## **Supplementary Information**

## Low Temperature and Solution-Processed Na-Doped Zinc Oxide Transparent Thin Film Transistors with Reliable Electrical Performance Using Methanol Developing and Surface Engineering

By Kyongjun Kim, Si Yun Park, Keon-Hee Lim, ChaeHo Shin, Jae M. Myoung and Youn Sang Kim\*

## The interstitial doping of Na in the ZnO semiconductors at low temperature

In the previous reports, the defect chemistry was explained with Li in ZnO.<sup>[1,2]</sup> Na defect mechanism in the ZnO is very similar to the case of Li as a kind of the alkali metal.

 $Na \rightarrow Na_i^+ + e^-$  (Interstitial) (1)  $Na \rightarrow Na_{zn}^+ + h^+$  (Substitutional) (2)

The Na defect mechanism could be demonstrated to both the interstitial doping of Na and the substitutional doping, that Na have potentials into the 4-fold coordinated O atoms in ZnO crystal structure by Equation (1 & 2). However, Na easily formed the interstitial defects more than the substitutional exchange of Zn in the ZnO matrix. Because the energy of Na substitution exchange is higher than the energy of Na interstitial doping like the case of Li defect mechanism.<sup>[3]</sup> It means that the interstitial doping is superior on Na doping in ZnO at low temperature. On the other hand, in order to achieve the substitutional doping of Na, more Na doping concentration and high temperature sintering are needed with oxygen gas like the case of P-type doping using the alkali metal.<sup>[4]</sup>



*Figure S1.* Optical microscopy images were magnified by a factor of 40. Cross-section and tilted( $\theta = 45^{\circ}$ ) FE-SEM microscopy images of patterned ZnO on a SiO<sub>2</sub> substrate. a–c) Drying of the solution in the air without methanol. d-f) Direct sintering of the solution in the air without methanol. d-f) Direct sintering of the solution in the



**Figure S2.** The optical microscopy(OM) images of various ZnO thin films, which fabricated by one run; (a) and (b) OM images of patterned ZnO thin films magnified by a factor of 40; (c) Enlarged OM image of side part of the patterned ZnO thin film of figure S5b magnified by a factor of 500.; (d) and (e) OM images to show the part of the gap between patterned ZnO thin films magnified by a factor of 40; (f) Enlarged OM image of side part of the patterned ZnO thin films of figure S5 magnified by a factor of 500.



**Figure S3**. Top views and 3D views of AFM images: (a) The sobel transform image of intrinsic ZnO thin film (RMS=1.261nm), (b) 3D view of intrinsic ZnO thin film, (c) The sobel transform image of Na-doped ZnO thin film (RMS=1.121nm), (d) 3D view of Na-doped ZnO thin film.



*Figure S4.* Transfer curves of the patterned intrinsic ZnO TFT after sintering at (a) 100 °C; (b) 200 °C; (c) 300 °C.



**Figure S5**. (a) Output curve of patterned Li doped ZnO TFT after sinterring at 100 °C. (b) Transfer curve of patterned Na doped ZnO TFT after sinterring at 100 °C. (c) The hysteresis-transfer curves of Na-doped ZnO TFT after sintering at 100 °C with a W/L ratio of 20.

## References

[1]G. Srinivasan, R. T. R. Kumar and J. Kumar, J. Sol-Gel Sci. Techn., 2007, 43, 171-177.

[2]P. Bonasewicz, W. Hirschwald and G. Neumann, *J. Electrochem. Soc.*, 1986, **133**, 2270-2278.

[3].J. R. Duclere, M. Novotny, A. Meaney, R. O'Haire, E. McGlynn, M. O. Henry and J. P. Mosnier, *Superlattice Microst.*, 2005, **38**, 397-405.

[4] J. S. Lee, S. N. Cha, J. M. Kim, H. W. Nam, S. H. Lee, W. B. Ko, K. L. Wang, J. G. Park and J. P. Hong, Adv Mater. **2011**, *23*, 4183.