RSC Advances


Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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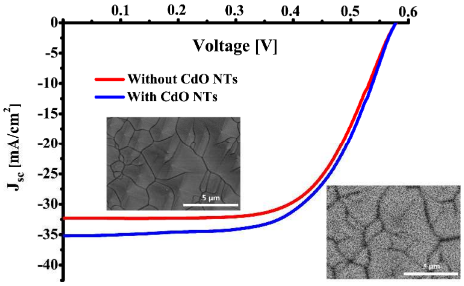

A composited CdO nanotips/mono-Si solar cell achieved 14% improvement in power conversion efficiency, compared to its none CdO nanotips counterpart.

Efficiency enhancement of mono-Si solar cell with CdO nanotips antireflection and down-conversion layer

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Keywords: CdO, nanotips, antireflection, down-conversion

Abstract

We propose a composited mono-Si solar cell that integrated with CdO nanotips (NTs). The substrate employed was mono-Si with Si_3N_4 antireflection (AR) layer already deposited on the topside. CdO NTs was synthesized on the surface of Si_3N_4 AR layer by chemical bath deposition (CBD). The CdO NTs composited solar cell achieved 14% enhancement in power conversion efficiency (PCE) compared to the none CdO NTs counterpart. With the investment of J-V curve, reflectance and photoluminescence, we demonstrate that the remarkable antireflection, down-conversion of CdO NTs and the slightly enhanced fill factor played significant roles in the PCE improvement. As the results, we believe that the PCE of Si solar cell remains a certain potential to be improved as materials with proper antireflection, down-conversion and conductivity on the topside.

1. Introduction

Even though Si based solar cell takes the main stream of the photovoltaic market, optical, recombination, series resistance, and thermal or quantum losses are the four insurmountable barriers that constrained the theoretical efficiency of Si solar cell to 31%.[1, 2]

Since bare Si substrate is a poor absorber, different kinds of surface texturing processes have been explored and carried out in large scale fabrication to provide superior light scattering. Apart from pyramid texturing, one-dimensional (1-D) Si nanostructure has been extensively studied in recent years.[3-5] However, the high recombination velocity restricts the PCE improvement regardless of its remarkable light trapping character.[6, 7] Absorption enhancement can also be achieved by using antireflection (AR) layer. With refractive index between air and crystalline Si, optical losses at the air-Si interface can be reduced.[8] For instance, the deposition of Si_3N_4 (n=2) AR layer has been widely carried out in commercial scale fabrication and reduced the reflectance of mono-Si solar cell from 35% to less than 10%.[9, 10] In recent years, other materials such as SiO_2 (n=1.5), TiO_2 (n=2.5), and Al_2O_3 (n=1.85) have also been reported as remarkable AR properties. However, the utility of ultraviolet (UV) region of the solar spectrum is quite low.[11-13]

According to Shockley–Queisser theory, thermal or quantum losses make up about half of the solar energy, in part due to the loss of photon energy that exceeds the Si band gap, especially in UV region.[1] Owing to the extension of operating spectral range toward ultraviolet and emit lower energy photons, down-conversion materials have the potential to improve the utility of the whole solar spectrum.[14] In the last decades, down-conversional rare earth-doped luminescent materials have been widely investigated,[15-17] but the integration of these materials on Si based solar cell is still far from practical. In addition to that, nano-materials with proper light trapping effects have also been applied to photo-voltaic devices and come into a spotlight.[18, 19] Nanocrystals such as ZnS and ZnSe have been introduced into bare Si substrate and was demonstrated with promising photoelectric properties. However, the fill factors of the devices were somehow decreased, which was mainly due to the hampered conduction phenomenon.[20, 21] As referenced with former studies, Cadmium oxide is quite a suitable material for solar cell applications due to its high electrical conductivity and optical transmittance in the visible region of the solar spectrum.[22, 23] With its N-type conductivity, proper refractive index and certain down-conversion performance,[24, 25] CdO is promising to further improve the PCE of Si based solar cell.

In the present study, we explore a strategy to improve the PCE of mono-Si solar cell by combining 1-D CdO NTs on the topside. Quite different from some former studies, which were mainly focus on the bare Si substrates, Si_3N_4 AR layer capped mono-Si solar cell with p-n active layer is employed as the reference specimen. 1-D CdO NTs was synthesized on the surface of Si_3N_4 to form a composited solar cell. The short-circuit current density (J_{sc}) of the CdO NTs composited solar cell enhanced remarkably and contribute greatly to the 14% PCE improvement. Based on the optical and spectra response characterizations, we demonstrate that CdO NTs on the top of the device not only act as AR layer for light trapping of incident photons, but also with the down-conversion property to make full use of the whole solar spectrum.

2. Experimental

The mono-Si solar cells employed in this work were purchased from Changzhou Yijing Optoelectronics Technology Co., Ltd., with Si_3N_4 antireflection layer already deposited by plasma enhanced chemical vapor deposition (PECVD). Frontside Ag electrode was printed and dried at 120 °C and went through rapid thermal annealing at 750 °C for 2s. Chemical vapor deposition was employed to evaporate Al as backside electrode, thus formed the reference specimen. The reference specimens were washed by double distilled water and cut into 2×2 cm. CdO NTs were synthesized by chemical bath deposition using cadmium chloride (0.02 M) as Cd^{2+} ion source. An excess ammonium hydroxide (30%) solution was added for the complex formation till to get clear solution. Two solar cells were attached together by waterproof to keep the backsides from the alkaline solution. As the result, 1-D CdO NTs will only grow on the Si_3N_4 surface. With 30-120 min deposit, whitish $Cd(OH)_2$ film was formed on both of the topsides, then heat treated in oxygen air-tight container at 623 K for 120 min. Finally, the whitish film was changed into brown, confirming the formation of CdO.

The in-situ synthesized CdO NTs were characterized by field emission scanning electron microscope (FESEM, Hitachi, Japan, operated at 15 kV). X-ray diffraction (XRD) patterns was recorded by D/MAX-2000 (Rigaku, Japan), using Cu-Kα radiation at a scan rate (2θ) of 4° min^{-1}. To study the electrical characterization, the J-V characteristics of the solar cells were investigated under the illumination of AM1.5G (100 mW/cm^2) and provided with Zennium electrochemical workstation (model: Xpot). The light intensity was calibrated with a silicon standard solar cell. The reflection spectra of the specimens were measured using CARY 500 Scan UV/VIS/NIR spectrophotometer with an integrating sphere (Labsphere) in a wavelength range of 300-1200 nm. Photoluminescence spectroscopy was carried out with a VARIAN Cary-Eclipse 500 fluorescence spectrophotometer equipped with a 60 W Xenon lamp as the excitation source. The sample was excited by a light beam at 510 nm. EQE measurement was carried out with CrownTech CCTH-150W in a wavelength range of 300-1100 nm.

3. Results and discussion

The one-dimensional CdO NTs were in-situ grown on the surface of Si_3N_4 AR layer. The CBD growth involved two steps as 0-D nucleation and 1-D NTs growth. Initially, the Cd^{2+} provided by cadmium chloride and the OH^- released from ammonium hydroxide underwent an rapid formation of the $Cd(OH)_2$ particles. With the increase of growth time, more and more adatoms were driven towards the nucleation points and formed 1-D $Cd(OH)_2$ NTs. Afterwards, the film was converted into CdO by 623 K annealing and the H_2O vapors are released during the heat treatment, the chemical reaction is shown as follow:

$$\mathrm{Cd(OH)_2} \xrightarrow{623\mathrm{K}} \left[\left(\mathrm{Cd}^{2+}+\mathrm{O}^{2-}\right)+\left(2\,\mathrm{H}^{+}+\mathrm{O}^{2-}\right)\right]^{\mathrm{Solid}} \longrightarrow \left[\mathrm{CdO}\right]^{\mathrm{Solid}}+\left[\mathrm{H_2O}\right]^{\mathrm{Gas}}$$

The surface morphologies are shown in Fig. 1(a) and (b) with two different magnifications. The 1-D nanostructure is composited together with the pyramid textured surface, this will theoretically provide much stronger light scattering to the incident photons than the barely pyramid textured surface. The high magnification cross-sectional image shows the 60 min deposited CdO nanotips are about 436 nm in length. The XRD pattern of CdO nanotips is shown in Fig. 1(c). The peak at 2θ values of 33.0°, 38.2°, 55.2° can be indexed to the (111), (200), (220) planes of CdO, indicating that the pure phase of CdO was obtained and no other impurity peaks were detected.

To obtain the optimum length of CdO NTs, we studied the impact of deposition time on electric performance of the CdO NTs composited solar cells. Specimens with different deposition time were investigated under the illumination of AM1.5G. The photovoltaic performance indicated by J_{sc} and FF as a function of deposition time are estimated and plotted in Fig. 3(a). With 1-D CdO NTs on the topside, J_{sc} enhanced dramatically. J_{sc} value of the reference solar cell is 32.81 mA/cm^2. The value of 34.71 mA/cm^2, 36.76 mA/cm^2, 36.05 mA/cm^2 and 36.29 mA/cm^2 are corresponding to 30 min, 60 min, 90 min, 120 min deposition of CdO NTs respectively. The mechanism of the enhancement will be discussed later. It also worth noticing that FF also increased to a certain extent, from the original 63.5% to 64.6%, 64.7%, 65.0% and 64.6% respectively. A slightly decrease of FF occurred in some former studies,[20, 21] which was regarded as the deterioration of the conduction of electrons in the N-type region toward the finger Ag electrode, resulting in a bigger series resistance. In our study, on one hand, the CdO NTs were grown on top of both AR layer and the finger Ag electrode, it didn't cause any handicap on the conduction of electrons from N-type Si to the Ag electrode, thus no extra series resistance produced. On the other, the remarkable conductivity of CdO has enabled it to be recognized as transparent conductive oxide, which will probably provide a better electron conduction phenomenon and contribute to the slightly increased FF.[22]

The PCE of the four integrated solar cells were improved from 12.1% to 13.0%, 13.8%, 13.4% and 13.7% respectively. Considering the experimental period, 60 min deposition with PCE of 13.8% should be the best measured composited solar cell and the optimum CdO NTs length is around 440 nm. Fig. 3(b) shows the J–V characteristics of the reference mono-Si solar cell and the best measured CdO NTs composited solar cell. Since the additional layer of CdO NTs in principle do not change the Fermi energy distribution in the Si p-n junction, it will not generate any extra built-in electric field. As the result, the open-circuit voltage (V_{oc}) stayed unchanged, which is shown in the two curves. Benefited from the enhanced J_{sc} and V_{oc}, the PCE of the CdO NTs composited solar cell achieved 14% increasement comparing to the none CdO NTs counterpart. According to the standard commercial mono-Si solar cell, which has reach to an average efficiency of around 16% in industrial fabrication, the PCE value in this study is much lower. This is probably due to the extra series resistance resulting from the interface of solder and wires during the J-V measurement. Since all the specimens were fabricated and measured in the same conditions, this deviation can be neglected.

In order to understand the underlying mechanism for the further enhanced PCE, we firstly investigated the antireflection property of the CdO NTs. Reflectance spectra of the reference Si solar cell and its integration with CdO NTs is shown in Fig. 4(a). It is well worth noticing that the reflectance reduction from 300 nm to 450 nm is remarkably improved. This is significant for the PCE enhancement. Rather than just targeting on the CdO NTs absorption edge, CdO NTs reduced the reflectance spectral ranging from 300 nm to 1000 nm. The reduction of reflectance probably lies in two aspects. Firstly, this is due to the additional light scattering provided from the one dimensional structure. Secondly, the refractive index of 1-D CdO NTs was measured to be in the range of 1.85 - 1.91 by spectroscopic ellipsometer, just between air and Si_3N_4 (n=2.0). The CdO NTs layer provided a gradual and continuous change of the effective refractive index from air to mono-Si (n=3.42) and acted as a graded index layer above the hierarchical structure. The Fresnel reflection over the broad spectral width can be effectively eliminated.[26] Consequently, CdO NTs provides extra antireflection effect over the Si_3N_4 AR layer.

With 2 hours annealing treatment in 350℃ oxygen air-tight container, which generally facilitated decrease in inhomogeneities and dislocations, the as-deposited amorphous $Cd(OH)_2$ thin film was converted into crystallizes CdO NTs. The indirect band gap is calculated to be 2.43 eV, which is quite in accordance with former studies.[27] The absorption and photoluminescence (PL) spectra are shown in Fig. 4(b) to understand the down-conversion character of CdO NTs layer. The absorption peak of CdO NTs is observed at 512 nm, as shown in Fig. 4(b). The fluorescence spectrum shows a peak at 695 nm with a 173 nm Stokes shift. In principle, the photon energy higher than Si band gap cools quickly to the band edges by sequential emission of phonons. The utility of the UV region is extremely low in the Si solar cell since one photon just excites single electron-hole pair in bulk c-Si. As the absorption depth is given by the inverse of the absorption coefficient, high-energy photons have relatively larger absorption coefficient and tend to be absorbed in shallower region.[9] UV lights tend to produce electron-hole pairs near the surface of the device where mass of surface defects concentrated in. The generated carriers would disappear easily through recombination. However, with the CdO NTs down-conversion layer, the emitted lower energy photons were absorbed in the deeper region, leading to more photons absorbed in the depletion region. Photo generated electron-hole pairs will be separated immediately with the help of a build-in-electric field, thus contribute to the J_{sc} enhancement.

The spectral response of the external quantum efficiency (EQE) was measured to understand the down-conversional property of CdO NTs in more details. As shown in Figure 5(a), The composited solar cell shows an enhanced EQE spectral response in the whole range from 300 nm to 1100 nm. According to Figure 5(b), the EQE enhancement curve peaks at 510 nm, which is quite accordance with the absorption peak of CdO NTs and implies that down-conversion took place in the device. To characterize the contribution of down-conversion effect, we calculated the effective current as the CdO NTs down-conversion layer on the top of the reference solar cell. The carries can be observed directly from J_{sc} of a solar cell.[28, 29] J_{sc} without and with CdO NTs are calculated as follows:

$$J_{sc} = \frac{e}{hc}\times\int_{300nm}^{1100nm}\lambda\times EQE(\lambda)\times I_{AM1.5G}(\lambda)d\lambda \tag{1}$$

$$\begin{aligned} J_{sc,CdO} = \frac{e}{hc}\times(&\int_{300nm}^{512nm}[1-A(\lambda)]\times\lambda\times EQE(\lambda)\times I_{AM1.5G}(\lambda)d\lambda + \\ &\int_{300nm}^{512nm}A(\lambda)\times\lambda\times EQE(\lambda)\times QY\times I_{AM1.5G}(\lambda)d\lambda + \\ &\int_{512nm}^{1100nm}\lambda\times EQE(\lambda)\times I_{AM1.5G}(\lambda)d\lambda) \end{aligned} \tag{2}$$

Where λ, c, h, e represent for the wavelength, the speed of light, Plank's constant and electric charge respectively. $A(\lambda)$ is the absorption of ultraviolet light of the CdO nanotips. $I_{AM1.5G}(\lambda)$ is the intensity of the AM1.5G solar spectrum and QY is the quantum yield of the NTs, the average QY is about 55%. The above equations tell that the portion of down-conversion photon make up to 13% of the J_{sc} enhancement.

To further characterize the possible candidates, we also studied the integration of ZnO nanotips. With high transmissivity and a wide band gap, 1-D ZnO NTs is also promising to be applied to our reference solar cell. However, the result was not as remarkable as CdO nanotips capped on the device. This is probably because the refractive index of ZnO is quite close or even bigger than Si_3N_4, thus didn't form a gradual refractive index change from air to c-Si and didn't provides extra antireflection effect. But according to CdO NTs, the more suitable refractive index provided better antireflection property over its counterpart. Comparing with the 14% PCE enhancement in lab scale, achieving such extent in commercial scale is quite difficult. On one hand, the quality of 1-D CdO NTs growth and the backsides protection will be relatively inferior. On the other, encapsulation materials are applied to the surface of the solar cell to provide certain protection. EVA, which is commonly used, with a refractive index also between air and Si_3N_4, the gradient change of refractive index from air to Si will be somehow changed. Thus, the reflectance improvement might be shrinked. But with the 1-D light trapping structure and remarkable down-conversion property, we believe that the advantages of CdO NTs definitly outwieght the drawbacks and the CdO NTs composited structure have a potential to be introduced for the PCE enhancement of Si solar cell in large scale fabrication.

4. Conclusion

In summary, a 4 cm^2 mono-Si solar cell achieved 14% PCE enhancement as composited with 1-D CdO NTs on the topside. The three main mechanisms of improvements including: (1) Extra antireflection effect of CdO NTs over Si_3N_4 AR layer. (2) Photon down-conversion of CdO NTs in the short wavelength region. (3) Slightly improvement of FF. We believe that the integration of 1-D nanomaterials with suitable refractive index, down-conversion and conductivity is promising to provide a new method for the PCE improvement of the Si based solar cell nowadays.

Acknowledgment

This work is supported by the Shanghai Science & Technology Committee (12521102501, 11ZR1426500), the first-class discipline construction planning in Shanghai University, PCSIRT (RT1269), the Program of Shanghai Normal University (DZL124) and the Key Laboratory of Resource Chemistry of Ministry of Education of China.

Notes and references：

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Figures

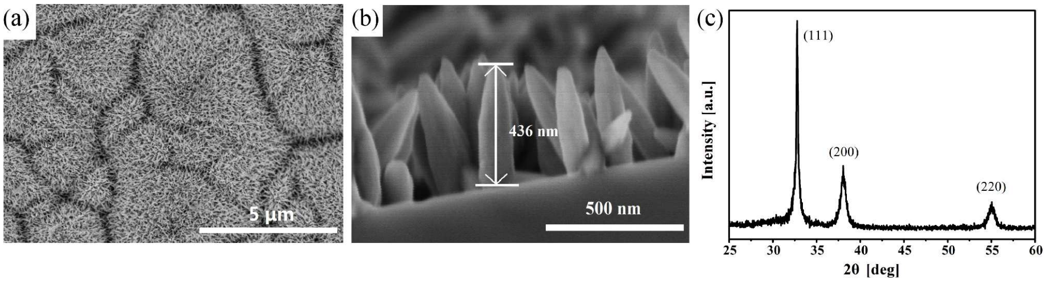

Fig. 1 (a), (b) Surface and cross sectional FESEM images of CdO NTs (the deposition time is 60 min). (c) X-Ray diffraction pattern of CdO NTs.

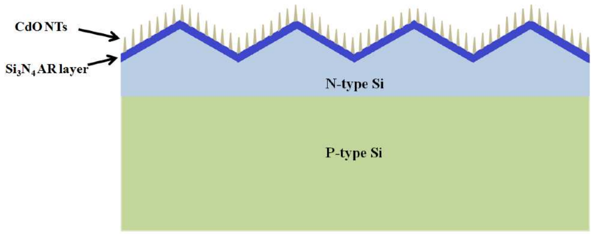

Fig. 2 Cross-sectional schematic illustration of CdO NTs composited mono-Si solar cell (with a pyramid textured surface). In general, Si_3N_4 AR layer was deposited by means of PECVD on top of the N-type mono-Si. With P-type on the botton, a semi-manufactured commercial mono c-Si solar cell is formed. In this device, 1-D CdO NTs synthesized only on the surface of Si_3N_4 AR layer.

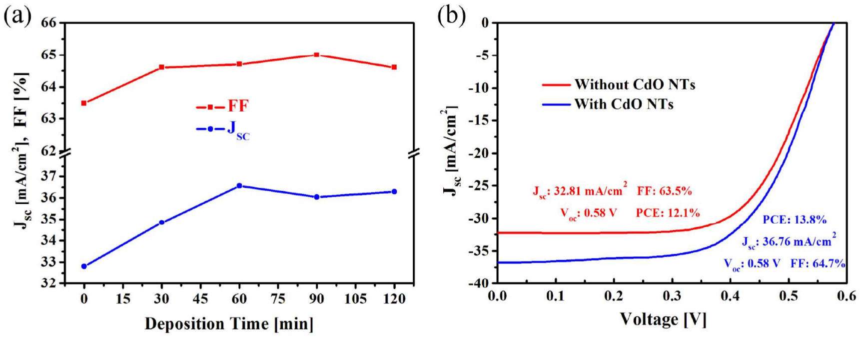

Fig. 3 (a) The effect of CdO NTs deposition time on the electrical performance of CdO NTs composited solar cell (FF & Jsc). (b) J–V characteristics of 2×2 cm reference solar cell and the best measured CdO NTs composited solar cell.

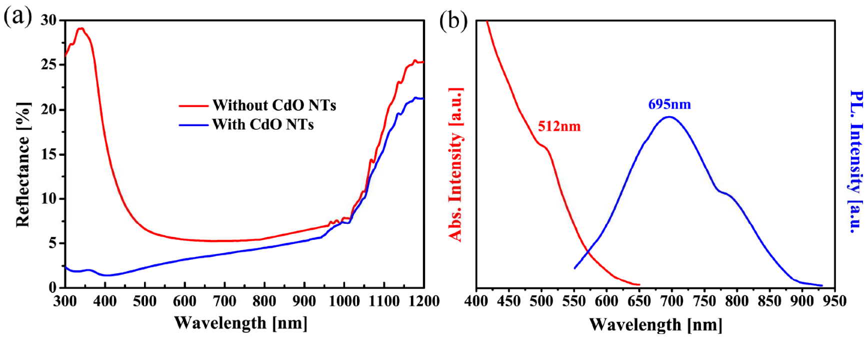

Fig. 4 (a) Reflectance spectra of reference solar cell and the CdO NTs composited solar cell. (b) Absorption and photoluminescence spectra of CdO NTs.

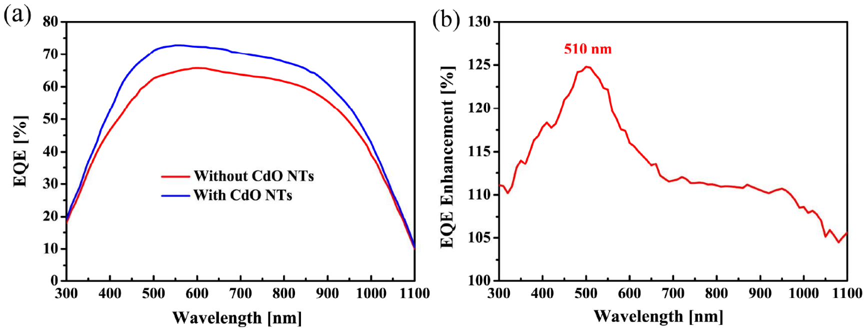

Fig. 5 (a) EQE spectra of the 2×2 cm reference solar cell and its integration with CdO NTs. (b) EQE enhancement of the CdO NTs composited solar cell.