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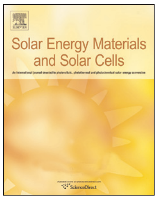

Review

Incorporation of alkali metals in chalcogenide solar cells

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ABSTRACT

Since 1993 it has been recognized that for solar cells based on the chalcogenide absorber material $Cu(In,Ga)Se_2$ (CIGSe) the incorporation of Na is crucial to obtain the highest values of power conversion efficiency. Since then, many reports have investigated the effects of Na in different chalcogenide solar cell materials. In the present review, we discuss the various sodium incorporation strategies for chalcogenide solar cells that have been reported. We briefly discuss the origin and the different interpretations of the positive effects that the presence of sodium provides in CIGSe and $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells. On the contrary, at the current stage of development of CdTe solar cells, Na is unwanted instead of incorporated. We review the various incorporation methods that have been reported: (a) diffusion from substrates like soda-lime glass, specialty glasses and sodium doped molybdenum (MoNa) layers; (b) external strategies by deposition of Na-containing compounds before, during and after the absorber growth; (c) other non-conventional methods. For each method, we present a literature review and critically present benefits and weak points. Finally, we provide an overview of characterization methods capable of directly probing the presence of sodium.

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1. Introduction

Na plays an important role in compound semiconductor thin film solar cells. Depending on the absorber material, the incorporation of Na into the solar cell stack can have a beneficial or harmful effect on the solar cell electrical performance. It also plays an important role how and at what time Na is introduced. For chalcopyrite $Cu(In,Ga)Se_2$ (CIGSe) based solar cells, it has been shown that an incorporation of Na into the absorber is beneficial for the electrical performance of the devices. However, for CdTe based solar cells Na degrades the properties of the transparent conductive oxide (TCO) and causes unwanted changes to the morphology of the absorber and is therefore avoided. For the kesterite $Cu_2ZnSn(S,Se)_4$ (CZTSSe) compound, a more recent studied material, the full effects of Na are still rather unknown, but preliminary results indicate a positive effect in the electrical performance as well. For these three types of solar cells, the most studied case is the one of CIGSe since in this case it is very well-known that the presence of Na within the CIGSe absorber layer is beneficial and is therefore desired. In this paper we review: (1) the general effects of Na on the different absorber materials, (2) the strategies that exist to incorporate Na in the absorber layer of thin film solar cells and (3) the characterization tools suitable to identify the presence of Na. The effects of Na in CIGSe, CZTSSe and CdTe, will be reviewed in the second chapter. We will describe how a doping concentration of Na in CIGSe was found to have a positive influence in CIGSe solar cells, briefly address some of these properties and explain why the amount of Na that is incorporated needs to be controlled. In the third chapter we will describe in detail the different approaches that have been presented for the incorporation of Na in CIGSe and CZTSSe solar cells. The discussed methods are: diffusion from the soda lime glass substrate or similar specialty glasses (Fig. 1a); the use of a precursor layer containing Na, i.e. a sodium doped Mo back contact (Fig. 1b) or a NaF precursor layer (Fig. 1c); external strategies for incorporation of Na as for example the evaporation of Na-compounds during the growth of the absorber layer (Fig. 1d) or after the growth of the absorber layer (Fig. 1e). In the fourth chapter we describe the techniques and tools used to directly measure the presence of Na.

2. Effects of Na in chalcogenide solar cells

2.1. Sodium in CIGSe solar cells

The importance of Na in the electrical performance of CIGSe was first observed in 1993 by Hedström et al. [1] and Holz et al. [2]. The work of Hedström et al. focused on solar cells properties: by comparing the growth of CIGSe solar cells on soda-lime glass (SLG), borosilicate, sapphire, and alumina substrates, the authors observed that CIGS solar cells grown on soda-lime glass leads to a better electrical performance, a stronger (112) texturing and a high concentration of Na throughout the CIGSe layer. Although the authors were not able to distinguish if the higher electrical performance was due to the (112) texturing or due to the presence of Na, the link between the presence of Na and high electrical performance was established. A more detailed study from the same authors showed that the improvement in the electrical performance was associated with an increase of the open voltage circuit (V_{oc}) and the fill factor (FF) and that in addition to the texturing the grain size of the CIGSe also improved [3]. Holz et al. focused on the electric properties of CIGSe and concluded that the presence of Na, even at a level of 10^{15} atoms/cm^{-3} increased the electrical conductivity either if Na was implanted on CIGSe grown on Na-free substrates or if the CIGSe was grown on SLG [2]. The relation between growth temperature and diffusion of Na from the SLG was introduced in 1995 by Zweigart et al. [4] by showing that Na diffusion is connected to the order of deposition of the elements. Several subsequent studies confirmed that the presence of Na improved the electrical performance of CIGSe solar cells [4–7]. At that point, several studies pointed to the fact that the increase in the open circuit voltage, V_{OC}, of solar cells was due to the higher built-in voltage (V_{bi}) of the junction created by Na increasing the free carrier concentration of CIGSe [8–10]. In 1997, a model was presented describing that by adding Na to CIGSe the number of acceptors does not change but the number of donors is

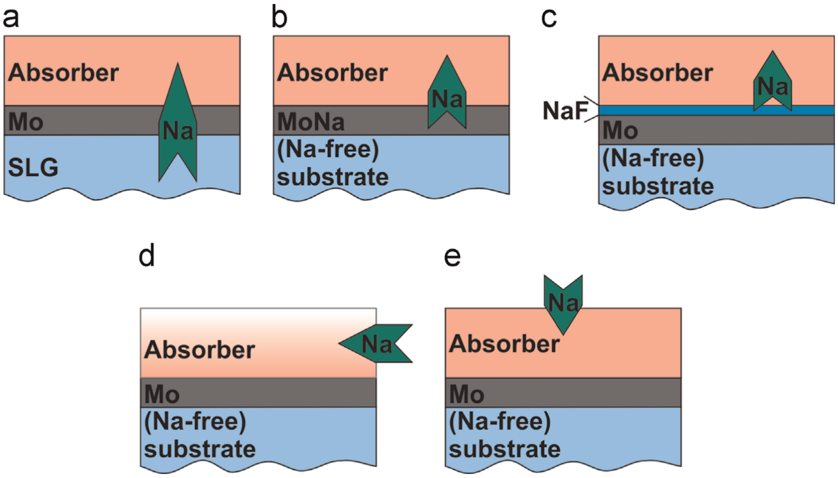

Fig. 1. Schematic representation of different Na incorporation strategies: (a) diffusion from the soda lime glass substrate; (b) diffusion from a sodium doped Mo layer; (c) diffusion from a NaF precursor layer; (d) introduction of Na during the growth of the absorber by evaporation of Na-containing compounds and (e) post-deposition evaporation of Na-containing compounds into the absorber.