

XRF and High Resolution TEM Studies of Cu at the Back Contact in Sputtered CdS/CdTe Solar Cells

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ABSTRACT

We have used the MR-CAT beam-line of the Advanced Photon Source (APS) at Argonne National Laboratory to study Cu x-ray fluorescence (XRF) in CdS/CdTe/Au structures on fused silica without transparent conductive oxide (TCO). After a "peel-off" process that separates the back contact at the CdTe/Cu interface both parts were studied by XRF. In order to locate the Cu spatially, we prepared TEM cross-sections and performed analytical electron microscopy at the Electron Microbeam Analysis Laboratory (EMAL) at the University of Michigan, to obtain high-resolution electron microscopy (HREM) imaging with a point-to-point resolution of 1.7 Å together with fine-probe energy-dispersive x-ray spectroscopy (EDX). We found direct evidence of an interfacial Cu-rich layer between CdTe and Au with thickness of ~ 4 Å and relatively high concentration of Cu in the Au layer. Based on previous EXAFS studies we suggest that a copper-oxide layer is formed at the CdTe/Au interface which might serve to inhibit diffusion of copper into the CdTe layer.

INTRODUCTION

High performance CdS/CdTe thin-film solar cells are usually completed with a low resistance Cu back contact. In our relatively thin (2-2.5 μm CdTe) sputtered cells, we have successfully used very thin evaporated Cu (3 nm) followed by evaporated Au (10-20 nm) to achieve 14% efficiency cells.[1] If all of the Cu were evenly diffused into the CdTe, one could expect a Cu density of ~10²⁰ cm⁻³ in the CdTe. However, C-V measurements of CdTe cells from several laboratories indicate maximum acceptor densities in CdTe of only ~5x10¹⁴ cm⁻³. [2] Thus most of the Cu is inactive. The location of the inactive must be determined to understand the behaviour of the cells.

Our previous studies of Cu K-edge extended x-ray absorption fine structure (EXAFS) from sputtered CdTe single layers on fused silica suggest that most of the ~30 Å of evaporated copper binds with oxygen in the chemical form of Cu₂O if the CdTe film has received a prior CdCl₂ treatment.[3] These studies were done on CdTe films deposited on high purity fused silica. Spectra from CdTe devices with the complete structure (glass/TCO/CdS/CdTe/metal contact) have not yet to be measured.

In this paper, we focused on the distribution of Cu in either a semi-cell-structure or complete structure. The semi-cell-structure sample was fabricated nearly identically

to our standard sputter-deposited cells except without a TCO layer and on fused silica rather than soda-lime.

In another paper for this conference,[4] we present x-ray fluorescence data on peeled-off metal back contact layers from complete cells that indicate 90% of the 3.5 nm evaporated Cu remains in the Cu/Au/(epoxy) back contact structure, so that only ~10% or an amount equivalent to ~0.35 nm of Cu adheres onto or diffuses into the CdTe. To obtain subnanoscale analyses of the Cu distribution in conventional cells, we have used HREM together with fine-probe EDX. High angle annular dark field (HAADF) imaging and EDX mapping are also employed to characterize the distribution of copper in the standard cell structure. An interfacial copper-rich layer of about four angstroms between CdTe and Au is observed. The significance of such layer will be discussed.

EXPERIMENTAL DETAILS

Typical magnetron sputter-deposited CdTe-based solar cells are fabricated with Cu and Au on the surface of CdCl₂ treated CdTe/CdS films on the top of SnO₂:F coated soda lime glass (TEC glass by Pilkington). Sputter-coated ZnO:Al on aluminosilicate glass is also occasionally used for better substrate transparency. No water rinse or acid etching is used after the Cl treatment and the depositions of the Cu and Au layers are completed without vacuum break. A heat treatment is employed to diffuse or activate the metal back contact as the last process of fabrication.

To study the distribution of copper in a cell structure using Cu K-edge EXAFS, samples with structure as close as possible to our standard cells are prepared with sputter-deposited 0.13 μm CdS and 2.3 μm CdTe layers on fused silica substrates without TCO coating, as shown in Fig. 1b. The substrate glass was heated to 250 °C during deposition, just as for regular TEC glass. Our standard vapor CdCl₂ treatment at 387 °C for 30 minutes was carried out, followed with 35 Å Cu and 200 Å Au depositions by evaporation onto the substrates held at room temperature. The process was finished with the same 45-minute thermal activation at 150 °C in ambient air. With such a "semi-cell" structure, a built-in field at the p-n junction is established, yet without x-ray fluorescence contamination from Cu impurities in the soda-lime glass. ZnO:Al is not included as a front contact in order to prevent signal contamination from Zn K_α, because the photon energy of the Zn K_α fluorescence (8639 eV) is very close to Cu K_α (8048 eV), which can affect the Cu signal detection. X-ray fluorescence (XRF) spectra were collected from these sam-