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THE EFFECT OF OXIDATIONS ON PHOSPHORUS-DIFFUSED CRYSTALLINE-SILICON SUBSTRATES

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ABSTRACT: We examined the effect of oxidations on phosphorus-diffused crystalline-silicon p-type substrates. Oxidations subsequent to the phosphorus diffusion are of interest for passivating surfaces, and are commonly found in both high-efficiency laboratory-cell and commercial-cell fabrication sequences. We found a degradation of the bulk lifetime due to the oxidation in a variety of crystalline-silicon substrates that were diffused in various laboratories. The degradation was avoided if there was aluminum present on the back surface of the wafer during the oxidation. The study suggests that impurities gettered during the phosphorus diffusion can be released back into the bulk during a subsequent oxidation, and that the aluminum suppressed the bulk lifetime degradation by reabsorbing these released impurities.

Keywords: Gettering – 1: c-Si – 2: Silicon – 3.

1. INTRODUCTION

Phosphorus diffusions are used in the fabrication process for nearly all crystalline-silicon (c-Si) photovoltaic solar cells to form the emitter on the front surface of the solar cell. These phosphorus diffusions are also well known to have beneficial gettering benefits – i.e., deleterious metallic impurities are removed from the bulk of the c-Si substrate and are incorporated into the phosphorus-doped layer, resulting in the improvement of the lifetime of injected carriers in the c-Si substrate ("bulk lifetime") [1].

Oxidations performed after the phosphorus diffusion are of interest for passivation of the surface of the phosphorus diffusion. Such an oxidation is a common feature in high-efficiency c-Si solar cells. Post-diffusion oxidations or moderate-temperature steps in oxidizing ambients (e.g., firing of screen-printed metallizations) are also commonly found in fabrication sequences of commercial c-Si solar cells.

We examined the effect of oxidations on phosphorus-diffused p-type Czochralski (Cz) c-Si substrates. A variety of phosphorus diffusion sources, types of oxidations, and sources of Cz c-Si substrates were examined. We also examined the effect of a post-diffusion oxidation on light-induced degradation in Cz silicon, which is an effect that has been recently described in Cz silicon solar cells [2]. This paper describes the experiments and results, and provides a possible physical explanation involving the effect of the oxidation on metallic impurities that were gettered during the phosphorus diffusion.

2. 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-Ωcm, (100)-oriented, p-type Cz silicon. One set of Cz wafers was very thick (640 μm), which facilitated determination of bulk diffusion length from the cell results. The second set of substrates was photovoltaic-grade Cz silicon from Siemens Solar Industries (SSI). The phosphorus diffusions were performed in different locations (Solarex, SSI, and Sandia) and with different processes (belt-furnace or tube-furnace diffusions). These diffusions have surface concentrations in the mid-10^{19} (Sandia) and low-10^{20} cm^{-3} (SSI and Solarex) range. Most of 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 high-resistivity float-zone (FZ) wafers [3]. The oxidations were generally performed in a separate step subsequent to the phosphorus diffusion in a furnace tube dedicated to oxidations. However, we also examined the effect of oxidations performed *in situ* with the phosphorus diffusion – i.e., the oxidation is performed immediately after the phosphorus diffusion in the same furnace tube without removing the wafers from the tube [4]. This experiment reduces uncertainties due to handling of the substrates between the phosphorus diffusion and the oxidation.

Cell processing was completed in the PDFL, which included a photolithographically defined, evaporated TiPdAg metallization for the front grid, an evaporated aluminum back contact, a contact sinter at 400°C in forming gas, and an evaporated double-layer TiO_2/Al_2O_3 antireflection coating. The cells were either isolated on or scribed from the 100-mm diameter c-Si wafers with laser-scribed grooves. This process sequence routinely achieves efficiencies in the 15% range using multicrystalline or Cz silicon substrates, planar surfaces, and passivated surfaces (oxide on the front surface and an aluminum-alloyed rear surface) [5]. 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 by analyzing the near-infrared internal quantum efficiency [6]. Figures 1 through 4 and Table 1 present some representative results from these experiments.

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

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were processed at Siemens for this experiment. LID refers to degradation of bulk diffusion length L due to illumination, and is found in some c-Si solar cells with p-type substrates. The bulk diffusion length 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 the centers that are responsible for LID. Fig. 5 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.

3. DISCUSSION

We consistently found a degradation in bulk lifetime due to a post-diffusion oxidation with Cz silicon substrates (Fig. 1 through 4, and Table 1). This degradation was found with different starting materials and with diffusions performed in different laboratories using very different processes. In addition, Schubert and Gee and Stocks *et al.* *both* found very similar behavior with *multicrystalline* silicon; i.e., degradation of bulk lifetime due to a post-diffusion oxidation unless there was Al present during the oxidation [7,8]. Hence, the effect is present in many different c-Si materials processed in different laboratories. The bulk diffusion length degraded from around 280 μm to around 80 μm in some 1-Ωcm Cz wafers, so the bulk lifetime degradation can be quite substantial. The presence of aluminum on the back surface during the oxidation completely prevented the bulk lifetime degradation (Fig. 2 and Table 1), while the presence of TCA during the oxidation was insufficient to prevent the lifetime degradation (Fig. 3 and Table 1). The degradation was also found for *in situ* post-diffusion oxidations, although the degradation was less pronounced (Fig. 4). Finally, we also found that the susceptibility of Cz silicon solar cells to LID was increased by the post-diffusion oxidation (Fig. 5). Annealing kinetics, degradation by forward biasing, thermal degradation, and other measurements are consistent with Fe-B pair dissociation as one cause of LID, although other mechanisms may also contribute to LID [2].

The above results collectively suggest that the interstitial Fe concentration and/or other metallic 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 and/or other metallic precipitates already present in the bulk. The wide prevalence of this phenomenon suggests that contamination is not responsible since contamination is likely to be laboratory and material specific. Numerical simulations of precipitation and dissolution find that that very long times are required for precipitate dissolution, which suggest that dissolution of precipitates is unlikely [9]. On the other hand, the time and temperature required for the oxidation is similar to the phosphorus diffusion step, so that redistribution of metallic impurities from the gettering site seems quite possible.

4. SUMMARY

We found that the bulk lifetime was degraded in Cz silicon due to a post-diffusion oxidation, and that the lifetime degradation could be avoided if aluminum was present on the back surface of the wafer during the oxidation. The degradation in diffusion length could be quite large – from 250 μm for the control cells to 80 μm for the oxidized cells in some experiments using 1-Ωcm p-type Cz substrates. We also examined the susceptibility of Cz silicon solar cells to light-induced degradation (LID) with and without a post-diffusion oxidation, and found that the susceptibility of Cz silicon solar cells to LID was increased by the post-diffusion oxidation. Our experiments collectively suggest that the interstitial Fe concentration and/or other metallic impurities are increased in the bulk of the solar cell due to a post-diffusion oxidation. Redistribution of gettered metallic impurities from the phosphorus diffusion during the oxidation is a possible mechanism to account for the observed bulk lifetime degradation.

5. ACKNOWLEDGEMENTS

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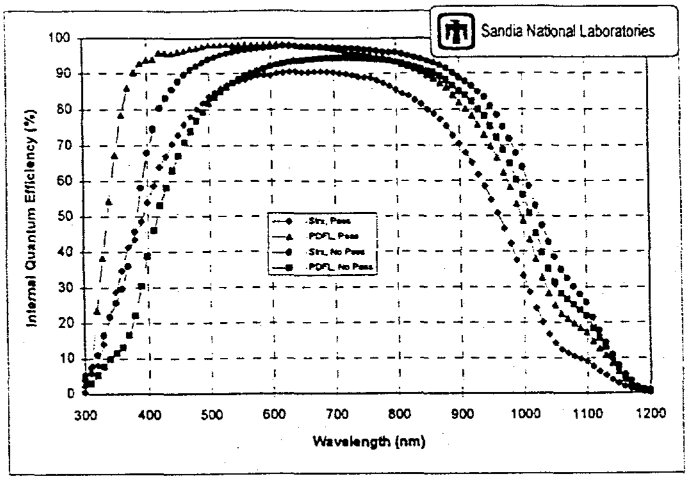
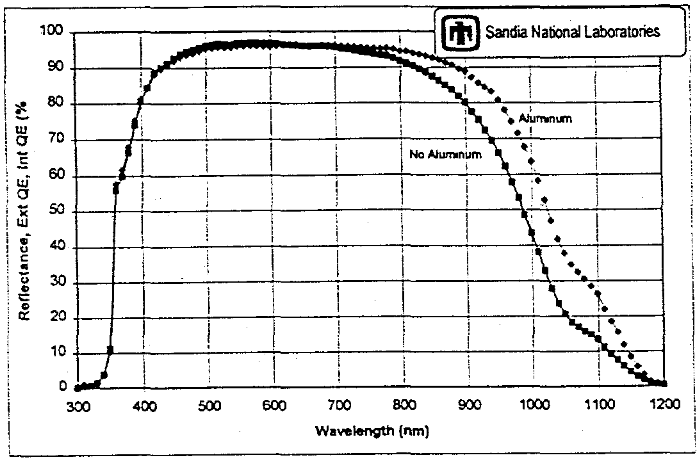
6. REFERENCES

1. J.M. Gee, "Phosphorus diffusions for gettering-induced improvement of lifetime in various silicon materials," 22nd IEEE Photo. Spec. Conf., pp. 118-123 (1991).
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).
3. J.M. Gee, *et al.*, "Process development for high-efficiency silicon solar cells," 6th Intern. PV Science and Engineering Conf. (PVSEC- 6), pp, 25-32 (1992).
4. P.A. Basore, *et al.*, "Simplified high-efficiency silicon cells processing," 7th Intern. PV Science and Engineering Conf. (PVSEC- 7), pp. 61-64 (1993).
5. W.K. Schubert *et al.*, "A simple single-photomask process for fabrication of high-efficiency multicrystalline-silicon solar cells," 25th IEEE Photo. Spec. Conf., pp. 1327-1330 (1995).
6. P.A. Basore, "Extended spectral analysis of internal quantum efficiency," 23rd IEEE Photo. Spec. Conf., pp. 147-152 (1993).
7. W.K. Schubert and J.M. Gee, "Phosphorus and aluminum gettering – investigation synergistic effects in single-crystal and multicrystalline silicon," 25th IEEE Photo. Spec. Conf. pp. 437-440 (1996).
8. Matthew Stocks, Andrew Blakers, and Andres Cuevas, "Minority carrier lifetimes of multicrystalline silicon solar cells during processing," this conference.
9. Teh Y. Tan, R. Gafiteanu, and U. Gösele, "Physical and numerical modeling of impurity precipitation, precipitate dissolution, and gettering of precipitated impurities in silicon," 6th NREL Workshop on the Role of Impurities and Defects in Silicon Device Processing, Snowmass, CO, August 12-14, 1996.



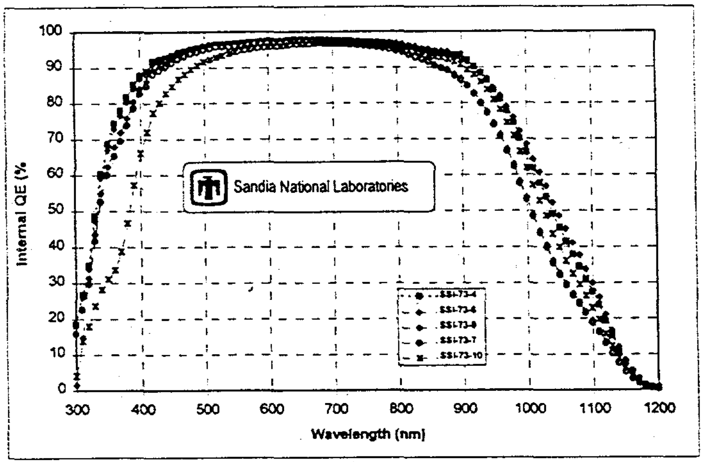
JSlrx-10: Passivation experiment using Solarex and PDFL diffusions.
Material: 1 *ohm*cm, p-type Cz.*
Pass = oxide passivation. No Pass = no oxide passivation.
Slrx = Solarex diffusion. PDFL = PDFL diffusion.

Figure 1. Representative internal quantum efficiency (IQE) spectra of an experiment that compared oxide passivation of Cz c-Si wafers diffused at Solarex and in the PDFL. The material was 1-Ωcm, p-type Cz silicon with a thickness (640 μm) 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 diffusion length of the Solarex-diffused wafers decreased from 280 to 80 μm due to the oxidation, while the diffusion length of the PDFL-diffused wafers decreased from 220 to 155 μm due to the oxidation.



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

Figure 2. Results of an experiment similar to Fig. 1, except that half of the wafers had Al 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 bulk 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.

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. Note that the analysis becomes insensitive to L or to S when L is greater than the device width W or when S is greater than the diffusion velocity (D/W), respectively. W is 280 μm.

Cell Name	TCA	Alum	L_{eff} μm	η_c %	L μm	S cm/s
SSI-73-10	Cntrl		280	49	>>W	$>10^6$
SSI-73-7	N	N	157	39	164	$3.7 \cdot 10^5$
SSI-73-9	N	Y	333	59	664	4100
SSI-73-6	Y	N	163	40	177	$4.1 \cdot 10^5$
SSI-73-4	Y	Y	397	54	>>W	4200

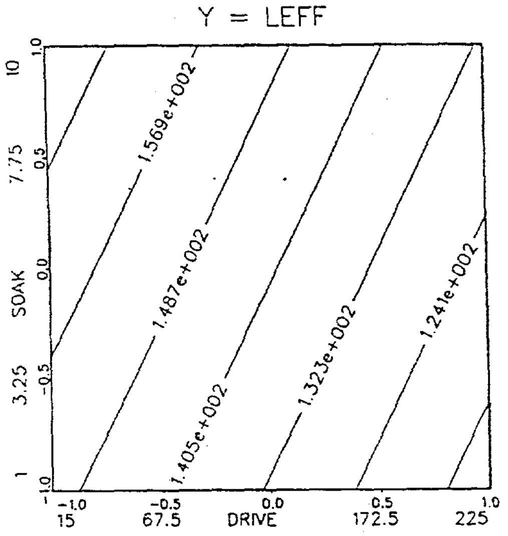


Figure 4. Representative response surface of an experiment that examined the effect of seven different diffusion and surface preparation parameters on bulk lifetime in SSI Cz silicon using a statistical experimental design. *Soak* and *Drive* refer to inert and oxygen soak times (minutes) of $POCl_3$ diffusion process, respectively. Contours are the effective diffusion length (L_{eff}) in μm. The diffusion length decreases with a longer oxygen soak time (i.e., longer *in situ* oxidation) and increases with a longer inert soak time (i.e., a heavier diffusion with more gettering). The 95% confidence limits on the contours is around 20 μm.

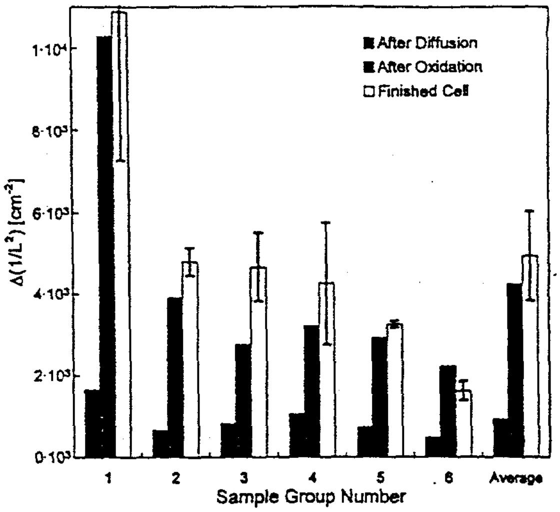


Figure 5. Change in concentration of recombination centers due to light-induced degradation of Cz silicon solar cells after a diffusion, after diffusion plus oxidation, and in complete cells that have both the diffusion and oxidation. "Sample Group" refers to a set of substrates from different portions of the ingot, and the error bars refer to the standard deviation of the group of cells.