Recent progress of crystal growth, conductivity control and solar cells of semiconducting barium disilicide

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Abstract

Semiconducting barium disilicide (BaSi₂) has attractive features for thin-film solar cell applications; both a large absorption coefficient comparable to copper indium gallium diselenide and a minority-carrier diffusion length much larger than the grain size of BaSi₂ can be used to improve solar cells properties. In this presentation, we explore the potential of semiconducting BaSi₂ films for thinfilm solar cell applications. We start by describing its crystal and energy band structure, followed by the optical and electrical properties of BaSi₂ films. Special attention was paid to the minority-carrier properties. Finally, we demonstrate the operation of p-BaSi₂/n-Si heterojunction solar cells and discuss prospects for future development.

1. Introduction

Silicon is safe, stable, and earth-abundant, and crystalline silicon (c-Si) solar cells will continue to play an important role for the sustainable supply of energy in the near future. However, there are two main drawbacks to using crystalline silicon. One drawback is that c-Si is an indirect band-gap semiconductor, which leads to it having a relatively low absorption coefficient. To efficiently absorb sunlight the wafer must therefore be thick, and the average wafer thickness for commercially available solar cells amounts to ~180 µm. Although further reduction in the wafer thickness to $\sim 100 \ \mu m$ in 2023 is predicted, there will be a lot of technical challenges. Even if one can reduce the wafer thickness down to 100 µm, c-Si wafers will still account for the majority of the cell's price and thus the thickness reduction will not have a drastic impact on decreasing manufacturing costs. Another drawback is the width of its band gap. The band gap of silicon (1.1 eV) is slightly narrower compared with the ideal band gap (~1.4 eV) for a single-junction solar cell. Kaneka recently reported a record efficiency of 26.33% using a back-contact heterojunction c-Si solar cell by utilizing advanced processing [1]. The achieved efficiency is already very close to the theoretical Shockley-Queisser limit for a 1.1 eV band gap [2], and thus there is little room for further improvement in this regard. To overcome the drawbacks of silicon, thin film solar cells using alternative materials with wider band gaps have been intensively studied and developed; for example, cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS) thin film solar cells have already been commercialized. However, these materials lack some important properties for global deployment. Solar cell materials should be safe, stable, and earth-abundant like silicon. The ideal alternative absorber material for thin film solar cells should have a high absorption coefficient, long minority carrier lifetime, and band gap close to 1.4 eV. Orthorhombic barium disilicide (BaSi₂) has all these properties, which will be described in the following sections.

2. Energy band structure

Figs. 1(a) and 1(b) show the partial densities of states (DOS) of Si *s*, *p*, and Ba *s*, *p*, and *d* states, and their energy band structures, respectively. The Si *p* state appears dominant in the valence band maximum (VBM), while the conduction band minimum (CBM) mainly consists of the Ba *d* state, leading to large values of the dipole matrix elements [3]. A direct transition occurs at approximately (0, 1/3, 0), and its gap value is higher than the band gap by approximately 0.1 eV. This might be the reason why experimental studies have revealed that BaSi₂ has high absorption coefficients in spite of its indirect band gap nature [4]. The effective mass for electrons and for holes are 0.41 and 0.53, respectively [3]. The effective density of states in conduction band and that in valence band is calculated to be 2.6×10^{19} cm⁻³ and 2.0×10^{19} cm⁻³, respectively.



Fig. 1(a) Partial DOSs and (b) energy band structure of BaSi₂ [5].

5. p-BaSi₂/n-Si solar cells

A pn homojunction diode is the most straightforward structure of a solar cell. In ref. 6, the spectral response of BaSi₂ p^+n abrupt homojunction diodes is discussed using experimentally obtained absorption coefficients, minority-carrier diffusion lengths, and minority-carrier lifetimes, where $\eta >$ 25% is expected for 2 µm thick BaSi₂ homojunction solar cells under ideal conditions. Here, we choose to begin with a p-BaSi₂/n-Si heterojunction structure. Fig. 2(a) shows the expected band alignment of a p-BaSi₂/n-Si junction diode when p is 2×10^{18} cm⁻³ for p-BaSi₂ and n is 2.0×10^{15} cm⁻³ for n-Si. There is a conduction band offset $\Delta E_{\rm C} = 4.05 - 3.2 \approx$ 0.9 eV and a valence band offset $\Delta E_V = (4.05 + 1.1) - (3.2 + 1.1)$ 1.3) \approx 0.7 eV at the heterointerface. The band offsets $\Delta E_{\rm C}$ and $\Delta E_{\rm V}$ promote the separation of photogenerated electrons and holes in p-BaSi₂, as well as those in n-Si, which is how it operates as a solar cell. Therefore, we anticipate that BaSi₂ will be useful as a hole selective contact for c-Si solar cells. On an n-Si(111) substrate, we formed B-doped p-BaSi₂ epitaxial layers with various layer thicknesses ranging from 10 nm to 50 nm by MBE, followed by a 3-4 nm thick a-Si capping layer. We set p in the p-BaSi₂ sample to 2×10^{18} cm⁻³. Finally, 1 mm diameter and 70 nm thick ITO electrodes were sputtered on the front surface, and Al electrodes were deposited on the backside of the n-Si substrate. The a-Si capping layer is necessary to prevent surface oxidation of the p-BaSi₂ and to ensure efficient hole transport to the ITO. Fig. 2(b) shows the TEM cross section of the sample when the p-BaSi₂ layer thickness is 20 nm. The a-Si/BaSi₂ and BaSi₂/Si interfaces are very smooth.



Fig. 2(a) band alignment and cross-sectional TEM image [7].

Fig. 3(a) shows the current-density versus voltage (J-V)curves under AM1.5 illumination. All the samples performed as solar cells [8]. This result clearly demonstrates that the p-BaSi₂/n-Si heterointerface does not hinder the transport of photogenerated electrons in p-BaSi2 to the n-Si side, and photogenerated holes in n-Si migrate to the p-BaSi2 side as expected. The efficiency reaches 9.9% when the p-BaSi₂ layer thickness is 20 nm. In the present device, p was set to a relatively large value of 2×10^{18} cm⁻³. So it becomes difficult for the photogenerated minority carriers (electrons) in p-BaSi2 to diffuse to the n-Si side before recombination. The minoritycarrier lifetime of B-doped p-BaSi₂ with various p quantities, measured by μ -PCD, increases from 0.07 μ s to 2 μ s [9] when p decreases from 3.9×10^{18} cm⁻³ to 1.4×10^{16} cm⁻³. Increasing the layer thickness of p-BaSi₂ with much smaller p values might be an effective way to enhance the contribution of p- $BaSi_2$ to the photocurrent. Note that we will be able to convert the present p-BaSi₂/n-Si heterojunction structure into a BaSi₂ pn homojunction diode by forming an n-BaSi₂ layer on a lightly-doped relatively thick p-BaSi₂ absorber-layer grown

on a Si substrate with small ρ , and further to a BaSi₂-pn/Si-pn tandem structure. Replacing half the Ba⁽¹⁾ sites with isoelectric Sr expands the band gap of BaSi₂ by 0.1 eV [10]. A broadening of the band gap by substituting Ba with Sr [11] and by substituting Si with C is theoretically expected [12]. There is still plenty of room for improvement in η as well as in BaSi₂ device structures. We therefore hope that many researchers will be interested in using this material.

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Fig. 3 (a) *J*-*V* curves under AM1.5 illumination. p-BaSi₂ layer thickness was varied as10, 15, 20, 30, and 50 nm. (b) *EQE*, *IQE*, and *R* spectra of the p-BaSi₂(20 nm)/n-Si heterojunction solar cell. The contributions of BaSi₂ and Si are also denoted by EQE(BaSi₂) and EQE(Si), respectively [8].

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