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Schottky junction photovoltaic devices based on CdS single nanobelts

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Abstract
Schottky junction photovoltaic (PV) devices were fabricated on single CdS nanobelts (NBs). Au was used as the Schottky contact, and In/Au was used as the ohmic contact to CdS NB. Typically, the Schottky junction exhibits a well-defined rectifying behavior in the dark with a rectification ratio greater than 10^3 at ± 0.3 V; and the PV device exhibits a clear PV behavior with an open circuit photovoltage of about 0.16 V, a short circuit current of about 23.8 pA, a maximum output power of about 1.6 pW, and a fill factor of 42%. Moreover, the output power can be multiplied by connecting two or more of the Schottky junction PV devices, made on a single CdS NB, in parallel or in series. This study demonstrates that the 1D Schottky junction PV devices, which have the merits of low cost, easy fabrication and material universality, can be an important candidate for power sources in nano-optoelectronic systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Photovoltaic (PV) devices are attractive candidates for clean and renewable power sources [1, 2]. One example is solar cells, which convert solar energy into electrical energy with a respectable conversion efficiency. The widespread concern about energy sources [3, 4] has created a surge in the efforts to exploring solar cells. For example, organic [5, 6], hybrid organic–inorganic [7], all-inorganic [8], and dye-sensitized [9, 10] solar cells have been developed. With the possibility of serving as integrated power sources for nano-optoelectronic systems, semiconductor nanowire (NW) or nanobelt (NB) PV devices have attracted intense attention [11–14]. Lieber *et al* reported axial [11] and coaxial [12, 13] p–i–n NW PV devices with a satisfactory efficiency. However, the high cost and complication of the material fabrication method involved would limit the device application. The Schottky junction is another alternative structure for a PV device. Basically, any semiconductor can form a Schottky junction with a certain metal if the difference between their work functions is large enough, and the carrier density of the semiconductor is moderate. In addition, the fabrication of Schottky junctions has the merits of low cost and simplicity. So far as we know, only two results were reported about the Schottky junction PV devices based on single NWs/NBs. Yu *et al* [14] observed the ZnO NW Schottky PV effect. However, the PV effect is so weak that neither open circuit photovoltage (V_{OC}) nor short circuit current (I_{SC}) could be clearly read out from their measured I–V curve. Atwater *et al* reported Si NW Schottky PV devices [15]. Their V_{OC} and fill factor (FF) were about 0.19 V, and 40%, respectively, comparable to those of ours ($V_{OC} = 0.16$ V, FF $= 42\%$). However, their devices were realized by destroying a certain part of the NW via applying an extremely high current density (>10 kA cm^{-2}), which was a less reliable method, and the nature of the induced junction was not explicitly understood. Here we report on the realization of CdS NB Schottky junction PV devices by microfabrication processes compatible with Si microelectronic integration. The as-fabricated Schottky junction exhibits a well-defined rectifying behavior in the dark, with a rectification ratio greater than 10^3 at ± 0.3 V. Under air mass 1.5 global (AM 1.5G) illumination from a calibrated solar simulator with an intensity of 100 mW cm^{-2}, a typical CdS NB Schottky junction PV device exhibits a V_{OC} of about 0.16 V, an I_{SC} of about 23.8 pA, a maximum output power (P_{max}) of about 1.6 pW, and a FF of about 42%. The output power can further be increased by fabricating more than one such kind of PV device on a single CdS NB and connecting them in parallel or in series according to the device desired. These NB Schottky

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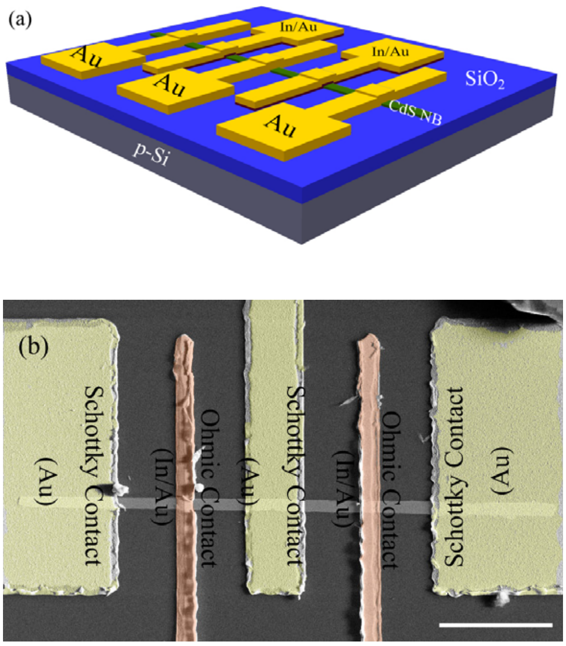

Figure 1. (a) Schematic illustration of the PV devices on a single CdS NB. Three Au Schottky contacts were fabricated on the CdS NB. Two In/Au ohmic contacts were fabricated between the Schottky contacts. (b) An SEM image of an as-fabricated device with three Schottky contacts and two ohmic contacts on a single CdS NB. Scale bar: 20 μm.

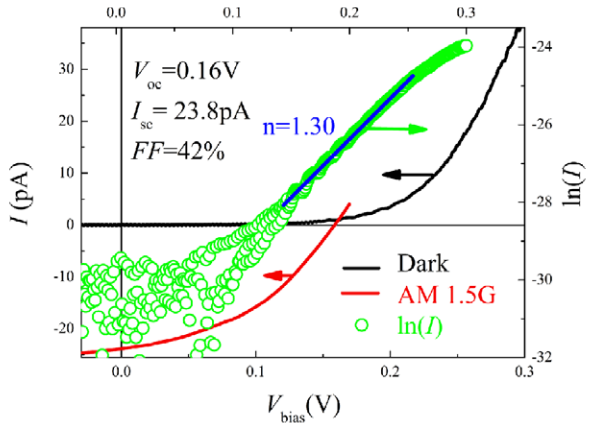

Figure 2. The I–V curves of a typical CdS NB Schottky junction PV device in the dark, and under AM 1.5G illumination. Circles: the I–V curve in the dark on a semi-log scale. The straight line shows the fitting result of the I–V curve by the equation $\ln(I) = qV/nkT + \ln(I_0)$.

junction PV devices provide a valuable example for solar-to-electric energy conversion and have potential applications in integrated nano-optoelectronic systems.

2. Experiments

The n-type CdS NBs used here were synthesized via the chemical vapor deposition method described previously [16]. The NBs had smooth surfaces and uniform width (1–2 μm) along the growth direction. The thicknesses of the CdS NBs as measured by an atomic force microscope were about 80–200 nm. To simultaneous fabricate more than one PV device on a single CdS NB, the CdS NBs were first dispersed in ethanol with an ultrasonic process. Next, the CdS NBs suspension solution was dropped onto oxidized Si substrates each having a 600 nm SiO_2 layer on the top. After that, several Au (100 nm) Schottky contact electrodes [17] with equal space distances were defined on one single CdS NB by UV lithography followed by thermal evaporation and lift-off processes. Finally, several In/Au (10 nm/100 nm) ohmic contact electrodes were defined in between the Schottky electrodes on the CdS NB by similar processes mentioned above. A single PV cell is defined as a Au/CdS NB Schottky junction together with an adjacent ohmic contact to the NB. The space between the Schottky and the ohmic contacts is about 10 μm. The effective area of each cell is defined by the area of the NB beneath the Schottky contact, which is determined by the lithography alignment process. Figure 1(a) shows a schematic illustration of the PV devices on a single CdS NB. Figure 1(b) shows a scanning electron microscope (SEM) image of an as-fabricated device with three Schottky contacts and two ohmic contacts on a single CdS NB. Room-temperature electrical transport and PV properties were characterized with a semiconductor characterization system (Keithley 4200) and a solar simulator (Newport 91160-1000) with a calibrated illumination power density of 100 mW cm^{-2}.

3. Results and discussions

The typical I–V characteristics of such a CdS NB Schottky junction PV device in the dark, and under AM 1.5G illumination, are shown in figure 2. During the measurement, the ohmic contact electrode was grounded. The I–V curve in the dark shows an excellent rectification characteristic. At a forward bias of +0.3 V, the current is about 39 pA; while the reverse leakage current at a reverse bias of −0.3 V is less than 10^{-2} pA. Hence, the rectification ratio is about 4×10^3 at ±0.3 V. The I–V relationship of a metal–semiconductor Schottky junction can be expressed as $\ln(I) = qV/nkT + \ln(I_0)$, where q is the electronic charge, k is the Boltzmann constant, I_0 is the saturation current, and n is the ideality factor. For an ideal Schottky barrier, $n = 1$ [18]. Here, by fitting the measured I–V curve in the dark with the above equation (the fitting result is the straight line in figure 2), we obtain $n = 1.30$. Under AM 1.5G illumination, the single NB Schottky junction PV device exhibits clear PV behavior. The obtained V_{OC}, I_{SC}, and FF of it are about 0.16 V, 23.8 pA, and 42%, respectively. The P_{max} is about 1.6 pW. Note that in the first quadrant, the current under AM 1.5G illumination tends to be higher than the dark current. This phenomenon results from the photoconductive behavior of the CdS NB [19, 20].

The principle of a Schottky junction PV device can be understood qualitatively by plotting the energy band diagrams. Because the electron density of the CdS NB used here is moderate, metals with a higher work function (herein the Au) tend to form a Schottky contact, while those with a lower work function (herein the In) tend to form an ohmic contact

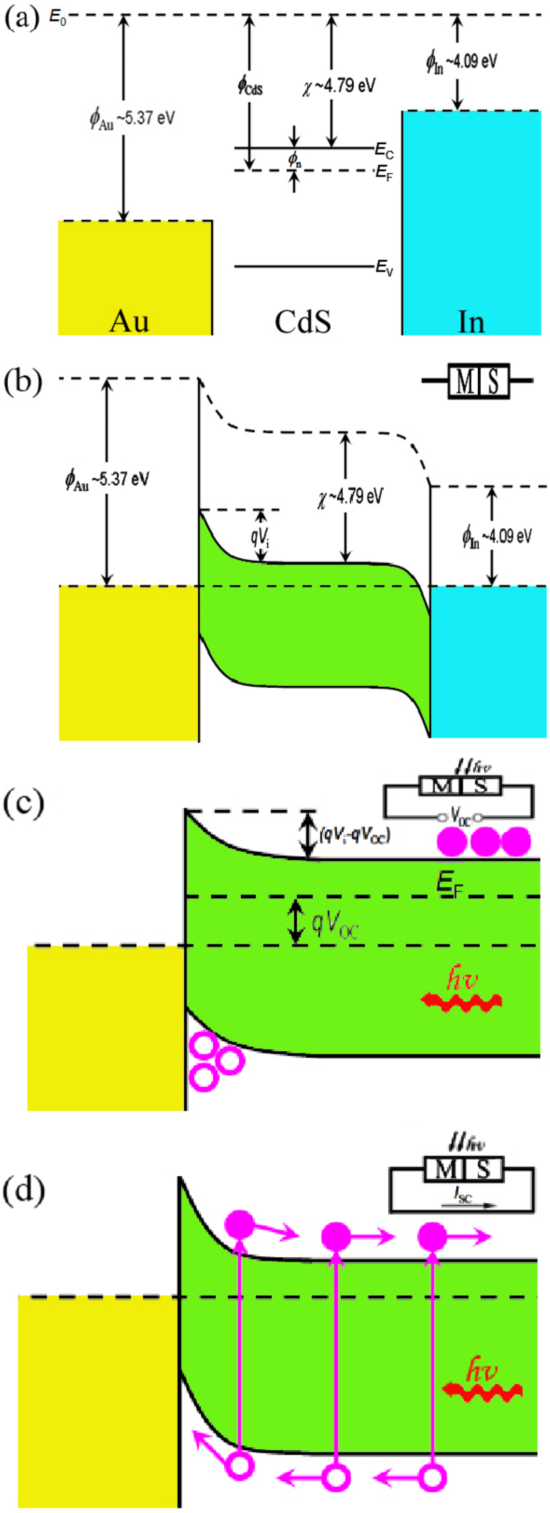

Figure 3. (a) The energy band diagrams of Au, CdS and In before contacting. (b) The thermal equilibrium energy band diagram of the Schottky junction in the dark. (c) and (d) The energy band diagrams of an open-circuited and a short-circuited Schottky junction PV device illuminated by light with photon energies higher than the bandgap energy of the semiconductor, respectively. Insets: the corresponding circuit schematics.

with the CdS NBs. Figure 3(a) shows the Au, CdS and In energy band diagrams prior to contacting. The electron affinity of the CdS is χ (4.79 eV) [21]. $\phi_n(=(k_B T)\ln(N_c/n_e))$ is the depth of the Fermi level below the CdS conduction band edge, where N_c is the effective density of state in the conduction band ($N_c \sim 2.44 \times 10^{18}$ cm^{-3}), and n_e is the electron density of CdS NB [16]. The work functions of Au (ϕ_{Au}) and In (ϕ_{In}) are about 5.37 and 4.09 eV, respectively [22]. E_C, E_V, E_F correspond to the conduction band edge, valence band edge, and Fermi level of the CdS. E_0 corresponds to the vacuum level. Figure 3(b) shows the thermal equilibrium energy band diagram after contacting. A space charge region (i.e., a junction) accompanied by a built-in field forms in the semiconductor near the Au/CdS interface. The built-in potential V_i of the Schottky junction can be described with the equation $V_i = (\phi_{Au} - \phi_{CdS})/e = (\phi_{Au} - \chi - \phi_n)/e$. Assuming $n_e \sim 10^{13}$ cm^{-3} (the measured resistivity is $\sim 10^3$ Ω cm, the electron mobility for CdS NB is about 300 cm^2 V^{-1}s^{-1} [16]), we can estimate ϕ_n to be about 0.3 eV. Thus, V_i can be obtained to be about 0.3 V. The photovoltaic effect is based on the separation of photogenerated electrons and holes in the built-in field of the junction (resulting a photocurrent) when the junction area is illuminated by light with photon energies higher than the bandgap energy of the semiconductor. In the semiconductor this requires the diffusion of the photogenerated minority carriers to the junction where they are swept to the other side. When the PV device is open-circuited (figure 3(c)), the separation of photogenerated electrons and holes will produce an open circuit voltage V_{OC}. At this state, the quasi-Fermi levels of metal and semiconductor are separated with an energy offset of qV_{OC}, corresponding to applying a forward bias (V_{OC}) to the Schottky junction. The photocurrent is opposite to the forward-biased current of the device. At $V = V_{OC}$, these two currents will cancel each other and result in a zero net current. When the PV device is short-circuited (figure 3(d)), the extracted photogenerated carriers can transit through the external circuit, generating a short circuit current I_{SC} [23]. The corresponding circuit schematic is plotted in the upper right corner of each figure.

We have fabricated dozens of this kind of Schottky junction PV devices; they exhibit similar PV behavior, with V_{OC} varying from 0.10 to 0.16 V, and I_{SC} varying from 10 to 60 pA. Basically, the output power of a PV device can further be multiplied by connecting two or more such Schottky junction PV devices in parallel or in series. For an example, the I–V characteristics of two PV devices (labeled as PV1 and PV2) connected in parallel, and two PV devices (labeled as PV3 and PV4) connected in series are shown in figures 4(a) and (b), respectively. The I–V characteristics of PV1 and PV2, and those of PV3 and PV4 are also plotted in figures 4(a) and (b), respectively, for comparison. The I_{SC} are about 11, 21, 24, and 55 pA, and V_{OC} are about 0.11, 0.13, 0.12, and 0.14 V, for PV1, PV2, PV3, and PV4, respectively. In the parallel device configuration, the V_{OC} is 0.14 V, close to the V_{OC} values of PV1 and PV2, while the I_{SC} is about 33 pA, equal to the sum of the I_{SC} values of PV1 and PV2. In the series device configuration, the I_{SC} is 24 pA, equal to the I_{SC} value of PV3 (the smaller one), while the V_{OC} is 0.24 V, about equal to the sum of the V_{OC} values of PV3 and PV4. SEM images of the devices together with the circuit connection schematics are plotted in the insets of the corresponding figures.

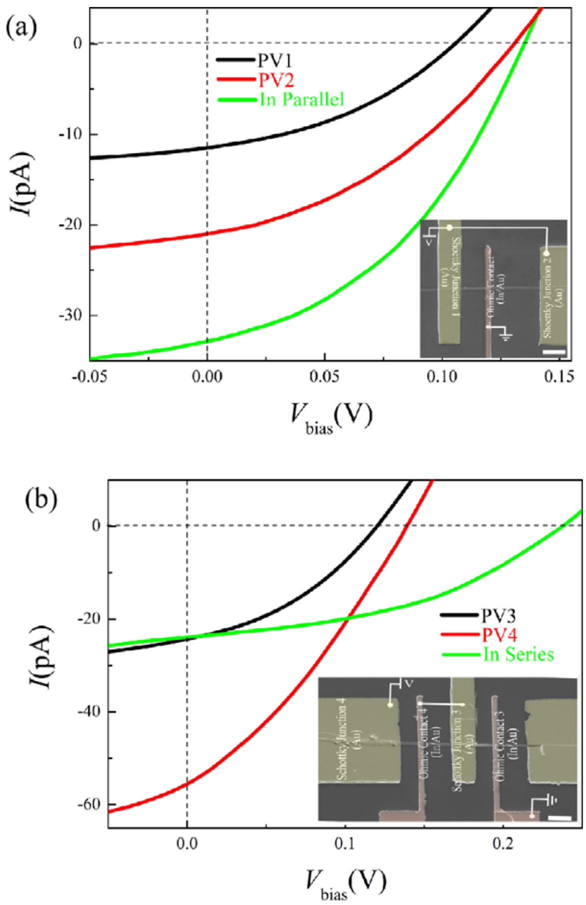

Figure 4. (a) The I–V characteristics of PV1, PV2, and the two PV devices (PV1 and PV2) connected in parallel under AM 1.5G illumination. (b) The I–V characteristics of PV3, PV4, and the two PV devices (PV3 and PV4) connected in series under AM 1.5G illumination. Insets: SEM images of the corresponding devices together with the circuit connection schematics. Scale bars: 10 μm.

Note that, in our case, the thickness of the Au Schottky contact metal film is about 100 nm, which will give a maximum transmission ratio of less than 0.5% in the simulated solar spectrum range (not shown here). This means that, in our case, most of the simulated solar energy is absorbed by the Au film, which greatly limits the performance of our PV devices. In order to further improve the performance of our PV devices, more experiments, including optimizing the Au film thickness and/or exploring new Schottky contact metal materials, are proceeding.

4. Conclusion

In summary, Schottky junction PV devices were fabricated on single CdS NBs. The Schottky junction exhibits a well-defined rectifying behavior in the dark, with a rectification ratio greater than 10^3 at ± 0.3 V. A typical such PV device exhibits a V_{OC} of 0.16 V, an I_{SC} of 23.8 pA, a P_{max} of 1.6 pW, and a FF of 42%. Moreover, the output power can be multiplied by connecting two or more of the PV devices made on a single NB in parallel or in series. The performance of the PV device can further be improved via straightforward methods, such as optimizing the Schottky contact electrode, etc. These single NB Schottky junction PV devices provide a valuable example for solar-to-electric energy conversion and have potential applications in integrated nano-optoelectronic systems.

Acknowledgments

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