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Microscale Spatially Resolved Characterization of Highly Doped Regions in Laser-Fired Contacts for High-Efficiency Crystalline Si Solar Cells

A. Roigé, J. Alvarez, J.-P. Kleider, I. Martín, R. Alcubilla, and L. F. Vega

Abstract—Laser-fired contact (LFC) processes have emerged as a promising approach to create rear local electric contacts in p-type crystalline silicon solar cells. Despite this approach has been successfully applied in devices showing efficiencies above 20%, there is still a lack of knowledge about some specific features of LFCs at the submicron level. In this study, we used micro-Raman and microphotoluminescence (PL) spectroscopies to carry out a high-resolution spatially resolved characterization of LFCs processed in Al_2O_3 -passivated c-Si wafers. Relevant information concerning features such as local doping distribution and crystalline fraction of the laser-processed region has been obtained. In particular, interesting qualitative and quantitative variations concerning the doping profile have been observed between LFCs processed at different laser powers. Finally, conductive-atomic force microscopy measurements have allowed to identify the existence of highly conductive zones inside the LFCs greatly correlated with highly doped regions revealed by Raman and PL data. This study gives a detailed insight about the LFCs characteristics at the submicron level and their possible influence on the performance of final devices.

Index Terms—Crystalline silicon, laser-fired contacts (LFCs), microphotoluminescence spectroscopy, micro-Raman spectroscopy.

I. INTRODUCTION

FROM an industrial point of view, one of the most interesting crystalline silicon (c-Si) solar cell technologies to obtain high-efficiency devices is the passivated emitter and rear cell concept. Recently, the industrial implementation of this cell type has been significantly simplified by using the so-called laser fired contact (LFC) approach for the creation of the back contacts of the cell [1], [2]. This method is based on firing the

rear Al metallization layer by a laser beam in order to create electrical point contacts between the Al layer and the silicon substrate through the passivation layer.

A key feature for the good operation of LFCs is the formation of an Al-doped p+ region under the contacted surface area. This is achieved by the diffusion of Al atoms from the predeposited Al layer into the molten Si. This p+ region not only creates a local back-surface field that induces a relatively low recombination velocity below the contacts, but also ensures a low-contact resistance.

LFC approach can be applied by using any of the dielectric layers that have demonstrated excellent c-Si passivating properties such as silicon oxide (SiO_2) [3], silicon nitride (SiN_x) [4], amorphous-silicon carbide (a- SiC_x) [5], and most recently, aluminum oxide (Al_2O_3) [6]. In the case of using the latter passivating material, an interesting alternative to the conventional LFC process can be applied. In this case, the Al_2O_3 layer itself can be used as Al-dopant source for the formation of the p+ region, and hence, the LFC can be done directly onto the Al_2O_3 /c-Si, instead of being done onto the Al/dielectric/c-Si stack. This approach enables a lower laser power operation in comparison with conventional LFC process where higher laser powers are needed to fire the aluminum through the dielectric layer. These type of LFC processes have been already used to fabricate solar cells showing efficiencies well above 20% [6].

Despite the evident success in the implementation of the LFC approach in real devices, there is still a lack of information about specific features of LFCs such as the doping profile of the p+ region, the level of induced-stress, and/or the structural properties of the laser-processed region. The most likely reason for that is the difficulty to find experimental techniques that match a high-lateral resolution (below 10 μm) and sensitivity to the parameters wanted to be studied. Recently, a study of LFC cross sections [7] have demonstrated that Raman and photoluminescence (PL) spectroscopies in microconfiguration are techniques that fulfill the mentioned requirements.

In this study, we have carried out high-resolution micro-Raman and micro-PL spectroscopy measurements on different LFCs processed in Al_2O_3 -passivated c-Si samples. Thanks to the high lateral resolution down to 1 μm achieved in our experiments, we have been able to perform a detailed study of relevant LFC properties such as the doping profile, induced-stress, and crystallinity fraction, giving an important insight about the LFC formation. Three LFCs processed at different incident laser power have been studied in order to analyze the influence of the laser power on the studied features. Finally, in

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81 order to complement the PL and Raman data, conductive-atomic
82 force microscopy (c-AFM) measurements have been performed
83 in order to study local resistance variations inside the LFCs.

84 It is worth to mention that the term LFC has been used since
85 more than a decade to describe the firing of the predeposited alu-
86 minum through a dielectric layer. Despite the process used here
87 is fundamentally different, its finality and application in solar
88 cell devices is the same. For simplicity, we have maintained the
89 term LFC to refer to our laser-processed locally doped regions.

90 II. EXPERIMENTAL METHODS AND MATERIALS

91 Samples under study were based on 2.5 $\Omega\cdot\text{cm}$ boron-doped
92 float-zone (FZ) crystalline Si (c-Si) wafers with a thickness of
93 250 μm and (1 0 0) crystal orientation. c-Si wafers were pas-
94 sivated by a 25-nm-thick aluminum oxide (Al_2O_3) film which
95 was grown by thermal atomic layer deposition. Laser fired spots
96 were processed on the top of the Al_2O_3 -passivated c-Si sam-
97 ples creating small apertures in the alumina layer and melting a
98 small part of the underlying c-Si subsurface region. LFCs were
99 processed by a 1064 nm Nd:YAG lamp-pumped laser working
100 at 100 ns of pulse duration. Each contact is a consequence of
101 six pulses at a repetition rate of 4 kHz. Three different LFCs
102 processed with a laser power of 0.98, 1.1, and 1.43 W were
103 studied, corresponding to pulse energies of 245, 275, and 357.5
104 μJ . The laser beam shows a Gaussian profile with a beam waist
105 characterized by a radius of 70 μm at the focus plane where all
106 the samples were processed. After laser processing and prior to
107 carry out the measurements, samples were immersed in an HF
108 1% solution bath during 40 s (or until obtaining an hydrophobic
109 silicon surface) in order to remove the Al_2O_3 layer. Addition-
110 ally, three boron-doped FZ c-Si wafers with doping densities
111 of 1×10^{15} , 5×10^{18} , and $1 \times 10^{20} \text{ cm}^{-3}$ were used in order to
112 obtain reference Raman and PL spectra.

113 Micro-Raman and microphotoluminescence experiments
114 were carried out with a WITEC alpha300. A diagram of the
115 Witec equipment setup can be found in [8]. A diode-pumped
116 laser with a wavelength of 532 nm was used as an excitation
117 source resulting in a penetration depth of about 1 μm . Micro-
118 Raman and micro-PL measurements were performed with a 100
119 \times VIS (visible), NA (numerical aperture) = 0.9 and a 20 \times IR
120 (Infrared), NA = 0.45, respectively. The resulting beam spot
121 size on the sample surface is in diameter below 1 and 2 μm for
122 Raman and PL measurements, respectively. Raman scattering
123 signal was recorded through a 300-mm imaging spectrometer
124 equipped with both a 600 lines/mm and 1800 lines/mm grat-
125 ing, and a 1024 \times 127 CCD (charge-coupled device) camera
126 visible-optimized, whereas PL signal was collected through an
127 additional 300-mm spectrometer composed of two gratings (150
128 and 300 lines/mm) and a 1024 \times 1 pixel linear InGaAs photodi-
129 ode array optimized for spectroscopy applications in the range
130 1–1.7 μm . It is worth to mention that the incoming laser power
131 on the sample surface for the Raman measurements was kept
132 below 3 mW. With our configuration, 3 mW was measured to
133 be the pumping limit to keep the photo-generated carrier den-
134 sity below threshold and, therefore, to avoid Fano resonances
135 induced by high injection conditions [15].

Local electrical measurements through the c-AFM technique 136
were performed using a Digital Instruments Nanoscope IIIa 137
Multimode AFM associated with the home-made conducting 138
probe extension called “Resiscope” [9]. This extension allows 139
us to apply a stable dc bias voltage (from -10 to $+10$ V) to the 140
sample and to measure the resulting current flowing through the 141
tip as the sample surface is scanned in contact mode, yielding a 142
local resistance map covering resistance values in the range 10^2 – 143
 $10^{12} \Omega$. Current–Voltage (I – V) measurements are also permitted 144
with this extension. Highly boron doped diamond-coated Si 145
AFM cantilevers, with an intermediate spring constant of about 146
3 N/m, proved to be the most suitable AFM tips for making 147
electrical measurements on LFCs. Due to the AFM tip radius 148
(~ 50 nm), c-AFM measurements offer a much greater lateral 149
resolution. This latter depends on the electrical contact radius 150
between the tip and the surface. In the particular case of flat 151
surfaces, the electrical contact radius can be much smaller than 152
AFM tip radius. The probed depth remains in the nanoscale 153
range, but it is linked, among other parameters, to the applied 154
voltage and the local electrical transport properties. 155

156 III. RESULTS AND DISCUSSION

157 A. Doping Characterization by Micro-Raman Spectroscopy

158 Doping profiles in c-Si can be monitored by studying both 158
the Full Width at Half Maximum (FWHM) [10] and the Fano 159
resonance [11] of the first-order Si Raman peak. In particular, 160
Fano resonances are evident in the Si Raman spectra at hole 161
concentrations above 10^{18} cm^{-3} by a characteristic asymmetry 162
in the first-order Si Raman line. This asymmetry results from 163
the resonant interaction between discrete phonon states and a 164
continuum of hole states [12], [13]. The Raman peak line shape 165
can be described by the following expression [11]: 166

$$167 \quad I(k) = I_0 \cdot \frac{[q + 2(k - k_{ph})/\Gamma]^2}{1 + [2(k - k_{ph})/\Gamma]^2} \quad (1)$$

168 where I_0 is a scaling factor, k_{ph} is the frequency associated to 167
the Raman peak maximum, Γ corresponds to the FWHM, and q 168
is the asymmetry parameter, which is correlated with the doping 169
level of the sample being studied. The lower the q parameter, 170
the higher the doping level. The first-order Si Raman peak can 171
be also influenced by stress and/or by the material crystalline 172
fraction. The former can be monitored by the peak frequency 173
shift, whereas the latter is evidenced by a peak broadening from 174
the c-Si to the amorphous-Si state. 175

176 Fig. 1 shows the optical microscope images (left-hand side) 176
and the corresponding Raman peak width maps (right-hand side) 177
of the three LFCs under study processed at 0.98 (a) and (b), 178
1.1 (c) and (d), and 1.43 W (e) and (f). Maps were obtained 179
from the raw Raman peak width, not from the fitted Γ . The 180
corresponding LFC diameters were 43.8, 54.5, and 74.2 μm , 181
respectively. For ensuring a good observation of the obtained 182
data, the microscope images and the Raman maps of the three 183
contacts have been represented with a slightly different scale. In 184
addition for clarity, the physical dimensions of the LFCs have 185
been represented in Raman maps by a green dotted circle. As 186
explained previously, the width of the first-order Raman peak 187

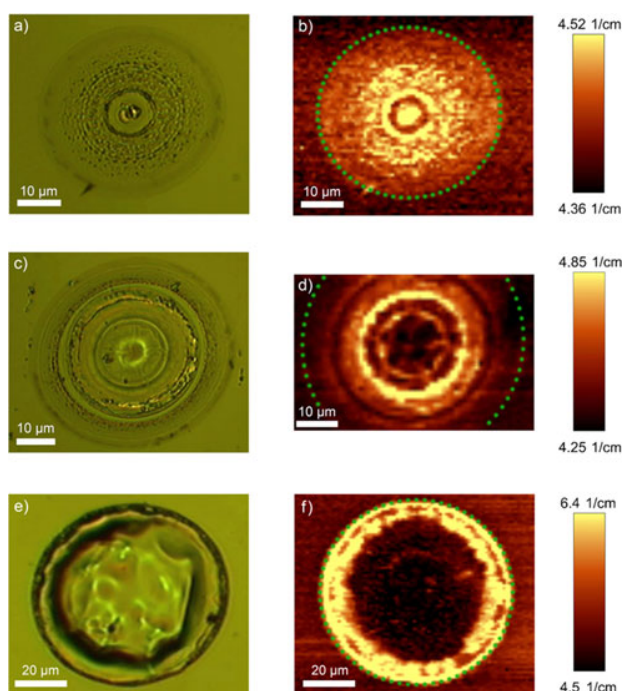


Fig. 1. Optical microscope images (left-hand side) and Raman peak width maps (right-hand side) of the three LFCs under study processed at 0.98 (a) and (b), 1.1 (c) and (d), and 1.43 W (e) and (f). Brighter zones in the Raman peak width maps correspond to zones with higher doping density.

188 can be used to monitor the doping level of the sample under
 189 study. Hence, the zones that evidence an increase of the Raman
 190 peak width in Fig. 1 (brighter zones) are qualitatively correlated
 191 with zones with a higher doping level. The LFC processed at
 192 0.98 W evidences slightly higher levels of doping at the central
 193 part of the contact. In contrast, the contact processed at 1.1 W
 194 [see Fig. 1(d)] evidences a brighter concentric corona pointing
 195 out a wider Raman peak and consequently an increase of the
 196 doping level. Following the same trend, for the contact processed
 197 using the higher laser power [see Fig. 1(f)], the border of the
 198 contact is the area that evidences a higher level of doping. The
 199 different Raman maps illustrated in Fig. 1 demonstrate that
 200 the laser power plays an important role on the distribution of
 201 the highly doped regions inside the contacts. More precisely,
 202 it seems that for higher laser powers, the highly doped regions
 203 move toward the border of the contact. Two-dimensional depth
 204 profiling across LFCs (maps not shown for space limitations)
 205 revealed the same results. This fact corroborates that the features
 206 of Raman maps shown in Fig. 1 were not affected by variations
 207 in surface topography of LFCs.

208 The correlation between the Raman peak widening observed
 209 in Fig. 1 and the expected increase in the doping density is con-
 210 firmed by data shown in Fig. 2. This figure shows the averaged
 211 Raman spectra corresponding to the zones with higher doping
 212 of images b, d, and f of Fig. 1. In particular, the averaged spectra
 213 were calculated from the yellow-colored areas of Raman maps.
 214 An averaged spectrum corresponding to an unprocessed area
 215 (outer region of LFC) is also shown (yellow dashed line). In

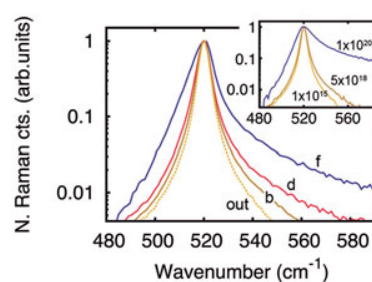


Fig. 2. Averaged Raman spectra corresponding to the brighter zones of maps b, d, and f of Fig. 1. For comparison, an averaged Raman spectra corresponding to an unprocessed surface area has been also represented (yellow dashed line). The inset shows the Raman spectra recorded from the three reference c-Si wafers with different doping level.

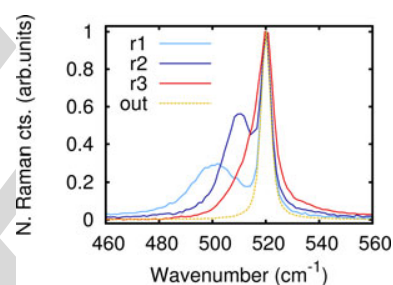


Fig. 3. Raman spectra obtained at specific points inside LFCs processed at 1.1 W (r1, r2) and 1.43 W (r3). In addition to the first-order Raman peak, a second peak characteristic of microcrystalline silicon sets in at lower wavenumbers. For comparison, a Raman peak related to an unprocessed area (outer region of LFCs) is also depicted.

216 order to facilitate the observation of Fano resonances, Raman
 217 spectra have been represented using a semilog scale. As it can
 218 be observed, the Fano resonance is clearly identified for all Raman
 219 spectra except for the one obtained out of the LFC, which
 220 shows a symmetric Raman line shape. This qualitatively con-
 221 firms that the brighter zones in maps of Fig. 1 are correlated
 222 with areas with a higher doping level. The increase in doping
 223 is also greatly confirmed by the inset, where the Raman spectra
 224 recorded from three reference c-Si wafers with doping levels of
 225 1×10^{15} , 5×10^{18} , and $1 \times 10^{20} \text{ cm}^{-3}$ clearly evidence the
 226 same trend concerning the Fano resonance. Another important
 227 feature observed in the main plot of Fig. 2 is that the LFCs
 228 processed with a higher laser power have associated a higher
 229 Fano asymmetry. Hence, the use of higher laser powers results
 230 in LFCs with higher doping densities.

231 In order to get further important information about the LFCs
 232 formation, we depict in Fig. 3 the Raman spectra recorded
 233 at three specific points (r1, r2, and r3) inside two LFCs pro-
 234 cessed at 1.1 W (r1, r2) and 1.43 W (r3) (contact images and
 235 point positions not shown). A fourth Raman spectrum corre-
 236 sponding to a nonprocessed surface area is also represented
 237 as a reference. As it can be observed, in addition to the first-
 238 order c-Si Raman line positioned at 520.9 cm^{-1} , new Raman
 239 bands can be identified at lower wavenumbers in the range be-
 240 tween 500 and 515 cm^{-1} . These latter bands are commonly as-
 241 signed to microcrystalline silicon [16], [17]. Indeed, the Raman

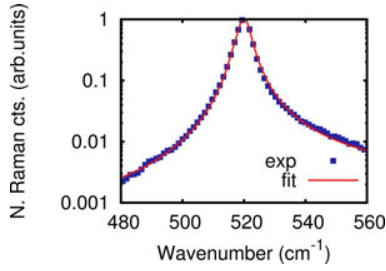


Fig. 4. Fitting using (2) of the Raman spectrum corresponding to the highly-doped region of the LFC processed at 1.1 W. Fit gave a q parameter of 59 which is correlated to a doping level of about $5.8 \times 10^{18} \text{ cm}^{-3}$.

spectra of microcrystalline-Si are currently decomposed into three bands: crystalline ($\sim 520 \text{ cm}^{-1}$), intermediate band ($500\text{--}515 \text{ cm}^{-1}$, usually interpreted as a signature of the grain boundaries or small crystallites grain size $< 10 \text{ nm}$), and amorphous (480 cm^{-1}). The following decomposition is used to quantify the crystalline fraction [18]. The observation of these new Raman bands at specific points inside the LFCs suggests that molten Si material fraction solidifies in a structure involving crystallites, grain boundaries, and an amorphous phase, at least in specific zones inside the contacts. However, the crystalline fraction in these zones reveals to be high indicating a negligible amorphous component.

The contribution of microcrystalline-Si components to the obtained Raman spectra is further confirmed by the fact that all Raman spectra recorded inside the LFCs could be significantly better fitted using a rewriting of (1) that considers a second Lorentzian function related to the contribution of the microcrystalline Si formation. In fact, the expression that has been used to fit the Raman data is the following:

$$I(k) = I_0 \cdot \frac{[q + 2(k - k_{ph})/\Gamma]^2}{1 + [2(k - k_{ph})/\Gamma]^2} + \frac{A}{1 + [2(k - k_m)/\Gamma_m]^2} \quad (2)$$

where A corresponds to the intensity, k_m is the frequency of the peak maximum, and Γ_m is the peak width of the Raman band related to the microcrystalline-like component. It is worth to mention that the position of the second Lorentzian function was limited to values between 505 and 517 cm^{-1} . As observed in Fig. 4 for a LFC processed at 1.1 W , the fit using (2) shows very good adjustment paving the way to obtain a reliable quantification about the doping level inside the LFCs.

Table I shows the q asymmetry parameters resulting from the best fit of (2) to the Raman spectra related to the highly doped regions of the three LFCs under study. Data were calculated from at least two LFCs for each one of the three values of laser power. The obtained q parameters clearly illustrate that the higher the laser power, the higher the doping density. According to the calibration tables reported in [10] and [11], we have obtained maximum doping levels in the range of $1.17\text{--}3.83 \times 10^{18}$, $4.58\text{--}6.06 \times 10^{18}$, and $2.15\text{--}5.02 \times 10^{19} \text{ cm}^{-3}$ for the LFCs processed at 0.98 , 1.1 , and 1.43 W , respectively. It is important to

TABLE I
 q ASYMMETRY PARAMETER OBTAINED FROM THE FITTING OF (2) TO THE AVERAGED RAMAN SPECTRA RELATED TO THE HIGHLY DOPED REGIONS OF THE THREE LFCs UNDER STUDY.

power (W)	q (arb.units)	doping ref. [10] ($\times 10^{18} \text{ cm}^{-3}$)	doping ref. [11] ($\times 10^{18} \text{ cm}^{-3}$)
0.98	90 ± 7	3.13 – 3.83	1.17 – 2.35
1.10	61 ± 4	5.19 – 6.06	4.58 – 6.03
1.43	16 ± 2	21.49 – 27.93	42.19 – 50.17

The corresponding doping densities were calculated using the calibration tables reported in [10] and [11].

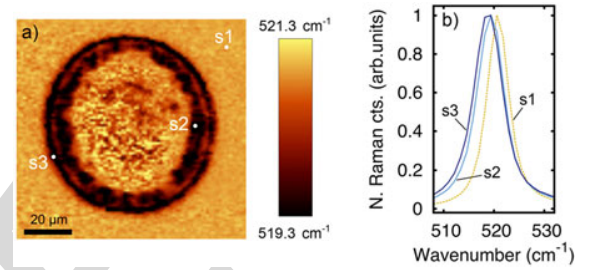


Fig. 5. (a) Raman spectra center of mass map of a LFC processed at 1.43 W . (b) Specific Raman spectra associated with points s1, s2, and s3 are also plotted.

remark that the intensity of the second Lorentzian peak related to the multicrystalline component was observed to increase with higher laser powers. This suggests that the use of higher laser powers decreases the crystalline fraction of the solidified Si volume.

Fig. 5(a) shows the Raman spectra center of mass map of a LFC processed at 1.43 W . The Raman spectra of the selected points (s1, s2, and s3) are represented in Fig. 5(b). The center of mass was calculated considering a frequency range between 480 and 560 cm^{-1} ; thus, as confirmed by Raman spectra of Fig. 5(b), it could be qualitatively correlated with the frequency shift of the first-order Si Raman peak. The first-order Raman line of s1, s2, and s3 Raman spectra is centered at 520.8 , 519.3 , and 518.7 cm^{-1} , respectively. Notice that the center of mass values represented by the color scale bar of Fig. 5(a) are shifted toward higher frequencies respect the Raman peak position values mentioned previously. This is induced by the contribution of the Fano resonance which moves the center of mass toward higher energies respect the peak maximum. As it can be seen, the Raman peak position suffers a red shift of about 2 cm^{-1} at the border of the contact. Interestingly, areas of the contact that show such a red shift exactly match with areas of the 1.43 W LFC that evidence higher levels of doping [see Fig. 1(f)]. It has been reported, that Raman spectra obtained from samples with doping levels above $5 \times 10^{18} \text{ cm}^{-3}$ not only exhibit the so-called Fano resonance, but also show a red shift in the Raman peak maximum [19]. The expected theoretical peak shift induced by an increase in doping satisfies:

$$k = k_0 + \frac{\Delta\Gamma}{2q} \quad (3)$$

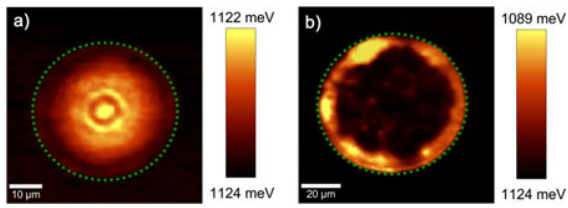


Fig. 6. PL center of mass maps of LFCs processed at (a) 0.98 W and (b) 1.43 W. The green dotted circles delimit the physical dimensions of the LFCs.

where k_0 is the peak position of the bulk un-doped and stress free c-Si and $\Delta\Gamma$ is the change in the Raman peak width due to doping. The expected theoretical peak shifts resulting from (3) for a q parameter of 16 (see Table I) takes values of about 0.5 cm^{-1} . These theoretical values are significantly lower than those observed in Fig. 5, i.e., about 2 cm^{-1} . This fact suggests that in addition to the red shift induced by an increase of the doping level, a second contribution in the Raman shift is also present. We correlate this second contribution with stress possibly induced by the laser process. LFCs processed at 0.98 and 1.1 W do not show any significant red shift in the first-order Raman peak maximum. Thus, the level of laser power used to process the LFCs probably plays an important role in the level of stress induced by the laser process.

321 B. Doping Characterization by 322 Photoluminescence Spectroscopy

Band-to-band photoluminescence spectroscopy senses the radiative recombination between photo-generated electrons in the conduction band (CB) and the corresponding holes in the valence band (VB). As an increase in doping density induces a reduction of the energy gap between CB and VB, PL has been proven as a reliable tool for monitoring the band-gap shift in heavily doped c-Si [14]. In this sense, micro-PL spectroscopy is also capable to characterize the high doping levels expected inside the LFCs. In fact, micro-PL has been applied to characterize the doping density in laser-induced highly doped regions cross sections [7]. In our study, we study the position and line shape of the PL emission line by monitoring the center of mass of the PL spectra recorded inside the LFCs.

Fig. 6 shows the PL center of mass maps corresponding to the LFCs processed at 0.98 (a) and 1.43 W (b). The averaged PL spectra obtained from the brighter zones of the PL maps are illustrated in Fig. 7. As it can be seen, the shift of the PL spectra center of mass revealed by the color scale bars of Fig. 6 is linked to an increase of the PL intensity at lower energies. In particular, the PL spectrum related to the 0.98 W LFC evidences a slight increase of the left PL spectrum shoulder, whereas the PL spectrum related to the 1.43 W LFC shows a significantly higher increase of the left PL spectrum shoulder plus a blue shift in the PL emission maximum. We correlate this shift of the PL line with a Si band-gap renormalization induced by a strong increase of doping in the measured material volume. The increase in the doping density is further confirmed by the inset of Fig. 7 which illustrates the PL spectra recorded from c-Si wafers with doping levels of 1×10^{15} , 5×10^{18} , and

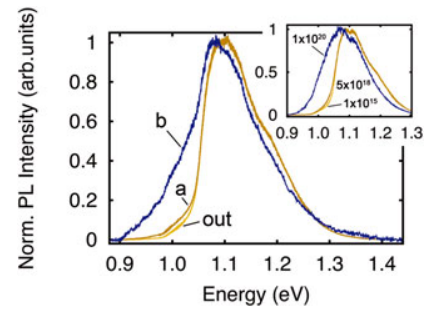


Fig. 7. Averaged PL spectra corresponding to the highly doped regions (yellow-colored regions) of PL center of mass maps a (0.98 W) and b (1.43 W) illustrated in Fig. 6. Additionally, a PL spectra recorded out of the processed LFC regions is also represented. The inset plot shows the PL spectra corresponding to three reference c-Si wafers with different doping level.

$1 \times 10^{20} \text{ cm}^{-3}$. As it can be seen, the inset and the main plot show the same trend. For all these reasons, we confirm that the brighter zones of the PL maps of Fig. 6 have associated a higher doping level. Interestingly, the two represented PL maps greatly correlate with the homologous Raman width maps of Fig. 1, demonstrating the successful application of micro-Raman and micro-PL techniques for studying doping-density variations above $1 \times 10^{18} \text{ cm}^{-3}$ with submicron resolution.

C. Laser-Fired Contact Characterization by Conductive-Atomic Force Microscopy

Finally, the study of LFCs was completed by their characterization by means of c-AFM measurements. The aim of these studies is to analyze if the laser-processed material volume shows preferential conductive zones, and if that is the case, to study their correlation with the highly doped regions deduced from Raman and PL data. C-AFM measurements have been divided in two groups. First, we have performed electrical maps of complete LFCs with the intention to qualitatively evidence differences in terms of electrical conductivity. In addition to the electrical maps, $I-V$ measurements were also performed. These measurements were done in static mode at various locations onto the LFCs. In order to minimize the well-known light scattering effects from the AFM laser, which can induce local photoconductivity [20], the laser was turned-off for a brief moment before the $I-V$ acquisition.

Representative c-AFM results obtained from a LFC processed at 1.43 W are shown in Fig. 8(a). The upper part of the image shows the topography map, whereas the lower part of the panel corresponds to the local resistance map recorded while applying a voltage of +2 V. In the latter, the darker zones indicate the areas with a low local resistance, i.e., high conductivity. In particular, the border of the contact shows the highest electrical conductivities which decrease as you move to the center of the contact. The highest local resistance was evidenced in outer region of the LFC (region that has not been processed). C-AFM data is in great agreement with Raman and PL data showed in the first part of the work, where highly doped regions of the contact processed at 1.43 W were detected at the border of the contact.

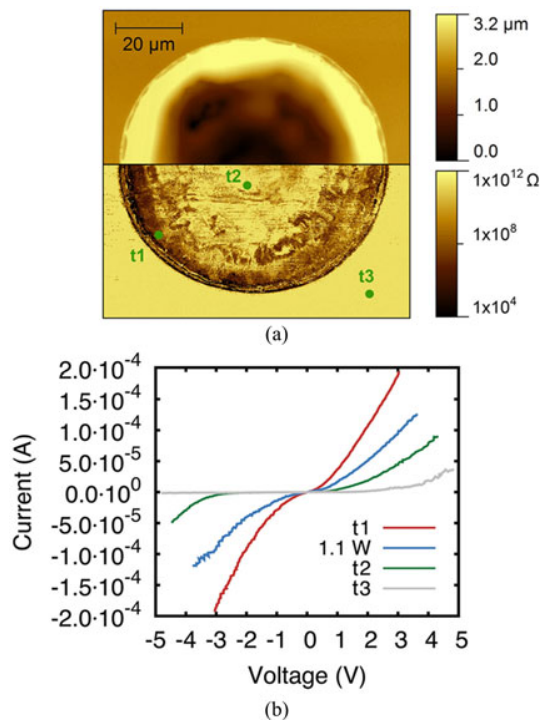


Fig. 8. (a) Topography (upper half) and local resistance (lower half) maps of a LFC processed at 1.43 W. (b) I - V characteristics of the selected points t1, t2, and t3 are represented. Additionally, an I - V curve (in blue) corresponding to a highly conductive area in a LFC processed at 1.1 W is also shown.

391 The I - V curves corresponding to the three points (t1, t2, and
 392 t3) depicted in the local resistance map of Fig. 8(a) are repre-
 393 sented in Fig. 8(b). The curves have been calculated from an
 394 average of at least 20 curves per point. As expected from the
 395 resistivity map, the curve recorded at point t1 is the one that
 396 shows a higher conductivity. Moreover, it also shows a good
 397 linearity evidencing an ohmic contact behavior between the di-
 398 amond tip and the sample. In contrast, the I - V curve recorded at
 399 point t2 (central part of the contact) evidences lower conductiv-
 400 ity than that obtained at point t1. In addition, t2 curve shows a
 401 rectifying behavior. This can be explained by a higher potential
 402 barrier between the diamond tip and the less doped Si region.
 403 Of course, this scenario is even more evident for the I - V curve
 404 measured on the unprocessed region (t3). The potential barrier
 405 between the diamond tip and the nonprocessed surface (with a
 406 related doping density of about $5 \times 10^{15} \text{ cm}^{-3}$) enlarges, creating
 407 a Schottky-like contact. In order to strengthen the consistency of
 408 the measurements, another I - V curve obtained onto the highly
 409 doped region of a contact processed at 1.1 W is also shown. As
 410 it was expected, the I - V curve shows a lower conductivity than
 411 the curve related to the LFC processed at 1.43 W. Again, the
 412 symmetry of the curve confirms the ohmic-like behavior of the
 413 contact between the tip and the highly doped sample region.

414 IV. CONCLUSION

415 In summary, the doping profiles in LFCs processed between
 416 0.98 and 1.43 W in Al_2O_3 -passivated p-type c-Si wafers have
 417 been studied. The laser power used to process the LFCs has been

found to play an important role in the distribution of the highly 418
 doped regions. At powers around 1 W, the highly doped regions 419
 that reach doping levels of $2 \times 10^{18} \text{ cm}^{-3}$ are preferentially lo- 420
 cated at the center of the LFCs. In contrast, for higher laser power 421
 values, the level of doping increases (levels of around 3×10^{19} 422
 cm^{-3} has been observed for contacts processed at 1.43 W), and 423
 the location of the highly doped regions moves toward the border 424
 of the contacts. The high spatial resolution associated with our 425
 micro-Raman measurements has allowed to obtain consistent 426
 doping density values. Hence, micro-Raman is preferably the 427
 more appropriate tool to quantify doping levels with submicron 428
 resolution. We consider an important result the observation of 429
 microcrystalline-like features in the Raman spectra recorded at 430
 specific points inside the LFCs, which suggests that the locally 431
 molten Si fraction solidifies in microcrystalline manner. 432

Highly doped regions revealed by Raman measurements have 433
 been further confirmed by micro-PL spectroscopy. Regions with 434
 a higher doping density evidenced a blue shift of the PL emission 435
 line, which we correlate with the Si band-gap renormalization 436
 induced by the strong increase in doping. Despite the sample 437
 volume measured by micro-PL is typically higher, and therefore, 438
 the spatial resolution is lower, micro-PL measurements have also 439
 shown a good sensitivity to doping variations. The high injection 440
 conditions and the subsequent reduction of the photo-generated 441
 carriers diffusion length [8] could favor to reduce the spatial 442
 resolution of micro-PL measurements. 443

Finally, Raman and PL data have been further confirmed by 444
 local I - V curves recorded through conductive-AFM. I - V char- 445
 acteristics obtained on highly doped areas featured an ohmic-like 446
 behavior, whereas I - V curves recorded at regions nonpro- 447
 cessed by laser, i.e., regions with lower doping level, revealed a 448
 Schottky-like behavior. 449

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REFERENCES 453

- [1] E. Schneiderlochner, R. Preu, R. Ldemann, and S. W. Glunz, "Laser-fired 454
 rear contacts for crystalline silicon solar cells," *Prog. Photovoltaic, Res. 455
 Appl.*, vol. 10, pp. 29–34, 2002. 456
- [2] D. Kray and S. Glunz, "Investigation of laser-fired rear-side recombination 457
 properties using an analytical model," *Prog. Photovoltaic, Res. Appl.*, 458
 vol. 14, pp. 195–201, 2006. 459
- [3] P. Ortega, A. Orpella, I. Martín, M. Colina, G. Lopez, C. Voz, 460
 M. I. Sanchez, C. Molpeceres, and R. Alcubilla, "Laser-fired contact 461
 optimization in c-Si solar cells," *Prog. Photovoltaic, Res. Appl.*, vol. 20, 462
 pp. 173–180, 2012. 463
- [4] M. Moors, K. Baert, T. Caremans, F. Duerinckx, A. Cacciato, and 464
 J. Szlufcik, "Industrial PERL-type solar cells exceeding 19% with screen- 465
 printed contacts and homogeneous emitter," *Sol. Energy Mat. Sol. C.*, 466
 vol. 106, pp. 84–88, 2012. 467
- [5] S. Glunz, A. Grobe, M. Hermle, M. Hofmann, S. Janz, T. Roth, O. Schultz, 468
 M. Vetter, I. Martín, R. Ferre, S. Bermejo, W. Wolke, W. Warta, and 469
 R. Willeke, "Comparison of different dielectric passivation layers for ap- 470
 plication in industrially feasible high-efficiency crystalline silicon solar 471
 cells," *Proc. 20th Eur. Photovoltaic Sol. Energy Conf.*, 2005, pp. 572–577. 472
- [6] P. Ortega, I. Martín, G. Lopez, M. Colina, A. Orpella, C. Voz, and 473
 R. Alcubilla, "P-type c-Si solar cells based on rear side laser process- 474
 ing of $\text{Al}_2\text{O}_3/\text{SiC}_x$ stacks," *Sol. Energy Mat. Sol. C.*, vol. 106, pp. 80–83, 475
 2012. 476

- 477 [7] P. Gundel, D. Suwito, U. Jger, F. D. Heinz, W. Warta, and M. C. Schubert, 502
 478 “Comprehensive microscopic analysis of laser-induced high doping 503
 479 regions in silicon,” *IEEE Trans. Electron Devices*, vol. 58, no. 9, 504
 480 pp. 2874–2877, Sep. 2011.
- 481 [8] P. Gundel, F. D. Heinz, M. C. Schubert, J. A. Giesecke, and W. Warta, 505
 482 “Quantitative carrier lifetime measurement with micron resolution,” *J.* 506
 483 *Appl. Phys.*, vol. 108, pp. 033705-1–033705-7 2010. 507
- 484 [9] F. Houzé, R. Meyer, O. Schneegans, and L. Boyer, “Imaging the local 508
 485 electrical properties of metal surfaces by atomic force microscopy with 509
 486 conducting probes,” *Appl. Phys. Lett.*, vol. 69, pp. 1975–1977, 1996. 510
- 487 [10] T. Kunz, M. Hessmann, S. Seren, B. Meidel, B. Terheiden, and C. Brabec, 511
 488 “Dopant mapping in highly p-doped silicon by micro-Raman spectroscopy 512
 489 at various injection levels,” *J. Appl. Phys.*, vol. 113, p. 023514, 2013. 513
- Q1 490 [11] M. Becker, U. Gosele, A. Hofmann, and S. Christiansen, “Highly p- 514
 491 doped regions in silicon solar cells quantitatively analyzed by small 515
 492 angle beveling and micro-Raman spectroscopy,” *J. Appl. Phys.*, vol. 106, 516
 493 p. 074515, 2009. 517
- 494 [12] U. Fano, “Effects of configuration interaction on intensities and phase 518
 495 shifts,” *Phys. Rev.*, vol. 124, pp. 1866–1878, 1961. 519
- 496 [13] F. Cerdeira, T. Fjeldly, and M. Cardona, “Effect of free carriers on zone- 520
 497 center vibrational modes in heavily doped p-type Si. II. Optical modes,” 521
 498 *Phys. Rev. B*, vol. 8, pp. 4734–4745, 1973. 522
- 499 [14] J. Wagner, “Band-gap narrowing in heavily doped silicon at 20 and 300 523
 500 K studied by photoluminescence,” *Phys. Rev. B*, vol. 32, pp. 1323–1325, 524
 501 1985.
- [15] V. Magidson and R. Beserman, “Fano-type interference in the Raman 502
 spectrum of photoexcited Si,” *Phys. Rev. B*, vol. 66, pp. 1952061–1952066, 503
 2002. 504
- [16] S. Veprek, F.-A. Sarott, and Z. Iqbal, “Effect of grain boundaries on the Ra- 505
 man spectra, optical absorption, and elastic light scattering in nanometer- 506
 sized crystalline silicon,” *Phys. Rev. B*, vol. 36, pp. 3344–3350, 1987. 507
- [17] Z. Iqbal, S. Veprek, A. Webb, and P. Capezzuto, “Raman scattering from 508
 small particle size polycrystalline silicon,” *Solid State Commun.*, vol. 37, 509
 pp. 993–996, 1981. 510
- [18] T. Kaneko, K. Onisawa, M. Wakagi, Y. Kita, and T. Minemura, “Crystalline 511
 fraction of microcrystalline silicon films prepared by plasma-enhanced 512
 chemical vapor deposition using pulsed silane flow,” *Jpn. J. Appl. Phys.*, 513
 vol. 32, p. 4907, 1993. 514
- [19] R. Agaiby, M. Becker, S. Thapa, U. Urmoneit, A. Berger, A. Gawlik, 515
 G. Sarau, and S. Christiansen, “Stress and doping uniformity of laser 516
 crystallized amorphous silicon in thin film silicon solar cells,” *J. Appl.* 517
Phys., vol. 107, p. 054312, 2010. 518
- [20] M. Ledinský, A. Fejfar, A. Vetushka, J. Stuchlík, B. Rezek, and J. Kocka, 519
 “Local photoconductivity of microcrystalline silicon thin films measured 520
 by conductive atomic force microscopy,” *Phys. Status Solidi RRL*, vol. 5, 521
 pp. 373–375, 2011. 522
- Authors’ photographs and biographies not available at the time of publication. 523
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Microscale Spatially Resolved Characterization of Highly Doped Regions in Laser-Fired Contacts for High-Efficiency Crystalline Si Solar Cells

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Abstract—Laser-fired contact (LFC) processes have emerged as a promising approach to create rear local electric contacts in p-type crystalline silicon solar cells. Despite this approach has been successfully applied in devices showing efficiencies above 20%, there is still a lack of knowledge about some specific features of LFCs at the submicron level. In this study, we used micro-Raman and microphotoluminescence (PL) spectroscopies to carry out a high-resolution spatially resolved characterization of LFCs processed in Al_2O_3 -passivated c-Si wafers. Relevant information concerning features such as local doping distribution and crystalline fraction of the laser-processed region has been obtained. In particular, interesting qualitative and quantitative variations concerning the doping profile have been observed between LFCs processed at different laser powers. Finally, conductive-atomic force microscopy measurements have allowed to identify the existence of highly conductive zones inside the LFCs greatly correlated with highly doped regions revealed by Raman and PL data. This study gives a detailed insight about the LFCs characteristics at the submicron level and their possible influence on the performance of final devices.

Index Terms—Crystalline silicon, laser-fired contacts (LFCs), microphotoluminescence spectroscopy, micro-Raman spectroscopy.

I. INTRODUCTION

FROM an industrial point of view, one of the most interesting crystalline silicon (c-Si) solar cell technologies to obtain high-efficiency devices is the passivated emitter and rear cell concept. Recently, the industrial implementation of this cell type has been significantly simplified by using the so-called laser fired contact (LFC) approach for the creation of the back contacts of the cell [1], [2]. This method is based on firing the

rear Al metallization layer by a laser beam in order to create electrical point contacts between the Al layer and the silicon substrate through the passivation layer.

A key feature for the good operation of LFCs is the formation of an Al-doped p+ region under the contacted surface area. This is achieved by the diffusion of Al atoms from the predeposited Al layer into the molten Si. This p+ region not only creates a local back-surface field that induces a relatively low recombination velocity below the contacts, but also ensures a low-contact resistance.

LFC approach can be applied by using any of the dielectric layers that have demonstrated excellent c-Si passivating properties such as silicon oxide (SiO_2) [3], silicon nitride (SiN_x) [4], amorphous-silicon carbide (a- SiC_x) [5], and most recently, aluminum oxide (Al_2O_3) [6]. In the case of using the latter passivating material, an interesting alternative to the conventional LFC process can be applied. In this case, the Al_2O_3 layer itself can be used as Al-dopant source for the formation of the p+ region, and hence, the LFC can be done directly onto the Al_2O_3 /c-Si, instead of being done onto the Al/dielectric/c-Si stack. This approach enables a lower laser power operation in comparison with conventional LFC process where higher laser powers are needed to fire the aluminum through the dielectric layer. These type of LFC processes have been already used to fabricate solar cells showing efficiencies well above 20% [6].

Despite the evident success in the implementation of the LFC approach in real devices, there is still a lack of information about specific features of LFCs such as the doping profile of the p+ region, the level of induced-stress, and/or the structural properties of the laser-processed region. The most likely reason for that is the difficulty to find experimental techniques that match a high-lateral resolution (below 10 μm) and sensitivity to the parameters wanted to be studied. Recently, a study of LFC cross sections [7] have demonstrated that Raman and photoluminescence (PL) spectroscopies in microconfiguration are techniques that fulfill the mentioned requirements.

In this study, we have carried out high-resolution micro-Raman and micro-PL spectroscopy measurements on different LFCs processed in Al_2O_3 -passivated c-Si samples. Thanks to the high lateral resolution down to 1 μm achieved in our experiments, we have been able to perform a detailed study of relevant LFC properties such as the doping profile, induced-stress, and crystallinity fraction, giving an important insight about the LFC formation. Three LFCs processed at different incident laser power have been studied in order to analyze the influence of the laser power on the studied features. Finally, in

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81 order to complement the PL and Raman data, conductive-atomic
82 force microscopy (c-AFM) measurements have been performed
83 in order to study local resistance variations inside the LFCs.

84 It is worth to mention that the term LFC has been used since
85 more than a decade to describe the firing of the predeposited alu-
86 minum through a dielectric layer. Despite the process used here
87 is fundamentally different, its finality and application in solar
88 cell devices is the same. For simplicity, we have maintained the
89 term LFC to refer to our laser-processed locally doped regions.

90 II. EXPERIMENTAL METHODS AND MATERIALS

91 Samples under study were based on 2.5 Ω -cm boron-doped
92 float-zone (FZ) crystalline Si (c-Si) wafers with a thickness of
93 250 μm and (1 0 0) crystal orientation. c-Si wafers were pas-
94 sivated by a 25-nm-thick aluminum oxide (Al_2O_3) film which
95 was grown by thermal atomic layer deposition. Laser fired spots
96 were processed on the top of the Al_2O_3 -passivated c-Si sam-
97 ples creating small apertures in the alumina layer and melting a
98 small part of the underlying c-Si subsurface region. LFCs were
99 processed by a 1064 nm Nd:YAG lamp-pumped laser working
100 at 100 ns of pulse duration. Each contact is a consequence of
101 six pulses at a repetition rate of 4 kHz. Three different LFCs
102 processed with a laser power of 0.98, 1.1, and 1.43 W were
103 studied, corresponding to pulse energies of 245, 275, and 357.5
104 μJ . The laser beam shows a Gaussian profile with a beam waist
105 characterized by a radius of 70 μm at the focus plane where all
106 the samples were processed. After laser processing and prior to
107 carry out the measurements, samples were immersed in an HF
108 1% solution bath during 40 s (or until obtaining an hydrophobic
109 silicon surface) in order to remove the Al_2O_3 layer. Addition-
110 ally, three boron-doped FZ c-Si wafers with doping densities
111 of 1×10^{15} , 5×10^{18} , and $1 \times 10^{20} \text{ cm}^{-3}$ were used in order to
112 obtain reference Raman and PL spectra.

113 Micro-Raman and microphotoluminescence experiments
114 were carried out with a WITEC alpha300. A diagram of the
115 Witec equipment setup can be found in [8]. A diode-pumped
116 laser with a wavelength of 532 nm was used as an excitation
117 source resulting in a penetration depth of about 1 μm . Micro-
118 Raman and micro-PL measurements were performed with a 100
119 \times VIS (visible), NA (numerical aperture) = 0.9 and a 20 \times IR
120 (Infrared), NA = 0.45, respectively. The resulting beam spot
121 size on the sample surface is in diameter below 1 and 2 μm for
122 Raman and PL measurements, respectively. Raman scattering
123 signal was recorded through a 300-mm imaging spectrometer
124 equipped with both a 600 lines/mm and 1800 lines/mm grat-
125 ing, and a 1024 \times 127 CCD (charge-coupled device) camera
126 visible-optimized, whereas PL signal was collected through an
127 additional 300-mm spectrometer composed of two gratings (150
128 and 300 lines/mm) and a 1024 \times 1 pixel linear InGaAs photodi-
129 ode array optimized for spectroscopy applications in the range
130 1–1.7 μm . It is worth to mention that the incoming laser power
131 on the sample surface for the Raman measurements was kept
132 below 3 mW. With our configuration, 3 mW was measured to
133 be the pumping limit to keep the photo-generated carrier den-
134 sity below threshold and, therefore, to avoid Fano resonances
135 induced by high injection conditions [15].

Local electrical measurements through the c-AFM technique 136
were performed using a Digital Instruments Nanoscope IIIa 137
Multimode AFM associated with the home-made conducting 138
probe extension called “Resiscope” [9]. This extension allows 139
us to apply a stable dc bias voltage (from -10 to $+10$ V) to the 140
sample and to measure the resulting current flowing through the 141
tip as the sample surface is scanned in contact mode, yielding a 142
local resistance map covering resistance values in the range 10^2 – 143
 $10^{12} \Omega$. Current–Voltage (I – V) measurements are also permitted 144
with this extension. Highly boron doped diamond-coated Si 145
AFM cantilevers, with an intermediate spring constant of about 146
3 N/m, proved to be the most suitable AFM tips for making 147
electrical measurements on LFCs. Due to the AFM tip radius 148
(~ 50 nm), c-AFM measurements offer a much greater lateral 149
resolution. This latter depends on the electrical contact radius 150
between the tip and the surface. In the particular case of flat 151
surfaces, the electrical contact radius can be much smaller than 152
AFM tip radius. The probed depth remains in the nanoscale 153
range, but it is linked, among other parameters, to the applied 154
voltage and the local electrical transport properties. 155

156 III. RESULTS AND DISCUSSION

157 A. Doping Characterization by Micro-Raman Spectroscopy

158 Doping profiles in c-Si can be monitored by studying both 158
the Full Width at Half Maximum (FWHM) [10] and the Fano 159
resonance [11] of the first-order Si Raman peak. In particular, 160
Fano resonances are evident in the Si Raman spectra at hole 161
concentrations above 10^{18} cm^{-3} by a characteristic asymmetry 162
in the first-order Si Raman line. This asymmetry results from 163
the resonant interaction between discrete phonon states and a 164
continuum of hole states [12], [13]. The Raman peak line shape 165
can be described by the following expression [11]: 166

$$167 I(k) = I_0 \cdot \frac{[q + 2(k - k_{ph})/\Gamma]^2}{1 + [2(k - k_{ph})/\Gamma]^2} \quad (1)$$

168 where I_0 is a scaling factor, k_{ph} is the frequency associated to 167
the Raman peak maximum, Γ corresponds to the FWHM, and q 168
is the asymmetry parameter, which is correlated with the doping 169
level of the sample being studied. The lower the q parameter, 170
the higher the doping level. The first-order Si Raman peak can 171
be also influenced by stress and/or by the material crystalline 172
fraction. The former can be monitored by the peak frequency 173
shift, whereas the latter is evidenced by a peak broadening from 174
the c-Si to the amorphous-Si state. 175

176 Fig. 1 shows the optical microscope images (left-hand side) 176
and the corresponding Raman peak width maps (right-hand side) 177
of the three LFCs under study processed at 0.98 (a) and (b), 178
1.1 (c) and (d), and 1.43 W (e) and (f). Maps were obtained 179
from the raw Raman peak width, not from the fitted Γ . The 180
corresponding LFC diameters were 43.8, 54.5, and 74.2 μm , 181
respectively. For ensuring a good observation of the obtained 182
data, the microscope images and the Raman maps of the three 183
contacts have been represented with a slightly different scale. In 184
addition for clarity, the physical dimensions of the LFCs have 185
been represented in Raman maps by a green dotted circle. As 186
explained previously, the width of the first-order Raman peak 187

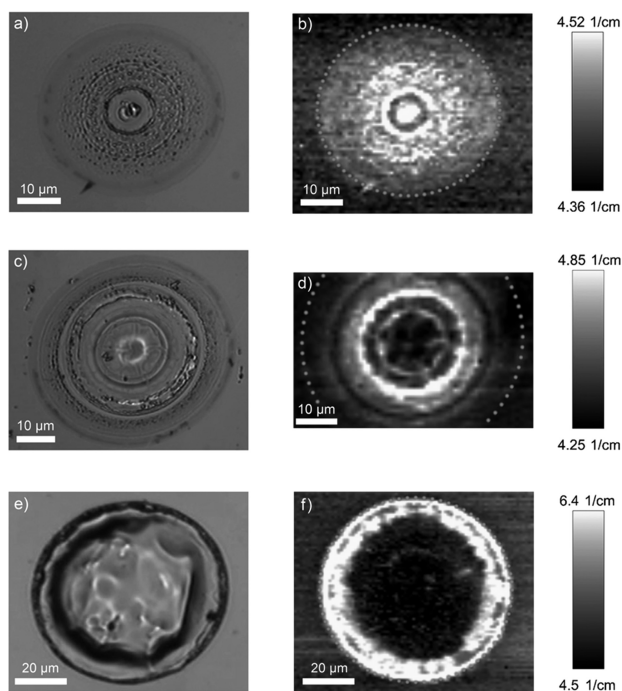


Fig. 1. Optical microscope images (left-hand side) and Raman peak width maps (right-hand side) of the three LFCs under study processed at 0.98 (a) and (b), 1.1 (c) and (d), and 1.43 W (e) and (f). Brighter zones in the Raman peak width maps correspond to zones with higher doping density.

188 can be used to monitor the doping level of the sample under
 189 study. Hence, the zones that evidence an increase of the Raman
 190 peak width in Fig. 1 (brighter zones) are qualitatively correlated
 191 with zones with a higher doping level. The LFC processed at
 192 0.98 W evidences slightly higher levels of doping at the central
 193 part of the contact. In contrast, the contact processed at 1.1 W
 194 [see Fig. 1(d)] evidences a brighter concentric corona pointing
 195 out a wider Raman peak and consequently an increase of the
 196 doping level. Following the same trend, for the contact processed
 197 using the higher laser power [see Fig. 1(f)], the border of the
 198 contact is the area that evidences a higher level of doping. The
 199 different Raman maps illustrated in Fig. 1 demonstrate that
 200 the laser power plays an important role on the distribution of
 201 the highly doped regions inside the contacts. More precisely,
 202 it seems that for higher laser powers, the highly doped regions
 203 move toward the border of the contact. Two-dimensional depth
 204 profiling across LFCs (maps not shown for space limitations)
 205 revealed the same results. This fact corroborates that the features
 206 of Raman maps shown in Fig. 1 were not affected by variations
 207 in surface topography of LFCs.

208 The correlation between the Raman peak widening observed
 209 in Fig. 1 and the expected increase in the doping density is con-
 210 firmed by data shown in Fig. 2. This figure shows the averaged
 211 Raman spectra corresponding to the zones with higher doping
 212 of images b, d, and f of Fig. 1. In particular, the averaged spectra
 213 were calculated from the yellow-colored areas of Raman maps.
 214 An averaged spectrum corresponding to an unprocessed area
 215 (outer region of LFC) is also shown (yellow dashed line). In

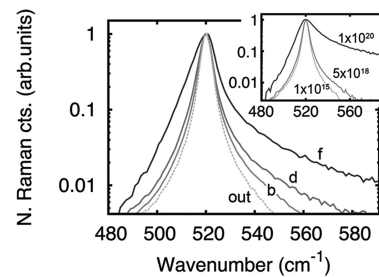


Fig. 2. Averaged Raman spectra corresponding to the brighter zones of maps b, d, and f of Fig. 1. For comparison, an averaged Raman spectra corresponding to an unprocessed surface area has been also represented (yellow dashed line). The inset shows the Raman spectra recorded from the three reference c-Si wafers with different doping level.

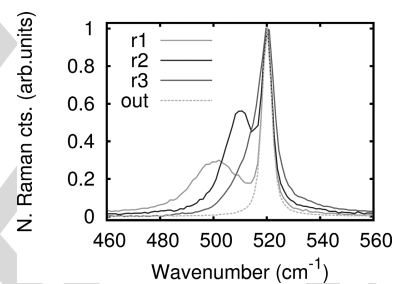


Fig. 3. Raman spectra obtained at specific points inside LFCs processed at 1.1 W (r1, r2) and 1.43 W (r3). In addition to the first-order Raman peak, a second peak characteristic of microcrystalline silicon sets in at lower wavenumbers. For comparison, a Raman peak related to an unprocessed area (outer region of LFCs) is also depicted.

216 order to facilitate the observation of Fano resonances, Raman
 217 spectra have been represented using a semilog scale. As it can
 218 be observed, the Fano resonance is clearly identified for all Raman
 219 spectra except for the one obtained out of the LFC, which
 220 shows a symmetric Raman line shape. This qualitatively con-
 221 firms that the brighter zones in maps of Fig. 1 are correlated
 222 with areas with a higher doping level. The increase in doping
 223 is also greatly confirmed by the inset, where the Raman spectra
 224 recorded from three reference c-Si wafers with doping levels of
 225 1×10^{15} , 5×10^{18} , and $1 \times 10^{20} \text{ cm}^{-3}$ clearly evidence the
 226 same trend concerning the Fano resonance. Another important
 227 feature observed in the main plot of Fig. 2 is that the LFCs
 228 processed with a higher laser power have associated a higher
 229 Fano asymmetry. Hence, the use of higher laser powers results
 230 in LFCs with higher doping densities.

231 In order to get further important information about the LFCs
 232 formation, we depict in Fig. 3 the Raman spectra recorded
 233 at three specific points (r1, r2, and r3) inside two LFCs pro-
 234 cessed at 1.1 W (r1, r2) and 1.43 W (r3) (contact images and
 235 point positions not shown). A fourth Raman spectrum corre-
 236 sponding to a nonprocessed surface area is also represented
 237 as a reference. As it can be observed, in addition to the first-
 238 order c-Si Raman line positioned at 520.9 cm^{-1} , new Raman
 239 bands can be identified at lower wavenumbers in the range be-
 240 tween 500 and 515 cm^{-1} . These latter bands are commonly as-
 241 signed to microcrystalline silicon [16], [17]. Indeed, the Raman

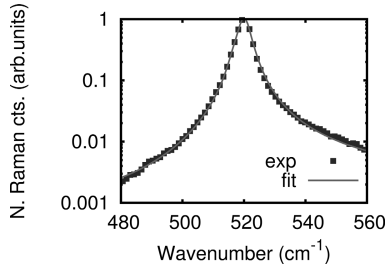


Fig. 4. Fitting using (2) of the Raman spectrum corresponding to the highly-doped region of the LFC processed at 1.1 W. Fit gave a q parameter of 59 which is correlated to a doping level of about $5.8 \times 10^{18} \text{ cm}^{-3}$.

spectra of microcrystalline-Si are currently decomposed into three bands: crystalline ($\sim 520 \text{ cm}^{-1}$), intermediate band ($500\text{--}515 \text{ cm}^{-1}$, usually interpreted as a signature of the grain boundaries or small crystallites grain size $< 10 \text{ nm}$), and amorphous (480 cm^{-1}). The following decomposition is used to quantify the crystalline fraction [18]. The observation of these new Raman bands at specific points inside the LFCs suggests that molten Si material fraction solidifies in a structure involving crystallites, grain boundaries, and an amorphous phase, at least in specific zones inside the contacts. However, the crystalline fraction in these zones reveals to be high indicating a negligible amorphous component.

The contribution of microcrystalline-Si components to the obtained Raman spectra is further confirmed by the fact that all Raman spectra recorded inside the LFCs could be significantly better fitted using a rewriting of (1) that considers a second Lorentzian function related to the contribution of the microcrystalline Si formation. In fact, the expression that has been used to fit the Raman data is the following:

$$I(k) = I_0 \cdot \frac{[q + 2(k - k_{ph})/\Gamma]^2}{1 + [2(k - k_{ph})/\Gamma]^2} + \frac{A}{1 + [2(k - k_m)/\Gamma_m]^2} \quad (2)$$

where A corresponds to the intensity, k_m is the frequency of the peak maximum, and Γ_m is the peak width of the Raman band related to the microcrystalline-like component. It is worth to mention that the position of the second Lorentzian function was limited to values between 505 and 517 cm^{-1} . As observed in Fig. 4 for a LFC processed at 1.1 W, the fit using (2) shows very good adjustment paving the way to obtain a reliable quantification about the doping level inside the LFCs.

Table I shows the q asymmetry parameters resulting from the best fit of (2) to the Raman spectra related to the highly doped regions of the three LFCs under study. Data were calculated from at least two LFCs for each one of the three values of laser power. The obtained q parameters clearly illustrate that the higher the laser power, the higher the doping density. According to the calibration tables reported in [10] and [11], we have obtained maximum doping levels in the range of $1.17\text{--}3.83 \times 10^{18}$, $4.58\text{--}6.06 \times 10^{18}$, and $2.15\text{--}5.02 \times 10^{19} \text{ cm}^{-3}$ for the LFCs processed at 0.98, 1.1, and 1.43 W, respectively. It is important to

TABLE I
 q ASYMMETRY PARAMETER OBTAINED FROM THE FITTING OF (2) TO THE AVERAGED RAMAN SPECTRA RELATED TO THE HIGHLY DOPED REGIONS OF THE THREE LFCs UNDER STUDY.

power (W)	q (arb.units)	doping ref. [10] ($\times 10^{18} \text{ cm}^{-3}$)	doping ref. [11] ($\times 10^{18} \text{ cm}^{-3}$)
0.98	90 ± 7	3.13 – 3.83	1.17 – 2.35
1.10	61 ± 4	5.19 – 6.06	4.58 – 6.03
1.43	16 ± 2	21.49 – 27.93	42.19 – 50.17

The corresponding doping densities were calculated using the calibration tables reported in [10] and [11].

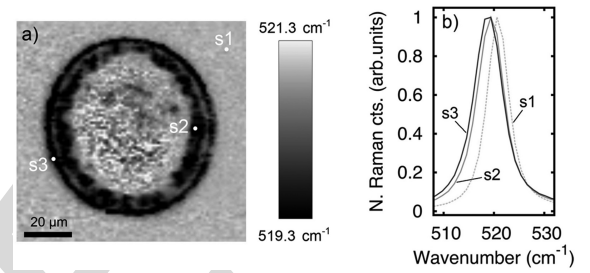


Fig. 5. (a) Raman spectra center of mass map of a LFC processed at 1.43 W. (b) Specific Raman spectra associated with points s1, s2, and s3 are also plotted.

remark that the intensity of the second Lorentzian peak related to the multicrystalline component was observed to increase with higher laser powers. This suggests that the use of higher laser powers decreases the crystalline fraction of the solidified Si volume.

Fig. 5(a) shows the Raman spectra center of mass map of a LFC processed at 1.43 W. The Raman spectra of the selected points (s1, s2, and s3) are represented in Fig. 5(b). The center of mass was calculated considering a frequency range between 480 and 560 cm^{-1} ; thus, as confirmed by Raman spectra of Fig. 5(b), it could be qualitatively correlated with the frequency shift of the first-order Si Raman peak. The first-order Raman line of s1, s2, and s3 Raman spectra is centered at 520.8 , 519.3 , and 518.7 cm^{-1} , respectively. Notice that the center of mass values represented by the color scale bar of Fig. 5(a) are shifted toward higher frequencies respect the Raman peak position values mentioned previously. This is induced by the contribution of the Fano resonance which moves the center of mass toward higher energies respect the peak maximum. As it can be seen, the Raman peak position suffers a red shift of about 2 cm^{-1} at the border of the contact. Interestingly, areas of the contact that show such a red shift exactly match with areas of the 1.43 W LFC that evidence higher levels of doping [see Fig. 1(f)]. It has been reported, that Raman spectra obtained from samples with doping levels above $5 \times 10^{18} \text{ cm}^{-3}$ not only exhibit the so-called Fano resonance, but also show a red shift in the Raman peak maximum [19]. The expected theoretical peak shift induced by an increase in doping satisfies:

$$k = k_0 + \frac{\Delta\Gamma}{2q} \quad (3)$$

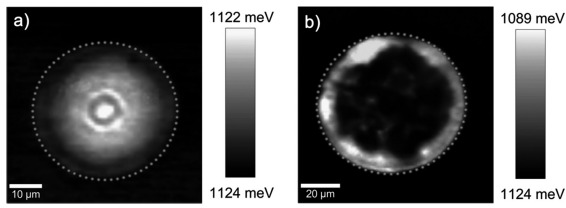


Fig. 6. PL center of mass maps of LFCs processed at (a) 0.98 W and (b) 1.43 W. The green dotted circles delimit the physical dimensions of the LFCs.

where k_0 is the peak position of the bulk un-doped and stress free c-Si and $\Delta\Gamma$ is the change in the Raman peak width due to doping. The expected theoretical peak shifts resulting from (3) for a q parameter of 16 (see Table I) takes values of about 0.5 cm^{-1} . These theoretical values are significantly lower than those observed in Fig. 5, i.e., about 2 cm^{-1} . This fact suggests that in addition to the red shift induced by an increase of the doping level, a second contribution in the Raman shift is also present. We correlate this second contribution with stress possibly induced by the laser process. LFCs processed at 0.98 and 1.1 W do not show any significant red shift in the first-order Raman peak maximum. Thus, the level of laser power used to process the LFCs probably plays an important role in the level of stress induced by the laser process.

321 B. Doping Characterization by 322 Photoluminescence Spectroscopy

Band-to-band photoluminescence spectroscopy senses the radiative recombination between photo-generated electrons in the conduction band (CB) and the corresponding holes in the valence band (VB). As an increase in doping density induces a reduction of the energy gap between CB and VB, PL has been proven as a reliable tool for monitoring the band-gap shift in heavily doped c-Si [14]. In this sense, micro-PL spectroscopy is also capable to characterize the high doping levels expected inside the LFCs. In fact, micro-PL has been applied to characterize the doping density in laser-induced highly doped regions cross sections [7]. In our study, we study the position and line shape of the PL emission line by monitoring the center of mass of the PL spectra recorded inside the LFCs.

Fig. 6 shows the PL center of mass maps corresponding to the LFCs processed at 0.98 (a) and 1.43 W (b). The averaged PL spectra obtained from the brighter zones of the PL maps are illustrated in Fig. 7. As it can be seen, the shift of the PL spectra center of mass revealed by the color scale bars of Fig. 6 is linked to an increase of the PL intensity at lower energies. In particular, the PL spectrum related to the 0.98 W LFC evidences a slight increase of the left PL spectrum shoulder, whereas the PL spectrum related to the 1.43 W LFC shows a significantly higher increase of the left PL spectrum shoulder plus a blue shift in the PL emission maximum. We correlate this shift of the PL line with a Si band-gap renormalization induced by a strong increase of doping in the measured material volume. The increase in the doping density is further confirmed by the inset of Fig. 7 which illustrates the PL spectra recorded from c-Si wafers with doping levels of 1×10^{15} , 5×10^{18} , and

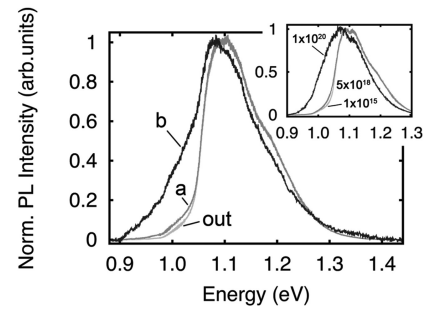


Fig. 7. Averaged PL spectra corresponding to the highly doped regions (yellow-colored regions) of PL center of mass maps a (0.98 W) and b (1.43 W) illustrated in Fig. 6. Additionally, a PL spectra recorded out of the processed LFC regions is also represented. The inset plot shows the PL spectra corresponding to three reference c-Si wafers with different doping level.

$1 \times 10^{20} \text{ cm}^{-3}$. As it can be seen, the inset and the main plot show the same trend. For all these reasons, we confirm that the brighter zones of the PL maps of Fig. 6 have associated a higher doping level. Interestingly, the two represented PL maps greatly correlate with the homologous Raman width maps of Fig. 1, demonstrating the successful application of micro-Raman and micro-PL techniques for studying doping-density variations above $1 \times 10^{18} \text{ cm}^{-3}$ with submicron resolution.

C. Laser-Fired Contact Characterization by Conductive-Atomic Force Microscopy

Finally, the study of LFCs was completed by their characterization by means of c-AFM measurements. The aim of these studies is to analyze if the laser-processed material volume shows preferential conductive zones, and if that is the case, to study their correlation with the highly doped regions deduced from Raman and PL data. C-AFM measurements have been divided in two groups. First, we have performed electrical maps of complete LFCs with the intention to qualitatively evidence differences in terms of electrical conductivity. In addition to the electrical maps, $I-V$ measurements were also performed. These measurements were done in static mode at various locations onto the LFCs. In order to minimize the well-known light scattering effects from the AFM laser, which can induce local photoconductivity [20], the laser was turned-off for a brief moment before the $I-V$ acquisition.

Representative c-AFM results obtained from a LFC processed at 1.43 W are shown in Fig. 8(a). The upper part of the image shows the topography map, whereas the lower part of the panel corresponds to the local resistance map recorded while applying a voltage of +2 V. In the latter, the darker zones indicate the areas with a low local resistance, i.e., high conductivity. In particular, the border of the contact shows the highest electrical conductivities which decrease as you move to the center of the contact. The highest local resistance was evidenced in outer region of the LFC (region that has not been processed). C-AFM data is in great agreement with Raman and PL data showed in the first part of the work, where highly doped regions of the contact processed at 1.43 W were detected at the border of the contact.

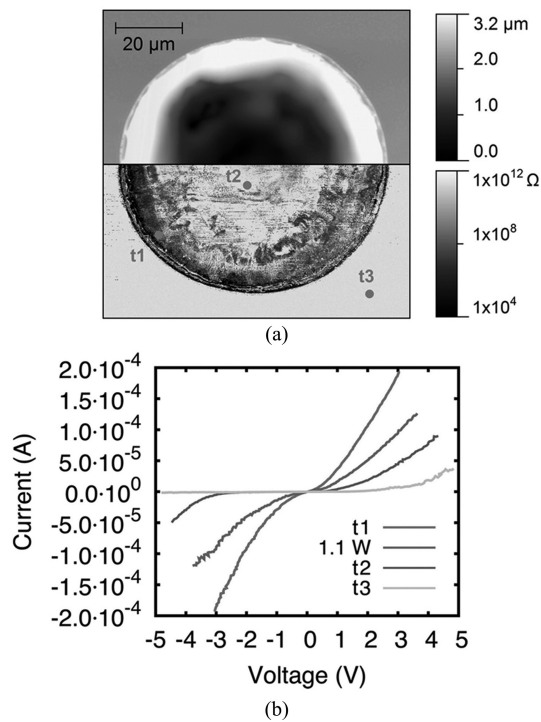


Fig. 8. (a) Topography (upper half) and local resistance (lower half) maps of a LFC processed at 1.43 W. (b) I - V characteristics of the selected points t1, t2, and t3 are represented. Additionally, an I - V curve (in blue) corresponding to a highly conductive area in a LFC processed at 1.1 W is also shown.

391 The I - V curves corresponding to the three points (t1, t2, and
 392 t3) depicted in the local resistance map of Fig. 8(a) are repre-
 393 sented in Fig. 8(b). The curves have been calculated from an
 394 average of at least 20 curves per point. As expected from the
 395 resistivity map, the curve recorded at point t1 is the one that
 396 shows a higher conductivity. Moreover, it also shows a good
 397 linearity evidencing an ohmic contact behavior between the di-
 398 amond tip and the sample. In contrast, the I - V curve recorded at
 399 point t2 (central part of the contact) evidences lower conductiv-
 400 ity than that obtained at point t1. In addition, t2 curve shows a
 401 rectifying behavior. This can be explained by a higher potential
 402 barrier between the diamond tip and the less doped Si region.
 403 Of course, this scenario is even more evident for the I - V curve
 404 measured on the unprocessed region (t3). The potential barrier
 405 between the diamond tip and the nonprocessed surface (with a
 406 related doping density of about $5 \times 10^{15} \text{ cm}^{-3}$) enlarges, creating
 407 a Schottky-like contact. In order to strengthen the consistency of
 408 the measurements, another I - V curve obtained onto the highly
 409 doped region of a contact processed at 1.1 W is also shown. As
 410 it was expected, the I - V curve shows a lower conductivity than
 411 the curve related to the LFC processed at 1.43 W. Again, the
 412 symmetry of the curve confirms the ohmic-like behavior of the
 413 contact between the tip and the highly doped sample region.

414 IV. CONCLUSION

415 In summary, the doping profiles in LFCs processed between
 416 0.98 and 1.43 W in Al_2O_3 -passivated p-type c-Si wafers have
 417 been studied. The laser power used to process the LFCs has been

found to play an important role in the distribution of the highly 418
 doped regions. At powers around 1 W, the highly doped regions 419
 that reach doping levels of $2 \times 10^{18} \text{ cm}^{-3}$ are preferentially lo- 420
 cated at the center of the LFCs. In contrast, for higher laser power 421
 values, the level of doping increases (levels of around 3×10^{19} 422
 cm^{-3} has been observed for contacts processed at 1.43 W), and 423
 the location of the highly doped regions moves toward the border 424
 of the contacts. The high spatial resolution associated with our 425
 micro-Raman measurements has allowed to obtain consistent 426
 doping density values. Hence, micro-Raman is preferably the 427
 more appropriate tool to quantify doping levels with submicron 428
 resolution. We consider an important result the observation of 429
 microcrystalline-like features in the Raman spectra recorded at 430
 specific points inside the LFCs, which suggests that the locally 431
 molten Si fraction solidifies in microcrystalline manner. 432

Highly doped regions revealed by Raman measurements have 433
 been further confirmed by micro-PL spectroscopy. Regions with 434
 a higher doping density evidenced a blue shift of the PL emission 435
 line, which we correlate with the Si band-gap renormalization 436
 induced by the strong increase in doping. Despite the sample 437
 volume measured by micro-PL is typically higher, and therefore, 438
 the spatial resolution is lower, micro-PL measurements have also 439
 shown a good sensitivity to doping variations. The high injection 440
 conditions and the subsequent reduction of the photo-generated 441
 carriers diffusion length [8] could favor to reduce the spatial 442
 resolution of micro-PL measurements. 443

Finally, Raman and PL data have been further confirmed by 444
 local I - V curves recorded through conductive-AFM. I - V char- 445
 acteristics obtained on highly doped areas featured an ohmic- 446
 like behavior, whereas I - V curves recorded at regions nonpro- 447
 cessed by laser, i.e., regions with lower doping level, revealed a 448
 Schottky-like behavior. 449

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REFERENCES 453

- [1] E. Schneiderlochner, R. Preu, R. Ldemann, and S. W. Glunz, "Laser-fired 454
 rear contacts for crystalline silicon solar cells," *Prog. Photovoltaic, Res.* 455
Appl., vol. 10, pp. 29–34, 2002. 456
- [2] D. Kray and S. Glunz, "Investigation of laser-fired rear-side recombination 457
 properties using an analytical model," *Prog. Photovoltaic, Res. Appl.*, 458
 vol. 14, pp. 195–201, 2006. 459
- [3] P. Ortega, A. Orpella, I. Martín, M. Colina, G. Lopez, C. Voz, 460
 M. I. Sanchez, C. Molpeceres, and R. Alcubilla, "Laser-fired contact 461
 optimization in c-Si solar cells," *Prog. Photovoltaic, Res. Appl.*, vol. 20, 462
 pp. 173–180, 2012. 463
- [4] M. Moors, K. Baert, T. Caremans, F. Duerinckx, A. Cacciato, and 464
 J. Szlufcik, "Industrial PERL-type solar cells exceeding 19% with screen- 465
 printed contacts and homogeneous emitter," *Sol. Energy Mat. Sol. C.*, 466
 vol. 106, pp. 84–88, 2012. 467
- [5] S. Glunz, A. Grobe, M. Hermlle, M. Hofmann, S. Janz, T. Roth, O. Schultz, 468
 M. Vetter, I. Martín, R. Ferre, S. Bermejo, W. Wolke, W. Warta, and 469
 R. Willeke, "Comparison of different dielectric passivation layers for ap- 470
 plication in industrially feasible high-efficiency crystalline silicon solar 471
 cells," *Proc. 20th Eur. Photovoltaic Sol. Energy Conf.*, 2005, pp. 572–577. 472
- [6] P. Ortega, I. Martín, G. Lopez, M. Colina, A. Orpella, C. Voz, and 473
 R. Alcubilla, "P-type c-Si solar cells based on rear side laser process- 474
 ing of $\text{Al}_2\text{O}_3/\text{SiC}_x$ stacks," *Sol. Energy Mat. Sol. C.*, vol. 106, pp. 80–83, 475
 2012. 476

- 477 [7] P. Gundel, D. Suwito, U. Jger, F. D. Heinz, W. Warta, and M. C. Schubert, 502
478 "Comprehensive microscopic analysis of laser-induced high doping 503
479 regions in silicon," *IEEE Trans. Electron Devices*, vol. 58, no. 9, 504
480 pp. 2874–2877, Sep. 2011.
- 481 [8] P. Gundel, F. D. Heinz, M. C. Schubert, J. A. Giesecke, and W. Warta, 505
482 "Quantitative carrier lifetime measurement with micron resolution," *J.* 506
483 *Appl. Phys.*, vol. 108, pp. 033705-1–033705-7 2010. 507
- 484 [9] F. Houzé, R. Meyer, O. Schneegans, and L. Boyer, "Imaging the local 508
485 electrical properties of metal surfaces by atomic force microscopy with 509
486 conducting probes," *Appl. Phys. Lett.*, vol. 69, pp. 1975–1977, 1996. 510
- 487 [10] T. Kunz, M. Hessmann, S. Seren, B. Meidel, B. Terheiden, and C. Brabec, 511
488 "Dopant mapping in highly p-doped silicon by micro-Raman spectroscopy 512
489 at various injection levels," *J. Appl. Phys.*, vol. 113, p. 023514, 2013. 513
- Q1 490 [11] M. Becker, U. Gosele, A. Hofmann, and S. Christiansen, "Highly p- 514
491 doped regions in silicon solar cells quantitatively analyzed by small 515
492 angle beveling and micro-Raman spectroscopy," *J. Appl. Phys.*, vol. 106, 516
493 p. 074515, 2009. 517
- 494 [12] U. Fano, "Effects of configuration interaction on intensities and phase 518
495 shifts," *Phys. Rev.*, vol. 124, pp. 1866–1878, 1961. 519
- 496 [13] F. Cerdeira, T. Fjeldly, and M. Cardona, "Effect of free carriers on zone- 520
497 center vibrational modes in heavily doped p-type Si. II. Optical modes," 521
498 *Phys. Rev. B*, vol. 8, pp. 4734–4745, 1973. 522
- 499 [14] J. Wagner, "Band-gap narrowing in heavily doped silicon at 20 and 300 523
500 K studied by photoluminescence," *Phys. Rev. B*, vol. 32, pp. 1323–1325, 524
501 1985.
- [15] V. Magidson and R. Beserman, "Fano-type interference in the Raman 502
503 spectrum of photoexcited Si," *Phys. Rev. B*, vol. 66, pp. 1952061–1952066, 504
2002.
- [16] S. Veprek, F.-A. Sarott, and Z. Iqbal, "Effect of grain boundaries on the Ra- 505
506 man spectra, optical absorption, and elastic light scattering in nanometer- 507
508 sized crystalline silicon," *Phys. Rev. B*, vol. 36, pp. 3344–3350, 1987. 509
- [17] Z. Iqbal, S. Veprek, A. Webb, and P. Capezzuto, "Raman scattering from 510
511 small particle size polycrystalline silicon," *Solid State Commun.*, vol. 37, 512
pp. 993–996, 1981. 513
- [18] T. Kaneko, K. Onisawa, M. Wakagi, Y. Kita, and T. Minemura, "Crystalline 514
515 fraction of microcrystalline silicon films prepared by plasma-enhanced 516
517 chemical vapor deposition using pulsed silane flow," *Jpn. J. Appl. Phys.*, 518
vol. 32, p. 4907, 1993. 519
- [19] R. Agaiby, M. Becker, S. Thapa, U. Urmoneit, A. Berger, A. Gawlik, 520
521 G. Sarau, and S. Christiansen, "Stress and doping uniformity of laser 522
523 crystallized amorphous silicon in thin film silicon solar cells," *J. Appl.* 524
Phys., vol. 107, p. 054312, 2010.
- [20] M. Ledinský, A. Fejfar, A. Vetushka, J. Stuchlík, B. Rezek, and J. Kocka, 525
526 "Local photoconductivity of microcrystalline silicon thin films measured 527
528 by conductive atomic force microscopy," *Phys. Status Solidi RRL*, vol. 5, 529
pp. 373–375, 2011.
- Authors' photographs and biographies not available at the time of publication. 530
531

526 Q1. Author: Please provide the complete page range in Refs. [10], [11], [18], and [19].

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