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Prospects for electron microscopy characterisation of solar cells: Opportunities and challenges ☆

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ABSTRACT

Several electron microscopy techniques available for characterising thin-film solar cells are described, including recent advances in instrumentation, such as aberration-correction, monochromators, time-resolved cathodoluminescence and focused ion-beam microscopy. Two generic problems in thin-film solar cell characterisation, namely electrical activity of grain boundaries and 3D morphology of excitonic solar cells, are also discussed from the standpoint of electron microscopy. The opportunities as well as challenges facing application of these techniques to thin-film and excitonic solar cells are highlighted.

1. Introduction

Despite its many benefits as a renewable energy source, solar photovoltaic energy harvesting can only be commercially viable if the cost per Watt (at peak performance) is reduced from its current value of ~$4/$W_p$ for the bulk silicon modules that account for ~85% of the present day market. Whereas thin-film CdTe modules are presently priced at ~$1/$W_p$ – and are beginning to be competitive with grid connected power – it remains the case that further increase in performance and decrease in cost are necessary to generate unsubsidised mass market conditions. In the case of bulk silicon, the advantages of high performance are countered by the high cost of purifying the material and the limits to production ultimately imposed by a wafer-based technology. Consequently 'thin-film' solar cells, that utilise more efficient light absorbing materials or novel light capturing mechanisms, are being intensely researched. Electron microscopy is vital for characterising the microstructure/morphology of these thin-film solar cells, as well as probing the physics governing device efficiency. In this review we focus on applications of electron microscopy to thin-film solar cells that have been partly brought about by recent advances in instrumentation. In some cases the techniques are yet to be applied to solar cells, but have been successfully demonstrated on other materials systems.

In Section 2 a brief introduction to solar cell operation and the various thin-film devices is presented. Here 'thin-film solar cell' is broadly defined as semiconductor thin-film solar cells and we have also included organic and dye-sensitised solar cells. Reviews for these devices can be found in [1–11]. A general review of physical techniques of analysis for thin-film solar cells including TEM and electron beam induced current measurements in the SEM is given in [145]. In Section 3 recent advances in electron–optic and related instrumentation, and their potential applications in solar cell characterisation are discussed. The instrument advances selected for review are: (i) aberration-corrected scanning transmission electron microscopy (STEM), (ii) monochromated electron energy loss spectroscopy (EELS), (iii) time-resolved cathodoluminescence in a dynamic scanning electron microscope (SEM) and (iv) focused ion-beam (FIB) microscopy. In Section 4 two widely encountered generic problems, namely electrical activity of grain boundaries in semiconductor thin-film solar cells and 3D morphology of excitonic solar cells, are discussed in light of electron microscopy characterisation. Conclusions are presented in Section 5.

2. Thin-film solar cells

2.1. Basic operating principles

The common feature of the great majority of solar cell devices is the *p–n* junction, the band diagram for a homojunction being shown in Fig. 1. Incident light of energy $h\upsilon$ greater than the band gap of the absorber material generates electrons in the conduction band and holes in the valence band. The photocurrent is due to the generation of minority carriers on each side of the junction. Minority carriers must diffuse towards the depletion region where the built-in electric field ε will inject them across the *p–n* junction. As an example minority carrier electrons photo-generated within the *p*-region will

☆ In memoriam Professor Gertrude Rempfer on the occasion of her 100th birthday.

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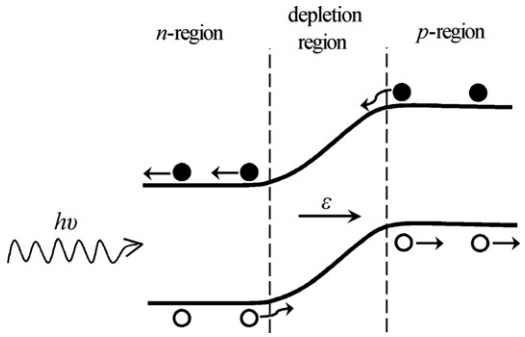

Fig. 1. Shematic illustrating the operating principle of a solar cell via the electronic band structure of the material. An incident photon of energy $h\upsilon$ greater than the band gap generates electrons (solid circles) and holes (open circles). Minority carriers that diffuse to the depletion region edge are injected across the p–n junction, which has a built-in electric field ε. See text for further details.

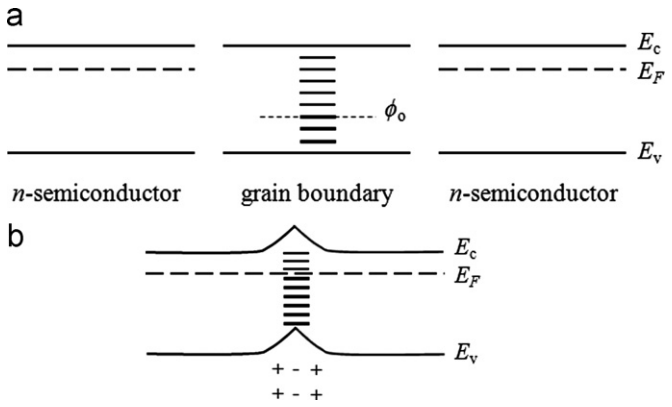

Fig. 2. (a) Schematic electronic band structure for a grain boundary region in isolation and the neighbouring n-type perfect crystals on either side. E_c, E_F and E_v denote the energies of the conduction band, Fermi level and valence band, respectively. ϕ_o is the quasi-neutrality level of the grain boundary. (b) Band structure diagram for a grain boundary in contact and in equilibrium with the two perfect crystals. Energy levels below E_F are occupied, which results in negative charge accumulated at the grain boundary plane. The figures are based on [13].

be injected into the n-region, where they become majority carriers, provided that the electrons are generated within a diffusion length away from the depletion region. Similar reasoning is applicable to holes photo-generated within the n-region. Solar cell efficiency is governed by the ability of photons to generate electron-hole pairs and by the successful separation and collection of the carriers. Electron-hole pair generation depends on the photon energy with respect to the band gap as well as the absorption coefficient (direct band gap materials have higher absorption coefficients since momentum is conserved during the optical transition). The ideal solar cell material for a single junction device has a band gap of $\sim$1.4 eV [12] and a high absorption coefficient. For further details see for example [13].

Separation and collection of carriers depends (amongst other factors) on the presence of crystal defects. Consider, for example, the effect of grain boundaries, which are common in inorganic semiconductor thin-film solar cells (Sections 2.2 and 4.1). The different atomic bonding environment at a grain boundary introduces additional energy levels within the band gap, so that for an electrically neutral grain boundary all energy levels below the quasi-neutrality level ϕ_o are occupied (Fig. 2a). At equilibrium however, the grain boundary and neighbouring bulk semiconductor must have a common Fermi energy level, so that, for the situation depicted in Fig. 2a, electrons are transferred from the bulk regions to the grain boundary plane. This results in a depletion region on either side of the grain boundary, and the resulting upward band bending repels the majority carrier electrons (Fig. 2b). Minority carrier holes are attracted towards the boundary, at a rate given by the so-called 'recombination velocity', where they undergo recombination. A higher recombination velocity means that photo-generated minority carriers have less probability of reaching the depletion region of the p–n junction and hence carrier separation is less efficient. On the other hand minority carriers which are injected across the p–n junction, where they become majority carriers, must overcome the potential barrier of any grain boundary along their path, and consequently carrier collection is also reduced. Apart from good optical absorption characteristics high efficiency solar cell materials must also contain a low density of electrically active defects.

2.2. Inorganic semiconductor thin-film solar cells

The inorganic semiconductor thin-film solar cells discussed in this review are: (i) amorphous silicon (a-Si), (ii) CdTe, (iii) plasmon enhanced and (iv) core-shell nanowire solar cells. Schematics of these devices are shown in Fig. 3 (note that in several cases variations in device structure, such as the nature of the individual layers, direction of light incidence, etc., are possible). Amorphous silicon solar cells have been in production for many years and have a long term stable efficiency as high as 9.3% [3,11]. Crystalline silicon has an indirect bandgap, but in the amorphous state atomic bond distortions lead to 'tail states' at the band edges, which can undergo optical transitions without the need for phonons. Consequently a-Si has a high absorption coefficient (10^4–10^5 cm^{-1} [14]) and can be used in thin-film form for solar cells. The a-Si is hydrogenated; hydrogen is accommodated at dangling bonds, thereby passivating deep level states within the optical gap and improving electrical conductivity. The material issues are degradation of optical and electrical properties of a-Si at high deposition

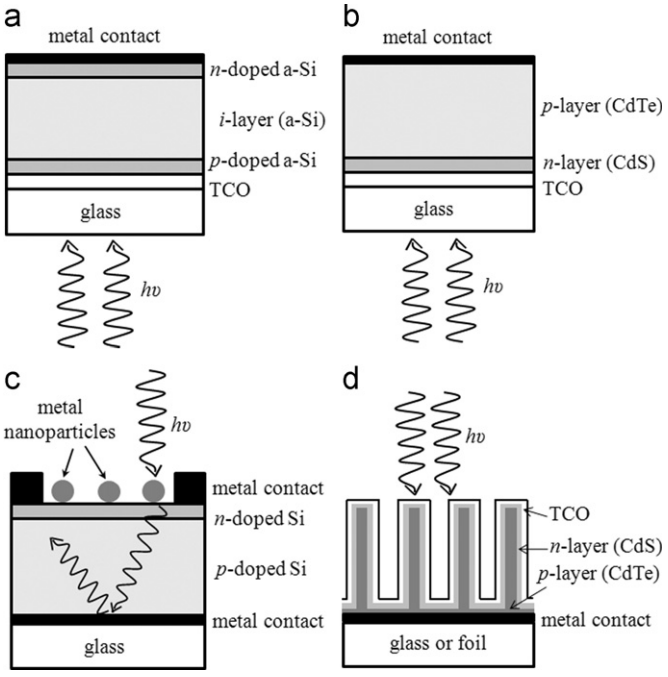

Fig. 3. Schematic thin-film solar cell device structures for (a) amorphous-Si (a-Si) solar cells, (b) CdTe solar cells, (c) plasmonic solar cells and (d) radial core-shell nanowire solar cells. TCO in Fig. 3a,b,d refer to transparent conducting oxide. The 'i-layer' in Fig. 3a refers to intrinsic layer, where the number of donors and acceptors are approximately equal. Note that variations in the device structure are possible.