

# Enhanced Performance of Small GaAs Solar Cells via Edge and Surface Passivation with Trioctylphosphine Sulfide

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**Abstract** — We have extended our previous work on trioctylphosphine sulfide (TOP:S) to further elucidate the mechanisms of this chemical passivation for small GaAs solar cells. Photoluminescence (PL) measurements indicate monolayers of TOP:S on GaAs significantly increases the electronic quality of both n- and p-doped wafers. TOP:S was also applied to an “ultra small” GaAs solar cell (0.31 mm<sup>2</sup>) to test its ability to passivate devices with the relevant dimensions for microconcentrator schemes. After the cells were briefly soaked in TOP:S, the efficiency of the cell was boosted by 1% (absolute), even after a rinse in toluene to remove all but a few monolayers of TOP:S, confirming sidewall passivation.

**Index Terms** — GaAs, passivation, photovoltaic cells, sulfur.

## I. INTRODUCTION

III-V compound semiconductors are the foundational materials for the highest efficiency single junction and multijunction concentrator solar cells. GaAs solar cells have set new single junction photovoltaic efficiency records, achieving efficiencies as high as 28.3% and multijunction solar cells based on III-V compound semiconductor heterostructures have reached efficiencies as high as 43.5% [1]. The high efficiency of these cells is achieved in part by effective passivation of the front and rear surfaces to mitigate recombination of photogenerated carriers. However, effective passivation remains a challenge for a variety of attractive III-V compound semiconductor materials.

Further, there has been growing interest in the design of small ( $\leq$  mm<sup>2</sup>) III-V thin film solar cells fabricated by transfer printing methods for microconcentrator applications because high efficiencies are attainable with smaller semiconductor area fractions and microscale optical components [2]. However, small cells introduce new optimization challenges. Typically the lateral side walls in large ( $\gg$  cm<sup>2</sup>) cells are not passivated since edge facets usually comprise a small fraction ( $\ll$  1 %) of the cell surface area and recombination there does not significantly compromise cell efficiency. However, minority carrier recombination is a significant loss mechanism for small III-V cells whose top and bottom surfaces are passivated by heterojunction windows but whose edges are exposed. In very small cells, the larger fraction of exposed sidewall surface area causes an increase of recombination dark current at the sidewalls and reduced efficiency that is highly dependent on the surface area of bare lateral semiconductor material. Traditional epitaxial growth of window layers does not passivate these sidewall facets. Thus alternate passivation

schemes are needed to realize small and highly efficient III-V based solar cells.

## II. BACKGROUND AND PREVIOUS WORK

Previous reports indicate that sulfur compounds provide excellent passivation of III-V compound semiconductors [3]. Unfortunately, the best treatment reported, immersion in aqueous solutions of Na<sub>2</sub>S, vigorously etches GaAs and is generally too corrosive for use in solar cell fabrication [3]-[4]. In earlier studies, we considered a class of long-chain surfactant molecules that are commonly employed for passivation of colloidal semiconductor nanocrystals. Specifically we identified trioctylphosphine sulfide (TOP:S), a clear, insulating liquid, as a candidate to improve the surface quality and prevent oxidation of III-V compound semiconductors, without etching or damaging the fabricated device. Through four independent measurements, we confirmed the effectiveness of the TOP:S treatment [5].

Importantly, we found that the addition of TOP:S mitigated the size-dependent loss of efficiency of GaAs cells ranging from 1 cm<sup>2</sup> to 1 mm<sup>2</sup> in active area size. Table 1 shows this trend of efficiency for a series of GaAs thin film cells, with and without TOP:S, characterized by a solar simulator under 1 Sun AM1.5G conditions. Without passivation, a decline in efficiency was observed with decreasing cell size because of the larger ratio of unpassivated surfaces. After being submerged in the TOP:S treatment, the efficiency in the smallest cell greatly increased from 12.3% to 16.82%, approaching the efficiency of the largest sized cell (17.2%). The large increases in efficiency of the small cells were primarily due to increases in short circuit currents arising from a significant decrease in recombination current at the device sidewalls.

TABLE I  
TREND IN EFFICIENCY AND  $J_{02}$  FIT PARAMETER TO DARK CURRENT-VOLTAGE RESPONSE OF GAAS DEVICES BEFORE AND AFTER TREATMENT WITH TOP:S [5].

Cell Size (cm <sup>2</sup> )	Efficiency (%)		$J_{02}$ [10 <sup>-10</sup> mA cm <sup>-2</sup> ]	
	Before	After	Before	After
1	17.25	17.2	0.12	0.09
0.02	14.8	17.82	1.3	0.3
0.01	12.3	16.82	1.5	0.4

TOP:S specifically eliminated the size-dependent losses measured before the treatment and we confirmed this was due to a decrease in sidewall recombination current. The sidewall contribution to the recombination current is given in Equation (1) by fitting the cell dark current response to a double diode model [6].

$$J = J_{01} \left( e^{qV/kT} - 1 \right) + J_{02} \left( e^{qV/n_2 kT} - 1 \right) \quad (1)$$

where  $J_{01}$  and  $J_{02}$  correspond to fit parameters for the “high” and “low” voltage saturation current densities, respectively. Additionally,  $n_2$ ,  $q$ ,  $k$ , and  $T$  are the quality factor (fit  $\approx 2$ ), electronic charge, Boltzmann’s constant, and the operating temperature (assumed 300 K). Our dark current analysis focused principally on the  $J_{02}$  “low voltage” saturation current density. The magnitude of this parameter is dominated by carrier recombination on the sidewalls of the device perimeter [6]. As shown in Table 1, the portion of the dark current affected by the sidewall surface recombination current is reduced after treatment. It should also be noted that the largest improvements occur in the smallest cells because they have the largest ratios of unpassivated semiconductor area. This agreement between the light and dark response of the cells verified that the efficiency increases in the small cells were due to effective passivation of the sidewall facets by TOP:S.

Additional insight was provided by light beam induced current (LBIC) measurements to extract the surface recombination velocities from a fractured GaAs solar cell with and without treatment by TOP:S. Using a confocal microscope, a 488 nm laser scanned the surface of the device near the cracked region and the measured photocurrent was correlated with the position of the laser beam, which is shown in Fig. 1. Treatment by TOP:S (soaking for 12 hours and then rinsing with toluene) was shown to decrease carrier recombination near exposed edges. Analysis of these photocurrent maps indicated that treatment by TOP:S significantly increased the collected current near the edge. We fit the data extracted from these maps in Fig. 1 to a simple 1-D carrier diffusion model and determined a 94% decrease in the surface recombination velocity from 8500 cm s<sup>-1</sup> before to 510 cm s<sup>-1</sup> after treatment with TOP:S [5].

These experiments give much understanding on the nature of passivation of GaAs through TOP:S. Sidewall passivation caused by TOP:S eliminates the size-dependent trend of efficiency down to an active area of 1 mm<sup>2</sup>. Additionally, treatment by TOP:S actively healed fractured cells, leading to a decreased surface recombination velocity at the sidewall. We extend this study through additional photoluminescence (PL) studies and characterization of even smaller cells to gain further understanding into the increased efficiency and robustness provided by sidewall passivation with TOP:S.

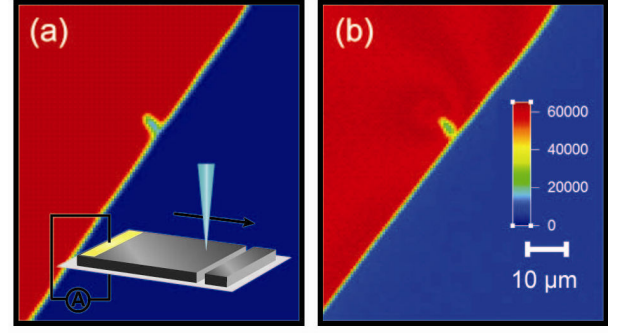


Fig. 1. Light beam induced current (LBIC) maps (a) before and (b) after treatment by TOP:S. The red regions indicate areas with the highest current collection while blue regions represent areas where no current is collected (i.e. where the cell is dead). Inset: schematic of experimental setup.

### III. SURFACE CHARACTERIZATION

When applied to the surface of GaAs wafers, PL yield indicates that TOP:S improves the surface electronic quality of sidewall facets. PL measurements were performed using excitation from a 633 nm laser source to probe for any change in non-radiative surface recombination due to treatment by TOP:S. Our previous work showed that TOP:S improved optical emission from the (011) facet of intrinsically doped GaAs wafers by 50%, which is comparable to treatments by Na<sub>2</sub>S [5]. However, GaAs-based solar cells are comprised of doped junctions, so it is necessary to understand the passivation mechanism as a function of the electronic properties of the layers.

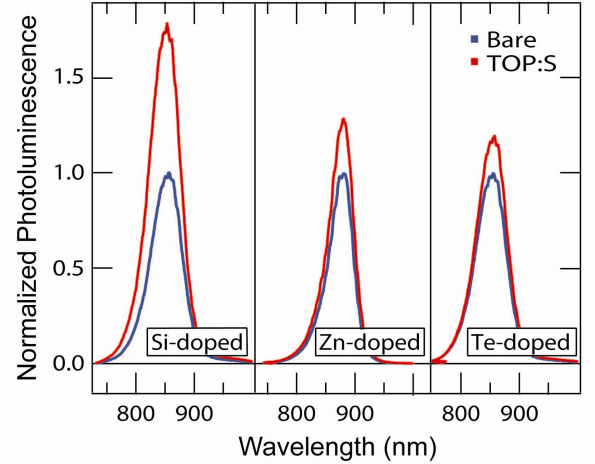


Fig. 2. Surface photoluminescence of doped GaAs wafer (011) facets (blue) shows significant enhancement when treated with TOP:S (red), indicating improved surface passivation.

The PL yields from cleaved (011) facets of GaAs wafers doped with Si, Zn, and Te are displayed in Fig. 2. The bare samples (blue) were cleaved under an inert atmosphere before

measurement. The TOP:S samples (red) were cleaved in the same fashion and subsequently soaked in TOP:S for 24 hours and rinsed in toluene to remove all but a chemically bonded monolayer. Both the Si- and Te-doped wafers are n-type ( $0.96 - 1.8 \times 10^{18}$  and  $0.62 - 2.6 \times 10^{18} \text{ cm}^{-3}$ , respectively), while the Zn-doped sample is p+-type ( $1.1 - 1.2 \times 10^{19} \text{ cm}^{-3}$ ). TOP:S improves the electronic quality regardless of dopant type. There is a striking enhancement across all samples, 77%, 29%, and 18% for the Si-, Zn-, and Te-doped samples, respectively. Possible dopant properties, such as the likelihood to oxidize, and how they affect the GaAs surface chemistry are under investigation to further elucidate this trend.

Because oxygen migration through the passivation layer can potentially lower device efficiency in III-V based devices, the PL yield over time was also studied. Fig. 3 shows the time-dependent integrated PL yield for the TOP:S treated wafers. The Te- and Zn-doped samples show a small improvement over time, indicating that the passivation may be photoactivated, which is consistent with observations of related sulfur treatments. However, there is a decline in the Si-doped samples after 20 minutes of exposure to atmosphere and light. This decline may indicate that oxygen is able to reach the surface, which was observed previously in studies of Na2S [3].

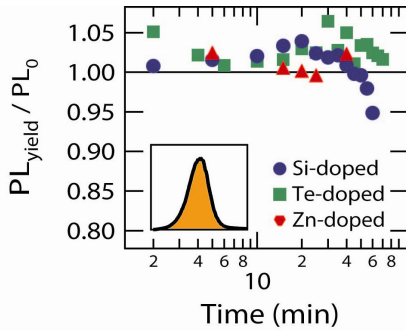


Fig. 3. Integrated photoluminescence yield over time of doped samples with TOP:S treatment. Inset: example PL curve. The curve is integrated (orange) and normalized to initial yield (time = 0 min).

#### IV. PASSIVATION OF ULTRA SMALL GAAS SOLAR CELLS

In our previous studies, we demonstrated effective passivation and healing for cells as small as  $1 \text{ mm}^2$ . Here, we have extended the study to “ultra small” cells ( $<1 \text{ mm}^2$  active area) to understand the limits of this passivation treatment. A  $1 \text{ mm}^2$  high quality, thin film GaAs cell was cleaved using a razor blade in order to form a small cell with approximately one-third of the original active area ( $0.31 \text{ mm}^2$ ). This cell was then characterized under the same solar simulator as in the previous study, and results are shown in Table 2 and Fig. 4. The open circuit voltage for this ultra small cell was much lower than similar cells of larger sizes, which was probably due to both the damage incurred during cleaving.

Furthermore, the contact pad shadows 46% of the cell, decreasing the effective absorption area. Future studies of these ultra small cells will employ smaller contacts and use an etching technique to define the size to provide the highest performance possible.

TABLE 2  
AVERAGE PARAMETERS FROM ULTRA SMALL GAAS  
SOLAR CELL UNDER AM1.5G ILLUMINATION, WITH AND  
WITHOUT PASSIVATION BY TOP:S.

	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	Eff. (%)
<b>Without Sidewall Passivation</b>	0.811	16.74	70.2	9.53
<b>Submerged in TOP:S</b>	0.820	20.2	67.2	11.1
<b>TOP:S Treated, Rinsed in Toluene</b>	0.809	20.0	65.6	10.6

Unlike our previous studies where wafers and devices were submerged for 12-24 hours, this cell was submerged in TOP:S for five minutes prior to characterization under the solar simulator. As shown by the increased performance between the absence of passivation and submerged in TOP:S cases, the effect of the treatment is nearly instantaneous, showing an increase in short circuit current and enhancement of the cell efficiency by over 1% (absolute). Other studies of sulfur-based treatments have shown that passivation occurs when the S-Ga interaction is activated in the presence of a light source. The exposure of the solution to light could explain the sudden improvement in the efficiency of this ultra small cell.

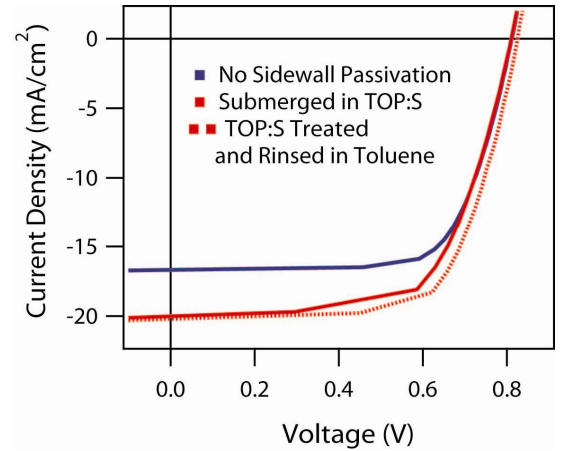


Fig. 4. I-V response of ultra small GaAs solar cell under AM1.5G conditions, before TOP:S treatment, while submerged in TOP:S, and after rinsing with toluene.

After measuring the cell submerged in the passivation liquid, the device was rinsed thoroughly in toluene to remove all but a few monolayers of TOP:S. XPS analysis has shown that even though TOP:S is very soluble in toluene, an extremely thin

layer remains on the surface and acts as the passivating layer [5]. This rinse was performed to both test the intensity and stability of the passivation of the thin layer as well as isolate the improvements of the sidewall passivation from any AR coating effects the liquid may induce. As shown by both Fig. 4 and Table 2, the short circuit current and efficiency show sustained improvement from the unpassivated case, though the improvements are slightly less than when the sample was submerged in TOP:S. The difference between the submerged and rinsed sample is due to a small antireflection coating effect because TOP:S has an index of refraction between that of air and GaAs. Nonetheless, improved efficiency (1% absolute) is still maintained without the antireflection coating effect. The improvement is maintained for at least 24 hours.

While the efficiency of the ultra small cell does increase with the sidewall passivation from treatment by TOP:S, the effect is much less dramatic than our previous studies as we are unable to recover efficiencies close to that of identically fabricated, but larger (1 cm<sup>2</sup>) sized cells. While part of this could be due to some damage the cell may have incurred during cleaving, this smaller efficiency enhancement could indicate the size limits of this chemical passivation strategy. Future work will focus on the limits and trends of this passivation on extremely small cells.

## V. CONCLUSIONS

We have demonstrated that TOP:S improves the electronic quality of GaAs sidewall facets and the efficiency of extremely small GaAs solar cells. Because GaAs wafers with different doping chemistries showed systematic improvements with TOP:S and relative time stability with the treatment, TOP:S is a promising molecule for effective passivation of GaAs-based and related semiconductors devices. Additionally, treatment with TOP:S followed by a toluene rinse improves current collection of extremely small (<mm<sup>2</sup>) solar cells.

## ACKNOWLEDGEMENTS

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## REFERENCES

- [1] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, "Solar cell efficiency tables (Version 38)," *Prog. Photovolt: Res. Appl.*, **19**, 2011, pp. 565-572.
- [2] J. Yoon, S. Jo, I. S. Chun, I. Jung, H. S. Kim, M. Meitl, E. Menard, X. L. Li, J. J. Coleman, U. Paik, and J. A. Rogers, "GaAs photovoltaics and optoelectronics using releasable multilayer epitaxial assemblies," *Nature*, **465**, 2010, pp. 329-U80.
- [3] S. Lunt, G. Ryba, P. Santangelo, and N. Lewis, "Chemical studies of the passivation of GaAs surface recombination using sulfides and thiols," *J. Appl. Phys.*, **70**, 1991, pp. 7449-7467.
- [4] C. Kirchner, M. George, B. Stein, W. J. Parak, H. E. Gaub, and M. Seitz, "Corrosion Protection and Long-Term Chemical Functionalization of Gallium Arsenide in an Aqueous Environment," *Advanced Functional Materials*, **12**, 2002, pp. 266-276.
- [5] M. T. Sheldon, C. N. Eisler, and H. A. Atwater, "GaAs Passivation with Trioctylphosphine Sulfide for Enhanced Solar Cell Efficiency and Durability," *Advanced Energy Materials*, **2** (3), 2012, pp. 339-344.
- [6] S. Tobin, S. Vernon, C. Bajgar, S. Wojtczuk, M. Melloch, A. Keshavarzi, T. Stellwag, S. Venkatesan, M. Lundstrom, and K. Emery, "Assessment of MOCVD-Grown and MBE-Grown GaAs for High-Efficiency Solar-Cell Applications," *IEEE T Electron Dev*, **37**, 1990, pp. 469-477.