

## Study on Sulfur Passivation for CuInSe<sub>2</sub> Polycrystalline Thin Film with (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> Solution

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### ABSTRACT

In this work, we studied the effect on polycrystalline CuInSe<sub>2</sub> thin films by KCN etching and subsequent chemical sulfurization with (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> solution on these films. The Auger Electron Spectroscopy and X-ray photoelectron spectroscopy studies showed that KCN removed the oxygen and the sulfurization prevented regrowth of the oxides. The optical bandgap of the sulfurized films increased about 0.27 eV. From these experiments, we concluded that sulfur atoms are incorporated in the CuInSe<sub>2</sub> to form a stable and higher bandgap layer, CuIn(S,Se)<sub>2</sub>.

### INTRODUCTION

Thin film solar cells based on CuInSe<sub>2</sub> (CISE) which is one of the promising candidates for high efficiency, stable thin film photovoltaic (PV) cells have been reported to have solar energy conversion efficiency up to 16%<sup>1,2</sup>. The role of surface oxide layers on the performance of CISE PV cells has not been investigated to date even though a KCN treatment is sometimes used to improve CISE cell performance. It is well known that KCN is a good etchant for copper selenides and copper sulfides and that it can remove oxides very effectively. In this investigation, we have followed the KCN etch with immersion in an (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> solution which we hoped would sulfurize the surface thus preventing regrowth of oxides removed by the KCN. We expected that sulfur atoms would replace the oxygen on the surface and in the grain boundaries of the thin films. What we found is that the KCN treatment did indeed remove the oxygen and that the sulfur atoms entered into the CISE grains to transform the layers into alloy of CISE and copper indium sulfide, CISu.

### EXPERIMENTAL

CuInSe<sub>2</sub> thin films were prepared by the three-source evaporation method. The films were divided into two groups. One group was etched in an aqueous solution of 5% KCN for 5 minutes at room temperature, followed by immersion in an (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub> solution containing about 5% excess sulfur for 1 hr and a deionized water rinse. After samples were taken out, the surface was blown dry with high purity nitrogen gas, and the samples were quickly loaded into the vacuum chamber of the surface analyzer. The second group of samples were left untreated and served as a control. Differences between the surface and bulk composition were determined with Auger Electron Spectroscopy (AES) compositional depth profiling. X-ray photoelectron spectroscopy (XPS) measurements were performed with PHI Model 1600 ESCA system using Mg K<sub>α</sub> for the determination of binding energies (E<sub>B</sub>). Ion-beam sputter etching was performed with a 3KV Ar<sup>+</sup> ion beam (10<sup>-2</sup> Pa Ar pressure). The optical bandgaps were determined from the Tauc plot using IR absorption spectrophotometry in the wavelength region from 800 to 1150 nm.

### RESULTS AND DISCUSSION

The qualitative AES compositional depth profiles of the CuInSe<sub>2</sub> thin film before and after KCN etching are shown in Figs. 1(a) and 1(b), respectively. No oxygen is observed in films subjected to KCN etching and sulfurization. Analysis of the binding energy of the O 1s before KCN etching reveals that the oxygen is present in a mix of carbonates and indium oxide (E<sub>B</sub> ≈ 530.4 eV)<sup>3</sup> as shown in Fig. 2a. After sputtering for 1 min, the carbonates decrease drastically as demonstrated by the fading away of the C 1s peak and the oxygen is present mainly as indium oxide. The oxygen peak disappears after sputtering for 15 min, which agrees with the AES depth profiles that show a large amount of oxygen present in the CISE films before KCN etching. After KCN etching and sulfurization, the O 1s peak is shifted to higher binding energy

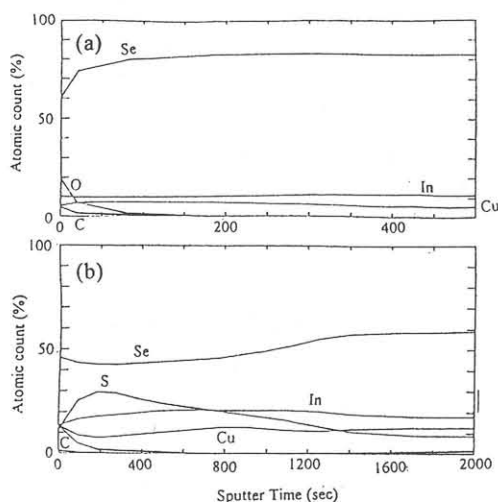


Fig. 1  
AES compositional depth profile on  $\text{CuInSe}_2$  thin film (a) before and (b) after etching in KCN solution and  $(\text{NH}_4)_2\text{S}_x$  sulfurization.

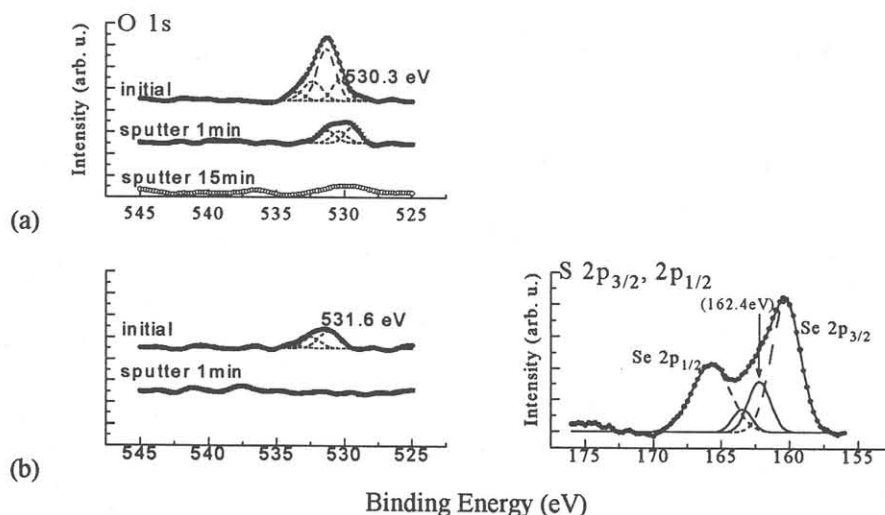


Fig. 2 Dependence of X-ray photoelectron spectra of O 1s and S  $2p_{3/2}$  on (a) before and (b) after etching in KCN solution and  $(\text{NH}_4)_2\text{S}_x$  sulfurized  $\text{CuInSe}_2$  thin film.

and removed by sputtering, i.e. oxygen is only present in a combination with carbon on the surface, as shown in Fig. 2b. Simultaneously, the In  $3d_{5/2}$  peak is shifted to a lower binding energy characteristic of  $\text{CuInSe}_2$ <sup>4</sup>). Those results demonstrate that KCN removes the native oxide and that the subsequent sulfurization can prevent the regrowth of the native oxide on the  $\text{CuInSe}_2$ . A significant amount of sulfur atoms diffused deeply into the  $\text{CuInSe}_2$  thin films after  $(\text{NH}_4)_2\text{S}_x$  treatment as shown in Fig. 1. Figure 2 indicates the copper is oxidized and the S  $2p_{3/2}$ ,  $2p_{1/2}$  peaks make their appearance in the  $(\text{NH}_4)_2\text{S}_x$  treated samples. Analysis of the energetic position of the Cu  $2p_{3/2}$  and S  $2p_{3/2}$ ,  $2p_{1/2}$  peaks leads to the conclusions that a copper sulfide layer is present in the sulfurized samples<sup>5</sup>).

We note that there are more sulfur atoms than oxygen atoms in the films after KCN etching and the Cu/In ratio is decreased by 17% (shown in Fig. 1). Based on the Cahen's defect chemical model<sup>6</sup>), all group VI elements are Lewis acids. They will react readily with Lewis bases, e.g.  $\text{V}_{\text{Se}}$  and  $\text{In}_{\text{Cu}}$ . Thus, after removal of oxygen  $\text{Cu}_x\text{Se}$  and/or excess copper phases by the KCN treatment, and consequently the Cu/In ratios are decreased<sup>7</sup>), i.e. the concentration of  $\text{Cu}_{\text{In}}$  which can neutralize  $\text{V}_{\text{Se}}$  is decreased, and the films becomes more sensitive to sulfur. Thus a portion of the selenide film is transformed into an alloy of  $\text{CuInSe}_2$  and  $\text{CuInS}_2$ . The optical bandgap as determined from a Tauc plot increases about 0.27 eV on the treated films. This supports the view that sulfur atoms are indeed incorporated in the  $\text{CuInSe}_2$  layer, transforming it into a stable, higher bandgap  $\text{CuIn}(\text{S},\text{Se})_2$  alloy.

## CONCLUSIONS

Polycrystalline  $\text{CuInSe}_2$  prepared by three-source evaporation were etched in a 5% KCN solution followed by sulfurization using an  $(\text{NH}_4)_2\text{S}_x$  solution. This treatment results in the removal of the native oxide by KCN solution followed by sulfurization which prevents the regrowth of the native oxide. As a result of the  $(\text{NH}_4)_2\text{S}_x$  treatment, a significant amount of sulfur atoms enter the  $\text{CuInSe}_2$  thin films and replace  $\text{Cu}_x\text{Se}$  with  $\text{Cu}_x\text{S}$ . Based on Cahen's defect chemical model, the substitution of S for Se may be the result of a higher sensitivity to sulfur caused by the KCN etching. The sulfur atoms are then incorporated into the  $\text{CuInSe}_2$  film to form a stable and higher bandgap film,  $\text{CuIn}(\text{S},\text{Se})_2$ . This hypothesis is supported by our observation that the optical bandgap increases by about 0.27 eV in the sulfurized films.

We conclude that a  $\text{CuIn}(\text{S},\text{Se})_2$  layer with a higher bandgap is formed as a result of KCN etching and the inorganic sulfurization. The effect of formation of this layer on the reduction of the surface recombination losses and improvement of the electrical properties of the films will be investigated in the future.

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