Evaluating Plasmonic Light Trapping With Photoluminescence

Chog Barugkin, Yimao Wan, Daniel Macdonald, Senior Member, IEEE, and Kylie R. Catchpole

Abstract—We use photoluminescence measurements to quantify the light trapping for a range of plasmonic structures. By combining Ag nanoparticles as a scattering structure and diffuse white paint as a back surface reflector (BSR) on silicon wafers, we can achieve absorption enhancement of 62% of the Lambertian value, which is comparable with literature values for inverted pyramids of 67%. Through measurements of the effective carrier lifetime, we also establish that plasmonic Ag particles do not degrade the electrical properties of the passivation layer.

Index Terms—Absorption, nanoparticles, photoluminescence, silicon.

I. INTRODUCTION

As high-efficiency solar cell technologies mature, harvesting the near-infrared (NIR) photons becomes essential to approach the theoretical limit of single-junction solar cells. To capture this proportion of the light, light-trapping structures are required to scatter light and increase the optical path length of photons within the solar cell.

Plasmonics has several advantages over conventional geometrical textures as it can be used for thin crystalline silicon and multicrystalline silicon, where pyramid texturing is not feasible. It can also be applied to a planar semiconductor layer, avoiding the need to etch the active region of the device. Furthermore, the surface plasmon resonance can be tuned to couple with the desired wavelength range by controlling the parameters of the plasmonic particles [1].

It is beneficial to apply plasmonic structures at the rear rather than front of a solar cell, as in this way the loss of short-wavelength light can be avoided [1]. To obtain good light trapping with plasmonic particles, it is necessary to include a reflector structure as well as the particles. There have been a limited number of works on applying plasmonic nanostructures with reflectors to solar cells. Ouyang et al. achieved 44% of photocurrent enhancement by applying Ag nanoparticles on the rear side of 2 μm-thick polycrystalline silicon (poly-Si) solar cells [2]. A 50.2% enhancement was reported by Rao et al. on a 2 μm-thick poly-Si-based solar cells with the optimized dielectric environment [3]. Ferry et al. reported photocurrent enhancement in ultrathin amorphous silicon solar cells by applying plasmonic nanostructures in the Ag/ZnO:Al back contact of the cell [4]. Later Paetzold et al. increased spectral response by employing a similar structure on μc-Si:H solar cells [5]. Recently, Yang et al. reported a maximum of fourfold external quantum efficiency enhancement at 1160 nm and 16% current enhancement in the 900–1200 nm wavelength region by applying silver nanoparticles and a detached silver reflector to wafer-based solar cells, in comparison with cells with an Al reflector [6].

In addition to metallic reflectors, dielectric reflectors are also promising for integrating with plasmonic structures. Diffuse coatings made from dielectric particles have been used as back surface reflectors (BSRs) in photovoltaic applications for over a decade due to their high reflectance over a broad spectral range, low cost, and chemical stability. In 1998, Cotter first applied dielectric particles as diffuse reflectors on solar cells [7]. Berger et al. increased the short-circuit current density by 41% for a very thin cell with a commercially available TiO2 white paint as a diffuse reflector, and experimentally demonstrated that the white paint is better than Al, air, TCO/Al stack, and detached mirror as a BSR [8]. Recently, Basch et al. achieved an enhancement of 35% in short-circuit current by applying TiO2 particles as the BSR on poly-Si thin-film solar cells [9], and increased this to 100% enhancement by combining plasmonic particles with the TiO2 reflector [10].

Plasmonic scattering is very sensitive to the size, shape, and location of the structures; therefore, there is a wide range of parameters that must be assessed in order to find the best structure [11]. It is therefore necessary to be able to easily quantify the light trapping achievable by any particular structure. In addition, for light trapping to be applicable to wafer-based solar cells, it is important that both effective light trapping and surface passivation can be simultaneously achieved. Therefore, it is important to be able to characterize both the light trapping and surface passivation achieved by a scattering structure.

In this study, we demonstrate experimentally that a back reflector structure with Ag plasmonic particles that is embedded between the dielectric and diffuse coating layers can support excellent light-trapping performance, which is comparable with the traditional inverted pyramid texturing structure. We use spectrally resolved photoluminescence to quantify the absorptance, which allows parasitic absorption to be excluded and provides a rapid method for assessing light trapping. Photoconductance-based measurements of the effective carrier lifetime at relevant injection levels also show that surface passivation is not degraded.
II. METHODS

A. Theoretical Background

With the conventional method for the determination of absorption (i.e., measurement of transmission and reflection spectra), it is impossible to avoid free-carrier and parasitic absorption, which do not contribute to the photocurrent. For useful absorption, which can generate electron and hole pairs, photons excite electrons from the valence band to the conduction band. In the inverse process, electrons transition between the conduction band and the valence band and can emit photons back into medium. According to Kirchhoff, a good absorber is a good emitter at the same condition, and Würfel has extended this to nonthermal emission such as luminescence [12]. Thus, any absorption enhancement within the semiconductor will be indicated in its emission, and any increase in emission corresponds to an increase in absorption. By studying the luminescence spectra of silicon wafers with and without light-trapping structures, we can derive the portion of photons that lead to effective electron–hole pair generation. This method is valid for solar cells in all the stages of the fabrication process, and is especially valuable for silicon wafers that have not acquired a complete p-n junction structure.

The method of extracting absorptance from luminescence was first developed and used by Trupke et al., using electroluminescence [13]. They derived the relationship between photoemitted current density and band-to-band transition absorbance

\[ dj, (E) = C \exp \left( \frac{\varepsilon_{F.C} - \varepsilon_{F,V}}{kT} \right) A(E) E^3 \exp \left( - \frac{E}{kT} \right) d(E). \] (1)

Here, \( C \) is a constant of proportionality, \( \varepsilon_{F.C} - \varepsilon_{F,V} \) is the difference of the quasi-Fermi energies, \( A(E) \) is absorptivity for band-to-band transitions, \( k \) is the Boltzmann constant, \( T \) is the temperature in kelvin, \( E = \hbar \omega \) (\( \hbar \) is the reduced Planck constant, and \( \omega \) is the angular frequency of the photon). Equation (1) is valid for situations where the difference in quasi-Fermi energies is constant across the device, which is the case for the high quality, passivated, silicon wafers we use in this study.

According to (1), the luminescence spectrum can be divided by \( E^3 \exp \left( - \frac{E}{kT} \right) \) to obtain the absorbance of the wafers with each type of light-trapping structure as a function of wavelength. The absorbance that we extract here are only relative values since the PL intensities we measure are arbitrary numbers. These need to be converted into absolute values by being normalized to 1–\( R \) at the high-energy range, where \( R \) is the front surface reflectance. The samples we consider here have light-trapping structures on the rear of the device, and we illuminate with a laser with photon energy well above the bandgap of silicon. Therefore, the absorption of the illuminating laser by a sample is the same whether the light-trapping structure is present or not. Our approach could also be used for light-trapping structures on the front of a sample, but in that case the difference in reflection for the cases with and without light trapping structures would need to be taken into account.

B. Experiments

A schematic diagram of the experimental structure is shown in Fig. 1. For this study, 1.5 \( \Omega \cdot \text{cm} \) 250 \( \mu \text{m} \) n-type Czochralski monocrystalline silicon wafers are used. The first step is saw-damage etching. Then, one of the four types of dielectric layers are coated on both sides of each wafer: plasma-enhanced chemical vapor deposited amorphous silicon (100 nm PECVD a-Si:H), PECVD silicon nitride (20 nm PECVD Si\(_3\)N\(_4\)), atomic layer deposited aluminum oxide (5-,10-, and-20 nm ALD Al\(_2\)O\(_3\), respectively), and thermally grown silicon dioxide (20 nm SiO\(_2\)). Ag films with thicknesses of 15, 21, 27, 33, and 39 nm are thermally evaporated on the rear side of wafers followed by an annealing at 250 °C for 50 min in a furnace with nitrogen atmosphere. Scanning electron micrographs of the resulting nanoparticles are shown in Fig. 1. After the nanoparticle fabrication process, a 200 \( \mu \text{m} \)-thick layer of barium sulfate-based nonluminescent diffuse white coating is uniformly sprayed on the samples as a BSR and dried at room temperature. Quasi-steady-state photoconductance measurement [14] is taken before and after the nanoparticle fabrication process to determine the effective minority carrier lifetime and hence examine the effect on the passivation property.

For measuring the photoluminescence spectra of the samples, a 252 mW high-powered free-running diode laser at 785 nm as a laser source illuminates the sample at room temperature. The laser spot size is approximately 1 mm in diameter. The emitted radiation is detected with a liquid nitrogen cooled InGaAs detector after having passed through an 800 nm grating blazed monochromator. The value of intensity is corrected for the spectral response of the detector across the measured wavelength range.

III. RESULTS AND DISCUSSIONS

A. Surface Passivation

The effective lifetime as a function of the excess carrier density for two samples with either Al\(_2\)O\(_3\) or a-Si:H passivation, before and after applying Ag nanoparticles, is shown in Fig. 2. The measured effective lifetime of the same samples remains constant (up to 6.6 ms at an injection level of 1 \( \times \) 10\(^{15}\) cm\(^{-3}\) for 10 nm Al\(_2\)O\(_3\)-passivated wafers) before and after the nanoparticle fabrication process, which shows that the excellent
Fig. 2. Measured effective lifetime for 10 nm Al₂O₃ and a-Si:H passivated samples with \( N_D = 2.6 \times 10^{15} \text{ cm}^{-3} \) before (Planar) and after (Ag) fabricating silver nanoparticles.

passivation of the Al₂O₃ and a-Si:H is maintained in the presence of the Ag nanoparticles. For samples with 20 nm thermally grown SiO₂ and 5 nm ALD Al₂O₃, the effective lifetime has significant degradation of up to 40% after Ag nanoparticles were applied. This could be because the dielectric films are too thin or because pin holes are present in the films, allowing the Ag to penetrate through and damage the passivation layers. Reduction in passivation quality may lead to disparity in the quasi-Fermi energy difference between the surface and bulk regions of the wafers, meaning (1) becomes increasingly invalid in these cases. Therefore, these passivation layers were not used in further experiments.

B. Photoluminescence Enhancement

The photoluminescence spectra for a sample with 10 nm Al₂O₃ passivation layer, with (magenta dashed line) and without (blue dash dot line) Ag nanoparticles and BSR, are shown in Fig. 3 (right axis). The spectra overlap at short wavelengths, but the photoluminescence for the sample with Ag nanoparticles and BSR is much larger at long wavelengths.

The intensity of photoluminescence emitted at a given wavelength is determined by both the carrier densities (which in turn are determined by the effective lifetime in the active layer) and the optical properties of the sample. In the short wavelength region (<1000 nm), where the absorption depth of photons is significantly less than the wafer thickness, the optical properties of the rear side are irrelevant, as photons reflected or scattered from the rear cannot reach the front surface to be emitted and detected. The overlapping PL spectra of both the planar and Ag+BSR samples therefore indicate that the effective lifetime \( \tau_{\text{eff}} \) of both samples is the same. This is expected, since we are measuring the photoluminescence spectra under high injection conditions (>6 \times 10^{16} \text{ cm}^{-3}), for which the lifetime is Auger dominated [15]. In order to sensitively detect changes in the surface recombination velocity, it is necessary to measure the lifetime under lower injection levels, such as with the QSSPC technique discussed in Section III-A.

Fig. 3 (left axis) shows the absorptance that is obtained from the PL spectra using (1). Since (1) contains an unknown constant \( C \), it is necessary to adjust the obtained absorptance spectrum to a separately measured value. In order to do this we measure the reflectance \( R \) using a PerkinElmer UV/Vis/NIR Lambda 1050 integrating sphere spectrophotometer and adjust the relative absorptance at 975 nm to 1 - \( R \) at the same wavelength. For comparison, we show the absorptance that would be expected for a Lambertian rear reflector, using the analytical method of Green [16]. For the Lambertian case, the absorptance is calculated for an ideal rear light-trapping structure with the same front surface reflectance as the experimental samples.

To quantify the light-trapping enhancement, we calculate the maximum possible photon current by multiplying the absorption spectra by the photon flux across the AM1.5 G solar spectrum and integrating from 400 to 1300 nm, and compare the results with the analytical Lambertian model. The absorption that is extracted from the PL spectra is within the region of 975 to 1300 nm. For the part of the spectrum from 400 to 975 nm, we use absorption obtained from reflectance and transmission.
measurements using a spectrophotometer, since parasitic absorption within this wavelength region is expected to be low.

We now compare the calculated currents for each case. \( J_P, J_{Ag+BSR}, \) and \( J_{Lam} \) are the maximum photon currents that the samples with planar surface, Ag + BSR, and the Lambertian rear surface could produce, respectively. By comparing the enhancement \( J_{Ag+BSR} - J_P \) with the enhancement for the Lambert case \( J_{Lam} - J_P \), we can evaluate the contribution of each light-trapping structure on the rear surface of the wafer. \( (J_{Ag+BSR} - J_P)/(J_{Lam} - J_P) \) is the experimental enhancement expressed as a fraction of the Lambertian enhancement.

Fig. 4 shows the experimental enhancement values as a function of the Ag film thickness, for various passivation layers. The best performing case is 62% of the Lambertian enhancement in absorption, obtained with 27 nm-thick Ag on 10 nm Al\(_2\)O\(_3\) passivated wafer (see Fig. 4). This case has a path length enhancement of 11, obtained by dividing the absorptance of the sample with nanoparticles and BSR by the absorptance of the planar sample in the weakly absorbed long-wavelength range.

We can compare this to the standard light-trapping scheme of an inverted pyramid texture, where the average path length enhancement of weakly absorbed light is 16 [13]. The inverted pyramid texture on the front surface of solar cells can provide both light trapping and antireflection. Since our Ag + BSR structure is only on the rear of the cell, we only consider the light-trapping properties between the two, not antireflection. The absorption in a substrate can be estimated by using

\[
A = \frac{1 - R(\lambda)}{1 - R(\lambda)_{\text{PLE}}} + 1. \quad (2)
\]

PLE refers to the path length enhancement, \( W \) is the width, \( \alpha(\lambda) \) is the absorption coefficient, and \( R \) is the front surface reflectance. Using PLE = 16 and the experimental front surface reflectance, calculating the maximum achievable photocurrent results in 67% of the ideal Lambertian enhancement.

The enhancement in absorption for the combination of plasmonic particles and BSR is much larger in all cases than for the BSR alone. This is because the Ag particles can scatter at high angles within the silicon, outside the escape cone. In contrast, although the BSR reflects light very effectively, much of the light reflected by the BSR is within the escape cone [10]. For 10 nm Al\(_2\)O\(_3\), 20 nm Al\(_2\)O\(_3\), and 20 nm Si\(_3\)N\(_4\) passivated wafers, the absorption increases with the Ag film thickness (15, 21, and 27 nm) until 27 nm, and then starts to decrease for thicker films (33 and 39 nm). The increase in absorption with Ag mass thickness is because larger mass thicknesses lead to larger particles (see Fig. 1). These larger particles have a red-shifted surface plasmon resonance that is better matched to the wavelength region where silicon can benefit from light trapping [17], [18]. For a-Si:H passivated samples, the optimum thickness is 21 nm, and then there is a clear degradation with thicker films. This is due to the higher refractive index film, which is also effective at red-shifting the surface plasmon resonance. In this case relatively smaller particles have the best coupling efficiency on a-Si:H compared with other types of dielectric layers.

For samples with Ag films thickness beyond 27 nm, the particles tend to form a continuous film, as shown in Fig. 1. This causes more reflection than scattering, which increases the possibility of incident light being reflected out of the silicon within the loss cone (see Fig. 5).

Passivated samples of 10 and 20 nm Al\(_2\)O\(_3\) show the same enhancement trend for Ag thickness less than 27 nm. We could not obtain reliable results for 10 nm Al\(_2\)O\(_3\)-passivated samples with Ag films 33 nm or thicker. The reason why the 10 nm passivated samples have better performance than 20 nm ones is that the coupling efficiency of nanoparticles with incident light gets stronger as the dielectric between nanoparticles and silicon gets thinner [11], [19]. The 100 nm a-Si:H case also results in good coupling between the Ag particles and the silicon because of the high refractive index of the a-Si:H. Since the a-Si:H
has a similar refraction index to c-Si, the coupling between the Ag particles and c-Si is expected to be about the same as if there were no a-Si:H film at all. (In contrast, if 100 nm of Al$_2$O$_3$ or Si$_3$N$_4$ were used, we would expect very little effect of the Ag particles due to poor coupling.) Overall, however, the performance of the a-Si:H passivated samples is lower than that of the 10 nm Al$_2$O$_3$. This could be due to parasitic absorption within the relatively thick a-Si:H layer.

IV. CONCLUSION

The method of extracting band-to-band absorption from photoluminescence spectra is a useful way to calculate the absolute absorption within the active layer, as free carrier absorption and parasitic absorption can be excluded. It allows the rapid comparison of a wide variety of light-trapping structures. With self-assembled plasmonic Ag particles, excellent optical enhancement can be achieved for photovoltaic applications without sacrificing the electrical performance of the device. 10 nm ALD aluminum oxide combined with nanoparticles formed from a 27 nm-thick Ag film, together with a diffuse back reflector, has provided the best light trapping among all those structures, with performance comparable with the light trapping provided by inverted pyramids. The combination of plasmonic particles with a back reflector is particularly promising for application to thin-film cells, and also interesting for multicrystalline silicon solar cells where conventional random pyramid texturing is not feasible.

ACKNOWLEDGMENT

This work is a part of an ARC Linkage Project. K. R. Catchpole acknowledges the support of an ARC Australian Research Fellowship. D. Macdonald acknowledges the support of ARC Future Fellowship. The authors would like to thank the Australian National Fabrication Facility for access to PECVD and WS Liang for depositing ALD Al$_2$O$_3$.

REFERENCES

Daniel Macdonald (M’10–SM’12) was born in Bendigo, Vic., Australia, in 1971. He received the Bachelor of Physical Science degree from La Trobe University, Melbourne, Vic., in 1993 and the Ph.D. degree in engineering from the Australian National University (ANU), Canberra, A.C.T, Australia, in 2001.

Since then he has been a Research Fellow with the ANU and a Research Scientist with the Energy Research Centre of the Netherlands, Petten, The Netherlands. He is also an Australian Research Council Future Fellow with the Research School of Engineering, ANU, where his research interests include defects and impurities in crystalline silicon solar cells and n-type silicon solar cells.

Kylie R. Catchpole received the B.Sc. degree in physics and the Ph.D. degree in engineering from the Australian National University, Canberra, A.C.T, Australia, in 1995 and 2001, respectively.

She was a Postdoctoral Fellow with the University of New South Wales and the FOM Institute for Atomic and Molecular Physics in the Netherlands. She is currently an Associate Professor with the Centre for Sustainable Energy Systems, the Australian National University. Her work on plasmonic solar cells was featured as one of the top ten emerging technologies in 2010 by MIT Technology Review. Her work has also been highlighted in the news sections of Science magazine and The Economist. Her research interests include using nanotechnology to increase the light absorption in solar cells in order to make them cheaper and more efficient.