Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2015, Article ID 263734, 6 pages
http://dx.doi.org/10.1155/2015/263734

Research Article

Efficiency Enhancement of Gallium Arsenide Photovoltaics Using Solution-Processed Zinc Oxide Nanoparticle Light Scattering Layers

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Received 10 September 2015; Revised 22 November 2015; Accepted 26 November 2015

Academic Editor: Xiaosheng Fang

We demonstrate a high-throughput, solution-based process for subwavelength surface texturing of a III-V compound solar cell. A zinc oxide (ZnO) nanoparticle ink is spray-coated directly on top of a gallium arsenide (GaAs) solar cell. The nanostructured ZnO films have demonstrated antireflection and light scattering properties over the visible/near-infrared (NIR) spectrum. The results show a broadband spectral enhancement of the solar cell external quantum efficiency (EQE), a 16% enhancement of short circuit current, and a 10% increase in photovoltaic efficiency.

1. Introduction

Gallium arsenide (GaAs) is a semiconductor used for a variety of optoelectronic applications (photodetectors, lasers, and solar cells) due to its high absorption coefficient and carrier mobility [1–3]. The best performing GaAs based solar cells have demonstrated efficiencies as high as 29% [4]. A critical loss mechanism in these devices is the reflection at the air-GaAs interface (over 30%), caused by the large refractive index mismatch between GaAs and air. This reflection loss significantly limits the performance of GaAs solar cells and makes the antireflective structure crucial to achieving high cell efficiencies. Multilayer antireflective coatings with low reflective index materials are generally used to reduce reflection losses, but these methods are sensitive to wavelengths and incident angles [5, 6]. Further, the precise thickness requirement for each layer makes depositing them economically unfavorable for solar cell production. Recently, nanoscale surface texturing [7–12] has been proposed as an alternative approach to achieving broadband wavelength and omnidirectional antireflection properties. However, this method typically requires complex processing techniques (such as e-beam, interference, or nanoimprint lithography) that are limited to smaller areas, making them incompatible with practical photovoltaic manufacturing approaches [7, 9]. Moreover, the textured nanoscale surfaces typically enhance surface recombination and reduce excess carrier lifetimes, resulting in decreased efficiencies [11–13]. To avoid these drawbacks, a variety of nondestructive inorganic nanoparticles coatings are being investigated for antireflection and texturing based absorption enhancements [14–17]. Among them, zinc oxide (ZnO) is a strong candidate, since its large band gap (E_g = 3.37 eV at room temperature) makes it transparent in the photovoltaically active regions of the solar spectrum. Further, porous films of ZnO nanoparticles provide a graded effective refractive index as a buffer for the air/GaAs index mismatch. Meanwhile, the ZnO nanoparticles with a range of feature sizes comparable to the wavelengths of the utilized solar spectrum can act as light scattering layers for broadband antireflection [14, 16].

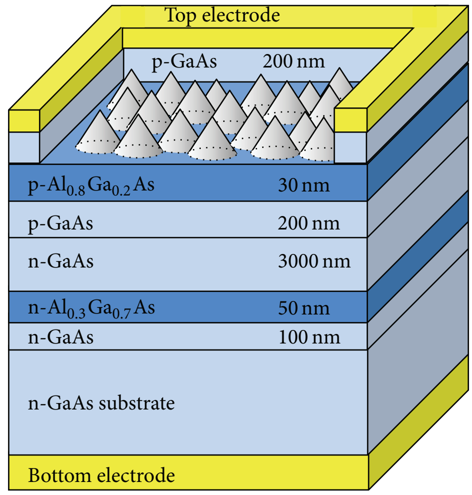

Figure 1: A schematic diagram of the ZnO nanoparticles coated GaAs solar cell.

By controlling the average nanoparticle size through the synthetic approach and film density through the deposition process, the optical properties of this film can be optimized for both antireflection and light scattering [18]. Here we show that the low-cost spray-deposited nanostructured ZnO film can enhance the performance of GaAs solar cells by its broadband antireflection and light scattering properties. The cell with optimized ZnO nanoparticles coating shows a 16.3% improvement in the short circuit current (J_{sc}) and a 10.3% increase in overall energy conversion efficiency (η). This low-temperature, solution-based process is compatible with other flexible substrates. These ZnO light scattering layers processed from nanocrystal inks could be extended to other poorly absorbing photovoltaic materials sets as well unconventional substrate materials [18].

2. Experimental

GaAs solar cells were grown on (100) n-GaAs substrate by metal organic chemical vapor deposition (MOCVD) with Zn as p-type dopant and Si as n-type dopant. The solar cell structure (Figure 1) includes the following: a 200 nm thick p-type heavily doped GaAs as a contact layer, a 30 nm thick p-type $Al_{0.8}Ga_{0.2}As$ window layer, a 200 nm thick GaAs emitter with p-type doping, and a 3000 nm thick GaAs base with n-type doping plus a 50 nm thick back side field layer of n-type $Al_{0.3}Ga_{0.7}As$. This shallow p-n junction employed in these experiments is designed to investigate the scattering effects of ZnO nanoparticles film. After MOCVD growth, a multilayer metal contact of Au/Ge/Ni/Au was e-beam evaporated as the bottom electrode. Metal fingers of Ti/Pt/Au were deposited as the top electrode. After both top and bottom contacts were formed, the GaAs cap layer was selectively etched in 4 : 1 citric acid (50%) and H_2O_2 (30%) solution.

ZnO nanoparticles were synthesized using a modified procedure from Andelman et al. [19]. Briefly, 1.95 g of zinc acetate dihydrate, 2.94 g of oleic acid (90%, technical grade), 115 mg of gallium nitrate hydrate, and 100 g of 1-hexadecanol were added to a 1 liter 3-neck flask, heated to 300°C for 1 hour under nitrogen gas flow, and cooled to room temperature. The ZnO nanoparticles were isolated from the reaction mixture by centrifugation. Ethanol was added to the reaction mixture to precipitate the nanocrystals, and the mixture was subsequently centrifuged at 4000 RPM for 10 minutes to precipitate the nanocrystal yield. The isolated nanocrystals were washed in ethanol two more times and subsequently dried overnight under vacuum [18]. The yield was dispersed in ethanol to create a nanocrystal dispersion of concentration 1.5 mg/mL. This ink formulation was the precursor solution for all spray-deposited coatings. The spray deposition process was performed using a pneumatic air-atomizing nozzle (Spraying Systems, 1/4JN-SUE15B). By independently controlling the nitrogen flow gas pressure and the precursor ink infusion rate, nanoparticle coatings with high levels of homogeneity can be achieved [18]. The process gas (N_2) was used at pressures of 2100 mBar and the ZnO nanoparticle solution was infused using a syringe pump at a rate of 1.8 mL/min. The GaAs solar cell substrates were placed on a heated X-Y stage 95 mm under the nozzle and rasterized throughout the deposition process. The resulting density of the nanoparticle coating on the substrate was calculated from the total infused volume of the ZnO nanoparticle precursor solution. The nominal coverage rate for the "medium concentration" optimized coating was 0.25 mg/cm^2. The insets in Figures 2(b)–2(d) show the scanning electron microscope (SEM) images of three sets of ZnO nanoparticles coating in which the nanoparticles have the average diameter of 250 nm–400 nm with the coverage fractions of nominally 35%, 70%, and 100%, respectively.

3. Results and Discussion

The optical properties of the ZnO nanoparticle layers were studied by characterizing films coated on a control glass substrate. All optical measurements were taken by a standard integrating sphere system. The sample in absorption

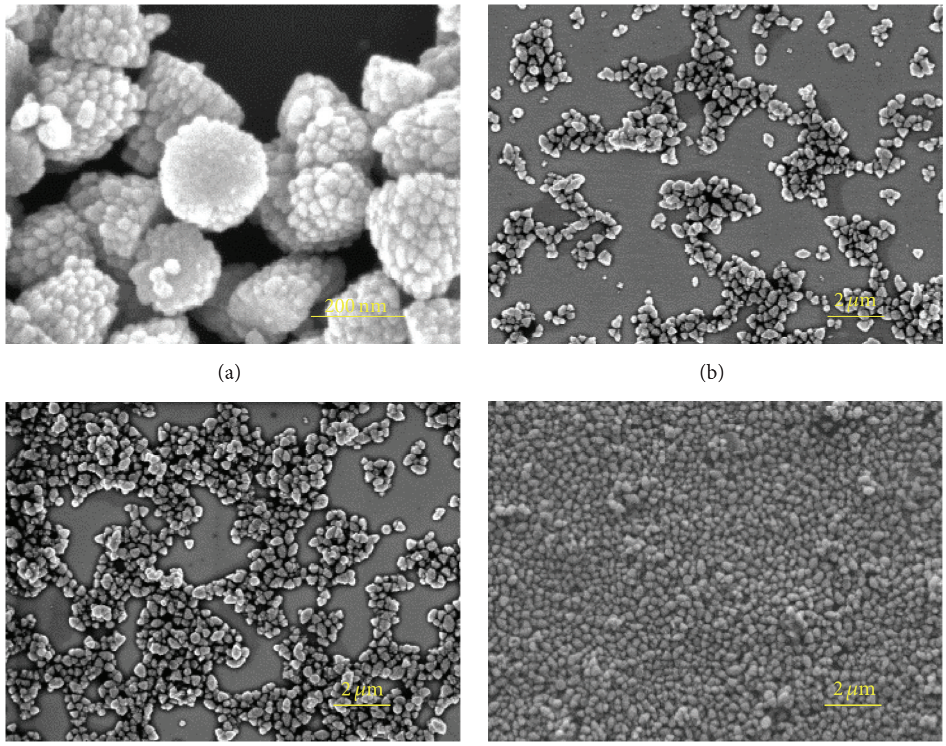

Figure 2: SEM top view images of ZnO nanoparticles coated on GaAs solar cells. (a) top view of ZnO nanoparticles; (b) low density coating, around 35% coverage; (c) medium density coating, around 70% coverage; (d) high density coating, 100% coverage.

measurement was mounted in the center of the sphere and illuminated by the normal incident light. All the reflected and transmitted light was collected by the integrating sphere and measured by a silicon detector mounted at the back of the sphere. The absorbance of ZnO nanoparticle layer is then calculated by subtracting reflected and transmitted light from the incident light. The reflectance of ZnO nanoparticle-coated GaAs cells was characterized by a similar method. In the total transmission measurement, the sample was placed at the opening of the sphere and illuminated by the normal incident light, thereby excluding the reflected light. Transmitted light is completely collected by the integrating sphere. The light scattered by the ZnO nanoparticles is characterized by subtracting direct transmission from total transmission, which is defined as the transmitted light within an angle of 2.5 degrees off-normal. In this measurement, an aperture mounted at the opening of the sphere is used to confine the angle of directly transmitted light [20]. The light scattering effect of ZnO nanoparticle film is illustrated by the haze ratio (H), which is defined as

$$H = \frac{(T - T_d)}{T}, \quad (1)$$

where T_d is the direct transmittance and T is the total transmittance.

Figure 3(a) shows absorption spectra of glass substrates coated with ZnO nanoparticles. Absorption peaks occur in ultraviolet (UV) regime (350 nm to 400 nm), which is attributed to the surface plasmonic resonance of ZnO nanoparticles. This absorption feature is also related to the coating densities. The lowest coverage densities result in the lowest light absorption at short wavelengths. In the visible and near-infrared (NIR) regime, nanoparticle films show gradually increased absorbance with the wavelength, which correspond to the free carrier absorption in ZnO. Figure 3(b) shows the reflectance of GaAs solar cells coated with varying ZnO nanoparticle film densities. Similarly, we observe that increased ZnO coating densities result in lower reflectance, which is expected from the improved index matching in high density film. At shorter wavelengths, particularly from 350 nm to 400 nm, the suppression of reflection is mainly caused by increased ZnO self-absorption. It is also important to note that the reflection properties are relatively flat across the visible and NIR light spectrum. We attribute the broadband decreases in reflection to improved index grading and reduced reflection at the top interface. This enhancement indicates that the ZnO nanoparticle films can reduce reflection losses and improve device absorption with minimal parasitic absorption from the nanocrystals.

In addition to improved antireflection characteristics, the ZnO coatings also effectively scatter the incident light due to the inherent submicron surface texturing in the porous nanoparticle films. When comparing the haze factors of the three films (Figure 4), all three samples show outstanding scattering properties with haze exceeding 0.4 over the whole spectrum. Increasing the coating coverage

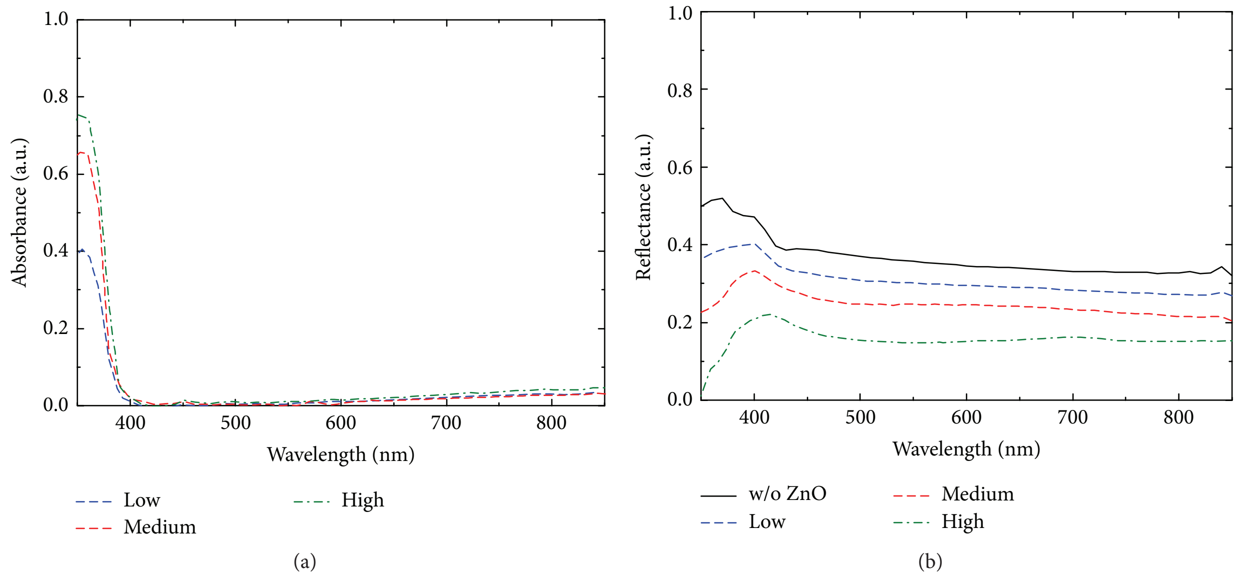

Figure 3: (a) Optical absorption of ZnO nanoparticle film on glass substrates; (b) reflectance of GaAs solar cells with ZnO nanoparticle film and control cell.

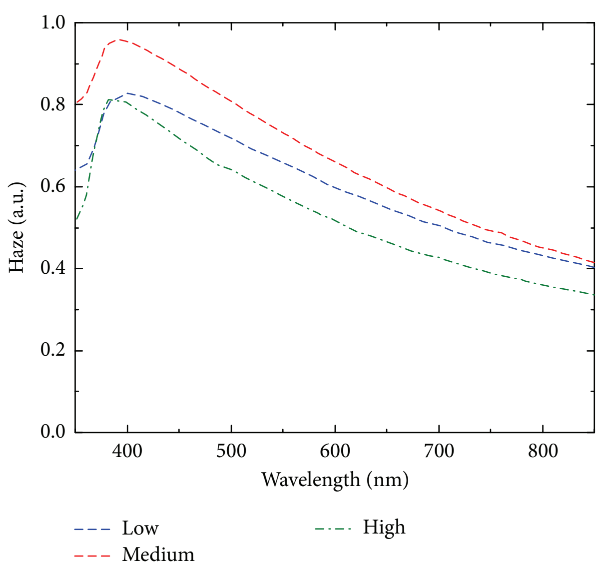

Figure 4: Haze of ZnO nanoparticle film coated on glass substrates with different density.

fraction from lower particle densities to medium particle densities enhances the haze factor across the visible spectrum, which indicates that stronger light scattering effects can be achieved by increasing the nanoparticle density. The highest density coating, however, is weakest in scattering power because it is more uniform than the other two coatings. This result suggests that the local nonuniformities in the moderate density coatings could be beneficial for light scattering purposes. Interestingly, the maximum haze factors of all three samples are at the wavelength of around 400 nm, which is close to the size of the nanoparticles. This indicates that the light scattering is mainly due to the plasmonic resonance of nanoparticles. This result motivates further work to evaluate the size dependence of light scattering effects in ZnO nanoparticle coatings.

The photovoltaic properties of the GaAs solar cells are given in Figures 5(a) and 5(b). The ZnO nanoparticle films had demonstrated great enhancements on the photocurrent of the cells. To understand these enhancements, the EQEs of solar cells with nanoparticle coatings were measured and normalized to that of the reference cell without coating (Figure 5(a)). The normalized EQEs show two different trends in the UV regime (350 nm to 400 nm) and visible to NIR regime (400 nm to 850 nm). In the UV regime, all the nanoparticle-coated cells have decreased photocurrent responses due to parasitic self-absorption of the ZnO coating. The trend is consistent with the absorption measurements in Figure 3(a). Specifically, the denser ZnO coating results in larger photocurrent losses. In visible and NIR regime, the medium density coating yields the highest photocurrent enhancement, which is consistent with the haze measurements of the nanoparticle films. The scattered transmitted light tends to be absorbed close to the depletion region of p-n junction, thus enabling easier separation of photogenerated electron-hole pairs and easier collection as part of the measured photocurrent. After all, the best photocurrent enhancement was induced by the ZnO nanoparticle thin film as medium density coating. Figure 5(b) shows the J-V curves of the GaAs solar cell measured before and after ZnO nanoparticle coating. The nanostructured ZnO coating demonstrated great influence on the photocurrent of the cells. The best performance was induced by the medium density nanoparticles coating with a short circuit current (J_{sc}) of 17.91 mA/cm^2, an open-circuit voltage (V_{oc}) of 0.94 V, and an efficiency of 10.73%. This cell with optimized ZnO

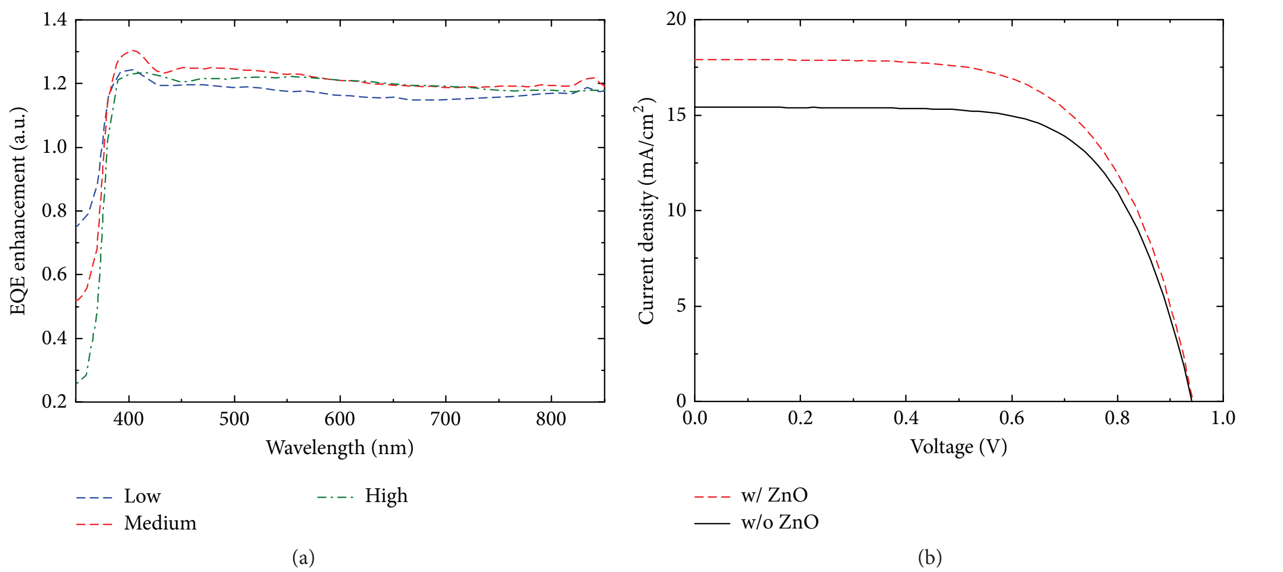

Figure 5: (a) EQE enhancement of the nanoparticle-coated GaAs solar cells compared with the reference cell without coating. (b) *J-V* characterization of GaAs solar cell before (black) and after (red) optimized ZnO nanoparticle coating (medium density) under AM 1.5 G at room temperature.

nanoparticle coating (medium density) demonstrated a 16.3% improvement in J_{sc} and a 10.3% increase in efficiency compared with the same cell without ZnO coating.

4. Conclusions

In conclusion, we have shown that low-temperature, solution-processed ZnO nanoparticle films deposited onto GaAs solar cells provide enhanced antireflection properties, increased active layer absorption, and improved device characteristics. The highly scattering ZnO nanoparticle coating results in a broadband enhancement of the GaAs solar cell's EQE. The optimized coating improves the photocurrent by 16% and cell efficiency by 10% relative to control devices. This result clearly shows the potential for solution-processed light scattering layers to enhance light absorption in other photovoltaic materials. We anticipate that this method of achieving submicron surface texturing can be extended to a variety of other nanoparticle scattering agents with different physical properties (index of refraction and band gap) and potentially useful for improving light emission profiles in light-emitting diodes [21].

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors gratefully acknowledge the technical assistance of P.-S. Wong and M. Riaziat of OEpic Semiconductors Inc. for MOCVD growth, the use of the processing facilities in the Stanford Nanofabrication Facility, and McGehee M.D. for use of optical characterization equipment.

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