Infrared Energy Harvesting in Millimeter-Scale GaAs Photovoltaics

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Abstract—The design and characterization of millimeter-scale GaAs photovoltaic (PV) cells are presented and demonstrate highly efficient energy harvesting in the near infrared (NIR). Device performance is improved dramatically by optimizing the device structure for the NIR spectral region and improving surface and sidewall passivation with the ammonium sulfide treatment and subsequent silicon nitride deposition. The power conversion efficiency of a 6.4-mm² cell under 660-nW/mm² NIR illumination at 850 nm is greater than 30%, which is higher than commercial crystalline silicon solar cells under similar illumination conditions. Critical performance limiting factors of submillimeter-scale GaAs PV cells are addressed and compared to theoretical calculations.

Index Terms—Gallium arsenide, photovoltaics (PVs), silicon, wireless energy harvesting.

I. INTRODUCTION

Wireless energy harvesting for biomedical implantable devices is an attractive technology for a wide range of biomedical applications for measuring physiological signals [1]–[5]. Fully implanted systems [4], [5] were developed recently with the aid of wireless energy harvesting methods [6]–[9] utilizing kinetic energy, ultrasonic mechanical vibrations for piezoelectric energy harvesting, thermal energy, and radio frequency (RF) electromagnetic radiation for inductive coupling link. The main hurdles [7], [8], [10] for these wireless energy harvesting are the robustness of ambient energy sources through the biological tissue or skull and miniaturization of implantable devices. Photovoltaic (PV) energy harvesting provides an alternative means of wireless power transfer (WPT) through the near-infrared (NIR) optical transparency window of the biological tissue between 650- and 950-nm range [11], [12], where the ambient solar irradiation or an intentional light-emitting diode (LED) illumination could provide energy to implantable PV cells and conventional high-efficiency PV cells [13] convert this NIR wavelength region efficiently with above 90% external quantum efficiency (EQE). The key challenges to obtaining highly efficient PV energy harvesting are that device performances of PV cells at millimeter scale or smaller under low-flux illumination are degraded by the shunt resistance [14]–[16] and sidewall/perimeter recombination losses [14], [17], [18]. Previous works on NIR PV WPT [19]–[22] are centimeter scale or larger and tested under extremely high intensity of laser illumination in milliwatt range producing skin heating [7], [22]. One of the previously reported silicon PV cells at millimeter scale [17], [23] addressed and relatively overcame these challenges, which had above 17% power conversion efficiency under low-flux NIR illumination below 1 μW/mm² at a wavelength of 850 nm. However, fundamental material characteristics of silicon such as higher dark current and shunt leakage compared to other III–V compound semiconductors limit the open-circuit voltage and corresponding power conversion efficiency. On the other hand, GaAs-based PV cells have a possibility to boost the NIR energy harvesting efficiency due to superior optical properties matched to desired NIR wavelength region, low dark current and low shunt leakage, which worked successfully under low-flux indoor conditions [14], [15]. The feasibility of subcutaneous energy harvesting utilizing fabricated silicon and GaAs PV cells through the NIR transparency window, and possible encapsulation methods for these PV cells were discussed and evaluated in previous papers [17], [23] and could provide sufficient power for millimeter-scale systems. In this paper, the details of submillimeter-scale GaAs PVs cells optimized for low-flux NIR energy harvesting at a wavelength of 850 nm and their performance limiting factors are explored.

II. EXPERIMENT

The material layer structure of GaAs PV cell for NIR energy harvesting was optimized based on simulation results using Synopsys Sentaurus Device [24] using widely accepted material parameters at 300 K and neglecting recombination effects from the surface/sidewall. The device structure grown by molecular beam epitaxy utilizing the structure of conventional high-efficiency GaAs solar cells [25] consists of n-base and...
Fig. 1. Fabricated variable size of PV cells from 0.001 to 6.4 mm².

Table I

<table>
<thead>
<tr>
<th>Type</th>
<th>Material</th>
<th>Thickness (nm)</th>
<th>Doping (cm⁻³)</th>
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<tr>
<td>p⁺⁺</td>
<td>GaAs</td>
<td>200</td>
<td>2 x 10¹⁸</td>
</tr>
<tr>
<td>p⁺</td>
<td>Al₀.₈Ga₀.₂As</td>
<td>30</td>
<td>2 x 10¹⁸</td>
</tr>
<tr>
<td>p⁻</td>
<td>GaAs</td>
<td>500</td>
<td>4 x 10¹⁴</td>
</tr>
<tr>
<td>n⁻</td>
<td>GaAs</td>
<td>200</td>
<td>1 x 10¹⁶</td>
</tr>
<tr>
<td>n⁺</td>
<td>GaAs</td>
<td>2750</td>
<td>1 x 10¹⁷</td>
</tr>
<tr>
<td>n⁺⁺</td>
<td>Al₀.₈Ga₀.₂As</td>
<td>150</td>
<td>1 x 10¹⁸</td>
</tr>
<tr>
<td>p⁻⁻</td>
<td>GaAs</td>
<td>300</td>
<td>2 x 10¹⁸</td>
</tr>
</tbody>
</table>

Fig. 2. Simulated maximum power density under 100-nW/mm² illumination at 850 nm.

Fig. 3. Measured current density versus voltage curves of different passivation studies of 6.4-mm² cell under 850-nm NIR-LED illumination with 660 nW/mm².

III. RESULTS

A. Passivation Layer

The J–V characteristics of 6.4-mm² GaAs PV cells passivated with the five different passivation layers under 660-nW/mm² illumination at a wavelength of 850 nm are shown in Fig. 3. A 100-nm PECVD Si₃N₄ passivation layer matched to the NIR tissue transparency window as shown in Fig. 4 increased the short-circuit current (Jsc) compared to control sample without passivation by reducing the surface reflectance and the surface recombination loss. The ammonium sulfide ((NH₄)₂S) treatment encapsulated with the PECVD from 0.001 to 6.4 mm², corresponding to perimeter/area (P/A) ratio from 125 to 1.69 mm⁻¹. Various passivation processes were studied including the dielectric passivation and chemical passivation methods to reduce the sidewall/perimeter recombination losses, including plasma enhanced chemical vapor deposition (PECVD) Si₃N₄, (NH₄)₂S [26]–[28], NH₄OH with subsequent PECVD Si₃N₄, and NH₄OH with subsequent atomic layer deposition (ALD) Al₂O₃ [29]. Further details of the different passivation processes are as follows:

1) 100-nm PECVD Si₃N₄ at 380 °C;
2) (NH₄)₂S (23% in H₂O) for 10 min at room temperature + 100-nm PECVD Si₃N₄ at 380 °C;
3) NH₄OH (29% in H₂O) for 3 min at room temperature + 100-nm PECVD Si₃N₄ at 380 °C;
4) NH₄OH (29% in H₂O) for 3 min at room temperature + 25-nm ALD Al₂O₃ at 150 °C; and
5) a sample without passivation.

Current–voltage (J–V) and power–voltage (P–V) characteristics of fabricated cells under dark and illumination conditions were measured using Keithley 2400 and 4200 semiconductor characterization tools. A microscope-compatible NIR-LED with 850-nm center wavelength and a calibrated power-meter were used to control low-flux illumination in increments of 5 nW/mm². Passivation effects on device performances of variable size cells were tested under 660 nW/mm² illumination at 850 nm, which is realistic under subcutaneous conditions and much lower flux than AM 1.5 sunlight at 1000-μW/mm² illumination [30]. The EQE was measured using a calibrated photodetector, lock-in amplifier, monochromator, optical chopper, and xenon white light source.
Si₃N₄ layer for long-term stability of passivation layers [31] improved both the short-circuit current density (J SC) and the open-circuit voltage (V OC), which results in the maximum power conversion efficiency above 30% under 850-nm NIR illumination with 660 nW/mm² and can supply sufficient power to a millimeter-scale system with the minimum power requirement of 50 nW/mm² [32].

The EQE measurement as shown in Fig. 4 on this (NH₄)₂S passivated sample shows that the device structure is well optimized for the first optical window in the NIR wavelength range with above 80% EQE and 5%–7% discrepancy between simulated and measured EQE values is observed over the desired wavelength region due to the surface reflection from metal fingers. Further studies of different passivation layer effects on device performance for variable size of cells from 0.0052 to 6.4 mm² corresponding P/A ratio 55.56 to 1.69 mm⁻¹ are shown in Fig. 5. The device performance of cells with varying size cells is strongly dependent on the P/A ratio, illustrating the critical impact of sidewall recombination loss as one of the most critical limiting factors for these small-area PV cells [14], [17], [18], as discussed further in Section IV. The (NH₄)₂S treatment improved V OC values of various size PV cells and this V OC improvement is closely relevant to the reduction in the reverse saturation current (J 0) as indicated in (1)

\[
V_{OC} = \frac{n k T}{q} \ln \left( \frac{J_{SC}}{J_0} + 1 \right) \tag{1}
\]

where n is the ideality factor, k is Boltzmann’s constant, T is the temperature, J 0 is the reverse saturation current density, and J SC is the short-circuit current density. The (NH₄)₂S treatment [26]–[28] etched the native oxide on the surface/sidewall and effectively passivated the dangling bonds with additional sulfur bonds, resulting in the reduction of J 0. The NH₄OH treatment reduced J SC due to increased optical scattering from the rough surface though the NH₄OH treatment etched the native oxide [29] to achieve more electronically favorable surface properties before the dielectric passivation. The 25-nm ALD Al₂O₃ did not provide an optimal antireflection match to the desired wavelength at 850 nm, which increased the surface reflectance over the desired wavelength region more than the optimized 100-nm PECVD Si₃N₄ layer, resulting in a reduction in J SC. The detailed device parameters regarding p-n junction diode equations and recombination losses were extracted from results of dark current measurement.

### B. Dark Current Measurements

Dark current measurements were conducted on all PV cells with varying P/A ratio to examine the impact of surface passivation properties. The dark J–V plots of 0.25-mm² samples are shown in Fig. 6(a) and the extracted J 0 parameters are shown in Fig. 6(b) obtained by curve fitting to the forward bias region between 0 and 0.7 V using the one-diode equation

\[
J = J_0 \left[ \exp \left( \frac{q V}{n k T} \right) - 1 \right] \tag{2}
\]

where J is the total current density, J 0 is the reverse saturation current, V is the applied voltage, k is Boltzmann’s constant, and T is the temperature. The extracted J 0 parameters for all passivation studies shown in Fig. 6(b) show the clear P/A ratio dependence due to increased sidewall/perimeter recombination losses as expected. The dramatic reduction in J 0 over all measured PV cells from (NH₄)₂S treatment was also observed in Fig. 6(b). For example, extracted J 0 of 6.4-mm² PV cells summarized in Table II was reduced from 0.9038 pA/mm² for the sample without passivation to 0.0673 pA/mm² for the sample passivated with (NH₄)₂S + PECVD Si₃N₄, agreeing with the improvement in V OC as indicated in Fig. 5.

### Table II

<table>
<thead>
<tr>
<th>Passivation</th>
<th>J 0 (pA/mm²)</th>
<th>n</th>
</tr>
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<tbody>
<tr>
<td>Si₃N₄</td>
<td>0.6157</td>
<td>1.939</td>
</tr>
<tr>
<td>(NH₄)₂S + Si₃N₄</td>
<td>0.0673</td>
<td>1.801</td>
</tr>
<tr>
<td>NH₄OH + Si₃N₄</td>
<td>0.5853</td>
<td>1.933</td>
</tr>
<tr>
<td>NH₄OH + Al₂O₃</td>
<td>0.4532</td>
<td>1.906</td>
</tr>
<tr>
<td>Unpassivated</td>
<td>0.9038</td>
<td>1.969</td>
</tr>
</tbody>
</table>

Fig. 4. Measured and Simulated (dashed) EQE characteristics of (NH₄)₂S + Si₃N₄ passivated sample along with the wavelength range between 400 and 900 nm.

Fig. 5. Measured power conversion efficiency values of various passivation studies versus P/A (mm⁻¹) ratio from 1.69 to 55.56 mm⁻¹ corresponding device size from 6.4 to 0.0052 mm².
Fig. 6. (a) Measured current versus voltage of 0.25-mm² sample under dark conditions. (b) Extracted reverse saturation current values of different passivation studies versus P/A (mm⁻¹) ratio from 1.69 to 125 mm⁻¹ corresponding device size from 6.4 to 0.001 mm².

The diode ideality factor \( n \) of 6.4-mm² cells summarized in Table II supported previous results that the ideality factor values near \( n = 2 \) for samples are dominated by the space charge region (SCR) recombination losses [14] mainly connected to the sidewall recombination losses and the (NH₄)₂S treatment with subsequent Si₃N₄ deposition reduced the diode ideality factor from 1.969 to 1.801, suggesting that the sulfur treatment unpinned the Fermi-level [31] and reduced the SCR recombination losses from surface and sidewall regions [33], [34]. Numerical parameters relevant to the perimeter recombination losses can be extracted by curve fitting to the forward bias region using the two-diode equation

\[
J = J_{01} \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right] + J_{02} \left[ \exp \left( \frac{qV}{2kT} \right) - 1 \right]
\]

(3)

where \( J_{01} \) and \( J_{02} \) are the saturation current densities for carrier recombination in the quasi-neutral region and the SCR, respectively. The extracted \( J_{02} \) along with P/A ratio are plotted in Fig. 7. The extracted \( J_{02} \) exhibiting the strong linear P/A dependence can be expanded as (4) [18], [35]

\[
J_{02} = J_{02B} + J_{02P} \left( \frac{P}{A} \right)
\]

(4)

where \( J_{02B} \) is the bulk recombination current density and \( J_{02P} \) (A/mm) is the perimeter recombination coefficient. These coefficients extracted using the linear curve fitting to \( J_{02} \) using (4) are summarized in Table III, which indicate that the effect of Si₃N₄ passivation mainly reduced the bulk recombination current density from 1.934 to 0.7831 pA/mm² rather than the perimeter recombination loss from 0.4882 to 0.4596 pA/mm compared to the control sample without passivation. The additional NH₄OH treatment with Si₃N₄ passivation also had a slight improvement in the perimeter recombination loss and made the optimized passivation to the bulk recombination only. ALD Al₂O₃ passivation reduced the bulk recombination losses significantly from 1.934 to 0.0438 pA/mm², but had a little impact on reducing the perimeter recombination loss. However, the (NH₄)₂S treatment reduced both for bulk and perimeter recombination losses dramatically from 1.934 to 0.1409 pA/mm² for the bulk recombination and from 0.4882 to 0.1714 pA/mm for the perimeter recombination, suggesting that the exposed mesa edges were effectively passivated with additional sulfur bonds.

The important parameters relevant to \( J_{02P} \) can be extracted using (5) [18], [35]

\[
J_{02P} = qn_iS_0L_S
\]

(5)

where \( n_i \) is the intrinsic carrier concentration, \( S_0 \) is the surface recombination velocity, and \( L_S \) is the effective surface diffusion length. The extracted \( S_0L_S \) product of the (NH₄)₂S treated sample was 5.09 cm²/s where the high-efficiency GaAs-based solar cells had \( S_0L_S < 1 \) cm²/s [18], [35], [36]. Further improvements in the device structure and passivation studies are still needed to overcome the perimeter recombination losses.

C. Shunt Resistance

The degradation from the parasitic shunt resistance dominating the device operation under low-flux illumination [14]–[16]...
was investigated for the sample with \((\text{NH}_4)_2\text{S} + \text{Si}_3\text{N}_4\) passivation varying the illumination intensities, as shown in Fig. 8. The simulated values for the comparison were calculated using the diode (6)

\[
J = J_{sc} - J_0 \left[ \exp \left( \frac{q (V + J A R_s)}{nkT} \right) - 1 \right] - \frac{V + J A R_s}{R_{sh}}
\]

where \(J_{sc}\) is the short-circuit current, \(R_s\) is the parasitic series resistance, and \(R_{sh}\) is the parasitic shunt resistance, using numerical extracted diode parameters from Table II and varying the shunt resistance values in \(\Omega \cdot \text{cm}^2\). As shown in Fig. 8, the performances of measured GaAs PV cell under various NIR illumination conditions from 30 nW/mm\(^2\) to 2.69 \(\mu\)W/mm\(^2\) were free of the shunt resistance degradation with above 10-M\(\Omega \cdot \text{cm}^2\) shunt resistance value that is consistent with the previous GaAs PV cell results [14] though the commercial crystalline silicon solar cell [37] with above 22% power conversion efficiency under AM 1.5 solar irradiation shows the clear performance degradation from the shunt resistance under dim NIR illumination below 1 \(\mu\)W/mm\(^2\).}

IV. DISCUSSION

The power conversion efficiency for a 6.4-mm\(^2\) cell is greater than 30% under 850-nm NIR illumination at 660 nW/mm\(^2\) through the optimization of device structures and improvement in \(V_{OC}\) from optimized sidewall passivation studies using \((\text{NH}_4)_2\text{S}\) and PECVD \text{Si}_3\text{N}_4. This efficiency approaches the expected value from simulation results neglecting surface/sidewall recombination, as shown in Fig. 10. The parasitic shunt resistance of optimized GaAs PV cell is on the order of 10-M\(\Omega \cdot \text{cm}^2\) range as shown in Fig. 8, which can sufficiently overcome the shunt resistance degradation under low-flux illumination conditions. The \(J_0\) and \(J_{02}\) values extracted from dark \(J-V\) measurements are gradually increased with increasing \(P/A\) ratio, which shows a dramatic reduction in dark current from 1.934 to 0.1409 pA/mm\(^2\) for the bulk recombination current and from 0.4882 to 0.1714 pA/mm for the perimeter recombination coefficient from the \((\text{NH}_4)_2\text{S}\) treatment encapsulated with PECVD \text{Si}_3\text{N}_4, attributed to the sulfur passivation of surface states [26]–[28].

The measured \(V_{OC}\) values in Fig. 9(a) agree with theoretically calculated values, showing a reduction from the increased reverse saturation current originated from the sidewall/perimeter recombination losses. The deviation of measured \(V_{OC}\) for small PV cells below 200-\(\mu\)m sidewall length is relevant to \(J_{SC}\) degradation. The measured \(J_{SC}\) values as shown in Fig. 9(b) exhibit a sharp drop as cell size decreases though theoretical \(J_{SC}\) should be independent of device size. One of the major \(J_{SC}\) limiting factors for small PV cells is optical shadowing from metal fingers and pads in the light harvesting area. However, recalculated values for \(J_{SC}\) accounting...
for optical shadowing effects still show a similar drop below 200-\(\mu\)m sidewall length. For these small micrometer-scale PV cells, a “dead area” [33] near the cell perimeter may be the cause of the substantial loss in photocurrent due to carrier diffusion to exposed sidewalls.

The overall power conversion efficiency values are shown in Fig. 9(c) and are limited by factors including an unavoidable sidewall recombination loss, optical shadowing from metal pads, and dead area near sidewall. Therefore, further improvements in power conversion efficiency approaching Shockley–Queisser (SQ) limit [38] indicated in Fig. 10 will require continued reduction in edge effects, where the surface and sidewall passivation using wide bandgap materials matched to the lattice constant of GaAs such as InGaP [39] or AlGaAs [40] may be required. The surface reflectance from metal pads might be reduced from transparent metal anode contacts such as indium tin oxide (ITO) [41], aluminum-doped zinc oxide [41], or Ti/ITO [39].

V. CONCLUSION

GaAs PV cells at millimeter-scale and micrometer-scale were optimized for wireless energy harvesting applications through the NIR optical transparency window of tissue between 650 and 950 nm. A power conversion efficiency beyond 30% and EQE over 80% were achieved under low-flux NIR illumination below 1 \(\mu\)W/mm\(^2\). The (NH\(_4\))\(_2\)S and PECVD Si\(_3\)N\(_4\) passivation methods improved the device performance dramatically by reducing the surface/sidewall recombination losses. The optimized device structure was free of performance degradation from shunt leakage under low-flux illumination. High-efficiency GaAs PV cell under NIR low-flux illumination makes wireless PV energy harvesting through a biological tissue into a feasible approach, where further improvements may be accomplished by further reduction in edge effects and optical shadowing from electrical contacts.

References


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