# Photoluminescence Enhancement towards High Efficiency Plasmonic Solar Cells

Chog Barugkin, Ngwe-Soe Zin and Kylie R. Catchpole

Centre for Sustainable Energy Systems, College of Engineering and Computer Science, The Australian National University, Canberra, ACT 0200, Australia

Abstract — We demonstrate enhanced absorption in silicon wafers when plasmonic nanoparticles are added to a conventional rear contact structure. A rear side light trapping with plasmonic nanoparticles and various thicknesses of  $\mathrm{Si}_3\mathrm{N}_4$  layer is studied and compared to a structure with combined plasmonics and diffused paint. Photoluminescence is applied to extract the absorptivity in order to exclude free carrier and parasitic absorption. Modeling shows that the absorption within a cell structure with plasmonic nanoparticles and optimum capping layer is expected to be enhanced by 53% of value for an ideal Lambertian reflector.

Index Terms — absorption, nanoparticles, photoluminescence, short circuit current, silicon.

#### I. INTRODUCTION

Plasmonics has been broadly studied to be applied as a light trapping structure in thin-film solar cells, as geometrical light trapping is not feasible for thin-films. However, a limited number of works have been reported on applying plasmonic particles to wafer based solar cells [1]. Plasmonics has several advantages over conventional geometrical textures for wafer based solar cells, as it is applicable for multi-crystalline wafers that are difficult to texture, and it does not increase the surface area that leads to surface recombination. Furthermore, the surface plasmon resonance can be tuned to the wavelength region that can most benefit from light trapping, by controlling the parameters of the plasmonic particles [2]. Therefore it is important to determine the extent to which plasmonic structures can enhance light trapping in wafer based cells.

In this paper we investigate the application of plasmonics on the back of a silicon wafer with a structure that mimics the rear of a high efficiency solar cell. The impact of capping layers with different thickness is studied to optimize the properties of the plasmonic rear side light trapping structure. The photoluminescence measurement technique we used in this paper provides a simple way to rapidly assess light trapping designs, speeding the development of optimal structures.

### II. BACKGROUND

For conventional cell design, geometrical scale surface texturing is used as a main technique to enhance the light absorption within the active layer, such as upright or inverted pyramids and random texture. The textured surface can randomize the direction of the light and reduce its chance of escape, thereby enhancing the path-length of the light and increasing the absorption probability. Material with high refractive index (n) like Si can increase the path length of light by a factor of up to  $4n^2$  or more due to the high density of optical modes in silicon, compared to the modes in air [3]. Scattering by plasmonic particles is an alternative method for increasing absorption in solar cells, with the advantage of avoiding the need to texture the active region of the cell. In the spectral region with wavelengths longer than the surface plasmon resonance wavelength of nanoparticles, the presence of nanoparticles leads to constructive interference between transmitted and scattered light, thereby increasing the photocurrent response in solar cells. But at wavelengths shorter than the particle resonance, a reduction in photocurrent response occurs due to the destructive interference between transmitted and scattered field components. This phenomenon can be prevented by applying the nanoparticles on the rear side of solar cells [2]. This means that plasmonic light trapping structures need to be applied at the rear of a solar cell, and therefore integrated with the rear reflector structure.

In industrial applications, it is important to include a capping layer, for example SiN<sub>x</sub>, to prevent the penetration of metal through the passivation layer [4] and increase the internal reflectance by reducing the penetration of the evanescent waves to the metal [5]. Therefore, we add a layer of plasma enhanced chemical vapor deposition (PECVD) deposited Si<sub>3</sub>N<sub>4</sub> as a capping layer between nanoparticles and reflector, and a plasmonic light trapping structure with various thickness of Si<sub>3</sub>N<sub>4</sub> layer is investigated in terms of absorption enhancement within silicon wafers. As a relevant comparison, we also include results of a rear side light trapping with combined plasmonics and diffuse coating reflector which was optimized in our previous work [6].

In order to rapidly optimize many parameters involved in such a structure, it is advantages to use wafers, rather than fully processed solar cells. However, using the measurement of transmission and reflection spectra, which is the conventional method for evaluating the absorption enhancement due to light trapping, it is impossible to avoid free-carrier and parasitic absorption, which do not contribute to the photon-current. For useful absorption that can generate electron-hole pairs, the absorbed photons excite electrons from the valence band to the conduction band. The inverse

process is band-to-band radiation, which can be directly quantified by measuring luminescence spectra. Therefore, by studying the luminescence spectrum of silicon wafers, we can derive the portion of the absorbed photons leading to the effective electron-hole generation in silicon wafers from the photoluminescence (PL) spectrum. This method is valid for solar cells in all stages of fabrication process, and is especially useful for silicon wafers that have not had a complete p-n junction structure. The intensity of PL emitted at a given wavelength is determined by both carrier densities, which in turn is determined by the effective lifetime in the active layer, and the optical properties of the sample. The relationship between spectral photoluminescence current density and band to band transition absorptivity is given by [7]:

$$dj_{e}(\hbar\omega) = C \exp\left(\frac{\varepsilon_{F,C} - \varepsilon_{F,V}}{kT}\right) A(\hbar\omega)(\hbar\omega)^{3} \exp\left(-\frac{\hbar\omega}{kT}\right) d(\hbar\omega) \qquad (1)$$

C is a factor of proportionality,  $\varepsilon_{F,C}$ - $\varepsilon_{F,V}$  is the difference of the quasi-Fermi energies, k is the Boltzmann constant, T is temperature in Kelvin,  $\hbar$  is the reduced Planck constant, and  $\omega$  is the angular frequency of the photon. According to equation (1), the photoluminescence spectrum can be divided

by 
$$(\hbar \omega)^3 \exp\left(-\frac{\hbar \omega}{kT}\right)$$
 to obtain the absorptivity of wafers

with each type of light trapping structure as a function of wavelength. The absorptivity as a function of wavelength that we extract here are only relative values as the PL intensities are arbitrary numbers, which need to be converted into absolute values by being normalized to 1-R at high energy range, where R is the front surface reflectance.

#### III. EXPERIMENT

A simplified device structure, mimicking a high efficiency rear contact silicon solar cell (Fig. 1) is fabricated by first saw damage etching 1.5  $\Omega$ cm 250  $\mu$ m n-type Cz mono-crystalline rear-side polished samples. A stack of 15 nm atomic layer deposited aluminum oxide is applied on both front and rear, followed by thermal evaporation of silver film having thickness of ~27 nm on the rear. The samples are then annealed in nitrogen ambient at 250°C for 50 min, which forms the Ag nanoparticles (AgNP), as shown in Fig. 1. Following the AgNP formations, PECVD silicon nitride is deposited on the front side of the sample (60 nm) as an anti-reflection coating (ARC) and on the rear (60, 90, 120 and 150 nm) as a capping layer using a standard PECVD process. Then a blanket Ag (~1  $\mu$ m) is thermally evaporated on the rear to form the back surface reflector (AgNP/Si<sub>3</sub>N<sub>4</sub>/Ag).

As a comparison, a 200  $\mu$ m commercially available barium sulfate based non-luminescent diffuse white coating (DWC) is used as back surface reflector instead of Si<sub>3</sub>N<sub>4</sub>/Ag structure. A layer of 60nm Si<sub>3</sub>N<sub>4</sub> is also deposited by PECVD on front side of these wafers.

The photoluminescence spectrum is then measured by illuminating the samples with a laser source powered by 252 mW free running diode at 785 nm. The emitted radiation is detected with a liquid nitrogen cooled InGaAs detector after having passed through an 800 nm blazed grating monochromator. The value of intensity is corrected for the spectral response of the detector across the measured wavelength range. (Fig. 1).

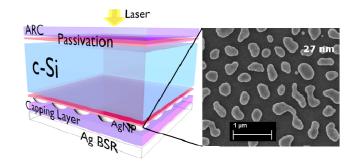


Fig. 1. (Left) The experimental structure with plasmonic Ag particles embedded between a thin  $Al_2O_3$  layer and a thicker  $Si_3N_4$  layer. (Right) SEM image of Ag nanoparticles with 27nm thickness deposited.

#### IV. RESULTS AND DISCUSSION

## A. Photoluminescence Enhancement for Plasmonic Cells Structures

Based on the photoluminescence spectrum of each structure measured, the absolute absorption within the silicon wafer is calculated using the equation (1), adjusted via the short wavelength reflectance measured with a spectrophotometer. For the planar sample (Fig. 2), we matched the relative absorptivity at 965 nm to 1-R at the same wavelength as measured using a PerkinElmer UV/Vis/NIR Lambda 1050 integrating sphere spectrophotometer. For sample with AgNP/Si3N4/Ag rear light trapping structure, we matched the relative absorptivity at 1050 nm to 1-R. As shown in Fig. 2, the PL intensity has a notable enhancement due to the present of plasmonics particles on the rear side compared with the planar back sample.

In the short wavelength region (<1000nm) where the absorption depth of photon is significantly less than the wafer thickness, the optical properties of the rear side are irrelevant, as these photons reflected or scattered from the rear cannot reach the front surface to be emitted and detected. The overlapping PLs of samples with and without AgNP therefore demonstrate that the effective lifetime  $\tau_{\rm eff}$  of both samples are the same. However, the absorption depths at above 1000 nm spectrum are much longer than the wafer thickness, meaning that reflectance and scattering form the rear side plays a large role in the intensity of photons emitted from the front. So the enhancement in wavelength range from 1000 to 1400 nm is

subjected to the light trapping effect of plasmonic nanoparticles.

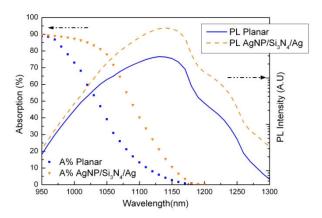


Fig. 2. Photoluminescence spectra of cell structure with planar rear side and sample with AgNP/120nm  $Si_3N_4/Ag$  and the absorptivity of each type of structures extracted from the photoluminescence spectra.

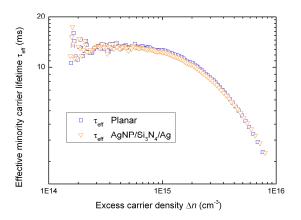


Fig. 3. Measured  $\tau_{\text{eff}}$  of planar silicon wafer and wafer with Ag nanoparticles as a function of  $\Delta n$ .

It was confirmed that the measured effective minority carrier lifetime of the same sample remains barely changed across the range of carrier injections before and after the application of AgNP on the structures using quasi-steady-state photo-conductance measurements (Fig. 3).

## B. Capping Layer Thickness Optimization

In order to quantify the light trapping enhancement for samples with different thickness of capping layer and rear structure, we calculate the maximum possible photon current by multiplying the absorption spectra by the photon flux across the AM1.5G solar spectrum and integrating from 400nm to 1300nm, and compare the results with an analytical

Lambertian model. The extracted absorption from PL spectra is only within the region of 1050 to 1300 nm. The remaining part of the spectrum from 400 to 1050nm uses absorption obtained from reflectance and transmission measurements using a spectrophotometer, since free carrier and parasitic absorption within this wavelength region is expected to be low. We calculate the maximum possible photon current for each type of sample  $(J_P,J_{AgNP/Si_{}^3\!N_4\!/Ag},\,J_{Lam}$  and  $J_{AgNP/DWC}$  of the with planar rear surface, AgNP/Si<sub>3</sub>N<sub>4</sub>/Ag, Lambertian and AgNP/DWC rear structures, respectively). By comparing the enhancement  $J_{AgNP/Si_3N_4/Ag}$  -J<sub>P</sub> with the enhancement for the Lambertian case  $J_{\text{Lam}}\text{-}J_{P}$  we can evaluate the contribution of each light trapping structure on the rear surface of the wafer.  $(J_{AgNP/Si_3N_4/Ag}-J_P)/(J_{Lam}-J_P)$  is the experimental enhancement expressed as a fraction of the Lambertian enhancement.

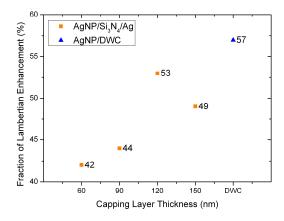


Fig. 4. The fraction of Lambertian enhancement in calculated photocurrent for  $(J_{AgNP/Si3N4/Ag}-J_P)/(J_{Lam}-J_P)$  in orange square and for  $(J_{AgNP/DWC}$  - $J_P)/(J_{Lam}-J_P)$  in blue triangle, as a function of  $Si_3N_4$  film thickness.

Fig. 4 shows the experimental enhancement values as a function of capping layer thickness, for AgNP/Si<sub>3</sub>N<sub>4</sub>/Ag and AgNP/DWC structures. The best performing case is 53% of Lambertian enhancement in absorption, obtained with sample with 120nm Si<sub>3</sub>N<sub>4</sub> film as capping layer at the rear, which is lower than DWC structure with 57% enhancement.

As an alternative way to quantify light trapping properties, we also calculate the path length enhancement (PLE) of each type of structures obtained by dividing the absorptance of the sample with AgNP/Si<sub>3</sub>N<sub>4</sub>/Ag and AgNP/DWC structures by the absorptance of the planar sample in longer wavelength range. PLE follows the same trend as the fraction of Lambertian enhancement in Fig. 4. The path length enhancement for the structures with Ag reflector varies from 4.7 to 5.8 depending on the capping layer thickness, with the best enhancement for the rear side plasmonic structure with 120nm. This compares to a value of 6.7 for the case of DWC.

## C. Modeled External Quantum Efficiency (EQE) Enhancement

Similar to the capping layer structure of the high efficiency solar cells [8], we use  $60 \text{nm Si}_3 N_4$  on the rear side of wafers to compare the light trapping properties of structures with and without AgNP.

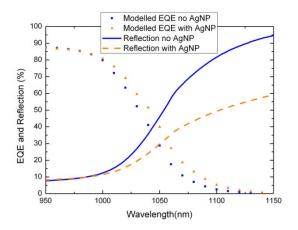


Fig. 5. Modeled EQE of cell structures with and without AgNP based on the absorption extracted from photoluminescence spectrum.

Since the absorption spectrum below 1000 nm is not determined by rear side light trapping, we combined the absorption spectrum measured with a spectrophotometer (300-1000 nm) with the spectrum extracted photoluminescence measurements (1000-1200 nm) to obtain the whole absorption spectrum of the structures. Based on the combined absorptance of the samples with and without AgNP, the external quantum efficiency (EQE) was modeled (Fig. 4). With an assumed collection efficiency of 95%, we calculated  $J_{\rm sc}$  of 2.2mA/cm<sup>2</sup> from 1000nm to 1200nm for the samples with conventional back structure and 2.6mA/cm<sup>2</sup> for with plasmonic light trapping on the rear side. The model indicates that in a solar cell, 18% enhancement in current density over this wavelength range could be expected when integrated with plasmonic nanoparticles at the rear surface. Higher enhancement in current density is also expected with the optimum capping layer of 120nm thickness.

## V. CONCLUSION

Adding Ag nanoparticles on the rear of solar cells can provide light trapping while avoiding additional recombination loss. It is a simple and effective light trapping structure that can be used in variety of solar cells, including thin-film and wafer based cells. In addition, the band to band absorptivity extraction from photoluminescence is a fast, non-destructive and reliable technique that can be applied in obtaining absolute absorption of solar cells in any fabrication stage.

By varying the thickness of capping layer, a maximum of 53% of fraction of the Lambertian enhancement is achieved with 120nm  $S_3N_4$  along with AgNP and Ag back reflector on the rear side of silicon wafers.

With plasmonic rear side light trapping, samples similar to high efficiency solar cell structures have an increase in estimated short circuit current density of 18% in the spectral range from 1000 nm to 1200 nm.

#### ACKNOWLEDGEMENT

This work is a part of an ARC Linkage Project. KRC acknowledges the support of an ARC Australian Research Fellowship. We would like to thank Australian National Fabrication Facility (ANFF) for access to PECVD.

#### REFERENCES

- [1] Y. Yang, S. Pillai, H. Mehrvarz, H. Kampwerth, A. Ho-Baillie and M.A. Green, "Enhanced light trapping for high efficiency crystalline solar cells by the application of rear surface plasmons," *Solar Energy Materials and Solar Cells* vol.101, pp.217-226, 2012.
- [2] F. J. Beck, A. Polman and K. R. Catchpole, "Tunable light trapping for solar cells using localized surface plasmons," *Journal of Applied Physics* vol. 105, pp. 114310-114315, 2009.
- [3] Z. Yu, A. Raman and S.H. Fan. "Fundamental limit of nanophotonic light trapping for solar cells," *Proceedings of the National Academy Sciences of United States of America*, vol. 107, pp. 17491–1749, 2010.
- [4] T. Lauerman, T. L'uder, S. Scholz, B. Raabe, G. Hahn, and B. Terheiden, "Enabling dielectric rear side passivation for industrial mass production by developing lean printing-based solar cell processes," in 35th IEEE Photovoltaic Specialist. Conference, 2010, pp. 28–33.
- [5] Z. Holman, M, Fillipic, A. Descoeudres, S. De Wolf, F. Smole, M. Topic, and C. Ballif, "Infrared light management in highefficiency silicon heterojunction and rear-passivated solar cells," *Journal of Applied Physics*, vol. 113, 013107, 2013.
- [6] C. Barugkin, Y. Wan, D, Macdonald, and K. Catchpole, "Evaluating plasmonic light trapping with photoluminescence," *Submitted*.
- [7] T, Trupke, E. Daub and P. Wurfel, "Absorptivity of silicon solar cells obtained from luminescence," *Solar Energy Materials and Solar Cells* vol.53, pp.103-114, 1998.
- [8] N. Zin, A. Blakers, K. R. Mcintosh, E. Franklin, T. Kho, K. Chern, J. Wong, T. Mueller, A. G. Aberle, Y. Yang, X. Zhang, Z, Feng, Q. Huang, and P. J. Verlinden, "Continued development of All-Back-Contact silicon wafer solar cells at ANU," *Accepted for publication in Energy Procedia 2013*.