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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, timeresolved 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 excitionic 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.

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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 \sim \$4/W_p for the bulk silicon modules that account for \sim 85% of the present day market. Whereas thin-film CdTe modules are presently priced at \sim \$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

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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 hv 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





Fig. 1. Shematic illustrating the operating principle of a solar cell via the electronic band structure of the material. An incident photon of energy hv 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 ~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 $(10^4-10^5 \text{ cm}^{-1} \text{ [14]})$ 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.

rates and the decrease in photocurrent on exposure to light, known as the Staebler–Wronski (S–W) effect [15,16]. The S–W effect is reversible, so that the material can be returned to its original state by annealing above 150 °C for several hours in the dark. The photodegradation is believed to be caused by breaking of Si–H bonds, although the details of the mechanism are poorly understood. Despite years of research the S–W effect remains the principal obstacle facing a-Si solar cells.

CdTe is the highest volume thin-film solar cell technology in production at the present time and the material has the advantage of being highly absorbing and amenable to large-scale deposition. It may be deposited using a number of cheap and efficient processes [2.11.17], with variants of vapour deposition processes being preferred for mass production. The CdTe absorber layer is a few micrometres thick and typically contains micron-sized grains, the exact size being a detail of growth and processing history (see Fig. 10b in Section 3.4 for a representative micrograph). In the asdeposited state the device efficiency is only \sim 1–3%, but is increased up to 16.5% by a 'chlorine activation' treatment. Chlorine activation involves depositing a thin layer of CdCl₂ on the CdTe back surface (prior to depositing the metal contact, Fig. 3b) and annealing at 400 °C for 20–30 min. Recently activation has also been enhanced by surface treatment [146] and carried out using chlorine containing gases instead of CdCl₂ [18,19]. Chlorine activation dopes the CdTe and radically alters the microstructure, the primary changes being sulphur inter-diffusion from CdS into CdTe to form a CdS_xTe_{1-x} interfacial layer of varying composition [20-23], segregation of chlorine to CdTe grain boundaries [22,23] and the acceleration of recrystallisation and grain growth in the CdTe [147,148] and CdS [114]. Chlorine has also been demonstrated to introduce continuously variable trap levels into the solar cells, these probably being grain boundary related [149]. There is also evidence that doping of the CdTe is influenced by inter-diffusion of CdS [24]. The presence of $CdS_{x}Te_{1-x}$ at the *p*-*n* heterojunction is likely to affect the width of the depletion region (Fig. 1) and thereby carrier separation as well. Chlorine segregation passivates the grain boundaries [24,121,150], so that the carrier lifetime and open circuit voltage are increased.

Semiconductors having the chalcopyrite structure are also under intense investigation and technological development for solar cell applications. Cu(In,Ga)Se₂ or CIGS has delivered the highest efficiency (19.5%; [25]) of all single junction thin-film solar cells under one sun illumination. CuInSe₂ has a band gap of 1.02 eV, but this can be increased to the optimum value of \sim 1.4 eV by alloying with Ga. The three stage deposition process for CIGS produces a variable Ga:(Ga+In) ratio (i.e. a graded band gap) through the film thickness, leading to a larger effective hole diffusion length. The disadvantage of CIGS however is the high cost of indium. Hence absorber layers consisting of cheaper, more abundant elements, such as Cu₂ZnSn(S,Se)₄ (CZTS), are being explored [26,27]. However, CZTS is stable in only a narrow region of the phase diagram [28] and depositing thin-films free of secondary phases is a considerable challenge. Other absorber materials include III-V compound semiconductors, such as GaAs, grown epitaxially on single crystal III-V or Ge substrates [4]. The substrate must be carefully chosen to minimise thermal and lattice mismatch with GaAs, so that the thin-film remains free of planar defects and interfacial misfit dislocations. The cost of the substrates, as well as the slow rates of epitaxial thin-film growth, means that the device area for III-V solar cells must be kept small, so that concentrator systems are required to obtain the desired efficiency in terrestrial applications. For space applications, where cost is not the primary concern, multi-junction devices based on III-V and hybrid III-V technology have been developed and have demonstrated efficiencies of greater than 30%.

In the case of thin-film silicon, the challenge is to take advantage of the high level of engineering knowledge for silicon, whilst reducing the specific cost $(\$/W_p)$. Since crystalline silicon is an indirect band gap material, this amounts to increasing the light capture in silicon thin-films. Light trapping schemes, such as forward scattering from the surface plasmon resonance of metal nanoparticles, have therefore been postulated to improve device efficiency (Fig. 3c) [29-31]. Noble metal nanoparticles, such as gold and silver, have surface plasmon resonances in the visible or near-visible part of the spectrum (the precise wavelength depends on the size and shape of the nanoparticle as well as the surrounding medium). Radiative decay of the surface plasmon gives rise to scattering, while non-radiative decay leads to absorption. Forward scattered light will travel a longer distance through the thin-film (Fig. 3c), thereby increasing absorption. This enables less efficient, but cheaper materials, such as silicon, to be used as the thin-film absorber layer. The suitability of a particular surface plasmon mode for light trapping depends on the crosssection for scattering with respect to that for absorption (the latter being undesirable) as well as the angular distribution of the scattering (i.e. there should be very little backscattering). For example, Temple et al. [31] found that the dipolar surface plasmon mode for silver, which has equal probabilities for forward and backscattering in vacuum, actually led to a decrease in quantum efficiency for a silicon thin-film solar cell at the plasmon resonance wavelength, despite the relatively small absorption cross-section.

Apart from the traditional planar junction, thin-film solar cells can also be fabricated as core-shell nanowire arrays [5,6,32-34] (a schematic of a CdTe-CdS core-shell nanowire solar cell is shown in Fig. 3d). As an example vertically aligned nanowires can be grown using the vapour-liquid-solid (VLS) technique from a gold catalyst and the shell subsequently deposited by the chemical bath method [34]. In a core-shell nanowire photon absorption takes place along the length of the nanowire, while carrier separation takes place in the orthogonal radial direction, so that the two processes are independent of one another. Compare this to a planar junction where a thicker film increases photon absorption but simultaneously leads to a decrease in the carrier separation efficiency for film thicknesses greater than the carrier diffusion length. The radius of a core-shell nanowire can be made less than the carrier diffusion length in order to maximise carrier separation (note that in some cases the nanowire radius can be smaller than the depletion region, so that carrier separation does not require any diffusion). Furthermore if the nanowire is single crystalline there will be no grain boundaries that limit carrier flow, although this could be offset by increased surface and interface recombination.

2.3. Organic solar cells

Organic materials have small dielectric constants and hence photo-generated electron-hole pairs are tightly bound as electrically neutral excitons. An electric field, such as that in a p-njunction, is required to dissociate the exciton and generate free carriers. Thin-film bulk heterojunction organic solar cells are a mixture of 'donor' polymer (the *p*-material, typically P3HT or MDMO-PPV) and 'acceptor' molecule (the *n*-material, typically PCBM, which is based on C_{60} [8,9]. Exciton dissociation takes place at the donor-acceptor interface (the lower ionisation energy of the donor results in exciton dissociation followed by electron transfer to the acceptor, with the hole remaining in the donor; Fig. 4a) [35]. Since the exciton diffusion length is only $\sim 10 \text{ nm}$ the donor and acceptor must be finely mixed within the thin-film. Once dissociation has taken place a contiguous pathway is required for free carriers to reach the electrodes without undergoing recombination at donor-acceptor interfaces. The requirements for efficient exciton dissociation and carrier transport

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Fig. 4. Schematic diagrams of (a) a bulk heterojunction organic solar cell consisting of a donor and acceptor phase and (b) a dye-sensitised solar cell. TCO in Fig. 4a refers to transparent conducting oxide, while solid and open circles denote electrons and holes, respectively. A thin layer of hole conducting PED-OT:PSS is deposited between the TCO and bulk heterojunction thin-film. See text for further details.

therefore oppose one another, so that thus far the maximum device efficiency achieved is only \sim 5%. Nevertheless organic solar cells are attractive materials, since they can be fabricated over large areas on flexible substrates using cheap one-step solution processing (e.g. spin coating, ink-jet printing and roll casting).

An alternative method is to use hybrid inorganic–organic solar cells, where the PCBM acceptor is replaced by an inorganic semiconductor, in the form of nanoparticles or nanorods [36–38]. There are several advantages to this approach, including that (i) inorganic materials have higher electron mobilities compared to PCBM, (ii) the inorganic semiconductor can be carefully chosen so that the band gap is in the infra-red part of the solar spectrum, thereby maximising photon absorption (solar cell organics typically absorb photons with wavelength \sim 550 nm and below), and (iii) in the case of nanorods, the high aspect ratio and large surface area satisfy the requirements of exciton dissociation and carrier transport simultaneously. Despite these benefits the performance of hybrid inorganic–organic solar cells is generally inferior to bulk heterojunction solar cells at the present time.

2.4. Dye-sensitised solar cells

Dye-sensitised solar cells are photoelectrochemical solar cells shown schematically in Fig. 4b [10,39]. A mesoporous network of sintered TiO₂ (anatase) nanoparticles are coated with a dye (typically a ruthenium containing compound, such as N3) that absorbs the photons. The photo-generated electrons are transferred from the dye to the TiO₂ semiconductor. The electrons diffuse through the TiO₂ network until they are collected at the electrode. The oxidised dye is reduced by the surrounding electrolyte, which in turn is reduced by the electrons flowing through the external circuit, so that the system is restored to its starting configuration and the cycle can commence once again. Research on dye-sensitised solar cells has focused on finding better dyes for optical absorption, on developing solid-state devices where the electrolyte is replaced by a hole conducting *p*-type semiconductor, as well as understanding the nature of the 'trap limited' electron diffusion through the TiO₂ network. The importance of the TiO₂ network morphology on electron diffusion has also been highlighted. For example, Benkstein et al. [40] found that the effective electron diffusion coefficient decreases with increasing porosity within the network, in a quantitative manner that is consistent with percolation theory.

3. Advances in instrumentation

3.1. Aberration-corrected scanning transmission electron microscopy (STEM)

The correction of third order spherical aberration (C_s) using non-round optical elements is one of the most significant breakthroughs in materials characterisation. Correctors for STEM are either of the quadrupole-octupole type [41-44] or a double hexapole type [45–49]. A multipole consisting of 2(n+1) elements produces a magnetic field that varies as r^n , where r is the radial distance from the optic axis. The deflection of the electron by the resulting Lorentz force can be made equal and opposite to that due to the *n*-th order aberration of the objective lens, so that the net deviation is zero, and the aberration is effectively 'corrected'. In a quadrupole-octupole corrector the octupoles introduce negative C_s , which cancel the positive C_s of the objective lens (in practice a small, but non-zero, defocus and C_s is used to compensate for fifth order spherical aberration). The primary aberrations of a hexapole are second order, but C_s can be corrected through the third order, residual aberrations by having two hexapoles separated by a round transfer lens doublet (an inverse image of unit magnification from the first hexapole is formed in the second hexapole via the transfer lens, so that the second order primary aberrations of the two hexapoles cancel one another). Aberration-corrected STEM instruments produce narrower probes with a higher current (due to the use of larger objective apertures), which has enabled high spatial resolution imaging (down to 50 pm [50]) as well as chemical analysis of individual atoms or atom columns over a region of interest [51-53].

High angle annular dark field (HAADF) imaging [54] in the STEM is particularly useful for characterising thin-film solar cells based on III-V and II-VI compound semiconductors (e.g. GaAs and CdTe) as well as chalcopyrite semiconductors (e.g. CIGS). Here an annular detector is used to collect the high angle scattered electrons, which are scattered from close to the atomic nucleus, so that the HAADF signal intensity varies as $\sim Z^{1.7}$, where Z is the atomic number of the scattering atom. Hence pseudo-chemical contrast can also be observed in HAADF images. This is especially useful for imaging crystal defects in thin-films as well as analysing polymorphs in III-V nanowires [55,56], which are potential candidates for nanowire-based solar cell devices (Section 2.2). HAADF has been used to image the atomic structure of interfacial misfit dislocations in epitaxial III-V thin-films, as well as identify the atomic species constituting any dangling bonds at the dislocation core [57,58]. Dangling bonds have an important effect on solar cell performance as they introduce deep energy levels within the band gap, consequently lowering the carrier lifetime through Shockley-Read-Hall recombination. As an example Fig. 5a shows misfit dislocations at the interface between GaSb and Si imaged using HAADF in an aberration-corrected STEM [57]. Since all the atom columns are resolved a Burgers circuit analysis can be carried out to determine the Burgers vector of the individual dislocations (Fig. 5b). Furthermore, the chemical contrast in the HAADF image enables the dangling bond at the dislocation core to be identified as an Sb atom (Figs. 5c and d). Despite the scan distortions present in STEM images due to electrical interference [59] a geometric phase analysis [60,61] can qualitatively reveal the strain tensor components at the

interface (Fig. 6). The strain between the Si substrate and GaSb thin-film due to lattice mismatch, as well as the tensile and compressive regions around the dislocation core are clearly evident. An alternative approach is to use a Nye tensor analysis



Fig. 5. (a) HAADF image of GaSb grown epitaxially on Si (inset shows the power spectrum), (b) an expanded view of the interface region showing misfit dislocations with corresponding closure failure of the Burgers circuit and (c) core structure of one such misfit dislocation. In (d) the Sb, Ga and Si atoms are superimposed on the HAADF image of Fig. 5c to reveal an Sb dangling bond at the misfit dislocation core. From Vajargah et al. [57] (reproduced with permission; copyright 2011 American Institute of Physics).

to map the dislocation density tensor components at the interface [62,63]. This method has the advantage that it is insensitive to compatible deformations, so that systematic scan distortions in a HAADF image are suppressed, leaving only the incompatible deformations of the dislocation core as the visible component.

The deposition and processing of thin-film solar cells, particularly CIGS and CdTe, lead to intermixing and chemical reactions at interfaces [20-23,64-68] as well as grain boundary segregation [22,23,69]. Characterisation has typically been carried out using energy dispersive X-ray (EDX) analysis in a non-aberration corrected STEM. Nevertheless it is clear that aberration-corrected STEM, with a smaller probe size and higher beam current, can increase the signal to background and signal to noise ratios of the spectra, thereby enabling more subtle chemical changes to be detected. The use of electron energy loss spectroscopy (EELS) can also provide complementary information on the local atomic bonding, through an analysis of the energy loss near edge fine structure (i.e. ELNES) [70,71]. Interfaces in CIGS and CdTe thinfilm solar cells generally have large projected width when tilted 'end-on', so that even in an aberration-corrected STEM the EDX and EELS signal measured at the 'interface' will contain a contribution from the surrounding matrix phase(s). In such cases the interface signal can be deconvolved through either multiple linear least squares (MLLS) fitting [72,73] or using the data analysis method developed by Mendis and co-workers [74,75], which, unlike MLLS, does not require a reference spectrum for the interface.

A further interesting application of aberration-corrected STEM is the use of 'optical sectioning' to determine the lateral and depth distribution of Au atoms in Si nanowires grown using the vapour-liquid-solid (VLS) method [76,77]. Metal catalysts (e.g. Au) are



Fig. 6. (a) and (b) denote the strain tensor components parallel (ε_{xx}) and perpendicular (ε_{yy}) to the GaSb–Si interface in Fig. 5. The vertical streaks in (a) are due to scan distortions in the HAADF STEM image. (c) is an expanded view of the strain ε_{xx} around a single interface misfit dislocation. The ε_{xx} strain perpendicular to the interface is plotted from within the box region (i.e. between the interface dislocations) of Fig. 6a and is shown in (d). This represents the lattice mismatch between GaSb and Si. From Vajargah et al. [57] (reproduced with permission; copyright 2011 American Institute of Physics).

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Fig. 7. (a) HAADF STEM composite image of a Si nanowire formed by aligning and summing each image in an optical sectioning experiment, where the probe defocus was varied through the thickness of the nanowire. The bright dots are individual impurity Au atoms. The scale bar is 5 nm. (b) plots the excess intensity (i.e. HAADF intensity above background) as a function of focal depth for Au atoms b_1 , d_1 and d_2 in Fig. 7a. A schematic diagram of the relative positions of Au atoms b_1 , d_1 and d_2 within the nanowire is also shown in Fig. 7b. From Allen et al. [76] (reproduced with permission; copyright 2008 Nature Publishing Group).

used in VLS, so that metal atom impurities are typically incorporated in the nanowire during growth. Au has a deleterious effect on the electrical properties of Si, and hence will have an impact on the efficiency of solar cell devices fabricated using VLS grown Si nanowires. The superior lateral spatial resolution of an aberration-corrected STEM can be used to image individual Au atoms in Si using HAADF. However, the large objective aperture required for such high spatial resolution imaging also reduces the depth of field, which varies as the inverse square of the probe convergence angle [78]. This means that the 3D distribution of Au atoms can be determined by systematically varying the probe defocus over the diameter of the nanowire, in a so-called optical sectioning experiment. Fig. 7a [76] is a composite image from such a focus-series (i.e. images at each defocus were aligned and superimposed) and shows a high concentration of Au atoms near a twin defect; the Au atoms run parallel to the lines of intersection of the twin with the free surfaces of the nanowire. The depth of field for the imaging conditions used in the above study is ~ 11 nm [76,78]. This explains the rather broad intensity distribution of individual Au atoms as a function of focal depth (Fig. 7b), and gives an indication of the depth resolution that can be achieved through optical sectioning (the depth resolution can be improved by increasing the accelerating voltage of the microscope and/or by increasing the probe convergence angle).

3.2. Monochromated electron energy loss spectroscopy (EELS)

The low-energy loss part of an EELS spectrum contains information on the optical band gap and absorption coefficient, excitons, as well as surface and bulk plasmons [70]. Combined with good spatial resolution it is therefore an ideal technique to probe the optical properties of graded bandgap solar cells (e.g. CIGS), plasmonic solar cells (Fig. 3c) and excitonic organic solar cells (Fig. 4a). Since the visible spectrum is between ~1.6 and ~3.2 eV, a narrow zero-loss peak (ZLP) is required for such analyses. The energy spread of thermionic and field-emitting sources are too large and hence a monochromator is required to select a fraction of the available electrons within a narrower energy spread (typically less than 100 meV). Commercial monochromators are based on either an electrostatic omega design [79–81] or Wien-type construction [82–84]. In the former electrostatic lenses are used to deflect the electrons along a trajectory in the shape of the Greek letter Ω , with the energy selecting slit inserted at the symmetry plane (energy dispersion is achieved due to the fact that the electrostatic field will deflect low energy electrons more than the high energy electrons). The monochromator has the desirable property that the beam is undispersed at the exit plane. In Wien-type monochromators an electric and magnetic field are superimposed on electrons travelling along the optic axis. Electrons of a fixed kinetic energy satisfy the 'Wien condition', where the forces due to the two fields are equal and opposite, and the electron trajectory is undeflected. A slit is inserted to block the deflected electrons of different energies. In practice satisfying the Wien condition within the entire length of the monochromator and in the outer fringing field region has only been achieved in the last few decades through significant instrument modification [82].

In general there are two factors that limit the accuracy of optical property measurement at high spatial resolution using EELS: (i) delocalisation of the inelastic signal and (ii) Čerenkov losses. The former was first treated classically by Neils Bohr [85,86], who considered the interaction of an incident electron of velocity v and impact parameter b, with an atomic electron oscillating at frequency ω . If the impact parameter is smaller than a critical value of $b_{\max} = (v/\omega)$, the atomic electron cannot adjust its oscillation frequency to that of the electric field of the incident electron and energy is transferred. For $b > b_{max}$ however the atomic electron will respond to the electric field, so that the energy transfer will be small, showing an exponential decay with distance, i.e. $exp(-2b/b_{max})$. Quantum mechanics predicts a similar behaviour, which has also been confirmed by experiment [87,88]. Delocalisation therefore depends on the energy loss $\hbar\omega$, such that b_{max} becomes progressively larger for smaller energy losses (for a 1 eV energy loss at 100 keV primary beam energy the delocalisation is more than 100 nm [88]). Since it is the low-loss part of the EELS spectrum that is used for optical property measurement, it is usually delocalisation, and not the electron probe size, that limits the spatial resolution. The other factor that needs to be considered is Čerenkov radiation, due to the electron travelling faster than the speed of light in the material [89–91]. Since the material refractive index is largest in the long wavelength limit, additional energy losses due to Čerenkov radiation are strongest in the low-loss part of the EELS spectrum, thereby potentially affecting band gap measurements. The scattering angle due to Čerenkov losses is extremely small ($\sim 10^{-2}$ mrad). Hence an EELS spectrum collected at a small (e.g. 0.23 mrad, [91]) scattering angle will be largely free of Čerenkov radiation, although this method is unlikely to be useful in a high resolution STEM experiment due to the large convergence angle (>10 mrad) of the incident probe. In such cases Čerenkov losses can be reduced using lower incident electron beam energies [92] and/or through the use of thin specimens. Total internal reflection of the Čerenkov radiation within the thin foil produces waveguide modes, which have a low-energy cut-off that varies inversely with the specimen thickness [93]. By selecting a suitably thin specimen, the cut-off energy can be made larger than the band gap energy, thereby giving reliable band gap measurements. However, care must be taken that the specimen is not too thin, such that the material deviates from its bulk properties.

The pitfalls associated with low-loss EELS at high spatial resolution are clearly illustrated in the case of optical property measurement near an interface. Interfaces can have different

optical properties due to chemical inter-diffusion, e.g. the CdS_xTe_{1-x} interfacial layer in CdTe solar cells (Section 2.2). Consider the case of an electron beam moving parallel to, but at a finite distance, from a sharp interface between two materials A and B (the electron is incident in material B). As the impact parameter decreases, an interface energy loss spectrum, of the form $Im\{-2/(\varepsilon_A + \varepsilon_B)\}$, is observed and increases in intensity at the expense of the bulk energy loss spectrum $Im\{-1/\varepsilon_B\}$ for material B, i.e. the *begrenzungs* effect (ε_{AB} is the complex dielectric function and 'Im' represents the imaginary part) [94,95]. A Kramers-Kronig analysis [70] on such an EELS spectrum would give dielectric constants that are different to the bulk material B, the difference being greater for smaller electron beam impact parameters. Band gap measurements could also be affected. To see this note that the condition $Im\{\varepsilon_B\}=0$ must be satisfied below the band gap of material B (this follows from the requirement that the bulk loss function is zero below the band gap, i.e. $Im\{-1/\varepsilon_B\}=0$). However, if material A has a lower band gap, then $\text{Im}\{\varepsilon_A + \varepsilon_B\} \neq 0$, and consequently $\text{Im}\{-2/(\varepsilon_A + \varepsilon_B)\} \neq 0$, for energies above the band gap of material A, i.e. a lower band gap is measured due to interface losses. The CdS_xTe_{1-x} inter-diffusion layer at the CdS-CdTe interface in CdTe solar cells is more complicated than the sharp A-B interface discussed above. In the simplest approximation, where the variation in sulphur concentration within the inter-diffused layer is neglected, the material can be represented as an A-B-C multi-layer, where 'A' is CdS, 'B' is $CdS_{x}Te_{1-x}$ of fixed composition and 'C' is CdTe. A–B as well as B–C interface losses are now present which, if the B-layer is sufficiently thin, will couple with one another to produce further perturbations [93,96]. Fortunately numerical methods are available to simulate the EELS spectrum in such multi-layer structures, provided the dielectric constants of the individual layers are known [97]. The dielectric constants for the A and C lavers can be directly extracted from EELS measurements made far from their respective interfaces. 'Best-fit' dielectric constants for the unknown B-laver can then be chosen to match experimental measurements made across the A-B-C multilayer, so that in principle a reliable estimate of the interfacial (i.e. B-layer) optical properties can be extracted.

Apart from optical property measurement monochromated EELS has also been used to characterise surface plasmons in metal nanostructures [98–100], which has applications in plasmonic solar cells (Section 2.2). Fig. 8 shows energy filtered TEM (EFTEM) images of a Au nanorod suspended at the edge of a holey



Fig. 8. (a) TEM bright field image of a Au nanorod suspended at the edge of a holey carbon film. Energy filtered images at energies of 0.97, 1.62 and 2.27 eV in (b), (c) and (d) show the distribution of different surface plasmon modes. The results were acquired using a monochromated TEM. From Schaffer et al. [99] (reproduced with permission; Copyright 2009 American Physical Society).

carbon film [99]. The images were acquired using a monochromated TEM with an energy slit width of 0.3 eV for the postcolumn imaging filter. Three surface plasmon modes are observed to be strongly excited (Fig. 8b–d). The EFTEM images give an indication of the relative intensity and spatial distribution of each surface mode. It should be noted than in an EELS experiment, where the energy loss of the incident electrons are measured, the intensity of a surface plasmon refers to extinction (i.e. scattering and absorption), while in plasmonic solar cells it is only the forward scattering component that is utilised [29–31]. The information that can be obtained from EELS is therefore incomplete, as far as plasmonic solar cells are concerned. Nevertheless, as has been clearly demonstrated, EELS is an invaluable tool for characterising surface plasmons as a function of particle shape and size at nanometre length scales.

Photo-excitation of organic solar cells results in exciton formation (Section 2.3), which can also be analysed using lowloss EELS. A particularly interesting application of momentumresolved EELS was developed by Fink and co-workers [101–103] to determine the spatial extent of excitons in π -conjugated molecules. The basis of these experiments is that the momentum dependent intensity of an EELS excitation (e.g. an exciton) can be expressed as [102,103]:

$$I_n \propto \frac{n!^{-2} (q \langle r \rangle)^{2n}}{N}, \quad N = \sum_n \frac{(q \langle r \rangle)^{2n}}{n!^2}$$
(1)

where I_n is the exciton intensity at momentum q (measured in reciprocal space [70]), which has a multipole character specified by *n* (e.g. n=1 for a dipole, n=2 for a quadrupole exciton and so on). $\langle r \rangle$ is the average size of the exciton and *n*! is the factorial of *n*. I_n depends on the dimensionless variable $q\langle r \rangle$, so that by comparing measurements of I_n as a function of q to the theoretical curves an estimate for $\langle r \rangle$ can be obtained. Fig. 9a shows exciton intensity vs momentum plots for a C_{60} molecule as well as the linear molecules TPD, β -carotene and 8 T, measured using momentum-resolved EELS [101]. The exciton intensity decreases monotonically with momentum for the linear molecules, consistent with a dipole exciton (Eq. (1)). In C₆₀ however the peak intensity is at non-zero momentum transfer, due to the quadrupole nature of the exciton. These curves are used to calculate the average exciton size $\langle r \rangle$, which are then plotted against molecular length for a number of π -conjugated systems (Fig. 9b, [101]). Surprisingly the exciton size is found to be of the order of the molecular size, which is counter-intuitive to the highly localised, Frenkel-type excitons expected for organic materials. However, as stated in [101–103], EELS transitions are purely electronic in nature (Frank-Condon principle [104]), so that structural relaxation of the molecule following excitation could still lead to localised excitons. The exciton size measured in EELS experiments is therefore due to electron-electron interactions alone.

3.3. Time-resolved cathodoluminescence (CL)

Section 2.1 described how the carrier lifetime at crystal defects, particularly grain boundaries, affected solar cell efficiency. A direct correlation between lifetime and device efficiency was found using time-resolved photoluminescence (PL) measurements for chlorine activated CdTe solar cells [105], i.e. the higher efficiency cells had longer carrier lifetimes. The lifetime (τ) was measured from the exponential decay of the luminescence intensity, i.e. $\exp(-t/\tau)$, where *t* is time following excitation. In PL the minimum spot size of the laser is typically a few µm, and hence only an average carrier lifetime for the specimen can be measured. In contrast a similar experiment in a scanning electron microscope (SEM), where the electron beam acts as the excitation



Fig. 9. (a) Intensity of the EELS exciton peak as a function of momentum transfer in the π -conjugated molecules C_{60} , TPD, β -carotene and 8 T. The exciton extension (i.e. $\langle r \rangle$ in Eq. (1)) is plotted against the molecule length in (b). See text for further details. From Knupfer et al. [101] (reproduced with permission; Copyright 2000 Elsevier).

source to produce cathodoluminescence, can be used to measure the lifetime at individual defects. Steckenborn [106,107] designed such an SEM where electrostatic plates positioned close to the gun were used to blank the beam. The beam rise and decay time (i.e. temporal resolution) was ≤ 200 ps and the pulse width could be varied between 1 ns and 10 µs, thereby enabling quasi-equilibrium of the carriers to be established [107]. An alternative method, where an optically excited gold photocathode is used to produce a pulsed electron beam has also been recently developed [108,109]. The optical source is a Ti:sapphire UV mode-locked laser, which enables a far superior beam rise time of 10 ps and beam current of ~ 100 pA per pulse. Both beam blanking and optical excitation methods have been used to measure carrier lifetime at crystal defects, such as dislocations [106] and stacking faults [110].

Using time-resolved cathodoluminescence, Bimberg et al. [106] demonstrated that attaining quasi-equilibrium of the excess carriers during excitation has an important effect on the measured lifetime in GaAs. Recombination pathways involving abundant species are the first to appear in the luminescence spectrum. For example, in *n*-type GaAs luminescence involving neutral and

ionised donors (e.g. the bound excitons (D^o, X) and (D^+, X)) appear within 2 ns of excitation. Further excitation (upto 50 ns) is required to observe the donor-acceptor pair luminescence from neutral donor and neutral acceptors, due to the lower concentration of the latter in *n*-type GaAs (in order to generate a neutral acceptor one of the few ionised acceptors in the starting material must capture a hole generated by the excitation source, which is an inherently slow process). The delayed appearance of additional recombination pathways could potentially have an effect on the overall carrier lifetime, until at the point of quasi-equilibrium the lifetime reaches a constant value. Solar cell devices operate under continuous solar illumination, so that quasi-equilibrium is inevitably established. However, the number of photo-generated electron-hole pairs is relatively small. This is in contrast to high energy electron beams (e.g. SEM) where, unlike a photon, the electron can lose only part of its energy to the material, so that one incident electron can generate many (~10,000) electron-hole pairs. Only a small beam energy and beam current is therefore required to achieve a guasi-equilibrium level that is equivalent to solar illumination. For example, Galloway et al. [111] calculated that a beam energy of 11 keV and beam current of 1 pA will produce an excess carrier profile similar to that of solar illumination in CdTe solar cells. For a measurable luminescence signal the beam current must be significantly above 1 pA, so that the quasiequilibrium level of solar illumination will most likely be established, or even exceeded, in cathodoluminescence experiments. In fact 'high injection' conditions, where the excess carrier concentration is of a similar magnitude to the dopant concentration, have also been observed in the SEM [24].

3.4. Focused ion-beam (FIB) microscopy

The majority of thin-film solar cells are deposited on glass substrates/superstrates (Fig. 3), which presents challenges for both sample preparation and electron microscopy characterisation. Cross-sections of semiconductor thin-film solar cells can be prepared by fracturing the glass and selecting fragments which have macroscopically flat free surfaces. Fig. 10a is a secondary electron SEM image of a CdTe solar cell prepared in this manner. The thin-film has fractured along the grain boundaries and the strong topographic features reduce the contrast between individual layers (in fact CdS can hardly be distinguished from the underlying transparent conducting oxide). Furthermore, delamination of the thin-film from the glass superstrate is also visible. Alternatively the Ga ion-source in a FIB microscope [112,113] can be used to mill a trench in the device structure, which then enables secondary electron imaging of the thin-film cross-section, as shown in Fig. 10b [114]. Individual layers as well as twinning defects within the CdTe grains are now clearly visible. Close examination of the CdS-ZnO interface reveals pores (Fig. 10c) that would not have been otherwise observed if the sample was prepared by glass fracturing. The flat surface topography of FIB milled cross-sections has also been used to correlate the grain structure in the secondary electron image with the electron beam-induced current (EBIC) signal in thin-film silicon solar cells [115]. Crystallographic contrast can be further improved by imaging with secondary electrons generated by the ion-beam, rather than the electron beam. This is due to the strong dependence of ion-beam channelling on crystal orientation (fewer secondary electrons are produced for strongly channelling orientations) [113,116], although it must be noted that some sputtering will take place as the image is acquired by scanning the ion-beam over the region of interest. Furthermore, 3D volume reconstruction from repetitive milling and imaging of 2D 'slices' has been used to analyse the distribution of cracks and voids in a CIGS solar cell [67].



Fig. 10. (a) SEM secondary electron image (J.D. Major, K. Durose, unpublished results) of a CdTe solar cell cross-section obtained by fracturing the glass superstrate. The image is dominated by surface topography, which also makes it hard to distinguish between the thin CdS and transparent conducting oxide (TCO) layers. Delamination of the thin-film from the glass superstrate has also taken place. In (b) Ga-ion milling in a FIB is used to expose the thin-film cross-section. All layers as well as twin defects in the columnar CdTe grains are clearly visible. Closer examination reveals the presence of small voids at the CdS–ZnO interface, which are shown circled in (c). From Major et al. [114].

The use of FIB for preparing TEM specimens [117] is well known. Much success has been achieved with 'hard' materials, but the technique has also been applied to 'soft' materials, including organic solar cells [118–120]. In these devices a PED-OT:PSS hole conducting layer is first deposited on an indium tin oxide (ITO) coated glass substrate, before depositing the organic layer. The PEDOT:PSS is water soluble, so that the organic film can be floated off in de-ionised water and collected with a copper grid for plan-view imaging in the TEM. This is by far the most convenient sample preparation method. However, as mentioned in Section 2.3 the 3D morphology of the organic thin-film is a crucial parameter in device performance. The limitations of planview imaging can be partly overcome by the use of FIB milled cross-sections (see however Section 4.2 on electron tomography of organic solar cells), which also enable characterising the

roughness of individual layers and their interfaces [119,120]. To the authors' best knowledge a systematic study on ion-beam damage and ion-beam heating during FIB sample preparation of organic solar cells has not been carried out. Ion-beams comprising of heavy Ga ions could potentially damage the covalent bonds along polymer chains and/or the much weaker inter-chain van der Waal's bonding. Furthermore, the temperature rise due to ion-beam heating varies approximately inversely with thermal conductivity of the material [113]. Ion-beam heating is therefore extremely important in organic solar cells, especially since they are subjected to a short (30 min–1 h) anneal at only \sim 150 °C, during which microstructural changes take place and the device reaches peak efficiency [9]. The temperature rise during FIB milling must therefore be kept well below the annealing temperature.

4. Generic problems in solar cell characterisation

4.1. Grain boundary electrical activity in semiconductor thin-film solar cells

The growth process for semiconductor thin-film solar cells, such as CdTe and CIGS, introduces a high density of grain boundaries that affects the device performance (Section 2.1) [17,22–24,65,121–125,150]. The recombination velocity of the grain boundary has an important effect on carrier separation,

i.e. grain boundaries with a high recombination velocity act as strong sinks for minority carries, so that the fraction of minority carriers reaching the depletion region is reduced. Furthermore, the grain boundary barrier height must be overcome during majority carrier transport and therefore affects carrier collection. The barrier height and recombination velocity are however not constant for a given grain boundary, but are dependent on the illumination intensity; above a threshold illumination the barrier height and recombination velocity decrease markedly [126]. This has consequences for the measurement of these parameters using high energy electron beams [24,111], where the generation rate is significantly higher than solar illumination (see also the discussion in Section 3.3). Indeed the threshold injection density for onset of high injection conditions has been used to form the basis of a method to map the local majority concentration in plan-view electron beam induced current (EBIC) imaging of CdTe/CdS solar cells [24]. More generally however, the fact that electron microscopy can simultaneously characterise the structure and chemistry of grain boundaries makes it an invaluable tool for probing the fundamental origins of grain boundary electrical activity, at least at a qualitative level.

A method for extracting the recombination velocity from EBIC linescans acquired across a grain boundary was developed by Donolato [127]. The experiment is carried out in 'plan-view' geometry (i.e. the p-n junction is perpendicular to the incident beam) and the EBIC signal is assumed to originate entirely from the diffusion of excess carriers towards the depletion region.



Fig. 11. (a) and (b) are simultaneously acquired secondary electron and panchromatic cathodoluminescence (CL) images of an 'end-on' grain boundary in a vapour grown CdTe thin-film (the grain boundary is invisible in Fig. 11a, due to a lack of grain boundary grooving and inter-grain contrast). The integrated CL intensity across the grain boundary is extracted from the box region in Fig. 11b and is shown in (c). This is used for plotting $\ln[\Delta I(x_b)]$ against distance of the electron beam position from the grain boundary (x_b), as shown in (d). See text for a definition of $\ln[\Delta I(x_b)]$. From Mendis et al. [128] (reproduced with permission; Copyright 2010 American Institute of Physics).

Using Green's function methods to solve the continuity equation for carrier diffusion Donolato obtained an expression for the EBIC signal due to a point source of generation, which also contains the minority carrier diffusion length and recombination velocity as materials parameters. The generation function for the electron beam, obtained from (say) Monte–Carlo simulations, is 'weighted' by the Green's function solution to give the theoretical EBIC intensity as a function of distance from the grain boundary. 'Best fit' values for the minority carrier diffusion length and recombination velocity can be obtained by matching the theoretical line profiles to the measurement (Donolato however used the variance and area of the EBIC line profile to extract these parameters [127]).

The recombination velocity has also been measured using the panchromatic cathodoluminescence (CL) intensity across a grain boundary [128]. This method is based on the van Roosbroeck model [129] for the steady state carrier distribution normal to a free surface, the excess carriers being generated uniformly in a plane parallel to and at a finite distance away from the free surface. Under certain approximations the parameter $\ln[\Delta I(x_h)]$ $(=\ln[1 - {I(x_b)/I(\infty)}])$ is predicted to vary linearly with distance x_b of the electron beam position away from the grain boundary, where $I(x_b)$ is the CL intensity for a beam at x_b and $I(\infty)$ is the asymptotic CL intensity far from the grain boundary. The gradient of a $\ln[\Delta I(x_b)]$ vs x_b plot gives the minority carrier diffusion length (L) and the intercept the 'reduced' recombination velocity (i.e. the recombination velocity divided by the diffusion velocity (L/τ) in the perfect crystal, where τ is the minority carrier lifetime). Fig. 11b is the panchromatic CL image of a grain boundary in vapour grown, p-type CdTe (the simultaneously acquired secondary electron image is shown in Fig. 11a) and Fig. 11c is the integrated line profile acquired across the grain boundary from the box region in Fig. 11b [128]. The line profile is used to plot $\ln[\Delta I(x_b)]$ vs x_b , which is shown in Fig. 11d. The gradient of the least squares fit straight line gave an L value of 550 nm, which is consistent with previously reported values for CdTe using other measurement techniques. The reduced recombination velocity, extracted from the intercept, was however only 0.23, which for $\tau = 20 \text{ ns}$ [130] gives a recombination velocity of 632 cm/s. Recombination velocities for high angle grain boundaries are typically $\sim 10^4 - 10^5$ cm/s [126], which suggests that the grain boundary in Fig. 11b could be a low angle boundary, as has been previously observed in vapour grown CdTe thin-films [131]. This is consistent with the invisibility of the grain boundary in the secondary electron image (Fig. 11a). The CL method has the advantage that it does not require any electrical contacts or built-in electric field (cf EBIC), although some of the approximations made, such as neglecting any variation in CL emission efficiency at the grain boundary compared to the perfect crystal and the assumption of a planar excess carrier generation volume, may limit the usefulness of the technique. The former assumption leads to a deviation of the $ln[\Delta I(x_b)]$ vs x_b plot from linearity for beam positions close to the grain boundary (i.e. small x_b ; Fig. 11d) [128], while the implications of assuming a planar generation volume have been discussed in detail in [132]. Both EBIC and CL measurements were carried out in an SEM, rather than a TEM, to minimise the effects of free surfaces (i.e. free surfaces acts as sinks for minority carriers, through the surface recombination velocity).

The recombination velocity affects minority carrier transport while the grain boundary barrier height affects majority carrier transport. Inline holography in the TEM has been used to measure the barrier height in CIGS grain boundaries [65,124]. Here a focus series of images is used to reconstruct the specimen exit wavefunction [133]. Energy filtering can be used to minimise inelastic scattering (the energy filtered image will still contain phonon losses), thereby improving the accuracy of the reconstruction. A phase object changes the phase of the incident parallel beam of



Fig. 12. (a) Phase map of the electron exit wavefunction for a random grain boundary in a CIGS solar cell determined from TEM inline holography. The phase is extracted from the box region in Fig. 12a and is used to plot the variation in specimen potential across the grain boundary, as shown in (b). The potential of the surrounding matrix has been arbitrarily set to zero. Also superimposed in Fig. 12b is the potential across a twin boundary in CIGS. From Abou-Ras et al. [124] (reproduced with permission; Copyright 2009 Elsevier).

Distance (nm)

electrons by an amount that is proportional to the local electrostatic potential. Hence the phase map of the exit wavefunction can be used to extract the change in mean inner potential at the grain boundary with respect to the surrounding grain interiors. This is an approximate measure of the grain boundary barrier height (changes in atomic density and/or segregation also affect the grain boundary mean inner potential). Fig. 12a shows the phase map of a random grain boundary in CIGS that was reconstructed from a focus series of images [124]. The phase and hence local potential is lower at the grain boundary. Fig. 12b shows the potential profile across the random grain boundary in Fig. 12a as well as a twin boundary. The latter has a smaller barrier height due to lower 'misfit' between the two adjoining grains. The full width at half maximum of the potential wells is 1–2 nm [65]. It is clear that inline holography can be used to analyse the barrier height as a function of grain boundary character, as well as measure any variations resulting from doping, device processing, etc.

4.2. 3D morphology of excitonic solar cells

As described in Section 2.3 the performance of bulk heterojunction organic and hybrid organic-inorganic solar cells depend on efficient exciton dissociation (i.e. carrier generation) as well as efficient carrier collection at the electrodes. Once an exciton is photo-generated within the polymer it must reach a donor–acceptor

interface within its diffusion distance (~ 10 nm), so that it can dissociate into a free electron and a free hole. The free carriers must then have a contiguous pathway to the electrodes, preferably parallel to the electrode field direction. In both cases the 3D morphology of the phase separated organic components (bulk heterojunction cell) or semiconductor nanomaterial (hybrid solar cell) within the thin-film is an important parameter. Electron tomography [134,135] is a suitable method for characterising the 3D morphology at nanometre spatial resolution and has been successfully applied to hybrid solar cells [136,137]. As an example Fig. 13a, b and c show tomography reconstructions for CdSe nanoparticle-P3HT polymer hybrid solar cells with 2:1, 3:1 and 6:1 semiconductor to polymer weight ratios, respectively (the coloured regions correspond to CdSe, while transparent voxels are used for P3HT) [137]. The tilt series was acquired in HAADF mode which gives good atomic number contrast between CdSe and P3HT and furthermore satisfies the tomography requirement of an analysis signal that varies monotonically with the projected

mass-thickness of the specimen (i.e. the 'projection criterion'). The effect of morphology on carrier generation and collection can be deduced through a quantitative analysis of the reconstructed tomograms. For example a plot of the cumulative percentage of P3HT voxels within a given distance from the nearest polymer-CdSe nanoparticle interface is shown in Fig. 13d for the hybrid solar cells in Figs. 13a-c. Since absorption primarily takes place within the polymer, a higher fraction of P3HT voxels within the exciton diffusion distance improves carrier generation, and from Fig. 13d it can be seen that the 6:1 hybrid cell has the more optimised morphology for this process. The volume fraction of CdSe percolation pathways in contact with the top (i.e. electron collecting) electrode can also be calculated and was found to be largest for the 6:1 hybrid solar cell, which suggests more efficient carrier collection as well. These results are consistent with the higher external quantum efficiency (EQE) measured for the 6:1 hybrid device [137]. In practice the 'missing wedge', due to the limited (i.e. $< 90^{\circ}$) tilt angles in a tomography experiment, could



Fig. 13. Tomography reconstructions for CdSe nanoparticle-P3HT polymer hybrid solar cells with 2:1, 3:1 and 6:1 semiconductor to polymer weight ratio are shown in (a), (b) and (c), respectively. CdSe is shown in purple while the P3HT is made transparent for visual clarity. In (d) the cumulative percentage of polymer voxels within a given distance from the nearest polymer-semiconductor heterojunction is plotted for the tomograms in Fig. 13a-c. From Hindson et al. [137] (reproduced with permission; Copyright 2011 American Chemical Society).

have an effect on the accuracy of such quantitative analyses. The missing wedge results in the reconstructed object to be elongated along the thin-film normal and can for example, lead to overestimates for the connectivity of the nanoparticle network. This is particularly relevant for carrier collection, since it is the connectivity of the nanoparticle network in the direction of the electrode field, parallel to the thin-film normal, that is important, rather than the total connectivity. Furthermore, nanorods lying approximately perpendicular to the tilt axis will only be weakly reconstructed due to the missing wedge. The missing wedge itself can be minimised using a higher tilt angle [134] or through dual-axis tomography experiments [138], which are however more time consuming.

Tomography of hybrid solar cells is relatively straightforward, since there is strong contrast between the inorganic and organic components in the HAADF signal. This is however, not necessarily the case for bulk heterojunction solar cells, especially P3HT-PCBM, where contrast is essentially due to small differences in mass-thickness between carbon-rich phases. Conventional bright field imaging has however been used for tomography experiments on P3HT-PCBM [139,140] and other systems [141–143] (diffraction contrast in the bright field signal does not satisfy the projection criterion and will therefore introduce artefacts in the reconstruction, although in the case of P3HT-PCBM diffraction contrast is relatively weak and is easily destroyed by electron beam damage of the specimen [135]). The quality of the reconstructed tomograms was suitable for extracting quantitative information, such as the distribution of P3HT 'nanowires' through the thickness of the thin-film [139,140]. An alternative method for analysing carbonaceous materials was developed by Gass et al. [144]. These authors used plasmon ratio maps as the signal for tomographic reconstruction of a multi-wall carbon nanotube (MWCNT)-nylon composite. The $(\pi + \sigma)$ plasmon energy for MWCNT is 28 eV while for nylon it is 22 eV, so that a (22 eV/28 eV) energy filtered TEM ratio map gives strong contrast between the two components (e.g. nylon-rich regions will appear bright in the ratio map etc). Furthermore, the plasmon peak intensity increases monotonically with specimen thickness upto the plasmon mean free path, which for carbon-based materials is \sim 180 nm for 300 kV electrons [144], so that with a suitably thin sample the projection criterion for a tomography experiment can be satisfied. However, the technique suffers from the red-shift of the plasmon energy close to surfaces (i.e. surface plasmons) as well as delocalisation (Section 3.2). Nevertheless the technique could be useful for bulk heterojunction solar cells, provided the plasmon energies for the donor and acceptor materials are sufficiently different.

5. Conclusions

Many applications of electron microscopy characterisation in a wide range of thin-film solar cell devices have been highlighted. The recent advances in instrumentation have had a major impact in the development of this field. In particular it is now possible to extract quantitative information, such as the electrical properties of grain boundaries, nano-scale optical properties and 3D morphology of excitonic solar cells. Correlating these results with other measurements on device performance, such as quantum efficiency and current-voltage characteristics, is important for understanding the fundamental physics governing device operation. This in turn could lead to the future development of higher efficiency solar cells.

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References

- A. Goetzberger, C. Hebling, H.W. Schock, Materials Science & Engineering R-Reports 40 (2003) 1.
- [2] R.W. Birkmire, E. Eser, Annual Review of Materials Science 27 (1997) 625.
 [3] S. Guha, J. Yang, A. Banerjee, Progress in Photovoltaics: Research and Applications. 8 (2000) 141.
- [4] M. Bosi, C. Pelosi, Progress in Photovoltaics: Research and Applications 15 (2007) 51.
- [5] K. Yu, J. Chen, Nanoscale Research Letters 4 (2009) 1.
- [6] Z. Fan, D.J. Ruebusch, A.A. Rathore, R. Kapadia, O. Ergen, P.W. Leu, A. Javey, Nano Research 2 (2009) 829.
- [7] A.I. Hochbaum, P. Yang, Chemical Reviews 110 (2010) 527.
- [8] H. Spanggaard, F.C. Krebs, Solar Energy Materials and Solar Cells 83 (2004) 125.
- [9] B.C. Thompson, J.M.J. Fréchet, Angewandte Chemie International Edition. 47 (2008) 58.
- [10] M. Grätzel, Progress in Photovoltaics: Research And Applications 8 (2000) 171.
- [11] S.K. Deb, in: Y. Hamakawa (Ed.), Thin-Film Solar Cells: Next Generation Photovoltaics and its Applications, Springer-Verlag, Berlin Heidelberg, 2004, pp. 15–42.
- [12] W. Shockley, H.J. Queisser, Journal of Applied Physics 32 (1961) 510.
- [13] J. Nelson, The Physics of Solar Cells, Imperial College Press, London, 2003.
- [14] Y. Hamakawa, in: Y. Hamakawa (Ed.), Thin-Film Solar Cells: Next Generation Photovoltaics and its Applications, Springer-Verlag, Berlin Heidelberg, 2004, pp. 15–42.
- [15] C. Wronski, D. Staebler, Applied Physics Letters 31 (1977) 292.
- [16] C. Wronski, D. Staebler, Journal of Applied Physics 51 (1980) 3262.
- [17] K. Durose, P.R. Edwards, D.P. Halliday, Journal of Crystal Growth 197 (1999) 733.
- [18] S. Mazzamuto, L. Vaillant, A. Bosio, N. Romeo, N. Armani, G. Salviati, Thin Solid Films 516 (2008) 7079.
- [19] N. Romeo, A. Bosio, A. Romeo, Solar Energy Materials and Solar Cells 94 (2010) 2.
- [20] M. Emziane, K. Durose, N. Romeo, A. Bosio, D.P. Halliday, Thin Solid Films 480–481 (2005) 377.
- [21] M.D.G. Potter, D.P. Halliday, M. Cousins, K. Durose, Thin Solid Films 361–362 (2000) 248.
- [22] M. Terheggen, H. Heinrich, G. Kostorz, A. Romeo, D. Baetzner, A.N. Tiwari, A. Bosio, N. Romeo, Thin Solid Films 431–432 (2003) 262.
- [23] M. Terheggen, H. Heinrich, G. Kostorz, D. Baetzner, A. Romeo, A.N. Tiwari, Interface Science 12 (2004) 259.
- [24] P.R. Edwards, S.A. Galloway, K. Durose, Thin Solid Films 372 (2000) 284.
- [25] M.A. Contreras, K. Ramanathan, J.A. Shama, F. Hasoon, D.L. Young, B. Egass, R. Noufi, Progress in Photovoltaics: Research and Applications 13 (2005) 209.
- [26] S. Schorr, Thin Solid Films 515 (2007) 5985.
- [27] D.B. Mitzi, O. Gunawan, T.K. Todorov, K. Wang, S. Guha, Solar Energy Materials And Solar Cells 95 (2011) 1421.
- [28] I.D. Olekseyuk, I.V. Dudchak, L.V. Piskach, Journal of Alloys and Compounds 368 (2004) 135.
- [29] S. Pillai, M.A. Green, Solar Energy Materials and Solar Cells 94 (2010) 1481.
 [30] S. Pillai, K.R. Catchpole, T. Trupke, M.A. Green, Journal of Applied Physics
- 101 (2007) 093105. [31] T.L. Temple, G.D.K. Mahanama, H.S. Reehal, D.M. Bagnall, Solar Energy
- [31] T.L. Temple, G.D.K. Mahanama, H.S. Reenai, D.M. Baghan, Solar Energy Materials and Solar Cells 93 (2009) 1978.
- [32] E.C. Garnett, P.D. Yang, Journal of the American Chemical Society. 130 (2008) 9224.
- [33] B.Z. Tian, X.L. Zheng, T.J. Kempa, Y. Fang, N.F. Yu, G.H. Yu, J.L. Huang, C.M. Lieber, Nature 449 (2007) 885.
- [34] B.L. Williams, B. Mendis, L. Bowen, D.P. Halliday, K. Durose, MRS proceedings, in press.
- [35] T.M. Clarke, J.R. Durrant, Chemical Reviews. 110 (2010) 6736.
- [36] W.U. Huynh, J.J. Dittmer, A.P. Alivisatos, Science 295 (2002) 2425.
- [37] N.C. Greenham, X. Peng, A.P. Alivisatos, Physical Review B 54 (1996) 17628.
- [38] Y. Yu, P.V. Kamat, M. Kuno, Advanced Functional Materials 20 (2010) 1464.
- [39] B. O'Regan, M. Grätzel, Nature 353 (1991) 737.
- [40] K.D. Benkstein, N. Kopidakis, J. van de Lagemaat, A.J. Frank, Journal of Physical Chemistry B 107 (2003) 7759.
- [41] O.L. Krivanek, P.D. Nellist, N. Dellby, M.F. Murfitt, Z. Szilagyi, Ultramicroscopy 96 (2003) 229.
- [42] P.E. Batson, N. Dellby, O.L. Krivanek, Nature 418 (2002) 617.
- [43] N. Dellby, O.L. Krivanek, P.D. Nellist, P.E. Batson, A.R. Lupini, Journal of Electron Microscopy 50 (2001) 177.
- [44] O.L. Krivanek, G.J. Corbin, N. Dellby, B.F. Elston, R.J. Keyse, M.F. Murfitt, C.S. Own, Z.S. Szilagyi, J.W. Woodruff, Ultramicroscopy 108 (2008) 179.
- [45] M. Haider, G. Braunshausen, E. Schwan, Optik 99 (1995) 167.
- [46] M. Haider, H. Rose, S. Uhlemann, B. Kabius, K. Urban, Journal of Electron Microscopy 47 (1998) 395.

B.G. Mendis, K. Durose / Ultramicroscopy & (****)

- [47] M. Haider, S. Uhlemann, E. Schwan, H. Rose, B. Kabius, K. Urban, Nature 392 (1998) 769.
- [48] J.L. Hutchison, J.M. Titchmarsh, D.J.H. Cockayne, R.C. Doole, C.J.D. Hetherington, A.I. Kirkland, H. Sawada, Ultramicroscopy 103 (2005) 7.
- [49] M. Haider, P. Hartel, H. Müller, S. Uhlemann, J. Zach, Philosophical Transactions of the Royal Society of London Series A 367 (2009) 3665.
- [50] U. Dahmen, R. Erni, V. Radmilovic, C. Kisielowski, M.D. Rossell, P. Denes, Philosophical Transactions of the Royal Society of London Series A 367 (2009) 3795.
- [51] M. Varela, S.D. Findlay, A.R. Lupini, H.M. Christen, A.Y. Borisevich, N. Dellby, O.L. Krivanek, P.D. Nellist, M.P. Oxley, L.J. Allen, S.J. Pennycook, Physical Review Letters 92 (2004) 095502.
- [52] M. Bosman, V.J. Keast, J.L. García-Muñoz, A.J. D'Alfonso, S.D. Findlay, LJ. Allen, Physical Review Letters 99 (2007) 086102.
- [53] D.A. Muller, L. Fitting Kourkoutis, M. Murfitt, J.H. Song, H.Y. Hwang, J. Silcox, N. Dellby, O.L. Krivanek, Science 319 (2008) 1073.
- [54] S.J. Pennycook, D.E. Jesson, Ultramicroscopy 37 (1991) 14.
- [55] G.E. Cirlin, V.G. Dubrovskii, B.Y. Samsonenko, A.D. Bouravleuv, K. Durose, Y.Y. Proskuryakov, B. Mendis, L. Bowen, M.A. Kaliteevski, R.A. Abram, D. Zeze, Physical Review B 82 (2010) 035302.
- [56] D. Spirkoska, J. Arbiol, A. Gustafsson, S. Conesa-Boj, F. Glas, I. Zardo, M. Heigoldt, M.H. Gass, A.L. Bleloch, S. Estrade, M. Kaniber, J. Rossler, F. Peiro, J.R. Morante, G. Abstreiter, L. Samuelson, A.F. Morral, Physical Review B 80 (2009) 245325.
- [57] S.H. Vajargah, M. Couillard, K. Cui, S.G. Tavakoli, B. Robinson, R.N. Kleiman, J.S. Preston, G.A. Botton, Applied Physics Letters 98 (2011) 082113.
- [58] S. Lopatin, S.J. Pennycook, J. Narayan, G. Duscher, Applied Physics Letters 81 (2002) 2728.
- [59] A.M. Sanchez, P.L. Galindo, S. Kret, M. Falke, R. Beanland, P.J. Goodhew, Journal of Microscopy 221 (2006) 1.
- [60] M.J. Hÿtch, J.L. Putaux, J.M. Penisson, Nature 423 (2003) 270.
- [61] M.J. Hÿtch, E. Snoeck, R. Kilaas, Ultramicroscopy 74 (1998) 131.
- [62] B.G. Mendis, Y. Mishin, C.S. Hartley, K.J. Hemker, Philosophical Magazine 86 (2006) 4607.
- [63] C.S. Hartley, Y. Mishin, Acta Materialia 5 (2005) 1313.
- [64] Y. Yan, K.M. Jones, M.M. Al-Jassim, R. Dhere, X. Wu, Thin Solid Films (2010) 10.1016/j.tsf.2010.12.108.
- [65] D. Abou-Ras, J. Dietrich, J. Kavalakkatt, M. Nichterwitz, S.S. Schmidt, C.T. Koch, R. Caballero, J. Klaer, T. Rissom, Solar Energy Materials and Solar Cells 95 (2011) 1452.
- [66] D. Abou-Ras, G. Kostorz, A. Romeo, D. Rudmann, A.N. Tiwari, Thin Solid Films 480–481 (2005) 118.
- [67] Z. Zhang, T. Wagner, Thin Solid Films 517 (2009) 4329.
- [68] V. Nadenau, D. Hariskos, H.W. Schock, M. Krejci, F.J. Haug, A.N. Tiwari, H. Zogg, G. Kostorz, Journal of Applied Physics 85 (1999) 534.
- [69] K. Durose, M.A. Cousins, D.S. Boyle, J. Beier, D. Bonnet, Thin Solid Films 403–404 (2002) 396.
- [70] R.F. Egerton, Electron Energy Loss Spectroscopy in the Electron Microscope, second edition, Plenum Press, New York, USA, 1996.
- [71] V.J. Keast, A.J. Scott, R. Brydson, D.B. Williams, J. Bruley, Journal of Microscopy 203 (2001) 135.
- [72] M. MacKenzie, A.J. Craven, D.W. McComb, S. De Grendt, Applied Physics Letters 88 (2006) 192112.
- [73] D.A. Muller, T. Sorsch, S. Moccio, F.H. Baumann, K. Evans-Lutterodt, G. Timp, Nature 399 (1999) 758.
- [74] B.G. Mendis, M. MacKenzie, A.J. Craven, Ultramicroscopy 110 (2010) 105.
- [75] B.G. Mendis, A.J. Craven, Ultramicroscopy 111 (2011) 212.
- [76] J.E. Allen, E.R. Hemesath, D.E. Perea, J.L. Lensch-Falk, Z.Y. Li, F. Yin, M.H. Gass, P. Wang, A.L. Bleloch, R.E. Palmer, L.J. Lauhon, Nature Nanotechnology 3 (2008) 168.
- [77] S.H. Oh, K. van Benthem, S.I. Molina, A.Y. Borisevich, W. Luo, P. Werner, N.D. Zakharov, D. Kumar, S.T. Pantelides, S.J. Pennycook, Nano Letters 8 (2008) 1016.
- [78] E.C. Cosgriff, P.D. Nellist, Ultramicroscopy 107 (2007) 626.
- [79] S. Uhlemann, M. Haider, in: Proceedings of ICEM-15, Durban, South Africa (2002), vol. 3, page 327.
- [80] T. Walther, E. Quandt, H. Stegmann, A. Thesen, G. Benner, Ultramicroscopy 106 (2006) 963.
- [81] E. Essers, G. Benner, T. Mandler, S. Meyer, D. Mittmann, M. Schnell, R. Höschen, Ultramicroscopy 110 (2010) 971.
- [82] M. Terauchi, M. Tanaka, K. Tsuno, M. Ishida, Journal of Microscopy 194 (1999) 203.
- [83] P.E. Batson, Review of Scientific Instruments 43 (1986) 43.
- [84] K. Tsuno, Review of Scientific Instruments 64 (1993) 659.
- [85] N. Bohr, Philosophical Magazine. 25 (1913) 10.
- [86] R.F. Egerton, Ultramicroscopy 107 (2007) 575.
- [87] H. Kohl, H. Rose, Advances in Electronics and Electron Physics 65 (1985) 173.
- [88] D.A. Muller, J. Silcox, Ultramicroscopy 59 (1995) 195.
- [89] E. Kröger, Zeitschrift fur Physik 235 (1970) 403.
- [90] M. Stöger-Pollach, H. Franco, P. Schattschneider, S. Lazar, B. Schaffer, W. Grogger, H.W. Zandbergen, Micron 37 (2006) 396.
- [91] M. Stöger-Pollach, Micron 39 (2008) 1092.
- [92] U. Kaiser, J. Biskupek, J.C. Meyer, J. Leschner, L. Lechner, H. Rose, M. Stöger-Pollach, A.N. Khlobystov, P. Hartel, H. Müller, M. Haider, S. Eyhusen, G. Benner, Ultramicroscopy (2011). doi:10.1016/j.ultramic.2011.03.012.

- [93] M. Couillard, A. Yurtsever, D.A. Muller, Physical Review B 77 (2008) 085318.
- [94] A. Howie, Ultramicroscopy 11 (1983) 141.
- [95] M.G. Walls, A. Howie, Ultramicroscopy 28 (1989) 40.
- [96] M. Couillard, M. Kociak, O. Stephan, G.A. Botton, C. Colliex, Physical Review B 76 (2007) 165131.
- [97] J.P.R. Bolton, M. Chen, Ultramicroscopy 60 (1995) 247.
- [98] J. Nelayah, M. Kociak, O. Stephan, F.J. Garcia de Adajo, M. Tence, L. Henrard, D. Taverna, I. Pastoriza-Santos, L.M. Liz-Marzan, C. Colliex, Nature Physics 3 (2007) 348.
- [99] B. Schaffer, U. Hohenester, A. Trügler, F. Hofer, Physical Review B 79 (2009) 041401.
- B. Schaffer, K. Riegler, G. Kothleitner, W. Grogger, F. Hofer, Micron 40 (2009) 269.
 M. Knupfer, J. Fink, E. Zojer, G. Leising, D. Fichou, Chemical Physics Letters. 318 (2000) 585
- [102] M. Knupfer, T. Pichler, M.S. Golden, J. Fink, M. Murgia, R.H. Michel, R. Zamboni, C. Taliani, Physical Review Letters 83 (1999) 1443.
- [103] M. Knupfer, J. Fink, Physical Review B 60 (1999) 10731.
- [104] M. Fox, Optical Properties of Solids, Oxford University Press, 2001.
- [105] D.P. Halliday, M.D.G. Potter, P. Dawson, in: Proceedings of the 28th IEEE
- Photovoltaics Specialists Conference, Alaska 200, pp. 521–524. [106] A. Steckenborn, H. Münzel, D. Bimberg, Journal of Luminescence 24–25
- (1981) 351.
 [107] D. Bimberg, H. Münzel, A. Steckenborn, J. Christen, Physical. Review. B 31 (1985) 7788.
- [108] M. Merano, S. Sonderegger, A. Crottini, S. Collin, P. Renucci, E. Pelucchi, A. Malko, M.H. Baier, E. Kapon, B. Deveaud, J.D. Ganiere, Nature 438 (2005) 479.
- [109] M. Merano, S. Collin, P. Renucci, M. Gatri, S. Sonderegger, A. Crottini, J.D. Ganiere, B. Deveaud, Review of Scientific Instruments 76 (2005) 085108.
- [110] P. Corfdir, P. Lefebvre, L. Balet, S. Sonderegger, A. Dussaigne, T. Zhu, D. Martin, J.D. Ganiere, N. Grandjean, B. Deveaud-Pledran, Journal of Applied Physics 107 (2010) 043524.
- [111] S.A. Galloway, P.R. Edwards, K. Durose, Solar Energy Materials and Solar. Cells 57 (1999) 61.
- [112] L.A. Giannuzzi, F.A. Stevie, Introduction to Focused Ion Beams: Instrumentation, Theory, Techniques and Practice, Springer, New York, USA, 2005.
- [113] C.A. Volkert, A.M. Minor, MRS Bulletin 32 (2007) 389.
- [114] J.D. Major, L. Bowen, K. Durose, Progress in Photovoltaics: Research and Applications (2011). doi:10.1002/pip.1164.
- [115] D. Inns, T. Puzzer, A.G. Aberle, Thin Solid Films 515 (2007) 3806.
- [116] B.W. Kempshall, S.M. Schwarz, B.I. Prenitzer, L.A. Giannuzzi, R.B. Irwin, F.A. Stevie, Journal Of Vacuum Science And Technology B 19 (2001) 749.
- [117] L.A. Giannuzzi, F.A. Stevie, Micron 30 (1999) 197.
- [118] J. Loos, J.K.J. van Duren, F. Morrissey, R.A.J. Janssen, Polymer 43 (2002) 7493.
- [119] G.F. Malgas, C.J. Arendse, S. Mavundla, F.R. Cummings, Journal of Material Sciences 43 (2008) 5599.
- [120] J.K.J. van Duren, J. Loos, F. Morrissey, C.M. Leewis, K.P.H. Kivits, L.J. van Ijzendoorn, M.T. Rispens, J.C. Hummelen, R.A.J. Janssen, Advanced Functional Materials 12 (2002) 665.
- [121] L.M. Woods, G.Y. Robinson, D.H. Levi, in: Proceedings of 28th IEEE Photovoltaic Specialists Conference, 2000, p. 603.
- [122] I. Visoly-Fisher, S.R. Cohen, A. Ruzin, D. Cahen, Advanced Materials 16 (2004) 879.
- [123] C.S. Jiang, R. Noufi, K. Ramanathan, J.A. AbuShama, H.R. Moutinho, M.M. Al-Jassim, Applied Physical Letters 85 (2004) 2625.
- [124] D. Abou-Ras, C.T. Koch, V. Küstner, P.A. van Aken, U. Jahn, M.A. Contreras, R. Caballero, C.A. Kaufmann, R. Scheer, T. Unold, H.W. Schock, Thin Solid Films 517 (2009) 2545.
- [125] M.J. Romero, M.M. Al-Jassim, R.G. Dhere, F.S. Hasoon, M.A. Contreras, T.A. Gessert, H.R. Moutinho, Progress on Photovoltaics: Research and Applications 10 (2002) 445.
- [126] J. Oualid, C.M. Singal, J. Dugas, J.P. Crest, H. Amzil, Journal of Applied Physics 55 (1984) 1195.
- [127] C. Donolato, Journal of Applied Physics 54 (1983) 1314.
- [128] B.G. Mendis, L. Bowen, Q.Z. Jiang, Applied Physical Letters 97 (2010) 092112.
- [129] W. van Roosbroeck, Journal of Applied Physics 26 (1955) 380.
- [130] D.R. Wight, D. Bradley, G. Williams, M. Astles, S.J.C. Irvine, C.A. Jones, Journal of Crystal Growth 59 (1982) 323.
- [131] C.C.R. Watson, K. Durose, Journal of Crystal Growth 126 (1993) 325.
- [132] B.G. Mendis, L. Bowen, Journal of Physics: conference series (2011). doi:10. 1088/1742-6596/326/1/012017.
- [133] C.T. Koch, Ultramicroscopy 108 (2008) 141.
- [134] P.A. Midgley, M. Weyland, Ultramicroscopy 96 (2003) 413.
- [135] S.S. van Bavel, J. Loos, Advanced Functional Materials 20 (2010) 3217.
- [136] S.D. Oosterhout, M.M. Wienk, S.S. van Bavel, R. Thiedmann, LJ.A. Koster, J. Gilot, J. Loos, V. Schmidt, R.A.J. Janssen, Nature Materials 8 (2009) 818.
- [137] J.C. Hindson, Z. Saghi, J.C. Hernandez-Garrido, P.A. Midgley, N.C. Greenham, Nano Letters 11 (2011) 904.
- [138] I. Arslan, J.R. Tong, P.A. Midgley, Ultramicroscopy 106 (2006) 994.
- [139] S.S. van Bavel, E. Sourty, G. de With, J. Loos, Nano Letters 9 (2009) 507.
- [140] S.S. van Bavel, E. Sourty, G. de With, K. Frolic, J. Loos, Macromolecules 42 (2009) 7396.
 [141] X. Verge L. Leas Macromolecules 42 (2007) 1052.
- [141] X. Yang, J. Loos, Macromolecules 40 (2007) 1353.
- [142] S.S. van Bavel, E. Sourty, G. de With, S. Veenstra, J. Loos, Materials Chemistry. 19 (2009) 5388.
- [143] B.V. Andersson, A. Herland, S. Masich, O. Inganäss, Nano Letters 9 (2009) 853.
 [144] M.H. Gass, K.K.K. Koziol, A.H. Windle, P.A. Midgley, Nano Letters 6 (2006) 376.

B.G. Mendis, K. Durose / Ultramicroscopy & (****)

- [145] K. Durose, S.E. Asher, W. Jaegermann, D. Levi, B.E. McCandless, W. Metzger, H. Moutinho, P.D. Paulson, C.L. Perkins, J.R. Sites, G. Teeter, M. Terheggen, Progress in Photovoltaics: Research and Applications. 12 (2004) 177.
- [146] J.D. Major, Y.Y. Proskuryakov, K. Durose, Progress in Photovoltaics: Research and Applications (2011). doi:10.1002/pip.1196.
- [147] H.R. Moutinho, F.S. Hasoon, F. Abulfotuh, L.L. Kazmerski, Journal of Vacuum Science and Technology A 13 (1995) 2877.
- [148] H.R. Moutinho, M.M. Al-Jassim, D.H. Levi, P.C. Dippo, L.L. Kazmerski, Journal
- of Vacuum Science and Technology A 16 (1998) 1251. [149] M.A. Lourenco, Y.K. Yew, K.P. Homewood, K. Durose, H. Richter, D. Bonnet, Journal of Applied Physics. 82 (1997) 1423.
- [150] L.M. Woods, D.H. Levi, G.Y. Robinson, V. Kaydanov, R. Ahrenkiel, in: Proceedings of the Second World Conference on Photovoltaic Energy Conversion, Vienna, Austria, 1998, p. 1043.