BAPVC Annual Project Report

Project Title: Earth abundant p-type transparent conductors
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Summary:
P-type transparent conductors based on Cu-Zn-S alloys have been synthesized which have world record combinations of transparency and hole conductivity. A scalable process for the deposition of these materials has been developed. Successful device integration work has been performed with Si and III-V photovoltaic absorbers.

Key Accomplishments:
The conductivity, of p-type transparent materials (TCMs) has historically lagged behind that of well-known n-type transparent conductors such as indium tin oxide (ITO), Al-doped ZnO (AZO), and F-doped tin oxide (FTO). Moreover, most of the p-type TCMs reported thus far require processing temperatures in excess of 400 C, which will limit their applications in devices with limited thermal budgets such as many solar cell architectures.

Cu alloyed ZnS ($Cu_xZn_{1-x}S$) is an attractive materials system to overcome these limitations. Leveraging the group's prior work on elevated temperature deposition,[1] the entire composition range from ZnS to CuS/Cu_2S was synthesized by pulsed laser deposition. As shown in Fig. 1, there is a "window" of p-type conductivity and excellent optical transmission for Cu contents in the range of 9-40%. For optimal films, the combination of optical transparency and p-type conductivity is the highest achieved for a transparent hole-conducting material deposited at room temperature and rivals that achieved for higher growth temperatures (Fig. 2).[2]

To increase the industrial relevance of the material, an inexpensive chemical bath deposition procedure was developed using mild conditions and earth-abundant precursors. Measurements performed within the BAPVC with M. Toney's group at SSRL were critical for determining the film microstructure and maximizing film conductivity and transparency. The transparency can be as high at 80% at 550 nm, with corresponding sheet resistivities of 400 Ω/sq; these values both meet project performance goals and represent state of the art performance for a p-type transparent conductor.

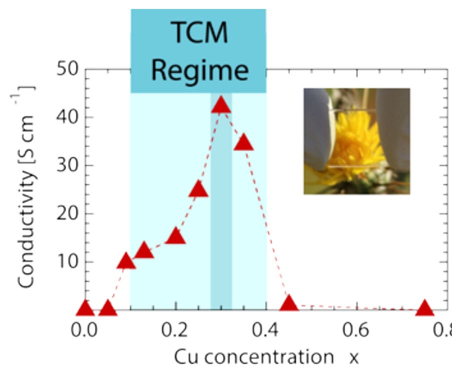

Fig. 1. Measurements of conductivity for transparent $Cu_xZn_{1-x}S$ films ($0 \leq x \leq 0.75$). The maximum hole conductivity, 42 S cm^{-1}, is observed at $x = 0.30$.

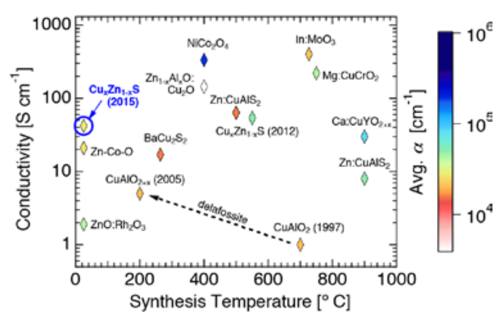

Fig. 2. Conductivity plotted against maximum processing temperature for the highest performing CuxZn1-xS films of this study (x = 0.30, circled in blue) and for a group of the highest performing p-type TCM films in the literature. The color scale represents increasing absorption coefficient (averaged over 400 – 800 nm), with white the lowest (most transparent) and blue the highest (least transparent).

An efficient PV device using a p-type TCM had not been reported in the literature, in particular with a low temperature process. In collaboration with BAPVC researcher Ali Javey's group, solar cell integration was performed by fabricating n-Si/p-CuZnS and np$^+$-Si/p-CuZnS structures. Excellent hole collection was found in the n-Si/p-CuZnS cells with 1 sun open circuit voltages exceeding 400 mV. Figure 3 shows current-voltage data from a np$^+$-Si/p-CuZnS structure, with the >30 mA cm^{-2} short circuit current, achieved without an anti-reflection layer, attesting to the transparency of the p-type contact.

The developments in this project eliminate the main barriers preventing the use of p-TCMs in device applications and thus will enable new applications such as thin film tandem solar cells based on abundant elements and, potentially, other applications, such as "invisible" electronics on flexible substrates.

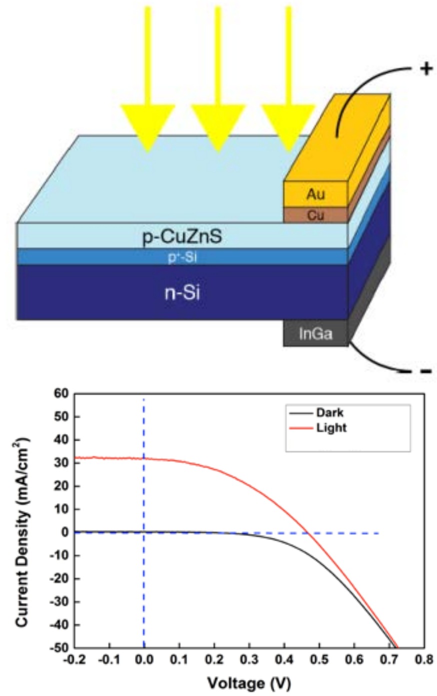

Fig. 3. Current-voltage data from a np$^+$-Si/p-CuZnS device. The p-type transparent contact was made by chemical bath deposition. Device size 1 cm x 1 cm, simulated AM1.5G illumination.

Future Work:

The focus of the future work will be further optimization of the chemical bath deposition process aiming at higher transparency while retaining the world-record level hole conductivity. The PV device integration work will focus on improving the fill factor for the Si-based devices. Also, the use of p-CuZnS as an ohmic (also electron-blocking) back contact to earth-abundant absorbers such CZTS will be explored. Ultimately, replacement of the Mo now used for this purpose may enable new types of thin film tandem architectures to be developed.

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[1] A.M. Diamond, L. Corbellini, K.R. Balasubramaniam, S. Chen, S. Wang, T.S. Matthews, L.-W. Wang, R. Ramesh, and J.W. Ager, Phys. Status Solidi **209**, 2101 (2012).

[2] R. Woods-Robinson, J. K. Cooper, A. Faghaninia, L. T. Schelhas, V. L. Pool, M. T. Toney, C. Lo, I. D. Sharp, and J. W. Ager, ms. under review.