Study of heterostructures of Cu$_3$BiS$_3$–buffer layer measured by Kelvin probe force microscopy measurements (KPFM)$^1$

F. Mesa and D. Fajardo

Abstract: The interface formed between Cu$_3$BiS$_3$ thin films and the buffer layer is a potentially limiting factor to the performance of solar cells based on Al/Cu$_3$BiS$_3$/buffer heterojunctions. The buffer layers of ZnS and In$_2$S$_3$ were grown by co-evaporation, and tested as an alternative to the traditional CdS deposited by chemical bath deposition. From the Kelvin probe force microscopy measurements, we found the values of the work function of ZnS, In$_2$S$_3$, and CdS, layers deposited into Cu$_3$BiS$_3$. Additionally, different electronic activity was found for different grain boundaries (GBs), from studies under illumination, we also found the net doping concentration and the density of charged GB states for Cu$_3$BiS$_3$ and Cu$_3$BiS$_3$/CdS.

PACS Nos.: 68.55.J-, 07.79.Lh, 73.30.+y.

Résumé: L'interface formée entre Cu$_3$BiS$_3$ couches minces et la couche tampon est un facteur limitant potentiel à la performance des cellules solaires au base de hétérogénéités de Al/Cu$_3$BiS$_3$/buffer. Les couches tampons de ZnS et In$_2$S$_3$ ont été cultivées par co-évaporation, et testés comme une alternative aux traditionnel CdS déposés par la CDB. A partir des mesures de microscopie à force Kelvin probe, nous avons trouvé les valeurs de la fonction de travail de ZnS, In$_2$S$_3$ et des CdS, des couches déposées sur Cu$_3$BiS$_3$. En outre, l'activité électronique différent a été trouvé pour les joints de grains (GBs) différents, à partir d'études de moins de éclairage, aussi nous avons constaté que la concentration de dopage net et la densité de charge états GBs pour Cu$_3$BiS$_3$, et Cu$_3$BiS$_3$/CdS.

1. Introduction

Recently, several studies have focused on obtaining new semiconducting materials that have good optoelectronic properties [1–4]. However, currently most semiconductors used for photovoltaic applications are Cu(In, Ga)Se$_2$, and CdTe [5–6], because these have reached the maximum conversion efficiency [7]. In this search we highlight Cu(In,Ga)S, Cu$_3$BiS$_3$, and AgInS$_2$ as an absorbent layer in solar cells [8–10], because elements such as Se, Te, and Cd are not included within their structures, which is beneficial because of the toxicity of these elements in high concentrations.

Moreover, the buffer layer that is usually composed of CdS [11] is also studied. Alternatively, a new study has suggested layers of In$_2$Se$_3$, ZnS, ZnO$_4$, and Zn$_{1-x}$Mg$_x$O, which have been deposited by different techniques, such as coevaporation, radio frequency sputtering, atomic layer deposition, spray ions layer gas reaction, spray pyrolysis, and chemical bath deposition [12–14]. However, it has been demonstrated that the electronic properties of the absorbent layer in solar cells strongly depend on the technique used to grow buffer layers [15].

Electronic properties have a very important aspect, because they have achieved considerable photovoltaic conversion efficiency despite the existence of many grain boundaries (GBs) [16]. On the surface of a pure CuGaSe$_2$ film area analysis has been made by the differences in work functions with crystal orientation, which has shown that for many grains there are electronic charges [17, 18]. In particular, studies under illuminated conditions have provided information about the charging and discharging of surface and defect states through the measurement of the surface photocurrent.

In this work, the topographic and electronic properties of Cu$_3$BiS$_3$ and the effect of the layers of CdS, ZnS, and In$_2$S$_3$ thin films on Cu$_3$BiS$_3$ were studied, measured by Kelvin probe force microscopy (KPFM). These layers were deposited through coevaporation and chemical bath deposition. However, In$_2$S$_3$ is very attractive because it has been proposed as a new buffer layer in solar cells [19] as a structure having TCO/In$_2$S$_3$/Cu$_3$BiS$_3$/Al.

2. Experimental

The Cu$_3$BiS$_3$ thin films were deposited on soda-lime substrates through the processes of evaporation of Bi and Cu metal precursors under a sulphur atmosphere (sulphurization) in two stages and keeping the substrate temperature at 300 °C during the entire process. In the first stage, Bi is evaporated leading to a Bi$_x$S$_y$ layer. In the second stage Cu is co-evaporated. The second stage is co-evaporation of Cu, creating a Cu$_x$S$_y$ layer that chemically reacts with the Bi$_x$S$_y$ layer, resulting in the formation of the compound Cu$_3$BiS$_3$. Al contacts were used for analysis by KPFM [20]. CdS thin films were deposited by chemical bath deposition on Cu$_3$BiS$_3$ thin films. The thickness of the films was approximately 80 nm. For specific experimental conditions see ref. 21; the thin film formation follows chemical reaction

$$[\text{Cd}^{2+}]_{\text{aq}} + \text{NH}_2\text{SCNH}_2\text{aq} + \text{OH}^- \rightleftharpoons [\text{CdS}]_{\text{film}} + \text{NCNH}_2 + \text{H}_2\text{O} \quad (1)$$

ZnS films were grown by co-evaporation of Zn into an atmosphere of S, which is evaporated by keeping the substrate temperature at 250 °C. A thickness monitor (Maxtec TM-400) with a quartz crystal sensor, was used to measure the deposition rate of Zn. The thickness of the films was ~120 nm. In ref. 22 the details of the procedure used to prepare the ZnS films are given.

On the other hand, In$_2$S$_3$ samples were deposited through the co-evaporation of In and S on a substrate heated at temperatures
around 300 °C. The deposition system configuration has the same components aforementioned for the manufacturing of films of ZnS. The thickness of the films was 150 nm. Finally, the aluminum contacts were deposited by sputtering DC magnetron. In ref. 23 details of the same procedure used to prepare the Mo films are given.

The KPFM measurements were accomplished by means of modified Omicron ultrahigh vacuum AFM/STM operating at a base pressure <10⁻¹⁰ mbar, using the amplitude modulation technique (AM mode). We used PtIr-coated cantilevers (nanosensors) with an initial resonance frequency of 75 kHz, measuring the contact potential difference (CPD) using the second resonance mode at 450 kHz. We obtained an energy resolution of 5 meV using ac-voltages as low as 100 mV. The lateral resolution of the contact potential signal was determined to be approximately 20 nm. KPFM was performed in ultrahigh vacuum to determine the surface morphology and the surface photovoltage, which was converted to a work function using a calibration of the tip with a curvature radius of 5 nm on a graphite sample [24, 25].

3. Results and discussion

Because any contamination can modify the results of the KPFM, KPFM images were taken in an ultrahigh vacuum 10⁻¹¹ mbar. Figures 1a and 1b show the difference in morphology and work function for two different regions at GB (G₁ and G₂). Fig. 1c shows changes in topography (solid line) and CPD (dotted line) at GB between G₁ and G₂ of Cu₃BiS₃ thin films. The topography of Cu₃BiS₃ polycrystalline samples exhibit a typical granular structure with the corresponding distribution of the work function measured in the dark. This work function presents variations between –110 and 78.4 meV (defined by the CPD). The results revealed that the work function obtained is of 4.36 ± 0.04 eV (determined in area A = 2μm × 2μm), which takes an average value of the entire distribution in the histogram, presented different values of Φ, which cannot be explained by sample homogeneity, giving rise to a nonuniform distribution.

Alternatively, to analyze the behavior of the electronic structure of the GBs of Cu₃BiS₃, following the model proposed by Seto [26] of Si, which explains the drop in the work function by the presence of intergrain states positively charged. Applying this model, can determine the net concentration of dopant impurities (P_net) of Cu₃BiS₃ and the charge density in the states of GB [18]

\[
P_{\text{net}} = \frac{2\varepsilon \Phi_{\text{gb}}}{e^2 w^2} \quad (2)
\]

\[
P_{\text{gb}} = \frac{1}{e^2} \left( \frac{8P_{\text{net}}}{P_{\text{gb}}} - \Delta \Phi_{\text{gb}} \right) \quad (3)
\]

where \( e \sim 10 \) is the electric permeability of the absorbent layer, \( \varepsilon_{\|} \) is the dielectric constant and \( e \) is the elemental charge, this model was already used by Fuertes Marrón [18] for CuGaSe₂ thin films. Using the experimentally obtained results for the potential drop \( \Delta \Phi \sim 91 \) meV and the space-charge region width \( w \sim 54.3 \) nm, we obtain the net doping concentration \( P_{\text{net}} = 3.86 \times 10^{16} \text{cm}^{-3} \) and the density of charged grain-boundary states \( P_{\text{gb}} = 4.19 \times 10^{11} \text{cm}^{-2} \), this is according to results obtained by Hall effect measurements on Cu₃BiS₃ absorbers [20].

Figure 2 shows a similar study of the Cu₃BiS₃–CdS system where the top layer is CdS, Fig. 2c shows changes in topography (solid line) and CPD (dotted line) at GB between G₃ and G₄, in this system

\[ \Delta z = 193 \text{ nm} \]

\[ \Delta z = 230 \text{ nm} \]

\[ \Phi = 4.30 - 4.42 \text{ eV} \]
the CPD profile is different to the Cu₃BiS₃ absorber layer, it presents a peak at GB contrary to Cu₃BiS₃ absorber, however, the work function takes on smaller values into the grain, which can be associated with sulphur vacancy in CdS induced by sulphur diffusion from CdS interior particle to GB, the sulphur diffusion passivate states at GBs. It was found that the CdS net doping concentration was \( N_{\text{net}} = 2.9 \times 10^{16} \text{cm}^{-3} \) and the density of charged GB states was \( N_{\text{gb}} = 3.2 \times 10^{11} \text{cm}^{-2} \). Sadewasser et al. [27], reported that these differences in magnitude of the work-function drop at GBs and doping concentrations estimated from the top and rear surfaces of this material may have their origin not only in the type of technology employed, but also and perhaps more significantly in the type of process followed for the film growth, particularly those leading to composition gradients within the layer thickness, such as sequential or multistage processes.

To obtain information regarding the homogeneity and topography of the samples with Cu₃BiS₃/buffer structure, scanning electron microscope measurements were taken, shown in Fig. 3. Figure 3a shows the thin film of Cu₃BiS₃ on top of the glass substrate. Figures 3b, 3c, and 3d show the structures of Cu₃BiS₃/CdS, Cu₃BiS₃/ZnS, and Cu₃BiS₃/In₂S₃ system analyzed.

Fig. 3. Scanning electron microscope images of (a) Cu₃BiS₃, (b) Cu₃BiS₃/CdS, (c) Cu₃BiS₃/ZnS, and (d) Cu₃BiS₃/In₂S₃ system analyzed.

Fig. 4. Histograms showing the work function distribution obtained by KPFM for: (a) Cu₃BiS₃; (b) Cu₃BiS₃, cleaning with ammonia; (c) Cu₃BiS₃/ZnS system; (d) Cu₃BiS₃/In₂S₃ system; and (e) Cu₃BiS₃/CdS system. (f) Work functions obtained for different samples obtained in dark and illuminated conditions.

![Histograms showing the work function distribution obtained by KPFM](image-url)
Cu$_2$Bi$_2$S$_3$/ZnS and Cu$_2$Bi$_2$S$_3$/In$_2$S$_3$, respectively. Starting with the scanning electron microscope images, it can be observed that the Cu$_2$Bi$_2$S$_3$ samples (Fig. 3a) grow presenting a scale-type formation, with very irregular and inhomogeneous grain size, showing fractures on the topmost region [28], which were confirmed in Fig. 1: while depositing buffer layers on the Cu$_2$Bi$_2$S$_3$, a formation of one substructure made up of much smaller grains (in the order of nanometres) which grow preferentially in the intergrain region, can be observed. This effect makes the electronic properties of the material change, which were determined by low of KPFM. Additionally, samples with Cu$_2$Bi$_2$S$_3$/In$_2$S$_3$ structure present the highest homogeneity, making this buffer layer an optimum layer that allows the defective states of Cu$_2$Bi$_2$S$_3$ [20] to be passivated.

Cu$_2$Bi$_2$S$_3$ samples exhibited a Bi$_2$O$_3$ layer when exposed to the atmosphere, which is clearly evidenced in previous studies [29]."