Surface characterization of epitaxial Cu-rich $CuInSe_2$ absorbers

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Abstract — **We investigated the electrical properties of epitaxial Cu-rich $CuInSe_2$ by Kelvin probe force microscopy (KPFM) under ambient and ultra-high vacuum conditions. We first measured the sample under ambient conditions before and after potassium cyanide (KCN) etching. In both cases, we do not see any substantial contrast in the surface potential data; furthermore, after the KCN etching we observed outgrowths with a height around 2nm over the sample surface. On the other hand, the KPFM measurements under ultra-high vacuum conditions show a work function dependence according to the surface orientation of the Cu-rich $CuInSe_2$ crystal. Our results show the possibility to increase the efficiency of epitaxial Cu-rich $CuInSe_2$ by growing the materials in the appropriated surface orientation where the variations in work function are reduced.**

I. INTRODUCTION

Polycrystalline Copper Indium Gallium Selenide (CIGS) is a well established material for photovoltaic applications, with record efficiencies above 23% [1]. Almost all absorbers and cells have been grown on glass substrates with a Mo back contact, which leads to a polycrystalline growth with many grain boundaries and different surface orientations of the individual grains [2], [3]. Only recently solar cells based on epitaxially grown of CIGS deposited on GaAs wafers have achieved an efficiency of 20% [4]. One of the main advantages of high quality single crystalline material is the absence of grain boundaries, leading to higher values of quasi-Fermi level splitting due to the reduction of carrier recombination sites [5]. However, so far the polycrystalline material outperforms the single crystalline in terms of power conversion efficiency. It is therefore important to investigate epitaxial material on the nanometer scale in order to identify the current bottleneck and to further improve the epitaxial absorber layers.

Different copper contents can be adjusted in the CIGS samples, in order to produce Cu-poor, stoichiometric and Cu-rich samples. Despite the higher efficiencies of the Cu-poor absorbers, Cu-rich material shows superior electrical properties, lower defects densities, less potential fluctuations and higher mobilities [6]. In this work, we concentrate on Cu-rich material, which denotes stoichiometric $CuInSe_2$ with an additional Cu_xSe secondary phase, which needs to be removed via a chemical etching, prior to device fabrication [7]. We will therefore also analyze the effect of potassium cyanide (KCN) etching on epitaxial absorbers on the nanometer scale.

In order to measure such small modifications, scanning probe microscopy based techniques are ideal due to their high spatial resolution [8]. One powerful technique to measure electrical properties of materials is Kelvin probe force microscopy (KPFM), which allows to directly investigate changes in the work function with lateral and energetic resolutions of around 20nm and down to 5meV respectively [9]–[12].

In this work, we applied the scanning probe microscopy based technique to directly probe the electrical and mechanical properties of single crystalline Cu-rich absorber. Is reported in the literature that $CuInSe_2$ absorbers degrade fast under ambient conditions, which is associated to the oxidation of the sample surface [13]. For this reason, we use two different setups, one under ambient conditions where the sample is exposed to air and also KCN etched, and another one under ultra-high vacuum (UHV) conditions with the sample never exposed to air.

II. EXPERIMENTAL DESCRIPTION

Epitaxial Cu-rich $CuInSe_2$ (CISe) films with a thickness of 650nm were grown by metal-organic vapor phase epitaxy (MOVPE) [14] on (100)-oriented semi-insulating GaAs wafers at 530°C and reactor pressure of 50mbar. From energy dispersive X-Ray analysis, we deduced a Cu/In ratio of 1.18. Low-temperature photoluminescence measurements corroborate that the samples are Cu-rich since we observe donor acceptor pair transitions and excitons, which is typical for Cu-rich material [6]. The topography and KPFM analyses under ambient conditions were carried out in a Bruker Multimode V, using a PPP-NCHR Nanosensors cantilever for intermittent contact mode AFM and a PPP-EFM Nanosensors cantilever for KPFM measurements. Amplitude modulation (AM-KPFM), applying an AC voltage of 5V at the resonance frequency of the tip in double pass mode with 100nm lift was used for the KPFM under ambient conditions. One piece of the sample was measured "as-grown" and a second piece was etched in 10% wt KCN for 5 minutes, in order to remove the Cu_xSe secondary phase. Large areas of the sample were measured by scanning electron microscopy (SEM) at 5kV in a JSM-6010LV Jeol apparatus. For the KPFM measurements under UHV conditions, we transferred the sample from the MOVPE directly to our ultra-high vacuum scanning probe microscopy system (Scienta Omicron VT-STM/AFM), via an inert gas transfer. Consequently, the samples were not exposed to air prior to the measurements. For the KPFM in UHV conditions, we used the frequency modulation technique (FM-KPFM), applying an AC voltage of 0.2V at 1.25kHz to the PPP-EFM Nanosensors cantilevers

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III. Results and Discussions

A. KPFM under ambient conditions

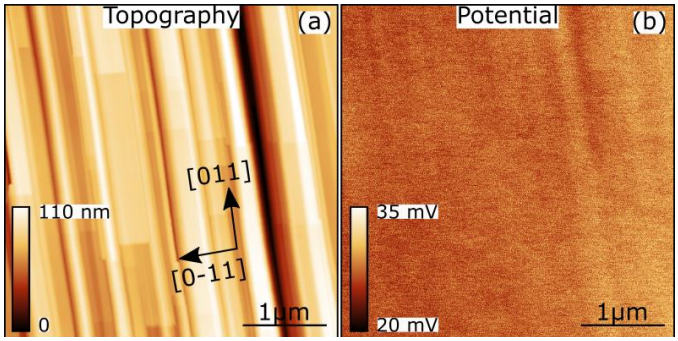

Fig. 1: Kelvin probe force microscopy (KPFM) of the epitaxial Cu-rich CISe sample under ambient conditions. (a) Topography and (b) surface potential images. The arrows indicate the crystallographic directions of the GaAs substrate

Fig. 1 shows the Kelvin probe force microscopy (KPFM) from the as-grown Cu-rich $CuInSe_2$ sample acquired under ambient conditions. The topography image (Fig. 1a) revealed trenches aligned in the [011] direction (cubic system) of the GaAs substrate with peak-to-peak height of up to 130 nm. Such patterns were already demonstrated for CIGS samples, where we can associate the alignment to the preferential growth direction during the epitaxial process and the facets to the spontaneous formation of a low energetic (112) polar surface [4],[15],[16]. Fig. 1b shows the surface potential map measured during double pass KPFM. We observed a homogeneous surface potential map with only a shallow contrast (in the resolution limit of the technique) in the top right side of the image. This result suggests a uniform work function all over the sample surface of our Cu-rich CISe. However, previous UHV-KPFM measurements on polycrystalline CIGS indicate that different surface orientations lead to different values in the work function [11]. In this way, we can propose two main reasons to explain the observed shallow contrast of our KPFM measurement on the epitaxial Cu-rich CISe sample. On the one hand, since the sample is exposed to air, oxidation or even a thin water layer can generate a homogeneous surface potential [17]. On the other hand, is largely reported in the literature that the excess of copper on Cu-rich CIGS samples forms a Cu_xSe secondary phase on the surface, which homogenizes the surface potential, and yields us this shallow contrast in the KPFM measurement.

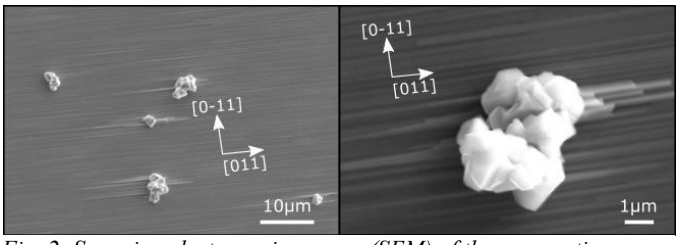

Fig. 2: Scanning electron microscopy (SEM) of the segregations on the surface of Cu-rich CISe sample.

From the Fig. 2 we clearly see that our Cu-rich CISe sample have segregated structures with more than 5µm in the size on top of the epitaxial layer which we associated to the Cu_xSe secondary phase.

The common procedure to remove the Cu_xSe secondary phase from the sample surface in chalcopyrite materials is by KCN etching. Thus, in order to understand the influence of the Cu_xSe secondary phase in the surface potential of the epitaxial Cu-rich CISe, we first performed SEM and AFM measurements before and after KCN etching depicted in Fig. 3a-b. From the as-grown sample (Fig. 3a), we observed material segregation (bright dots in the SEM image) over the entire surface, slightly oriented in the [011] direction. After 5 minutes of KCN etching, the white dots were partially removed, as showed in the SEM image (Fig. 3b). Longer etching times do not completely removed the structures, although they were further reduced. We attribute this to the fact that the Cu_xSe grains are very large, at least several micrometers in height, and a prolonged KCN etching is necessary to remove those structures.

Thus, intermittent contact mode AFM was used to check if the KCN is etching only the segregated structures, or if it is also etching the flat region of the sample. From the topography images (Fig. 3c,d), we can identify similar trenches for the as-grown as well as for the KCN etched samples, in other words, there are no massive changes related to the shape of the sample surface. However, from amplitude signal (which removes the influence of the roughness and therefore we are much more sensitive to small changes in the topography), we observed small structures on the surface of the etched sample (Fig. 3f). Looking in more detail in the topography image, it means, adjusting the scale bar to the range of a few nanometers, we could measure small dots with around 2nm height. Interestingly, in the phase image we can also identify the small structures with distinct color contrast compared to the CISe facets. As the phase signal is proportional to the differences in mechanical properties, we can associate the observed contrast to a different chemical composition between the dots and the surrounding. These results show that KCN etching does not only remove the big Cu_xSe secondary phase from the Cu-rich CISe, but it also modifies the rest of the surface. Currently, we can only speculate about the nature of this segregation. We attribute the changes in the surface area to a partial decomposition of the CISe due to KCN. Measurements on Cu-rich $CuInSe_2$ grown on polycrystalline glass show that a the strong KCN etching induces a substantial Cu-depletion [18]. Furthermore, we have identified a substantial amount of Indium oxides/hydroxides present at the surface after KCN. A possible explanation could therefore be that the small grains are related to Indium oxides/hydroxides. Another possibility is the presence of the elemental Selenium that cannot be completely

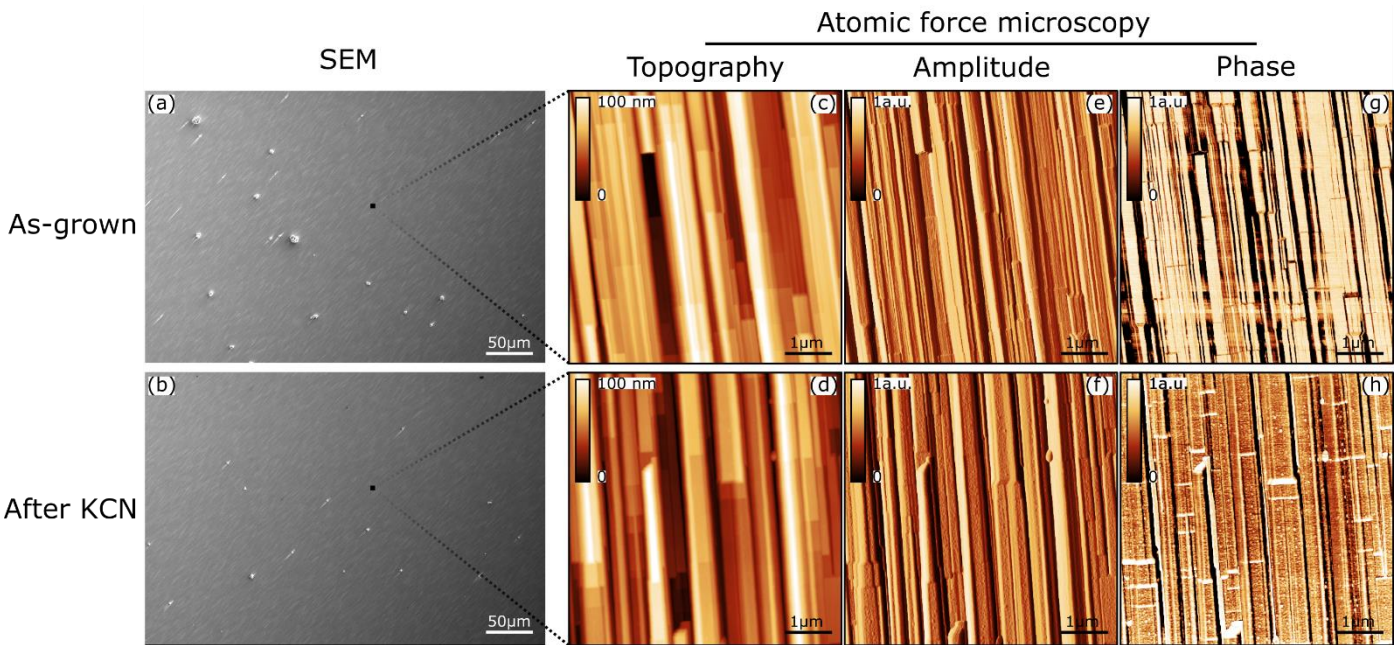

Fig. 3: (a) Scanning Electron microscopy (SEM) of the Cu-rich CIS sample. Atomic force microscopy in a flat region of the SEM image (c-d) topography, (e-f) amplitude and (g-h) phase contrast. Features with 2nm height are observed in the sample after KCN chemical etching.

removed by the KCN etching. However, more measurements are necessary to corroborate this speculation.

Fig. 4 shows the KPFM after KCN etching. As described in the Fig. 1, we do not see massive changes in the topography (Fig. 4a) when compared to the as-grown sample. From the potential image (Fig. 4b) we again observed only a shallow contrast along the image indicating that, even if we have Cu_xSe secondary phase, the oxidation or the thin water layer on top of the sample surface have stronger influence in the surface potential. Meaning that again, the observed variations are within the resolution limit of the machine.

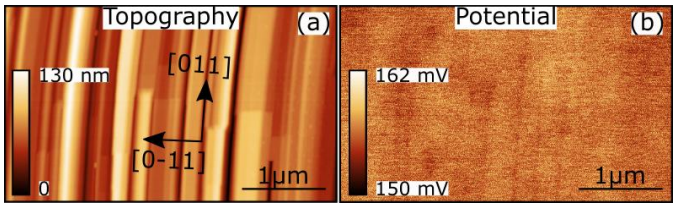

Fig. 4: Kelvin probe force microscopy (KPFM) of the epitaxial Cu-rich CISe sample under ambient conditions and after KCN. (a) Topography and (b) surface potential images.

B. KPFM under UVH conditions

To avoid any influence of the atmosphere in our KPFM measurements we moved one piece of the sample, without expose to air, directly from the MOVPE to our UHV KPFM machine. The topography image (Fig. 5a) shows the expected trenches pattern aligned in the [011] direction (cubic system) of the GaAs substrate with step height of up to 100 nm, which is shown in blue line profile of Fig. 5c. Simultaneously to the topography, the surface potential information is acquired, which also shows contrast along the direction [011] and some small features along the direction $[0\bar{1}1]$ (Fig. 5b). We can easily identify from the surface potential image at least three predominant contrasts in the work function that we associated

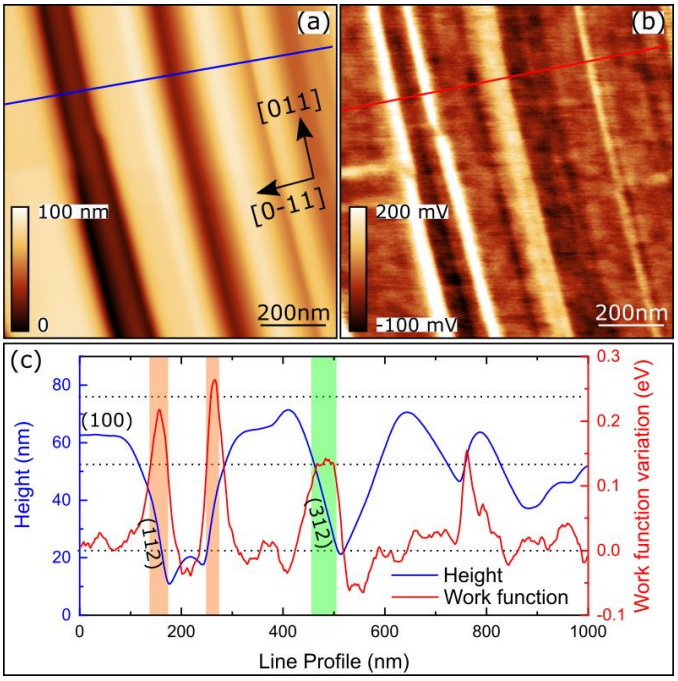

Fig. 5: Kelvin probe force microscopy (KPFM) image under vacuum conditions. (a) Topography and (b) surface potential images. The arrows indicate the crystallographic directions of the GaAs substrate. From the line profile, we related the difference in the surface potential to the different facets of the crystal. Differences up to 250 meV is measured between the facets (100) and (112).

to the crystal orientation of the facet. We measured the angles between the surfaces from the height line profile, assuming the horizontal plane as the GaAs (100) substrate. From this assumption, we found two major values, 27 and 54 degrees, which we can associate to the planes (312) and (112)/($1\overline{1}\overline{2}$) respectively. In the Fig. 5c, the orange regions represent the plane (112)/($1\overline{1}\overline{2}$) and green region represents the plane (312). We can associate a work function variation of 140meV between the planes (100) and (312), and up to 250meV between the planes (100) and (112)/($1\overline{1}\overline{2}$). For all the other surface orientations, the characteristic work function is similar to the work function in the plane (100).

From these results, we assume two possibilities for the difference in the work function. One hypothesis is that the crystal orientation surface is inducing the change in the work function. The same behavior was observed for the $CuGaSe_2$ grown on ZnSe (110) surface[11]. Another hypothesis is that Cu_xSe secondary phase is growing on one preferential surface orientation. In this way, we are measuring the work function difference between the $CuInSe_2$ and Cu_xSe that could be preferentially growing on the surface (112). Is important to note here that our KPFM measurements under UHV differs from our measurements under ambient conditions. We attribute this difference to the oxidation and/or water layer on the surface of the sample exposed to air, which homogenize the surface potential.

IV. Summary

Our KPFM measurements under ambient conditions show that the surface potential in the Cu-rich epitaxial CISe is strongly influenced by the oxidation and/or water layer, even after KCN etching. In accordance with the literature, the KCN etching removed most of the Cu_xSe secondary phase from Cu-rich CISe, however we have shown that the sample surface is modified, with the appearance of outgrowths which exhibit a height of approximately 2nm. UHV-KPFM measurements reveal a strong dependence of the work function according to the surface orientation of the crystal, which cannot be resolved in the KPFM measurements in air. We found from the AFM topography images three main orientations of the crystal surface, which correspond to three different values in the work function. We propose two hypotheses for the observed effect: different surface have different work functions or the Cu_xSe secondary phase grows preferentially on different surface. This observation can open a new field of investigation with the possibility to increase the conversion efficiency of the CIGS solar cells since different work functions lead to different band alignments, which is detrimental for solar cells. As we have shown in the KPFM measurements, the work function is strongly related to the surface orientation, meaning that ideal surface orientation of the crystal can be critical in the energy band alignment[19]. Our results show higher values for the work function in the surface (112) in analogy to CuGaSe2 grown on ZnSe(110)[11]. On the other hand, the observed differences in the work function could be related to the well-oriented growth of the Cu_xSe secondary phase in one preferential surface orientation. One hint for this affirmation is the presence of 2nm structures on the sample surface after KCN etching.

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