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Effect of interface incorporation of cadmium nanocrystallites on the photovoltaic performance of solar cells based on CdS/Si multi-interface nanoheterojunction

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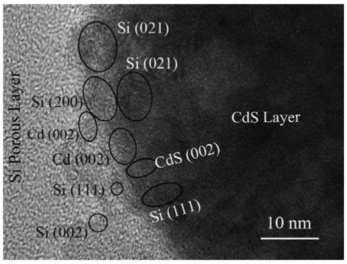
HIGHLIGHTS

- Solar cells based on CdS/Si multi-interface nanoheterojunctions are prepared.
- Cd nanocrystallites (nc-Cd) are incorporated naturally into the heterojunction interface.
- The cell energy conversion efficiency is greatly promoted because of nc-Cd incorporation.

GRAPHICAL ABSTRACT

A multi-interface CdS/Si nanoheterojunction is prepared through growing CdS nanocrystallites (nc-CdS) onto silicon nanoporous pillar array (Si-NPA) by a chemical bath deposition method. Utilizing the surface reducibility of Si-NPA, Cd nanocrystallites (nc-Cd) are incorporated naturally into CdS–Si interface. The experimental results show that the interface incorporation of nc-Cd can promoted greatly the energy conversion efficiency of the solar cells based on CdS/Si-NPA.



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ABSTRACT

A non-planar and multi-interface CdS/Si nanoheterojunction was prepared by growing CdS nanocrystallites (nc-CdS) onto silicon nanoporous pillar array (Si-NPA) using a chemical bath deposition (CBD) method. Utilizing the surface reducibility of Si-NPA, small quantities of Cd nanocrystallites (nc-Cd) were incorporated naturally into the CdS–Si interface during the CBD process. Solar cells with a device construction of ITO/CdS/Si-NPA/Al were prepared based on CdS/Si-NPA and their photovoltaic performances, including open circuit voltage, short circuit current density, external quantum efficiency and energy conversion efficiency, were measured under simulated AM 1.5 G illumination. Compared with CdS/Si-NPA cells without nc-Cd incorporation, an energy conversion efficiency promotion by two orders of magnitude was achieved, which was ascribed to the reduction of the series resistance resulted from the nc-Cd incorporation at the interface. Our results show that the incorporation of nc-Cd at CdS–Si interface might be an effective path for obtaining high-efficiency solar cells based on CdS/Si multi-interface nanoheterojunctions.

1. Introduction

Solar cells have long been thought a promising clean and renewable energy source to replace the traditional fossil fuels in the future. Nevertheless, the realization of the blueprint depends

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highly upon the low-cost and environment-friendly fabrication of solar cells with high energy conversion efficiency and long device lifetime. Besides the traditional solar cells based on silicon (Si) bulk materials [1,2] and thin films [3], some newly appeared solar cells such as those based on polymers [4], semiconductor quantum dots [5] and various nanostructures [6,7] also attracted much attention. In recent years, mainly due to the technical maturity and remarkable physical and chemical properties differed from bulk Si, various Si nanostructures were extensively studied as building blocks for high-performance electronic and photonic devices [8–11]. In particular, the strong light absorption and efficient charge separation found in various Si-based heterojunctions, which were constructed by growing compound semiconductors on Si nanostructures, make the fabrication of high-efficiency Si-based nano solar cells be hopeful [12–15]. Some recent progresses demonstrated that efficient light absorption and enhanced electron harvesting were achieved in solar cells based on p-Si nanopillar array/cadmium sulfide (CdS)/zinc oxide (ZnO) [15], and relatively high energy conversion efficiency was obtained in solar cells based on zinc selenide (ZnSe) nanoribbon/Si nanowire [16]. In these experiments, the promoted photovoltaic performances were all attributed to the improvement of bandgap matching and the enhancement of light absorption caused by the formation of compound semiconductor/Si nanoheterojunctions.

In the previous study, we reported the preparation and characterization of Si nanoporous pillar array (Si-NPA), a Si hierarchical structure characterized by a regular array of micron-sized, quasi-identical and highly nanoporous Si pillars [17]. The light reflectance of Si-NPA was reduced to as low as ~2% in the wavelength range of 400–1000 nm [17]. The optical and electrical properties observed in both Si-NPA and the nanoheterosystems based it demonstrated that Si-NPA might be a promising functional substrate in constructing Si-based optoelectronic devices [18–20]. Similar to the discussion on other nanosystems [21], there the specific physical properties of light absorption and electron transport were ascribed to the quantum effect of nanostructures. Especially, through constructing a CdS/Si nanoheterostructure based on Si-NPA (CdS/Si-NPA), a high-efficiency separation of photon-generated carriers was realized and an obvious photovoltaic effect was observed [20]. Nevertheless, only a relatively small short circuit current and a low energy conversion efficiency were achieved by the system, and the apparent reason was due to the big series resistance in magnitude of $\sim 10^5\ \Omega\,\mathrm{cm}$ [20]. Just as pointed out by other groups [22,23], the big series resistance of a solar cell could lead to the shortening of the carrier diffusion length and the strengthening of the carrier recombination probability, both of which would result in the decreasing of short circuit current and energy conversion efficiency. In the case of CdS/Si-NPA solar cell [20], because the adopted initial Si wafers were heavily boron-doped ones, the series resistance should mainly originate from CdS thin film. To reduce the resistance of CdS thin films or nanostructures, the introduction of foreign atoms was a usually adopted method [24–26]. It has been reported that a resistivity as low as $4.6 \times 10^{-2}\ \Omega\,\mathrm{cm}$ was obtained by introducing aluminum into CdS films [24], and the electrical conductivity of CdS nanopillars was promoted by 4 orders of magnitude through indium doping [25]. Clearly, the above mentioned examples were typical semiconductor doping method, in which the choice of doping elements and the control of the doping concentration were important factors for obtaining an optimal doping effect without damaging the crystallinity seriously [27].

Besides the usually used doping method, the incorporation of metal nanocrystallites at the interface might also be an effective method to improve the electrical conductivity across a nanoheterojunction [28,29]. In this paper, we report that a non-planar and multi-interface CdS/Si nanoheterojunction, whose interface was constructed by alternatively and randomly dispersed Si and CdS nanocrystallites (nc-Si and nc-CdS), was prepared through growing hexagonal CdS on Si-NPA by a chemical bath deposition (CBD) method. Owing to the strong surface reducibility of Si-NPA, small amount of hexagonal cadmium nanocrystallites (nc-Cd) were formed and embedded at Si-CdS interface. The photovoltaic effect of the samples prepared with different CdS deposition time were studied by measuring the open circuit voltage, short circuit current, external quantum efficiency and energy conversion efficiency, and the according physical mechanism was analyzed. Our results show that the incorporation of nc-Cd at CdS–Si interface might be an effective path for obtaining high-efficiency solar cells based on CdS/Si multi-interface nanoheterojunctions.

2. Experiments

The Si-NPA substrate was prepared by hydrothermally etching (1 1 1)-oriented, p-type single crystal silicon (sc-Si) wafers in the aqueous solution of hydrofluoric acid containing ferric nitrate. The procedure and conditions have been described in detail elsewhere [17]. The CdS thin film was deposited on Si-NPA by a CBD method and the preparing procedures were described as the followings. The bath solution was prepared by mixing the solutions of cadmium chloride ($0.04\ \mathrm{mol\,l^{-1}}$, 75 ml) and aqueous ammonia (25–28%, 15 ml). The mixing process was lasted for 60 min under continuous magnetic agitation, during which the bath temperature was kept at 80 °C. Then 5 ml ammonium chloride ($0.1\ \mathrm{mol\,l^{-1}}$) and 5 ml thiourea ($2.0\ \mathrm{mol\,l^{-1}}$) were added to the mixed solution in turn. In the chemical reaction process, ammonium chloride was used as a buffering agent to slow down the chemical reaction rate. Five minutes later, Si-NPA wafers were immersed in the solution for 30, 40, 50 and 60 min, respectively, to grow CdS thin films with different thickness. After the CBD process, the samples were taken out of the solution, washed with de-ionized water, and dried in nitrogen flow. Through growing indium tin oxide (ITO, ~100 nm) and aluminum (Al, ~500 nm) thin films on CdS/Si-NPA as front transparent electrode and back electrode by magnetron sputtering and vacuum electron evaporation methods, respectively, solar cells with a structure of ITO/*n*-CdS/*p*-Si-NPA/sc-Si/Al were prepared.

The morphology and structure of as-prepared CdS/Si-NPA were characterized by a field-emission scanning electron microscope (FE-SEM, JSM 6700F), a high-resolution transmission electron microscope (HR-TEM, JEM-2100) and a powder X-ray diffractometer (XRD, Panalytical X'Pert Pro) using Cu*k*α as the X-ray source ($\lambda = 1.5046$ Å), respectively. The integral diffuse reflection spectra of CdS/Si-NPA were measured with an UV–vis–IR spectrophotometer (Shimadzu, UV-3150) equipped with an integrating sphere. The photovoltaic performance was investigated in air under simulated AM 1.5 G solar irradiation ($100\ \mathrm{mW\,cm^{-2}}$) at room temperature, and the illumination of light was precisely calibrated by a standard silicon solar cell.

3. Results and discussions

The XRD spectra of CdS/Si-NPA prepared with four different deposition times, 30, 40, 50 and 60 min, respectively, were shown in Fig. 1. Here each spectrum has been normalized according to the intensity of its strongest diffraction peak. Clearly, two sets of diffraction peaks were observed in each spectrum, which were indexed to diffractions from hexagonal CdS and hexagonal Cd, respectively. The peaks located at 26.65°, 44.16° and 52.38° were due to the reflections from the crystal family planes of CdS (0 0 2), (1 1 0) and (1 1 2), and those located at 31.72°, 34.69° and 38.39°