INFLUENCE OF Na ON THE ELECTRO-OPTICAL PROPERTIES OF Cu(In,Ga)Se$_2$

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ABSTRACT

Polycrystalline Cu(In,Ga)Se$_2$ (CIGS) thin films, grown by coevaporation of the constituent elements with different amounts of sodium (Na), were investigated. In some devices, an increased Na content was achieved through the incorporation of a thin layer of NaF deposited on the substrate prior to the growth of CIGS. The effect of Na on the electro-optical properties was addressed through characterization of the finished devices using photoluminescence (PL) and capacitance techniques. Results indicate the beneficial effect of Na as evidenced by increases in the device efficiency, open-circuit voltage, and PL intensity. Furthermore, these measurements provide evidence that Na 1) increases the net carrier concentration, and 2) reduces the number of gap states including those that act as minority-carrier traps.

INTRODUCTION

The presence of Na in polycrystalline Cu(In,Ga)Se$_2$-based photovoltaic devices correlates with numerous changes in material and device quality. The observed changes include increases in the open-circuit voltage [1-4], conversion efficiency [3-6], grain size [2-5,7], and conductivity [4], as well as preferential grain orientation [2, 7], and a reduced sensitivity of the device performance to the Cu/(In+Ga) ratio [4-6]. While explanations based on Na incorporation into the CIGS lattice exist to explain the increase in carrier concentration [8], the complete role of Na in these devices is far from understood. Furthermore, it is unclear whether the improvement in device performance is caused by the observed increase in conductivity, an increase in material quality, or both. This study will attempt to clarify this by correlating the electrical and optical properties of Na-containing devices.

EXPERIMENTAL APPROACH

Seven sets of polycrystalline ZnO/CdS/ CuIn$_{0.75}$Ga$_{0.25}$Se$_2$ thin-film devices have been grown on Mo/soda-lime glass substrates. The sodium content in one member of each set is intentionally increased by the addition of a 180Å-thick NaF layer deposited on top of the Mo, prior to the deposition of the CIGS absorber layer. All CIGS layers for these sets were grown by coevaporation of the constituent elements during a single deposition run. The only expected variation in composition between different sets is a continuous change in the Cu/(In+Ga) ratio from approximately 0.95 for set #1 to approximately 0.85 for set #7. Compositional measurements on similar structures have shown that the NaF layer is fully consumed, and the amount of fluorine remaining in the film is undetectable by Auger electron spectroscopy. The devices are completed with the addition of a chemical bath deposited CdS layer followed by a sputtered ZnO layer. Explicit details of this deposition process have been previously published [9].

Device-related electrical properties were determined through current-voltage (I-V) and conversion-efficiency (η) measurements. CIGS-material-related electrical properties were determined through capacitance-voltage (C-V) and deep-level transient spectroscopy (DLTS) measurements.

Optical properties of the finished devices were obtained through room temperature Fourier–Transform Photoluminescence measurements [10]. For these measurements, the excitation source was an AlGaAs diode laser (840 nm) driven to provide 7 mW of continuous power incident on the sample. This excitation energy is below the bandgap of CdS and the average excitation density within the CIGS absorber was less than 10^{10} cm^{-3}.

RESULTS

The device performance data for both members of all sets are summarized in Table I. These data show that the addition of Na, via a NaF layer, results in an overall increase in device performance. Furthermore, this improvement manifests itself mainly as an increase in the open-circuit voltage, with little change in the short-circuit current. This increased performance demonstrates an improvement above that which occurs as a result of the out-diffusion of Na from the soda-lime substrate.

Table 1. Summary of device parameters.

set #	Efficiency (%)		Voc (mV)		Jsc (mA/cm²)	
	no NaF	w/NaF	no NaF	w/NaF	no NaF	w/NaF
1	11.2	14.2	528	621	30.3	31.0
2	10.6	13.4	510	604	30.8	30.4
3	9.3	13.2	510	602	27.4	30.0
4	10.1	13.2	515	602	29.0	29.7
5	10.0	13.1	517	599	28.6	29.8
6	10.6	12.9	518	594	30.3	29.9
7	10.2	12.1	514	589	30.0	28.4

It has been previously observed that the addition of Na results in an increase in the conductivity of CIGS films[4]. It is possible that the increase in V_{oc} observed for these devices is due solely to this increased carrier concentration. To determine this, room-temperature C–V measurements were taken at 100 kHz and in the dark for all devices in this study.

From the C-V measurements, we found that the introduction of Na results in an increased capacitance. The majority-carrier concentration of the CIGS layer can be derived by assigning this capacitance to a free-carrier population in the CIGS layer. This carrier concentration data is plotted in Fig. 1 as a function of depth into the device for the two devices of set #1. Comparing the region of the film where data for both samples were obtainable, shows that the incorporation of Na has increased the majority-carrier concentration by about 1 order of magnitude. The increase in conductivity at the depletion edges, a factor of 3, is considerably lower than this. While the actual enhancement in the depletion region was not obtainable because of the large current generated from
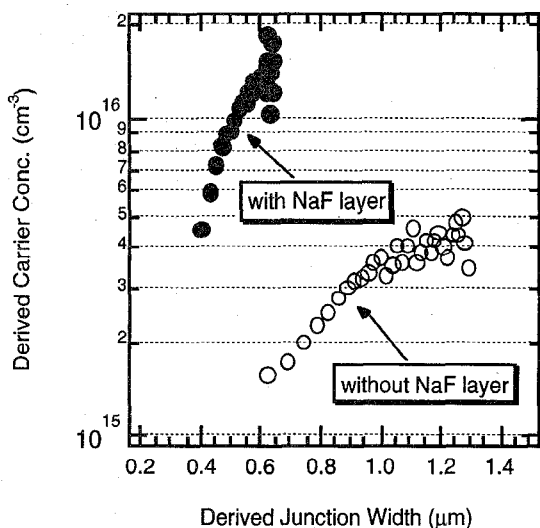

Fig. 1. Derived carrier concentrations from C-V data of sample set #1.

forward biasing the device, the reduction in depletion width is comparable to that expected for an increase in the carrier concentration by a factor of about 3.

The factor-of-3 increase in the majority-carrier concentration at the respective depletion edges should result in a change in V_{oc}, through a change in the built-in potential, of about 30 mV. The actual increase in V_{oc} is greater than this for all of these devices. Comparing the data between like samples (Table I), the increase in V_{oc} ranges from about 75 to 95 mV. Thus, only some of the improvement in device performance can be explained by the increase in conductivity.

It is possible that Na is having a beneficial effect on the CIGS material quality. To investigate this possibility, PL and DLTS measurements were performed.

Room-temperature steady–state PL data have been taken on all devices. The integrated PL intensity (I_{PL}) is found to increase in the samples with increased Na content. The magnitude of this increase varies from a factor of between 4 and 10. This increase can be related to material parameters through a simple analysis of the radiative recombination process. Here, the integrated PL intensity is proportional to the radiative recombination rate within the sample. This can be expressed as

$$I_{PL} \propto \delta / \tau_{rad} , \qquad (1)$$

where δ is the photoexcited carrier density and τ_{rad} is the radiative lifetime. The radiative lifetime under low-injection conditions is inversely proportional to the majority-carrier concentration (N_{maj}). Furthermore, δ can be expressed as G•τ, where G is the generation rate per unit volume from the laser excitation, and τ is the overall minority-carrier lifetime. The end result is that

$$I_{PL} \propto N_{maj}\tau. \qquad (2)$$

Thus, the observed increase in the integrated PL intensity is caused by an increase in the carrier concentration and/or an increase in the material quality of the CIGS absorber, as measured by the minority-carrier lifetime. While the increases in PL intensity are in agreement with the measured increases in carrier concentration, the complexity of the test structure prohibits an accurate determination of any increase in lifetime from this data.

Figs. 2a and 2b show the normalized PL spectra for the devices grown with and without the NaF layer, respectively. For the films grown without the NaF layer, the spectra are relatively complex with emission occurring at several distinct peak wavelengths. The main luminescence peak occurs at an energy of about 1.09 eV with evidence of a higher energy peak at about 1.10 eV. Both of these peaks are in the region of the expected bandgap energy of 1.1 eV [11]. The remaining portion of
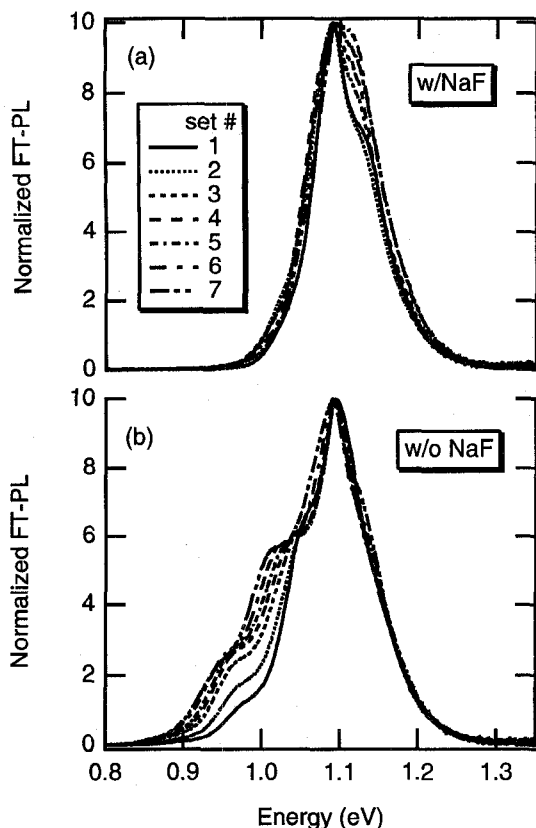
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Fig. 2. Normalized room-temperature PL spectra.

Fig. 3. DLTS spectra for sample set #7 with one minority-carrier peak, (a), and two majority-carrier peaks, (b) and (c).

the spectra is composed of two broad peaks, the positions of which vary between sample sets, ranging from about 1.05 to 1.01 eV and 0.99 to 0.96 eV. These shifts to lower peak energies correlate with the expected decrease in Cu/(In+Ga) ratio from set #1 to #7.

Upon inspection of the FT-PL spectra from the samples deposited with the NaF layer, it is evident that the signal from the lower energy peaks is no longer observed. This removal of the lower energy peaks could be the result of a reduction in the number of shallow-defect states, or an increase in the relative radiative contribution of the higher energy states, or both. As these peaks were no longer visible from the NaF-grown sample that exhibited an increase in PL intensity of only a factor of 4, it is most likely that their number has been reduced significantly as a result of the additional Na.

Finally, DLTS data were taken for two companion devices. Figure 3 contains the rate window analysis spectra for the two devices in set #7. For these data, a positive (negative) change in the measured capacitance corresponds to the presence of a minority-carrier (majority-carrier) trap. The location of the peak, in degrees K, is related to the emission rate of the contributing trap. The spectra for the sample grown without the NaF layer exhibits one minority-carrier trap,
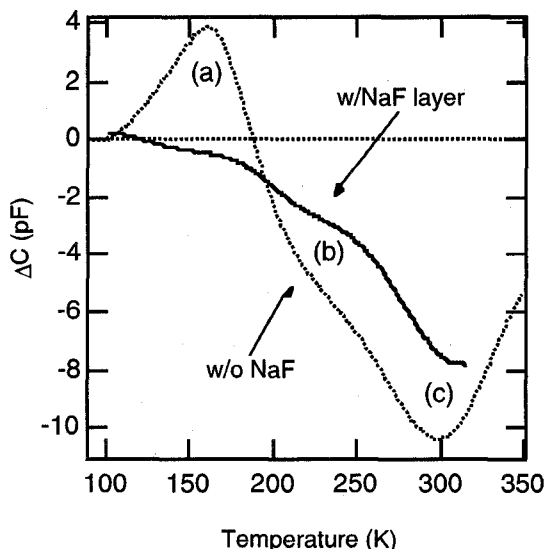
(a), and two majority-carrier traps, (b) and (c). With the addition of Na, the majority-carrier traps are reduced, but more significantly, the minority-carrier trap is no longer detectable. This is of particular importance for a minority-carrier device, such as a solar cell. Further analysis of these samples determined the activation energies of the minority-carrier trap (a), and dominant majority-carrier trap (c), to be 305 and 400 meV, respectively.

DISCUSSION

As has been the case with other researchers, we found the addition of Na to be beneficial to device performance. In addition, this increase is observed for a Na content above that resulting from growth on Mo/soda-lime glass substrates. Also in agreement with previous work, C-V data have determined that at least part of this improvement is due to the measured increase in carrier concentration that comes with the increase in Na content. The point of interest is that the improvement in device performance is too great to be explained simply by an increase in carrier concentration. Analysis of the PL intensity provides some evidence of changes in material quality, but the complexity of the structure and the nonuniform carrier concentration prohibit an accurate measurement of the improvement.

It is likely that any improvement in material quality will be accompanied by a reduction in the nonradiative recombination rate. This improvement will be manifested as a reduction in the number of defect states

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acting as efficient recombination centers. Evidence for specific changes in the electronic states comes from the normalized-PL and DLTS spectra. In both cases, the data provide direct evidence of the removal of midgap states. The normalized-PL spectra show that Na significantly reduces the number of states found between 40 and 140 meV below the bandgap. It is possible these are compensating donor states that have been passivated with the addition of Na. Such an act would result in an increase in the carrier concentration without Na having to act as an acceptor. Even more interesting, because it relates directly to the material quality, is the DLTS spectra. From these data, it can be seen that the addition of Na completely removes a strong minority-carrier trap having an activation energy of about 305 meV. While more work needs to be done on this, the removal of such a trap is precisely to be expected when the material quality is increased.

CONCLUSION

It has been shown that Cu(In,Ga)Se2 solar cells can be improved by the addition of Na beyond that incorporated by diffusion from the soda-lime substrate. This increase can be partly explained by an increase in the carrier concentration as determined by C-V measurements. PL-intensity measurements provide further evidence of increases in carrier concentration and/or material quality. Further analysis of the PL spectra reveal that Na incorporation results in the removal of shallow subgap sates. Finally, DLTS spectra show that a strong minority-carrier trap, with an activation energy of 305 meV, is removed with the addition of Na.

ACKNOWLEDGEMENTS

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