Enhancement of photocurrent in GaInNAs solar cells using Ag/Cu double-layer back reflector

Timo Aho, Arto Aho, Antti Tukiainen, Ville Polojarvi, Turkka Salminen, Marianna Raappana, and Mircea Guina

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III–V multijunction solar cells are the solution of choice for space and concentrator photovoltaic (CPV) systems, owing to their high power-to-mass ratio, radiation durability, and high efficiency. The continuous progress of multijunction solar cell technology has reached a high level of maturity using approaches involving, e.g., GaInP/GaAs/GaInAs or GaInP/GaAs/Ge designs, which have enabled the efficiencies of over 30% for space and over 40% for CPV. However, these achievements are still far from the theoretical potential, prompting for new approaches to increase the number of junctions for better matching to the solar spectrum. Amongst the recent approaches to increase the efficiency of multi-junction solar cells, the use of lattice-matched Ga1-xInxNyAs1-y layers grown by molecular beam epitaxy (MBE) has emerged as a very promising design.4,5 More recently, a combination of MBE and metalorganic vapor deposition (MOVCD) epitaxy was developed as a practical approach to fabricate GaInNAs-based solar cells, exploiting the key features that are established in the production of commercial solar cells.6 The main advantages offered by GaInNAs rest upon their ability to tailor the bandgap in a wide range from approximately 0.8 eV to 1.42 eV while remaining lattice-matched to GaAs and Ge.4,7 Despite the recent achievement and good potential for future developments, at high N compositions (y ≥ 0.04) required for bandgaps below 0.9 eV, the photovoltaic operation of GaInNAs solar cells is reduced due to relatively low charge carrier lifetimes (below 1 ns) leading to short minority carrier diffusion lengths of under ~1 μm, and high p-type background doping of the order of 10^{16} cm^{-3} or higher.8-10 High background doping level narrows the depletion region, which together with the short diffusion length limits the thickness of an optimized absorption layer, resulting in lower quantum efficiencies.9-12 To obtain wider depletion regions and higher quantum efficiencies, the p-type background doping should be reduced down to the order of 10^{15} cm^{-3} or below, which still remains a challenging task at high N compositions (y ≥ 0.04). This issue can be mitigated by adding a reflector on the back side of the solar cell that would allow the use of a thinner absorber with enhanced photogeneration.13 Highly reflective back surface reflectors effectively double the absorption length in the photogenerating layer. As a result, the charge collection efficiency is improved, which increases the short-circuit current density (J_{sc}).14 Furthermore, the open circuit voltage (V_{oc}) will theoretically increase as a consequence of higher effective light concentration in the junction and the absorption in average occurs closer to the depletion region, which decreases the nonradiative recombination.15

In this paper, we report the operation of a GaInNAs solar cell with a Ag/Cu back surface reflector. Amongst the options for developing non-alloyed back surface reflectors, Ag, Au, and Cu provide almost ideal reflectivity at wavelengths longer than 800 nm.16 Au as a reflector material17 is known to be expensive, and therefore, to reduce the solar cell fabrication costs the use of other metals, such as Ag and Cu, would be an attractive alternative. The Ag back reflector has already been reported to work well in GaAs and GaInP solar cells,18,19 but Ag has not been applied to GaInNAs solar cells. Furthermore, Cu has also been used as a part of the back side contact in GaAs solar cells, but Cu is also known to diffuse easily into III–V semiconductors and thus to reduce the V_{oc}.20-22 In our approach, we have studied GaInNAs solar cells with double-layer Ag/Cu reflectors exhibiting high reflectance, good adhesion, and low contact resistance. Moreover, a thin Ag layer acts as a diffusion barrier, preventing Cu diffusion into the semiconductor structure even when the cell is subjected to thermal annealing.

Single-junction GaInNAs solar cells were grown by MBE following the process described in Ref. 9. A generic sample structure is presented in Fig. 1. In our benchmark process, as a back contact we used Ti/Au annealed at 420 °C for 90 s to ensure formation of an ohmic contact. Here, we have replaced Ti/Au contact layers with higher-reflectivity metals and fabricated the contact without annealing. Four different metal reflectors were deposited using an electron
beam evaporator: Ag/Cu/Ni/Au (denoted as Ag/Cu), Cu/Ni/Au (denoted as Cu), Au (100 nm), and Ti/Au (50 nm/100 nm). Thicknesses of individual layers for the Ag/Cu and Cu samples were: 100 nm for Cu layers, 10 nm for Ni, and 50 nm for Au. Moreover, for the Ag/Cu reflector, we studied three different Ag layers, with thicknesses of 10 nm, 30 nm, and 50 nm. The purpose of Ag is to act as a diffusion barrier for Cu and to provide high reflectance in combination with the Cu layer. The Cu layer acts as a current spreader and conductor. Ni is required between the Au and Cu layers as an adhesion layer and Au acts as a protective layer and bonding surface.

Indium contacts were deposited on the top of the solar cells and the surface was coated with a double-layer TiO2/SiO2 antireflection coating by an electron beam evaporator. External quantum efficiency (EQE) measurements were performed with a setup equipped with a 250 W quartz tungsten halogen lamp. The narrow excitation wavelength span for the probe beam was selected by using a Digikrom DK240 monochromator and an 800 nm long-pass filter placed before the monochromator. The signals from the solar cells and from the reference detectors were measured using an SRS SR830 lock-in amplifier and chopped light. A NIST-calibrated Ge reference detector was used for the whole wavelength range of 800–1500 nm.

Fig. 2 shows the EQE results of GaInNAs solar cells with the back reflectors. In addition, the reflectance results of double-side polished semi-insulating GaAs samples with back surface reflectors are shown in Fig. 2 for comparison of the optical properties of the reflectors. The reflectance was measured using an SRS SR830 lock-in amplifier and chopped light. A NIST-calibrated Ge reference detector was used for the whole wavelength range of 800–1500 nm.

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The \( J_{sc} \) values at AM1.5G, AM1.5D, and AM0 spectral conditions were deduced from the EQE measurements by integrating over the given spectrum and assuming a thick GaAs filter on top of GaInNAs cell. The results are shown in Table I. The solar cell with the 30 nm Ag/Cu reflector exhibited a \( J_{sc} \) value of \( \sim 14 \text{ mA/cm}^2 \) at AM1.5D (1000 W/m\(^2\)), which is 28% higher compared to the reference solar cell with the Ti/Au reflector. These values are similar to the current that can be generated by GaInP/GaAs top cells, which is \( \sim 14 \text{ mA/cm}^2 \) at AM1.5D (1000 W/m\(^2\)).\(^{24}\) The enhanced photocurrent of the GaInNAs solar cells with the back reflector is proven. This improvement is valid for the bottom junction of a multijunction solar cell. When comparing the conversion efficiency of an optimized GaInP/GaAs/GaInNAs triple-junction solar cell with the Ti/Au back reflector to the cell with the Au/Cu back reflector, 10 percentage points higher efficiency would be reached at \( \sim 1000 \times \text{AM1.5D} \) resulting in an efficiency of 45% instead of 35%.

Back reflectors that are simultaneously used as ohmic contacts require a low contact resistivity. Conventional ohmic
contacts are made of alloyed metals but annealing is shown to lower reflectivity due to the reduction of interface sharpness in comparison to non-alloyed contacts.25 Although non-alloyed contacts usually suffer from higher contact resistivity,26 high doping levels can be employed in GaAs to attain low contact resistivity.20 Typical contact resistivities for p-GaAs are of the order of $10^{-6}$ Ω-cm$^2$, which are lower than reported contact resistivities of non-alloyed contacts.27 These results show that an ohmic contact is formed even without annealing due to high doping in the GaAs layer and high reflectivity of the metal reflector is retained.

Adhesion of the metal reflectors was studied by the Scotch tape peel test.28 None of the samples showed notable metal peeling, as revealed in Fig. 3. The Au reflector also passed the adhesion test even though Au has been reported to have weak adhesion to GaAs.20 We observed a small piece of metal peeled off from the sample with 10 nm Ag/Cu as shown in Fig. 3(c). However, this was because of the small cracks on the edge of the sample caused by cleaving. The results indicate that an additional adhesion promoting metal layer, which could reduce the reflectivity, is not needed between the semiconductor and Ag.

The diffusion of Cu and Ag into the semiconductor was investigated by examining the cross-section of the metal-semiconductor interface with a focused ion beam scanning electron microscope (Zeiss Crossbeam 540 FIB-SEM) equipped with an energy-dispersive x-ray spectroscopy detector (EDS) from Oxford Instruments. Samples with similar metals to those for the solar cells were studied. Some of the samples were annealed at 200°C and 420°C for 90 s to test the effect of the processing conditions on the atomic diffusion.

The cross-section SEM images and EDS data of the metal-semiconductor interface are presented in Figs. 4 and 5.

![FIG. 3. The samples after the Scotch tape adhesion test. The back surface reflector materials were: (a) 50 nm Ag/Cu, (b) 30 nm Ag/Cu, (c) 10 nm Ag/Cu, (d) Cu, (e) Au, and (f) Ti/Au.](image)

![FIG. 4. SEM images of the cross-sections of metals on top of p-GaAs: (a) Cu, (b) Cu annealed at 200°C, (c) Cu annealed at 420°C, (d) 50 nm Ag/Cu, (e) 50 nm Ag/Cu annealed at 200°C, (f) 50 nm Ag/Cu annealed at 420°C, (g) large scale SEM image of the FIB-processed sample slice to clarify the measurement configuration (10 nm Ag/Cu annealed at 420°C), (h) 10 nm Ag/Cu annealed at 200°C, and (i) 10 nm Ag/Cu annealed at 420°C.](image)

### Table I: Measured contact resistivity results and $J_{sc}$ values at AM1.5G (1000 W/m$^2$), AM1.5D (1000 W/m$^2$), and AM0 (1366 W/m$^2$) calculated from the EQE data.

<table>
<thead>
<tr>
<th>Back Surface Reflector</th>
<th>Contact Resistivity ($\Omega$-cm$^2$)</th>
<th>$J_{sc}$ AM1.5G (mA/cm$^2$)</th>
<th>$J_{sc}$ AM1.5D (mA/cm$^2$)</th>
<th>$J_{sc}$ AM0 (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/Au</td>
<td>$3 \times 10^{-6}$</td>
<td>10.1</td>
<td>10.7</td>
<td>12.7</td>
</tr>
<tr>
<td>Au</td>
<td>$1 \times 10^{-6}$</td>
<td>11.8</td>
<td>12.4</td>
<td>14.8</td>
</tr>
<tr>
<td>Cu</td>
<td>$4 \times 10^{-6}$</td>
<td>12.8</td>
<td>13.4</td>
<td>15.9</td>
</tr>
<tr>
<td>10 nm Ag/Cu</td>
<td>$4 \times 10^{-6}$</td>
<td>12.9</td>
<td>13.6</td>
<td>16.1</td>
</tr>
<tr>
<td>10 nm Ag/Cu*</td>
<td>$1 \times 10^{-6}$</td>
<td>12.7</td>
<td>13.3</td>
<td>15.8</td>
</tr>
<tr>
<td>30 nm Ag/Cu</td>
<td>$4 \times 10^{-6}$</td>
<td>13.0</td>
<td>13.7</td>
<td>16.2</td>
</tr>
<tr>
<td>50 nm Ag/Cu</td>
<td>$5 \times 10^{-6}$</td>
<td>13.0</td>
<td>13.7</td>
<td>16.2</td>
</tr>
</tbody>
</table>

*Annealed at 200°C for 90 s
Cu, Ni, and Au layers remained separated in the non-annealed Cu sample and in Cu sample annealed at 200 °C (Figs. 4(a) and 4(b)). This is also seen in the EDS data (Fig. 5). After annealing the 50 nm Ag/Cu sample at 420 °C (Fig. 4(f)), the layers are still separated but Ag has formed triangular spikes into GaAs. The EDS data, in Figs. 5(c) and 5(d), for the samples annealed at 200 °C and 420 °C, did not show mixing of Ag and GaAs, as indicated by the SEM images. Similar behavior was observed for the 10 nm Ag/Cu samples (Figs. 4(h), 4(i), 5(e), and 5(f)). Consequently, even 10 nm of Ag acts as an effective diffusion barrier for Cu and GaAs enabling process temperatures of at least 200 °C.

In conclusion, we have demonstrated the applicability of a double-layer Ag/Cu back contact reflector to enhance the EQE of the GaInNAs solar cell. The solar cell with the 30 nm Ag/Cu reflector resulted in the calculated $J_{sc}$ of $\sim$14 mA/cm$^2$ at AM1.5D (1000 W/m$^2$) under a GaAs filter. This value is 28% higher than that for the reference Ti/Au reflector. Furthermore, the adhesion tests showed no notable peeling of metals and the contact resistivity values were of the order of $10^{-8}$ 2·cm$^{-2}$. Moreover, the reflector withstands annealing temperatures of at least 200 °C. The results enable current-matching for GaInNAs materials with a high amount of N corresponding to bandgaps below 0.9 eV, ultimately allowing the development of lattice-matched solar cells with more than three junctions.

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