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**Light absorption enhancement in ultra-thin layers  
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of an enhanced hot-carrier effect with light trapping**

**Maxime Giteau**<sup>1,4</sup>, Kentaroh Watanabe<sup>1,4</sup>, Naoya Miyashita<sup>1,4</sup>, Hassanet Sodabanlu<sup>1,4</sup>,  
Julie Goffard<sup>2,3,4</sup>, Amaury Delamarre<sup>2,4</sup>, Daniel Suchet<sup>3,4</sup>, Ryo Tamaki<sup>1,4</sup>, Zacharie Jehl<sup>1,4</sup>,  
Laurent Lombez<sup>3,4</sup>, Masakazu Sugiyama<sup>1,4</sup>, Andrea Cattoni<sup>2,4</sup>,  
Stéphane Collin<sup>2,4</sup>, Jean-François Guillemoles<sup>3,4</sup>, Yoshitaka Okada<sup>1,4</sup>

<sup>1</sup>RCAST, The University of Tokyo, Komaba 4-6-1, Meguro-ku, Tokyo 153-8904, Japan,  
<sup>2</sup>C2N, CNRS, University Paris-Sud/Paris-Saclay, Route de Nozay, 91460 Marcoussis, France,  
<sup>3</sup>CNRS, IPVF, UMR 9006, 30 route départementale 128, 91120, Palaiseau, France,  
<sup>4</sup>NextPV, The University of Tokyo, Komaba 4-6-1, Meguro-ku, Tokyo 153-8904, Japan

**ABSTRACT**

Hot-carrier solar cells (HCSC) can potentially overcome the Shockley-Queisser limit, by having carriers at a higher temperature than the lattice. To this end, the carriers need to thermalize slower than power is generated by absorbing photons. In thin films, a hot-carrier distribution can only be achieved with very high incident power, by saturating the thermalization channels. Ultra-thin absorbers have a smaller thermalization rate, due to fewer channels. However, they typically absorb only a limited amount of light, which prevents them from reaching high efficiencies. Light trapping is an excellent way to increase significantly the amount of light absorbed in an ultra-thin material. Yet, studies on the coupling between light trapping and hot carriers are still lacking, due to the complexity of the whole system. We analyze numerically and experimentally how light trapping can enable high-efficiency HCSC. This manuscript presents the progress towards the experimental demonstration of the enhancement of the hot-carrier effect with light trapping.

280 nm-thick devices have successfully been reported on a gold mirror using epitaxial lift-off (ELO) and gold-gold bonding. These devices have been characterized by photoluminescence spectroscopy. Hot carriers with a temperature 37 K above lattice temperature were measured, in accordance with theoretical predictions. We are now working towards the ELO of absorbers 10 times thinner, on which we will implement light trapping to increase the carrier temperature.

**KEYWORD LIST**

Hot-carrier solar cells / thermalization / ultra-thin / light trapping / epitaxial lift-off

## INTRODUCTION AND THEORETICAL BACKGROUND

A hot-carrier solar cell (HCSC) is a concept of photovoltaic cell where the carriers have a temperature higher than that of the lattice. This extra temperature can be seen as extra kinetic energy which, if converted into potential energy (voltage), results in a higher efficiency. Therefore, HCSC promise efficiencies above the Shockley-Queisser limit provided we can overcome two major challenges: maintaining a hot-carrier population, and extracting the carriers with their extra energy.

The first step towards a high-efficiency HCSC is the generation of a hot-carrier population under continuous illumination. In thin absorbers, a hot-carrier distribution can only be achieved with very high incident power, close to or higher than that of fully concentrated sunlight ( $4.5 \text{ kW} \cdot \text{cm}^{-2}$ ), by saturating the electron-phonon interaction<sup>1</sup>. Ultra-thin (<50 nm) absorbers can reduce the thermalization by limiting the number of phonon modes, but at the cost of a strongly reduced absorption<sup>2</sup>.

By increasing the average optical path inside the material, light trapping allows the enhancement of the light absorbed by a material of a given thickness. Several strategies can provide this absorption enhancement. In all cases, the presence of a reflector at the back of the solar cell (usually a mirror) is a great way to prevent photons from escaping. In thick materials, where ray optics can be applied, light trapping consists in diffusing the light in all directions to increase the average light path of light, and increase the chance of total internal reflection<sup>3</sup>. In thin materials, whose thickness is smaller than the wavelength of light, multi-resonant light trapping can be applied, whereby light is coupled to resonant modes (Fabry-Pérot, guided modes) in the absorber, so it can be absorbed much more efficiently<sup>4</sup>. Theoretically, with multi-resonant absorption, the effective absorption thickness of a material could be multiplied by a factor higher than 100 at a broadband level<sup>5</sup>.

Light trapping has a lot of advantages for all types of solar cells. The reduction of absorber volume leads to cost reductions, as well as improved efficiency due to the reduction of non-radiative bulk recombinations (that scale with the absorber volume). Also the presence of a back mirror leads to an increase in the open-circuit voltage due to a reduction of the angle of radiative emission. Because HCSC require ultrathin absorbers to limit thermalization, light trapping is not only advantageous, but necessary for them.

We previously developed a theoretical framework based on detailed balance calculations in order to understand the role of light trapping and thermalization rate in HCSC<sup>6</sup>. A conclusion of this work is that by keeping the absorption constant while reducing the thickness, we can expect an efficiency boost coming purely from a hotter carrier population. However, if no light trapping is implemented, the cell efficiency decreases with the thickness, as a lower thermalization does not compensate for the lower absorption (inset of figure 1).

The experimental observation of hot carriers can be made directly by observing the temperature of the carriers. A reduction of thickness leads to an increase of temperature, whether light trapping is implemented or not (figure 1). However, the temperature will be significantly higher with light trapping, especially for ultra-thin absorbers. This gives us an experiment roadmap to demonstrate the benefit of light trapping on HCSC. In a first step (A), we will measure the carrier temperature in a 200 nm GaAs absorber without light trapping, then (step B) in a 20 nm GaAs absorber, still without light trapping, and implement light trapping in the last step (C) to recover the same absorption as in step A. For each successive step, the model predicts a higher carrier temperature under identical experimental conditions.

In this proceeding, we present our latest experimental results. We have been able to characterize a GaAs absorber for step A, and are working towards the implementation of steps B and C. We present the grown samples, the epitaxial lift-off (ELO) and gold-gold bonding methods we developed to study ultra-thin layers, and measure the temperature of the carriers.

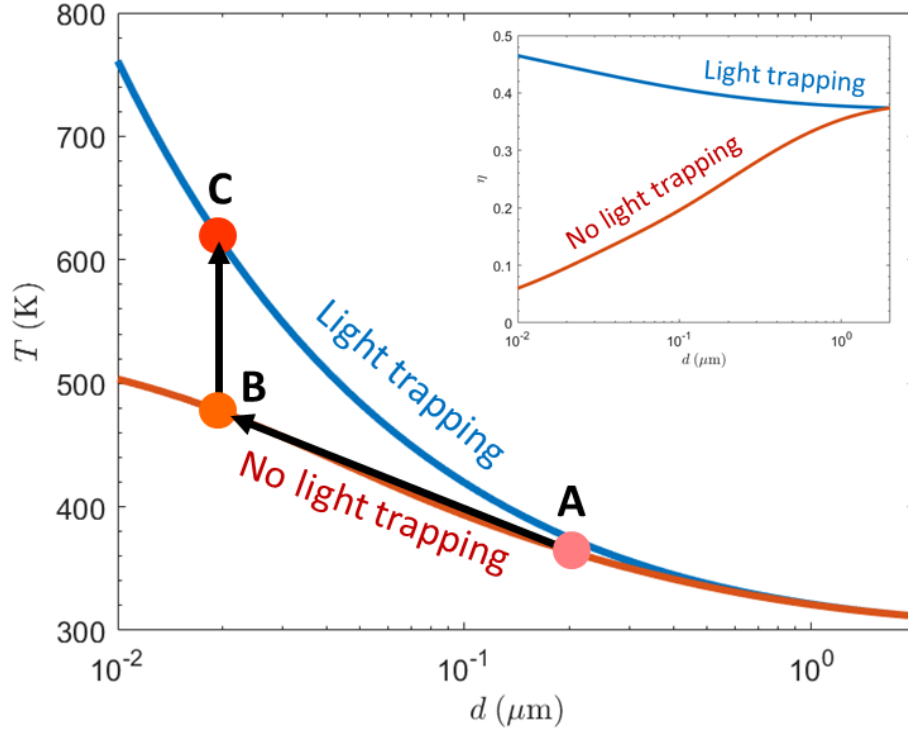


Figure 1: Temperature of the carriers in a GaAs absorber as a function of the absorber thickness, in the radiative limit, and for an illumination intensity of 45000 suns. The blue line corresponds to a constant absorption whichever the thickness, while the red line is calculated without any light trapping. For thicknesses below 200 nm, an important temperature difference starts to appear between the two cases. Our experimental plan follows the steps indicated with the capital letters. In step A, we make a 200 nm absorber without light trapping, in step B a 20 nm absorber, still without light trapping, and in step C we implement light trapping on the 20 nm absorber in order to have the same absorption as in a 200 nm absorber. For each step, we expect the temperature of the carriers to increase. Inset: Ideal efficiency achievable for the same conditions, with and without light trapping. Only if we implement light trapping can we expect an efficiency gain in HCSC.

## EXPERIMENTAL RESULTS

We have grown samples by metalorganic chemical vapor deposition (MOCVD) on GaAs substrates (figure 2, left and middle). The absorber is made of GaAs, with barriers consisting of  $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$ . Before the active region, we grew a layer of  $\text{Al}_{0.53}\text{In}_{0.47}\text{P}$ , which will be used as the release layer for the ELO. All the layers are grown lattice-matched on GaAs and without doping. We choose a GaAs absorber in the first place, as it is a well-known material which can be grown with a quality very close to its radiative limit (even though its band gap is too high for an HCSC).

The barriers on each side of the GaAs absorber prevent the thermal escape (or non-radiative recombination) of the carriers, enabling the hot-carrier population (figure 2, right). The requirement for the barrier height for electrons and holes is not the same. Because the electrons have a much lower effective mass than the holes, most of the extra energy received from a photon is transferred to the electron. Therefore, the kinetic energy of the electrons in the conduction band is much higher than the kinetic energy of the holes in the valence band. The electrons tend to heat more, while the holes remain relatively cold<sup>7</sup>. Therefore, the barrier height is more critical on the electron side than on the hole side.

The Al composition in the AlGaAs layers is chosen to maximize the conduction band offset between the absorber and the barrier. The conduction band offset with GaAs starts decreasing for an Al content above 50%, even though the bandgap of

AlGaAs increases as more Al is introduced. With this composition, we calculate a conduction band offset of 0.33 eV, and a valence band offset of 0.21 eV. It is also higher than what can be achieved with InGaP (0.20 eV) or InAlP (0.31 eV). We are currently working on calculating whether the height of this barrier should be sufficient to limit the thermal escape of the electrons, and if so, up to which temperature.

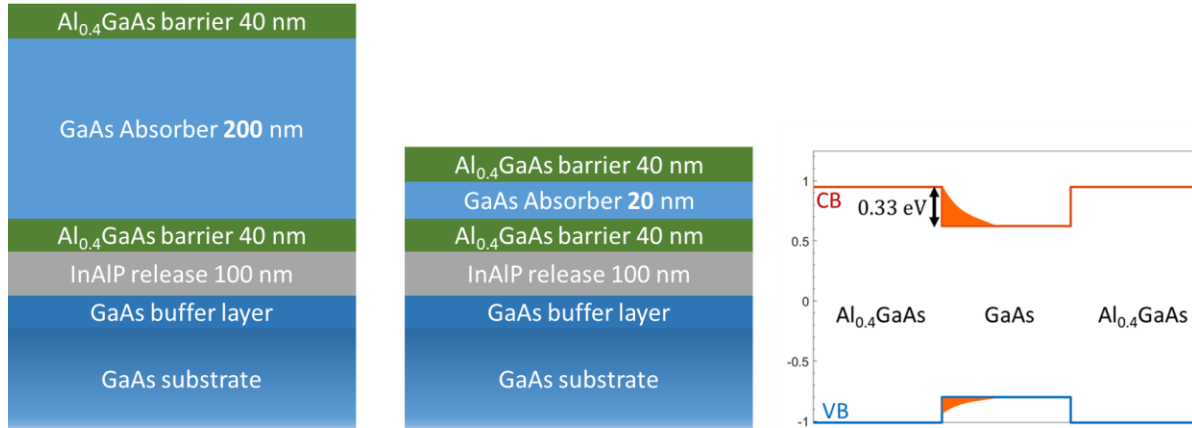


Figure 2: Left and middle: structures grown in MOCVD. The device is composed of a GaAs absorber sandwiched between two Al<sub>0.4</sub>GaAs. An InAlP layer, lattice matched to GaAs, is grown before the device for the ELO. Right: band offset for holes and electrons for a barrier-absorber barrier system consisting of a GaAs absorber and Al<sub>0.4</sub>GaAs barriers. Al<sub>0.4</sub>GaAs provides a conduction band offset of 0.33 eV, the highest among materials lattice matched to GaAs.

Light trapping methods require the presence of a mirror at the back of the cell in order to prevent the photons from escaping. This mirror needs to be put right at the back of the device, which requires to remove the substrate. Even in the samples in which we do not implement light trapping, a back mirror should be integrated for fair comparison. Also, this allows to suppress the substrate parasitic photoluminescence signal.

Substrate removal can be done in several ways. The simplest consists in chemically etching the substrate up to an etch stop layer grown between the device and the substrate. The etch rate of the solution being much lower for the etch stop layer, one can effectively remove the substrate without damaging the device.

A more challenging approach consists in using a release, or sacrificial, layer, again in between the device and the substrate. The device is designed so that the substrate and the device are not etched by the solution that etches the release layer. The main advantage of this technique is that it enables to recover the substrate, a costly part in III-V solar cells, and to use it for multiple growths<sup>8</sup>. This epitaxial lift-off (ELO) technique is not a fundamental requirement for our objective, but a very nice step towards improving the competitiveness of III-V solar cells overall.

ELO requires a solution that etches a release layer without etching any layer of the device, nor the substrate. Because the etch is relatively long (we want to etch several mm to cm-large samples), the selectivity should be really high. Two main routes are considered for the ELO from GaAs substrates.

The most common ELO method combines a HF solution with an AlAs release layer<sup>9</sup>. This method works relatively well, but is not perfectly selective with GaAs<sup>9</sup> and even less so with our Al<sub>0.4</sub>GaAs barriers. Other demerits are the deposition of residues<sup>10</sup>, and the need for applying a strain between the substrate and the device.

An alternative approach is the combination of an HCl solution with a InP-based release layer. This method, if using highly concentrated HCl, can be considered infinitely selective with GaAs<sup>11</sup>, with no residues. In order to maximize the speed of the reaction, AlInP should be considered over GaInP, with an etching about 2 orders of magnitude faster<sup>12</sup>. A specificity of this reaction is that it only occurs in the <100> direction, while almost non-existent in the <110> direction<sup>11</sup>.

We first deposit a 300 nm gold layer on top of the structures shown in figure 2. On the other hand, we prepare a silicon wafer, on which we also deposit a 300 nm gold layer. In order to maximize the adhesion of the metal, the materials are carefully deoxidized in dilute HF solutions right before the metal evaporation. We then bond the grown structure to the silicon

substrate by putting the two gold layers in contact and applying pressure ( $1000 \text{ N. cm}^{-2}$ ) and temperature ( $170^\circ\text{C}$ ) for about 30 minutes. We then proceed to the ELO by immersing the sample in 37% hot (about  $40^\circ\text{C}$ ) HCl until substrate and device are separated, without any strain.

We successfully etched a  $5 \times 6 \text{ mm}^2$  200 nm-thick (figure 2, left) absorber after about 1.5 hours. The resulting sample looks damaged on the surface (figure 3). We attribute this damage to the direct AlInP-AlGaAs interface in our samples, which we suppose not as selective as AlInP with GaAs. Also, the method did not work so far for the 20 nm-thick absorber, possibly because the release layer gets covered with gold during the bonding. We will modify our process so as to modify this interface and hopefully improve the overall device quality, and be able to separate even thinner layers. Still, the device quality was enough so that the hot-carrier measurement could be conducted.

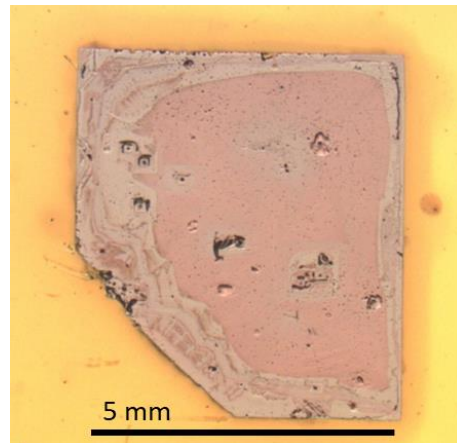


Figure 3: Optical microscope picture of a  $5 \times 6 \text{ mm}^2$  sample after epitaxial lift off. A corner is cut with a  $45^\circ$  angle before the etch due to the directional dependence of the etch rate. The surface of the sample looks damaged, which we attribute to the direct AlInP-AlGaAs interface.

The temperature of the carriers is a parameter which can be obtained experimentally through photoluminescence characterization. In this measurement, a laser beam is focused on the sample, generating photocarriers. We then measure the power which is radiated from a material, due to the recombination of the generated photocarriers. This signal is spectrally resolved using a spectrometer. As such, it is directly a measurement of Planck's generalized law<sup>13</sup>. Therefore, the extraction of charges is not required to access the temperature of the cell: the measurement can be conducted in a purely optical way, in open-circuit condition.

A first approximation of the temperature can be obtained by fitting the slope of the high-energy tail of the photoluminescence spectrum. In log scale, this slope is inversely proportional to the carrier temperature<sup>14</sup>. This can be understood as a higher temperature will correspond to more populated high-energy states, thus to a shallower decrease in the photoluminescence spectrum with increasing energy.

We measure the photoluminescence spectrum of the sample in figure 3 for illumination intensities of 40, 400 and  $4000 \text{ W. cm}^{-2}$  under a 532 nm laser (inset of figure 4). In power, this corresponds to equivalent light concentrations of 400, 4000 and 40000 suns, respectively. The spot size for the illumination is around  $50 \mu\text{m}$ .

For illumination powers of 400 and 4000 suns, the slope of the photoluminescence spectra is identical, meaning that the carriers are at room temperature for both of these intensities. However, when the intensity is increased by one more order of magnitude, the slope becomes slightly shallower, and a carrier temperature 37 K above the lattice temperature is obtained. We confirm the lattice temperature does not increase, because the peak energy of the photoluminescence is not shifted towards a lower energy.

These hot carriers are of the same magnitude as the one expected from the model (figure 1), where step A corresponds to 365 K. However, the conditions are quite different: the calculation is made for a broadband illumination, no front reflection is supposed, while no back mirror is considered. Still, the fact we obtain temperatures slightly above the lattice temperature in both cases is a good sign and suggests the validity of our approach.

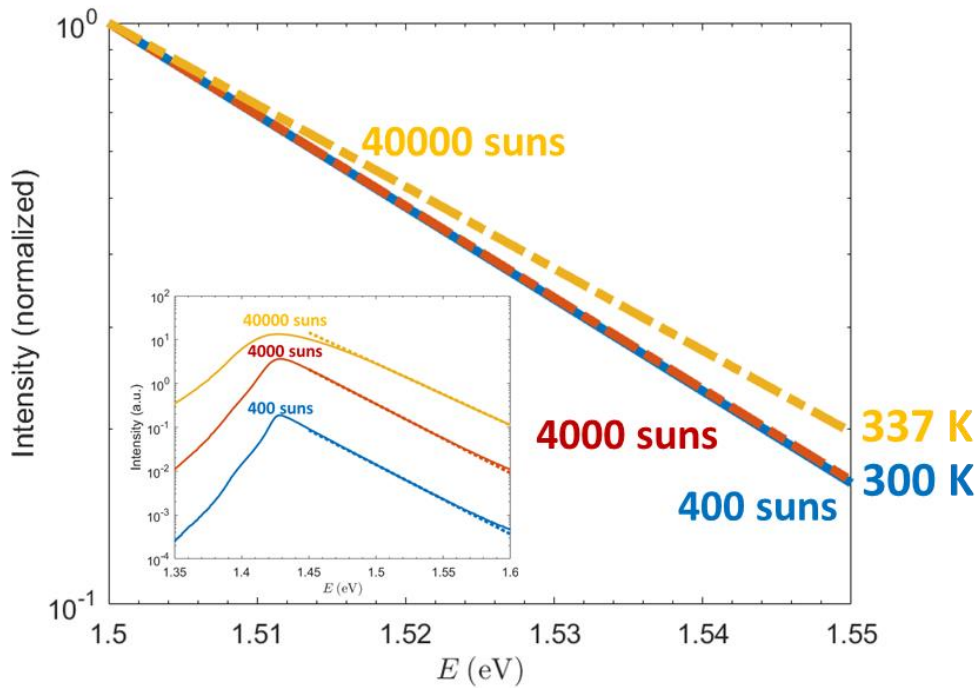


Figure 4: High-energy fit of the photoluminescence spectra obtained from the 200 nm absorber reported on a gold mirror. The spectra (inset) are obtained with a 532 nm laser illumination, with equivalent intensities of 400, 4000 and 40000 suns. Up to 4000 suns, the slope remains identical, suggesting carriers in thermal equilibrium with the lattice. For the highest illumination power, a carrier temperature 37 K higher than that of the lattice is measured. The energy peak remains the same, so that no lattice heating seems to occur.

## CONCLUSION

In this work, we investigated the influence of light trapping in HCSC. Using a previous theoretical work based on a detailed balance model, we show the need for light trapping in HCSC, in order to reach efficiencies higher than conventional cells. When considering the temperature of the carriers, we show that a thickness reduction leads to a higher temperature, with an even higher temperature if light trapping is implemented to maintain high absorptivity.

We presented the experiments which have been conducted so far. We grew heterostructures with 20 nm and 200 nm-thick GaAs absorbers on top of a GaAs substrate, with a release layer in-between. We justify the use of  $\text{Al}_{0.4}\text{GaAs}$  as the barrier, and of  $\text{AlInP}$  as a release layer for ELO. We report the gold-gold bonding of a  $5 \times 6 \text{ mm}^2$  sample with a 200 nm-thick absorber on a Si substrate using ELO, resulting in a device with a back mirror. We measure hot carriers for a 40 000 sun equivalent illumination, with a temperature 37 K above the lattice temperature.

The next step of this work is to manage the ELO of 20 nm-thick absorbers, which we expect to have a hotter carrier temperature. Then, we will implement light trapping on these ultra-thin absorbers to show an even higher carrier temperature. We will also work on the epitaxial structures in order to improve the surface quality of the device after the ELO.

We believe high-efficiency light trapping is one of the most critical components to be integrated into a HCSC in order to develop devices working in real conditions, and is a very important feature for any kind of solar cell. As such, we hope this work will contribute to the development of HCSC in particular, and III-V solar cells in general.

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