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ScienceDirect

Energy Procedia 60 (2014) 81 – 84

Energy Procedia

E-MRS Spring Meeting 2014 Symposium Y "Advanced materials and characterization techniques for solar cells II", 26-30 May 2014, Lille, France

Impact of grown-in point-defects on the minority carrier lifetime in Czochralski-grown silicon wafers

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Abstract

In this study, we investigate the nature of some recombination active defects limiting the lifetime in Czochralski (CZ) silicon wafers, in the millisecond range. Due to their low concentrations, the observed defects are unlikely to be identified through Deep-Level Transient Spectroscopy (DLTS) or Electron Paramagnetic Resonance (EPR), hence we use lifetime spectroscopy combine with several annealing steps to help identify the defect. We demonstrate that the defect can be deactivated by annealing above 300°C. Our experimental findings suggest that vacancy-related pairs incorporated during ingot growth may be responsible for the decreased minority carrier lifetime.

Peer-review under responsibility of The European Materials Research Society (E-MRS)

Keywords: Czochralski, Silicon, defect, nitrogen, vacancy, minority carrier lifetime

1. Introduction

Due to its very high minority-carrier lifetime, high purity n-type monocrystalline silicon is used for very high efficiency solar cells possesses[1]. The intrinsic lifetimes for such wafers (resistivities greater than 3Ω.cm) is above 10ms and greater than 20 ms for higher resistivities[2]. However, in reality the typical lifetime of such wafers rarely

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Peer-review under responsibility of The European Materials Research Society (E-MRS)
doi:10.1016/j.egypro.2014.12.346

reaches the intrinsic lifetime meaning that the electronic quality is still limited by the presence of defects, which have been much less studied in terms of their impact on silicon solar cells.

In this paper we investigate defects limiting the lifetime of high purity Czochralski (CZ) silicon. Considering the high lifetime of the wafers, the defects present are likely to be below the detection limit of DLTS. We use lifetime spectroscopy combined with different annealing step to determine the nature of the recombination active defects preventing the wafers from reaching the intrinsic limit.

2. Experimental method

The silicon samples used in this work were sourced from two CZ grown *n*-type silicon ingots grown for high efficiency solar cells, with resistivity ranging from 4.1 Ω.cm -3.6 Ω.cm, and thicknesses ranging from 955 μm – 1022 μm. The CZ *n*-type samples were annealed for 30 minutes at different temperatures ranging from 150°C to 650°C in a quartz tube furnace using a nitrogen ambient. To determine the remaining defect density after annealing at any given temperature, the effective defect concentration was first calculated by, $N_{t,initial}^{*}=1/\tau_{asgrown}-1/\tau_{max}$ and $N_{t,anneal}^{*}=1/\tau_{anneal}-1/\tau_{max}$, where $\tau_{asgrown}$ is the measured lifetime in the as grown state, $\tau_{annealed}$ refers to the annealed lifetime after a given annealing time, and τ_{max} is the maximum lifetime measured at a given temperature. The remaining normalised defect density after annealing was then determined by $N_{t,anneal}/ N_{t,initial}$. In this work, the normalised defect concentration was determined at an injection level of 10% of the net doping $\Delta p=0.1\times n_0$.

The minority carrier lifetime was measured using a room-temperature surface-passivation technique[3] where wafers were immersed in a plastic container filled with 150 ml of 20 wt% HF and subsequently illuminated to activate the passivation, as outlined by Grant *et al.*[3]. Post illumination, the samples were measured by a transient photoconductance method using a WCT-120 Sinton lifetime tester[3, 4]. To achieve very high effective lifetimes, the samples were etched in a 25 wt% TMAH solution at 80–90 ºC for 10 minutes prior to immersing the silicon wafers in the HF solution, in order to remove surface defects. The surface recombination velocity of the passivation technique measured on n-type Floating Zone (FZ) samples with similar resistivity was found to be injection independent with a value of $S_{eff} = 1.1 \pm 0.2$ cm.s^{-1}.

3. Results and discussion

Figure 1. shows the minority carrier lifetime in the as-grown and annealed state after 150°C and 450°C. While the minority carrier lifetime remains constant after annealing at 150°C the lifetime increases from 1.6±0.4ms to 4.7±0.4ms (at $\Delta p=1\times10^{15}$cm^{-3}) after annealing at 450°C. It is hard to reconcile such low deactivation energy with metallic impurities. Indeed if metallic impurities were limiting the lifetime they would be gettered or altered (for eg precipitate or move to the surface) at much higher temperatures. This indicates that the defect present in these particular CZ wafers is unlikely to be related to metallic defects. The low deactivation temperature also excludes most extended defects (stacking faults and oxygen precipitates) as well as thermal donors as responsible for the lower lifetime in the as-grown state. The most likely cause of such a low deactivation energy is the dissociation or transformation of pairs or complexes of defects with low binding energies.

There are many complexes of light elements and grown-in defects that could be responsible for the observed defect. If we assume the ingot is a vacancy-rich ingot, which most commerial ingots are, potential candidates are VV, V_XO_Y, V_XP_Y, V_XH_Y. However assuming a midgap defect and a typical capture cross section of $\sigma_p = \sigma_n = 1\times10^{-14}$ cm^2 we estimate the defect concentration to be $N = 1\times 10^{10}$ cm^{-3}, which is below the detection limit of DLTS for this sample of doping 1.2×10^{15} cm^{-3}. Hence we must use indirect methods in order to identify the nature of the defects in high lifetime silicon samples. Indicators of the nature of the defect could be its deactivation energy and temperature, recombination activity from lifetime measurements and spatial distribution.

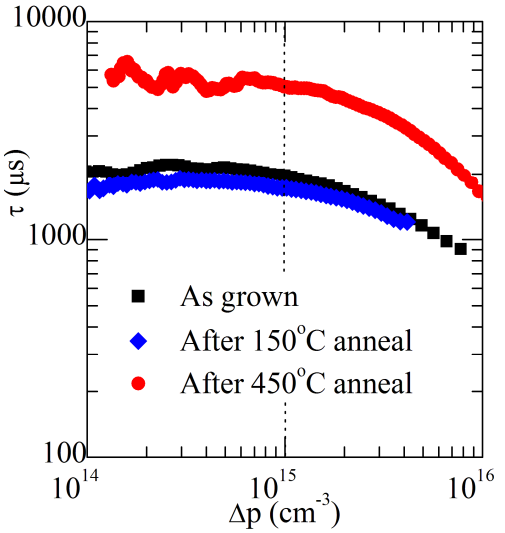

Fig. 1. Measured injection dependence of the carrier lifetime in Czochralski grown n-type silicon samples before and after annealing for 30 minutes at 150°C and 450°C.

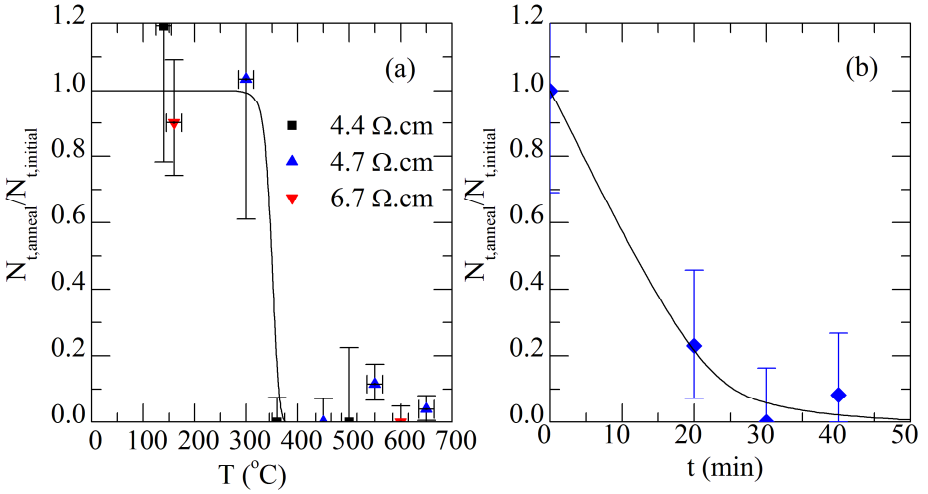

Fig. 2. (a) Remaining defect density after 30 min isochronal anneal for temperature ranging from 150°C to 650°C measured by lifetime measurements. The line is a guide to the eye. For temperatures above 360°C, the defect is annealed, while the defect remains recombination active for temperatures below 300°C (b) Remaining defect density after annealing at 360°C for different lengths of time. The line is an exponential fit.

In order to further investigate the nature of the defect, figure 2a shows the remaining defect density after isochronal annealing of 30 minutes for temperatures ranging from 150°C to 650°C. The samples came from two different ingots and had resistivities of 4.4Ω.cm (black square), 4.7Ω.cm (blue upward triangle) and 6.3Ω.cm (red downward triangle). This graph clearly shows that for temperatures above 360°C, the defect is annealed, while the defect remains recombination active for temperatures below 300°C. Figure 2b shows the injection dependence of the minority carrier lifetime after annealing at 360°C for different lengths of time. After a 30 min anneal at 360°C, the defect is completely deactivated. Additionally we observe no significant lifetime degradation of the deactivated samples after 8 months of storage.

As shown in our previous study[5], a possible scenario for the observed lifetime increase upon annealing is as follows. During ingot cooling (assuming it is a vacancy-rich ingot, which most ingots are today), vacancies pair with a range of available impurities in the crystal. Upon reaching 360°C, many of the vacancies will therefore pair with oxygen interstitials[6], creating the recombination active vacancy-oxygen defect observed. The remaining free vacancies, if any, will then pair with, for example, other vacancies at 270°C, and potentially phosphorus at 140°C. Upon annealing above 360°C, all of these pairs are dissociated[6]. However, as the sample is subsequently rapidly cooled, vacancies not only pair with oxygen, but also with other vacancies to form divacancies VV, and phosphorus to form vacancy-phosphorus pairs VP[7], and other possible compounds. Thus the proportion of vacancies paired with point defects other than oxygen may increase. Provided that these other vacancy-related complexes are less recombination active than VO pairs, the lifetime would therefore increase upon such annealing.

4. Conclusion

In summary, we demonstrate the presence of a lifetime limiting grown-in defect in n-type CZ wafers. We estimate the defect concentration to be below $N = 1\times10^{10}$ cm^{-3} and hence below the DLTS detection limit. In order to help identify the defect we anneal the samples between 150°C and 650 °C and demonstrate that the defect can be thermally deactivated by annealing above 360°C. Note that this defect is unlikely to have been observed before through lifetime measurements due to the fact that typical surface passivation steps, which are generally performed at around 400 °C, would already de-activate it. Silicon self-interstitials and vacancy-related defect pairs with low binding energies and are likely to be responsible for the observed lifetime recovery upon annealing. A potential candidate showing a deactivation energy between 300°C and 360°C is the vacancy-oxygen pair VO, however further independent results are needed to confirm this conjecture.

Acknowledgements

This work was supported by the Australian Renewable Energy Agency postdoctoral fellowship program (ARENA), and the Australian Research Council future fellowship program (ARC).

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