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Letter

Effect of oxygen precipitation on the performance of Czochralski silicon solar cells

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ABSTRACT

We have demonstrated the effect of oxygen precipitation on the performance of Czochralski (CZ) silicon solar cells. The oxygen precipitates in silicon substrates were formed by a low–high two-step annealing. With the increase of oxygen precipitation, the minority carrier diffusion length of CZ silicon solar cells decreases and, meanwhile, the leakage currents due to the carrier recombination at the defect states get increased. The external quantum efficiency (EQE) measurement shows that the decrease of the solar cell efficiency due to oxygen precipitates mainly takes place in the long wavelength range of light. The short-circuit current and open-circuit voltage of solar cells both become smaller, while the fill factor does not significantly change. The efficiency of solar cells is reduced to 12.7% from an original value of 17.5%. All these results suggest that the oxygen precipitation is a limitation factor for the improvement of solar cell efficiency, which should be strictly controlled during the crystal growth and cell fabrication.

1. Introduction

Czochralski (CZ) silicon solar cells still occupy a large portion of photovoltaic market [1], since it has a higher efficiency than those based on multicrystalline silicon due to the absence of defects such as dislocations and grain boundaries. Oxygen is one of the main impurities in CZ silicon, which mainly originates from the contamination of silica crucibles and cannot be avoided during crystal growth [2,3]. In general, oxygen atoms with the concentration up to 10^{18} cm^{-3} in CZ silicon stay at the interstitial sites to form covalent bonds with two silicon atoms and are therefore electrically neutral [4]. The excess interstitial oxygen in silicon can form precipitates during crystal growth and cell fabrication, which consists of two stages, i.e., nucleation and growing-up [5,6]. Nucleation is the early stage of oxygen aggregation, driven by oxygen supersaturation [7]. The precipitate density detected in silicon wafers subjected to different thermal treatments is directly related to the initial nuclei density. The growing-up of oxygen precipitates is controlled by oxygen diffusion [8]. As we know, the formation of oxygen precipitates within the bulk of silicon wafers can affect both the generation and the recombination lifetimes since they can cause deep energy levels in band gap and become the recombination centers for minority carriers [9]. It has also been reported that the degree of lifetime degradation was more pronounced in p-type silicon than in n-type silicon [10]. Since the recombination of oxygen precipitates takes place through their interface states, the existence of positive fixed charges around oxygen precipitates will help the lifetime degradation in p-type silicon. Although the detrimental effect of oxygen precipitation on minority carrier lifetime has been demonstrated, it is still necessary to systematically understand the impact of oxygen precipitates on the performances of solar cells, specially in gallium-doped CZ silicon.

In this paper we have intentionally formed oxygen precipitation in CZ silicon wafers by a two-step annealing, and meanwhile inspected its effect on the performances of solar cells. Compared to the referenced solar cells based on the as-received wafers the short-circuit currents and open-circuit voltages of solar cells containing oxygen precipitates are lower, but the fill factors almost remain constant. Based on these results, we have discussed the role of oxygen precipitates in the degradation of solar cell efficiency.

2. Experimental details

The experimental samples were 125 mm × 125 mm gallium (Ga)-doped CZ silicon wafers with a thickness of ~200 μm, which were sliced from the same part of an ingot. The resistivity of wafers was ~3.0 Ω cm, measured by the four-point probe method, and the initial interstitial oxygen concentration ($[O_i]_0$) was $\sim 9.0\times10^{17}$ cm^{-3}, determined by a Fourier Transform Infrared Spectroscope (FTIR, Bruker, IFS 66v/S) at room temperature with a calibration factor of 3.14×10^{17} cm^{-2}. The samples were firstly etched in 20% NaOH solution for 1 min to remove the

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damaged layer and cleaned by a standard RCA cleaning. Then the samples were divided into six groups. Five of them were subjected to two-step annealing in argon ambient for formation of different oxygen precipitate densities, i.e., 750 °C for 0–16 h followed by 1050 °C for 16 h. Another one was used as a reference, without any thermal treatment. The evolutions of interstitial oxygen concentration in these wafers were inspected by FTIR measurement at room temperature. Meanwhile, the bulk microdefects (BMDs) related to oxygen precipitates were observed by an optical microscope (Olympus, MX-50) after Secco etching for 7 min. These silicon wafers were then fabricated into solar cells by Sunflower Company using the standard process, including alkaline texture, phosphorus diffusion, anti-reflection coating deposition, screen-printing and contact firing. The minority carrier diffusion lengths of all the CZ silicon solar cells were measured by a light beam induced current (LBIC) technique. The external quantum efficiencies (EQE) of solar cells were obtained from the spectral responses. The characteristics of cell performance were measured under the standard conditions (one sun, AM 1.5 Global spectrum, 25 ± 1 °C), using a Berger Flasher PSS 10 solar simulator. The illumination intensity was calibrated using a reference cell obtained from FISE, Germany.

3. Results and discussion

Fig. 1 shows the variation of interstitial oxygen concentrations (Δ[Oi]) as a function of annealing time at 750 °C in the samples subjected to 750 °C+1050 °C two step thermal treatments compared to the referenced sample. It can be seen that with the increase of the annealing time, the amount of Δ[Oi] increases. Compared to the referenced wafer with [Oi] $\sim 9.0\times10^{17}\,\mathrm{cm}^{-3}$, $\Delta[O_i]$ increases significantly when the 750 °C pre-anneal exceeds 2 h and then it reaches a relatively stable value after 8 h. However $\Delta[O_i]$ increases slightly in the wafer subjected to only 1050 °C anneal, indicating that it is difficult to form a large amount of oxygen precipitates without sufficient nucleation centers. It is well known that oxygen precipitates firstly nucleate at low temperatures and then grow up at higher temperatures. At a very low temperature (below 600 °C) the diffusion of interstitial oxygen in the bulk of silicon is too slow to form many oxygen precipitate nuclei, while at a relatively high temperature (above 900 °C) oxygen atoms are difficult to form the nucleus sites due to the poor driving force related to their supersaturation. Meanwhile, the growing-up of oxygen precipitates is dominated by oxygen diffusion at high temperatures where diffusivity of oxygen is extraordinarily high. This suggests that the low temperature thermal treatment with enough time for nucleation benefits the formation of oxygen precipitates [11].

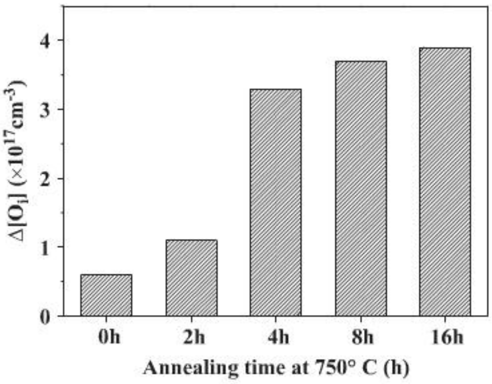

Fig. 1. Variation of interstitial oxygen concentration $\Delta[O_i]$ as a function of annealing time at 750 °C after 750 °C+1050 °C two-step thermal treatments.

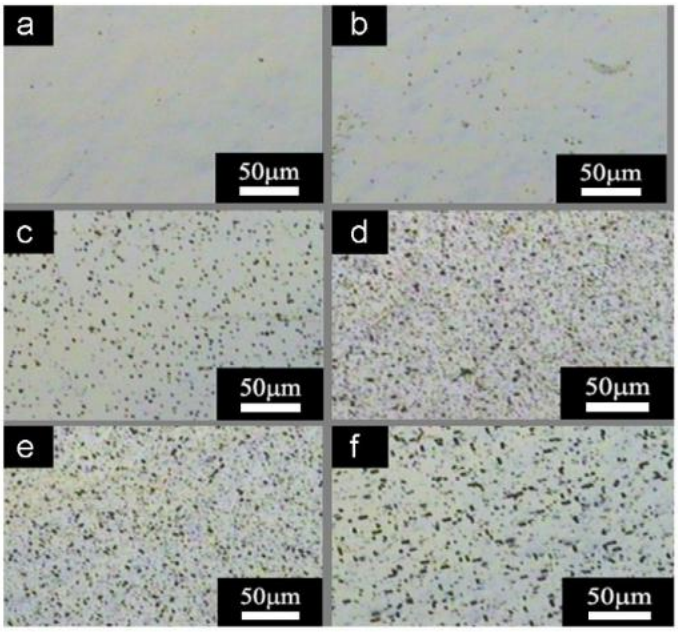

Fig. 2. Optical micrographs of BMDs in silicon after different two-step anneals. (a) The referenced wafer without any thermal treatments, (b) 1050 °C/16 h, (c) 750 °C/2 h+1050 °C/16 h, (d) 750 °C/4 h+1050 °C/16 h, (e) 750 °C/8 h+1050 °C/16 h, (f) 750 °C/16 h+1050 °C /16 h.

The optical micrographs (OMs) of BMDs related to oxygen precipitates in the samples after different thermal treatments are shown in Fig. 2. Obviously, the referenced sample has lower BMD density while the annealed samples have higher density. Moreover it can be clearly seen that the longer the nucleation time at 750 °C, the higher the BMD density. In the case of sample subjected to only 1050 °C anneal few oxygen precipitates were observed, while the density was much higher in the sample that experienced a pre-anneal at 750 °C for 16 h, which is consistent with the results shown in Fig. 1.

In order to investigate the influence of oxygen precipitates on the performance of cells, the electrical properties of these cells were further examined. Fig. 3 shows the LBIC measurements for all kinds of solar cells. The dark red regions in the LBIC images correspond to high carrier recombination zones where the minority carrier diffusion length is low, while the blue regions are related to low carrier recombination regions. As clearly seen from this figure the average diffusion length of the referenced cell is up to 973 μm, which is much larger than the wafer thickness, suggesting that a high cell performance can be achieved without oxygen precipitates. However, a significant decrease in diffusion length for solar cells containing oxygen precipitates was clearly observed. As the oxygen precipitation density increases, the minority carrier diffusion length becomes smaller. It is reported that oxygen precipitates can act as effective recombination centers to enhance the bulk recombination and reduce the minority carrier lifetime [12,13]. Besides, oxygen precipitates not only induce secondary defects but also produce a compressive stress due to the fact that the volume of each oxygen precipitate (SiO_2) is about 1.25 times larger than that of a silicon atom. Thus, the carrier diffusion length could also be seriously affected by those secondary defects and compressive stress.

The measured EQE as a function of wavelength for three types of cells is demonstrated in Fig. 4. It is known that EQE in the short wavelength range denotes information about the recombination in the emitter junction as well as at the front surface [14], while the long wavelength region reveals messages about the quality of bulk materials and recombination at the rear side of the cells [15]. Fig. 4 shows that the referenced cell exhibits a better external

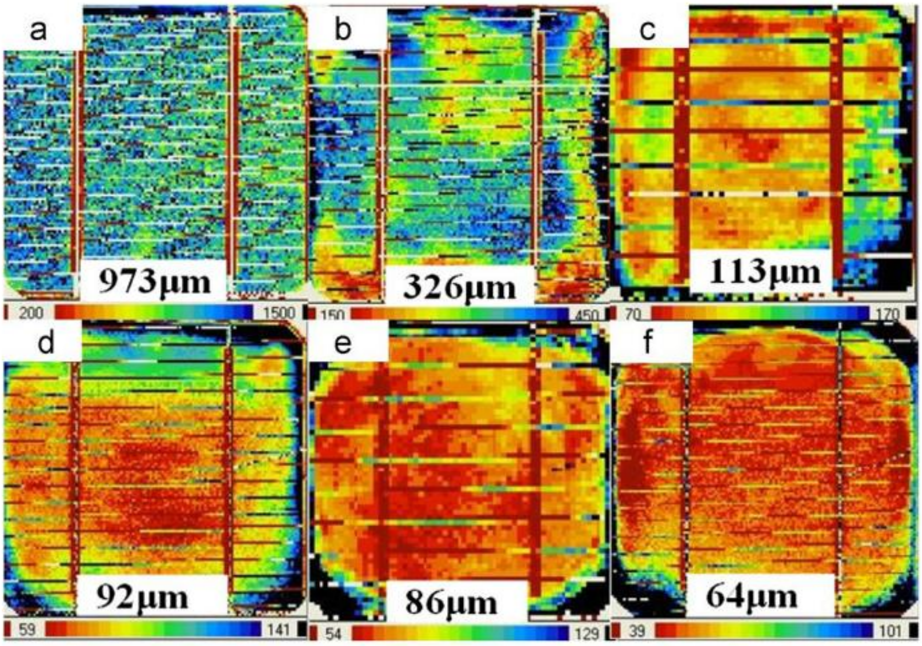

Fig. 3. Mappings of light beam-induced current (LBIC) measurement for different solar cells suffered from 750 °C + 1050 °C two step annealing. (a) The referenced solar cell, (b) subjected to pre-anneal 750 °C/0 h, (c) pre-anneals 750 °C/2 h, (d) pre-anneals 750 °C/4 h, (e) pre-anneals 750 °C/8 h and (f) pre-anneals 750 °C/16 h (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

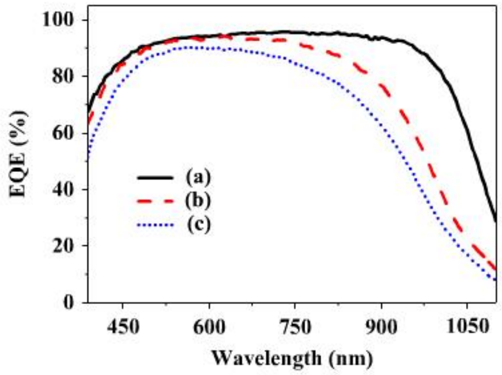

Fig. 4. Representative external quantum efficiency (EQE) of the solar cells made from: (a) the reference sample, (b) the sample subjected to 1050 °C annealing for 16 h without pre-annealing and (c) the sample subjected to 750 °C pre-annealing for 16 h followed by 1050 °C annealing for 16 h.

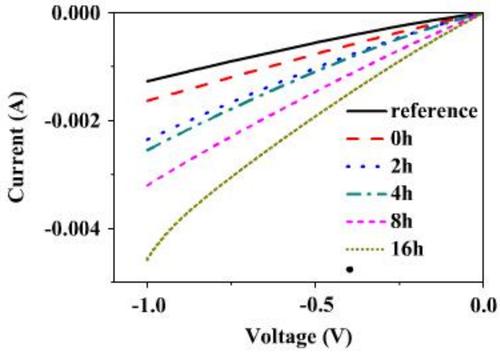

Fig. 5. Inverse current–voltage characteristics of solar cells from the reference sample and the samples are subjected to pre-annealing for different durations at 750 °C followed by 1050 °C annealing for 16 h, which contains different oxygen precipitate concentrations.

quantum efficiency ranging from 400 to 1100 nm, especially in the region from 700 to 1100 nm. Compared to the referenced cell, the long wavelength response of the cells containing oxygen precipitates becomes much lower. It should be pointed out that the reflectivity of all cells is almost the same. As mentioned above, oxygen precipitates and its related extended defects as effective recombination centers have a significant impact on the bulk carrier recombination. Thus, the poor response at long wavelength is ascribed to the decrease of lifetime in the bulk with oxygen precipitates. Although all the cells experienced the same processes, including diffusion and front surface passivation, there are still some differences of the short wavelength response. After long time pre-anneal to form high density oxygen precipitates in the wafers, a slight decrease of EQE at the short wavelength is also observed. In view of the homogeneous distribution of oxygen precipitates in the whole bulk of silicon substrates, the recombination in the space charge region due to the presence of oxygen precipitates cannot be ignored. Therefore, it can be concluded that the degradation at long wavelength mainly accounts for the increase of the oxygen precipitate density.

Fig. 5 shows the leakage current of silicon solar cells with the different oxygen precipitation concentrations. It is found that the leakage current of cells containing oxygen precipitates is larger than that of the reference cell. Besides, the higher the precipitate density, the more pronounced the leakage current. Generally, the increase of the recombination centers results in an increase in the leakage current accordingly. Shimura [16] considered that crystalline defects are related to leakage current and pointed out that the leakage current drastically increases with increasing defect density. Thus it is easy to understand that the oxygen precipitates can increase the leakage current obviously and affect the electrical properties of silicon solar cells.

Fig. 6 shows the characteristic parameters of solar cells with different oxygen precipitations. Compared to the referenced solar cell, the solar cells containing oxygen precipitates have lower values of J_{sc} and V_{oc}. The J_{sc} and V_{oc} decrease with an increase of oxygen precipitate concentration. Nevertheless, permitting an examination of how photons of different wavelengths (energy) contribute to J_{sc} in solar cells is the spectral response and J_{sc} can

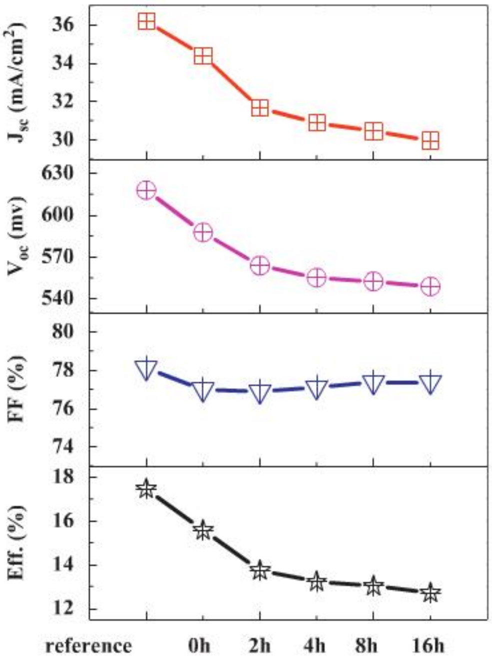

Fig. 6. Characteristic parameters of the solar cells from the reference sample and the samples subjected to pre-annealing for different durations at 750 °C followed by 1050 °C annealing for 16 h, which contains different oxygen precipitate concentrations.

be written in terms of the external spectral response as

$$J_{SC} = \int_{\lambda} EQE(\lambda) f(\lambda) d(\lambda) \tag{1}$$

where $EQE(\lambda)$ is the external spectral response and $f(\lambda)$ is the incident photon flux (number of photons incident per unit area per second per wavelength) [17]. Thus a high J_{sc} of solar cells should be associated with a good external spectral response. Therefore, this change trend in J_{sc} is strongly supported by the results obtained from Fig. 5. Meanwhile, it is well known that the open-circuit voltage (V_{oc}) can be written as

$$V_{oc} = (kT/q) \ln((J_{SC}/J_o)+1) \tag{2}$$

where k is Boltzmann's constant, q is electronic charge, T is the absolute temperature and J_o is the saturation current. Thus, V_{oc} is logarithmically proportional to the reciprocal of J_o, indicating that reducing the saturation current will increase the open circuit voltage. Taking into consideration the fact that J_o is inversely proportional to the minority carrier diffusion length [18], it is not surprising that as the minority carrier diffusion length decreases with more oxygen precipitate formation (in Fig. 3), V_{oc} decreases. However, the fill factor is unaffected by the existence of oxygen precipitates. This suggests that the formation of oxygen precipitates would not influence the shunt and series resistances. An average efficiency of 17.5% in referenced solar cells has been achieved, which was 1.9–4.7% higher than in those subjected to different annealings. These results indicate that the formation of oxygen precipitates is detrimental to the performance of silicon solar cells. Considering the impact of oxygen precipitates on the efficiency of cells, it is necessary to avoid the formation of oxygen precipitates during the crystal growth and cell fabrication.

4. Conclusions

The effect of oxygen precipitates on the performance of CZ silicon solar cells was investigated. It was found that the higher the oxygen precipitation density, the lower the minority carrier diffusion length. The EQE result shows that the degradation at long wavelength is ascribed to the presence of oxygen precipitates. Moreover, oxygen precipitates can amplify the leakage current effectively thus affecting the electrical properties of solar cells. At last, we also found that the efficiencies of solar cells with oxygen precipitates decrease sharply compared to those referenced cells. Therefore, it is necessary to control the thermal treatment processes to avoid the formation of oxygen precipitates in solar cell fabrication.

Acknowledgements

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