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A direct measurement of higher photovoltage at grain boundaries in CdS/ CZTSe solar cells using KPFM technique

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ABSTRACT

A direct mapping of photovoltage in a complete Mo/CZTSSe/CdS/ZnO/Al:ZnO solar cell device is carried out using Kelvin probe force microscopic (KPFM) measurements in surface and junction modes. Four cells having different values of open circuit voltage (V_{OC}) have been studied, and nanoscale variation of photovoltage have been obtained from the difference of surface potential (SP) images in the two modes. The maps exhibit a higher photovoltage at grain boundaries in general. Observed SP image of pristine CZTSe layer reveals downward band bending resulting in reduction of carrier recombination, and thus, lower J_{dark} at grain boundaries (GB). The observed downward band bending resulting in low J_{dark} at GB in CZTSe layer is used to explain the increase in photovoltage (V_{OC}) at the GB. KPFM measurements of CZTSe and CZTSe/CdS layers show that the surface potential of CZTSe layer and its variation can be affected by CdS deposition and further device processing, in addition to surface adsorption and contamination effects. The photovoltage mapping obtained from Kelvin probe force microscopic measurements on the final device without any interfering effects, is an important advantage of the present method.

1. Introduction

The kesterite-based $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells are composed of earth-abundant elements, and therefore, is a potential which can replace $Cu(In,Ga)Se_2$ (CIGS) absorber layers [1]. In addition, the optical and electronic properties of CZTS are comparable to those of CIGSe solar cell [2]. Junction location is a critical factor for the photovoltaic (PV) efficiency, especially in thin film solar cells because the junction is formed between different material partners and the defects at the hetro-interfaces can significantly affect the open circuit voltage (V_{OC}) by changing the carrier transport over the junction [3]. It has been shown in a number of studies that the high PV efficiency of CdTe, $CuInSe_2$, CIGSe and CZTS solar cells is due to higher carrier collection at benign grain boundaries in the absorber layers [4–8]. It is assumed that defects at grain boundaries (GB) do not always act as recombination centres, as expected in conventional semiconductor devices [9–11]. Presence of impurities (O and Na) has been observed to lead to a passivation effect [9–11].

KPFM is a specialized AFM based technique which is used to study the surface electronic properties of bulk, thin film and hetrostructures by measurement of contact potential difference between the samples and tip [12]. During KPFM measurements, the sample and AFM tip which act as two metallic electrodes, are brought in contact which results in alignment of their Fermi levels, and electron flow from the material with a lower work function to the material with higher work function. This Fermi level alignment causes a finite potential difference between two materials (AFM tip and sample), known as contact potential difference or surface pontential. A feedback dc voltage is applied to nullify the resultant potential force between AFM tip and sample, which is proportional to the square of fields. This nullifying voltage, is equivalent to the surface potential and is given by the relation, $\Phi_S = \Phi_t + SP$, for the case when it is applied to the sample, where Φ_t and Φ_s are work function of the tip and sample, respectively [12].

Scanning probe techniques, including, conductive atomic force microscopy (CAFM) and Kelvin probe force microscopy (KPFM) have been extensively employed to study the nanoscale electrical properties of CZTSe, as discussed below. In a study CAFM and KPFM measurements of CZTS layer have shown a significant increase in conductivity and lower work function at the grain boundaries [13,14]. These changes in the CZTS layer are shown to be a major factor for the increase in PV efficiency of the corresponding CZTSSe/CdS cells [2,14]. In another study, surface potential mapping of CZTS layer obtained using KPFM

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reveals higher work function at grain boundaries because of Li doping [15]. This is expected to form a depletion region resulting in lower recombination of majority carriers, and thus, higher current along the GB in the corresponding CAFM measurement [16]. It is clear that, the above studies explain the increase in PV performance at GB of CdS/CZTS cells, by indirect measurements of surface potential/ conductivity of bare CZTS layers. However, there is no direct evidence of measurement of photovoltage/photocurrent at GB present at CdS/CZTS junction in the finished solar cell device [2,16,17]. The deposition of CdS onto CZTSe layer can significantly affect the nanoscale variation of electrical properties (conductivity/SP) at the grain or grain boundaries in CZTSe. Multiple processing steps (sputtered deposition of ZnO layer) can also affect the average value, especially point to point variation at nanoscale.

The objective of this study is the use of KPFM to directly measure nanoscale variation of photovoltage at the CZTSe/CdS interface in the final cell comprising of Mo/CZTSe/CdS/i-ZnO/AZO [18]. The SP of the cell is measured in two different modes, i.e., surface and junction modes. By taking the difference in the two images under light conditions, a photovoltage map of the CZT(S)Se/CdS interface is obtained. As the measurements are carried out in the final cell, the effects of post deposition changes on the hetero-interface are completely eliminated.

2. Experimental section

For the present study, four test samples having different photovoltaic parameters were chosen. The CZTSe (Sample A) and CZTSSe (Samples B, C, D) based solar cells were fabricated from co-sputtered and solution-processed precursors, respectively [19,20]. The final solar cell devices comprise of a SLG/Mo/CZT(S)Se/CdS/i-ZnO/AZO/Ni-Al stack, where, SLG/Mo indicates a Mo coated soda lime glass substrate and AZO means aluminium doped ZnO layer. The current-voltage (J-V) measurements of the fabricated solar cells were carried out using a 2400 source meter (Keithley Instruments, Inc., Cleveland, OH, USA) under simulated AM1.5G source illumination at 100 mW/cm^2 by Xenon Arc lamp in ambient atmosphere. A Nanoscope IIIa (Veeco Metrology Group, USA) instrument was used to carry out KPFM measurements. Fig. 1 shows the schematic diagram of the solar cell device structure and the measurement scheme. The SP images of the solar cells were recorded in KPFM using Pt-Ir coated silicon cantilevers (ANSCM-Pt from Applied Nanostructures Inc, USA) and WSxM software was used for analysis of the recorded data. KPFM measurements provide a map of SP (contact potential difference V_{CPD} or SP) which is equal to difference between the work functions of sample (Φ_s) and tip (Φ_T). Prior to the imaging of samples, the work function of the Pt/Ir tip was calibrated using highly ordered pyrolytic graphite (HOPG) sample with a known function value. The average value of the work function of the tip is found to be ~5.5 eV. The tip radius of curvature is around ~20 nm. A white light fibre-optic source (Intensity ~ 28 mW cm^{-2}), which has been calibrated using standard commercially available Si solar cells, was used for all KPFM measurements under light conditions. Before recording the SP images, a sufficient initial stabilization time has been provided to make effect of thermal drift negligible. The KPFM measurements were carried out in homogeneous environmental conditions with stable temperature. The morphology of the samples are also recorded during KPFM measurements. Difference in height histograms obtained from morphology reflect the thermal drift, which is minimized. Here, we employ two different configurations to carry out the KPFM measurements in dark and light conditions. In the first configuration, referred to as 'surface mode' configuration, the bias is applied between the top contact (Al/Ni) grid and the KPFM tip (Fig. 1). In the second configuration, referred as 'Junction mode' bias is applied between the Mo-back contact and the KPFM tip (Fig. 1). In both configurations, shown in Fig. 1, the compensating DC bias is applied to the sample for obtaining the contact potential difference. The photovoltage map is obtained by subtraction of the SP images corresponding to surface and junction modes in light conditions. The advantage of using this two configuration measurement scheme is that the effects of buffer layer and surface contamination are nullified by using subtraction method. In addition, the above method also ensures that the obtained results are independent of the work function of the KPFM tip.

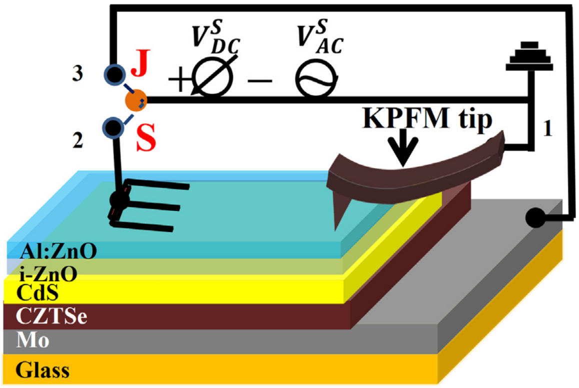

Fig. 1. Schematic diagram of the fabricated CZTSe/CZTSSe based solar cell and the two modes used for KPFM measurements: The bias is applied between the tip-1 and the top contact −2 in the Surface mode (S). In the case of Junction mode (J), the bias is applied between the tip-1 and the bottom Mo contact-3.

3. Results and discussion

The absorber layer CZT(S)Se in Sample A exhibits ZnSe as secondary phase on the surface. For Samples B-D, no secondary phases were detected. All samples have a composition of Cu/(Zn + Sn) = 0.7–0.8 and Zn/Sn = 1.2–1.3. The macroscopic J-V measurements of the fabricated solar cell samples (A-D) were carried out in dark and light conditions and the results of the latter are presented in Fig. 2. Energy band diagram of the fabricated device structure (under light conditions) is given in Fig. 3, showing band alignment of constituent layers with respect to Fermi level in the device structure comprising of CZT(S)Se p-type layer, CdS, ZnO and a highly doped n-type AZO layer. All the cells show a rectifying behaviour in dark (not shown) and photovoltaic response with downward shift of the J-V curve upon exposure to light. The solar cell performance parameters of open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (FF), and efficiency (η) are given in Table 1. Samples A-D are arranged in terms of increasing V_{OC}.

In order to gain insight into the phenomena responsible for the variation in the performance of the cells, especially nanoscale variation in V_{OC} (photovoltage), KPFM measurements have been carried out in dark and light conditions. To ensure minimal cantilever shadow effect during light exposure, the light source is kept at an oblique angle with respect to the horizontal plane during the measurements. In addition,

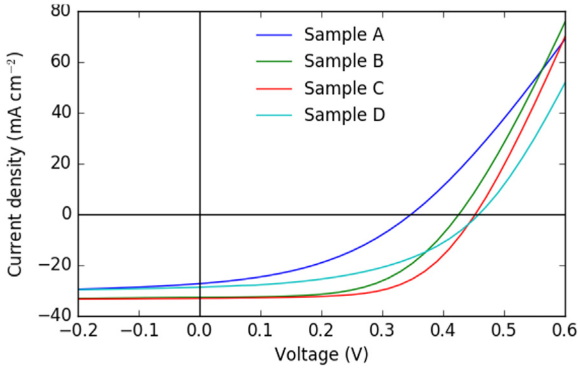

Fig. 2. Comparison of J-V characteristics of CZTS/CZTSSe thin film solar cell samples (A, B, C and D). The V_{OC} values of samples A, B, C and D are 347, 426, 453 and 459 mV respectively.(see Table 1).