Supporting Information

An electrochemical route to *p*-type doping of ZnO nanowires

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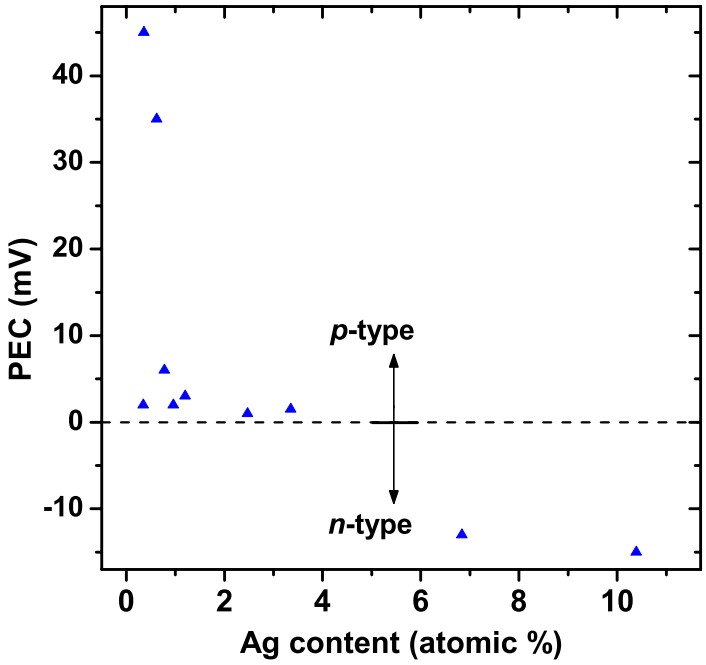

Figure S1. Photoelectrochemical cell (PEC) responses as a function of Ag content in the doped ZnO nanowires.

Figure S1 shows the conductivity type trends of the doped ZnO as the Ag content in the nanowires changes. Only the doped samples with relatively low Ag content, around 1% or less,

display distinct, positive PEC responses. As the Ag content increases in the nanowires, their *p*-type properties begin to diminish. Eventually the doped nanowires become *n*-type when the Ag content is too high. The increasing Ag content produces ZnO nanowires of lower material quality, in turn effecting hole conduction and quenching the *p*-type behavior of the samples.

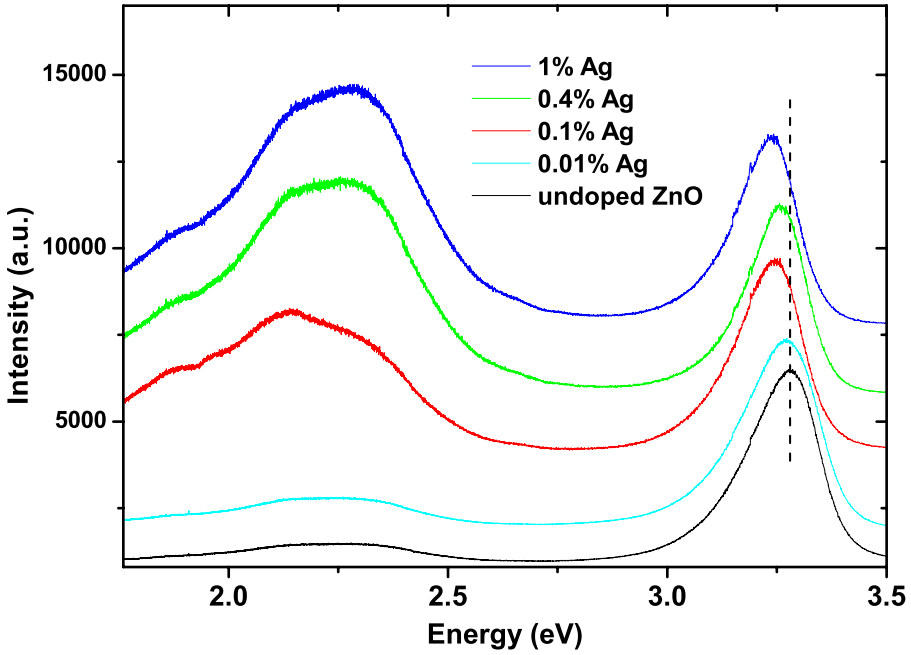

Figure S2. Room temperature photoluminescence (PL) spectra of as grown undoped and Ag-doped ZnO. The spectra are vertically offset for clarity.

Figure S2 displays representative PL spectra of the ZnO nanowires. All the samples were obtained at an applied potential of -1.13 V but with increasing Ag concentrations in the growth solution as indicated in the figure. Both doped and undoped ZnO nanowires possess two main emissions in their spectra, the near band edge emission (NBE) above 3.2 eV and the broader emission in the visible range typically associated with defects. All the spectra have been normalized to the NBE emission in order to more easily compare relative intensities of the defect

bands among the samples. The vertical line represents the NBE peak position of the undoped sample.

The undoped ZnO sample has an NBE peak at 3.28 eV and weak defect emissions. The nanowires obtained with only 0.01% Ag during growth display very similar PL to the undoped sample, indicating such a small amount of Ag did not lead to significant Ag doping. But the doped nanowires grown with 0.1% Ag have a clear NBE peak shift and increased defect emissions. It is evident at this Ag concentration doping begins to occur in the nanowires. The other doped samples grown at even higher Ag concentrations also show NBE peak shifts and a further increase in the relative intensity of defect emissions. It is clear from these observations that a continued increase in the Ag concentration during the growth of the ZnO nanowires produces material of a lower quality with more defects. This trend eventually affects the *p*-type properties of the nanowires as too many defects offset the available acceptors created by doping.