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Microscopic measurements of variations in local (photo)electronic properties in nanostructured solar cells

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ABSTRACT

Modern nanostructured designs of solar cells improve photovoltaic conversion by better light trapping and collection of photogenerated charges. Illustrative example may be cells composed of radial junctions on semiconductor nanowires. In other cells the structural elements can be nanowires, nanorods or random light trapping structures. The elements have sizes from nm to μ m. Inevitably, they exhibit variations of shape, size and properties which influence local photovoltaic conversion. The cells operate as random arrays of microscopic photodiodes connected in parallel with overall performance limited by weak diodes. Microscopic measurements of photoresponse are needed to assess the distribution of the local photodiodes, their connections and influence of weak diodes. We demonstrate the use of atomic force microscopy (AFM) with conductive cantilever for study of local (photo)electronic properties of silicon nanostructures: p–i–n radial junctions of amorphous Si grown on Si nanowires or mixed phase microcrystalline films. We have used the conductive AFM to study the local photoresponse of the microcrystalline grains in mixed phase thin films to changes of external illumination. We have observed variations of the conductivity of the radial junction solar cells based on Si nanowires. Finally, we discuss possibilities of comparing the local photoresponse to local photovoltaic conversion efficiency.

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1. Introduction

Modern thin film solar cells are designed to use microscopic structures for increasing photovoltaic conversion efficiency by better light trapping and photogenerated charge collection. Attention is focused to solar cells based on semiconductor nanowires (NWs) which offer a possibility of surpassing the Shockley-Quiesser limit [1-5]. The cells are typically composed of huge number of nanowire based junctions with sizes comparable to visible light wavelengths. In other cells the structural elements with similar sizes can be transparent conductive oxide (TCO) nanocones [6] or nanorods [7,8] or modulated [9–12] or random light trapping structures [13]. Substantial research effort is invested into developing TCO structures leading to efficient light trapping which would not compromise the electronic properties by structural defects of the active Si layer [14,15], e.g., by multiscale architecture [16] or by flattened light-scattering substrates [17]. Silicon solar cells without the TCO electrodes use other ways of structuring the substrates,

e.g., by bead coating or plasma texturing [18]. Light trapping may be also designed using plasmonic scattering from metallic nanoparticles [19]. Several examples of these structures are illustrated in Fig. 1.

For all the structures described above, local variations of microstructural elements are either an inherent part of the cell or they will occur due to imperfections of the structuring. Optical and electronic properties of microstructural elements (e.g. nanowires) often strongly depend on both dimensions, occurrence of defects etc. The cells thus operate as parallel-connected random photodiode arrays [20] with overall performance limited by weak elements. The exponential sensitivity of the diode to local parameters means that even small fluctuations can significantly impact the resulting photovoltaic conversion efficiency, as illustrated in Fig. 2 for the case of radial junctions in Si nanowire based solar cells.

The lateral sizes of the cells' structural elements (nanowires, crystallites, light trapping features) range from tens of nanometers to few micrometers and few experimental data are available for assessing the distribution of local electronic properties at these scales. The conversion efficiency always tends to be smaller for larger cells and so the officially recognized solar cell record efficiencies must have a minimum size of 1 cm² for one-sun cells to be included into the record tables published in Progress in

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Fig. 1. Examples of the thin film based solar cells with microscopic structure designs: (a) radial junctions of a-Si:H on Si nanowires [3], (b) ZnO nanorods for conformal a-Si:H p-i-n coating [7], (c) Swiss cheese design of ZnO electrode for tandem cells [7], (d) hexagonal dimple arrays as back reflectors [12], quartz beads light trapping structure for crystalline silicon on glass solar cells [18].

Photovoltaics [21]. While the main development effort is aimed on improving uniformity and thus also the efficiency of the large area thin film panels, novel solar cells open an opposite direction of research measuring properties and efficiency at microscopic scale [22]. Development of a technique capable of measuring the efficiency down to the size of the structural elements would help us to understand the nanostructured solar cells and their limitations.

The required resolution can be easily achieved by scanning probe methods, in particular atomic force microscopy (AFM) with conductive cantilever (C-AFM) [23,24]. C-AFM has been used to study local electronic properties of photovoltaic materials, e.g., μ c-Si:H [25–27], Cu(In,Ga)Se₂ [28–30] and organic blends [31,32]. Photoresponse was probed by C-AFM first for organic bulk heterojunctions [33,34] and recently for a number

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