RESEARCH ARTICLE

Microstructured ZnO coatings combined with antireflective layers for light management in photovoltaic devices

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ABSTRACT

We describe microstructured ZnO coatings that improve photovoltaic (PV) device performance through their antireflective properties and their tendency to scatter incoming light at large angles. In many PV devices, reflection from the transparent conductive top contact significantly degrades performance. Traditional quarter-wave antireflective (AR) coatings reduce surface reflection but perform optimally for only a narrow spectral range and incident illumination angle. Furthermore, in some types of devices, absorption far from the junction increases the rate of recombination, and light management strategies are required to remedy this. The randomly patterned, microstructured ZnO coatings described in this paper, formed via a simple wet etch process, serve as both an AR layer with superior performance to that of a thin film AR coating alone as well as a large angle forward scatterer. We model formation of the coatings and evaluate their AR properties. When combined with a traditional quarter-wave MgF2 coating, these microstructured ZnO coatings increase short circuit currents of example Cu(In,Ga)Se2 (CIGS) devices by over 20% in comparison to those of uncoated devices at normal incidence. A similar improvement is observed for illumination angles of up to 60°. While demonstrated here for CIGS, these structures may prove useful for other PV technologies as well. Published 2016. This article is a U.S. Government work and is in the public domain in the USA.

KEYWORDS

antireflective coatings; light management; CIGS

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1. INTRODUCTION

Many photovoltaic (PV) devices employ a transparent conductive oxide film, most commonly tin-doped indium oxide (ITO) or aluminum-doped zinc oxide (AZO), as a top electrode. Both ITO and AZO have refractive indices of around two at a wavelength of 500 nm, resulting in Fresnel reflections with a magnitude of ~11% at normal incidence. In uncoated devices, therefore, a significant fraction of the incoming light is lost to reflection.

In high-performance devices, a thin film dielectric AR coating is applied to reduce surface reflection. In CIGS devices, for example, a quarter-wave MgF2 AR coating results in an improvement in performance at normal incidence associated with an increase in the short circuit current density, $J_{SC}$, of approximately 5% [1]. While single-layer AR coatings may exhibit excellent performance for a particular wavelength at a fixed incident angle, performance typically suffers away from the design wavelength and incident angle [2]. For applications without tracking and in environments with significant scattered light, performance at non-normal incidence is important. A coating that improves performance across both wide spectral and angular ranges is therefore desirable. One approach is to use multilayer AR coatings that offer better performance than a single quarter-wave AR
film [3,4]. While such coatings can potentially extend AR performance across a wider spectral and angular range, the difficulty of obtaining large-area uniformity as well as the cost of such coatings make them impractical for manufacturing.

In addition to surface reflection, another consideration for light management relates to the position at which light is absorbed within the device. It has been well established that sub-wavelength structures can dramatically enhance light trapping in PV devices [5]. Light management considerations differ depending on the PV material. In amorphous silicon (a-Si), for example, which has an absorption coefficient ranging from approximately \(10^2 \text{ to } 4 \times 10^6 \text{ cm}^{-1}\) for above band gap light [6], low absorption necessitates increasing path length within the absorber. Depositing the absorber on a textured back contact has been used to accomplish this for a variety of thin film materials with low absorption. For instance, V-shaped grooves [7,8] and pyramidal structures [9,10] have been shown to significantly improve light trapping in thin film absorbers. Randomly textured back contacts have also been shown to be effective for this application [11]. Front surface structures such as microlens arrays [12] have also been used to increase path length and absorption in thin film PV.

In contrast, the high absorption coefficient of CIGS, approximately \(10^3 \text{ cm}^{-1}\) for above band gap light, means that nearly all of the useable solar radiation is absorbed in a thickness of \(1 \mu m\) [13]. Practical considerations, such as avoiding the formation of shunt paths usually dictate that CIGS absorber thicknesses are closer to \(2 \mu m\). As a result, large angle scattering is not necessary in order to increase path length. It is, however, potentially useful for a different reason; the minority carrier diffusion length in high quality CIGS devices has been measured to be as short as \(0.3 \mu m\) [14], which is small compared with the \(\sim 1 \mu m\) absorption depth. This discrepancy is especially significant for long wavelength light which is absorbed closer to the back contact. If photons can be absorbed, on average, closer to the p-n junction near the front surface, we can increase charge collection, therefore increasing efficiency as a result of reduced recombination. Because the majority of useable solar radiation is absorbed before it reaches the back surface, scattering should ideally occur at the front surface of the device.

Given the need for broadband AR performance and scattering in CIGS PV devices, a front side structure that can accomplish both is desirable. Such an antireflective surface structure (ARSs), whether its structure is ordered or random, can achieve high AR performance across a broad spectral and angular range [15]. These sub-wavelength structures create a gradual transition in effective index between the sample and air. As Lord Rayleigh hypothesized, the reflectance at an abrupt transition between two media with differing indices of refraction can be reduced via a gradual index transition between the two materials [16]. Ordered ARSSs, often referred to as “moth eye” structures because they are inspired by the naturally occurring morphology found on the surface of a moth’s eye, typically require lithographic patterning or imprinting to produce. Randomly patterned arrays of peaks can achieve similar AR performance to ordered ARSSs yet may be fabricated by random etch processes.

At the short wavelength edge of their transparency region, ARSS structures typically exhibit a scattering edge; for wavelengths smaller than this edge, the non-scattered transmittance and specular reflectance are low and the forward scattered field is large [17]. By designing a coating to operate in this regime, we can ensure both good AR properties and a significant amount of scattered light.

A variety of ARSS structures for PV devices have been proposed. Examples in the literature include lithographically patterned ARSS on silicon [18] and CIGS [19] and arrays of depressions patterned directly into silicon [20]. Textured ZnO top contacts have been described previously as well. Various methods of achieving such texturing have been proposed. These include growth of ZnO nanostructures via an aqueous process on silicon [21] and on CIGS devices [22]; direct sputter deposition of textured AZO [23]; etching of ZnO structures on silicon [24]; and nanomoulding [25]. A theoretical treatment of the effects of increased surface roughness due to etching has been described by Campa [26].

In order to best match the refractive index of the existing device surface, it is especially advantageous to create a structured layer of the same material present at the device/air interface, that is, the top contact material. To do so, we take advantage of the ability of HCl to texture the surface of ZnO during wet etching [11]. In this work, we fabricate ARSSs with features up to \(~500 \text{ nm}\) deep on glass substrates and on CIGS devices and characterize their optical properties. This method is distinct from previous work on textured ZnO for thin film PV in that, rather than requiring photolithographic processing, controlled growth of nanostructures, or stamping, it relies only on a fast wet etch and is thus easily scalable to a large device size. Further, we demonstrate enhanced same-device performance with and without ZnO ARSSs at normal and non-normal incidence. The contributions of both the AR and large-angle scattering properties of the coatings and their impact on device performance are evaluated. We show that it is important to consider both the AR properties of the ARSS structures and the improvement resulting from large-angle scattering.

### 2. EXPERIMENT

Soda lime glass (SLG) substrates with a sputtered Mo bottom contact were coated with \(2 \mu m\) of CIGS via either single-step evaporation or quaternary sputtering [27]. Approximately \(50 \text{ nm}\) of CdS was then deposited by chemical bath deposition. For the top contact, \(60 \text{ nm}\) of ZnO was deposited by reactive sputtering with flowing \(O_2\) in order to increase resistivity and transparency, and this was followed by a conductive \(200 \text{ nm}\) thick layer of AZO deposited by sputtering. Both ZnO and AZO were deposited at a calibrated substrate temperature of \(200^\circ \text{C}\). Ni/Al grids, composed of \(60 \text{ nm}\) of Ni followed by \(400 \text{ nm}\) of...
aluminum, were deposited via electron beam evaporation. Samples were scribed by hand to obtain individual cells, each with an area of approximately 0.5 cm². PV devices were then characterized prior to ARSS coating.

Next, with the contact pads for the grids protected with photoresist or polyimide tape, ZnO ARSS structures were formed on top of the devices. At least 500 nm of ZnO was sputtered on top of the complete CIGS device, again with flowing O₂ and at a substrate temperature of 200 °C. This layer was chemically etched in a 0.5% HCl solution at room temperature for 0–30 s while agitating the solution slightly, resulting in a textured ZnO surface. On some samples, a 100 nm thick layer of MgF₂ (a quarter wave at a wavelength of approximately 550 nm) was deposited via electron beam evaporation. The photoresist or tape protecting the contact pads was removed, and devices were characterized. A schematic diagram of the device cross section is shown in Figure 1(a). Figure 1(b) shows a schematic cross section of the device in which the various fields are identified. Eᵢ represents the incident field, Eᵣ,spec the reflected specular field, Eᵣ,diff the reflected diffuse field, Eₜ,reg the regularly transmitted (non-scattered) field, and Eₜ,diff the transmitted diffuse field.

In order to perform spectral characterization of the ZnO ARSSs, some samples were fabricated on top of CIGS stacks without grids or contact pads. For transmittance measurements, other ARSS samples were fabricated on top of SLG substrates that were previously coated only with the AZO/ZnO top contact, not an entire CIGS device. Spectral characterization was performed on a PerkinElmer Lambda 950 spectrometer. An integrating sphere in the instrument permitted the separate measurements of scattered and non-scattered transmitted and reflected light. During near-normal incidence measurements, the sample is placed at the rear of the sphere and held at a fixed angle of 8°. A plug on the opposite side of the sphere may be removed, allowing specularly reflected light to exit, permitting the separate measurement of the diffuse reflectance. For non-normal incidence measurements, the sample is placed within the sphere and held in a rotating mount. In this case, the total reflectance, including both the specular and diffuse components, is measured. Feature height on ARSS samples without the CIGS layer was measured using an atomic force microscope (AFM) in tapping mode. Samples for cross sectional scanning electron microscope (SEM) analysis were obtained by mechanically breaking samples.

Light J-V curves were obtained using a xenon-arc solar simulator under collimated one sun (100 mW/cm²) AM 1.5G illumination calibrated using a Si reference cell. The setup was configured to allow for angular measurements of up to 60° from normal incidence. Dark current measurements were obtained with a Keithley 2400 SourcMeter in a darkened enclosure in order to evaluate diode properties of the devices. External quantum efficiency (EQE) measurements were performed on a laboratory-built system using a quartz tungsten halogen source lamp coupled through an Oriel Cornerstone 260 monochromator. A white light bias of ~1/3 sun intensity was applied to the sample during EQE measurements. Illumination angle was varied up to 60° from normal incidence. During these measurements, the illuminated spot was kept significantly smaller than the device area so that it did not intersect the metallic collection grid, even in the case of non-normal illumination.

3. RESULTS AND DISCUSSION

Samples consisting of a thick ZnO layer deposited on an AZO/ZnO electrode were etched for times varying from 0–30 s in 0.5% HCl. SEM images showing cross sections and images taken at 20° from normal incidence as well as AFM images for various etch times are shown in Figure 2. Prior to etching, the as-deposited ZnO exhibits a small amount of surface roughness, and the roughness increases with etch time. Features are subwavelength and consistent across the etched surface. For the 20 and 30 s etches, some features extend through the entire ZnO film but not the underlying electrode, indicating that the etch rate of AZO is smaller than that of ZnO. This is fortuitous in that the slower etch rate of the AZO prevents the HCl etch from damaging other layers of the device. Note that
for samples left in the etch bath for significantly longer, for times approximately twice the etch times used here, the AZO and underlying ZnO begin to be removed.

The depth of ARSS features may be understood from a simple model, illustrated in Figure 3. In this model, the film has an initial thickness of $D$ and an initial roughness of $d_0$. The features form as a result of grains in the ZnO film etching at different rates, presumably as a result of different grain orientations. The slowest-etching grains are etched at a rate of $\nu_{\text{min}}$ while the fastest-etching are etched at a rate of $\nu_{\text{max}}$. During Phase 1 of the etch, both sets of grains are etched at their respective rates. During Phase 2, the material comprising the fastest etching grains is depleted and only the slower-etching material remains. The feature depth, $d$, increases during Phase 1 and begins to decrease during Phase 2.

Therefore, the feature depth may be represented by the expression in Eq. (1), as

$$d = d_0 + (\nu_{\text{max}} - \nu_{\text{min}}) t_{t \leq t'}$$
$$= d_0 + \nu_{\text{max}} t' - \nu_{\text{min}} t_{t' < (D/\nu_{\text{max}})}$$
$$= 0\mid (D/\nu_{\text{max}}) \leq t$$

where $t$ is the elapsed etch time and $t'$ is the etch time at which maximum feature depth is achieved. It is thus expected that a larger difference between $\nu_{\text{max}}$ and $\nu_{\text{min}}$ will lead to greater feature depth. It is also evident that if $\nu_{\text{min}}$ is too large compared with $D$, the entire ZnO film will be etched in a short time, leaving no remaining surface structure.

Measurements of feature depth as a function of etch time were obtained by performing AFM measurements on $2 \times 2 \mu\text{m}$ regions on each sample. The feature height is taken to be the average peak-to-valley height from three different locations on each sample. Feature height initially increases with etch time, peaks at approximately 350 nm for an etch time of 25 s, and decreases with further etching. This data is shown in Figure 4 where the red line shows a fit obtained by Eq. (1), where the least-squares method is used to determine the etch parameters. The error bars represent the standard deviation from three measurements at different locations on each sample. We obtain values of $d_0 = 109$ nm, $\nu_{\text{max}} = 14.4$ nm/s, and $\nu_{\text{min}} = 5.1$ nm/s, indicating that the fastest-etched grains are etched at a rate of approximately three times that of the slowest-etched grains. The capability to measure the precise etch rates will allow for better comparison and further optimization of these ARSS coatings in the future.

The optical properties of the ZnO ARSS structures on quaternary sputtered CIGS samples were characterized. For the purposes of this study, it is important to understand how much of the incident light is scattered into the diffuse
The transmitted haze parameter, $H_T$, may be defined in terms of the irradiance of the transmitted diffuse light, $I_{T,diff}$, and the regularly transmitted light, $I_{T,reg}$ as

$$H_T = \frac{I_{T,diff}}{I_{T,reg} + I_{T,diff}}. \quad (2)$$

Figure 5(a) shows $H_T$ plotted for various etch times. $H_T$ was also measured for untreated SLG and for SLG coated only with an AZO/ZnO top contact and in both cases was found to be near zero and is not shown on the plot. For samples with a thick ZnO layer, even the un-etched sample produced some scattered light due to its inherent surface roughness, while samples etched for 10 s or more produced significant scatter. For instance, $H_T$ for samples etched for 20 or 30 s was greater than 0.2 at a wavelength of 500 nm, and greater than 0.4 at a wavelength of 400 nm.

An analogous haze factor for reflected light, $H_R$, may be defined as

$$H_R = \frac{I_{R,diff}}{I_{R,reg} + I_{R,diff}}. \quad (3)$$

$H_R$ is plotted for the same samples in Figure 5(b). There are some fringes in the data due to interference in the multi-layer structure. Also shown in the figure for comparison are $H_R$ for a standard CIGS device and for a CIGS device with a ZnO ARSS coating with an etch time of 15 s. We are primarily interested in $H_T$ because we are interested in light that enters the device. However, examining $H_R$ is still instructive; the scatter for the coated CIGS devices is significantly higher than those of the coated AZO/ZnO electrodes alone. This increase is due to the fact that the CIGS surface itself is highly scattering as evident from the figure. This data implies that $H_T$ for a CIGS device is also considerably higher than that measured for a coated electrode.

The reflectance properties of the ZnO ARSS structures on quaternary sputtered CIGS samples were characterized. Figure 6 shows the reflectance measured at near-normal incidence, an angle of 8°, for several samples—an untreated sample with a AZO/ZnO top contact and those with a MgF$_2$ AR coating, a ZnO ARSS coating with an etch time of 15 s, and a ZnO ARSS coating with an etch time of 15 s followed by a MgF$_2$ AR coating. The sum of the specular and diffuse reflected light is shown. Photographs of an untreated CIGS sample, a CIGS sample with an AR coating, and another with both ARSS and an AR coating are also shown. Between 300 and 1000 nm, the reflectance of the untreated sample varies from approximately 5–12%, with an average of 6.9% in this range. Both the AR coating and the ARSS coating, significantly decrease the reflectance, resulting in average reflectances in the 300–100 nm range of 2.7% and 3.0%, respectively. The combination...
of the ARSS and an AR coating results in by far the lowest reflectance, with an average value of 1.4% in this range. The performance at non-normal incidence is similarly improved. Data for incident angles of 30° and 60° is shown in the supplemental information in Figure S1 and Figure S2, respectively.

Light J-V measurements were obtained for CIGS devices treated with both a combinations ARSS layer (20 s etch time) and an AR film for angles ranging from 0–60°. Figure 7 shows light J-V results as a function of illumination angle for the same device both before and after coating with the ARSS and AR layers. Note that ideally, we would compare the treated film to one with an AR coating alone. However, in this case, it is critical to measure same-device efficiency before and after treatment to avoid errors caused by sample-to-sample variation that could be larger than the measured effects. This precludes a direct comparison to devices coated with only AR coatings because these coatings are difficult to remove without damaging the underlying devices. However, the effects of standard AR coatings on CIGS devices are well-understood, typically resulting in an increase in $J_{SC}$ of approximately 5% [1]. Figure 7 shows (a) $J_{SC}$, (b) open circuit voltage, $V_{OC}$, (c) fill factor (FF), and (d) efficiency. The increase in $J_{SC}$ is partially counteracted by a decrease in $V_{OC}$ of 2–3% and in FF of 5–12%. The degradation in $V_{OC}$ and FF is likely caused by the extra anneal that occurred during ZnO deposition. It is well-established that interdiffusion at the CIGS/CdS junction during annealing can degrade device performance. In order to check whether the anneal did indeed damage
the junction dark current measurements were made before and after ARSS deposition. It was found that the diode ratio was reduced from $10^3$ to $10^2$ after ARSS deposition, consistent with slight damage to the junction. The data is shown in the supplemental information in Figure S3. It is expected that further optimization of ZnO deposition parameters, for example, reducing deposition temperature or decreasing deposition time for the thick ZnO layer, will reduce this effect. When combined, the increase in $J_{SC}$ together with the decreases in $V_{OC}$ and FF resulted in an increase in efficiency from 10.4% to 11.0% at normal incidence and from 4.47% to 4.96% at a 60° illumination angle—relative increases of 5.8% and 11.0%, respectively.

External quantum efficiency measurements were also performed on device samples for different incident angles to evaluate the spectral response of the coatings. In order to eliminate the possibility of edge effects, the EQE was re-measured with several different aperture sizes. It was determined that the change in EQE was within the uncertainty in the measurement, indicating that spot size and edge effects are not a significant source of error for these devices. Data for samples before and after ZnO ARSS and AR coating, measured at both 0° and 60° incident angles, is shown in Figure 8. Each plot represents the average for three samples with identical processing. The shaded band for each plot indicates the standard deviation. For both normal incidence and 60° incidence, EQE is significantly improved across most of the spectral range. The inset in Figure 8 shows the ratio of EQE after to that before ARSS and AR fabrication. The enhancement in EQE is as high as 17% for normal incidence and 12% for 60° incidence. The EQE for normal incidence is slightly degraded at wavelengths less than 500 nm, likely because scattering increases the path length and thus the absorption within the CdS.

Note that the peak in enhancement for normal incidence lies near 680 nm—the same location as the peak in reflectance for the untreated sample evident in Figure 6. For 60° incident angle, this peak is blue-shifted to approximately 620 nm, also matching the peak in reflectance which can be seen in the supplemental information in Figure S2. A similar enhancement is evident corresponding to a peak near 500 nm. These observations support the idea that part of the improvement in performance results from a significant decrease in reflectance. The total increase in current, however, is greater than the elimination of reflectance can account for. At 680 nm and near-normal incidence, for instance, the enhancement in EQE is approximately 17%, while the enhancement in transmitted light, $E_T$, given by

$$E_T = \frac{1 - (R_{\text{reg}} + R_{\text{diff}})}{1 - (R_{\text{reg}}' + R_{\text{diff}}')},$$

where the primed variables denote values after coating, is only 9.1%. The scattering properties of the coatings are necessary to fully explain the observed increase in $J_{SC}$.

The improvement in device performance, therefore, can be attributed to both a decrease in reflectance and the scattering of incident light. This conclusion is at odds with the conclusion reached by Campa et al. in [26] based on their simulations—that the increase in efficiency from a textured ZnO coating would result primarily from its AR properties as opposed to its scattering properties. It is possible that the scattering profile resulting from the structures tested here differs from that used in the previous work, and this difference merits further study.

4. CONCLUSION

The effects of ZnO ARSSs in combination with MgF$_2$ AR coatings, formed via a wet etch in dilute HCl, on CIGS devices were evaluated. The spectral properties of films and the performance of PV devices with and without these coatings, at normal and non-normal incidence, were characterized. The combined coatings provide a significant reduction in reflectance, greater than that from either the ARSS coating or AR coating alone. They also scatter a significant portion of the incident light. For devices, the most pronounced effect of the coatings is an increase in $J_{SC}$ of approximately 20%. This effect results in an increase in efficiency from 10.4% to 11.0% at normal incidence and from 4.47% to 4.96% at a 60° illumination angle—relative increases of 5.8% and 11.0%, respectively. EQE measurements indicate that it is necessary to consider both the AR properties of the ARSS structures and large-angle scattering in order to account for the 20% increase in $J_{SC}$. Further processing refinements are expected to result in improved performance, maintaining the large gains in $J_{SC}$ while...
Mediating the losses in $V_{OC}$ and FF. In addition to their use described here for CIGS-based devices, these coatings may prove useful in other thin film PV applications as well due to their combination of low and spectrally flat surface reflection and desirable optical scatter.

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