Solar Energy Materials & Solar Cells 136 (2015) 17–24

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Achieving graded refractive index by use of ZnO nanorods/TiO_2 layer to enhance omnidirectional photovoltaic performances of InGaP/GaAs/Ge triple-junction solar cells

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ARTICLE INFO

Article history:
Received 2 December 2014
Accepted 13 December 2014
Available online 13 January 2015

Keywords:
Antireflection coating
Zinc oxide (ZnO)
Nanorod
Triple-junction solar cell

ABSTRACT

In this study, we theoretically and experimentally demonstrate high performance of antireflection (AR) coating composed of the ZnO nanorods (NRs) and TiO_2 layers applied on InGaP/GaAs/Ge triple-junction solar cells. The high performance of this AR coating is due to the realization of a smooth gradient profile of refractive index fabricated by only two physical layers. First, due to the inherent inhomogeneous-nanoporous geometry along the surface normal, the ZnO NRs are reasonable to be considered as discrete multiple optical layers with low scattering loss, leading to the index smoothly increasing from air ambient toward down to the solar cells. Second, to compensate the gap of index between ZnO and solar cells, an additional TiO_2 layer with index in between is hence necessary to insert under ZnO NRs, significantly further reducing the Fresnel reflection loss of the entire device. The ZnO NRs/ TiO_2 layer shows a low wavelength-averaged (solar spectrum weighted) reflectance of 6.00% (4.78%) over a wide spectral range of λ=380–1800 nm, and exhibits a hydrophobic surface with a water contact angle of 128.2°. At device level, we compared the photovoltaic performance of solar cells with and without AR coating, the short-circuit density (J_{SC}) is enhanced by 31.8% and 23.8% for solar cells integrated with the ZnO NRs/TiO_2 layer and conventional SiO_2/TiO_2 double-layer AR (DLAR) coating, respectively. Under a very large incident angle of solar illumination (θ=80°), the ZnO NRs/TiO_2 layer remains static with J_{SC} enhancement of 35.2%, whereas the J_{SC} enhancement of conventional DLAR coating drops down to 9.4%. In addition, the ZnO NRs/TiO_2 layer barely affects the open-circuit voltage and fill factor of the solar device. Therefore, the proposed ZnO NRs/TiO_2 layer with a smoother graded refractive index change is highly promising for the AR coating applications for the next-generation solar cells.

1. Introduction

III–V compound tandem solar cells, taking advantage of the bandgap tunability by elemental multi-junction compositions to achieve a better utilization of the solar spectrum, have been demonstrated showing high power conversion efficiency over 40% [1,2]. However, to take the advantage of fully utilizing solar spectrum of multiple junctions, a much improved deign of anti-reflection (AR) coatings, which successfully reduces the Fresnel reflection between the air and the semiconductor materials over broad solar spectrum becomes extremely important. In general, the quarter-wavelength (λ/4) and the double-layer (DL) AR coatings have been widely used to reduce the Fresnel reflection of solar cells. However, these conventional AR coatings only can achieve low reflectance (by the destructively optical interference) at certain spectral range and limited angles-of-incidence (AOIs). For incident wavelengths and AOIs out of these designed ranges, the measured reflectance is considerably increased, hindering the fully optical absorption of solar energy for realization of the high power conversion efficiency of the solar device. Recently, an oblique-angle electron deposition methodology was reported to create a four-layer AR coating, which exhibits an excellent refractive index matching between the ambient air and

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http://dx.doi.org/10.1016/j.solmat.2014.12.019
0927-0248/

semiconductor materials, and demonstrates a broadband and omnidirectional AR performance [3,4]. Yet the fabrication cost of multiple-discrete-layer and deposition uniformity [5] could be considerable issues for manufacturing solar cells on large-scale chip sizes. On the other hand, inspired by the nature creatures of wild world, various biomimetic nanostructures (such as vertical nanorods) with random or periodic alignments were widely reported to suppress the optical reflectance of incident sunlight [6–15]. Since the featured size of such nanostructures is generally smaller than the optical wavelengths of solar light, the incident light cannot resolve the individual nanostructure of the ensemble. Thus the ensembles of these nanostructures provide a continuous gradient of refractive index from their tops to the semiconductor materials, dramatically alleviating the Fresnel reflection loss of the devices. In principle, to minimize the self-absorption of incident solar light, such nanostructured AR coatings have to be fabricated by the wide band-gap (optical transparent) materials. Zinc oxides (ZnO) nanorods (NRs) have been popularly used as AR coatings in the photovoltaic applications [16–20], because ZnO is well recognized as the wide band-gap material (E_g=3.37 eV) [21,22], and the ZnO NRs are easy to grow or synthesize via various approaches such as chemical vapor deposition, [23] electrochemical deposition [24] and a low-temperature hydrothermal method [25]. Although the ZnO NRs have been demonstrated exhibiting a broadband AR characteristic [16], their application on the III–V triple-junction solar cell, which requires low reflectance of AR coating for a wide range of solar spectrum (λ=300−1800 nm), was seldom reported [18,19]. Meanwhile, the mismatch of refractive index between the ZnO NRs and the semiconductor materials underneath is rarely discussed, inevitably degrading the AR performance of the ZnO NRs. Consequently, the enhancement of ultimate power conversion efficiency of solar devices integrated with the ZnO NRs is barely comparable to that of the traditional DLAR coating.

In this study, we report the design and fabrication of a smoothly graded refractive index ZnO NRs/TiO_2 layer to enhance the photovoltaic performances of the InGaP/GaAs/Ge triple-junction solar cell. From the spectroscopic ellipsometry measurement, it was found that the effective refractive index of ZnO NRs grown by the low-temperature hydrothermal method can be perceived as discrete multiple optical layers. Moreover, by adding an insertion of TiO_2 layer with appropriated refractive index and optical thickness, the Fresnel reflection loss, occurring at the interface between the ZnO seed layer and the AlInP window layer of the triple-junction solar cell, is able to further reduce. The low wavelength-averaged diffuse reflectance of ~0.74% validates the ZnO NRs with small feature sizes induces a low scattering loss under the solar illumination, and the ZnO NRs can therefore be conceived as discrete multiple optical planar layers. In order to demonstrate the potential of the ZnO NRs/TiO_2 layer for the photovoltaic applications, a theoretically and experimentally comparative study of AR performances for the InGaP/GaAs/Ge triple-junction solar cells integrated with the conventional DLAR coating, the ZnO NRs, and the ZnO NRs/TiO_2 layer was performed. Both of theoretical and experimental results are in good agreement and show that the ZnO NRs/TiO_2 layer is highly promising to achieve good AR performances over broadband spectrum and omnidirectional incidence, and is readily applicable to other kinds of solar cells.

2. Experiment

Fig. 1(a) shows a schematic configuration of the proposed solar device. The three lattice-matched subcells of the triple-junction solar cell from top to bottom in order are the InGaP, GaAs, and Ge subcells grown on the p-type Ge substrate by low-pressure metal-organic chemical vapor deposition (MOCVD) for absorbing the incident light in short, intermediate, and long wavelength regimes of solar spectrum, respectively. Trimethylaluminum (TMAl), trimethygallium (TMGa) and trimethyindium (TMIn) were used as group-III precursors, and arsine (AsH_3) and phosphine (PH_3) were used for the group-V reaction agents. Silane (SiH4) and diethylzinc (DEZn) were used as the n-type and p-type dopant sources, respectively. The InGaP and GaAs subcells are connected to each other by a p-AlGaAs ($p=4\times10^{20}$ cm^{-3}, 20 nm)/n-InGaP ($n=1\times10^{20}$ cm^{-3}, 20 nm) tunnel junction, whereas the GaAs middle subcell is connected to the Ge bottom subcell by a p-GaAs ($p=6\times10^{19}$ cm^{-3}, 30 nm)/n-GaAs ($n=1\times10^{20}$ cm^{-3}, 30 nm) tunnel junction. Finally, Ge/Au and Ti/Pt/Au were deposited by e-beam evaporator for front (n-type) and backside (p-type) contacts, respectively. After that, the intermediate layer of 55-nm-thick TiO_2 was deposited on the top of $Al_{0.5}In_{0.5}P$ window layer by RF magnetron sputtering with a deposited rate of 2 nm/s. The solar device was then subjected to the hydrothermal process for the growth of ZnO NRs. Initially, a 50 nm ZnO seed layer was sputtered onto the TiO_2 intermediate layer followed by suspending the substrate in an aqueous solution of 400 mL zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot6H_2O$, 0.025 mol/L) and 100 mL hexamethylenetetramine ($(CH_2)_6\cdot N_4$, 0.025 mol/L) at 90 °C for 60 min in an oven. The randomly aligned ZnO NR arrays were then grown and the process was finished by dipping the substrate into deionized water to remove the residual salts and dried by N_2 gas flow. For comparison, the solar cell deposited with the traditional DLAR coating, composed of TiO_2 (55 nm) and SiO_2 (92 nm) layers in sequence on top of the cell, was fabricated by the RF sputtering. The solar device with ZnO NRs of hydrothermal growth but without an insertion of TiO_2 intermediate layer was also fabricated to evaluate its influence on the refractive index profile along the impinging direction of solar light. The chip size of the individual cell is designed to be 1 cm × 1 cm. The device's performance was characterized by an Oriel Sol3A solar simulator. The current density vs. voltage (J–V) characteristic was obtained by a Keithley 2400 multi-meter in four-wire sensing mode to eliminate the resistance from the contribution of probes and the contact resistances. Fig. 1(b) shows the cross-sectional scanning-electron microscopy (SEM) image of the completed AR structure of ZnO NRs/TiO_2 layer grown on the InGaP/GaAs/Ge triple-junction solar cell. Accordingly, the ZnO NRs are randomly aligned, and a distinct boundary between TiO_2 intermediate and ZnO seed layers is clearly identified. The thickness of ZnO NRs layer is determined to be 300 ± 10 nm. The variation of the layer thickness is mainly attributed to ZnO NRs with different growth rates along different crystallographic directions [26]. Fig. 1(c) shows the top-view SEM image of ZnO NRs. The corresponding X-ray diffraction (XRD) scan of ZnO NRs is also inserted in the figure. The ZnO NRs exhibit the typical crystallography of hexagonal structure with a feature size (i.e. diameter of the nanorods) of 40 ± 10 nm, which is much smaller than the wavelengths of visible light. The XRD scan dominated by the (002) peak at 2θ=34.11° indicates that the ZnO NRs are preferentially grown along c-axis parallel to the surface normal direction. A relative weak peak at 2θ=36.09° is attributable to the (101) planes to terminate and form the truncated hexagonal pyramid at the tips of ZnO NRs [27]. Analysis on the measured XRD scan agrees well with the SEM observation on the structural morphology of ZnO NRs. Most importantly, some ZnO NRs grow in the off-surface-normal directions, and thus we can expect that the gradient of effective refractive index of the ZnO NRs film is varied along the surface normal direction, which can be simulated as discrete multiple optical layers that provides AR functionality.

3. Results and discussion

To quantitatively examine the optical characteristics of all of the different AR structures, we first measured the refractive index (n) and extinction coefficient (κ) of our fabricated samples. Fig. 2 plots