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A Comparative Study of Zn(O,S) Buffer Layers and CIGS Solar Cells Fabricated by CBD, ALD, and Sputtering

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***Abstract* —Zn(O,S) thin films were deposited by chemical bath deposition (CBD), atomic layer deposition, and sputtering. Composition of the films and band gap were measured and found to follow the trends described in the literature. CBD Zn(O,S) parameters were optimized and resulted in an 18.5% efficiency cell that did not require post annealing, light soaking, or an undoped ZnO layer. Promising results were obtained with sputtering. A 13% efficiency cell was obtained for a Zn(O,S) emitter layer deposited with 0.5%O_2. With further optimization of process parameters and an analysis of the loss mechanisms, it should be possible to increase the efficiency.**

***Index Terms* — Buffer layers, copper indium gallium diselenide, thin film solar cells, wide bad gap emitters, zinc oxysulfide.**

I. INTRODUCTION

High conversion efficiency has been demonstrated for CIGS thin film solar cells [1]. An integral part of the device is a chemically deposited CdS layer. In the last decade, several alternative approaches have been taken to replace the CdS with more transparent emitter layers grown by different methods [2]. In principle, one can surpass the current efficiency levels because more current can be collected with transparent emitter layers. This is particularly beneficial to higher bandgap devices. ZnS-based layers grown by chemical bath deposition (CBD) and atomic layer deposition (ALD) have demonstrated the potential to be viable alternatives [3,4]. Sputtering is arguably the most attractive in terms of its suitability for inline, high throughput, low-cost processing of the junction. While the CBD CdS process is favored because of its simplicity, excellent process control, and low-cost, CBD of Zn compound films is more complicated and not as well developed to replace CdS in manufacturing. The same comment can be made for ALD, although large-area deposition tools have been demonstrated. Sputtering can be easily adopted if convincing evidence is provided to show that stable, high efficiency solar cells can be made. To clarify the above questions, a concerted effort in the basic science of junction formation is needed. Specifically, a correlation between the emitter process conditions and the electrical properties of the solar cells, and an identification of the root cause(s) of the differences would be valuable.

Previous work has demonstrated the effect of interfacial reactions during CBD CdS deposition [5]. We showed that the combination of Cd and ammonia in the CBD bath enhanced the inversion or n-type doping of the near-surface region of the absorbers. This was corroborated by photoemission measurements that showed enhanced band bending as a result of the Cd partial electrolyte treatment [6]. A similar effect can be expected in the CBD Zn(O,S) deposition because Cd and Zn are donors in CIGS. It will be instructive to compare the CBD CdS and Zn(O,S) devices in a step-wise manner as they go through the different stages of device fabrication. More importantly, if electrical properties of the surface region and the changes caused by the processing can be measured, one can describe the device and model it in terms of the measured properties and phenomena. This basic knowledge will help identify the most important elements of the device and the relative magnitude of the various effects. A comparative approach is taken in this work. Because CBD Zn(O,S) solar cells have shown the greatest potential for making high efficiency cells, it would be prudent to fully characterize the emitter layers and the junctions. This knowledge can be applied to understand what is different about the interfaces produced by ALD and sputtering and how the gap can be bridged.

II. EXPERIMENTAL

CBD Zn (O,S) films were grown from an aqueous bath containing zinc sulfate, thiourea and ammonium hydroxide in the temperature range 65°C-95°C. Bath composition was similar to those described in the literature [3]. ZnS and Zn(O,S) films were deposited by ALD at 120°C using DEZn, H_2S and H_2O precursors in a Beneq reactor. R.F. sputtered films were deposited from a ZnS target at different target powers, pressures, and substrate temperatures. Moderate levels of oxygen were incorporated by adding O_2 to the Ar process gas. Typical film thickness for CBD was 20 to 30 nm and ~50 nm for sputtering. Films were characterized by optical absorption, ellipsometry, Auger electron spectroscopy, XPS, and X-ray diffraction. Solar cells were completed by depositing only the conductive ZnO layer. Current-voltage measurements were made in our laboratory and the data reported here are not certified by NREL.

III. RESULTS AND DISCUSSION

Zn(O,S) films deposited on witness substrates were characterized by a variety of techniques to determine the

composition and optical properties. Film composition needed to be measured with good confidence because it is a critical parameter in controlling the solar cell properties. Auger sensitivity factors were first established from a measurement of a ZnS crystal. Fig. 1 shows the Auger depth profile of a CBD Zn(O,S) film deposited on a 3-stage CIGS absorber. Fig. 2 shows the Auger depth profiles for a film deposited on Mo-coated glass. It is clear there is a close correspondence between the two. Our CBD films were reproducible and contained ~30% O and 20% S. This has also been corroborated by XPS.

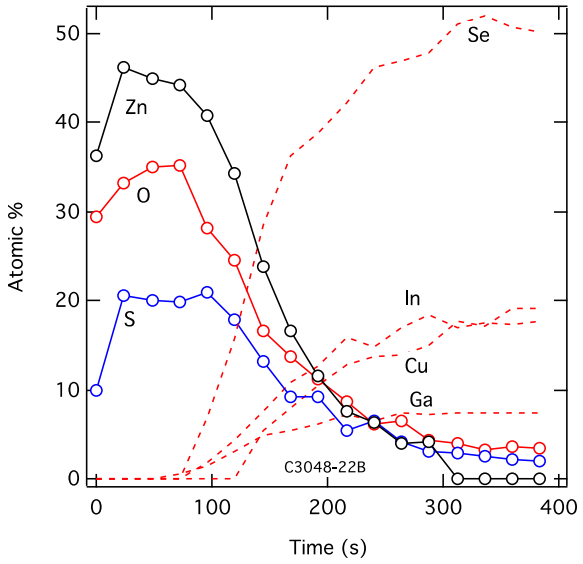

Fig. 1. Auger depth profile of a Zn(O,S) film deposited on CIGS

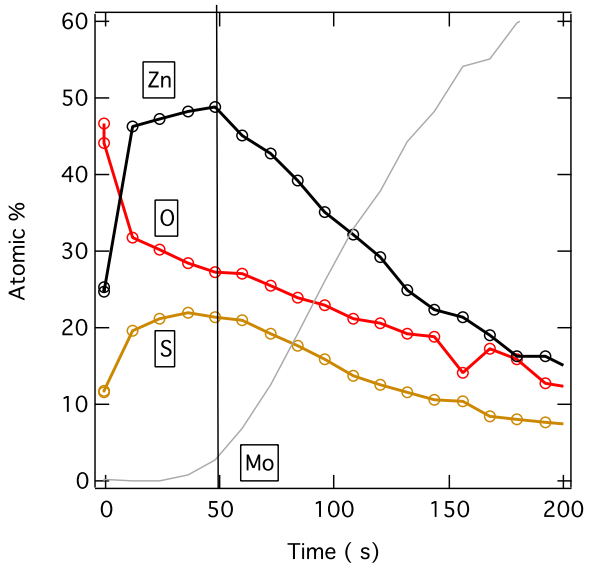

Fig. 2. Auger depth profile of Zn(O,S) film on Mo.

ALD films over a range of compositions were prepared by choosing a cycle of deposition according to the desired ratio of H_2S/H_2O and repeating the cycles to get the final thickness. As shown in Fig. 3, it was possible to vary the band gap and the composition of the films. Fig. 4 shows the optical absorption in Zn(O,S) films deposited by sputtering. All the films have also been characterized by spectroscopic ellipsometry and those results are presented elsewhere in this Conference [7]. The variation of band gap is consistent with the literature reports [8,9]. Film composition was measured by AES in both cases and was found to vary over the entire range, depending on the process conditions.

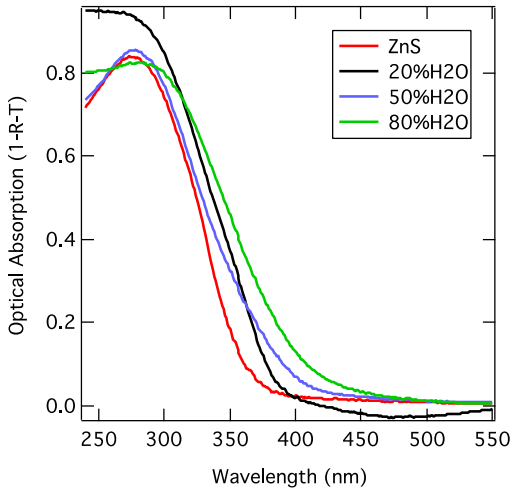

Fig. 3. Optical absorption in ALD Zn(O,S) films

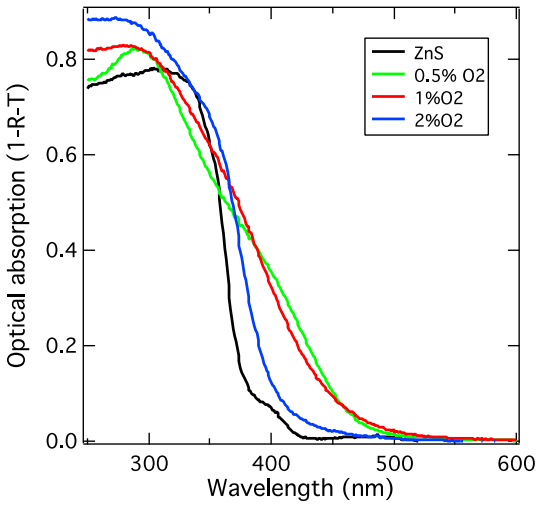

Fig. 4. Optical absorption in sputtered Zn(O,S) films.

We now turn to a discussion of solar cells made by CBD and sputtering. We investigated the dependence of solar cell properties on the CBD conditions. Deposition temperature (65°C-95°C) and film thickness (immersion time) had an effect. Longer deposition time and high temperatures resulted in a loss of fill factor and lower efficiency as shown in Fig. 5 and Fig. 6, respectively.

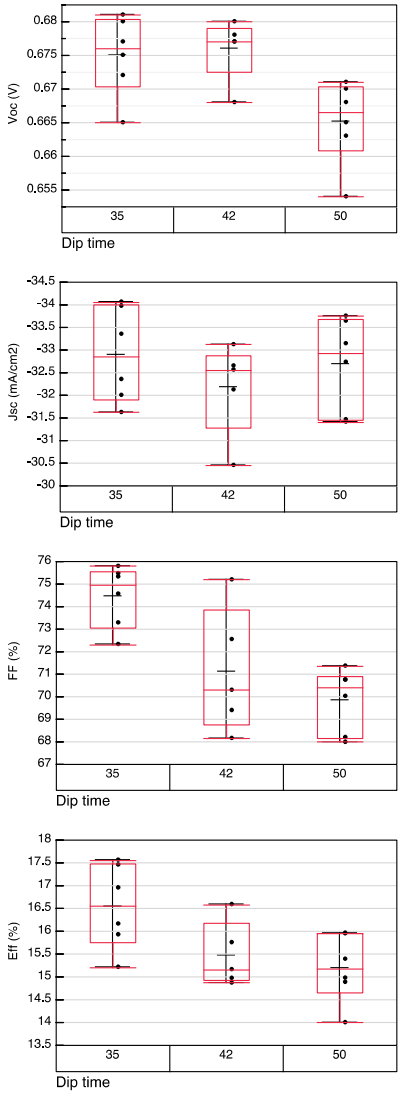

Fig. 5. Effect of CBD thickness on solar cell parameters.

We have obtained contradictory results regarding the effect of post annealing after CBD deposition. In some samples, cell performance improved after an anneal and in others it degraded. This effect appears to be absorber dependent and needs more careful scrutiny. There are some differences between our devices and those reported elsewhere. The addition of the undoped ZnO layer is detrimental to our Zn(O,S) devices. The solar properties do not show much change upon light soaking. By optimizing the deposition conditions, we are able to reproducibly fabricate solar cells with efficiency of ~18%; the highest efficiency measured was 18.5%. The solar cell parameters are: V_{oc} 692 mV; J_{sc} 34 mA/cm^2, FF 78.5%, and efficiency 18.5% after an antireflection coating. At present, some loss is encountered in the long wavelength collection and in front surface reflection. These losses are significant and amount to > 2 mA/cm^2. Hence, the efficiency can be increased to more than 20%.

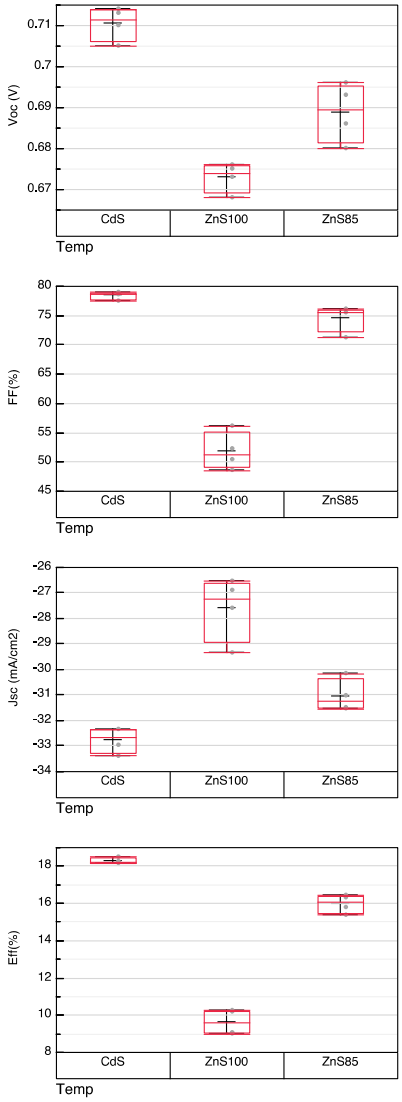

Fig. 6. Effect of CBD temperature on solar cell parameters.

In sputtering, we have experimented with pure ZnS films, stacked layers of ZnS and ZnO, and Zn(O,S) films reactively sputtered in Ar/O_2 ambient. The last approach has yielded the best results so far in our preliminary work and the process has not been fully optimized. We have found that pure ZnS layers block the photocurrent, and pure ZnO layers give rise to leaky cells with low barrier height. We have made very good working devices in the range of 0.5% to 1% O_2/Ar in which we observe a strong dependence of solar cell parameters as shown in Fig. 7.

Cell efficiency decreases sharply because of a loss of V_{oc} and FF as the oxygen content is increased. Compositions measured by AES were: $ZnO_{0.45}S_{0.55}$ for the 0.5% O_2 and

$ZnO_{0.9}S_{0.1}$ for the 1% O_2 conditions, respectively. The highest conversion efficiency we have obtained is 13% with the following parameters: V_{oc} 587 mV; J_{sc} 36.1 mA/cm^2, FF 60% without any antireflective coating. This can be compared to the CdS devices on the same absorber. Average values for 10 cells were: V_{oc} 684 mV; J_{sc} 32.5 mA/cm^2, FF 74%. It is apparent that the performance difference comes from reductions in V_{oc} and fill factor. These results were obtained in the beginning of this study and the process is not optimized.

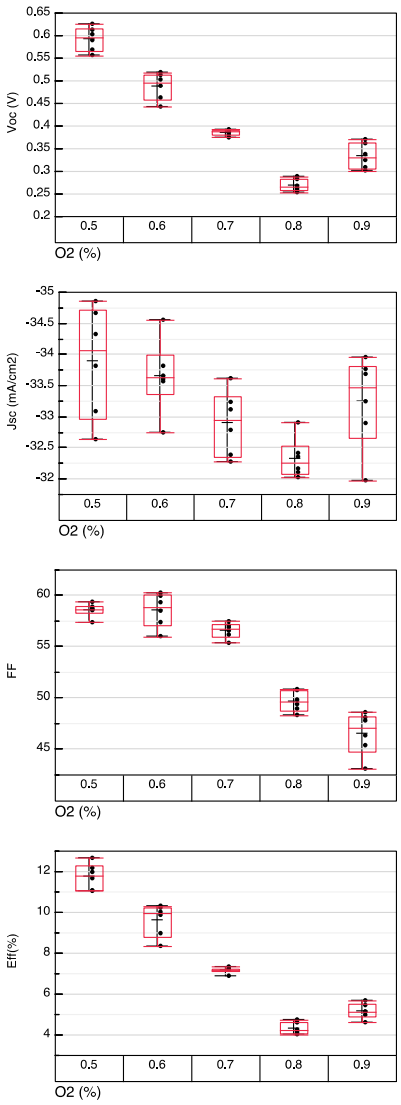

Fig. 7. Dependence of solar cell parameters on O_2 content.

IV. CONCLUSIONS

We have summarized the results from our studies of Zn(O,S) films and emitter layers deposited by CBD, ALD, and sputtering. We have determined their composition and optical properties. Aspects of the CBD Zn(O,S) process were studied so as to understand the effect of deposition temperature and thickness. Reactive sputtering of ZnS in O_2 produced Zn(O,S) films with varying oxygen content and band gap. The highest conversion efficiency obtained was 18.5% for CBD and 13% for sputtering. We have yet to optimize the sputter and ALD depositions.

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