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Review on Alkali Element Doping in Cu(In,Ga)Se$_2$ Thin Films and Solar Cells

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ABSTRACT

This paper reviews the development history of alkali element doping on Cu(In,Ga)Se$_2$ (CIGS) solar cells and summarizes important achievements that have been made in this field. The influences of incorporation strategies on CIGS absorbers and device performances are also reviewed. By analyzing CIGS surface structure and electronic property variation induced by alkali fluoride (NaF and KF) post-deposition treatment (PDT), we discuss and interpret the following issues: ① The delamination of CIGS thin films induced by Na incorporation facilitates CuInSe$_2$ formation and inhibits Ga during low-temperature co-evaporation processes. ② The mechanisms of carrier density increase due to defect passivation by Na at grain boundaries and the surface. ③ A thinner buffer layer improves the short-circuit current without open-circuit voltage loss. This is attributed not only to better buffer layer coverage in the early stage of the chemical bath deposition process, but also to higher donor defect (Cd_{Cu}^+) density, which is transferred from the acceptor defect (V_{Cu}^-) and strengthens the buried homojunction. ④ The KF-PDT-induced lower valence band maximum at the absorber surface reduces the recombination at the absorber/buffer interface, which improves the open-circuit voltage and the fill factor of solar cells.

1. Introduction

In 2013, Chirilă et al. [1] of the Swiss Federal Laboratories for Materials Science and Technology (Empa) achieved an energy conversion efficiency of 20.4% on a polyimide (PI)-substrate-based Cu(In,Ga)Se$_2$ (CIGS) solar cell by alkali fluoride (NaF and KF) post-deposition treatment (PDT), which is excellent progress for CIGS-based solar cells. This world-record-setting device, fabricated by the low substrate temperature process, was not only the most efficient CIGS-based solar cell, but also equaled the champion cell efficiency of polycrystalline silicon-based solar cells. As researchers continued to study the PDT process, several institutes rapidly boosted the best device efficiency. In the past three years, the efficiency increments that have been achieved are even larger than those made during the prior 15 years, thus establishing a milestone in pro-

gress. In June 2016, Jackson et al. [2] of the Center for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW) set the current world record for efficiency for CIGS-based solar cells, of up to 22.6%, by using heavy alkali element fluoride RbF-PDT treatment.

In 1993, Hedström et al. [3] found that the crystalline structure and device performance of CIGS absorber developed on soda lime glass (SLG) substrate is significantly better than that developed on borosilicate glass. The reason for this phenomenon is the incorporation of sodium (Na), which increases the open-circuit voltage (V_{OC}) and the fill factor (FF), and therefore increases device efficiency [4]. In 1994, Holz et al. [5] revealed that no matter whether the Na was diffused from SLG or introduced by other methods, the material conductivity increased only when the atom density of Na approached 10^{15} cm^{-3}. In 1997, Granata et al. [6] suggested that the device performance deteriorated as the Na concentration approached 1 at%.

The optimal concentration was in the range of 0.05 at% to 0.5 at%. In the same year, Contreras et al. [7] from the National Renewable Energy Laboratory unprecedentedly investigated doping with other alkali elements, and revealed that potassium (K) and cesium (Cs) also improved the device V_{OC}, but that Na improved it the most. In 2005, Rudmann et al. [8] from Empa improved the efficiency of CIGS devices on PI substrates up to 14.1% by doping Na on absorbers with PDT treatment. In 2013, as mentioned earlier, Chirilă et al. [1] from Empa demonstrated that the KF-PDT process could improve the conversion efficiency of flexible CIGS devices on a PI substrate to 20.4%.

It is commonly agreed that alkali element doping passivates the defects at the p-type CIGS absorber surface or at grain boundaries. It does not change the acceptor concentration, but decreases the compensating donor concentration [9]. As the free carrier density is determined by the difference in acceptor and donor concentration, the p-type carrier concentration increases; as a result, the Fermi level (E_F) is lowered. Thus, an enlarged E_F differential will produce higher V_{OC} and FF. In this article, we summarize some outcomes achieved by alkali incorporation, such as surface chemical composition and electronic structure variations, and analyze the reasons behind the boost to CIGS-based solar cell efficiency by the induction of alkali PDT.

2. Influences of incorporation strategies on Cu(In,Ga)Se₂ absorbers

There are three commonly adopted alkali incorporation methods: pre-deposition, co-evaporation, and post-deposition. Pre-deposition means that the alkali element diffuses from an alkali-containing substrate. Co-evaporation means that the alkali element is evaporated during the absorber deposition. Post-deposition means that the absorber is deposited first and then annealed with the alkali element (also called the PDT method).

2.1. Pre-deposition incorporation

It is commonly recognized that diffusing Na from the SLG substrate during CIGS evaporation, without intentional incorporation, is a good Na doping method. However, for large-scale SLG, the Na content uniformity is insufficient and deteriorates the module efficiency. The solution is to deposit a thin layer of aluminum oxide (Al_2O_3) or silicon nitride (Si_3N_4) on SLG to prevent elements in SLG from diffusing into deposited CIGS absorbers. Next, Na is distributed uniformly via a method such as sputtering a Na-containing molybdenum (Mo) (MoNa) back contact, which acts as a Na source. Another method is to deposit a NaF layer (NaF precursor), with a certain

amount on the Mo back contact to ensure a sufficient supply of Na during the absorber deposition. NaF is stable, and the residual fluorine ion (F⁻) reacts with selenium (Se) to form vaporous SeF_6 that can desorb from the absorber [10]. The Na doping is controlled by the NaF layer thickness. Insufficient NaF amount results in low V_{OC} and FF, and an excess amount leads to peeling-off problems during absorber deposition. Moreover, an excess amount of NaF also deteriorates the solar cell performance [11]. Due to the good controllability of the NaF precursor, this method has been commonly adopted.

Salomé et al. [12] compared the performance of CIGS-based solar cells prepared with different Na supply methods, including using SLG, NaF precursor, and a MoNa layer. According to Table 1[12] (where cell parameters are mean values), Sample 3, which is a Na-free device, shows the lowest V_{OC} and FF. Thus, the average conversion efficiency is only 8.8%. Of the rest of the samples with pre-deposition incorporation methods, the NaF precursor sample (Sample 4) shows the best performance, with a significantly higher V_{OC} and FF than the other devices. The second-best performer is the SLG sample (Sample 1), and the worst device among the Na-doped samples is the sample with the MoNa structure (Sample 5). This sample is doped with Na diffused from the Mo back contact layer. The lowest device parameters indicate the lowest doping content. In addition, Sample 2, which was prepared with a MoNa layer on SLG, shows inferior performance compared with Sample 1. We deduce that the MoNa layer blocks the diffusion of Na from SLG to the absorber.

2.2. Co-evaporation incorporation

In 2010, Güttler et al. [13] prepared CIGS absorbers on PI substrate using the three-stage co-evaporation process, and incorporated Na by co-evaporation during the first, second, and third stages, respectively. They compared the film structures with Na-free CIGS film (Fig. 1) [13].

The scanning electron microscope cross-sections in Fig. 1 show that incorporating Na during the first and second stages deteriorates the CIGS crystallinity. Fine grains were found at the film surface and back interface. However, incorporation at the third stage only slightly affects the crystallinity at the film surface, and the corresponding solar cell shows the best performance. The Na-free sample shows larger grain sizes with no stratification. By analyzing the secondary ion mass spectrum (SIMS) profiles (Fig. 2) and comparing the results with Fig. 1, we deduced that gallium (Ga) accumulates at the Cu(In,Ga)Se₂ (CIGS)/Mo interface if Na is incorporated at the first or second stage. These fine grains were composed of high-Ga-content CIGS or $CuGaSe_2$ (CGS). For the samples in which Na co-evaporated at the third stage, fine grains were located at the film surface, and

Table 1
Effects of different Na incorporation methods on the performance of CIGS solar cells [12].

Sample	Substrate	Back contact	Temperature (°C)	V_{OC} (mV)	J_{sc} (mA·cm⁻²)	FF (%)	Conversion efficiency (%)
1	SLG	Mo	540	678 (674–681)	32.48 (32.29–32.68)	76.0 (72.6–77.0)	16.8 (15.8–17.1)
2	SLG	MoNa/Mo	540	625 (605–634)	32.32 (31.93–32.81)	71.0 (63.8–72.2)	14.4 (12.9–15.1)
3	Al_2O_3	Mo	540	480 (393–492)	31.46 (29.15–32.17)	57.8 (38.6–58.7)	8.8 (4.7–9.1)
4	Al_2O_3	Mo/NaF	540	698 (684–703)	32.23 (32.02–32.64)	76.4 (74.9–77.5)	17.1 (16.8–17.5)
5	Al_2O_3	MoNa/Mo	540	590 (577–601)	32.42 (32.13–32.72)	70.0 (67.2–72.7)	13.4 (12.6–14.0)
6	Al_2O_3	MoNa/Mo	600	520 (507–529)	32.55 (32.32–32.78)	65.1 (61.5–67.3)	11.0 (10.1–11.3)
7	Al_2O_3	MoNa/Mo	640	556 (525–574)	32.53 (31.79–32.77)	65.2 (63.3–69.1)	11.8 (10.8–12.7)

J_{sc}: the short-circuit current density.