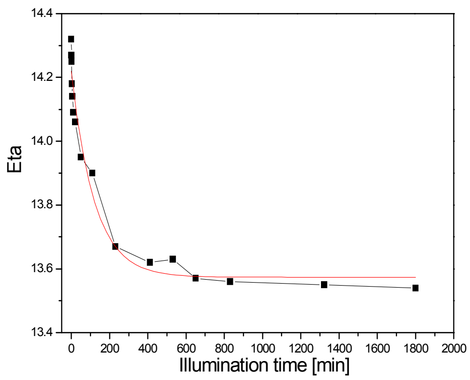

Figure 1. Evolution of the efficiency under illumination for the SoGM multicrystalline silicon solar cell and exponential curve fitted to data (line)

From Fig. 1, we can conclutate relative degradation of the efficicency is about 5.5%, which is greater than the value of EG multicrystalline silicon solar cell (2～4%)[11]. This significant light-induced efficiency degradation due to the high net doping concentration[2].

In order to determine the activation energy E_{gen} of defect generation process, and to compare it with available results on EG-Si from carrier lifetime and the V_{oc} measurements. The efficiency−t measurements on solar cells is performed at various sample temperatures. From the measured data the defect generation rate R_{gen} as well as the activation energy of the defect formation process E_{gen} are determined. R_{gen} can be represented by the expression

$$R_{gen}(T) = k_0 \exp(-\frac{E_{gen}}{k_B T}) \qquad (1)$$

where the pre-exponential factor k_0 is a characteristic of the physical mechanism of the defect formation[8]. The initial very fast decay of the efficiency, observed during the first few seconds of light soaking, was not analyzed in this study. The variation of R_{gen} with T is plotted in Fig.2. R_{gen} is found to follow an Arrhenius law with an activation energy of 0.44ev. The value is in good agreement with the activation energy of 0.4 ev from the carrier lifetime measurements [6]and 0.47 ev from the V_{oc} measurements[8]. We find that the activation energy E_{gen} is independent of the boron concentration, but R_{gen} is found to increase with increasing net boron concentration.

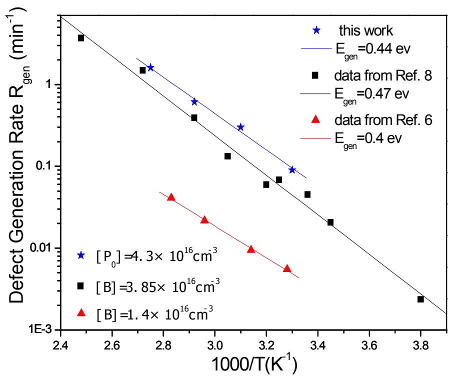

Figure 2. Arrhenius plot of the defect generation rate R_{gen}

B. Defect annihilation

Similarly, to determine the activation energy E_{ann} of defect annihilation process, and compare it with available results on EG-Si. We have first locally degraded the cells until efficiency reaches a stable minimum value. Starting from this fully degraded state, the recovering anneals in darkness were performed on a hot plate that was set at 140, 160, 180 and 200 °C. Where the complete efficiency degradation state by light inducation or the recovery process of efficiency on the hot plate, FeB pairs have been dissociated completely. So the recovery of efficiency only duo to the dissociation of BO_{2i} defects, not the association of the FeB pairs.

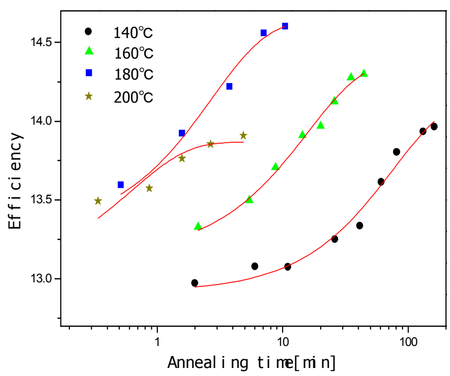

Figure 3. Temperature dependence of efficiency recovery from the the fully degraded state of a solar cell at annealing temperatures of 140 to 200°C (symbols) and exponential curves fitted to data (lines).

Fig. 3 show efficiency recovery property from the degraded state. It is clearly seen that the efficiency of all the samples are not consistence, there are two reasons(i) The chemical composition distribution of the SoGM-Si is less uniform than chemical EG-Si; (ii) the solar cells size is not strictly equal, this impact is much marked for small size cells. We can see that the sample temperature strongly affected the recovey time of defect annihilation process: at 140 °C, the final state was reached after more than 100 min but at 200 °C, it was reached after 10 min.

E_{ann} can then be obtained from an Arrhenius plot of the variation of R_{ann} with T according to a similar expression of defect generation[12].

$$R_{ann}(T) = \nu_0 \exp(-\frac{E_{ann}}{k_B T}) \qquad (2)$$

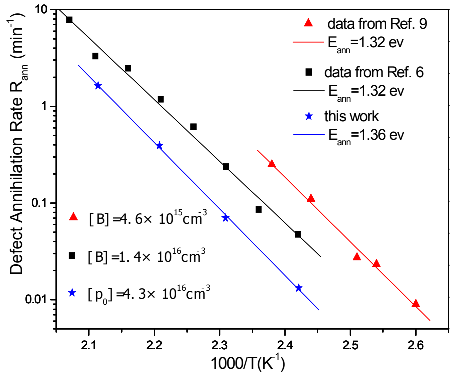

Figure 4. Arrhenius plot of the defect annihilation rate R_{ann}

The measured linear dependence in Fig. 4 clearly proves that the physical mechanism responsible for the defect annihilation in SoGM-Si solar cells is also a thermally activated process, and the activation energy Eann=1.36 eV. This is in good agreement with the values of 1.32 and 1.36ev reported by [6,11] and [7], so the value of E_{ann} is independent of the boron concentration. Another important finding from Fig. 4 is that R_{ann} decreases approximately linearly with p_0, this have been reported successively by Schmidt [13]and Lim [7].

C. EQE test

LID on SoGM-Si cell level is mainly based on the formation of BO_{2i} defects and Fe_i under illumination. In our experiment we compared the EQE of a cell at different states: State 1, the cell was annealed in the dark at 200 ℃for 20 min; State 2, the cell was placed under a 75 w halogen lamp in a distance of about 20 cm (about 70 mw/ ㎝ ^{2}) and are illuminated for 24 hours; State 3, the cell is kept one day in the dark to enable Fe-B formation. Three of these states are listed in Table I. For simplicity, we use the terms ''not active'' and ''active'' to refer to defect states corresponding to reduced and enhanced recombination activity, respectively. The EQE is shown in Fig. 5.

Table Ⅰ. Selected defect states for EQE measurements

State 1	BO_{2i} not active	Fe active
State 2	BO_{2i} active	Fe active
State 3	BO_{2i} active	Fe not active

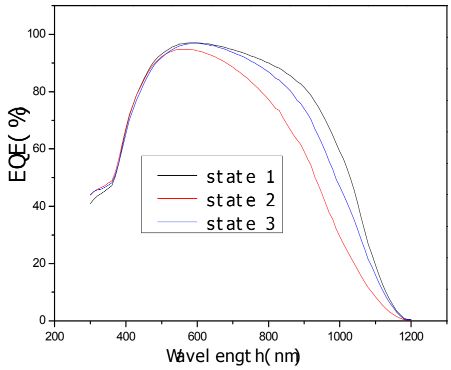

Figure 5. EQE development during the different states of a degradation experiment

From Fig. 5 we can see that the EQE of long-wave region degradated obviously after 24 hours illumination, but there has no impact on the EQE of Short-wave region. This is becaues that the minority carriers produced by long wavelength photons are far from the p-n junction, the lifetime of the minority carriers becamed shoter when the BO_{2i} defects formation, resulting in diffusion length degradation at long wave lengths; As for Short-wave region, the minority carriers produced by short wavelength photons are near from the p-n junction, so that injected carriers have diffusion lengths much longer than the distance between the minority carriers and the p-n junction even in the degraded state, therefore, illumination has no impact on the EQE of Short-wave region. This is good agreement with Hashigamis' result [14].

We can see that there have some recovery of EQE when leaving the degraded cell in the dark for 24 hours, this is because the isolated and paired form of interstitial iron have markedly different recombination properties, the recomation parameters listed in Table 2.

Table Ⅱ. Main energy levels and capture cross-sections for Fe_i and the acceptor state of the Fe_iB_s pair

Recombination centre	Energy level (eV)	$\sigma_n cm^2$	$\sigma_p cm^2$
Fe_i	E_V+0.38	5×10^{-14}	7×10^{-17}
Fe_iB_s(acceptor state)	E_C-0.23	3×10^{-14}	2×10^{-15}

Data taken from the literature[15, 16]

From Table 2, we observe that the energy level of the FeB center is relatively shallow and capture cross sections is relatively small, this characteristic behaviour leads to significant rise in carrier lifetime and diffusion length after forming the FeB pairs, So the EQE of state 3 greater than stae 2. It is also can be seen that EQE has not comepeletly recovery in state 3, this means that the degraded value of EQE induced by the dissociation of FeB pairs is less greater than the formation of BO_{2i} defects. In other word, the formation of BO_{2i} defects is the main facor for the electricial parameters degradation of this SoGM-Si solar cell.

Ⅳ. CONCLUSION

The light-induced efficiency degradation specific to B-doped SoGM-Si solar cell was investigated. Both BO_{2i} defect generation and annilation, the corresponding activation energy calculated from efficiency measurements are consistent with the values calculated from minority carrier lifetime measurements. The BO_{2i} defect and FeB pairs are the two key centers that contribute to LID in SoGM-Si, but the BO_{2i} defect is the main facor. As for the LID induced by BO_{2i} defect, the results revealed that using phosphorus to compensate boron was an effective way to reduce the LID of the solar cells. As for the LID induced by FeB pairs, optimizing the purification process and phosphorus gettering treatment are the efficive measures to reduce Fe concentration and corresponding LID.

ACKNOWLEDGMENT

This work is supported by National Natural Science Foundation of China (No.61076056) and the Key Science and Technology Project of Fujian Province (No.2007HZ0005-2)

REFERENCES

[1] H. Fischer, W. Pschunder. Investigation of photon and thermal induced changes in silicon solar cells. Conference Record of 10th IEEE Photovoltaic Specialists Conference, pp. 404-411, 1973.

[2] D. Macdonald, F. Rougieux, A. Cuevas, et al., “Light-induced boron-oxygen defect generation in compensated p-type Czochralski silicon”. J. Appl. Phy. 105, 093704, 2009. I. S. Jacobs and C. P. Bean, “Fine particles, thin films and exchange anisotropy,” in Magnetism, vol. III, G. T. Rado and H. Suhl, Eds. New York: Academic, 1963, pp. 271–350.

[3] B. Lim, F. Rougieux, .D Macdonald, et al., “ Generation and annihilation of boron–oxygen-related recombination centers in compensated p- and n-type silicon”. J. Appl. Phy. 108, 103722, 2010.

[4] J. Schmidt. “Effect of Dissociation of Iron–Boron Pairs in Crystalline Silicon on Solar Cell Properties”. Prog. Photovolt: Res. Appl. vol. 13, pp. 325–331, 2005.

[5] H. Savin, M. Yli-Koski, and A. Haarahiltunen. “Role of copper in light induced minority-carrier lifetime degradation of silicon”. Appl. Phys. Lett., 95, 152111, 2009.

[6] J Schmidt and K Bothe. “Structure and transformation of the metastable boron-and oxygen-related defect center in crystalline silicon”. Phys. Rev. B., 69, 024107, 2004.

[7] B. Lim, V. V. Voronkov, R. Falster, et al., “Lifetime recovery in p-typeCzochralski silicon due to the reconfiguration of boron–oxygen complexes via a hole-emitting process”. Appl. Phys. Lett., 98, 162104, 2011

[8] D. W. Palmer, K. Bothe, and J. Schmidt, “Kinetics of the electronically stimulated formation of a boron-oxygen complex in crystalline silicon”. Phys. Rev. B. 76, 035210, 2007

[9] S. Rein, T. Rehrl, W. Warta, et al., “Electrical and thermal properties of the metastable defect in boron-doped Czochralski silicon”. *Proc. 17th European Photovolt. Solar Energy Conf.* (WIP-ETA, Munich, 2001) p. 1555.

[10] J. Schmidt, K. Bothe, D. Macdonald. Mechanisms of light-induceddegradation in mono-and multicrystalline sillicon solar cells. 20th European Photovoltaic Solar Energy Conference, Barcelona, Spain, 2005.

[11] Y. Kayamori, M. Dhamrin, H. Hashigami, et al., “Rapid initial light-induced degradation of multicrystalline silicon solar cells.” in Proc.3rd World Conf. Photovoltaic Energy Convers, Osaka, Japan, pp. 1511–1514. May 2003.

[12] T. Schutz-Kuchly, J. Veirman, S. Dubois, et al., “Light-Induced-Degradation effects in boron–phosphorus compensated n-type Czochralski silicon”. Appl. Phys. Lett., 96, 093505, 2010 .

[13] J Schmidt, K. Bothe, and R. Hezel. “Formation and annihilation of the metastabledefect in boron-doped czochralski silicon”. Proc 29th IEEE PVSC, pp. 178-181, 2002.

[14] H. Hashigami, Y. Itakura, T. Saitoh, et al., “Interpretation of light-induced cell performance degradation by means of spectroscopic light illumination”. Sol. Energy Mater. Sol. Cells. Vol. 75, pp. 351–356, 2003 .

[15] A. A. Istratov, H. Hieslmair, E. R. Weber, et al., “Iron and its complexes in silicon”. Appl. Phys. A., 69, pp. 13–44. 1999.

[16] D. Macdonald, A. Cuevas, J. Wong-Leung, et al., “Capture cross sections of the acceptor level of iron-boron pairs in p-type silicon by injection-level dependent lifetime measurements”. J. Appl. Phys. 89, pp. 7932–7939, 2001.