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RESEARCH, DEVELOPMENT AND FABRICATION OF LITHIUM SOLAR CELLS

FIRST QUARTERLY REPORT

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OF LITHIUM SOLAR CELLS

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from

Centralab Semiconductor Division

under JPL Contract 952546

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ABSTRACT

In this quarter, most attention was concentrated on various acceptor sources, and the interaction of these sources with subsequent lithium solar cell properties. It appears possible now to obtain increased output from oxygen-poor silicon, and to provide cells with a gradual transition from earlier cells which used standard BCl_3 processes. The shipments scheduled and much of the work for the next period will continue the emphasis of the present period.

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1.0 INTRODUCTION

The present contract continues development of high efficiency solar cells using lithium doping to maintain high output in the charged particle space environment.

Previous JPL contracts led to improved cell performance and consistency, and showed the areas needing improvement. One problem was to understand why, after equivalent lithium diffusion schedules, cells using oxygen-poor silicon generally had lower Voc (and usually also Isc) than cells made from crucible grown silicon. The main reason was thought to be the boron diffusion method used to form the P+ layer, and the interaction of the resulting N-silicon with the in-diffused lithium.

Therefore, most recent work has been concentrated on evaluating various methods of boron diffusion. In addition to selecting the correct diffusion conditions to realize the best P+ layer qualities, the overall cell performance has to be monitored, and in some cases the fabrication sequence adjusted, to best match the boron diffusion method used.

2.0 TECHNICAL DISUCSSION

2.1 BORON DIFFUSION METHODS

The boron trichloride source used mostly on Centralab's previous contracts has been used successfully for producing large numbers of good performance P/N solar cells for space use. Any alternate system chosen must reduce the disadvantages of BCl_3, while retaining its important advantages. The final choice of the best boron diffusion method will be determined by the quality of the lithium cells produced, and the repeatability of the process for large numbers.

2.1.1 Advantages of BCl_3

a. It is a proven source, capable of good control for large production quantities.

b. Chlorine-containing gases in the diffusion tube react with the silicon giving gas-etching. This makes the process less dependent on the surface finish of the starting slices, and enables good cells to be formed even when the silicon has a lapped surface finish.

c. BCl_3 forms a boron-rich layer ½ to 1 mil thick at the silicon surface. This layer acts as the boron source for in-diffusion, and also as a sink for impurities gettered from the silicon. This layer is mechanically removed when the slices are cooled and boiled in nitric acid. The gettering may increase the minority carrier diffusion length, or the perfection of the P/N junction region.

d. The surface left on the silicon when the layer in (c) is removed has low reflectivity over the solar spectrum range. Thus, high cell currents can be obtained either by leaving this surface film intact, or by removing some of the film and over-coating it with an additional SiO antireflective coating.

2.1.2 Disadvantages of BCl_3

a. The etching in 2.1.1 (b) makes it difficult to form complex structures in lithium solar cells. Such structures include those needing a thin N+ or oxygen layer under the P+ layer, to increase cell stability after exposure to high particle fluences.

b. The BCl_3 process can introduce stresses into the silicon, probably from the layer formation described in 2.1.1 (c). These stresses show as increased etch pit density (increased dislocation density) or in extreme cases as warpage, or as decreased breaking stress. The stresses impose a limit on how thin the original slice can be and make the process more dependent on surface finish for thinner slices. It is also believed that these stresses can affect the behavior of lithium subsequently diffused into the cell, particularly for oxygen-poor silicon, and can lead to lower I-V parameters and reduced ability to recover after irradiation.

c. The antireflective boron layer may reduce the bonding of titanium to the surface, leading to decreased contact adhesion.

NOTE: The "normal" defects (mismatch, strain, and non-ionized precipitates) resulting from the high concentration of boron needed in the very shallow P+ surface layer required for good space solar cell operation are probably comparable for BCl_3 to those resulting from any alternate boron source.

2.1.3 Other Boron Sources

Several alternate sources have been used successfully for other devices. These sources include solid forms (boron oxide, boron nitride) in suspension or used as vapor sources, liquid forms (boron tribromide, trimethyl borate) or gaseous forms (diborane).

In preliminary tests, boron nitride, trimethyl borate and diborane were not promising. Boron oxide and boron tribromide showed more promise, and are discussed below.

In general, the lack of gas etching requires taking more care in surface finish and cleanliness. To obtain similar diffused layer properties to those used on present good space cells, it was necessary to adjust the temperature time cycle for each source. There was often irregular gas flow, causing nonuniformity in diffused layers. Some sources left surface films which did not have beneficial antireflective properties, and which were tenacious and difficult to remove without harming the shallow P+ layer. Often when the diffusion conditions were comparable to those obtained with BCl_3 the resultant I-V properties of the cells was poor.

2.1.3.1 Boron Oxide

Although some cells comparable to BCl_3 cells were made, generally the I-V values were lower and often an uneven surface layer was formed. However, the etch pit density was not increased seriously in contrast to the standard BCl_3 process. These were also some encouraging signs that Voc was increased for oxygen-poor silicon after standard lithium diffusion cycles.

2.1.3.2 Boron Tribromide (BBr_3)

Other contractors in the previous year supplied good quality lithium cells using this source. At first, in the present work, there was some difficulty in acquiring the necessary consistency of diffusion parameters, and of Isc and Voc values. The liquid BBr_3 was maintained at 28°C, and the vapor was carried into the diffusion tube by nitrogen, with small addition of oxygen. The important variables are the slice temperature, the flow rate of BBr_3 (too much leaves a boron stain film) and adjustment of the oxygen flow rate between the extremes of too little (where insufficient B_2O_3 is formed at the silicon surface) and too much (where the thicker SiO_2 layer formed reduces the boron surface concentration).

Later tests have shown success in adjusting these variables, to allow good I-V characteristics for all three forms of silicon growth, with small increase in etch pit density. More work continues on BBr_3 processed cells.

2.1.3.3 Modified BCl_3 Process

The conventional BCl_3 process includes three periods, a warm-up time in inert gas, a deposition time during which BCl_3 is introduced into the inert gas flow, and the diffusion time when the BCl_3 is switched off. Typical times are 8 minutes for each of the first two periods, and 10 minutes for the diffusion time. Analysis of the process showed that the boron layer forms during the deposition time, and this time was determined by the need to provide excess boron for interaction at the silicon surface, both for high surface concentration and for formation of a good antireflective coating. The deposition time was systematically reduced and the effects studied.

As the time was decreased the amount of boron layer decreased linearly. The blue boron layer left after diffusion, also became fainter and for short times left the silicon surface close to bare silicon in color. There were occasional stains and visual effects from gas etching, but these were not serious, and the bonding strength of titanium-silver seemed greater than for "normal" BCl_3 cells.

The measured etch pit density fell drastically for deposition times below 4½ minutes. Typical values for deposition times of 8, 5, and 2 minutes were 60,000, 45,000, and $<$ 10,000 etch pits per cm^2 respectively. If no lithium was introduced, control cells made from all these forms of silicon showed gradually increasing Isc as the deposition time was increased; this was mainly from increased short wavelength response, caused by the thicker boron film.

When lithium was added, for increasing deposition time, oxygen-rich silicon showing increasing Isc (as for the control cells) and slight increase in Voc. On the other hand, for lithium cells with increasing deposition times, oxygen-poor silicon showed decreasing Isc (mainly in long wavelength response) and steady decrease in Voc. The results for short deposition times were encouragingly close to the best values found for non-BCl_3 sources. This modified BCl_3 process will be continued, because of its ability to control the interaction of boron with silicon, thus allowing good comparison of the real effects of boron diffusion on other parameters (especially on the silicon, and the lithium cycle) with fewer perturbing variables. It also has the advantage of giving continuity between older and newer lithium cells. and should help in understanding the physical mechanisms operating.

2.2 LITHIUM INTRODUCTION

In this period, the lithium diffusion cycles used have been maintained to give moderate lithium concentrations ($\sim 5X10^{14}cm^{-3}$ near the P/N junction as measured by capacitance) to allow comparison of the various acceptor methods. Later, more low temperature diffusion schedules will be used.

Using similar schedules lithium was diffused into several slices of N- silicon, including all three forms of crystal growth, and a wide range of initial donor concentrations. The lithium concentration near each face of the slice was measured and did not show dependence on either the silicon growth method or the background concentration.

Some additional conclusions have been drawn concerning the effect of lithium on etch pit formation:

a. The P+ layer etched differently when lithium had been diffused from the back of the slice towards the P+ layer. The background was bumpy, and contained oriented hillocks, compared to well defined oriented etch pits when no lithium was near the P+ layer.

b. The lithium drastically reduced the apparent etch pit density at the back surface, where it was introduced. However, where pits did remain they were the same size as those in the lithium-face area, suggesting an equal etch rate.

Tests continue to find the reason for these differences.

2.3 OTHER TOPICS

Some crucible grown ingots were purchased from outside suppliers and are being processed for comparison with Centralab ingots.

Continuous refinement is proceeding in the techniques for applying optimum antireflective coatings, and also contacts with the best adhesion and lowest resistance.

Some of the earlier conclusions drawn on control cells made with no lithium may have been incorrect because of contact barriers. These tests are being repeated.

Breaking tests were performed on thirty crucible-grown slices, fifteen slices being chemically polished, fifteen with a lapped finish. Five slices of each surface finish were given three different BCl_3 deposition times. Unexpectedly, the breaking weights did not show any consistent dependence on the deposition time.

More tests were made on front surface introduction of lithium, and of oxygen layer cells. These will be continued. Tests will also be continued on aluminum contacts.

Some cells were made with deeper P/N junctions (0.7 and 1.0 microns). As expected the short wavelength response decreased, the bulk response remained steady, and the curve fill-factor only increased slightly.

2.4 CELL SHIPMENTS

The first sixty cells of the 600 scheduled under the contract are being completed.

The first shipment will use F.Z. silicon and the same lithium diffusion schedule for all cells. Half the cells will use the standard BCl_3 cycle, the other half will be diffused using BBr_3.

3.0 CONCLUSIONS

There has been improvement in control and understanding of various methods for in-diffusing boron. There are encouraging signs that the oxygen-poor silicon will have improved performance over earlier tests, and it is now possible to bridge the gap completely between the last contract BCl_3 methods and the methods being used currently. This continuity is important because it allows stabilization of all the other cell fabrication variables, as well as consistency in irradiation and storage conditions. The interaction of the other cell fabrication procedures with the acceptor diffusion is being studied in detail to optimize all the cell properties.

4.0 RECOMMENDATIONS

Work will continue on the interaction of all the cell fabrication steps. Cells with various acceptor diffusion methods will be submitted for irradiation.

5.0 NEW TECHNOLOGY

Most of the advances have been the result of application of already existing technology. Therefore, no new technology is reportable in this period.