Energy & Environmental Science

Dynamic Article Links

Cite this: *Energy Environ. Sci.*, 2012, **5**, 6850

www.rsc.org/ees

COMMUNICATION

Piezo-phototronics effect on nano/microwire solar cells

Yan Zhang, Ya Yang and Zhong Lin Wang*

Received 7th January 2012, Accepted 7th February 2012
DOI: 10.1039/c2ee00057a

Wurtzite structures, such as ZnO, GaN, InN and CdS, are piezoelectric semiconductor materials. A piezopotential is formed in the crystal by the piezoelectric charges created by applying a stress. The inner-crystal piezopotential can effectively tune/control the carrier separations and transport processes at the vicinity of a p–n junction or metal–semiconductor contact, which is called the *piezo-phototronic effect*. The presence of piezoelectric charges at the interface/junction can significantly affect the performances of photovoltaic devices, especially flexible and printed organic/inorganic solar cells fabricated using piezoelectric semiconductor nano/microwires. In this paper, the current–voltage characteristics of a solar cell have been studied theoretically and experimentally in the presence of the piezoelectric effect. The analytical results are obtained for a ZnO piezoelectric p–n junction solar cell under simplified conditions, which provide a basic physical picture for understanding the mechanism of the piezoelectric solar cell. Furthermore, the maximum output of the solar cell has been calculated numerically. Finally, the experimental results of organic solar cells support our theoretical model. Using the piezoelectric effect created by external stress, our study not only provides the first basic theoretical understanding about the piezo-phototronic effect on the characteristics of a solar cell but also assists the design for higher performance solar cells.

School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, USA. E-mail: zlwang@gatech.edu

1. Introduction

Typical piezoelectric semiconductor crystals, such as ZnO, GaN, InN and CdS, have non-central symmetric wurtzite structure, and they are important optoelectronic materials for solar cells, photodetectors, and light emitting diodes. At the nanoscale, piezoelectric semiconductor nanowires have been utilized as basic building blocks for fabricating a series of novel nano/microdevices,[1–4] such as nanogenerators,[5–9] piezoelectric field effect transistors,[10,11] piezotronic logic devices,[12,13] piezotronic photodetectors,[14] and piezotronic light emitting diodes.[15] Most recently, solar cells and photocells fabricated using piezoelectric semiconductors have demonstrated that the inner-crystal piezoelectric potential can be used effectively for enhancing charge separation.[4,16,17]

There are several key parameters to evaluate the performance of a solar cell: photocurrent (short circuit current), open circuit voltage, maximum output power, fill factor and ideal conversion efficiency. The fill factor is defined as the ratio of the maximum output power to the product of short circuit current and open circuit voltage. The ideal conversion efficiency is defined as the ratio of the maximum power output to the incident solar power.

From materials and device structural point of view, there are two approaches to optimize the solar cell performance: developing new energy efficient materials and designing new structures. The metal–insulator–semiconductor (MIS) structure has been used to decrease the saturation current density in silicon solar cells.[18] Thickness dependence of p–n junction solar cells had been discussed

Broader context

Wurtzite structures, such as ZnO, GaN, InN and CdS, are piezoelectric semiconductor materials. A piezopotential is formed in the crystal by the piezoelectric charges created by applying a stress. The inner-crystal piezopotential can effectively tune/control the carrier separations and transport processes at the vicinity of a p–n junction or metal–semiconductor contact, which is called the *piezo-phototronic* effect. The presence of piezoelectric charges at the interface/junction can significantly affect the performances of photovoltaic devices, especially for flexible and printed organic/inorganic solar cells fabricated using piezoelectric semiconductor nano/microwires. The current–voltage characteristics of a solar cell have been studied theoretically and experimentally with the presence of piezoelectric effect. The analytical results are obtained for ZnO piezoelectric p–n junction solar cell under simplified conditions, which provide a basic physical picture for understanding the mechanism of the piezoelectric solar cell. Furthermore, the maximum output of the solar cell has been calculated numerically. Finally, the experiment results of organic solar cells support our theoretical model. Using the piezoelectric effect created by external stress, our study not only provides the first basic theoretical understanding about the piezo-phototronic effect on the characteristics of a solar cell, but also assists the design for higher performance solar cells.

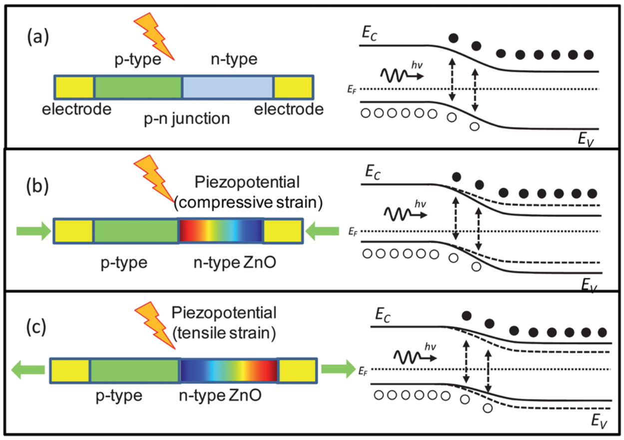

Fig. 1 Schematic and energy band diagram of (a) a general nanowire piezoelectric solar cell fabricated using a p–n junction structure. Schematics and energy band diagram of the piezoelectric solar cells under (b) compressive strain and (c) tensile strain, where the polarity and magnitude of the piezopotential can effectively tune/control the carrier generation, separation and transport characteristics. The color code represents the distribution of the piezopotential at the n-type semiconductor nanowires.

theoretically for optimization of open circuit voltages using the thermodynamic theory.[19] Polymer solar cells are constructed based on the structure of a low-band gap polymer, PBDTTT4, to increase the open-circuit voltage as high as 0.76 V combined with a power conversion efficiency as high as 6.77%.[20] Theories and experiments have been developed to understand the origin of the open-circuit voltage of polymer–fullerene solar cells.[21] Recently, a brand new method has been developed by using piezoelectric and ferroelectric materials for enhancing the performance of organic solar cells: piezoelectric solar cells (PSCs)[17] and ferroelectric polymer solar cells.[22] The core idea is to use the intrinsic potential provided by the material itself for enhancing charge separation. Developing the basic theory for understanding the experimental phenomena is needed.

Take a typical nano/microwire solar cell (Fig. 1a) as an example, the basic structure is a p–n junction or metal–semiconductor (M–S) contact. The working principle of the solar cell is to use the high electric field in the depletion region to assist the separation of electron–hole pairs generated by incident photons. The piezoelectric charges created at the junction area under strain can effectively tune/control the solar cell performance. For example, ZnO nanowire solar cells are shown in Fig. 1b and c, which are made of a p-type non-piezoelectric and n-type piezoelectric heterojunction. The piezopotential significantly modifies the band structure at the interface, resulting in a control over the carrier generation, separation and transport at the p–n junction or M–S interface, which is the fundamental piezo-phototronic effect.

The piezopotential distribution and the dynamic transport properties of the carriers have been discussed in our previous report.[23] In this paper, we present a theoretical model for semi-quantitatively understanding the piezo-phototronic effect on the carrier generation and transport behavior. The analytical results are obtained for a ZnO piezoelectric p–n junction solar cell under simplified conditions, which provide a basic physical picture for understanding the mechanism of the PSC. Furthermore, the maximum output of the PSC has been calculated numerically. Finally, the experimental results of organic solar cells support our theoretical model. Using the piezoelectric effect created by external stress, our study not only provides the basic physics for understanding the characteristics of the solar cell but also assists the design for higher performance solar cells.

2. Theoretical model of the piezoelectric solar cell

Piezoelectric theories and semiconductor physics are used for describing the properties of a PSC that is fabricated using piezoelectric semiconductors. The behaviors of the piezoelectric material under dynamic straining are described by piezoelectric theories.[24] The static and dynamic transport behavior of the charge carriers and the interaction of a photon and an electron in semiconductors are described by the basic equations of semiconductor physics.[25]

2.1. Basic equations

The piezoelectric and constituter equations under a small uniform mechanical strain are given by:[24,26,27]

$$(\boldsymbol{P})_i = (\boldsymbol{e})_{ijk}(\boldsymbol{S})_{jk} \quad (1a)$$

$$\begin{cases} \boldsymbol{\sigma} = \boldsymbol{c}_{\mathrm{E}}\boldsymbol{S} - \boldsymbol{e}^{\mathrm{T}}\boldsymbol{E} \\ \boldsymbol{D} = \boldsymbol{e}\boldsymbol{S} + \boldsymbol{k}\boldsymbol{E} \end{cases} \quad (1b)$$

where $\boldsymbol{P}$ is the polarization vector, $\boldsymbol{S}$ is the uniform mechanical strain, the third order tensor $(\boldsymbol{e})_{ijk}$ is the piezoelectric tensor, $\boldsymbol{\sigma}$ and $\boldsymbol{c}_{\mathrm{E}}$ are the stress tensor and the elasticity tensor, respectively. $\boldsymbol{E}$, $\boldsymbol{D}$ and $\boldsymbol{k}$ are the electric field, the electric displacement, and the dielectric tensor, respectively.

The electrostatic behavior of charges in a piezoelectric semiconductor is described by the Poisson equation:

$$\nabla^2\psi_i = -\frac{\rho(\vec{r})}{\varepsilon_s} \quad (2)$$

where ψ_i, $\rho(\vec{r})$ and ε_s are the electric potential distribution, the charge density distribution, and the permittivity of the material.

The drift and diffusion current density equations that correlate the local fields, charge densities and local currents are:

$$\begin{cases} \boldsymbol{J}_{\mathrm{n}} = q\mu_n n\boldsymbol{E} + qD_n\nabla n \\ \boldsymbol{J}_{\mathrm{p}} = q\mu_p p\boldsymbol{E} - qD_p\nabla p \\ \boldsymbol{J} = \boldsymbol{J}_{\mathrm{n}} + \boldsymbol{J}_{\mathrm{p}} \end{cases} \quad (3)$$

where $\boldsymbol{J}_{\mathrm{n}}$ and $\boldsymbol{J}_{\mathrm{p}}$ are the electron and hole current densities, q is the absolute value of unit electronic charge, μ_n and μ_p are electron and hole mobilities, n and p are concentrations of free electrons and free holes, D_n and D_p are diffusion coefficients for electrons and holes, respectively, $\boldsymbol{E}$ is the electric field, and $\boldsymbol{J}$ is the total current density.

The charge transport under the influence of a field is described by the continuity equations.

$$\begin{cases} \dfrac{\partial n}{\partial t} = G_n - U_n + \dfrac{1}{q}\nabla\cdot\boldsymbol{J}_{\mathrm{n}} \\ \dfrac{\partial p}{\partial t} = G_p - U_p - \dfrac{1}{q}\nabla\cdot\boldsymbol{J}_{\mathrm{p}} \end{cases} \quad (4)$$

where G_n and G_p are the electron and hole generation rates, U_n and U_p are the recombination rates, respectively.

2.2. Piezoelectric solar cells based on the p–n junction

According to our theoretical work about piezotronic effect,[23] an ideal p–n junction is taken as an example to understand the unique property of a PSC. There are two typical effects in a piezoelectric semiconductor material under applied external stress: piezoresistance effect and piezotronic effect. Piezoresistance effect is about the strain induced change in bandgap, density of states and/or mobility.[28,29] Piezoresistance is mostly a volume effect and it is not sensitive to the reversal of the piezoelectric polarity in the semiconductor, thus, it can be truly considered as a change in resistance of the semiconductor bulk, and it has a little effect on the contact property. Although the change in bandgap can affect the saturation current density and the open circuit voltage of a solar cell, the change of bandgap is independent of the sign of piezoelectric charges created at the contact of the device. The second effect is the piezotronic effect,[3,30] which is about the polar direction dependence of an inner-crystal piezoelectric potential arising from the piezo-charges created at the contacts. Owing to the sign reversal of the piezo-charges at the two ends of the device, a non-symmetric effect is induced at the two ends. This means that the output of the solar cell depends on the polarity of the crystal.

Recent experiments on a P3HT/ZnO solar cell show a strong dependence of the open circuit voltage on the orientation of the ZnO microwire once it is subjected to a strain,[17] suggesting the key role played by the piezo-phototronic effect on the solar cell output. The open circuit voltage and maximum output power sensitively depend on the strain applied to ZnO, while the short circuit current density does not. Therefore, for a p–n junction nano/microwire solar cell to be used for following theoretical study, the photocurrent density (short circuit current density) is assumed to be independent of the external strain. Here the p-type material is assumed to adsorb solar light. For simplicity, we used a p–n junction model for easily describing the piezo-phototronic effect on a solar cell and neglected the difference in bandgaps between the p-type and n-type materials, but our approach can be extended to general heterojunction.

Theoretically, the short circuit current density results from the excitation of excess carriers by solar radiation.[25] For simplicity, we assume the electron and hole generation rates (G_n and G_p) as constant:

$$G_n = G_p = \frac{J_{\text{solar}}}{q(L_n + L_p)} \tag{5}$$

where J_{solar} is the short circuit current density, L_n and L_p are the electron and hole diffusion lengths respectively. We assume no radiative process, which means no photon emission in our model $U_n = U_p = 0$. In our previous work, the piezoelectric p–n junction model was developed for understanding the physics of the piezoelectric semiconductor using the Shockley theory.[23,25] The current density of the p–n junction has been obtained in the presence of piezoelectric polarization charges inside the p–n junction. Using the one-dimensional piezoelectric p–n junction model in the presence of photocurrent density J_{solar}, the total current density had been derived by solving above basic eqn (1)–(5) under simplified conditions for an ideal p–n junction PSC:

$$J = J_{\text{pn}}\left[\exp\left(\frac{qV}{kT}\right) - 1\right] - J_{\text{solar}} \tag{6a}$$

$$J_{\text{pn}} \equiv \frac{qD_p p_{\text{n0}}}{L_p} + \frac{qD_n n_{\text{p0}}}{L_n} \tag{6b}$$

where J_{pn} is the saturation current density, D_p and D_n are diffusion coefficients for electrons and holes, respectively, p_{n0} and n_{p0} are the thermal equilibrium hole concentration in n-type semiconductors and the thermal equilibrium electron concentration in p-type semiconductors, respectively. For organic solar cells based on the polymer as a p-type material and the ZnO micro/nanowires as the n-type material, the ZnO micro/nanowires have a high level n-type conductivity.[30] Thus, we assume the p-type side has an abrupt junction with donor concentration N_{A}, which means $n_{\text{p0}} \gg p_{\text{n0}}$ inside the p–n junction, $J_{\text{pn}} \approx \frac{qD_n n_{\text{p0}}}{L_n}$, where $n_{\text{p0}} = n_i \exp\left(-\frac{E_i - E_{\text{F}}}{kT}\right)$, n_i is the intrinsic carrier density and E_i is the intrinsic Fermi level. According to our previous theoretical work about piezotronics, the total current density is rewritten as:

$$J = J_{\text{pn0}} \exp\left(-\frac{q^2 \rho_{\text{piezo}} {W_{\text{piezo}}}^2}{2\varepsilon_s kT}\right)\left[\exp\left(\frac{qV}{kT}\right) - 1\right] - J_{\text{solar}} \tag{7a}$$

$$J_{\text{pn}} = J_{\text{pn0}} \exp\left(-\frac{q^2 \rho_{\text{piezo}} {W_{\text{piezo}}}^2}{2\varepsilon_s kT}\right) \tag{7b}$$

where the Fermi level and the saturation current density in the absence of piezopotential are defined as E_{F0} and $J_{\text{pn0}} = \frac{qD_n n_{\text{p0}}}{L_n}\exp\left(-\frac{E_i - E_{\text{F0}}}{kT}\right)$, respectively. Different from the original equation, the negative sign appearing in the exponential term in eqn (7) is to be elaborated as follows.

For PSCs, eqn (7a) and (7b) present that the saturation current density J_{pn} decreases exponentially with the piezoelectric charges at the interface of the p–n junction. It must be mentioned that the term inside the exponential function of eqn (7b) has a negative sign compared to our previous piezoelectric p–n junction.[23] The mechanism in terms of semiconductor physics is that the saturation current density J_{pn} depends on two parts: the thermal equilibrium hole concentration p_{n0} in the n-type semiconductor and the thermal equilibrium electron concentration n_{p0} in the p-type semiconductor. There are two approximate cases that can be obtained directly from eqn (6b): first case is $n_{\text{p0}} \gg p_{\text{n0}}$, which means that the thermal equilibrium electron concentration n_{p0} in the p-type semiconductor dominates the current characteristic. This case corresponds to our PSC model. Second case is $p_{\text{n0}} \gg n_{\text{p0}}$, which means that the thermal equilibrium hole concentration p_{n0} in the n-type semiconductor dominates the current characteristic. This case had been presented in our previous study on piezoelectric p–n junction solar cells.[23] As for the negative strain (compressive strain) case in our model, the positive piezoelectric charges attract the electrons and repel the holes. Alternatively, for the positive strain (tensile strain) case, negative piezoelectric charges attract the holes and repel the electrons. A distinction between positive and negative piezoelectric charges results in the opposite effects for the two cases, which is represented by the reversal in sign of the term in the exponential function of eqn (7b). According to eqn (7a) and (7b),

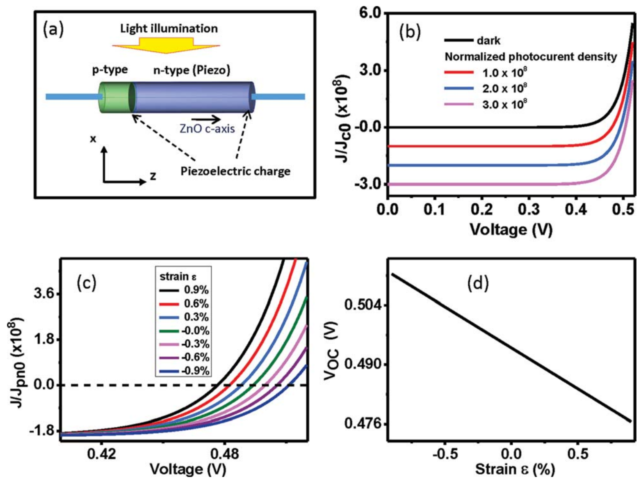

Fig. 2 (a) Schematic of a ZnO nanowire piezoelectric solar cell based on a p–n junction with the n-side being piezoelectric and the *c*-axis pointing away from the junction; (b) calculated current–voltage characteristics of the piezoelectric solar cell under various photocurrent densities; (c) relative current density as a function of voltage under various applied strains (−0.9% to 0.9%); (d) open circuit voltage as a function of the applied strain.

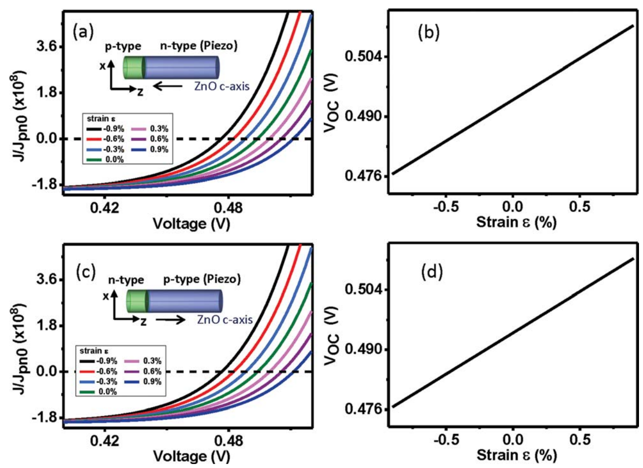

Fig. 4 (a) Current–voltage curves and (b) open circuit voltage of a p–n type solar cell, with the n-side (ZnO) being piezoelectric and the *c*-axis pointing toward the junction, under various applied strains (−0.9% to 0.9%). (c) Current–voltage curves and (d) open circuit voltage of a p–n junction solar cell, with the p-side being piezoelectric and the *c*-axis pointing away from the junction, under various applied strains (−0.9% to 0.9%).

by setting $J = 0$, the open circuit voltage of a PSC can be obtained as:

$$V_{\mathrm{OC}} = \frac{kT}{q}\ln\left(\frac{J_{\mathrm{solar}}}{J_{\mathrm{pn}}}+1\right) \tag{8a}$$

For typical solar cells with $J_{\mathrm{solar}} \gg J_{\mathrm{pn}}$, the open circuit voltage is approximately given by:

$$V_{\mathrm{OC}} \approx \frac{kT}{q}\ln\left(\frac{J_{\mathrm{solar}}}{J_{\mathrm{pn}}}\right) = \frac{kT}{q}\left\{\ln\left(\frac{J_{\mathrm{solar}}}{J_{\mathrm{pn0}}}\right) + \frac{q^2\rho_{\mathrm{piezo}}{W_{\mathrm{piezo}}}^2}{2\varepsilon_s kT}\right\} \tag{8b}$$

Eqn (8b) presents the open circuit voltage as a function of the piezoelectric charges. The open circuit voltage can be effectively tuned or controlled by not only the magnitude of the strain but also the sign of the strain (tensile *vs.* compressive). Though the above results are given by using a one-dimensional nano/microwire model, the mechanism of the piezo-phototronic effect can also be applied to bulk and thin film solar cells.

For GaN or ZnO nanowire grown along the *c*-axis, with a strain s_{33} along the *c*-axis, solving piezoelectric equation (eqn (1a)) gives $q\rho_{\mathrm{piezo}}W_{\mathrm{piezo}} = -e_{33}s_{33}$. Thus, the current density and open circuit voltage of the solar cell are calculated using typical material constants: piezoelectric constant $e_{33} = 1.22$ C m^{-2} and relative dielectric constant $\varepsilon_{\mathrm{S}} = 8.91$. The width within which the piezo-charges are distributed uniformly is taken as $W_{\mathrm{piezo}} = 0.25$ nm, which is about one atomic layer in thickness. The temperature is $T = 300$ K. For all of the calculations, the lengths of the left-hand and right-hand side segments of the p–n structure are taken as 20 nm and 80 nm, respectively. The diameter of the nanowire is 20 nm. Fig. 2a shows a schematic model for the calculation. A *z*-axis is defined along the *c*-axis of ZnO nanowire, with $z = 0$ representing the end of the p-type. The p–n junction is located at $z = 20$ nm along the axis and the n-type ends at $z = 100$ nm. For simplicity, we assume that the normalized photocurrents depend on the density of light and are chosen as 0.6×10^8, 1.8×10^8, and 3.0×10^8, respectively. Fig. 2b present the calculated current–voltage curve as a function of voltage and varied light intensity. The short circuit current density increases with light intensity. However, for a given J_{pn}, the open circuit voltage increases logarithmically with the increase of photocurrent J_{solar}. Decreasing the saturation current density is likely to slightly increase the open circuit voltage of the solar cell. At a fixed short circuit current density, the *J*–*V* characteristics of the p–n junction solar cell are presented in Fig. 2c with applied strain varying from −0.9% to 0.9%. Fig. 2d shows the open circuit voltage as a function of the externally applied strain, which clearly demonstrates the piezo-phototronic effect on the performance of the solar cell. The open circuit voltage drops from 0.48 V to 0.51 V when the strain increases from −0.9% to 0.9%, as shown in Fig. 2d.

Based on the analytical results, the output power of the PSC can be obtained from eqn (7a). Fig. 3a shows the output power as a function of voltage at a fixed photocurrent density. The output power curve rises with the increase of strain, and each has its maximum at a specific voltage. By calculating the extreme-value using eqn (7a), the maximum output power is shown as a function of applied strain in Fig. 3b. It is obvious that the external strain can effectively tune the maximum output power of the solar cell.

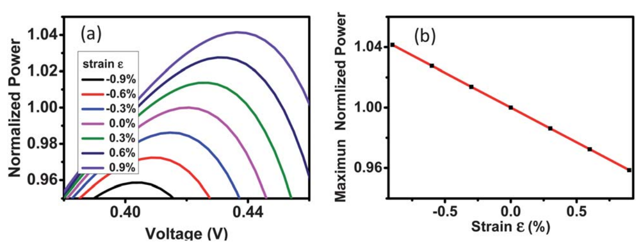

Fig. 3 (a) Output power of a ZnO nanowire p–n junction piezoelectric solar cell as a function of voltage and (b) relative maximum output power under various applied strains (−0.9% to 0.9%).

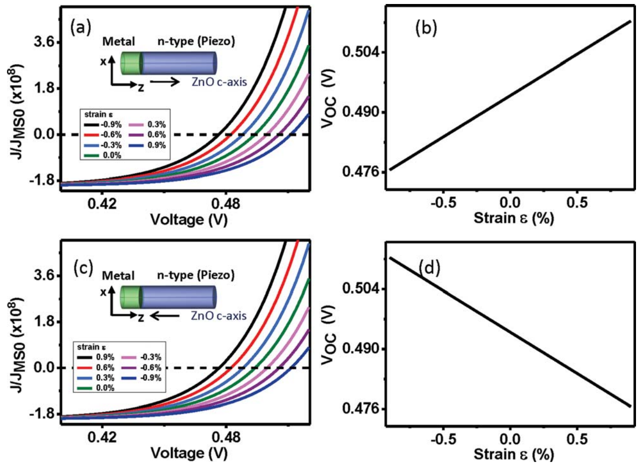

Fig. 5 (a) Schematic of a piezoelectric solar cell based on metal–semiconductor (ZnO) contact with the *c*-axis pointing away from the interface and (b) the open circuit voltage under various applied strains (−0.9% to 0.9%). (c) Schematic of a piezoelectric solar cell based on metal–semiconductor (ZnO) contact with the *c*-axis pointing toward the interface and (d) open circuit voltage under various applied strains (−0.9% to 0.9%).

As a comparison to the case shown in Fig. 2a, we reverse the *c*-axis polarity of the n-type side (Fig. 4a) or exchange the n and p segments (Fig. 4c). The corresponding models are the inset in the figures. The current–voltage curves and the open circuit voltage of the two cases are plotted in Fig. 4a and b, respectively. In the case of Fig. 4a that has a reversal *c*-axis in comparison to that of Fig. 2a, the trend of the current density depending on the strain as shown in Fig. 4a is opposite to that shown in Fig. 2c, because the sign of the piezoelectric charges is reversed.

For non-piezoelectric n-type material and piezoelectric p-type semiconductor solar cell case, as shown in Fig. 4c and d, the calculated *I*–*V* curve and the open circuit voltage show the same trend as for Fig. 4a and b. The results indicate a choice of n- or p-type piezoelectric semiconductor materials and their corresponding piezoelectric polar directions may be used effectively for improving solar cell performance.

2.3. Metal–semiconductor Schottky contacted solar cells

The metal–semiconductor (M–S) contact is an important component in solar cell devices. According to our theoretical work about the piezotronic effect,[23] for an n-type piezoelectric semiconductor nanowire, the total current density of an ideal M–S under simplified conditions is given by eqn (9) for a PSC:

$$J = J_{\text{MS}}\left[\exp\left(\frac{qV}{kT}\right) - 1\right] - J_{\text{solar}} \tag{9a}$$

$$J_{\text{MS}} = J_{\text{MS0}}\exp\left(\frac{q^2\rho_{\text{piezo}}{W_{\text{piezo}}}^2}{2\varepsilon_{\text{s}}kT}\right) \tag{9b}$$

where J_{MS} is the saturation current density and J_{MS0} is defined as the saturation current density in the absence of piezoelectric charges:

$$J_{\text{MS0}} = \frac{q^2 D_n N_{\text{C}}}{kT}\sqrt{\frac{2qN_{\text{D}}(\psi_{\text{bi0}} - V)}{\varepsilon_{\text{s}}}}\exp\left(-\frac{q\phi_{\text{Bn0}}}{kT}\right) \tag{10}$$

where ψ_{bi0} and ϕ_{Bn0} are the built-in potential and Schottky barrier height in the absence of piezoelectric charges. In our case, the effect of piezoelectric charge can be considered as perturbation to the conduction-band edge E_{C}. Note the sign of the exponential term in eqn (9b) is reversed in comparison to that in eqn (7a) for the reasons discussed in the last section.

Thus, the open circuit voltage of an M–S contact PSC can be obtained as:

$$V_{\text{OC}} \approx \frac{kT}{q}\left\{\ln\left(\frac{J_{\text{solar}}}{J_{\text{MS0}}}\right) - \frac{q^2\rho_{\text{piezo}}{W_{\text{piezo}}}^2}{2\varepsilon_{\text{s}}kT}\right\} \tag{11}$$

Under a positive strain (tensile strain) case, the negative local piezoelectric charges increase the barrier height at the M–S contact, and thus result in a decrease in the saturation current density J_{MS} as shown in eqn (9b); correspondingly, the open circuit voltage of the M–S contact solar cell is increased according to eqn (11). Alternatively, under a negative strain (compressive strain) case, the positive local piezoelectric charges decrease the barrier height at the M–S contact, resulting in an increase in the saturation current density J_{MS}, which reduces the open circuit voltage of the M–S contacted solar cell. Therefore, the current density and the open circuit voltage can be controlled not only by the magnitude of the strain but also by the sign of the strain (tensile *vs.* compressive).

For GaN or ZnO nanowire grown along the *c*-axis, with a strain s_{33} along the *c*-axis, the typical material constants for calculations are the same as for the p–n junction cases. The schematics of the calculated model are shown in Fig. 5a and c. Fig. 5a shows the calculated

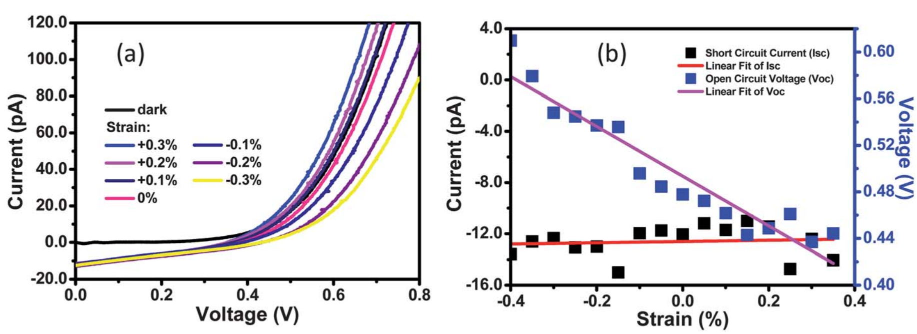

Fig. 6 Experimentally measured current–voltage characteristics of a P3HT/ZnO microwire solar cell under simulated AM 1.5 illumination. The experiment was done for a single microwire to show the piezo-phototronic effect on the solar cell output. (a) Current–voltage curves of the piezoelectric solar cell device under various applied strains (−0.3% to 0.3%) and (b) dependence of the short circuit current I_{sc} and open circuit voltage V_{oc} on the applied strain; red and pink lines are linear fittings for I_{sc} and V_{oc} as a function of the applied strain, respectively.

J/J_{MS0} as a function of voltage V at fixed light intensity. The current curves drop as the external applied strain changes from −0.9% to 0.9%. The open circuit voltage increases as a function of the externally applied strain, as shown in Fig. 5b. By switching the polar direction of the c-axis, the open circuit voltage drops with the increase of strain (Fig. 5c and d). The theoretical result agrees qualitatively with our previous experiments.[16]

3. Experimental results

In order to verify the theoretical model, p–n type solar cells have been fabricated by using poly(3-hexylthiophene) (P3HT) as a p-type material and the ZnO micro/nanowires as the n-type material. Details have been reported previously.[17] A ZnO microwire growing along the [0001] direction was laid down on a polystyrene substrate with a length of 4 cm, width of 8 mm and thickness of 0.5 mm. Silver paste served as an electrode at the other end of the ZnO microwire. Then, a thin layer of PDMS was used to pack the device. Applying a tensile or compressive strain by a three-dimensional mechanical stage (with a displacement resolution of 1 μm) on the PS substrate, the device was mechanically deformed under simulated AM 1.5 illumination with 100 mW cm^{-2} light intensity.

Fig. 6a shows the current–voltage curves of the device under different applied stress applied transversely across the diameter of the microwire, which produces an axial strain in the microwire. The I–V curve shifts to higher voltage by changing the strain from 0.3% to −0.3%. As expected from our theoretical discussion presented above, for the ZnO microwire growing along the [0001] direction that is pointing away from the P3HT–ZnO interface, positive piezoelectric charges are created at the interface of the p–n junction under compressive strain, which result in an increase in the open circuit voltage but a drop in the saturation current density. Alternatively, for the tensile strain case, negative piezoelectric charges are created at the p–n junction, which increase the saturation current density but reduce the open circuit voltage. Fig. 6b shows the experimentally measured dependence of the short circuit current I_{sc} and open circuit voltage V_{oc} under different applied strains for the corresponding configuration. The short circuit current is approximately a constant under the strain, *e.g.*, J_{solar} is a constant, thus, according to eqn (8b), the linear decrease in the open circuit voltage is due to the linear change of the piezoelectric charge density.

Alternatively, by switching the orientation of the microwires with their c-axis pointing toward the P3HT, we have studied the effect of sign reversion in piezoelectric charges on the solar output, as reported previously.[17] A reversal in microwire orientation does not affect the piezoresistance, if any, present in the microwire, because piezoresistance has no polarity. Experimentally, the presence of the open circuit voltage increased linearly with a linear increase in strain,[17] in agreement with the expected result from eqn (8b). Again, the performance of the solar cell was dominated by the piezo-phototronic effect. The above model can also be applied to explain the output of a ZnO microwire that grows along the [01$\bar{1}$0] direction.[17]

4. Conclusions

In summary, we have presented a theoretical model about the piezoelectric effect on solar cells by studying carrier transport in two configurations: the p–n junction and metal–semiconductor Schottky contact. The analytical results of current density and open circuit voltage under simplified conditions are derived for understanding the core physics about the piezo-phototronic effect on the solar cell output. The theoretically expected results have been verified by experiments. We have presented the basic principle of piezoelectric solar cells: the inner-crystal piezoelectric potential inside the region of the junction can be used effectively for enhancing charge separation. The mechanism can be applied to most of the junctions for using the built-in electric field in the crystal to separate charges, including p–n junction, metal–semiconductor contact, and heterojunction. Our study not only provides the first basic understanding on the piezoelectric effect on the characteristics of a solar cell but also assists the design for higher performance solar cells.

Acknowledgements

Research was supported by Airforce, U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-FG02-07ER46394, NSF (CMMI 0403671).

References

1 C. M. Lieber and Z. L. Wang, *MRS Bull.*, 2007, **32**, 99–108.
2 F. Qian, Y. Li, S. Gradecak, H. G. Park, Y. Dong, Y. Ding, Z. L. Wang and C. M. Lieber, *Nat. Mater.*, 2008, **7**, 701–706.
3 Z. L. Wang, *Nano Today*, 2010, **5**, 540–552.
4 F. Boxberg, N. Søndergaard and H. Q. Xu, *Nano Lett.*, 2010, **10**, 1108–1112.
5 Z. L. Wang and J. H. Song, *Science*, 2006, **312**, 242–246.
6 X. D. Wang, J. H. Song, J. Liu and Z. L. Wang, *Science*, 2007, **316**, 102–105.
7 Y. Qin, X. D. Wang and Z. L. Wang, *Nature*, 2008, **451**, 809–U805.
8 D. Choi, M. Y. Choi, W. M. Choi, H. J. Shin, H. K. Park, J. S. Seo, J. Park, S. M. Yoon, S. J. Chae, Y. H. Lee, S. W. Kim, J. Y. Choi, S. Y. Lee and J. M. Kim, *Adv. Mater.*, 2010, **22**, 2187–2192.
9 V. Dallacasa, F. Dallacasa, P. Di Sia, E. Scavetta and D. Tonelli, *J. Nanosci. Nanotechnol.*, 2010, **10**, 1043–1050.
10 X. D. Wang, J. Zhou, J. H. Song, J. Liu, N. S. Xu and Z. L. Wang, *Nano Lett.*, 2006, **6**, 2768–2772.
11 S.-S. Kwon, W.-K. Hong, G. Jo, J. Maeng, T.-W. Kim, S. Song and T. Lee, *Adv. Mater.*, 2008, **20**, 4557–4562.
12 N. Liu, G. Fang, W. Zeng, H. Zhou, H. Long, X. Zou, Y. Liu and X. Zhao, *Appl. Phys. Lett.*, 2010, **97**, 243504.
13 W. Wu, Y. Wei and Z. L. Wang, *Adv. Mater.*, 2010, **22**, 4711–4715.
14 Q. Yang, X. Guo, W. H. Wang, Y. Zhang, S. Xu, D. H. Lien and Z. L. Wang, *ACS Nano*, 2010, **4**, 6285–6291.
15 Q. Yang, W. H. Wang, S. Xu and Z. L. Wang, *Nano Lett.*, 2011, **11**, 4012–4017.
16 Y. F. Hu, Y. Zhang, Y. L. Chang, R. L. Snyder and Z. L. Wang, *ACS Nano*, 2010, **4**, 4220–4224.
17 Y. Yang, W. Guo, Y. Zhang, Y. Ding, X. Wang and Z. L. Wang, *Nano Lett.*, 2011, **11**, 4812–4817.
18 R. B. Godfrey and M. A. Green, *Appl. Phys. Lett.*, 1979, **34**, 790–793.
19 R. Brendel and H. J. Queisser, *Sol. Energy Mater. Sol. Cells*, 1993, **29**, 397–401.
20 H. Y. Chen, J. H. Hou, S. Q. Zhang, Y. Y. Liang, G. W. Yang, Y. Yang, L. P. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649–653.
21 K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganas and J. V. Manca, *Nat. Mater.*, 2009, **8**, 904–909.
22 Y. B. Yuan, T. J. Reece, P. Sharma, S. Poddar, S. Ducharme, A. Gruverman, Y. Yang and J. S. Huang, *Nat. Mater.*, 2011, **10**, 296–302.
23 Y. Zhang, Y. Liu and Z. L. Wang, *Adv. Mater.*, 2011, **23**, 3004–3013.
24 T. Ikeda, *Fundamentals of Piezoelectricity*, Oxford University Press, Oxford UK, 1996.
25 S. M. Sze, *Physics of Semiconductor Devices*, Wiley, New York, 1981.
26 G. A. Maugin, *Continuum Mechanics of Electromagnetic Solids*, North-Holland, Amsterdam, 1988.

27 R. W. Soutas-Little, *Elasticity, XVI, 431*, Dover Publications, Mineola, NY, 1999.
28 A. D. Bykhovski, V. V. Kaminski, M. S. Shur, Q. C. Chen and M. A. Khan, *Appl. Phys. Lett.*, 1996, **68**, 818–819.
29 R. Gaska, M. S. Shur, A. D. Bykhovski, J. W. Yang, M. A. Khan, V. V. Kaminski and S. M. Soloviov, *Appl. Phys. Lett.*, 2000, **76**, 3956–3958.
30 A. Janotti and C. G. Van de Walle, *Rep. Prog. Phys.*, 2009, **72**, 126501.