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Xuegong Yu, Dong Wang, Dong Lei, Genhu Li and Deren Yang*  

Abstract
An efficient antireflection coating is critical for the improvement of silicon solar cell performance via increased light coupling. Here, we have grown well-aligned ZnO nanowisker (NW) arrays on Czochralski silicon solar cells by a seeding-growth two-step process. It is found that the ZnO NWs have a great effect on the macroscopic antireflection effect and, therefore, improves the solar cell performance. The ZnO NW array-coated solar cells display a broadband reflection suppression from 500 to 1,100 nm, and the minimum reflectance smaller than 3% can easily be achieved. By optimizing the time of ZnO NW growth, it has been confirmed that an increase of 3% relatively in the solar cell efficiency can be obtained. These results are quite interesting for the application of ZnO nanostructure in the fabrication of high-efficiency silicon solar cells.

Keywords: Silicon, Solar cell, Antireflection, ZnO nanowhisker, Efficiency.

Background
Antireflection (AR) technology plays an important role in the fabrication of high-efficiency solar cells by increasing light coupling into the active region of devices. Generally, a relatively low-light reflectivity can be obtained for crystalline silicon solar cells by combining surface texturization with Si,Ny-thin-film deposition [1,2]. However, in order to further reduce the light reflectivity for the improvement of solar cell efficiency, a variety of nanostructures with size comparable to the wavelength of most of the utilized solar spectrum have been proposed, such as photonic crystals [3], porous structures [4], plasmonics [5-8], etc. The subwavelength structures can be nanowires [9], nanocones [10,11], frustum nanorods [12], biomimetic nanostructures [13-16], dielectric nanoparticles [17,18] etc. All these nanostructures should be based on the wide bandgap materials which, themselves, cannot absorb sunlight.

The ZnO material has a wide bandgap, which has been popularly used in the fields of photocatalysis [19] and optoelectronic nanodevices [20]. For photovoltaic application, the ZnO nanostructures as antireflective layers could be fabricated by various approaches like pulsed laser deposition [21], chemical vapor deposition [22], vapor–liquid-solid growth [23], hydrothermal method [24], and electrochemical deposition technique [25]. Among them, a seeding and growth two-step process in zinc salt and amide mixed solutions seems quite acceptable for photovoltaics due to its low cost and good potential for scale-up [26,27]. Experiments have shown that ZnO nanorod arrays can exhibit better antireflective properties than other oxide compounds [28]. A weighted global reflectance of 6.6% has been achieved in the broadband range from 400 to 1,200 nm [29]. However, most work on ZnO nanorod arrays as antireflective layers is performed on the naked silicon wafer by now [29,30]. The application of ZnO nanostructures in the practical silicon solar cells is seldom reported.

In this work, we have grown ZnO nanowiskers (NWs) with different lengths by the seeding and growth two-step process, and meanwhile have integrated the ZnO NW technique into the fabrication of Czochralski (CZ) silicon solar cells based on the current standard celling technology. The density and the length of ZnO NWs have been optimized for the improvement of solar cell performances by controlling the time of growth. The result shows that the efficiency of CZ silicon solar cell can be improved by a value of 3% relatively using the ZnO NWs as the AR layer in practice.

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Methods

The starting samples are p-type CZ silicon solar cells fabricated by a standard process including surface texturization, phosphorus diffusion, Si$_x$N$_y$ film deposition, screen printing, and metallization. The size of solar cells is 4 × 4 cm$^2$. The seed layer of ZnO was first deposited on the front surface of solar cells by a magnetron sputtering system. The deposition temperature is 150°C, and the seed layer thickness is about 10 nm. After protecting the parts without the ZnO seed film with waterproof tapes, the samples were immersed in the solution of zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) and (CH$_2$)$_6$N$_4$ mixture for 30 to 60 min for the growth of ZnO NW. The ZnO NW growth temperature is 90°C.

For characterization, a scanning electron microscope (SEM; Hitachi S-4800, Hitachi, Ltd., Chiyoda, Tokyo, Japan) was used to observe the ZnO NWs on the solar cells. The reflection spectra of the samples were measured by a UV–vis spectrophotometer (Hitachi U-4100) in the wavelength range of 300 to 1,100 nm. The external quantum efficiencies (EQEs) of the final solar cells were obtained from the spectral responses. The current–voltage characteristics of the cells under the dark and illumination circumstances were measured. For illumination, one sun (100 mW/cm$^2$) with AM 1.5 Global spectrum was used.

Results and discussion

Figure 1 shows the SEM micrographs of a silicon solar cell with the ZnO NWs after a two-step growth process. It can be seen that the ZnO NWs are uniformly fabricated on the surface of silicon solar cell. Generally, the fabrication of ZnO NWs based on aqueous solution consists of nucleation [31] and growth. The main chemical reactions through the whole process can be described as follows:

\[ \text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + 2\text{NO}_3^- + 6\text{H}_2\text{O} \quad (1) \]

\[ (\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 6\text{HCHO} + 4\text{NH}_3 \quad (2) \]

\[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \quad (3) \]

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad (4) \]

\[ \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (5) \]

Zn$^{2+}$ is provided by Zn(NO$_3$)$_2$·6H$_2$O through its ionization in the solution. The decomposition of hexamethylenetetramine produces ammonia that can supply the OH$^-$ needed for the ZnO NW formation reaction and acts as a pH buffer to regulate the pH value of the solution [32]. The pH value of the solution should be 6 or 7 for the whole reaction process. During the process, the ZnO nanocrystals existing in the seed layer serve as the nucleation centers where the growth of ZnO NWs takes place. Due to its growth habit, c-axis is the most preferred growth orientation [33], which leads to the formation of ZnO NWs.

Figure 2 shows the SEM micrographs of ZnO NWs on the solar cells after growing at different times. Figure 2a, d shows the plan view and its cross-sections of ZnO NWs after growing 30 min, respectively. One can see that the tapered ZnO NWs with the length of approximately 100 nm are obtained on the pyramid-like textured surface of solar cell via this method. With the growth time increasing, the density of ZnO NWs increases (see Figure 2b,c,e,f). Meanwhile, the length of ZnO NWs becomes larger, e.g., approximately 200 nm after 45 min and approximately 300 nm after 60 min.

Figure 3 shows the reflectance spectra of the solar cells without or with the ZnO NW coating. It can be seen that, compared with the solar cell without ZnO NW coating (reference), all the solar cells with ZnO NW coating exhibit lower reflectance than in the whole wavelength range. The reflectivity of ZnO NW-coated solar cells decreases with an increase of ZnO NW growth time. The solar cell with ZnO NWs grown for 45 min has the lowest reflectivity. However, when the
ZnO NW growth time reaches to 60 min, the reflectivity of coated solar cell becomes higher in the wavelength range of 500 to 1,100 nm. Since the density and length of ZnO NWs increase with an increase of growing time, it is suspected that the ZnO NWs grown for 60 min could have formed something like ‘film’ on the CZ silicon solar cell. Therefore, the effect of trapping light based on the ZnO nanostructure becomes weaker. This finally results in a higher reflection of ZnO NW grown for 60 min. Nevertheless, these results clarify that the ZnO NW-coated solar cells have better antireflection effect than the reference without ZnO NW coating. The decrease of reflectivity in the long wavelength range mainly results from the effect of ZnO NW trapping light by the multiple scattering of the incident light. Meanwhile, their gradually and continuously changing refractive index profile from the air to the substrate is also beneficial for its antireflection property. The drastic decrease of reflectance in the low-wavelength range should be mainly attributed to the absorption of light by ZnO NWs, themselves, which hardly makes any contribution to the improvement of the solar cell performance. After a prolonged growing time, e.g., 60 min, the light absorption of long ZnO NWs becomes even stronger, and therefore, their contribution to the solar cell efficiency is further smaller.

Figure 4 shows the EQEs of the solar cells with ZnO NWs grown for different times. It can be seen that the solar cells with ZnO NWs grown for 30 and 45 min generally have higher EQEs than the referenced one in the whole spectral region. The result is quite consistent with the reflectance data above. It signifies that ZnO NWs on CZ silicon solar cells can effectively improve the response of light spectrum. For the solar cell with ZnO NWs grown for 60 min, the EQEs in the short-wavelength range are smaller than that of the referenced due to the stronger light absorption of long ZnO NWs. Table 1 lists the detailed parameters of the solar cells coated with ZnO NWs grown for different times. It can be seen that even though the open-circuit voltages for all the solar cells keep the same, the short-circuit current density of the solar cells coated by ZnO NWs are higher. This finally results in that the efficiency of the solar cells coated by ZnO NWs grown for 30 and 45 min are improved by a value of 0.1% and 3.0%, respectively, in
comparison with the referenced cell. Figure 5 examples the current density as a function of bias voltage for the solar cells with ZnO NWs grown for 45 min. It reveals that ZnO NW-coated solar cells have higher short-circuit current density than the referenced one, while the open-circuit voltages keep constant. The improvement of short-circuit current density is obviously a result of ZnO NWs suppressing the light reflectivity. In the case of ZnO NWs grown for 60 min, the fill factor of the cell has a low fill factor and, therefore, a low efficiency. This deterioration of the cell performance should be related to the long-time immersion of the solar cell in the 90°C aqueous solution during the ZnO NW growth process.

Conclusions
In summary, around 100 to 300 nm ZnO NWs are grown on the surface of Czochralski Si solar cells based on a low cost aqueous solution method. ZnO NWs grown for different times, such as 30, 45, and 60 min, can reduce the reflectivity of the solar cells effectively ($R < 3\%$) in a large spectral region and improve the external quantum efficiency in the corresponding range. Furthermore, ZnO NWs with 45-min growth time can improve the efficiency of the solar cells by 3%, corresponding to their increment of short-circuit current density and fill factor. Finally, long-time immersion of solar cells in aqueous solution during the ZnO NW growth process can deteriorate the solar cell performance drastically.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
XY carried out the fabrication of solar cells. DW and GL carried out the growth of ZnO NWs. DL carried out the measurement of solar cell performances. DY carried out the design of experiments. All authors read and approved the final manuscript.

Authors’ information
Deren Yang and Xuegong Yu are both professors and doctorate degree holders in the State Key Laboratory of Silicon Materials, Department of Materials Science & Engineering, Zhejiang University. Dong Wang, Dong Lei, and Genhu Li are masters degree holder candidates of the same university.

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**Table 1 Performance parameters of c-Si solar cells with and without ZnO NWs**

| ZnO growth time (min) | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF (%) | η (%) | Δη (%) |
|-----------------------|----------------------|-------------|--------|-------|--------|
| 0                     | 35.66                | 0.61        | 75.76  | 16.30 | 0      |
| 30                    | 36.00                | 0.61        | 74.84  | 16.31 | 0.1    |
| 45                    | 36.75                | 0.61        | 74.90  | 16.79 | 3.0    |
| 60                    | 36.54                | 0.61        | 71.24  | 15.83 | −2.9   |

FF fill factor, $J_{SC}$ short-circuit current density, $V_{OC}$, open-circuit voltage.
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