

Full paper

ZnO nanowire based CIGS solar cell and its efficiency enhancement by the piezo-phototronic effect



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ABSTRACT

Cu(In,Ga)Se₂(CIGS)-based heterostructures have been thought to be one of the most prospective thin film solar cells. However, considering cost competitiveness, researchers are still seeking for new methods to improve the power conversion efficiency (PCE). In this work, the ZnO nanowires are first introduced into the CIGS-based solar cells to substitute the ZnO film for well developing the piezoelectric effect. Interestingly, the solar cells exhibit very good photovoltaic performances with PCE of 9.83% for rigid device and 5.43% for flexible device, the PCE of which is even larger than that of the corresponding ZnO film CIGS devices. Moreover, by exerting piezo-phototronic effect of the ZnO nanowires, the PCE of the rigid device is modulated from 9.83% to 11.40% with vertical pressure increasing from 0 to 2 MPa, and the PCE of the flexible device improves from 4.82% to 5.96% with external strain changing from a 0.74% tensile strain to a -0.74% compressive strain. This study demonstrates that introducing ZnO nanowires as well as the associated piezo-phototronic effect provides an ideal approach for improving the performances of CIGS-based solar cells.

1. Introduction

With the advent of energy crises and global warming, solar cells, which can be used for the direct conversion of sunlight into electricity as a renewable and green energy, are gaining intensive interest and considered to be an alternative to other sources of energy [1–3]. Recently, it is even expected that thin-film solar cell technologies would be capable of competing with traditional energy manufacture methods due to their lower producing costs [4]. Among them, one of the most prospective thin film photovoltaics is the high power conversion efficiency (PCE) and low price solar cell based on polycrystalline chalcopyrite copper indium gallium selenide (CIGS). As it is demonstrated that CIGS exhibits many excellent properties, e. g., large optical absorption coefficients ($\geq 10^5 \text{ cm}^{-1}$), [5] direct bandgap semiconductor with tunable band energy (1.04–1.67 eV) [6,7], long-term thermal, environmental and electrical stabilities [8,9]. Moreover, the CIGS heterojunction has been leading in PCE simultaneously gaining widespread

reputation as a mature solar cell technology [10], and can be manufactured on both rigid and flexible substrates [11]. Although PCE exceeding 22% for CIGS solar cells has been achieved by several groups [12,13], considering the important role of PCE in cost competitiveness, researchers are still trying best to seek for different methods to improve it, such as adjusting bandgap [14], modifying interface quality [15], changing buffer layer or transparent conducting layer [16], introducing K or Na ions [17], and even combining CIGS with perovskite or two dimensional material structures [13,18,19]. However, a new emerging technology based on piezoelectric effect, which can be used to tune/control the separation and transport behaviors of photo-excited carriers by operating a three-way coupling among photonic excitation, charge transport, and piezoelectricity in the piezoelectric semiconductors [20–24], has not been used in the CIGS-based solar cells. More importantly, the recent studies have already verified the great potential of piezo-phototronic effect on photovoltaic devices by effectively tuning the generation, separation, recombination, and transport of carriers at

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the interface of the heterojunction via strain-induced piezo-potential in piezoelectric semiconductors [25–32]. For CIGS solar cell, the currently acknowledged structure is a multilayer heterostructure composed of substrate/Mo/CIGS/CdS/ZnO/ITO, it seems that the piezo-phototronic effect of both CdS and ZnO layers may be utilized to modulate the photovoltaic performances. However, the CdS layer is an amorphous or polycrystalline buffer layer usually grown by chemical bath deposition (CBD) with a very thin thickness [10–12], thus it is not suitable to tune the PCE of CIGS-based solar cells by the piezoelectric effect of the CdS layer. While, different from it, the ZnO layer is a window layer with slightly modulated thickness, and can be grown by numerous different methods. Therefore, the ZnO film could be substituted with the ZnO nanowires for well developing the piezoelectric effect, which may also provide another novel insight to modulate the PCE of CIGS-based solar cells. Besides, the strong piezo-phototronic effect of the ZnO nanowires is capable of improving the photovoltaic properties by applying external pressure or strain on the device.

In this work, the CIGS heterostructure solar cells with four different ZnO nanowire heights (350 nm, 850 nm, 1400 nm, and 2000 nm) were grown on the rigid glass substrates. It is found that the 850 nm ZnO nanowire CIGS solar cell exhibits the best PCE of 9.83%, which is even better than that of ZnO film CIGS solar cell. More importantly, by utilizing piezo-phototronic effect of the ZnO nanowire, the PCE improves quickly from 9.83% to 11.40% with adding an external pressure from 0 to 2 MPa. Besides, we also successfully prepared the ZnO nanowire CIGS structure on the flexible steel substrates with PCE of 5.43%, and the PCE can also be modulated from 4.82% to 5.96% with external strain changing from a 0.74% tensile strain to a $-0.74%$ compressive strain. These results can be attributed to the lowered and heightened junction barrier between the CdS and ZnO layers induced by the negative and positive polarization charges generated at the $-c$ end of the (0002)-oriented ZnO nanowires under external pressure or strain. Our study demonstrates that adding ZnO nanowires as well as applying the piezo-phototronic effect may bring an insight for enhancing the photovoltaic performances of CIGS-based multilayer heterostructures via strain-modulated piezoelectric effect of the ZnO nanowire.

2. Experimental sections

The thickness of glass and steel substrate was about 2 mm and 25 μm , respectively. During the flexible CIGS solar cell preparation, the steel plate was fixed on the glass substrate to make sure its flatness and similar preparing condition as that of glass substrate. Firstly, a 800 nm-thick metallic Mo back contact was prepared on the substrates; then an about 2 μm -thick CIGS layer was deposited on it by co-evaporating Cu, In, Ga, and Se sources; then the CdS was prepared with a thickness of about 80 nm by the CBD method. For ZnO film CIGS solar cell preparation, an intrinsic ZnO layer was then sputtered with a thickness of about 100 nm, and followed by ITO top electrode layer. Details of the preparing conditions are shown in Ref. [33]. The process for fabricating the ZnO nanowire CIGS solar cells is illustrated in Fig. 1. A thin ZnO seed layer of a thickness of 50 nm was sputtered, then the sample was put into a mixed solutions (hexamethylenetetramine (HMTA) of 60 mM/L and $\text{Zn}(\text{NO}_3)_2$ of 60 mM/L) keeping at $\sim 90^\circ\text{C}$ with 1.0 h, 1.5 h, 2.5 h, and 4.0 h for preparing different heights of ZnO nanowires. The ZnO nanowires was then spin-coated with the polymethylmethacrylate (PMMA), followed by Ar ion etching to expose heads of the ZnO nanowires, and the ITO layer was prepared by RF magnetron sputtering. At last, the sample was cleaned by acetone to remove the PMMA. In order to prevent the device from damage and strengthen the mechanical property, the CIGS solar cells were packaged with polydimethylsiloxane (PDMS) so that the strains or pressures can be softly added on the surface of the device.

The structure and morphology of the ITO/ZnO/CdS/CIGS/Mo heterojunction were carried out by X-ray diffraction (XRD) with (Bruker, D8 Advance) and scanning electron microscopy (SEM, Hitachi SU8020).

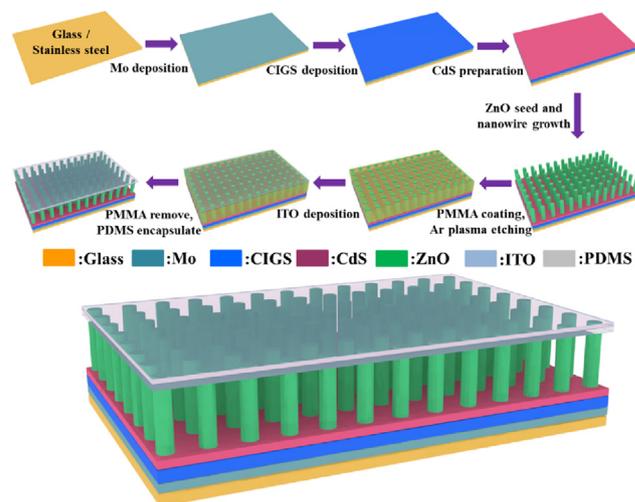


Fig. 1. Fabrication process illustration of the ZnO nanowire CIGS solar cells.

The J-V (I -V) curves of the devices were measured by a low noise current source (SR570) combined with a voltage source (SR560), and an air mass (AM) 1.5 solar simulator (Newport, 91260, 300 W) was used to provide the light source with a $100 \text{ mW}/\text{cm}^2$ power density. To employ piezoelectric effect on the CIGS solar cells, a home-made mechanical stage was used in the measurements to produce the pressures or strains.

3. Results and discussion

Fig. S1 (Supporting information) gives the cross-section SEM image of the solar cells with different ZnO nanowire lengths on the glass substrates. Each layer is well prepared with distinct interface, and the ZnO nanowire arrays are perpendicularly prepared on the CdS layer with lengths of 350 nm, 850 nm, 1400 nm, 2000 nm, respectively. In order to well identify them, the devices were named as #1, #2, #3, #4, #5 for ZnO film and 350 nm, 850 nm, 1400 nm, 2000 nm ZnO nanowire samples. The crystal structures and phase purity of the samples was characterized by the XRD, as shown in Fig. S2, Supporting information. It is clear that there are mainly CIGS and Mo diffraction peaks for #1 sample without any obvious CdS or ZnO peaks due to their weak crystalline and thinner thickness. However, for other four samples, besides the CIGS and Mo peaks, a new peak at 34.35° is observed, which can be indexed to the ZnO (0002) diffraction peak with c -axis oriented hexagonal wurtzite structure, enabling the potential application of piezoelectric effect on the CIGS solar cells.

The photovoltaic performances were investigated under a full sunlight illumination, with a schematic of the measurement presented in Fig. 2a, b shows the J-V curves of these five devices. The PCE is about 9.37% for ZnO film CIGS solar cell (#1 device), and decreases to 8.56% when first introducing ZnO nanowire, then reaches to a maximum of 9.83% for #3 device, but at last decreases dramatically with increasing ZnO nanowire length again. The J_{SC} , V_{OC} , and fill factors show nearly the same changing tendency as that of PCE, as shown in Fig. 2c and d, respectively. As far as we know, this is the first time that the ZnO nanowires were introduced into the CIGS solar cell, especially with an excellent photovoltaic response. The novel preparing structure results in the best photovoltaic performances for the #3 solar cell, which can be ascribed to the high crystalline quality as well as the enhanced light absorption effect of the ZnO nanowire arrays compared with the ZnO film, as illustrated in the external quantum efficiency (EQE) results of Fig. S3, Supporting information. However, it is less sufficient to transport and collect the photo-excited carriers for ZnO nanowires with longer lengths, meaning that the devices with a relatively shorter length are beneficial to the device performance in electrical transport.

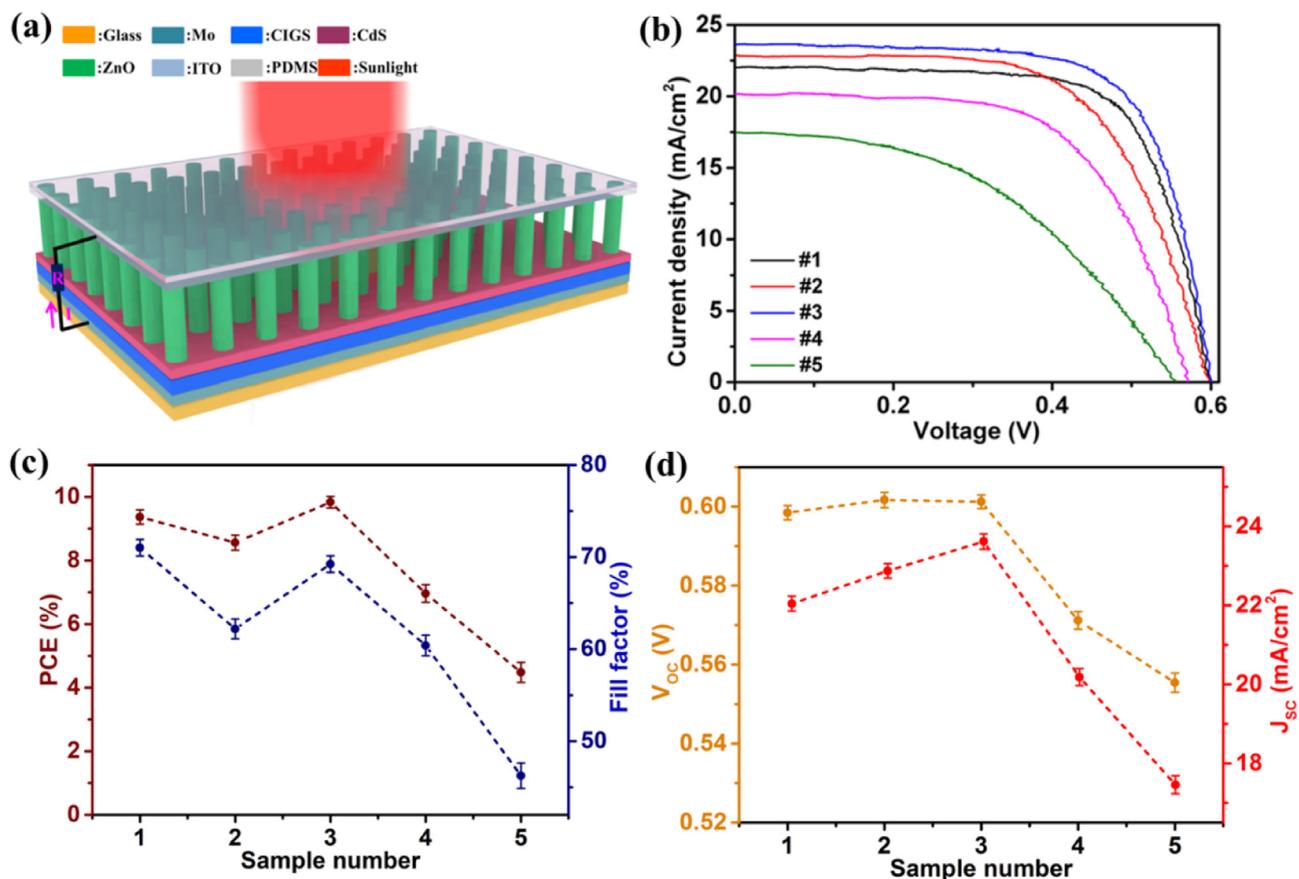


Fig. 2. (a) The measurement diagram of the solar cell under illumination of a sunlight. (b) J-V curves of the CIGS solar cells. (c) PCEs and fill factors, and (d) V_{OC} and J_{SC} for different devices.

Therefore, considering the advantages of strong light absorption as well as suitable carrier collection for moderate length ZnO nanowire sample, the # 3 device with 850 nm length ZnO nanowires should exhibit the best photovoltaic properties.

To investigate the role of piezo-potential on the photovoltaic response of CIGS solar cells with #3 sample structure, vertical pressures were applied on the device with a high-transparent acrylic equipment. The measurement schematic for studying the piezoelectric effect was illustrated in the inset of Fig. 3a. The J-V curves of the #3 solar cell under various external compressive pressures ranging from 0 to 2 MPa were characterized under illumination of AM 1.5 G, as presented in Fig. 3a. The photovoltaic performances of the CIGS solar cell were enhanced obviously when subjecting to a vertical pressure, and the PCE, fill factor, V_{OC} , and J_{SC} under various pressures were extracted and given in Figs. 3b and 3c, respectively. The J_{SC} increases from 23.62 mA/cm² to 26.44 mA/cm² for an about 11.9% improvement, and the V_{OC} changes from 0.601 V to 0.605 V with only a 0.67% fluctuation, meanwhile the fill factor also increases slightly from 69.25% to 71.16%. As a result of the dominated enhancement of the J_{SC} , the PCE is tuned from 9.83% to 11.40% with a maximal relative improvement of 15.9%, as summarized in Fig. 3d. It is suggested that such an enhanced property of the ZnO nanowire CIGS device under external vertical pressures can be attributed to the effective modulation of the interface built-in field of the junction between the ZnO and the CdS layers resulted from the pressure-induced polarization-charges at both ends of ZnO nanowires.

In order to well understand it, a theoretical model of energy band diagram of the CIGS heterostructure is proposed and carefully analyzed to illustrate the enhanced performances of the device. Different from most of other solar cell structures [25–32], there are mainly two depletion regions located in the interfaces of CIGS/CdS and CdS/ZnO,

which can be labeled as “depletion region I” and “depletion region II”, respectively. When the solar cell is illuminated under a sunlight, the energy is mainly absorbed by the CIGS layer, thus generating electron-hole pairs there. These charge carriers could diffuse into “depletion region I” at first, and be separated by its built-in field, then part of separated electrons transmit into “depletion region II”, and are swept to the ITO side of the heterojunction again, as shown in Fig. 4a. It is clear that the raised triangle barrier at the conductive band of the ZnO/CdS interface would hinder electrons transmitting from the junction, resulting in less transmitted carriers and lower PCE. However, when a vertical pressure is applied, negative charges would emerge at +c direction of the ZnO nanowires and positive charges yielded at -c direction of the ZnO nanowires due to piezoelectric polarization effect, the generated piezoelectric potential causes valence and conductive bands of the ZnO nanowires to go downward (blue line) and the barrier height in the ZnO/CdS interface is lowered, as shown in Fig. 4b. Then the transport and tunneling of these separated electrons is propelled in the CdS/ZnO junction, so that more carriers would be transmitted and the PCE of the device is enhanced accordingly.

Then, we also studied the photovoltaic performances of the flexible solar cell prepared on the steel substrate with structure the same as that of sample #3. The PCE of the flexible device was about 5.43% (the PCE of the corresponding ZnO film device was 5.01%), which is lower than that of the #3 rigid device probably due to the non-suitable or non-optimal preparing condition. Here, the influence of the piezo-photonic effect on the photovoltaic properties of such a flexible CIGS device was also investigated with applying a variety of bending strains. And the bending strains can be divided into compressive strains and tensile strains based on the device surface bending downward and upward, with the experimental schematic diagram shown in the insets of Fig. 5a and b, respectively. Moreover, considering the illumination

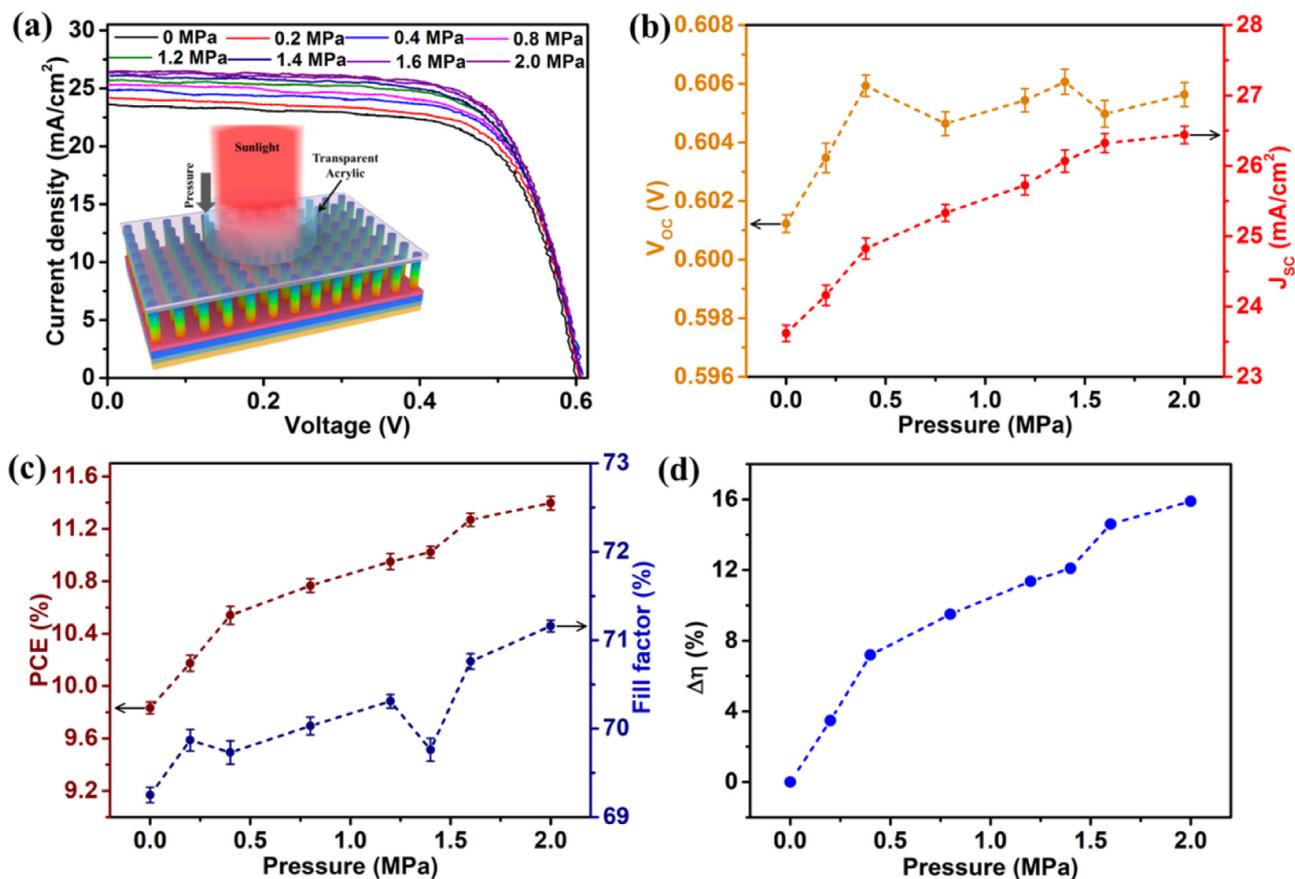


Fig. 3. (a) J-V curves of the #3 device under different vertical pressures with inset the measurement diagram. External pressure-dependent (b) efficiencies and fill factors, (c) V_{oc} and J_{sc} , and (d) relative PCE changes ($\Delta\eta$).

area change during bending deformation, the photovoltaic parameters were all calculated based on the effective illumination areas. The measured J-V curves of the flexible CIGS device with applying different tensile and compressive strains (ranging from 0.74% to -0.74%) were presented in Fig. 5a and b, respectively. It can be found that the photovoltaic performances in compressive strains exhibit the similar increasing tendency as that of the rigid CIGS solar cell under the vertical pressures, but the photovoltaic response decreases with increasing

tensile strains. The strain-dependent photovoltaic parameters (PCE, V_{oc} , J_{sc} , and fill factor) were extracted and given in Fig. 5c and d. The V_{oc} increases from 0.505 V to 0.523 V for a 3.56% improvement, the J_{sc} increases from 18.81 mA/cm² to 22.22 mA/cm² for an increment of 18.12%, while the fill factor always remains at around 51%. Owing to the associated modulation of both the output voltage and current density, the PCE increases quickly from 4.82% to 5.97% for an about 23.8% enhancement when an external strain is changed from a 0.74%

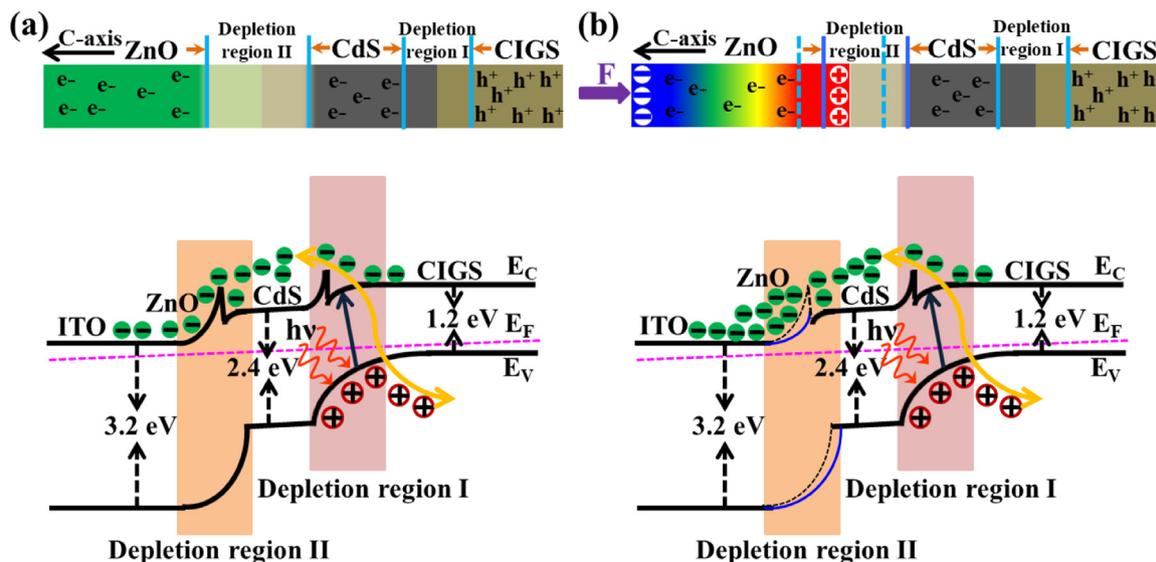


Fig. 4. Schematic diagram of the CIGS solar cell and the corresponding band diagram under (a) no external pressure, and (b) vertical pressure.

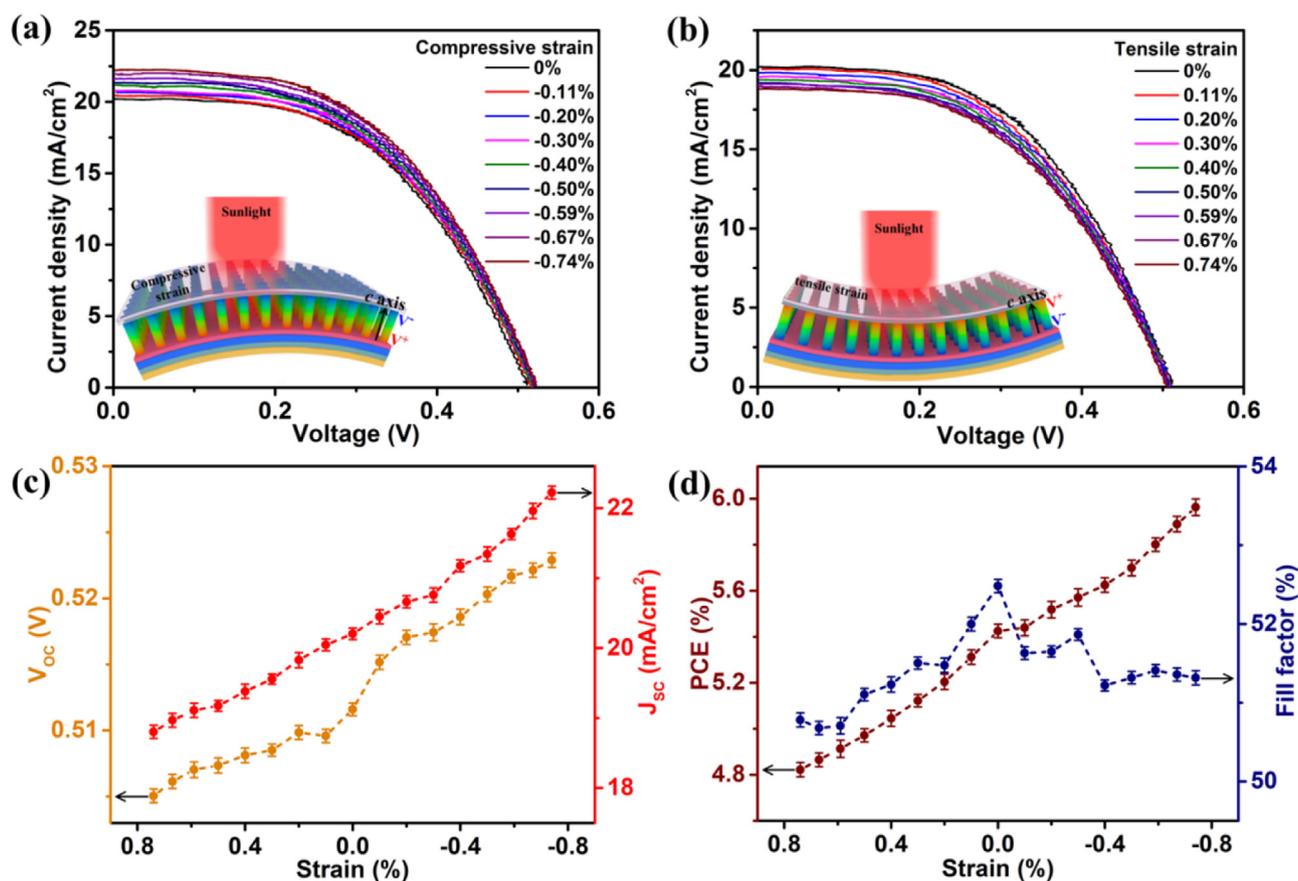


Fig. 5. J-V curves of flexible CIGS solar cell under (a) different compressive strains, and (b) different tensile strains (with inset the corresponding measurement diagram). External strain-dependent (c) PCEs and fill factors, and (d) V_{oc} and J_{sc} .

tensile strain to a -0.74% compressive strain. It is indicated, as the external pressure-modulated PCE in rigid CIGS solar cell, that the performances of the flexible device can also be effectively tuned by bending the solar cell, indicating its great potential application in multifunctional devices. Besides, the PCE enhancement is larger than that of the rigid CIGS device, which can be ascribed to the stronger effect of piezo-phototronic effect on the lower PCE or lower fill factor devices [25,26,29,31].

To well understand the observed strain-modulated performances in the flexible device and explain the different effects of compressive and tensile strains, a physical model was also proposed on the basis of the piezo-phototronic effect by using energy band diagram of the CIGS heterostructure. When the solar cell is subjected to a compressive strain, the interface energy band of “diffusion region II” is changed. The positive piezoelectric charges induced by the compressive strain appear at the interface of ZnO/CdS, and both valence and conduction bands of ZnO go downward, resulting in a decreased triangle barrier height at the interface, as shown in Fig. 6a. This is equivalent to enlarging the “depletion region II”, so that the transport and tunneling of the separated electron-hole pairs in the junction is propelled effectively. However, different from that of the compressive strain, the negative piezoelectric charges are generated under a tensile strain, then both the valence and conduction bands of ZnO would go upward at the interface, leading to an increased triangle barrier height, as shown in Fig. 6b. Therefore, the separation process would be slowed down, and then the output current density as well as the PCE is decreased when a tensile strain is applied.

As is known that ZnO and CdS are all wurtzite-structured semiconductors, so that either of the film layers may also exhibit the piezoelectric properties and be responsible for the modulated photovoltaic performance in the CIGS solar cell structure. Therefore, to prove the

piezo-phototronic effect is resulted from the ZnO nanowires but not the CdS film or ZnO film, the J-V curves of #1 device were also investigated under different vertical pressures, as shown in Fig. S4a, Supporting information. Even under the largest pressure of 2 MPa, there still seems no clear changing of photovoltaic performances. Moreover, the structure of Mo/CIGS/CdS/ZnO/ITO is a very classical, mature, and high-PCE photovoltaic structure whether with flexible or rigid substrate, so that the performance modulation is usually carried out on the basis of maintaining its layer structure [10–12,16,34,35]. However, in order to further verify the piezo-phototronic effect of the ZnO nanowires, another ZnO nanowire CIGS solar cell was also fabricated without preparing the CdS layer. The performances of this device were evaluated under no pressure and different vertical pressures, with the J-V curves shown in Fig. S4b, Supporting information. It is clear that the photovoltaic properties are all very bad with PCE of only about 0.57% under no external pressures, demonstrating the very important roles of the CdS layer (though no exhibited piezoelectric effect), which is used to increase the band bending, to serve as an insulating buffer layer, and to protect the interface from preparing damage in the CIGS heterostructure. Therefore, omission of the CdS layer would result in the very poor photovoltaic responses of the CIGS solar cell [36]. However, the performances can still be greatly modulated by piezo-phototronic effect of the ZnO nanowires with PCE increasing from 0.57% to 0.94% for an enhancement of about 64.9%. From the above results and analysis, it is suggested that the performance modulation of the CIGS-based solar cells can be ascribed to the piezo-phototronic effect of c-axis preferential ZnO nanowires whether through indirectly propelling the transport and tunneling of the separated electrons in the CdS/ZnO junction or directly accelerating the separation and transport of the photo-generated electron-hole pairs in the CIGS/ZnO junction.

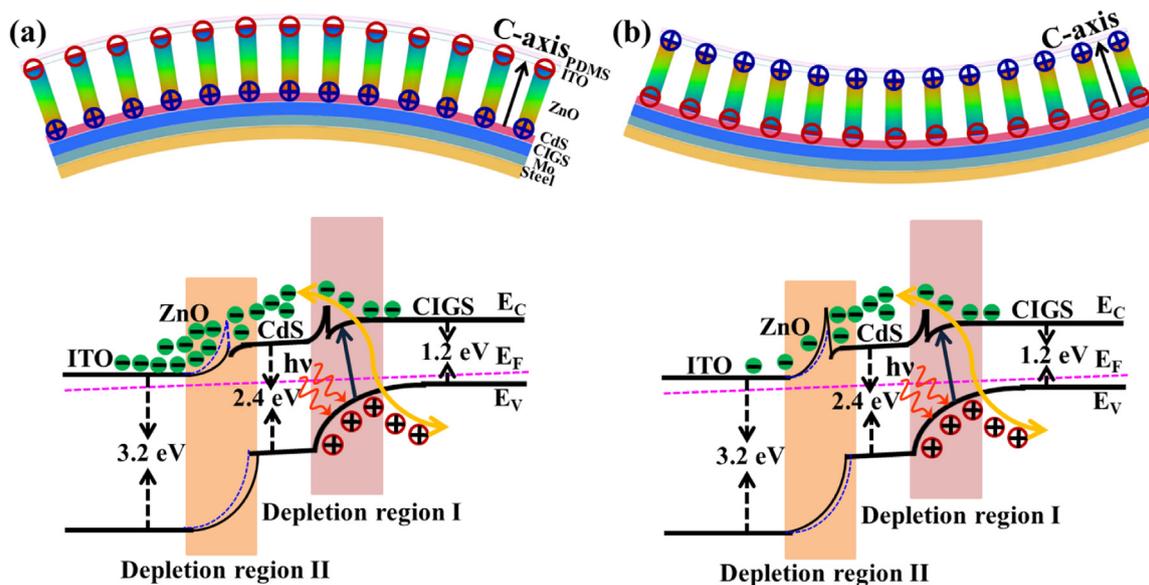


Fig. 6. Schematic diagram of the flexible CIGS solar cell and the corresponding band diagram under (a) compressive strain, and (b) tensile strain.

4. Conclusion

In conclusion, we first introduced the ZnO nanowires into the CIGS solar cells to substitute the ZnO film layer on both glass and stainless steel substrates. It is observed that the ZnO nanowire CIGS solar cells exhibit very good photovoltaic performances, with PCE even larger than that of the ZnO film CIGS solar cells. Moreover, the photovoltaic performance is largely enhanced by using piezo-phototronic effect of the ZnO nanowires under external pressures or strains. The PCE is modulated from 9.83% to 11.40% with adding vertical pressures from 0 to 2 MPa in the rigid device, and increases from 4.82% to 5.96% when external strain is added from a 0.74% tensile strain to a -0.74% compressive strain in the flexible solar cell. These results can be ascribed to the piezo-phototronic effect of the (0002) oriented ZnO nanowires, which can be used to modulate the separation, recombination, and transport of carriers in the CdS/ZnO junction. Our results not only provide an ideal method for increasing PCE of CIGS solar cells by introducing ZnO nanowires, but also shed light on enhancing its photovoltaic properties via the piezo-phototronic effect.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the

online version at <http://dx.doi.org/10.1016/j.nanoen.2018.04.070>.

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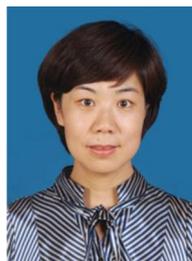
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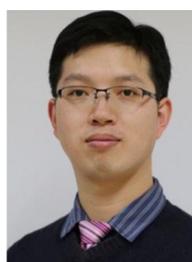
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