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# Electrochemical etching of copper indium diselenide surface

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## Abstract

$CuInSe_2$ thin films were grown onto ITO surface by electrodeposition and annealed in the hydrogen atmosphere at 400 °C. The influence of traditional chemical etching (KCN etchant) and electrochemical etching at various potentials and values of solution pH (0.8–13) on the surface composition and morphology was studied using the EDX and SEM methods. The mechanism of $CuInSe_2$ decomposition at various pH values was examined by cycling voltammetry. The influence of chemical and electrochemical etchings on electrical and optical characteristics of thin films was analyzed.

## 1. Introduction

Thin film solar cells based on $CuInSe_2$, $Cu(In,Ga)Se_2$ have been reported to demonstrate an efficiency of over 19.5% [1] for small-scale laboratory devices and 15% for a 100 $cm^2$ solar cell [2]. To develop solar cells with a higher efficiency, better composition control and improved reproduction of properties of the interface $CuInSe_2$/buffer layer are required.

$CuInSe_2$ films prepared with an excess of Cu to promote the grain growth, need another processing step to remove separate binary phases like $Cu_2Se$ segregated to the surface. The prevalent method for removing segregated Cu–Se and Cu–S phases is chemical etching in KCN solutions [3, 4]. Another approach to modify the surface is an exposure of the surface to strong oxidants, such as Br [3], $H_2O_2$ [5], permanganates [5] or complexes [6]. Electrochemical oxidation is a useful surface treatment technology. Although different research groups [7–10] have used electrochemical etching of $CuInSe_2$ and $CuInS_2$ films for surface modification, detailed analytical studies of the electrochemical process have not been conducted.

Two different processing solutions and technologies were used for electrochemical etching: oxidation in alkaline solutions (I) and electrochemical reduction–oxidation cycling in an acid solution (II). The influence of both electrochemical etchings on the surface morphology and elemental composition of thin films and on the electrical parameters of complete solar cell structures on their base are discussed in the following.

## 2. Thermodynamical aspects and background

The pH-potential diagram of $CuInSe_2$, CuSe and Se in an aqueous medium is mapped in Fig. 1. For simplicity and readability of data, only data of immunity, passivity and corrosion of stoichiometric (selected) elements are shown.

The data of stability of the $Se–H_2O$ system were calculated using the methodology of Pourbaix [12], the data of stability of the $Cu–Se–H_2O$ and $Cu–In–Se–H_2O$ system — by data from publications of Mishra [11] and Sardi [8]. Concentrations of Cu, In and Se species in the aqueous solution at 25 °C were assumed to be $10^{-4}$ M.

It should be noted that in aqueous solutions selenium could form soluble species in any pH region on both, the highest and lowest oxidation levels. Copper (II) and indium (III) species are soluble both in an acidic medium ($pH<5.5$ and $pH<3.5$, correspondingly) and in an alkaline medium at $pH>13$ (Fig. 1). The formation of metallic oxides on the surface, which may probably block the etching process, could be expected.

Separate phases of selenium and copper selenides could be present at the surface of $CuInSe_2$ films, since domains in which they are stable are adjacent to the $CuInSe_2$ stability domain. The pH-potential diagram shows two domains of the stability of $CuInSe_2$, which are not covered by the domains of Se and CuSe and could be used for separate dissolution of concurrent phases. In the range of oxidation potentials the $CuInSe_2$ domain proceeds at

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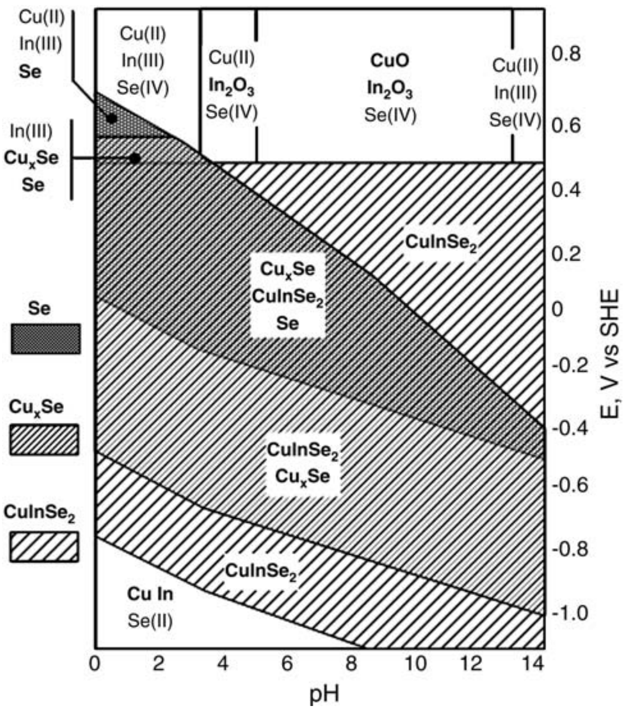

Fig. 1. Theoretical condition of corrosion, immunity and passivation of $CuInSe_2$, CuSe, and Se phases in an aqueous solution.

potentials more negative 0.4 V vs. SCE for pH values from pH = 4.5 and higher.

In the cathodic area, the reduction of $CuInSe_2$ is preceded by the hydrogen evolution and the reduction of metal oxides (including ITO) (−0.4 V and −0.6 V*)* that restricts the applied potential.

The relevant electrochemical reactions occurring in these systems are indicated as a list in Table 1. As the different selenium species could be expected in solutions on the dependence of solution pH, the reactions are listed as they proceed in basic ($SeO_3^{2-}$, pH = 13) and in acidic ($H_2SeO_3$, pH = 1.5) solutions.

Table 1
Thermodynamic data for selected reactions

| Reaction | | E/V (vs. SCE) | Ref. |
|---|---|---|---|
| 1O | $H_2SeO_3+4H^++4e^-\leftarrow Se^0+3H_2O$ | 0.50 | [12] |
| 2O | $2Cu^{2+}+H_2SeO_3+4H^++4e^-\leftarrow Cu_2Se+3H_2O$ | 0.45 | [13] |
| 3O | $Cu^{2+}+H_2SeO_3+4H^++6e^-\leftarrow CuSe+3H_2O$ | 0.45 | [13] |
| 4O | $Cu^{2+}+In^{3+}+Se^0+3e^-\leftarrow CuInSe_2$ | 0.42 | [8] |
| 5O | $2Cu^{2+}+In_2Se_3+Se^0+4e^-\leftarrow 2CuInSe_2$ | 0.4 | [8] |
| 6O | $Cu^{2+}+Se^0+6e^-\leftarrow CuSe$ | 0.32 | [13] |
| 7O | $SeO_3^{2-}+6H^++4e^-\leftarrow Se^0+3H_2O$ | 0.13 | [12] |
| 8O | $2Cu^{2+}+SeO_3^{2-}+6H^++4e^-\leftarrow Cu_2Se+3H_2O$ | 0.08 | |
| 9O | $Cu^{2+}+SeO_3^{2-}+6H^++6e^-\leftarrow CuSe+3H_2O$ | 0.08 | |
| 1R | $2CuSe+2H^++2e^-\rightarrow Cu_2Se+H_2Se$ | −0.2 | [8] |
| 2R | $Cu_2Se+2H^++2e^-\rightarrow 2Cu^0+H_2Se$ | −0.4 | [11] |
| 3R | $Se^0+2H^++2e^-\rightarrow H_2Se$ | −0.66 | [12] |
| 4R | $2CuSe+2e^-\rightarrow Cu_2Se+Se^{2-}$ | −1.0 | |
| 5R | $Cu_2Se+2e^-\rightarrow 2Cu^0+Se^{2-}$ | −1.2 | |
| 6R | $Se^0+2e^-\rightarrow Se^{2-}$ | −1.2 | [12] |
| 7R | $CuInSe_2+2H^++4e^-\rightarrow Cu^0+In^0+H_2Se$ | – | – |
| 8R | $CuInSe_2+4e^-\rightarrow Cu^0+In^0+Se^{2-}$ | – | – |

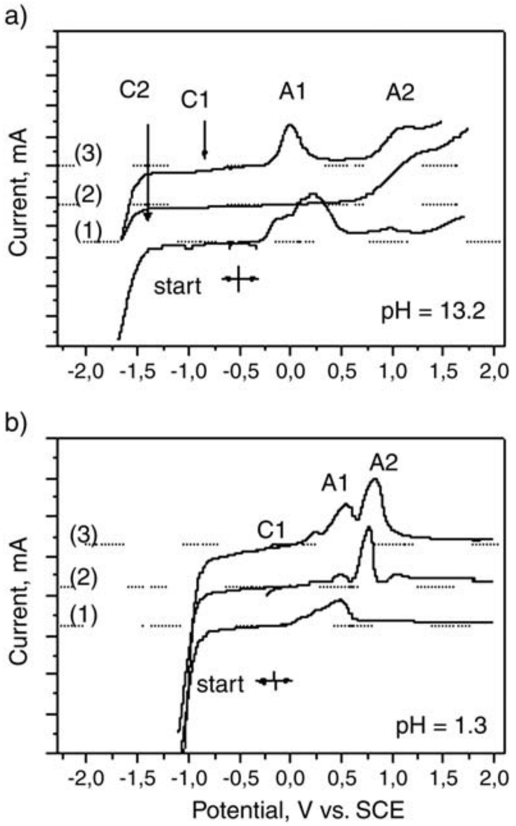

Fig. 2. Voltammograms of $Cu_{2-x}Se$ (1), $CuInSe_2$ (2) and un-etched CISe film (3). Scan rate is 10 mV/s. The active square of films is 1 $cm^2$.

## 3. Experimental

A standard three-electrode cell configuration was used for the voltammetry studies. A Pt-plate electrode was used as the counter

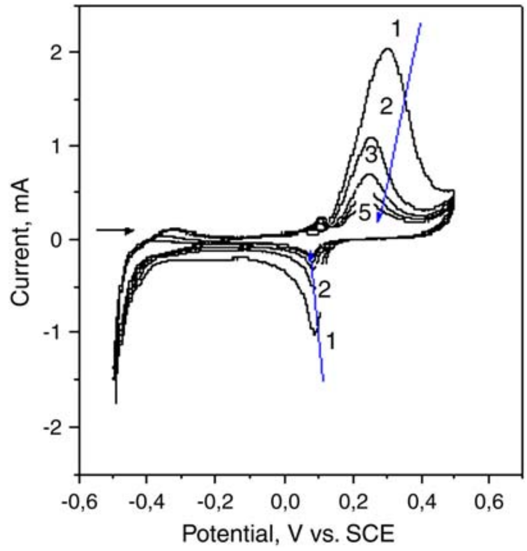

Fig. 3. Voltammetric protocol of electrochemical etching of CISe film in 0.1 M $H_2SO_4$ electrolyte. Scan rate is 10 mV s.