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Argon ion beam and electron beam-induced damage in $Cu(In,Ga)Se_2$ thin films

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Abstract

Ar ion beam and electron beam-induced damages in $Cu(In,Ga)Se_2$ thin films are investigated by transmission electron microscopy and X-ray energy-dispersive spectroscopy. We find that a high-energy Ar ion beam can cause severe damage in $Cu(In,Ga)Se_2$ surface regions by preferentially depleting Se and In. The depletion can occur with an Ar ion beam at energy as low as 0.5 keV. High-energy electron beams also cause damage in $Cu(In,Ga)Se_2$ thin films by preferentially depleting In and Ga. Our results imply that special care must be taken for measurements involving surface treatments using high-energy Ar ion beams or electron beams.

Keywords: CIGS; Ion beam damage; TEM; Electron beam

1. Introduction

Polycrystalline $Cu(In,Ga)Se_2$ (CIGS) related materials are the leading photovoltaic material for high-efficiency thin-film solar cells. The efficiency of the polycrystalline CIGS-based device is approaching 20% [1]. This remarkable performance of polycrystalline CuInSe2 (CIS) solar cells has been puzzling because polycrystalline solar cells usually exhibit poor performance compared to their single-crystalline counterparts [2]. To understand the origin of this performance, a large number of experimental techniques, such as X-ray photoelectron spectroscopy, secondary ion mass spectroscopy, scanning electron microscopy, scanning probe microscopy, and transmission electron microscopy (TEM), have been employed to investigate the structural, chemical, electronic, and optical properties of CIGS thin films [3–12]. In many cases, the CIGS samples measured have to encounter interaction with high-energy ion beams and/or electron beams. For example, for surface measurements, surface cleaning using a high-energy Ar ion beam is often required. For TEM studies, samples are often prepared by high-energy Ar ion-beam thinning and investigated by a high-energy electron beam. It is known that the composition of a CIGS film can range from the α phase region to the β phase region in the equilibrium CIS phase diagram [12]. The CIGS films with different compositions can have very different properties [13]. For example, electron and proton irradiation-induced property changes have been observed [14,15]. If surface cleaning and sample preparation using a high-energy ion beam can cause severe damage (such as compositional change), then the measured property may not truly represent the actual property of the films. Therefore, it is important to investigate the possible damage effects that may be caused by Ar ion and electron beams.

In this paper, we report on our TEM and energy-dispersive X-ray spectroscopy (EDS) study of Ar ion beam and electron beam-induced damage in CIGS thin films. We find that high-energy Ar ions can cause severe preferential depletion of In and Se from CIGS films and result in serious damage in CIGS surface regions. The preferential depletion of Se can even occur with Ar ions with energies as low as 0.5 keV. A high-energy electron beam (200 kV) can also cause damage in $Cu(In,Ga)Se_2$ thin films by preferentially driving out In and Ga. Our results indicate that special care must be taken for measurements involving surface treatments using Ar ion or electron beams.

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2. Experimental procedures

The CIGS thin films used in this study were grown by a 3-stage, physical vapor deposition growth process in a bell jar. To avoid any potential damage caused by the Ar ion beam, cross-sectional TEM specimens were made by directly cleaving CIGS devices. These cleaved TEM samples were examined in an FEI Tecnai TF20-UT microscope operating at 200 kV. Suitable samples were chosen for Ar ion milling at various conditions for various periods of time using a Fischione low-angle ion milling and polishing system. These samples were then examined again in TEM to investigate Ar ion beam-induced damage. EDS measurements were carried out to analyze compositional changes. Electron beam-induced damage was carried out by focusing the electron beam on freshly cleaved samples for various periods of time.

3. Results

We first look at Ar ion beam-induced damage in CIGS thin films. Fig. 1(a) shows a bright-field TEM image obtained from a freshly cleaved sample. This sample is not exposed to any Ar ion beam; thus, it is free of any damage. EDS measurements reveal that the average composition is about Cu:In:Ga:Se=22:18:9:51, which is very close to the composition measured by other techniques, confirming that no damage is present in this sample. The image also shows a very smooth morphology, indicating that a relatively flat surface can be achieved by the cleaving method. Nanoprobe EDS measurements revealed that local compositions fluctuate around the average composition [16]. However, the fluctuation is only within ±6%. This sample was first milled using 0.5 keV Ar ions at currents of 3 μA/cm^2 and an inclination angle of 7° for 5 min. Fig. 1(b) shows a bright-field TEM image of the sample after Ar ion-beam milling. The area is the same as that shown in Fig. 1(a). The image reveals that the sample is thinned, but also, that some nonuniform features started to form. From the results of a large number of ion-milling experiments, we know that these nonuniform features indicate damage. However, the EDS measurements from large areas did not show any significant compositional change. Our explanation is that the 0.5 keV ion beam is very gentle and 5 min is a short period of time. The ion-beam-induced damage is only within the very thin surface layers. To confirm this, we carried out nanoprobe EDS measurements by scanning the nanoprobe along straight lines in thin regions and in thick regions. In this case, the measured compositions are averaged compositions along the lines. Two lines, line1 and line2, are marked on Fig. 1(b). Line1 is at the sample edge, which is the thin region. Line2 is in the thick region. The composition obtained is Cu:In:Ga:Se=25:16:9:50 from the line 1, whereas it is Cu:In:Ga:Se=22:18:10:50 from the line 2. It shows that there is a clear compositional change in the thin region, but the change in the thick region is not visible. We then milled the sample at the same conditions for another 20 min. We found that the damage become more significant. The nonuniform features became even clearer. The composition

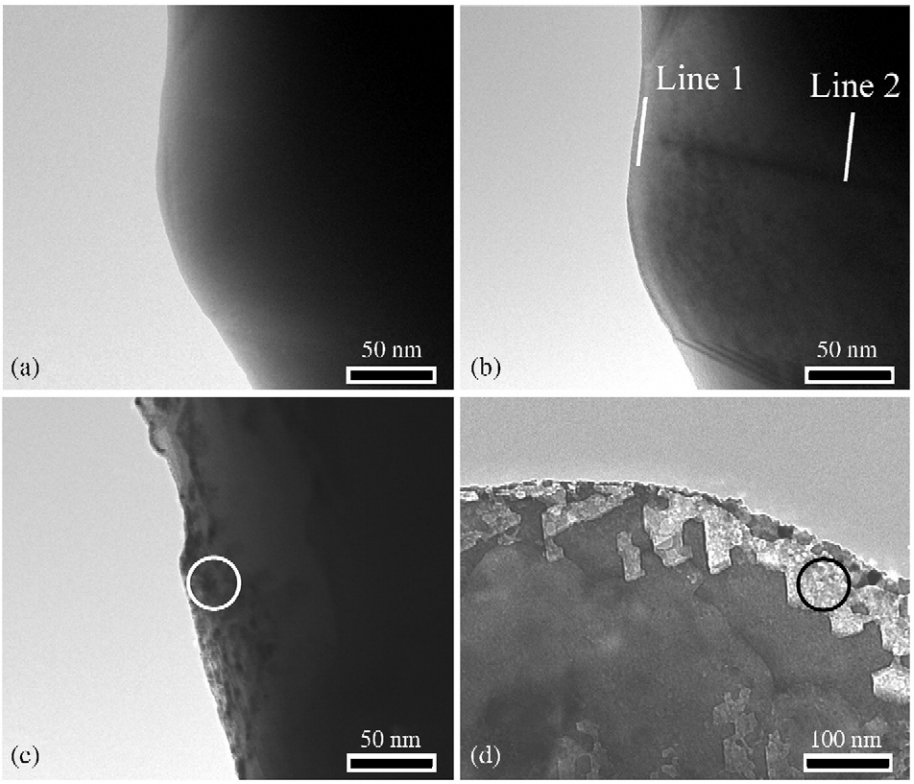

Fig. 1. Bright-field TEM images obtained from (a) a freshly cleaved CIGS sample; (b) the sample milled for 5 min by Ar ions with energies of 0.5 keV and currents of 3 μA/cm^2; (c) the sample milled for 10 min by Ar ions with energies of 1 keV and currents of 4 μA/cm^2; (d) the sample milled for 10 min by Ar ions with energies of 2 keV and currents of 10 μA/cm^2.