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$CH_3NH_3PbI_3$/GeSe bilayer heterojunction solar cell with high performance

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ABSTRACT

Perovskite ($CH_3NH_3PbI_3$) solar cells have made significant advances recently. In this paper, we propose a bilayer heterojunction solar cell comprised of a perovskite layer combining with a IV-VI group semiconductor layer, which can give a conversion efficiency even higher than the conventional perovskite solar cell. Such a scheme uses a property that the semiconductor layer with a direct band gap can be better in absorption of long wavelength light and is complementary to the perovskite layer. We studied the semiconducting layers such as GeSe, SnSe, GeS, and SnS, respectively, and found that GeSe is the best, where the optical absorption efficiency in the perovskite/GeSe solar cell is dramatically increased. It turns out that the short circuit current density is enhanced 100% and the power conversion efficiency is promoted 42.7% (to a high value of 23.77%) larger than that in a solar cell with only single perovskite layer. The power conversion efficiency can be further promoted so long as the fill factor and open-circuit voltage are improved. This strategy opens a new way on developing the solar cells with high performance and practical applications.

1. Introduction

Photovoltaic (PV) devices are used to convert the solar energy into electricity. How to choose appropriate materials is an indispensable issue in design of PV devices. A number of properties are required for candidate PV materials, such as strong optical absorption over a wide range of light wavelength and good collection properties for carriers and low cost in large-scale applications (Reithmaier et al., 2011). Single crystal and polycrystalline Si have dominated the PV industry for long time owing to its mature manufacturing technology and abundant sources. Due to the indirect band gap of Si, the absorption of light has to be mediated by phonon-assisted processes, giving rise to limitations on the efficiency. Therefore, it is highly desired to look for better materials with direct band gap for a replacement of Si in solar cells, and much effort was paid over the years. To name a few, GaAs is a kind of semiconductor with direct band gap and shows good optical properties, and the efficiency in GaAs-based thin-film solar cell has been realized at 28.8% (Moon et al., 2016). However the high price is one of main obstacles to restrict massive applications of GaAs-based solar cells. The polycrystalline CdTe-based solar cell can absorb 90% of the solar spectra with only 1 μm thick (Asim et al., 2012), but the main obstacle is the toxicity of cadmium, and thus, CdTe is not suitable for a large-scale and green PV application (Shah et al., 1999). Organic solar cells have developed rapidly in recent decades due to technical developments of semiconducting polymers (Nunzi, 2002; Hoppe and Sariciftci, 2004), which have many advantages, including low cost materials, high-throughput roll-to-roll production, mechanical flexibility and light weight (Zhao et al., 2016), but high stability and long cyclic lifetime are still big challenges. So, the mixed organic-inorganic halide perovskites ($CH_3NH_3PbX_3$, X = Cl,Br,I) jump into the stage and become booming PV materials in short time, where the conversion efficiency of perovskite-based solar cells rises rapidly from 3.8% to 22.1% in past few years (Lin et al., 2015; Li et al., 2016).

$CH_3NH_3PbI_3$ as an ambipolar semiconductor (n- or p-type) has intense light absorption and long diffusion length and lifetime of carriers. These advantages lead to a high power conversion efficiency (PCE) in $CH_3NH_3PbI_3$-based solar cells. Perovskite solar cells have various structures such as liquid-electrolyte dye-sensitized cells, mesoporous structure, planar n-i-p structure, planar p-i-n structure, HTL-free cells, and ETL-free cells (Zuo et al., 2016). The planar p-i-n structure solar cell uses $CH_3NH_3PbI_3$ as an active layer to absorb light, while the layers above and beneath it play the role in conducting holes and electrons (Lin et al., 2015). The semi-transparent planar perovskite solar cells (Fu et al., 2015) are also pursued for further improving the efficiency of

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perovskite solar cells.

The wavelength of light absorbed by perovskite solar cells ranges from 300 nm to 800 nm. This means the absorption energies are limited to the visible light, and most infrared light are actually wasted. Besides, the absorption coefficient of perovskites drops over 90% at wavelengths beyond 650 nm (Green et al., 2014; Yin et al., 2014). However, it is well known that the invisible "near-infrared" (700–2500 nm) radiation carries more than half of the power of sunlight (Santamouris, 2008). Therefore, to improve the efficiency of energy utilization in a solar cell, recycling such wasted energies is an imperative choice. Unfortunately, it is impossible to reach this goal in a single-layer perovskite solar cell since the absorbers have fixed bandgaps that may bring limitations on absorbing energies.

One idea is to combine more solar cells serially connected into a tandem (multi-junction (MJ)) solar cell. MJ solar cells are made of multiple p-n junctions from different semiconductors. Each p-n junction produces electric current in response to different range of wavelengths of solar spectrum, aiming to improve the total energy conversion efficiency. Usually, there are two ways for MJ solar cell fabrication: series connection and parallel connection. For the former, a single current passes and only two electrodes are required. The single current is in fact determined by the weakest current generated in one sub-cell subject to the current match condition, constraining the performance of entire MJ solar cell. While for the latter, each sub-cell is connected by separate electrodes and the output from each sub-cell can be independently optimized. But it is not easy to fabricate the middle electrode in practice (Bremner et al., 2008).

We propose, in this work, a solar cell based on a bilayer p-n heterojunction serving as an active layer. One layer is selected to be perovskite, i.e. $CH_3NH_3PbI_3$, whose band gap is 1.5 eV, and the cut-off wavelength is 827 nm according to $\lambda = \frac{hc}{E_g}$, where h is the Planck constant, c is the velocity of light, and E_g is the band gap of the material. To recycle the unabsorbed energies of the light after penetrating into the perovskite layer, it is instructive to add another layer which should absorb the energies ranging in 800–1200 nm. To achieve this aim, we notice that the narrow-band-gap IV-VI group semiconductors constitute an important class of materials for photovoltaic applications (Vaughn et al., 2015). IV-VI group layered semiconducting compounds (e.g., SnS, SnSe, GeS, and GeSe) have attracted much attention due to their interesting optical and electrical properties (El-Rahmana et al., 2014; Deng et al., 2012), which can be efficient PV materials with suitable bandgaps ranging from 0.5 eV to 1.5 eV (Huang et al., 2016). In particular, GeSe is a layered semiconductor that is predicted to bear a high chemical stability (Ulaganathan et al., 2016) and can be used as low-cost components of photovoltaic cells (Vaughn et al., 2015). The experimental bandgap of GeSe is 1.1 eV (Elkorashy, 1989), implying that it is suitable for an active absorber in a solar cell. It was also shown to be promising materials for ultrathin-film flexible photovoltaic applications with high conversion efficiency, and can compete with organic and dye-sensitized solar cells (Shi and Kioupakis, 2015). Therefore, we select these kind of IV-VI group semiconductors as another layer in our bilayer heterojunction solar cell structure. Here it is interesting to mention that we are pursuing to improve the efficiency of a *single* p-n junction solar cell rather than a multi-junction solar cell. This may increase the output energy density, and there is no current match requirement for such a single p-n junction solar cell in our study.

2. Optical absorption of the bilayer solar cell

The structure of the bilayer solar cell we propose here is shown in Fig. 1. The top layer is a glass with thickness 100 nm, and the second layer is 80 nm thick Indium tin oxide (ITO) which is taken as the anode of the solar cell. Perovskite ($CH_3NH_3PbI_3$) layer and IV-VI group semiconductor layer constitute a n-p heterojunction and are taken as active layers expected to absorb almost all light through the whole cell device. As $CH_3NH_3PbI_3$ as a semiconductor with wide band gap absorbs relatively short wavelength visible light, the layer of narrow-band-gap IV-VI group layered semiconductors under the $CH_3NH_3PbI_3$ layer can absorb the infrared light. The thickness of $CH_3NH_3PbI_3$ is taken to be 350 nm according to a previous experiment (Lin et al., 2015), and that of the IV-VI group semiconductor layer is set as 450 nm. On the top of $CH_3NH_3PbI_3$, there is an electronic transport layer (ETL): PC60BM ((6,6)-phenyl-C61-butyric acid methyl ester), and under the IV-VI group semiconductor layer, there is a hole transport layer (HTL): PCDTBT (poly(N-9′-heptadecanyl-2,7-carbazole-alt- 5,5-(4′,7′-di(thien-2-yl)-2′,1′,3′-benzothiadiazole))) (Lin et al., 2015). The bottom layer is 100 nm thick Ag as cathode.

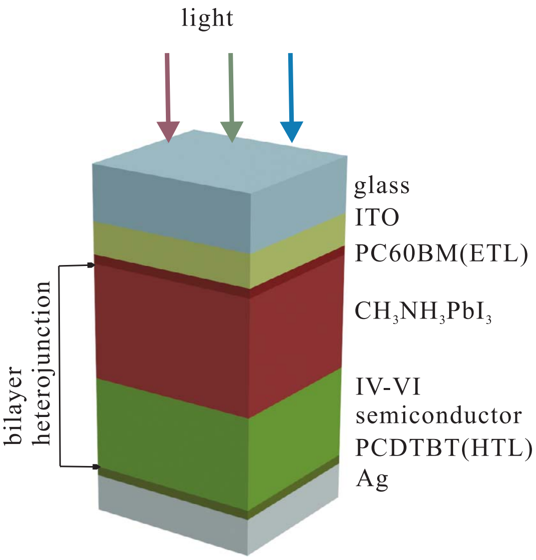

Fig. 1. The schematic structure of the bilayer solar cell device. The active layer is a bilayer heterojunction comprised of $CH_3NH_3PbI_3$ layer and a IV-VI group semiconductor layer. A p-n junction is formed in the bilayer heterojunction.

For IV-VI group semiconductor layers, here we consider GeSe, SnSe, GeS and SnSe due to their suitable direct bandgaps. The dielectric constants of these materials are taken from Ref. Eymard and Otto (1977). According to the following equation

$$n = \frac{1}{\sqrt{2}}\left(\epsilon_1 + (\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}}\right)^{\frac{1}{2}},$$
$$k = \frac{1}{\sqrt{2}}\left(-\epsilon_1 + (\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}}\right)^{\frac{1}{2}}, \tag{1}$$

we can get the refractive index of materials (Fox, 2001), where ϵ_1 and ϵ_2 are the real and the imaginary part of dielectric constants, respectively, and n and k are the real and imaginary part of the refractive index. Taking the refractive index as an input parameter, we use the methods described in Wang and Su (2014) and Wang et al. (2015, 2016) to calculate the absorption efficiency. The other parameters are taken from Ref. Wang et al. (2016).

We summarize the experimental bandgaps and corresponding cutoff wavelengths for bulk IV-VI group layered semiconductors, namely GeS, SnS, GeSe, and SnSe in Table 1. As the cutoff wavelengths in the range of 1000–1200 nm are proper, GeSe and SnSe may be better choices for the present purpose. This can be seen clearly in Fig. 2 in which the absorption of the solar cell is calculated. "Device" labels the entire absorption for the solar cell consisting of the bilayer heterojunction of $CH_3NH_3PbI_3$/IV-VI group semiconductor layers. The curves labeled by "$CH_3NH_3PbI_3$" or IV-VI group semiconductors represent the contributions of these two materials in the cell device. Fig. 2(a) gives the absorption efficiency in the case of GeSe and $CH_3NH_3PbI_3$ as active layers. One may see that $CH_3NH_3PbI_3$ shows a strong absorption in the range of 300–800 nm in accordance with the bandgap. However, there is no