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Evaluation of vanadium substituted In_2S_3 as a material for intermediate band solar cells

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ABSTRACT

The potential of vanadium substituted In_2S_3 as the active material in intermediate band solar cells (IBSCs) is investigated. The study is performed with a detailed balance model developed by Cuadra et al. that takes into account the shape and overlap of the absorption coefficients. Despite having values of the band gaps that could in principle lead to highly efficient IBSCs, it is found that cells with a practical thickness made of $V_2In_{14}S_{24}$ have a lower efficiency limit than conventional single band gap solar cell materials. It has previously been explained why overlapping absorption coefficients requires the cell thickness to be optimized. In this work it is shown that the thickness dependency of the cell efficiency can have two peaks. In this particular case the two peaks occur at cell thicknesses around 1 μm and 1 m. The reason for this double peaked dependency is processes where photons are emitted over one band gap and reabsorbed over another. Some of these processes can happen at very low rates and thus not give a significant contribution before a very thick cell is considered. For cells with a reasonable thickness, maximum efficiencies of 20.8% and 26.4% are found for light intensities corresponding to 1 and 1000 suns.

1. Introduction

Through theoretical solid state physics a number of semiconductors with a partially filled intermediate band (IB) between the valence band (VB) and conduction band (CB) have been identified by various research groups [1–17]. If possessing the right properties, a material with an intermediate band can be used in solar cells called intermediate band solar cells (IBSC) with a theoretical efficiency higher than that of conventional cells [18]. Due to the IB such a material have three band gaps, one for each pair of bands, over which photons can excite electrons. In the following we denote these band gaps E_{cv}, E_{ci} and E_{iv}, where the subscripts indicate the respective pairs of bands. In IBSCs the energy gap between the VB and CB can be larger than in conventional cells, which reduces thermalization losses. Photons with lower energy can still be utilized in a two-step generation process, via the IB, in which two photons create one electron-hole pair. Recently, experimental results showing an IB electronically isolated from the CB and VB were presented for GaN_xAs_{1-x} [19]. This is a an important finding because it shows that the investigated material fulfills a requirement for the two-step process to be effective [20,21].

A decisive criterium for high efficiency is the positioning of the IB relative to the CB and VB and the energy gap between these two bands. See for example Ref. [22]. From the size of the three band gaps it is possible to make a fast initial evaluation on whether a material has potential for use in highly efficient IBSCs or not. But there is also another fundamental and important issue that should be taken into account when looking for interesting IB-materials: the overlap and shapes of the three absorption coefficients related to excitations over the different band gaps [23,24]. Overlapping absorption coefficients lead to processes that are associated with irreversible losses of energy. When photons with sufficient energy to excite electrons over the two largest band gaps excite electrons over a smaller band gap, energy is lost when the excited electron–hole pair thermalizes to the band edges. The impact of such processes depends on the degree of overlap and on the mutual sizes of the absorption coefficients. A full evaluation of the theoretical efficiency of a material in the radiative limit, that is where radiative recombination is the only recombination process, must therefore take the sizes and shapes (i.e. the energy dependence) of the absorption coefficients of the material into account.

The energy of photons emitted in a radiative recombination process in a conventional solar cell is recycled if the photon is reabsorbed before leaving the cell. The cell thickness of ideal conventional cells can therefore go toward infinity without reduction in the efficiency. In IBSCs with overlapping absorption coefficients this is different due to the possibility of photon

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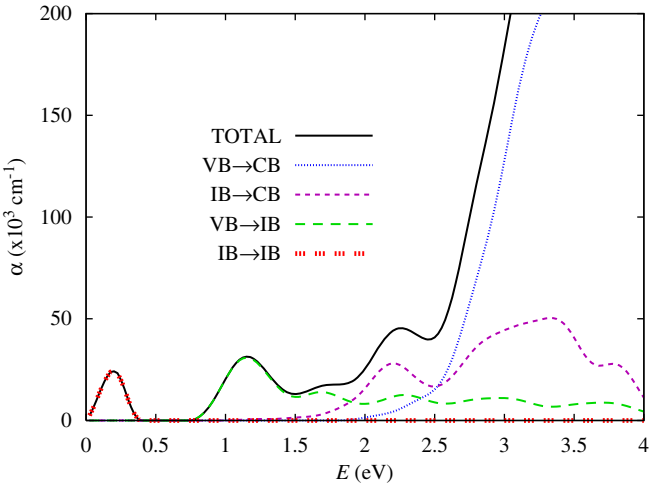

Fig. 1. Theoretical absorption coefficients of $V_2In_{14}S_{24}$.

emission followed by absorption over another band gap. The amount of radiative recombination, and thus photon emission, reabsorption and irreversible losses increase with the volume of the cell. With overlapping absorption coefficients the efficiency can therefore decrease with the cell thickness in some energy intervals, i.e. when the cells become very thick, and the thickness becomes a parameter to optimize [23].

While the band gaps of IB-materials are often used as an evaluation criterium, the issue with shape and overlap of the absorption coefficients has not been paid much attention so far. In this work, the absorption coefficients of $V_2In_{14}S_{24}$ (Fig. 1) calculated with density functional theory (DFT) [25,26] are used to investigate the potential of this material for use in IBSCs by using a method that takes the mentioned properties of the absorption coefficients into account. $V_2In_{14}S_{24}$ has previously been shown to possess an intermediate band and is therefore an interesting material for use in IBSCs.

2. Method

The modeling is performed using a detailed balance model, presented by Cuadra et al. [23], that takes into account the overlap between the absorption coefficients. The model is based on the following assumptions: radiative recombination is the only recombination mechanism, carriers can be extracted from the cell without loss, reflection losses are absent and all photons coming from the sun propagate normal to the cell surface. The back side of the cell is assumed to be a perfect reflector, so the optical path length for incoming photons equals two times the cell thickness. The equations from the original paper have been used without modification. The reader is therefore referred to the original paper for a mathematical description of the model.

The absorption coefficients, index of refraction, spectrum of the incoming photons, cell temperature and the cell thickness are the input parameters of the model, of which the three first are energy dependent. The model requires the computation of several integrals over the photon energy. Since the absorption coefficients and the refractive index are given as a set of discrete values, these integrals have been computed stepwise, with constant parameters within each interval. The boundaries for the steps are halfway between neighboring points. The incoming photons are assumed to be distributed according to the 6000 K black body spectrum. The cell temperature and ambient temperature have been set to 300 K.

3. The material

In_2S_3 is a semiconductor with a direct bandgap around 2.0 eV wide. In its most stable phase it is a defect spinel structure with cation vacancies ordered in the tetrahedral sites, producing a body-centered tetragonal structure (space group I41/amd). Most of the indium in it (75%) has thus octahedral coordination. In_2S_3 is frequently used as a window layer material in thin film photovoltaic (PV) cells so that the preparation methods, well adapted to PV cell manufacture, are already known.

Vanadium-doped In_2S_3 has been proposed [8], by means of DFT calculations, as a good candidate to make an IB material. Optical characterization of vanadium-doped In_2S_3 has confirmed the expectations from DFT results [9].

We have used DFT, where the exchange-correlation potential has been approximated with the generalized gradient approximation (GGA) [27], to obtain the IB electronic structure of vanadium-doped In_2S_3, which is shown in Fig. 2. As already predicted in [8], the electronic structure of $V_2In_{14}S_{24}$ presents an intermediate band, which is partially filled and it is formed by t_{2g} states of vanadium.

GGA calculations underestimate band gaps, but this mainly affects the separation between the occupied and unoccupied levels; consequently, the energy difference between the VB and the IB is not expected to be affected by this underestimation [16,28,29]. However, the IB-CB real gap will be larger than that calculated with GGA. To estimate its real value, a shift in the CB has been applied by an amount appropriate to reproduce the VB-CB gap in the original semiconductor.

This electronic structure has then been used to obtain, through the random-phase approximation, the input parameters required for the present work: the absorption coefficient and the refractive index. The spectra found can be seen in Figs. 1 and 3 respectively. The plane-wave code VASP [30–32] was used for the calculation of the electronic structure and the optical spectra.

4. Results and discussion

Fig. 4 shows calculated cell efficiencies plotted as a function of the cell thickness for light intensities of 1 sun and 1000 suns. The curves have two peaks, one at around 1 μm and the other for around 1 m thick cells. For 1 sun, the first peak, at 0.91 μm, gives an efficiency of 20.8%. This is considerably lower than the detailed balance efficiency limit for ideal IBSCs with similar bandgaps and non-overlapping absorption coefficients, calculated as in Ref. [18], which is around

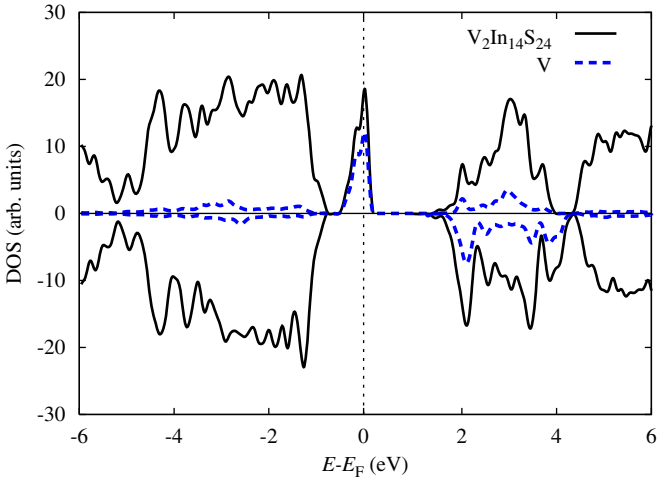

Fig. 2. Theoretical total and vanadium-projected density of states (DOS) of $V_2In_{14}S_{24}$. The energy is zero at the Fermi level E_F which is inside the intermediate band.