Response to “Comment on ‘Unraveling the conduction mechanism of Al-doped ZnO films by valence band soft X-ray photoemission’” [Appl. Phys. Lett. 86, 216101 (2005)]

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In the Comment by Lin, it is said that, as shown in Fig. 6 of Ref. 2 (Ref. 10 in the original Letter), the optical band gap of the 3% Al-doped ZnO film is bigger than that of the 1% Al-doped film. From this figure, it is easily seen that the absorption edge shift toward higher values as the aluminium concentration increases but is not possible to deduce an increase or a reduction of the optical band gap. That should be done with the function

$$\alpha \sim (h\nu - E_m)^{1/2}$$

where $\alpha$ is the absorption coefficient, $h\nu$ is the incident energy and $E_m$ is the measured optical band gap. The shift in the absorption edge is mainly attributed to the Moss-Burstein effect. There is a second phenomenon that affects the measured optical absorption edge in heavily doped $n$-type semiconductors, which is the change in the nature and strength of the interaction potentials between donors and the host crystal. Thus, the effective measured band gap of a doped semiconductor suffers shrinkage and this is our interpretation of the changes in the valence band. Of course, Mondragón-Suárez et al. do not measure a decrease in the optical gap, but a shift in the absorption edge. In their work, the detected shift in absorption edge with increasing aluminium doping is attributed to the combination of the two competing effects, Moss-Burstein upwards shift and the band gap shrinkage. Note that a few percent Al doping would, following Roth et al., give rise to a smaller measured effective band gap.

In our Letter, we do not study the changes in the band gap width using photoelectron spectroscopy. Band-edge emission in undoped and doped ZnO has been done, and is cited in our Letter. We measure the position of the valence band maximum. Our principal conclusion is that the hybridization between the Al dopant orbitals and ZnO matrix leads to an upwards shift of the chemical potential. The band gap persists in spite of doping and no semiconductor–metal transition has been detected. As a consequence, the band conduction mechanism should be the principal contribution to the conduction process in doped films, as is the case in the undoped ZnO.

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