Electric Field-Driven Defect Diffusion at Oxide Semiconductor-Metal Interfaces

H. Gao,[1] G. M. Foster[1], G. Mackessy[2], A. Hyland[3,4], M. Allen[3,4], and L.J. Brillson[1,5]
[1] *Department of Physics, The Ohio State University, 191 W. Woodruff Ave., Columbus, OH 43210, USA*
[2] *Columbus School for Girls, 56 S. Columbia Ave, Columbus, OH 43209, USA*
[3] *Department of Electrical and Computer Engineering, University of Canterbury, Christchurch 8140, NZ*
[4] *The MacDiarmid Institute for Advanced Materials and Nanotechnology, NZ*
[5] *Dept. Electrical & Computer Engineering, The Ohio State University, Columbus, OH 43210, USA*

We used depth - resolved cathodoluminescence spectroscopy (DRCLS) to measure how native point defects move under applied electric fields at metal-ZnO and metal-$SrTiO_3$ interfaces. Native point defects can be electrically active, acting as donors or acceptors that increase[1]or compensate[2]free carrier densities, altering Schottky barrier depletion regions[3] as well as forming interface states that "pin" Fermi levels.[4] For many compound semiconductors, these defects exhibit pronounced segregation toward free surfaces and metal contacts, amplifying their interface electronic effects.[4] Here we report that native point defects in ZnO and $SrTiO_3$, representative wide band gap semiconductors with and without built-in polarization fields, respectively, can move hundreds of nanometers under applied electric fields that are comparable to electric fields in conventional Schottky barriers. In turn, such voltage gradients can account for the pronounced defect segregation typically reported at oxide semiconductor interfaces.[1,3,4,5]

To gauge how electric fields can affect defect distributions in ZnO, we measured DRCLS vs. increasing incident electron beam energy E_B and increasing depth below a 20 nm Pt electrode on a 0.5 mm thick commercial (MTI) ZnO single crystal. Without bias, DRCLS through the Pt showed significant increases in zinc vacancies (V_{Zn}) and Cu on Zn sites (Cu_{Zn}), analogous to previous studies.[3] An applied bias of +917V corresponding to 18.3 kV/cm across the entire crystal width increased this segregation by > 2x nearest the Pt/ZnO interface. This enhancement extends tens of nanometers into the bulk – comparable to the semiconductor depletion width, suggesting that the applied field falls primarily across the Schottky depletion region. With bias removed, these defects redistribute. Applied bias up to 2.5 kV/cm produces analogous oxygen vacancy (V_O) diffusion in commercial (Crystek) $SrTiO_3$ wafers. Here, positive bias drives the positive donors away from the anode, but with bias removed, these defects don't redistribute.

Electric fields applied laterally across ZnO surfaces also drive defect diffusion. Hyperspectral imaging (HSI) maps of V_{Zn} and Cu_{Zn} spatial distributions between a 32 nm thick, 300 nm diameter IrO_x Schottky diode and ground on a low-Li Tokyo Denpa Ltd. single crystal wafer displayed acceptor movement toward the diode with increasing positive bias corresponding to 10^4V/cm. These effects have general significance since voltage gradients of this magnitude are comparable or less than those in conventional band bending regions.

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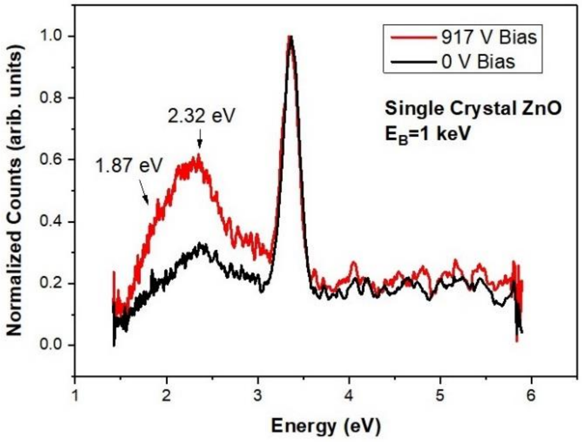

Fig.1. 1 keV DRCL spectra under the Pt-ZnO contact. Positive bias increases Cu_{Zn} and V_{Zn}

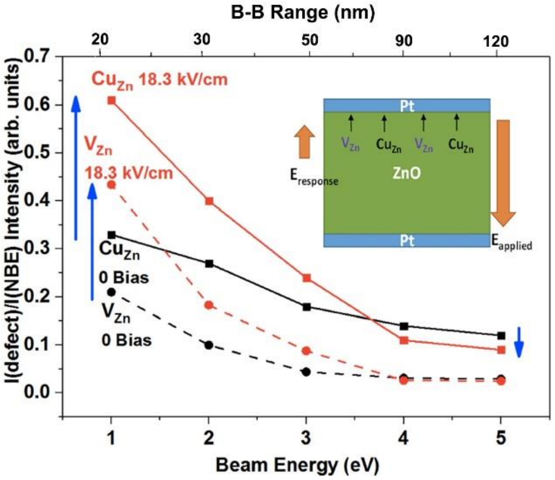

Fig. 2. Normalized defect intensities vs. depth below the metal-ZnO interface. Positive bias increases acceptor diffusion toward interface. Inset depicts V_{Zn} and Cu_{Zn} response to applied field.[3]

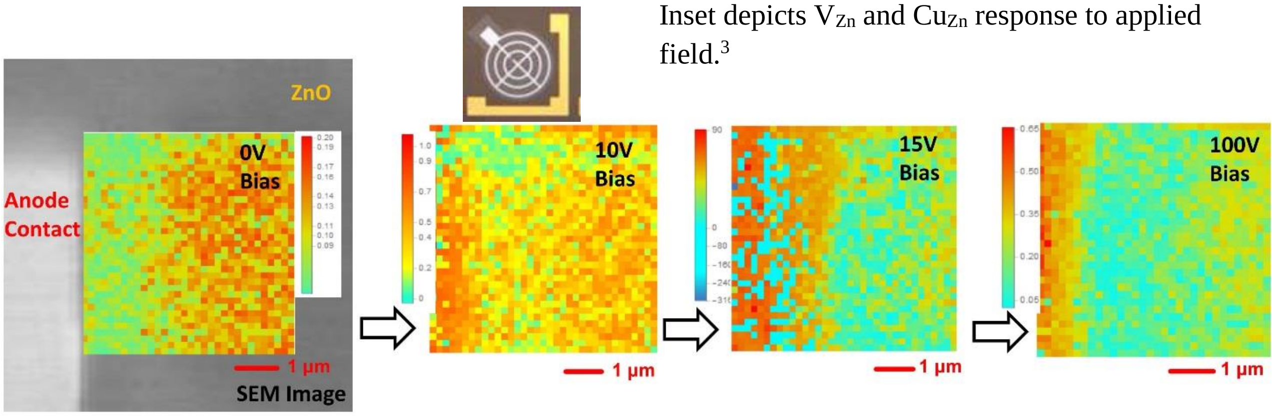

Fig. 3. ZnO HSI maps of V_{Zn} and Cu_{Zn} intensities vs. voltage gradients up to 10^4V/cm. Inset: anode & ground.

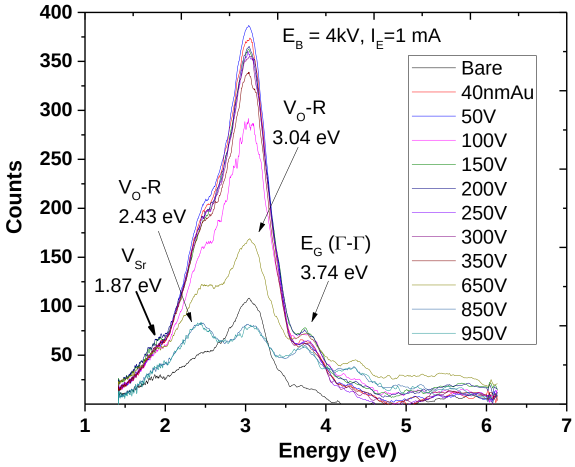

Fig. 4. DRCLS through 40 nm Au into $SrTiO_3(100)$ under positive bias.

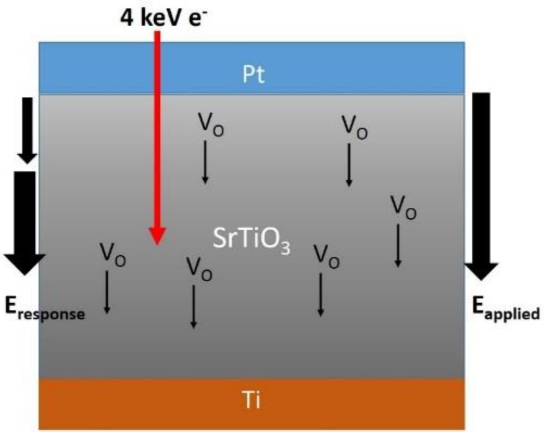

Fig. 5. V_{Zn} and Cu_{Zn} acceptor response in $SrTiO_3$ to positive applied bias.