Transparent Conducting Fe-F Codoped ZnO Films Deposited by Spray Pyrolysis

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Zinc oxide (ZnO) is a promising candidate to replace indium tin oxide as the transparent conducting oxide in photovoltaic solar cells. Although, by adding a dopant, the resistivity of ZnO can be significantly reduced, further reduction in ZnO resistivity is desired for better-performance solar cells. Codoping ZnO is an attractive approach. Two dopants, one cationic and one anionic, can go separately into the Zn and O sublattices and introduce double doping effects. A number of growth techniques, such as sputter, CVD and sol-gel, have been used for co-doping ZnO films [1-3]. Although spray deposition is a low-cost technique for large-area deposition of ZnO films, there are few papers regarding codoping ZnO in spray deposition. One of the limitations with codoping ZnO by spray deposition is that all the chemicals have to be compatible in one solution without precipitation. This limits the choices of dopants for spray-deposited ZnO.

In this paper, we report a novel spray deposition technique, co-spray deposition, to codope ZnO films with Fe and F. Since the co-presence of Fe^{3+} and F^{-} in the same solution leads to precipitation of FeF_3, two starting solutions were prepared and sprayed through two spray heads. One contains Zn^{2+} and Fe^{3+}, and the other contains only F^{-}. This technique bypasses the incompatible chemistries and for the first time, Fe-F codoped ZnO is demonstrated by spray deposition.

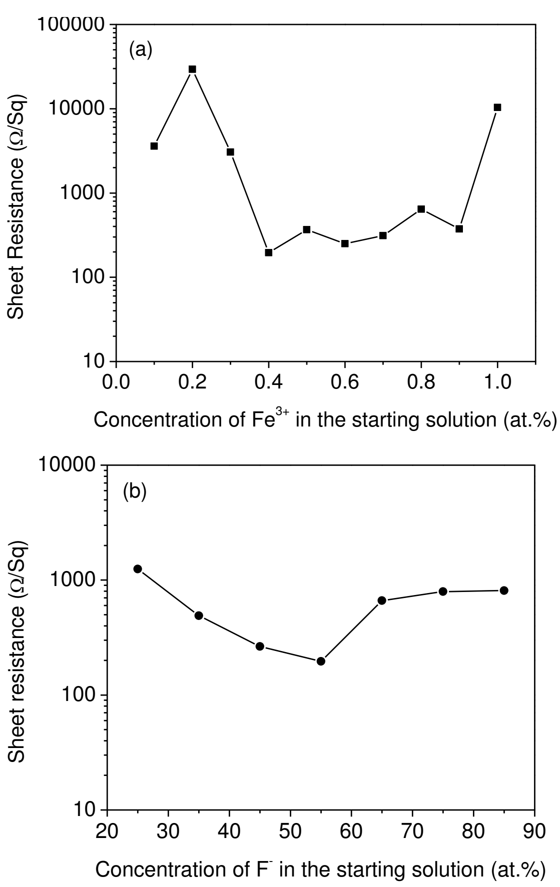

Figure 1. Sheet resistance of annealed ZnO:Fe:F films as a function of doping concentration in starting solution: (a) 0.1–1.0 at.% Fe with F fixed at 55 at.%; (b) 25–85 at.% F with Fe fixed at 0.4 at.%.

The sheet resistance of codoped ZnO as a function of Fe and F concentrations in the starting solutions and after vacuum annealing at 400°C for 1 hour is shown in Figure 1. The minimum sheet resistance, 196 Ω/□, is obtained for at 0.4 at.% Fe and 55 at.% F. Compared to ZnO doped with 0.4 at.% Fe only (185 kΩ/□) and ZnO doped with 55 at.% F only (609 Ω/□), Fe and F codoped ZnO resulted in much a lower sheet resistance. It is believed that cationic Fe^{3+} substitutes Zn^{2+} ions and anionic F^{-} substitutes O^{2-} ions in the ZnO lattice. This double doping enhances the carrier concentration in ZnO films leading to a lower sheet resistance. Figure 2 shows the FESEM image of the ZnO film with the lowest sheet resistance. The thickness of the sample is ~400 nm (insert in Figure 2) and the resistivity is 7.84×10^{-3} Ω·cm correspondingly. The optical transmittance of the same sample is in Figure 3. The average transmittance is ~90 % in the visible range. Our co-spray technique results in Fe-F codoped ZnO films with a lower sheet resistance compared to single-doped ZnO and high transmittance.

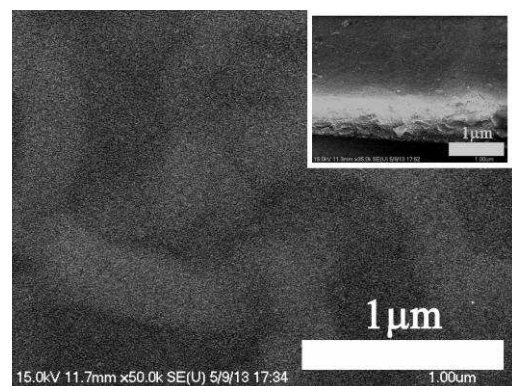

Figure 2. FESEM image of a ZnO film deposited at 0.4 at.% Fe and 55 at.% F in the starting solutions.

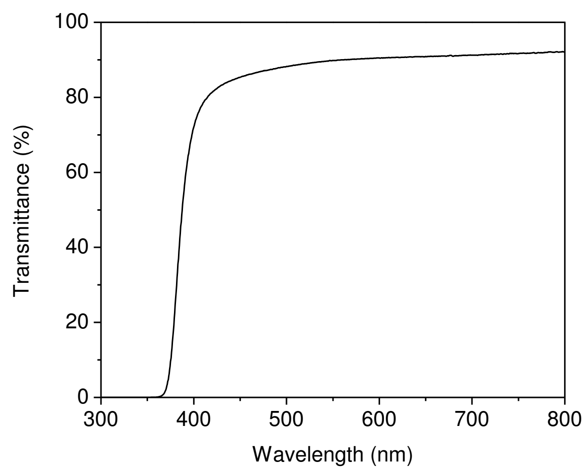

Figure 3. Transmittance of an as-deposited ZnO film with 0.4 at.% Fe and 55 at.% F in the starting solutions.

References:
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