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In and Ga diffusion in Cu(In, Ga)Se_2 and Cu(In, Ga)S_2 films instantaneously prepared in a non-vacuum process

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Abstract

When Cu(In,Ga)$(S,Se)_2$ is prepared by heating metal precursor films in chalcogen atmosphere (sequential process) the resulting films typically show a gradient in the Ga/(In+Ga) ratio over the depth of the film. This is generally observed for reaction periods ranging from a few minutes (rapid thermal processing) to several hours. In this work we have investigated the Ga distribution in films where the reaction period was reduced to one second. The ultra-fast reaction was achieved by passing a high electrical current through the Mo foil substrate after depositing metal and chalcogen precursors.

Keywords: Cu(In,Ga)Se_2; Cu(In,Ga)S_2;non-vacuum process; solar cell; Chalcopyrite; metal substrate; instantaneous synthesis

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1. Introduction

Chalcopyrite thin films for solar cells are typically prepared by vacuum-based methods such as evaporation. Vacuum-based methods are costly in terms of equipment and raw materials utilisation. With a view to lower-cost fabrication processes [1], thin films were fabricated from precursors deposited by non-vacuum processes using selenization with H_2Se or selenium vapour, such as deposition of oxide precursor film and selenization [2,3], or paste coating and heat treatment [4,5]. Other groups have synthesized nanoparticle precursors, deposited those onto the substrate using a non-vacuum process, and finally sintered the films using a mechanochemical process [6-8]. We have previously reported that $CuIn(Se_x, S_{1-x})_2$ solid solution films were prepared by means of non-vacuum, instantaneous, direct synthesis from elemental In, Cu, Se, S particle precursor films without prior synthesis of $CuIn(Se_x, S_{1-x})_2$ nanoparticle precursors and without selenization [9,10]. The process was performed using metal substrates and a spot welding machine.

When $Cu(In,Ga)(S,Se)_2$ is prepared by heating metal precursor films in chalcogen atmosphere (sequential process) the resulting films typically show a gradient in the Ga/(In+Ga) ratio over the depth of the film [11-13]. This is generally observed for reaction periods ranging from a few minutes (rapid thermal processing) to several hours. Up to now, the Ga distribution in films prepared instantaneously has not been reported nor has there been a direct comparison between $Cu(In,Ga)Se_2$ (CIGSe) and $Cu(In,Ga)S_2$ (CIGSuf). In this study we have investigated the Ga distribution in CIGSe and CIGSuf films where the reaction period was reduced to one second.

2. Experimental details

Pieces of Molybdenum foil (10 mm×10 mm×1 mm) were used as substrates. Elemental metals were evaporated onto the Mo substrate (sequence: Cu/Ga/In/Mo substrate, Cu/(In+Ga) ratios =1.0 or 1.8 [14], Ga/(In+Ga) ratio = 0.2). Spraying solutions were prepared from commercial elemental powders, S or Se or Cu+S (> 99.9 % pure) dissolved in ethylene glycol mono-phenyl ether. The chalcogen part of the precursor films was deposited onto the Mo substrates already coated with the evaporated metallic films by spraying the suspension. Following that, precursor films were dried in a desiccator. To proceed with the reaction, an electrical current was passed through the metal substrate from one of the substrate edges to the opposite edge using a spot welding machine. Each of the two 10×1 mm^2 substrate edge areas was contacted with an electrode. Our spot welding power source (MEA-100A manufactured by MIYACHI) can be set to supply power ranging between 0.5 kVA and 9.25 kVA in intervals of 0.025 kVA. The reaction time can be adjusted between 1/60 seconds and 99/60 seconds in intervals of 1/60 second. The reaction time was 1 second for all films. We measured and verified current (0.75 kA-1.20 kA), voltage (1.09 V-1.45 V), and reaction time by a tester (MM-380A manufactured by MIYACHI) during the reaction. Thicknesses of reacted films were in the range from 1 μm to 5 μm. The phases present and the lattice constants were determined by X-ray diffraction (XRD) using Cu-K_α radiation. Depth profiles of the elements of Ga and In were measured by secondary-ion mass spectroscopy (SIMS) using a Cameca ion microprobe (IMS-4f). The primary ion was $^{133}Cs^+$ having an effective acceleration energy of 5.5 kV and the positive secondary ions were monitored. The analyzed area was about 30 μm in diameter.