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Art J. Nelson
(303)231-7128 FAX: (303)231-1231

CORRELATION OF POLYCRYSTALLINE $Cu(In,Ga)Se_2$ DEVICE EFFICIENCY WITH HOMOJUNCTION DEPTH AND INTERFACIAL STRUCTURE: X-RAY PHOTOEMISSION AND POSITRON ANNIHILATION SPECTROSCOPIC CHARACTERIZATION

Art J. Nelson, P.E. Sobol, A.M. Gabor and M.A. Contreras
National Renewable Energy Laboratory, Golden, CO 80401

P. Asoka-Kumar and K.G. Lynn
Department of Physics, Brookhaven National Laboratory, Upton, NY 11973

The ternary $A^{I}B^{III}X_2^{VI}$ chalcopyrite semiconductor, $CuInSe_2$ (E_g = 1.1 eV), has proved to be a superior absorber for heterojunction photovoltaic device applications.[1] Technical advances in polycrystalline thin-film technology have demonstrated photovoltaic devices with measured efficiencies exceeding 16% (total area).[2] This has been realized by developments in physical vapor deposition and processing. Furthermore, these devices have exhibited homojunction behavior and thus it has been proposed that there exists a moderately doped ($N_d \geq 10^{17}$ cm^3) n-type surface layer. Proper engineering of this n-type surface region could result in further improvements in device performance. Specifically, the presence of an optimized n-type surface region will effectively move the recombination region away from the highly defective $CdS/Cu(In,Ga)Se_2$ heterojunction interface.

Deviations from the ideal $CuInSe_2$ stoichiometry introduces defects in the chalcopyrite lattice, e.g. incorporation of excess In results in unoccupied Cu-sites.[3] These defect chalcopyrite phases have a tendency to segregate at the surface of polycrystalline thin-films.[4] In addition, the lattice defects (Cu vacancies) can have well defined positions (ordered), which has lead to the term "ordered vacancy compound" or OVC. Two such phases have been identified in the literature, specifically, $CuIn_3Se_5$ (5) and $CuIn_2Se_{3.5}$ (6).

In order to further improve our understanding of device performance, the surface versus bulk composition and electronic structure of polycrystalline $Cu(In,Ga)Se_2$ thin-film interfaces were studied by X-ray photoemission spectroscopy (XPS) and positron annihilation spectroscopy (PAS).

Angle-resolved high resolution photoemission measurements on the valence band electronic structure and Cu 2p, In 3d, Ga 2p and Se 3d core lines were used to evaluate the surface and near surface chemistry of $CuInSe_2$ and $Cu(In,Ga)Se_2$ device grade thin films. XPS compositional depth profiles were also acquired from the near surface region and the bonding of the Cu, In, Ga and Se was determined as a function of depth. These films were all grown on Mo-coated soda lime glass and results clearly show an accumulation of Na on all of the surfaces with typical surface concentrations of ≥10 at. %. Na concentrations in the bulk material were <1 at. %. In addition, non-destructive angle resolved compositional analyses of the surface chemistry reveals a Cu poor region indicative of $CuIn_5Se_8$ (or a mixture of $CuIn_3Se_5$ and In_2Se_3). Of

Art J. Nelson
(303)231-7128 FAX: (303)231-1231

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particular interest were the results of the high resolution XPS compositional depth profiles (sputter rate of 1 Å/sec.) which show a remarkable trend. Specifically, a correlation between the depth of the metallurical interface between the Cu poor region and bulk stoichiometric material, and the device efficiency was performed. This analysis revealed that the depth of the metallurgical interface was 115 Å for a 16.4% CIGS device, 240 Å for a 15.0% CIGS device, and 300 Å for a 14.0% CIGS device (Fig. 1). Similar trends were observed for the CIS films as well. Photoemission results also show that the surface region is n-type and that the bulk material is p-type and that there is a 0.5 eV valence band offset between the n-type surface layer and the p-type bulk. These results clearly show that the depth of the homojunction may be the determining factor in device performance.

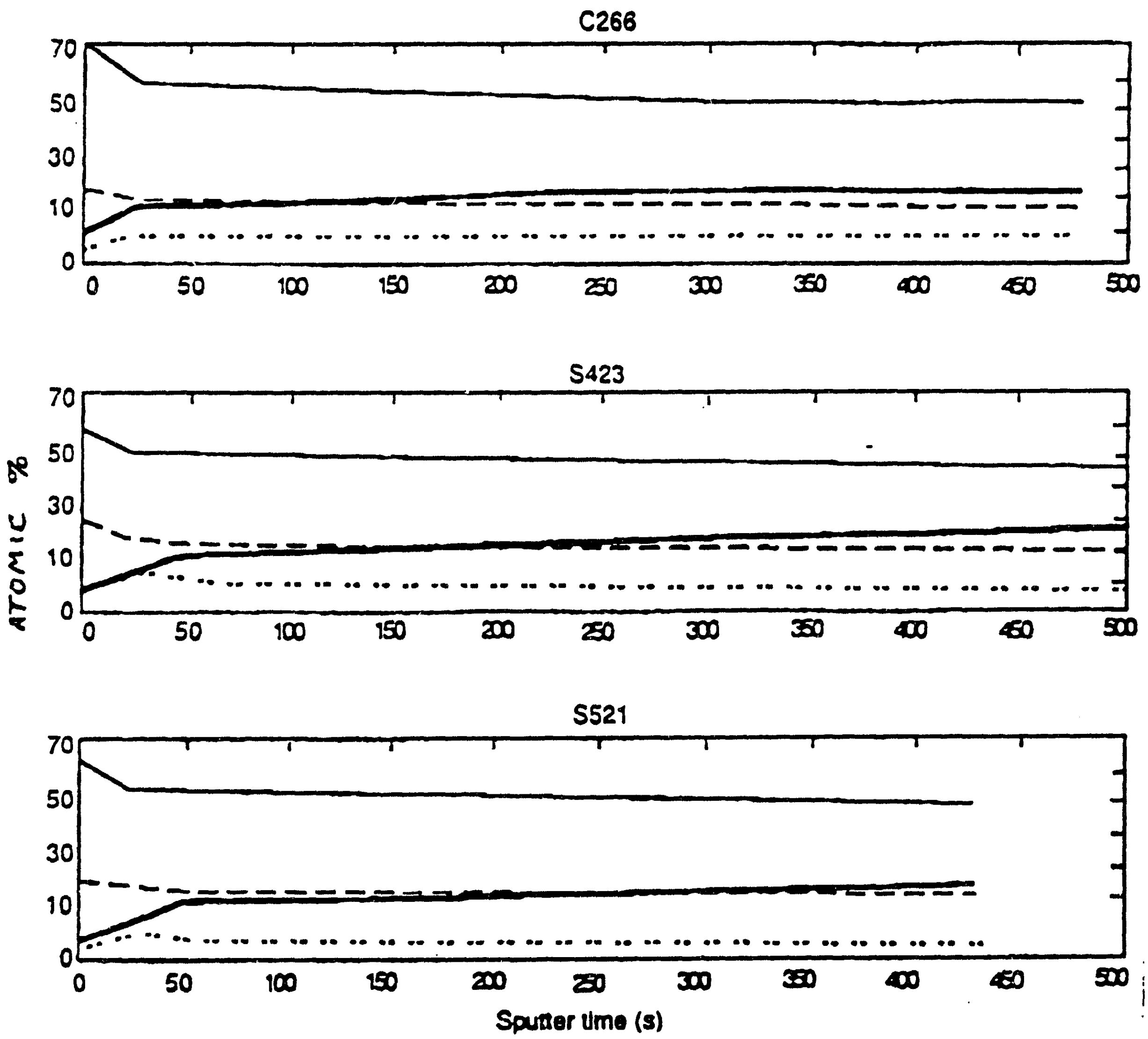

Figure 1. XPS compositional depth profiles showing depth of $CuIn_5Se_8/CuInSe_2$ metallurgical junction.

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Positron annihilation spectroscopy was used as a nondestructive, depth-sensitive probe for open-volume-type defects with a sensitivity of 5×10^{15} cm^{-3}(7). This technique examines changes in Doppler broadening of the annihilation γ rays that originate from various depths of a test material. The Doppler broadening is characterized by an S (for shape) parameter, defined as the ratio of counts in a fixed central region (of width ~1.59 keV and centered around 511 keV) of the annihilation photopeak to the total number of counts in the annihilation photopeak. When positrons annihilate after being localized near open-volume-type defect sites, annihilation occurs predominantly with low momentum electrons as opposed to the defect-free crystal where positrons are more likely to annihilate with core electrons. As a result, in the presence of open-volume defects, the annihilation photopeak is sharp and produces a higher S parameter.

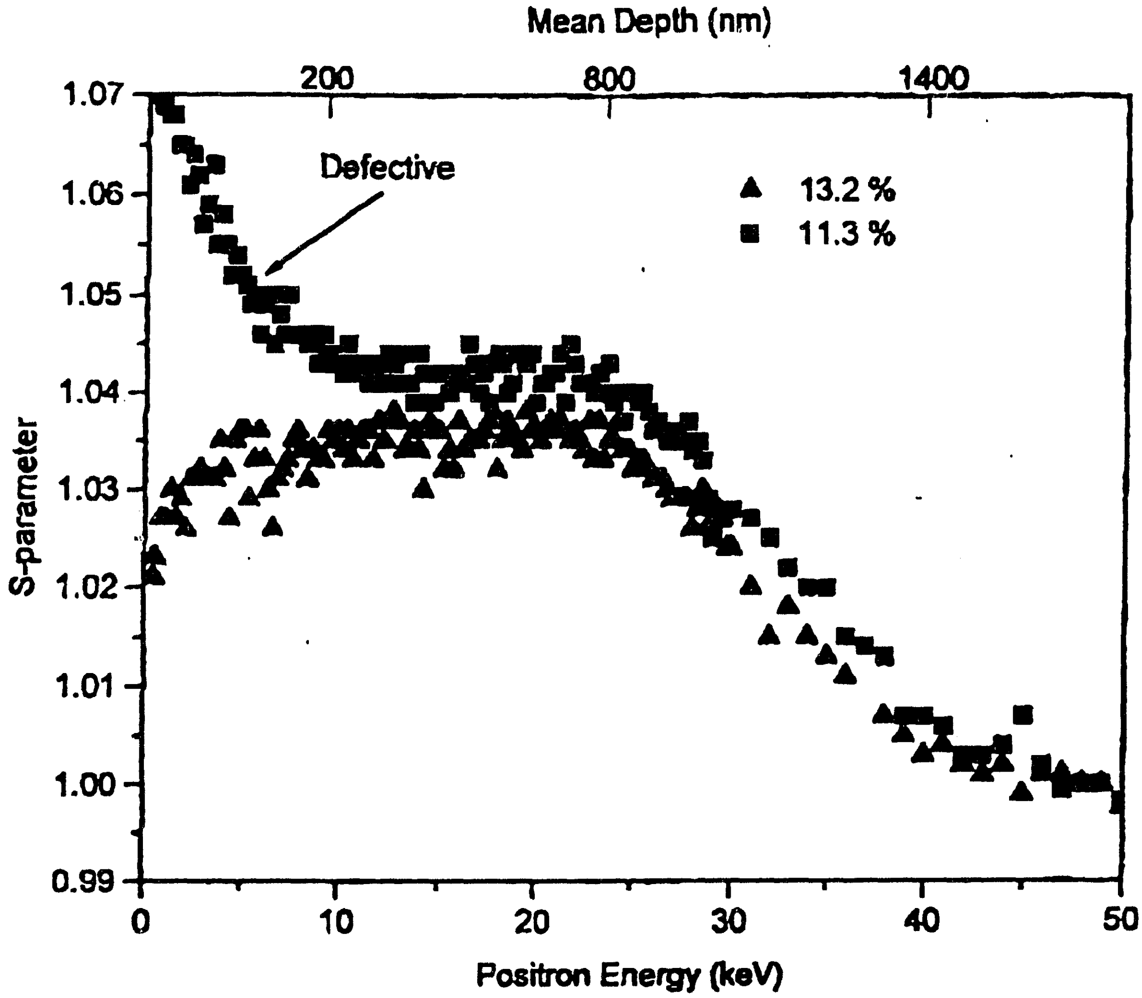

Figure 2. S-E data for polycrystalline $CuInSe_2$ thin-film devices.

Figure 2 shows the PAS results from a polycrystalline $CuInSe_2$ thin-film device which had a total area efficiency of 11.3%. XPS results for this device revealed a Cu-poor surface consisting of a thin In_2Se_3 layer on a $CuIn_3Se_5$ layer on bulk $CuInSe_2$. Correlation of the XPS results with the PAS results reveal that the In_2Se_3 surface layer is highly defected as evidenced by the large S value. The highest efficiency $Cu(In,Ga)Se_2$

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device (16.4% total area) had the lowest S value, which suggest more homogeneous composition near the surface.

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References

1. A. Rockett and R.W. Birkmire, J. Appl. Phys. 70, R81 (1991).
2. A.M. Gabor, J.R. Tuttle, D.S. Albin, A.L. Tennant and M.A. Contreras, Proceedings of the 12th PV AR&D Review Meeting, Denver, CO, AIP Conference Proceedings No. 306, 59 (1994).
3. E. Parthe, Proceedings of the 7th Int. Conf. Ternary and Multinary Compounds, Snowmass (MRS, Pittsburgh, 1987), p. 3
4. A.J. Nelson, J.R. Tuttle, R.Noufi, D. Rioux, and Hartmut Hochst, J. Appl. Phys. 74, 5757 (1993).
5. L.S. Palatnik and E.I. Rogacheva, Neorgan. Mat. 2, 478 (1966).
6. B. Schumann, G. Kühn, U. Boehnke and H. Neels, Sov. Phys. Crystallogr. 26, 678 (1981).
7. P.J. Schultz and K.G. Lynn, Rev. Mod. Phys. 60, 701 (1988).

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