Supplementary Information

ZnO Nanoparticle-Decorated HfO₂/Sn-Doped In₂O₃ Core-Shell Nanowires by Atomic Layer Deposition: Enhancement of Field Emission Behavior by Surface Modification Engineering Wen-Chih Chang⁺, Chi-Hsin Huang⁺, Chih-Chung Lai, Hsu-Sheng Tsai, Shih-Min Lin, Su-Jien Lin, and Yu-Lun Chueh*

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<u>Microstructural analysis and electrical properties of the ALD-ZnO films with different</u> temperatures :

The crystal structure of ALD-ZnO films was characterized by X-ray diffractometer (XRD) as shown Figure S1a.[1] ALD-ZnO film always exhibits a polycrystal wurtzite (WZ) structure at all process temperatures from 100 to 250 °C.[1] Obviously, no distinctly preferred orientation in the ALD-ZnO films was found at low temperature, compared with that from the sputtered-ZnO films, with which the preferred (002) peak obviously appears. However, the intensity of (002) peak increases as the deposition temperature increases because the (002) plane has the lowest formation energy in the WZ hexagonal-packed structure. The films deposited at 250 °C show a much stronger intensity than that of the film deposited at other temperatures. The results imply that films deposited at 250 °C could get much better crystalline quality to have better field emission properties. For the electrical device application, the quality of film is quite important, especially resistivity. Figure S1b shows the four-point-probe resistivity measurements at different heating temperatures from 100°C to 250 °C.[1] Obviously, lower resistivity and higher mobility of ZnO films deposited at higher temperature than the films deposited at lower temperature can be achieved due to much better crystalline quality.

Consequently, the good crystallinity and better electrical properties (lower resistivity, better conductivity and mobility) are important parameters for the good field emission behavior. As we discussed above, the ALD-ZnO films deposited at 250°C with good crystallinity and better conductivity is an effective parameter for our research to obtain better field-emission performance.

Usually, ALD reaction breaks the CVD reaction into two half-reactions, keeping separation of precursor materials during the reaction. Separation of the precursors is accomplished by pulsing a purge gas (ex: nitrogen or argon) after removal of excess precursor from the process chamber and thus prevents CVD deposition on the substrate during each precursor pulse. Although, high temperature will result in thermal decomposition of diethylzinc while it would be a minor effect in this process in our study.



Figure S1 (a)XRD spectra for the growth of ALD-ZnO films with different temperatures. (b)The resistivity of ALD-ZnO films with different temperatures.



Figure S2 (a) A TEM image of a ZnO/ITO core-shell nanowire. Inset shows a HRTEM image (b) The corresponding HAADF image. (c)-(e) The correspond EDS mappings at Sn, In, and Zn, respectively. (f) A TEM image of a HfO₂/ITO core-shell nanowire. Inset shows the corresponding HRTEM image (g) The corresponding HAADF image (h)-(j) The corresponding EDS mappings at Sn, In, and Hf, respectively.



Figure S3 A high resolution TEM image of HfO_2/ITO core-shell nanowire. Inset shows the corresponding fast Fourier transform image of HfO_2 shell.



Figure S4 (a) HRTEM image of ZnO NPs-decorated HfO₂/ITO core-shell NW. (b) HRTEM image of the ZnO nanoparticle. Inset shows the diffraction pattern of ZnO nanoparticle.



Figure S5 XRD spectrum of ZnO NPs-decorated HfO₂/ITO core-shell NWs.

References:

[1]H.-W. Huang, W.-C. Chang, S.-J. Lin and Y.-L. Chueh, J. Appl. Phys, 2012,112, 124102-124107.