

Effect of Oxidations on Phosphorus-Diffused Crystalline-Silicon Substrates

James M. Gee*
Sandia National Laboratories
Albuquerque, NM

Richard R. King, Joerg H. Reiss,
and Kim W. Mitchell
Siemens Solar Industries
Camarillo, CA

S. Narayanan
Solarex
Frederick, MD

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INTRODUCTION

Phosphorus diffusions are used in the fabrication process for nearly all crystalline-silicon (c-Si) photovoltaic solar cells to form the emitter of the solar cell. These phosphorus diffusions are also well known to have beneficial gettering benefits – i.e., deleterious metallic impurities are gettered from the bulk of the c-Si substrate into the phosphorus doped layer.

In this study, we examined the effect of oxidations performed after the phosphorus diffusion. We were particularly interested in using the oxidation to passivate the surface of the phosphorus diffusion. Post-diffusion oxidations or moderate-temperature steps in oxidizing ambients are also commonly found in commercial fabrication sequences of c-Si solar cells. We found that the bulk lifetime was degraded in Czochralski (Cz) silicon due to the post-diffusion oxidation unless there was a gettering agent present during the oxidation. Possible explanations for these results are presented at the end of the paper.

EXPERIMENT

We performed several experiments to examine the effect of post-diffusion oxidations on bulk lifetime. The starting material included two different batches of 1- Ω cm, p-type Cz silicon. The phosphorus diffusions were performed in different locations (Solarex, Siemens, and Sandia) and with different processes (belt-furnace or tube-furnace diffusions). The oxidations were performed in the Photovoltaic Device Fabrication Laboratory (PDFL) at Sandia National Laboratories. The PDFL maintains control charts to verify high-lifetime processing, and routinely obtains photoconductance decay (PCD) lifetimes over 1 msec for oxidized intrinsic float-zone (FZ) wafers. Cell processing was completed in the PDFL, which included a photolithographically defined, evaporated TiPdAg metallization for the front grid, an evaporated aluminum back contact, and a contact sinter at 400°C in forming gas. The illuminated-IV, dark-IV, hemispherical reflectance, and absolute spectral

response of the completed cells were measured. The spectral data were analyzed to determine bulk diffusion lengths and back-surface recombination velocities. Some representative results of these experiments are presented in Fig. 1-3, and in Table 1.

We also examined the susceptibility of Cz silicon solar cells to light-induced degradation (LID) with and without a post-diffusion oxidation. The wafers and cells were processed at Siemens Solar Industries (SSI) for this experiment. LID refers to degradation of bulk diffusion length L due to illumination, and is found primarily in p-type c-Si solar cells with high concentrations of oxygen [1,2]. The bulk diffusion length L was determined by internal quantum efficiency measurements both before light exposure, and after sufficient light exposure to saturate the LID effect. According to a model of LID in which an inactive or less-active recombination center is converted to a state which is more effective at causing recombination, the change in $(1/L^2)$ is proportional to the concentration of these centers that are responsible for LID [2]. Fig. 4 shows the quantity $\Delta(1/L^2)$ for SSI Cz wafers after diffusion only, after diffusion and oxidation, and for finished cells with oxide passivation. These measurements indicate that the post-diffusion oxidation increases the susceptibility of the solar cells to LID.

DISCUSSION

We consistently found a degradation in bulk lifetime due to a post-diffusion oxidation with Cz silicon substrates (Fig. 1-3 and Table 1). This degradation was found with different starting materials and with diffusions performed in different laboratories using very different processes. The presence of aluminum on the back surface during the oxidation completely prevented the bulk lifetime degradation (Fig. 2 and 3, and Table 1), while the presence of TCA during the oxidation was insufficient to prevent the lifetime

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degradation (Fig. 3 and Table 1). We also found that the susceptibility of Cz silicon solar cells to LID was increased by the post-diffusion oxidation (Fig. 4). Annealing kinetics, degradation by forward biasing, thermal degradation, and other measurements are consistent with Fe-B pair dissociation as the cause of LID [2].

The above results collectively suggest that the interstitial Fe concentration and/or other impurities are increased in the bulk of the solar cell due to the post-diffusion oxidation. These impurities degrade the bulk lifetime unless there is a gettering agent (i.e., aluminum on the back surface) present during the post-diffusion oxidation. Similarly, a higher concentration of metallic impurities due to the post-diffusion oxidation would contribute to the increased susceptibility to LID.

There are several mechanisms that could account for the increase in impurity concentration by a post-diffusion oxidation. These mechanisms include the

following: (1) redistribution of the gettered Fe from the phosphorus-doped surface layer; (2) contamination of the wafer during the oxidation; or (3) dissolution of Fe precipitates already present in the bulk. We are currently examining higher concentrations of TCA during the oxidation to help prevent the lifetime degradation during the post-diffusion oxidation.

REFERENCES

1. James M. Gee, High-Efficiency One-Sun Photovoltaic Module Demonstration Using Solar-Grade Cz Silicon, final report, CRADA #1248, Sandia National Laboratories, Albuquerque (1996).
2. J. H. Reiss, R.R. King, and K.W. Mitchell, "Characterization of diffusion length degradation in Czochralski silicon solar cells," *Applied Physics Letters* 68, 3302-3304 (1996).

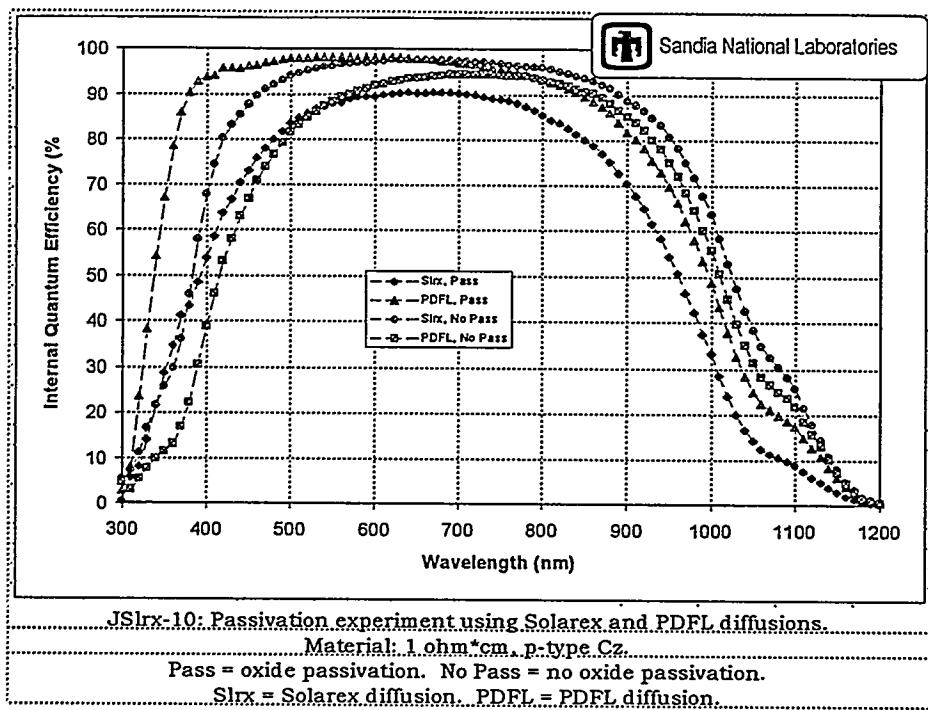
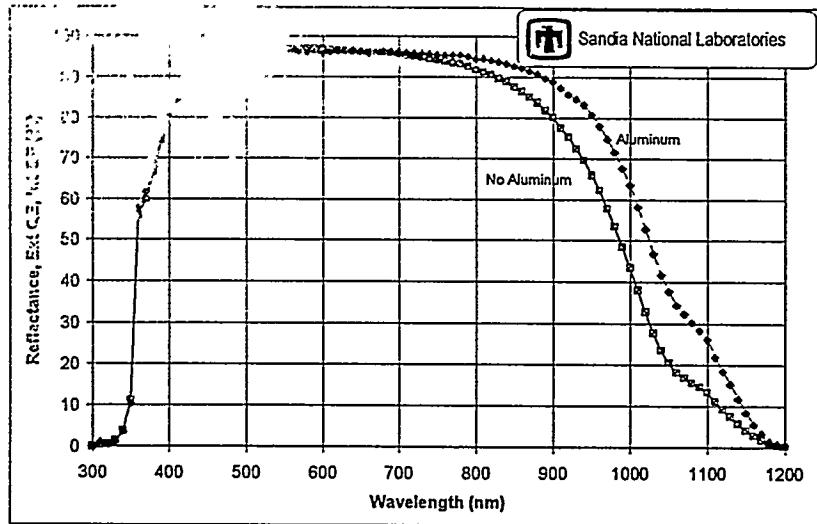
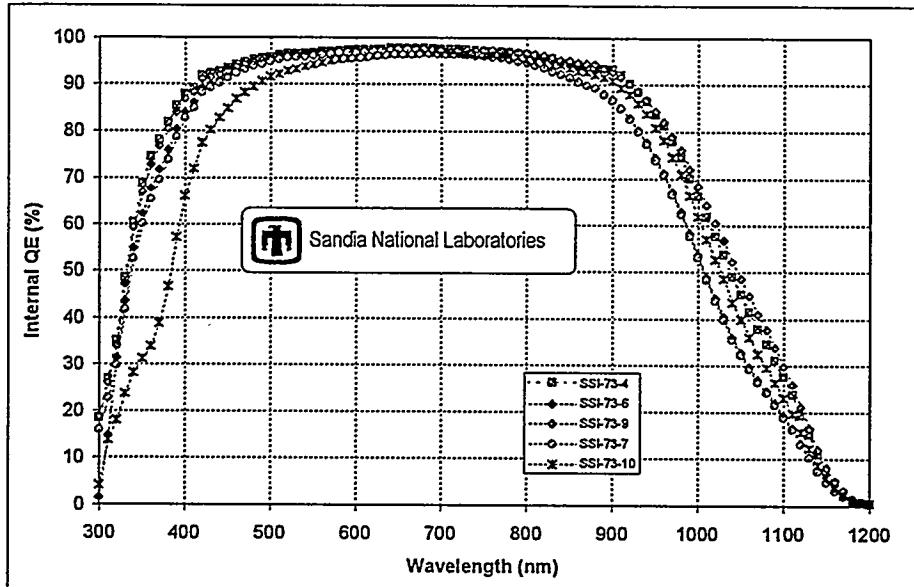


Figure 1. Representative internal quantum efficiency (IQE) spectra of an experiment that compared thermal-oxide passivation of Cz c-Si wafers diffused at Solarex and in the PDFL. The material was 1- Ω cm, p-type Cz silicon with a thickness (640 μ m) much greater than the diffusion length. The large thickness means that the effective diffusion length estimated from analysis of the IQE spectra is essentially the same as the bulk diffusion length. The effective diffusion length of the Solarex-diffused wafers decreased from 280 to 80 μ m due to the oxidation, while the effective diffusion length of the PDFL-diffused wafers decreased from 220 to 155 μ m due to the oxidation.



Lot: JSIrx-13
Split: 15 min, 750C oxidation.

Figure 2. Results of an experiment similar to Fig. 1, except that half of the wafers had aluminum on the back surface during the post-diffusion oxidation, all the wafers were diffused at Solarex, and a variety of oxidation schedules were used (15 to 45 minutes at 750 and 850°C). The effective diffusion lengths for this particular split (15-minute 750°C oxidation) were 117 and 269 μm for the cells without and with aluminum during the oxidation, respectively. The other oxidations exhibited similar trends; i.e., degradation in lifetime unless aluminum was present.



SSI-73-4	TCA and Al-alloy.
SSI-73-6	TCA and no Al-alloy.
SSI-73-9	No TCA and Al-alloy.
SSI-73-7	No TCA and no Al-alloy.
SSI-73-10	Control.

Figure 3. Representative IQE spectra from an experiment that compared oxidations with and without aluminum, and with and without trichloroethane (TCA) during the oxidation. TCA is a source of chlorine during oxidations, which is useful for gettering and preventing contamination during the oxidation. The TCA concentration was equivalent to 2% HCl. The c-Si material was 280- μm 1- Ωcm p-type Cz from Siemens Solar Industries, and the wafers were diffused at Siemens and oxidized in the PDFL. The control cell was not oxidized, and therefore has poor front- and rear-surface passivation. Table 1 presents estimates of L and S for these cells.

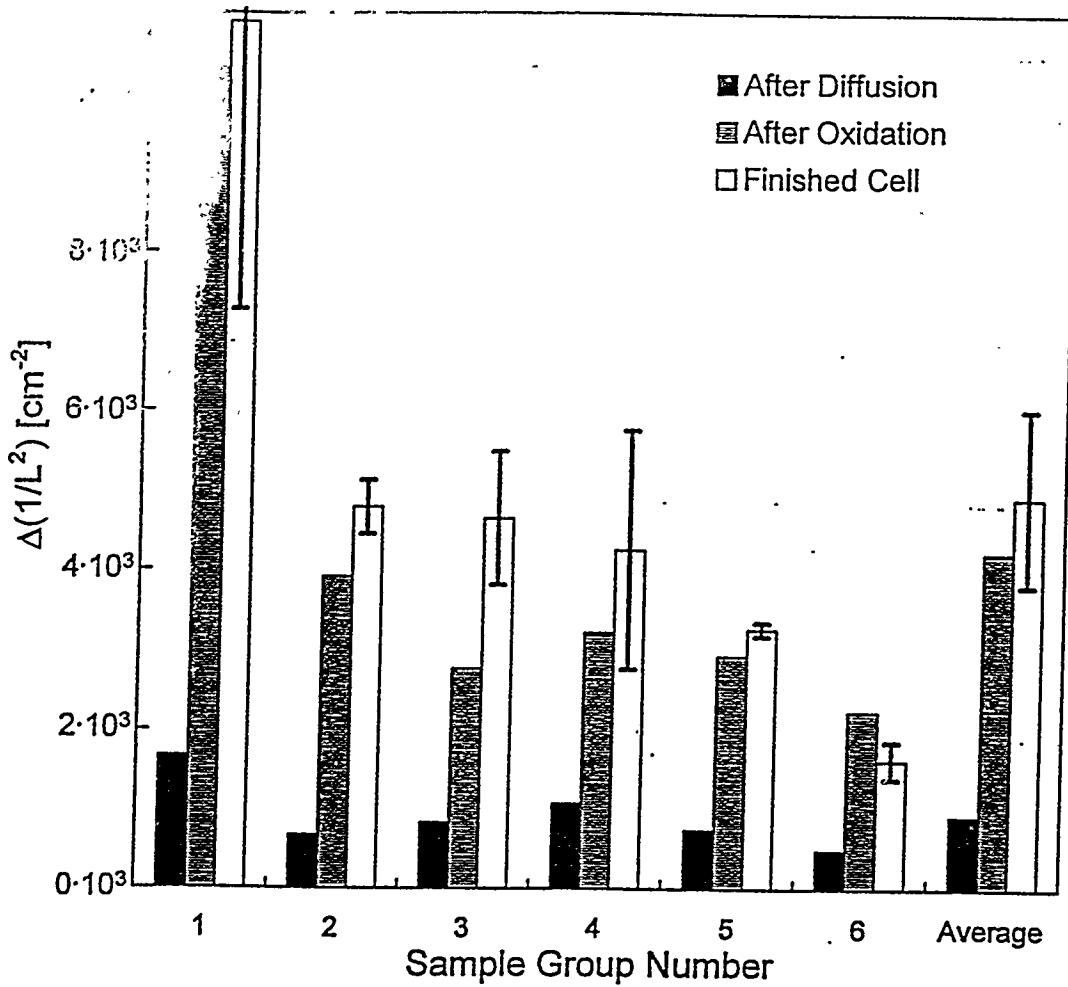


Figure 4. Change in concentration of recombination centers due to light-induced degradation of Cz silicon solar cells after a diffusion, after diffusion plus oxidation, and in complete cells that have both the diffusion and oxidation. "Sample Group" refers to a set of substrates from different portions of the ingot, and the error bars refer to the standard deviation of the group of cells.

Table 1. Summary of analysis of IQE data of Fig. 3. L_{eff} and η_c are the effective diffusion length and the internal collection efficiency for uniform photogeneration, and are derived from analysis of the IQE spectra. L and S are the bulk diffusion length and back-surface recombination velocity, and are estimated from L_{eff} and η_c . Back refers to the percentage recombination at the back surface at open circuit. Note that the analysis becomes insensitive to L or to S when L is much greater than the device width or when S is much greater than the diffusion velocity (D/W), respectively. W is the device thickness, and is equal to 280 μm .

Cell Name	TCA	Alum	L_{eff} μm	η_c %	L μm	S cm/s	Back %
SSI - 73 - 10	Cntrl		280	49	$\gg W$	$>10^6$	89
SSI - 73 - 7	N	N	157	39	164	$3.7 \cdot 10^5$	35
SSI - 73 - 9	N	Y	333	59	664	4101	83
SSI - 73 - 6	Y	N	163	40	177	$4.1 \cdot 10^5$	39
SSI - 73 - 4	Y	Y	397	54	$\gg W$	4165	85