FINAL TECHNICAL REPORT "ENGINEERED ELECTRODES AND ELECTRODE-ORGANIC INTERFACES FOR HIGH-EFFICIENCY ORGANIC PHOTOVOLTAICS"

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Inorganic Hole-Extracting Electron-Blocking Nanolayers in Bulk-Heterojunction Organic Solar Cells. Thin (5-80nm) layers of p-type semiconducting NiO films have been synthesized in a collaboration between the Chang and Marks groups using pulsed laser deposition. These films have been used as hole-transporting/electron-blocking interfacial layers in bulk-heterojunction solar cells of the type [ITO/NiO/P3HT:PCBM/LiF/Al]. The NiO film is polycrystalline in nature and is significantly planarized by the deposition process on the glass/ITO surface with a measured RMS roughness of 1-1.5 nm. The optimal NiO interlayer thickness for the solar cell was found to be 5-10 nm, where an 80% increase in power conversion efficiency (to 5.2%) versus the control was observed. The external quantum efficiency (EQE) was measured on a device containing a 10nm NiO layer and was found to reach a maximum of 87% between 400 and 700 nm. These results highlight the importance of suppressing cell losses, and their adverse effects on power conversion efficiency. The highest power conversion efficiency measured on these cells was 5.2%, and was confirmed by NREL.

Surface dipole modifications in In_2O_3-based TCOs. In a three-way collaboration between the Mason group (ceramic target synthesis), the Chang group (pulsed-laser deposition), and the Klein group at the Technical University of Darmstadt (RF

sputtering), we have demonstrated, for the first time in In_2O_3-based TCOs, the ability to independently modify the Fermi level (by varying the oxygen content during in situ film growth) and the ionization potential or "external work function" (by post-growth annealing in oxygen at intermediate temperatures—400°C in air). The ionization potential is defined as the difference between vacuum level and the valence band maximum (VBM). The experimental XPS/UPS results are shown in Fig. 1, plotted as work function vs. Fermi level (referenced to the VBM). The lower box on the left shows data for in situ 10% and 30% Zn,Sn co-substituted In_2O_3 (ZITO 10,30) films deposited by RF magnetron sputtering, and measured without breaking vacuum. It can be seen that the Fermi level can be varied substantially between 2.2 eV (oxidizing conditions) and 3.0 eV (reducing conditions). The films grown under oxidizing conditions proved to be highly resistive in comparison to the conductive (and degenerate) films grown under reducing conditions. When subjected to a post-growth oxidizing anneal at 400°C in air, the Fermi levels of the degenerate films remain relatively constant, however the work functions increase dramatically (to as high as 5.4 eV!). (Note that post-treated films now closely resemble ex situ PLD films and bulk ceramics synthesized in air at much higher temperatures!) We have attributed the rise in work function to "surface dipole modification" (SDM), the origins of which are under investigation. Potential factors include changes in surface termination and extra oxygen species at the surface (e.g., peroxide and hydroxide species). Regardless of origin, these results point the way to "engineered" bixbyite-based TCOs, employing a two-step process: 1) adjusting the Fermi level by film growth under reducing conditions (step ① in Fig. 1) followed by 2) a brief post-growth oxidation anneal at intermediate temperatures (step ② in Fig. 1). These results have major ramifications for TCO anodes in organic LEDs and solar cells, where large work functions (>5 eV) are required for band alignment with the HOMO levels of the p-type organics employed. This work is the subject of a forthcoming publication.

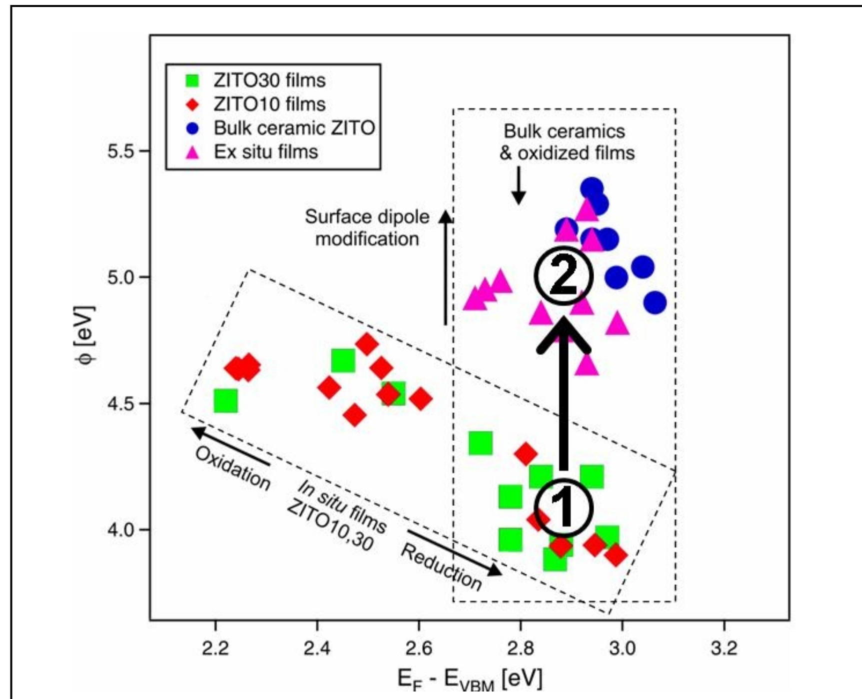

Figure 1. Work function vs. Fermi level (vs. VBM) by XPS/UPS for in situ sputtered ZITO thin films (lower left set), degenerate ZITO films subjected to brief post-synthesis O_2 treatments (vertical left set), which also agree with bulk values.

New TCO Synthetic Routes. Transparent conducting oxides (TCOs), such as In_2O_3:Sn (ITO) are essential to many devices, such as flat-panel displays, OLEDs and OPVs, but the scarcity of indium has necessitated the development of indium-free TCO materials. New chemical methodologies to form $In_{2-2x}Sn_xZn_xO_3$ ($x \leq 0.4$), (ZITO), are under investigation by Poeppelmeir to further reduce the indium content, yet maintain their high performance. The synthesis of ZITO at low temperatures has been explored for both ambient and hydrothermal conditions as outlined in the flow chart in Figure 2. In both cases, an oxyhydroxide or hydroxide Zn-In-Sn precursor is precipitated from an aqueous solution. Adjusting the initial conditions of the low temperature synthesis, however, yields distinct phases that convert on calcination to either the cubic form of ZITO or the novel metastable hexagonal polymorph. Recent reports have demonstrated the formation of hexagonal In_2O_3 and ITO, however; this is the first study of hexagonal ZITO. The hexagonal polymorph may offer increased Zn/Sn substitution ($x > 0.4$) because $ZnSnO_3$ ($x = 1$), the fully substituted end-member, is isostructural with hexagonal In_2O_3.

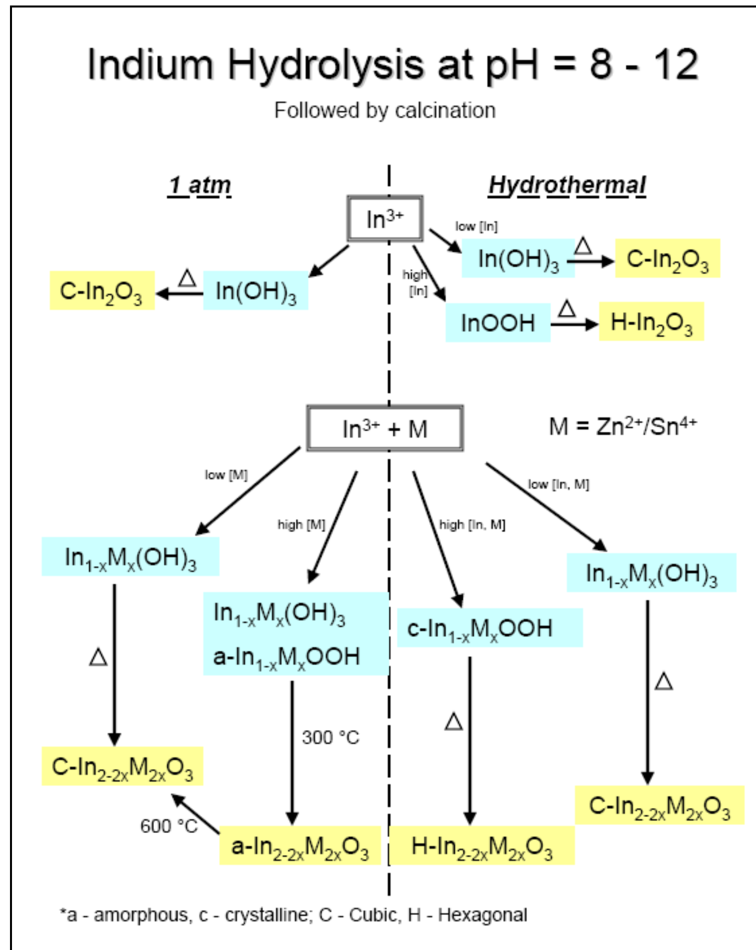

Figure 2. Flow chart for low temperature ZITO synthetic products

Recent experimental studies and first-principles calculations (Da Silva, Yan, Wei, *Phys. Rev. Lett.*, 100, 255501 (2008)) have revealed the fundamental structural motifs and bonding rules in the layered $InMO_3(ZnO)_n$ materials, with M=In, Ga, or Al and n an integer number. In these structures, sheets of InO2 octahedra alternate with layers of ZnO

which tend to preserve the hexagonal structure of bulk ZnO. The In or Ga within the ZnO layers are five-fold coordinated and their spatial arrangement modulates the hexagonal structure so as to accommodate an inversion domain boundary. The combination of these structural motifs gives an overall structure that obeys the octet rule.

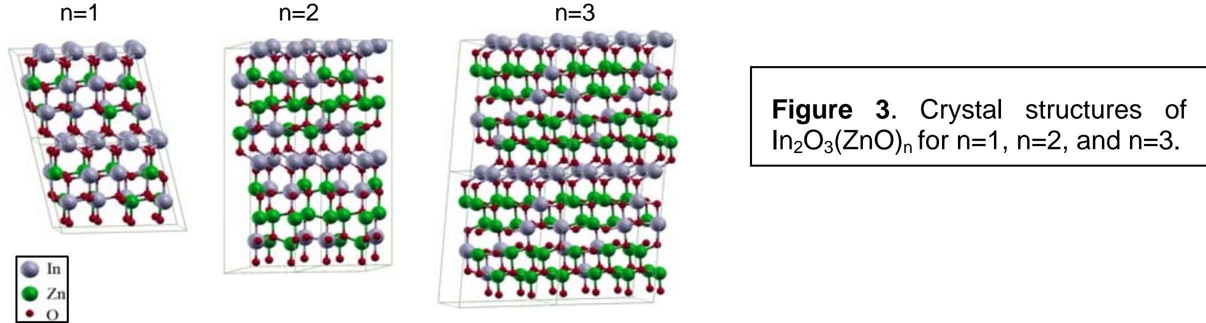

Figure 3. Crystal structures of $In_2O_3(ZnO)_n$ for n=1, n=2, and n=3.

Theoretical Studies. In collaboration with Mason, Poeppelmeier, and Marks, Freeman has investigated the electronic structures and transport properties of the layered In-Zn-O using the aforementioned structural rules to build models of their crystal structures. A detailed analysis of angular-momentum-resolved density of states (DOS) reveals that oxygen anions (blue) hybridized with Zn cations show ionic characteristics as a sharp peak at the valence band maximum (VBM) while those hybridized with In cations show relatively covalent characteristics and dispersed bands. On the other hand, all cation *s*-states and O *p*-states contribute to the conduction band minimum (CBM). The very large band dispersion near the CBM is a key feature for n-type TCOs, which originates from strong antibonding interactions between the cation *s*-states and the anion *p*-states.

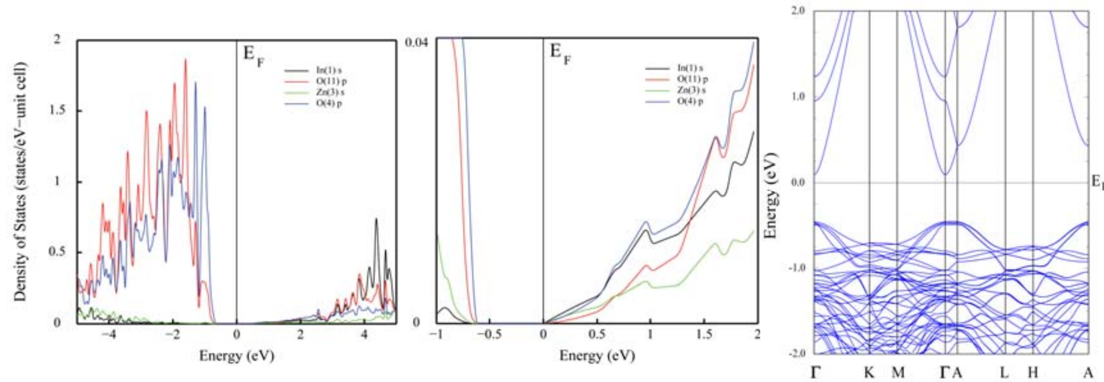

Fig. 4. Projected density of states for individual elements and band structure of $In_2O_3(ZnO)_2$.

The charge density distribution of $In_2O_3(ZnO)_3$ near the CBM in Figure 5 shows a consistent picture with the DOS. That is, the comparable contributions to the conduction band minimum from both InO_2 and $(MZnO)_{n+1}$ layers yield a three-dimensional charge density distribution, i.e., isotropic electronic properties in these compounds. This should

lead to nearly the same transport properties in all crystallographic directions as in Figure 6. However, note the decrease in the out-of-plane conductivity picture with the DOS.

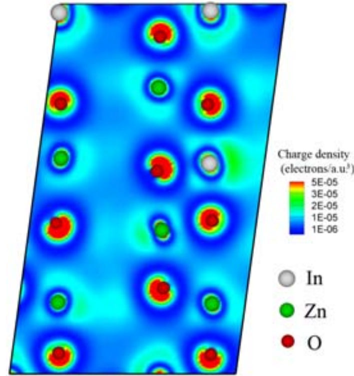

Figure 5. Charge density distribution of $In_2O_3(ZnO)_3$ for an energy interval 0.2 eV above the conduction band minimum

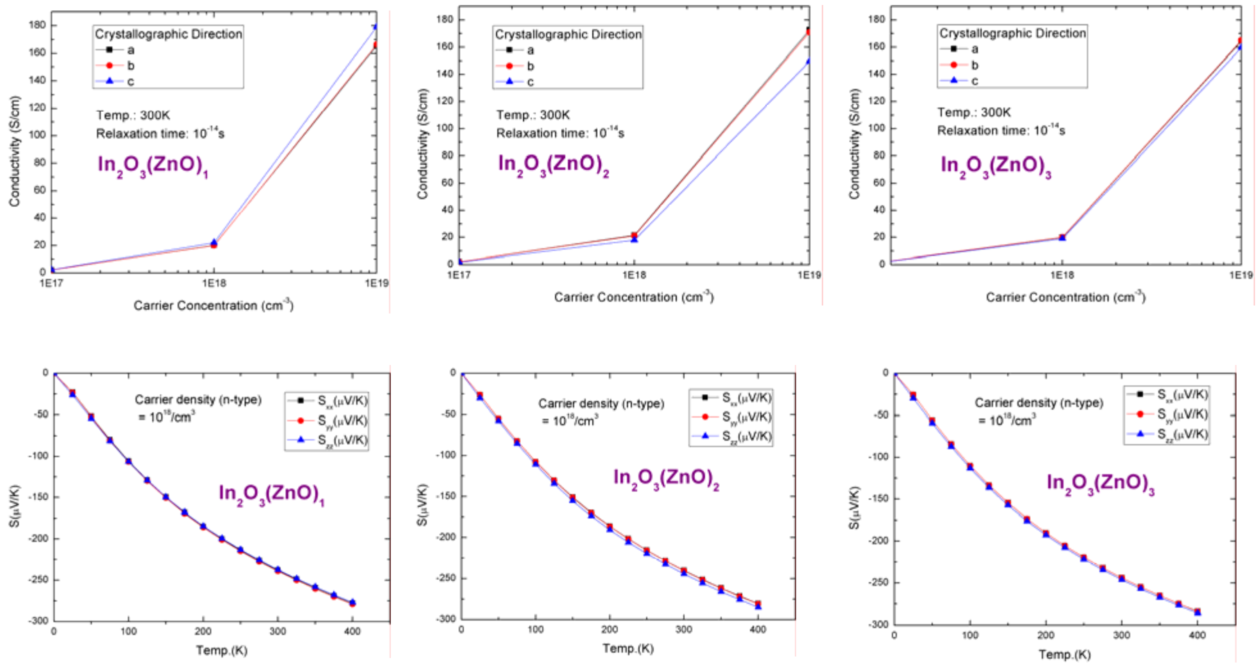

Figure 6. Computed transport properties (conductivities and Seebeck coefficients) as a function of different number (n) of ZnO layers in $In_2O_3(ZnO)_n$.

That is, comparable contributions to the conduction band minimum from both InO_2 and $(MZnO)_{n+1}$ layers yield a three-dimensional charge density distribution, i.e., isotropic electronic properties in these compounds. This should lead to nearly the same transport properties in all crystallographic directions as in Figure 6. However, the noticeable decrease in the out-of-plane conductivity of $In_2O_3(ZnO)_2$ compared to the in-plane

directions indicates that the modulation pattern of In or Ga impurities in ZnO layers may play an important role in transport properties; there is a pure ZnO layer in $In_2O_3(ZnO)_2$ without any In impurities while there is no such ZnO layer in $In_2O_3(ZnO)_1$ or $In_2O_3(ZnO)_3$ as shown in Figure 3. The anisotropy in the conductivities should be further investigated with different modulation patterns and possible intrinsic defects such as O vacancies and In in Zn sites.

Of particular interest is the effect of the content of Ga on the carrier concentration of GIZO. It is believed that the lower carrier concentration in the GIZO material with respect to the IZO systems originates from the fact that Ga increases the formation energy of the electron-donor oxygen vacancies, thereby lowering their equilibrium concentration and the related carrier content. Freeman's preliminary results already show that, in $InMO_3(ZnO)_2$, the presence of Ga impurities (M = Ga) in ZnO layers causes significantly the higher formation energy, 0.63 eV, of the O vacancy than In impurities (M = In).

In the continued effort of this work under the recent DOE grant, Freeman's LDA calculations will quantify the formation energy of the oxygen vacancies. Specifically, investigating the difference in the formation energy of the oxygen vacancies in the homologous layered compounds $In_2O_3(ZnO)_n$ and $InGaO_3(ZnO)_n$ as a function of thickness n of the ZnO layer will help understand the effect of Ga on the nonstoichiometry of the IZO systems. Also our theoretical electronic structure scheme, based on the FLAPW method, includes the so-called screened-exchange LDA (sX-LDA) method that allows us to reliably estimate features of the electronic structure as band gaps and electronic levels of impurities with respect to the host band edges. Having at hand reliable values for the latter quantities is crucial for an accurate description of the impurity formation energies. His study with the sX-LDA will provide a reliable picture of the energetics of the intrinsic defects, of the related carrier concentration, and of the structure-transport relationships in these materials.

Publications During the Grant Period

Irwin, M.D.; Buchholz, D.B.; Hains, A.W.; Chang, R.P.H.; Marks, T.J. p-Type Semiconducting Nickel Oxide as an Efficiency-Enhancing Anode Interfacial Layer in Polymer Bulk-Heterojuction Solar Cells, *Proc. Nat. Acad. Sci*, **2008**, *105*, 2783-2787.

Hains, A.W.; Marks, T.J. High-Efficiency Hole Extraction/Electron-Blocking Layer to Replace Poly (3,4-ethylenedioxythiophene):Poly (styrene sulfonate) (PEDOT:PSS) in Bulk-Heterojunction Polymer Solar Cells, *Appl. Phys. Lett.*, **2008**, *92*, 023504.

Poster – C. A. Hoel, J.-F. Gaillard, K. R. Poeppelmeier, "Synthesis and Characterization of Zinc-Indium-Tin Oxide." *Atomic, Molecular, Optical and Chemical Sciences at the APS*. Nov. 5, 2008, Argonne National Laboratory.