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PROCESSING EXPERIMENTS FOR DEVELOPMENT OF HIGH-EFFICIENCY SILICON SOLAR CELLS

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Abstract

Fabrication of high-efficiency silicon solar cells requires processing technology capable of maintaining long bulk carrier lifetime and low surface recombination. Development of long-lifetime processing techniques using experimental designs based on statistical methods is described. The first three experiments investigated pre-oxidation cleans, phosphorus gettering, and a comparison of different phosphorus diffusion sources. Optimal processing parameters were found to depend on type of silicon material.

Introduction

The achievement of high efficiencies in silicon solar cells requires minimizing recombination losses simultaneously throughout the solar cell. Emitter recombination can be reduced through clever cell design, while surface and bulk recombination losses are minimized through processing techniques. Surface recombination is minimized by growth of high-quality SiO_2 passivation layers, while bulk recombination losses are controlled by using long-lifetime silicon and by using processing technology that maintains a long bulk lifetime through the cell fabrication sequence.

Sandia National Laboratories operates a silicon fabrication laboratory (Photovoltaic Device Fabrication Laboratory, PDFL) for the United States Department of Energy. The purpose of the PDFL is to assist industry in development and adoption of new processing technologies for both higher performance and lower cost silicon solar cells. These new technologies were typically first demonstrated at university or government R&D laboratories; the intent of the PDFL is therefore to decrease the time between laboratory advances and commercial adoption. The strategy employed in operation of the PDFL is to perform process research in conjunction with university and industrial partners in a facility with a carefully controlled environment and demonstrated high-quality processing. The latter requirement ensures that the experiments are meaningful and are readily transferrable.

In this paper, we briefly report results of three experiments conducted in the PDFL investigating high-lifetime processing. These experiments examined pre-oxidation cleans, gettering, and different sources for phosphorus diffusions.

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Pre-Oxidation Cleans

The surface and bulk of a silicon wafer are well known to be very sensitive to the cleaning steps immediately prior to a high-temperature process. A wafer cleaning sequence widely used in industry involves several elevated-temperature chemical baths using hydrogen peroxide (i.e., RCA clean) and is relatively expensive. An experiment was designed using a multi-factorial experimental-strategies approach to investigate the effectiveness of different wafer preparations on the post-oxidation PCD lifetime of four different silicon materials. (PCD lifetime refers to the decay constant of a photoconductive decay measurement. This value is related to both the surface recombination velocity and to the bulk lifetime.) The experiment consisted of 23 different factors (Table 1). The statistical nature of the experimental-strategies approach requires only 24 trials to determine which factors are "main effects." Each trial represents an individual lot and consists of a specific wafer-cleaning sequence, an oxidation in dry O_2 with post-oxidation anneal for 15 minutes in argon, a forming-gas anneal, and measurement of the PCD lifetime. The experiment is described more fully by McBrayer (1).

An example of results from the experiment is presented in Figure 1. This figure shows the more significant factors affecting PCD lifetime for high-resistivity float-zone silicon wafers. From this experiment, we were able to define a cleaning sequence capable of producing post-oxidation lifetimes in excess of 2 ms that is also significantly simpler than the RCA sequence. Results of this experiment have already been transferred to an industrial research partner. Other silicon materials had different factors that were significant. In general, though, the post-oxidation PCD lifetime of silicon materials with lower starting lifetimes was less sensitive to the cleaning sequence.

Gettering

Gettering refers to a process step that improves the quality of a crystal by removing impurities or defects from device regions. Gettering requires two actions to occur: (1) inducing impurities and/or defects to migrate from one region of the crystal to a less important region, and (2) trapping these impurities in the less important region. Movement and trapping of impurities and defects is accomplished through surface and/or thermal treatments of the crystal.

Phosphorus diffusion is well known to act as a gettering agent in silicon wafers. We examined phosphorus diffusion as a gettering agent for six different silicon materials. The experiment consisted of the following process sequence: wafer clean, phosphorus diffusion (950°C, 30 min, $POCl_3$), KOH etch, wafer clean, dry oxidation (950°C, 75 min, dry O_2), forming-gas anneal, and measurement of the PCD lifetime. Each process lot included a split where the wafers did not receive the phosphorus gettering diffusion. Table 2 summarizes results of the experiment. Initial conclusions are that high-quality materials (float-zone and magnetic-Czochralski) are not affected by phosphorus gettering while low-quality materials (Czochralski) are significantly improved. Continuing experiments are examining the effect of further thermal treatments on lifetime of gettered wafers and of the gettering action of other surface treatments. Future work will examine silicon materials provided by industry (e.g., polycrystalline silicon).

Diffusion Sources

A variety of dopant sources is available for diffusions. These sources have different characteristics that affect their cost and the quality of the wafer after processing. Note that the total cost of a diffusion source includes material costs, process throughput, capital costs, and costs associated with handling, storage, and environmental and safety systems.

A study has been initiated to compare the relative merits of different diffusion sources. The initial experiment examined phosphorus diffusions using PH_3 and $POCl_3$. PH_3 is a highly toxic gas that requires special storage, delivery, safety, and environmental control systems. $POCl_3$ is a relatively safe liquid that requires a temperature-controlled bubbler. High-lifetime wafers (high-resistivity FZ and MCz) were processed with the following sequence: (1) wafer clean, (2) phosphorus diffusion, (3) deglaze, (4) oxidation (950°C, 65 min, dry O_2) with in situ Ar anneal (15 min), (5) forming-gas anneal, and (6) measurement of lifetime and J_{oe} (saturation current density associated with emitter recombination) by means of PCD. The experiment is described more fully by Ruby (2). Figure 1 shows J_{oe} as a function of sheet resistance. The electrical characteristics of the emitters formed by the two different diffusions sources are largely equivalent, although the $POCl_3$ diffusions occasionally produced poor results. Analysis of the costs associated with the two sources showed that PH_3 is less expensive than $POCl_3$. Future work will compare other phosphorus diffusion sources (solid source and phosphorus-doped CVD oxide) and will investigate boron diffusions.

Conclusions

We have reviewed the operational strategy of the PDFL and of several processing experiments in progress. By use of an experimental-strategy approach in a clean and closely controlled environment, we have shown that advanced processes can be readily transferred to industry. The importance of this activity is demonstrated by the fact that there are now six different photovoltaic companies involved in cooperative research programs with the PDFL.

References

1. J.D. McBrayer et al., in 1990 DOE/Sandia Crystalline Photo. Techn. Project Review Meeting, D.S. Ruby ed., SAND90-1821, Albuquerque, NM (July 1990).
2. D. S. Ruby, J. M. Gee, P. A. Basore, and J. D. McBrayer, ibid.

Table 1. Factors in main effects wafer-cleaning experiment.

No.	Factor	Low	High
1.	Condition	Clean	Contam.
2.	Estek Rinse/Dry	No	Yes
3.	$HF:H_2O$ Ratio	1:100	1:10
4.	$HNO_3:HF$ Ratio	20:1	200:1
5.	Degrease	Low	High
6.	Unused	——	——
7.	BOE etch time	0	HPO+1min
8.	$HNO_3:HF$ time	0	20min
9.	$H_2SO_4:H_2O$ time	0	20min
10.	H_2SO_4 Ratio	3:1	5:1
11.	1st-HF time	0	2min
12.	Summa time	0	20min
13.	Summa temperature	25	50°C
14.	RCA1 time	0	20min
15.	RCA1 temperature	40	80°C
16.	2nd-HF time	0	2min
17.	RCA2 time	0	20min
18.	RCA2 temperature	40	80°C
19.	$HNO_3:HF$ time	0	20min
20.	3rd-HF tie	0	2min
21.	R/D storage time	0	60min
22.	Dry oxidation	950	1100°C
23.	Forming-gas anneal	FGA1	FGA2

Table 2. PCD lifetime (μsec) of oxidized silicon wafers with and without phosphorus gettering. A total of 10 wafers of each type in five different process runs are included in the statistical analysis. The p-type Cz wafers show the largest benefit of gettering. Low-, mid-, and high-resistivity refer, respectively, to 0.2, 10, and 100 Ωcm.

Wafer Type	Gettered	Average	Std.Dev.
p, low-ρ, FZ	Y	10.21	3.60
	N	9.25	1.82
n, high-ρ, FZ	Y	3975	853
	N	3845	737
p, low-ρ, MCz	Y	5.71	1.68
	N	7.10	4.98
n, high-ρ, MCz	Y	3235	964
	N	2633	465
p, mid-ρ, Cz	Y	240.2	117.7
	N	44.5	19.7
n, mid-ρ, Cz	Y	487.6	260.7
	N	372.9	169.8

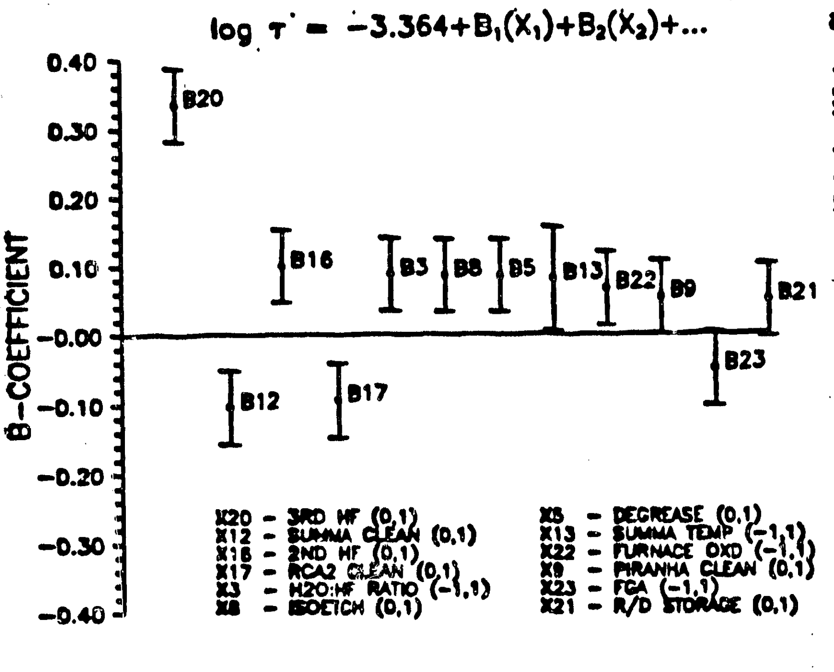

Figure 1. Regression coefficients for PCD lifetime from main effects experiment using high-resistivity FZ silicon (12 largest factors).

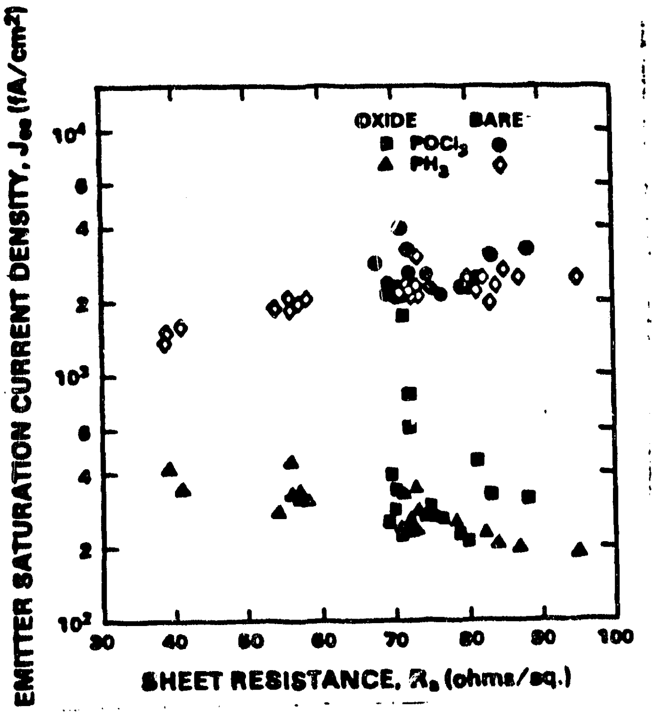

Figure 2. Emitter saturation current density versus emitter sheet resistance for PH_3 and $POCl_3$ diffusions. Oxide and bare refer to phosphorus-diffused wafers with and without an oxide.

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