Analysis of Selective Phosphorous Laser Doping in High-Efficiency Solar Cells

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***Abstract*—This paper focuses on the analysis of local phosphorous laser doping in high-efficiency solar cells. Those so-called selective emitters are intended to reduce the contact recombination and resistance in order to increase the solar conversion efficiency. Sample solar cells are prepared using laser chemical processing as the laser doping technique and analyzed via analytical models and *suns*–V_{oc} measurements at high illumination densities. It can be shown that fully ohmic contacts can be manufactured on the investigated selective emitters which exhibit low dark saturation currents. The specific recombination current density of the local laser doping is determined experimentally to be $< 8.5 \times 10^{-13}$ A/cm^2 for planar surfaces.**

***Index Terms*—Doping, laser chemistry applications, photovoltaic cells.**

I. INTRODUCTION

SELECTIVE emitters are incorporated into many types of silicon solar cells. These include UNSW's PERT and PERL [1], [2] cells, the buried-contact cells developed by UNSW and commercialized by BP Solar [3], [4], Stanford's point-contact cells [5], ANU's Sliver cells [6], and some screen-printed cells via doped-finger [7] and "semiconducting" finger technologies [8]. A selective emitter mitigates contact resistance [9], [10] and recombination [11] by being heavily doped under metal contacts, while ensuring low recombination elsewhere by being lightly doped in optically active regions [12].

In this paper, we explore a recently developed and relatively inexpensive means to attain a selective emitter by laser chemical processing (LCP) [13]. Following a light diffusion over the entire front surface, a liquid-jet-guided laser is used to simultaneously open small regions in a front passivation layer (such as silicon dioxide or silicon nitride) and to heavily dope the underlying silicon. Based on a technique realized by Richerzhagen [14], the procedure is fast and reliable and requires neither a damage etch nor a furnace step.

This paper investigates whether the recombination and contact resistance associated with LCP selective emitters are sufficiently low to make them compatible with high-efficiency solar cells. Following a description of experimental solar cells fabricated with LCP diffusions, the recombination and contact resistance associated with those diffusions are quantified for both planar and textured solar cells.

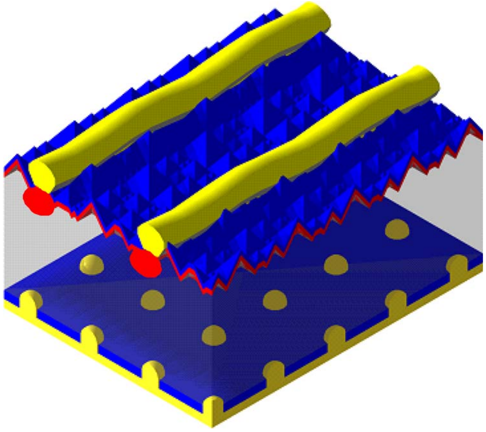

Fig. 1. Sketch of the solar cell structure. The (red) emitter is lightly doped except in shallow and heavily doped grooves under the fingers, as formed by LCP. The cell has (blue) 105 nm of silicon oxide that acts as an antireflection layer and a passivating layer. The (yellow) metal is contacted to the silicon by local laser firing on the rear and evaporation and electroplating on the front.

II. EXPERIMENTAL

A. Solar Cell Structure

Fig. 1 shows the structure of the cells investigated in this paper, and Fig. 2 shows the fabrication process. This follows the procedure described in [15], employing the high-efficiency features of thermal-oxide passivation, local laser-fired contacts (LFC) [16] at the rear, and evaporated and plated front Ti–Pd–Ag contacts defined by photolithography. However, rather than being defined by photolithography and doped by furnace diffusion, the local heavy phosphorus diffusion under the front fingers was defined by LCP. The pulses of the laser were closely spaced, forming shallow and highly doped grooves in the silicon with a width of 55 μm. The solar cells were manufactured from 0.5- and 1-$\Omega \cdot$ cm FZ(B) wafers of 250 μm thickness, where the front surface of some wafers was textured with random pyramids while others were left planar.

B. Grid Geometry

To investigate the recombination and contact resistance of the heavily doped LCP grooves, cells were manufactured with a varied number of front metal fingers. Seven cells of 2 × 2 cm^2 area were fabricated on each 4-in wafer, with 10, 15, 20, and

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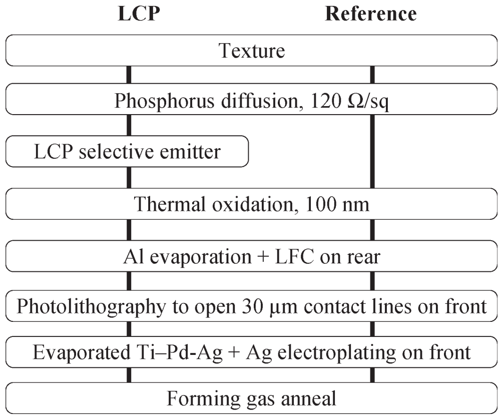

Fig. 2. Fabrication procedure of the cells in this paper.

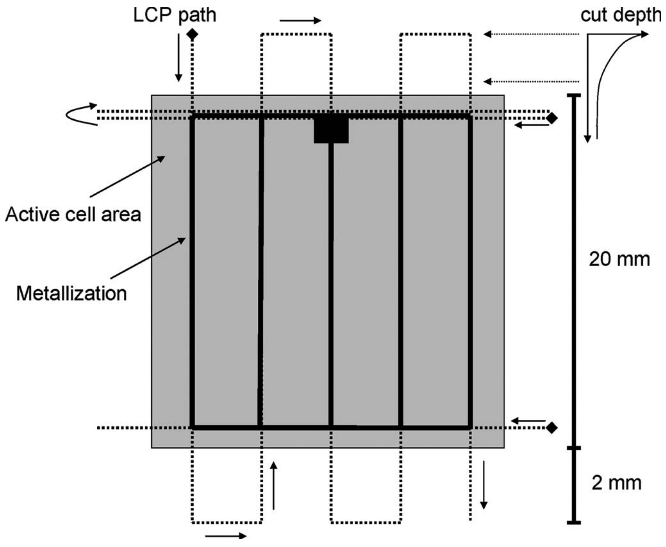

Fig. 3. Laser path for LCP. A snaking path extending beyond the active cell area is chosen to locate the areas with larger cut depth outside the active area.

25 fingers, corresponding to an LCP groove area of 0.11, 0.17, 0.22, and 0.28 cm^2. The LCP groove width was $\sim$55 μm to ensure successful alignment of the contact openings and evaporated fingers to the grooves. The contact openings were then formed by oxidizing the surface and using photolithography to define 30-μm-thick lines within the grooves. While it is possible to employ LCP to create openings through SiO$_2$, photolithography was used here to permit comparison between the LCP and reference cells (described as follows).

Fig. 3 shows the general scheme of the (solid lines) front metal and (dotted lines) LCP grooves on the cells. It illustrates how the LCP grooves of each cell were conducted in three sweeps—one for the fingers, one for the redundant line, and one for the main bus bar—resulting in a snaking path that extended beyond the active area of the cell. The deceleration of the laser prior to making 90° and 180° turns, and the subsequent acceleration afterward, led to deeper LCP grooves in the “U-turns” beyond the active area. These turning points were deliberately conducted outside the cell area to avoid introducing high recombination associated with the extra deep grooves (this is why the contact pad was not grooved). Even so, when the cells were not removed from the wafer, the regions of high recombination could still affect the cell performance due to the conduction of carriers along the grooves to these regions. Their contribution is assessed in the following section.

TABLE I
ILLUMINATED I–V PARAMETERS OF THE MOST EFFICIENT SOLAR CELL FROM EACH WAFER

Cell ID	Front	Fingers	Base res. [Ωcm]	V$_{oc}$ [mV]	J$_{sc}$ [mA/cm^2]	FF [%]	η [%]
25.4	Planar, no LCP (reference)	10	0.5	668.3	33.7	79.1	17.8
21.4	Planar	10	0.5	664.0	33.0	80.5	17.7
14.3	Textured	10	0.5	668.0	37.7	79.0	19.9
15.3	Textured	10	0.5	664.9	38.7	79.2	20.4
6.1	Textured	10	1.0	598.3	38.1	64.1	14.6

To provide a reference, the cells of one wafer were manufactured using the complete procedure described in [15], where the front contact openings were defined to the same width of 30 μm by photolithography but without applying any heavy diffusion. Fig. 2 compares its fabrication procedure to the cells manufactured with LCP.

The current–voltage $(I–V)$ characteristics of the completed cells were measured under dark and one-sun conditions. The results of the most efficient solar cell from each wafer are listed in Table I. While the texturization and LFC rear contacts in these cells were suboptimal [17], an efficiency in excess of 20% was still achieved. The table lists the open-circuit voltage V_{oc}, short-circuit current density J_{sc}, fill factor FF, and cell efficiency η.

III. ANALYSIS

The impact of the LCP grooves on cell performance is now addressed, first in terms of recombination and, then, in terms of contact resistance.

A. LCP Recombination: Planar Cells

Fig. 4 shows the dark I–V curve and its associated local ideality factor for two planar cells with ten fingers: one with heavy diffusions made by LCP and the other without local heavy diffusion (the reference). The local ideality factor is defined as

$$m(V) = [(kT/q)(d\ln J/dV)]^{-1} \qquad (1)$$

which is proportional to the inverse slope of the $\ln(I)V$ curve.

Both dark I–V curves in Fig. 4 exhibit near-ideal behavior, with m being $\sim$1 over a wide voltage range. This indicates the following: 1) The recombination is dominated by a single mechanism that is either SRH or Auger recombination in low injection and 2) recombination through that mechanism does not saturate due to any resistive path or asymmetrical capture cross sections. At high voltage, the I–V curves flatten due to series resistance, while at low voltage, the shunt resistance impacts slightly on the curves.

Most importantly, the dark I–V curves of Fig. 4 are nearly identical and so too is the cells’ open-circuit voltage. This indicates that recombination associated with the heavily doped LCP grooves is no greater than that associated with the homogeneous

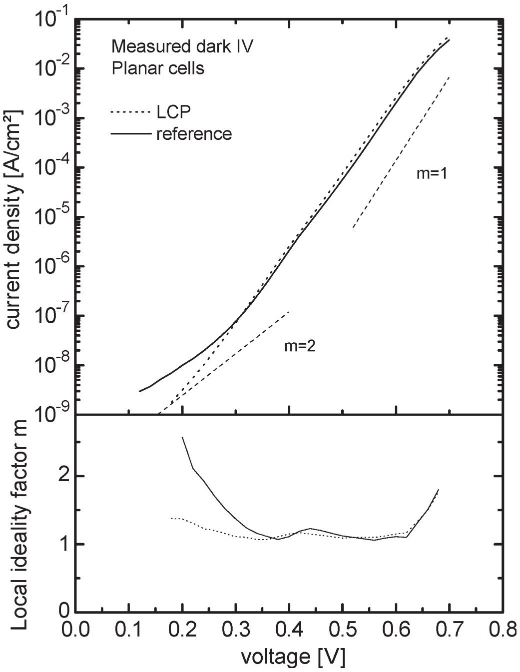

Fig. 4. Comparison of dark I–V curves of planar solar cells with ten fingers, one with LCP doping and the other without.

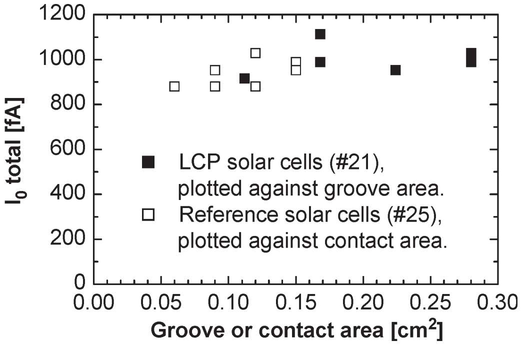

Fig. 5. Dark saturation current $i_{0,\mathrm{total}}$ for planar solar cells with heavy front diffusion by LCP plotted against groove area and without heavy front diffusion (reference) plotted against contact area.

furnace diffusion. This is true even though the LCP groove width of ~55 μm is larger than the reference contact opening of 30 μm. It also indicates that the recombination associated with the U-turns of the LCP cell is insignificant.

To quantify the recombination rate associated with the heavy doping of the front contact, Fig. 5 shows the total saturation current $i_{0,\mathrm{total}}$ against the groove area of the planar LCP cells, and the contact area of the planar reference cells, where

$$i_{0,\mathrm{total}} = i_{\mathrm{sc}}/\exp(qV_{\mathrm{oc}}/kT). \quad (2)$$

This definition assumes that m would be equal to one at V_{oc} if series resistance was not present—a justifiable assumption given the results of Fig. 4.

The intercept of a linear fit to the data of Fig. 5 gives the recombination current if the cells had no grooves or contacts. We expect this value to be the same for both sets of data since the cells are identically fabricated other than the LCP grooves. We find the y-axis intercept to be 958 ± 98 fA for the LCP cells and 826 ± 76 fA for the reference cells, where the uncertainty represents the 95% confidence limits. Thus, to within the accuracy of the experiment, the recombination outside the groove or contact area is the same for each cell type. (Dividing these values by the cell area gives the recombination current densities of 240 ± 25 and 207 ± 19 fA/cm^2, respectively.)

The slope of a linear fit to the data of Fig. 5 gives the recombination current density associated with the grooves and contacts of the LCP cells (or with the contacts of the reference cells), minus the recombination current density of the light emitter diffusion that they replace. This slope is 158 ± 455 fA/cm^2 for the LCP cells and 997 ± 657 fA/cm^2 for the reference cells. These current densities are higher than those for the remainder of the cell (calculated earlier), as is expected due to Auger recombination in the heavy diffusion and high Shockley–Read–Hall recombination at the contacts.

The uncertainty in the slope is too large to conclude that recombination associated with the LCP grooves is significant. We can, at best, place an upper limit on the recombination current density to be 613 fA/cm^2 if the emitter recombination is negligible (upper limit to slope) and 853 fA/cm^2 if the emitter recombination dominates the recombination elsewhere (sum of upper limits to slope and intercept/area). Although this recombination current density is large compared to elsewhere in the cell, it has little impact on the cell efficiency due to its small area (evidenced by Fig. 5). In fact, the groove width of 55 μm could even be reduced to 6.5 μm by proven LCP processes. In such case, it would be possible to achieve a groove fraction of 1%, limiting the V_{oc} to > 749 mV (for a J_{sc} of 40 mA/cm^2).

While recombinations in the LCP and reference cells are nearly identical, we note that the LCP cells exhibit a lower J_{sc} and a higher FF (see Table I). The lower J_{sc} is due to the width of the LCP grooves of 55 μm that exhibits lower quantum efficiency. The higher FF results from a smaller specific contact resistance (0.9 rather than 4 $\Omega \cdot \mathrm{cm}^2$), as measured via the transmission line method (TLM) [18] on test structures.

B. LCP Recombination: Textured Cells

LCP on textured substrates is challenging because the laser intensity is inhomogeneously imparted on the silicon. Nevertheless, successful LCP can be attained, as testified by the high cell efficiencies listed in Table I. These are the first laser-doped silicon cells with efficiencies greater than 20%.

The dark I–V and mV curves of one 20% cell are shown in Fig. 6. Interestingly, the data exhibit a strong $m = 2$ component at low voltage followed by a transition to an $m = 1$ component at ~0.6 V, above which the curve is influenced by a series resistance. The curves are consistent with the equivalent circuit of Fig. 7, which describes a solar cell with a resistance-limited region (or regions) of high recombination [19]. In such case, current flows predominantly through the region of high recombination at low voltage, adequately modeled by $m_H = 2$, $I_{0H} = 1.2 \times 10^{-7}$ A, and $R_H = 500\,\Omega$, as shown by the dotted line in Fig. 6. At higher voltage, the current through this region saturates due to the series resistance R_H, and most current flows through the main part of the solar cell, adequately modeled by $R_{\mathrm{sh}} = 5 \times 10^5\,\Omega, m_1 = 1, j_{01} = 1.8 \times 10^{-13}$ A/cm$^2, m_2 = 2,$

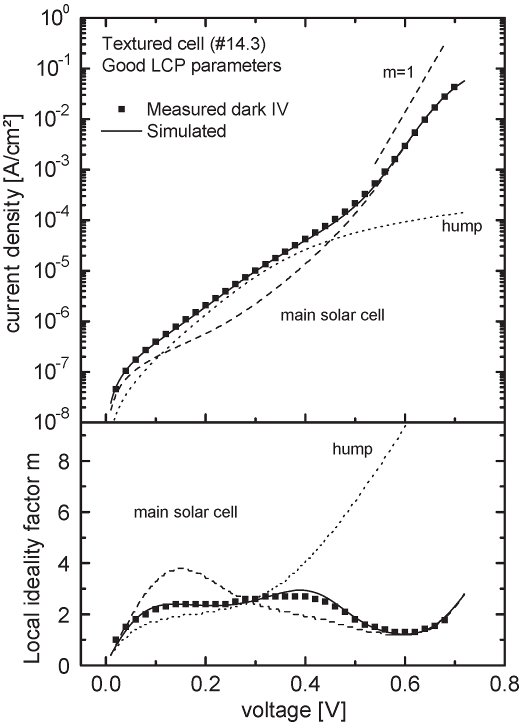

Fig. 6. Dark I–V and local ideality factor of textured solar cell with LCP selective emitter.

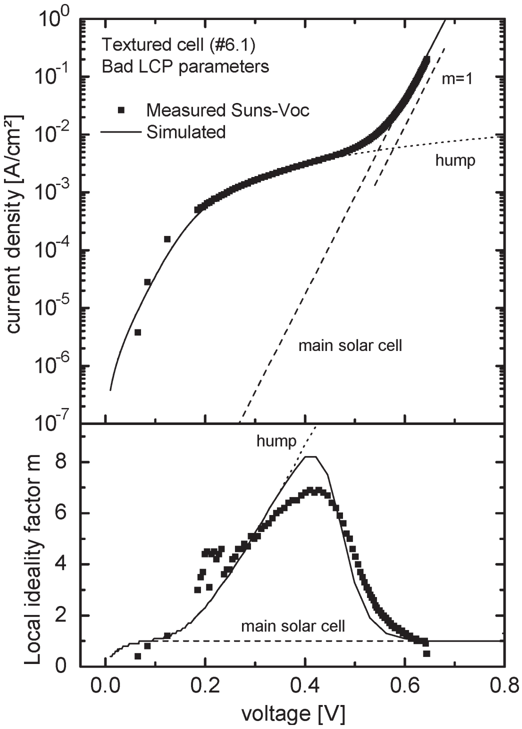

Fig. 8. Suns–V_{oc} and mV curve of textured solar cell with suboptimal LCP selective emitter.

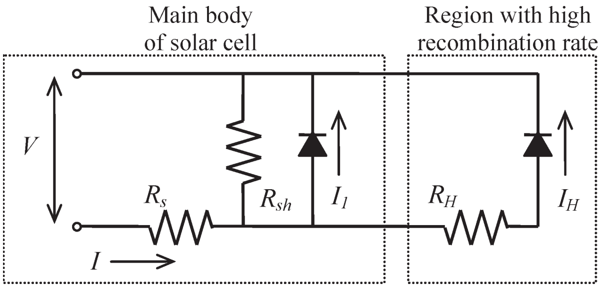

Fig. 7. Equivalent circuit of solar cell with a resistance-limited region of high recombination in the dark. A second diode can be added to the main body of the solar cell.

$j_{02} = 5 \times 10^{-9}$ A/cm^2, and $R_s = 0.7\ \Omega$ (dashed line). The currents through these parallel components sum to give the solid line. The general shape of this curve is similar to that observed by Hernando *et al.* [20], who attributed the $m = 2$ component to defects associated with broken pyramids, presumably due to the intersection of the p-n junction with the defect (it cannot be due to the intersection of the p-n junction with the edge of the cells since they are not removed from the wafers). We do not assign great importance to the best fit values for I_{0H} and R_H since any defected pyramids are probably unevenly distributed, but we do note that the best fit R_H is much too large to be attributed to the paths down the grooves into the U-turns. Their resistance was ~20 Ω for this cell, as calculated from the grooves' dimensions and sheet resistance determined from SIMS measurements. Most importantly, it can be concluded that any regions of high recombination have little impact on the cell efficiency, because their effect on the cell is minimal at and above the maximum power point voltage (0.56 V). Furthermore, the difference in V_{oc}'s between 10 and 15 fingers on textured cells is below 1 mV, so that we can state that, also for textured surfaces, the recombination current density associated with LCP grooves is negligible.

For interest, we also present the *suns*–V_{oc} [21] and equivalent mV curve of a textured sample with suboptimal LCP parameters in Fig. 8. In this case, the grooves were deeper ($> 100\ \mu$m), being formed over a longer surface melt duration, causing the surface melt flow due to the liquid jet momentum [22]. Adequate contact to these grooves was not attained, preventing the measurement of a dark I–V curve, and hence, the *suns*–V_{oc} technique was employed. The curves of Fig. 8 present a classic example of a cell with a resistance-limited region(s) of very high recombination, evidenced by the large shoulder or hump in the curves. The cell is adequately modeled by a region of high recombination: $m_H = 1$, $I_{0H} = 3.2 \times 10^{-6}$ A, and $R_H = 15\ \Omega$ (dotted line), and the main body of the solar cell: $R_{\mathrm{sh}} = 2.5 \times 10^{10}\ \Omega$, $m_1 = 1$, and $I_{01} = 1.2 \times 10^{-11}$ A (dashed line). The series resistance R_s cannot be inferred because it does not influence a *suns*–V_{oc} curve [21]. The region(s) of high recombination might be the ends of the U-turns, given that the modeled value of R_H is of similar magnitude to the resistance along the grooves (5–20 Ω) and that the ideality factor is one (consistent with the recombination in a heavily doped region). We discard the possibility that the regions of high recombination are the rear contacts since they were formed by the same LFC procedure that was used on all other cells in this study.

C. Contact Recombination

To investigate whether the contacts exhibited ohmic or Schottky behavior, *suns*–V_{oc} measurements were performed

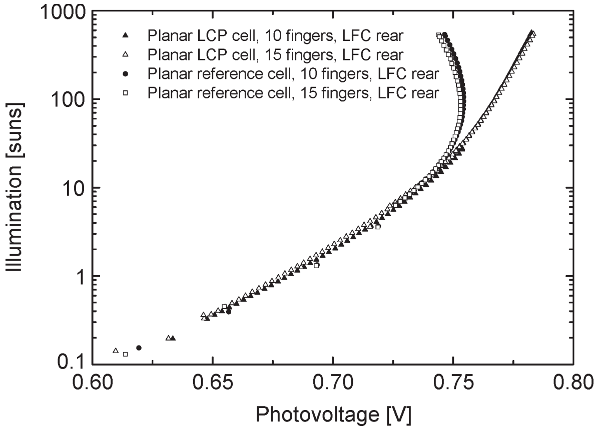

Fig. 9. Suns–V_{OC} measurements at high illumination densities of planar cells with and without LCP selective emitter. (Rear side) LFC point contacts.

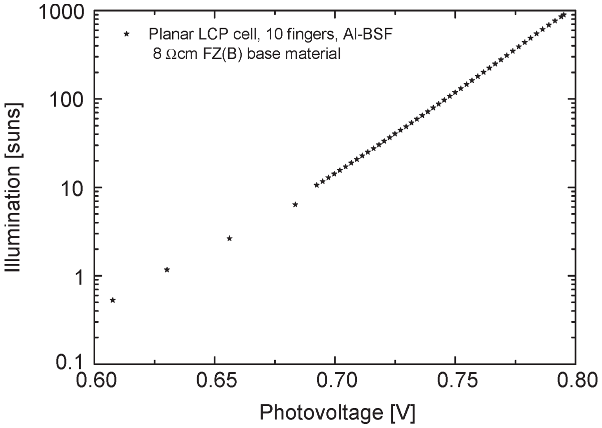

Fig. 10. Suns–V_{OC} measurement of planar solar cell with LCP selective emitter. (Rear side) Full area Al-BSF.

under high illumination intensities. Any Schottky behavior is apparent in such measurements if the external voltage begins to decrease with increasing light intensity, a result of the Schottky diode "switching on" and opposing the main junction [23].

Fig. 9 shows the *suns*–V_{OC} measurements for four planar cells at very high injection. Schottky behavior is observed for all four cells, as evident from the departure from linearity, but much more so for the two reference cells (with no heavy diffusion) than for the two LCP diffused cells. Thus, the LCP contacts are superior to the reference contacts.

To ascertain whether the Schottky behavior resulted from the front LCP contacts or from the rear LFC contacts, a sample was manufactured with LCP contacts on the front but with screen-printed aluminum contacting the entire rear surface. Fig. 10 shows the *suns*–V_{OC} curve of this cell. It does not depart from linearity, even at 1000 suns, indicating that these LCP contacts are highly ohmic. As mentioned before, the specific contact resistance was determined from TLM measurements to be just $0.9\ \Omega \cdot \mathrm{cm}^2$. This resistance is too small to have a deleterious effect on cell performance, even for contact areas of just 1% of the total cell area.

IV. CONCLUSION

This paper has presented the I–V characteristics of high-efficiency solar cells manufactured with LCP doped heavy diffusions. It was shown that the recombination current density associated with LCP grooves was at most 8.5×10^{-13} A/cm^2 on planar silicon. For small LCP diffused areas, this recombination is almost negligible in comparison to other source of recombination in a silicon cell, which could also be shown for textured samples. It has also been demonstrated that ohmic contacts can be attained on LCP diffusions, even at intensities as high as 1000 suns, with a specific contact resistance of $0.9\ \Omega \cdot \mathrm{cm}^2$. These features make LCP processing consistent with high-efficiency silicon solar cells. Its industrial implementation is expected to greatly reduce the cost of manufacturing selective-emitter solar cells.

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