FORMATION OF IN SITU MN-DOPED ZnO STRUCTURES BY RAPID HEATING METHOD

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In recent years, ZnO nanostructures have attracted much interest. ZnO with wurzite structures is an n-type semiconductor material with both good electrical and optical properties. To enhance the electrical/optical properties ZnO was usually doped with some dopants such as Al, Si, In [1]. Recently many investigations have paid attention to Mn-Doped ZnO and expect it to be one promising transparent diluted magnetic semiconductor to be used potentially in spintronic [2]. Several methods are used to fabricated structures, including aqueous solution growth methods, metal- organic chemical vapour deposition, thermal evaporation, hydrothermal method, and pulsed laser deposition, etc. In practicum it is no easy to control its shape and order its orientation of growth into three-dimensional arrays.

In this work Mn-doped ZnO multipods were produced from metallic Zn in air atmosphere. MnO_2 was used as substrate where metallic Zn wire was embedded by uniaxial double load pressing to obtain a disk shaped pellet. There is no other metal catalyst in the process. The MnO_2 disk containing the Zn wire was heated in an alumina crucible sealed with another alumina crucible. The oxidation process was attempted by a rapid temperature cycle at 1220º 6 minutes with heating and cooling rates >50ºC/min. After thermal cycling a yellowish structure was observed in the manganese disk. This structure had carpet type fibre morphology, figure 1. The fibres were supported directly on the manganese oxide sintered substrate. EDX microanalysis confirms the presence of nearby 2 wt % of manganese ions in the fibres.

If the experiment were performed with metallic Zn powder as reported previously [3] but under the same rapid thermal heating proposed in this work, two white and yellowish tetrapods type structures were obtained, figure 2. The white like cotton was collected outside of the alumina crucible and the yellowish one inside the alumina crucible.

To elucidate the influence of manganese in the fibres formation, XRD diffraction patterns were realized. The calculated lattice parameters of pure ZnO tetrapods were a=3.250 Å, c=5.207 Å that are similar than pure ZnO wurzite, meanwhile the lattice parameters of the carpet type fibres were a=3.251 Å, c=5.210Å that suggest an effective incorporation of Mn ions into ZnO structure.

Raman Spectroscopy shown a characteristic vibration spectra for ZnO tetrapopds but when carpet type fibres were analyzed a new vibration state at 521,5 cm^{-1} can be observe characteristic of the Mn-doping in ZnO [3].

In summary it is possible to in situ synthesize Mn-doped ZnO structures having a carpet type fibre morphology by rapid heating method in air by using metal Zn and MnO_2 as substrate without additional catalyst system. Based on EDS microanalysis, XRD and Raman spectroscopy, the carpet type fibres were ZnO having Mn^{2+} ions occupying the Zn sites.

References:

[1] J. Zhong, S Muthukumar, Y. Chen, Y. Lu, H.M.. NG, W. Jiang, E.L. Garfunel, Appl. Phys. Lett. 83 (2003) 3401
[2] P. Sharma et al., Nat Mat. 2(2003) 639
[3] L.W. Yang, X.L. Wu, G.S. Huang, T. Qiu, and Y.M. Yang, J. Appl. Phys. 87(2005)014308

Figures:

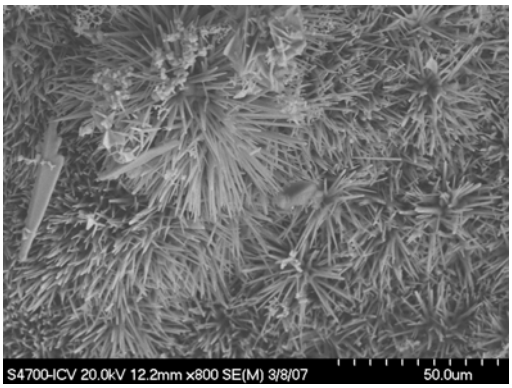

Fig 1: MEB micrograph of Mn-doped ZnO fibres.

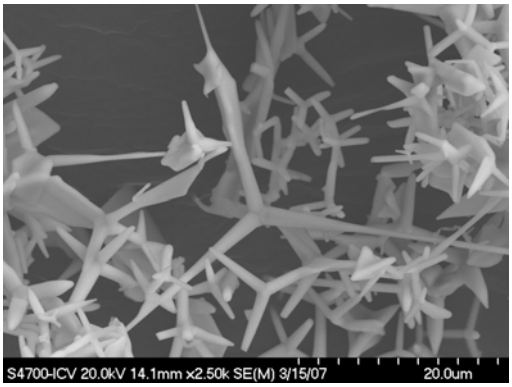

Fig 2: MEB micrograph of pure ZnO tetrapod

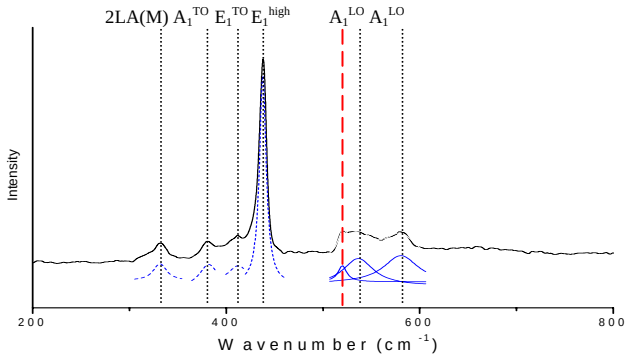

Fig3. Room temperature Raman spectra of Mn:ZnO carpet type fibres. The black line corresponds to the experimental spectra and the blue lines to the Lorentz fitting.