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Influence of Ring Oxidation-Induced Stack Faults on Efficiency in Silicon Solar Cells *

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We observe a strong correlation between the ring oxidation-induced stack faults (OISF) formed in the course of phosphor diffusion and the efficiency of Czochralski-grown silicon solar cells. The main reason for ring-OISF formation and growth in substrate is the silicon oxidation and phosphorus diffusion process induced silicon self-interstitial point defect during $POCl_3$ diffusion. The decreasing of minority carrier diffusion length in crystal silicon solar cell induced by ring-OISF defects is identified to be one of the major causes of efficiency loss.

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Terrestrial solar cells are an excellent means to provide clean energy. Based on cost and solar cell efficiencies, silicon is one of the most promising materials for this application with the silicon being photovoltaic (solar) grade in multicrystalline (polycrystalline) or single crystal forms. The efficiency of a silicon solar cell depends to a large extent on its bulk minority carrier lifetime, especially for low lifetime silicon. Schroder[1] has pointed out that the carrier recombination lifetime (minority carrier lifetime) is a property of the carrier within the semiconductor, rather than a property of the semiconductor.Many factors may cause low minority carrier lifetime in Czochralski silicon and polysilicon. Dissolved transition metals degrade carrier lifetime through Shockley–Read–Hall recombination,[2,3] although they are rarely found in concentrations high enough to account for observed low minority carrier lifetime in solar cell silicon. However, when these transition metal precipitated at the structure defects in silicon, such as dislocation, grain boundaries, etc., these defects become highly recombination-active.[4] Furthermore, grain boundaries in large-grained silicon can reasonably be ruled out as efficiency-limiting defects.[5] Additionally, in single crystalline silicon, especially Czochralski solar grade silicon, the carrier lifetime in boron-doped oxygen contaminated crystalline silicon is limited by a specific recombination centre that forms under illumination or injection of minority carriers in the dark (forward-biased p-n junction).[6−8]

Oxidation-induced stacking fault (OISF) ring has been important research topics in the past in complementary metal-oxide-semiconductor devices.[9] It was found that defects could affect gate oxide integrity and device performance, yield, and reliability.[10] In integrated-circuit (IC) process, a ring can be formed during thermal oxidation of silicon wafers at the boundary that separates the vacancy-rich area near the centre of the wafer and the interstitial-rich area near its edges; radius of the ring is determined by the growth conditions of the ingot, i.e. ratio of the pull rate to the interfacial axial temperature gradient at the melt/crystal interface.[11] The existence of vacancy/interstitial (V/I) boundary and the oxygen precipitates inside the V/I boundary are the two major criteria,[12] ring-OISF cannot be forms if any one of the two criteria is not fulfilled. These defect types are not new to silicon technology but the demands on their control increase dramatically in recent years[13] in ICs.

For silicon solar cells, the ring-OISF was observed after phosphorus diffusion in some types of silicon substrates. The solar cells made from these materials tend to have energy conversion efficiency lower than the value of the normal silicon. However, there have been few reports focused on the generation of ring-OISF in silicon solar cells and the effect of ring-OISF on solar cell efficiency. In this Letter, we address ring-OISF defects in solar grade silicon and study the mechanism of ring-OISF forming during solar cell process and the impact on efficiency of solar cells.

The solar cells were fabricated with a p-type ⟨100⟩ substrate with resistivity of 1 Ωcm using industry single crystalline silicon solar cell process, including alkaline etching damage layer and alkaline texture, emitter diffusion, phosphorous glass removed, oxidation, deposing TiO_2 anti-reflectance layer, front side print and rear side print and firing. Current-voltage ($I-V$) tester was used to test this set of solar cell at AM1.5 (1000 W/m^2), 25°C. The laser microwave-detected photoconductance decay (MW-PCD)[14] method was used to monitor the changes in the minority carrier

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lifetime before metallization.

Saw damage etching and the texturing of silicon wafer are realized in alkaline solution. Then, the effective lifetime of silicon wafer was measured by passivation with 1% iodine/ethanol solution. The incidence light source in the MW-PCD technique is 904 nm, which ensures the carrier generation in silicon bulk. Then the substrates were again cleaned and subjected to double-face phosphor diffusion. The effective lifetime of silicon after phosphorus diffusion was measured by passivation with phospho-silicate glass. The solar cells process was carried on to produce the cells after the effective minority carrier lifetime measurement. The short circuit current map of solar cells was measured by light beam induced current (LBIC)[15] in a WT-2000 system. The measured short circuit current I_{SC}, the power of the incident light and the reflection coefficient R are converted into the local internal quantum efficiency (IQE)

$$\mathrm{IQE} = \frac{1}{1-R} \cdot \frac{I_{SC}/e}{P_L(h \cdot c/\lambda)}, \tag{1}$$

where e represents the elementary charge, h is Planck's constant, c is the velocity of light in vacuum, λ is wavelength of the incident light. The second factor in Eq. (1) is called the external quantum efficiency (EQE).

After measuring the short circuit current and the reflection, the IQE map was obtained by EQE corrected with $1/(1-R)$. The measuring head includes up to four light sources (405 nm, 880 nm 956 nm and 979 nm) with a spot size of 100 μm. The 405 nm wavelength of laser corresponds to a penetration depth of about 0.5 μm in textured cells which mainly in the front surface and the emitter region of cells. The penetration lengths of three other light sources in silicon are from 30 to 80 μm, which means that the detected region is mainly in the bulk of cells. The results of LBIC for the four light sources with poor spatial revolution (2 mm) show that the ring-OISF presents in the solar cells for the three infrared light sources except for the 405 nm light sources. Thus the LBIC measurement was carried on in the wavelength of 979 nm.

In order to more clearly verify that the relation of minority carrier lifetime in bulk with the short circuit current I_{SC}, open circuit voltage V_{OC} and solar cell efficiency, these photovoltaic (PV) parameters as functions of the bulk lifetime are obtain by numeric simulation software Afors–Het. In the Afors–Het calculation the value of back surface recombination velocity (SRV) is 10^5 cm/s, without considering the anti-reflectance of the SiO_2/TiO_2 layer. We can obtain a set of curves displaying the relationship between the PV parameters and bulk lifetime by changing the value of SRV in front surface of solar cell from 10 cm/s to 10^4 cm/s.

From the current-voltage ($I-V$) curves under illumination, the solar cell parameters, short circuit current, open circuit voltage, curve fill factor, maximum output power, series resistance and shunt resistance are derived for each cell. The average values of the parameters for each group of cells A and B are calculated. Samples A and B are denoted the solar cell with lower efficiency and the solar cell with higher efficiency respectively. Table 1 shows the $I-V$ characteristics of the Czochralski solar cells measured under standard illumination conditions (AM 1.5 and 25°C). In solar cell A, the average efficiency is lower than 15%, whereas the average efficiency of solar cells increases to about 16% after changing the substrate to B.

Table 1. Average electrical parameter of the Czochralski solar cells prepared by the same solar cell process with different types of silicon substrates.

Solar cell	V_{OC}(V)	J_{SC}(A)	$P_{\max}$(W)	FF	η
A	0.611	4.884	2.224	0.74	14.9%
B	0.613	5.143	2.389	0.76	16.0%

Figure 1 shows the result of IQE for types A and B. The EQE and reflection map of solar cells are not shown here. The existence of four different IQE ring-like distributions is shown in the result of solar cell A, and the value of IQE increases from 55% to 85% from the centre of cell to the edge of cells. However, for solar cell B, except for the lower value of IQE in the horizontal and vertical contact fingers, the variation of IQE value is small, which is from about 87% to 97%. In a word, solar cell A contains ring-like patterns with uniformly reduced quantum efficiency. However, for solar cell B, except for that the quantum efficiency in the contact fingers is low, the efficiency in the area between fingers is high and similar.

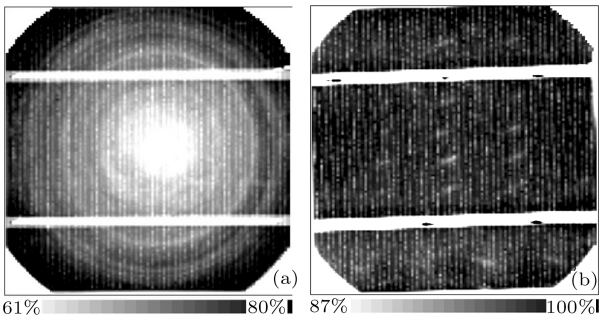


Fig. 1. LBIC result of silicon solar cells: (a) the internal quantum efficiency map and distribution of solar cell A, (b) the internal quantum efficiency map and distribution of solar cell B. The contact fingers are visible as horizontal lines, but the fingers as vertical lines are unclear because of the lower spatial resolution of 250 μm.

In order to discuss the nature of the ring-like defect, MW-PCD technique was used to monitor the changing of silicon bulk lifetime just prior to metallization. In the result of silicon A before phosphorus diffusion, the uniform distribution of effective lifetime in the silicon wafer can be observed except for the edge of wafer (Fig. 2(a)). The same map of effective lifetime is shown in the type of silicon B (Fig. 2 (b)).

The value of bulk lifetime in sample B is larger than the value of sample A. The lower effective lifetime in the edge of wafer may be resulted from the residual damage produced in the incising silicon ingot or rupture. After phosphorus diffusion, the effective lifetime measurement reveals the ring-like area which can be seen in the result of LBIC (Fig. 1) with lower bulk lifetime value existing in phosphor-diffused silicon substrate of cell A (Fig. 3). However, this is not observed in the result of silicon B dealt with the same process (Fig. 4). From these results, it can be concluded that the substrate property is the main factor of the ring-like defect origin during $POCl_3$ diffusion.

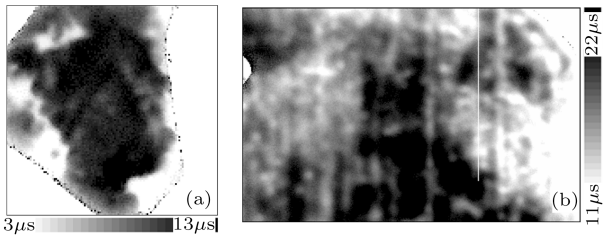


Fig. 2. MW-PCD effective lifetime map of sample after texture: (a) sample A, (b) sample B.

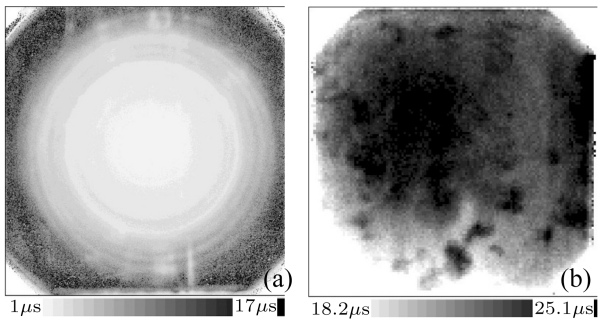


Fig. 3. Effective lifetime maps and distributions of sample after phosphorus diffusion: (a) effective lifetime of sample A, (b) effective lifetime of sample B.

The present study shows that for the solar grade silicon, the concentration of oxygen interstitial atom will reduce largely after silicon annealed at the temperature of 850–900°C because of formation of oxidation precipitates from these interstitial atoms.[16] In the silicon solar cell, $POCl_3$ diffusion process usually occurs in the temperature range of 850–900°C. If the substrate contains enough oxygen interstitial atoms, the oxidation precipitates will form and grow during this thermal treatment process. Furthermore, the ring-OISF will be formed if the existence of the ring- distribution oxygen precipitates inside the V/I boundary.[10] Therefore, it can be concluded that in the solar cell A, a ring-like pattern is the ring-OISF defect although the V/I boundary cannot not observed in sample A from the result of MW-PCD.

The main reason for forming OISF is that thermal oxidation silicon self-interstitials are produced and diffuse to the sites having a stress field or crystal lattice, which is the nucleating centre of OISF.[17] In the silicon solar cells, the ring-OISF forming may have different characteristics from IC process because not only oxidation but also phosphorus diffusion are in the thermal process. In the process of flash memory,[10] when phosphorus doped by implantation, the ring-OISF formation is significantly enhanced. Nishi and Antoniadis[18] found that the silicon self-interstitial point defects are dominant during phosphorus diffusion. Since OISF grows by absorbing interstitials or by emitting vacancies, the phosphorus diffusion also promotes to form OISF or to enhance the growth of OISF during the thermal treatment process. From the two major criteria that determine the ring-OISF forming: the existence of V/I boundary and the oxygen precipitates inside the V/I boundary, there are three methods that can be used to eliminate the ring-OISF from the crystal history of the wafer substrate and solar cell fabrication processes. The first one is to obtain the defect equilibrium between vacancies and self-interstitials. The second one is to identify the processing conditions that lead to the formation of relatively defect-free crystals. The last one is based on solar cell fabrication processes, such as driving oxygen out of wafer in the non-oxidation atmosphere so that oxygen precipitates are difficult to form in the region. However, this method may be inappropriate for the process of silicon solar cell, because the higher temperature (above 1100°C) or more thermal process will degrade the properties of silicon substrates, especially for solar grade silicon.

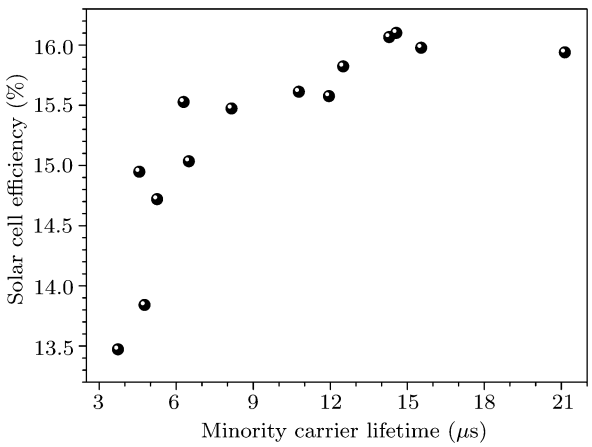


Fig. 4. Relationship between the efficiency of silicon solar cell and minority carrier lifetime of silicon after phosphorus diffusion prepared in solar cell factory.

In the result of MW-PCD and LBIC for solar cell A, the lower I_{SC} distributing area corresponds to the lower effective minority carrier lifetime. As a result, in order to make accurate co-relation between substrate lifetimes and final cell parameters, the lifetime measurement and finished cell characterization were performed. As shown in Fig. 4 , When τ varies from

10 μs to 20 μs, efficiency η increases from 14.6% to 15% only by 0.4%.

Figure 5 shows the relation of minority carrier lifetime in bulk silicon with the PV parameters obtained by the help of numerical simulation. The three figures show that when minority carrier lifetime in bulk silicon is $\tau_b < 5\,\mu$s, I_{SC} and V_{OC} increase dramatically with lifetime, and when $\tau_b > 10\,\mu$s the two parameters increase slowly. In these results, the dependence of the solar-cell efficiency with the recombination lifetime is dominated by the effect on I_{SC}. For example, when the lifetime increases from 1 μs to 10 μs, I_{SC} is increased by 0.307 A, while V_{OC} only by 0.028 V. The SRVs in front surface of the solar cell from 10 cm/s to 10^4 cm/s hardly have any influence on the performance of the solar cell, and the curves denote various SRVs in front surface of the solar cell almost lapping over each other.These theoretical results agree well with the experimental results shown in Fig. 4.

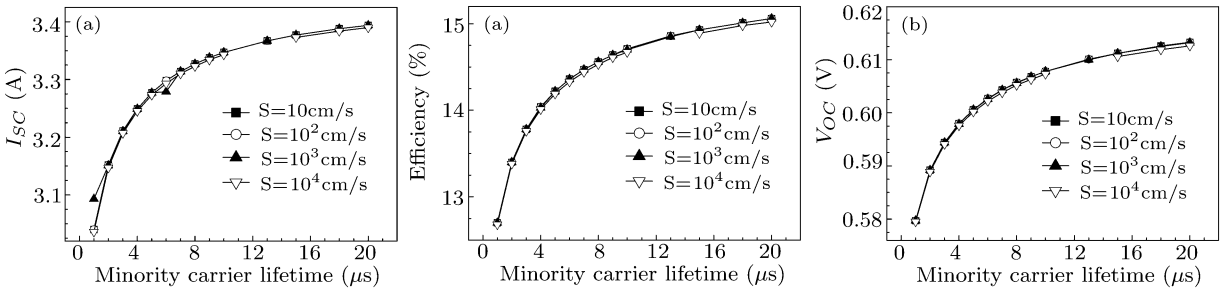


Fig. 5. Electric parameter of silicon solar cells as a function of minority carrier lifetime τ_b in silicon bulk, simulated by using four values for the front surface recombination (S) in Afors–Het software: (a) characteristics of short circuit current I_{SC}, (b) open circuit voltage V_{OC}, (b) solar cell efficiency η.

The ring-OISF area contains stack fault and the high bulk micro-defects density, such as oxidation precipitates.[10] The presence of defects within a semiconductor crystal produces discrete energy levels within the bandgap. These defect levels, also known as traps, greatly facilitate recombination through a two-step process (SRH recombination).[19] The minority carrier lifetime degradation will occur if the SRH recombination in bulk enhances. It is well known that the short circuit of a solar cell is determined by the number of minority carriers (either generated in the base or the emitter) that diffuse to the junction edge before recombining. If the lifetime of minority carrier decreases, which corresponds to the decreasing of minority carrier diffusion, only a few fraction of carriers can take part in the process of diffusion. This should make the decrease of short-circuit carrier I_{SC}. In a simple case, the short circuit current is proportional to the square root of the minority carrier lifetime (proportional to the minority carrier diffusion length). In contrast, the open circuit voltage continues to increase logarithmically with increasing lifetime in the base. Therefore, in the ring-OISF area, the more prominent impact of minority carrier lifetime on solar cell efficiency is mainly resulted from the effect on short-circuit current I_{SC}.

In a word, the conversion efficiency of light to electricity in such a cell is strongly affected by ring-OISF, which degrades the cell efficiency. During phosphorus diffusion in silicon solar cell process, silicon self-interstitials induced by oxidation and phosphorus diffusion promote the formation of ring-OISF defects and growth on silicon substrates which contain V/I boundary and high oxygen concentration. The results indicate that the ring-OISFs, i.e. the centres of carrier recombination, play a role of degradation of the efficiency of solar cells by reduction of the number of effectively collected carriers. The ring-OISF creating is associated with not only the solar cell fabrication process, such as phosphorus diffusion, but also the crystal history of the wafer substrate. This indicates that the solar cell fabrication process as well as the silicon wafer selection is critical to minimize the device failures induced by ring-OISFs.

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