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Elucidation of the highest valence band and lowest conduction band shifts using XPS for ZnO and $Zn_{0.99}Cu_{0.01}O$ band gap changes

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ABSTRACT

ZnO and $Zn_{0.99}Cu_{0.01}O$ nanostructures were prepared by a simple sol–gel method. The band gaps of the materials were systematically studied based on the dependence of the dimensions of the nanostructures as well as the presence of a dopant material, Cu. ZnO and $Zn_{0.99}Cu_{0.01}O$ nanostructures were found to exhibit band gap widening whilst substitution of Cu in the lattice of ZnO caused its band gap to narrow with respect to the pure ZnO materials. In order to understand the phenomenon of band gap change, structural, spectroscopic, particle size and morphological studies were done. The band gap change occurring when the materials were in the nanostructured phase was proven to be mainly due to the downward shift of the valence band. Interestingly, when the band gaps of the pure ZnO and Cu doped ZnO were compared, the band gap changes were due to different shifts of the valence bands.

Introduction

ZnO is a very interesting material to study due to its unique physical and chemical properties resulting in applications such as blue and ultra-violet optical devices, sensors, solar cells and other new nanotechnology based devices [1–5]. ZnO is said to have a direct band gap of 3.37 eV [1–4] but this value has been found not to be unique and lately, using more accurate modern instruments, the values have been revised to between 3.1 and 3.4 eV [2,6]. Thus, the band gap of ZnO is found to be sensitive to the route of synthesis and preparation conditions as well as its physical dimensions. The band gap of ZnO can be changed by either decreasing the size of the crystallites [2,7–9] or by doping [10–12]. There are two types of doping of which the first is when a foreign ion replaces a host cation or anion in its position in the crystal lattice site and the second type is when the foreign ion is placed in the interstices of the crystal structure. Substitutional doping can be done by a chemical reaction method that forces the dopant element to be introduced into the crystal lattice sites of the material [10,11]. If the dopant is a cation, it will replace the host cation site and if the dopant is an anion, it will likewise replace the anion at its particular site in the crystal lattice. Single phase materials that are isostructural to the initial material will be produced. However, these new compounds will exhibit novel characteristics which will be useful for future applications.

Much work on ZnO doping has been done [13–20]. Doping can cause either an increase or decrease of band gaps. As an example, according to Shan et al. Cd doping in ZnO causes the band gap of the material to decrease while Mg doping in ZnO causes it to increase [15]. Therefore, band gap tuning via dopant materials is quite possible. Several synthesis methods such as hydrothermal [1], combustion [21], spray pyrolysis [22], sol–gel [19], etc. have been employed to produce ZnO. Among these techniques, catalysts are used [23,24] contaminating the final products. In this work, the ZnO and Cu doped ZnO materials are synthesized without using any catalysts, thus, simplifying the synthesis route and ensuring purity to a high degree. Since this work investigates the band gaps and changes in band gap of materials, and band gaps are very sensitive to the presence of impurities and multi phases [25], it is very important that the final product must be single phase and pure. Contributions from other minor phases or impurities are detrimental to the experimental results because band gaps are affected by minor presence of impurities or the presence of other phases.

Although much work has been published on ZnO and ZnO doped materials [14–25], there are still many unresolved issues on this subject. As an example, there are no clear explanations of the band gap widening of nanostructured ZnO in the literature

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Table 1
Sample ID for ZnO and $Zn_{0.99}Cu_{0.01}O$ annealed at various temperatures for 24 h.

Samples	Annealing temperature (°C)	Sample ID
ZnO	400	Z400
	500	Z500
	600	Z600
	700	Z700
	800	Z800
	1200	Z1200
$Zn_{0.99}Cu_{0.01}O$	400	ZC400
	500	ZC500
	600	ZC600
	700	ZC700
	800	ZC800
	1200	ZC1200

beyond the presence of vacancies [26,27] but with no experimental proofs of the existence of the vacancies given. For Cu doped materials, it is very difficult to force Cu into the lattice of ZnO producing pure powders. For our $Zn_{1-x}Cu_xO$, we can only manage a Cu content of $x = 0.01$. Yan et al. [25] and Chow et al. [28] said that they have produced $Zn_{(1-x)}Cu_xO$, with $x = 0.03$ but since no XRD results were shown by Yan, and low intensity XRD results showing the presence of Cl_2 (albeit, it was not explained how Cl_2 can produce a peak in an XRD pattern!) was shown by Chow, it has not been established if the samples are really pure or of single phase. Thus, it is hard to say if the observed band gap change was due to the impurities, multiphases or the materials themselves. In addition, no energy dispersive X-ray spectroscopy (EDS) or equivalent methods in the work have been shown to prove that a substitution of

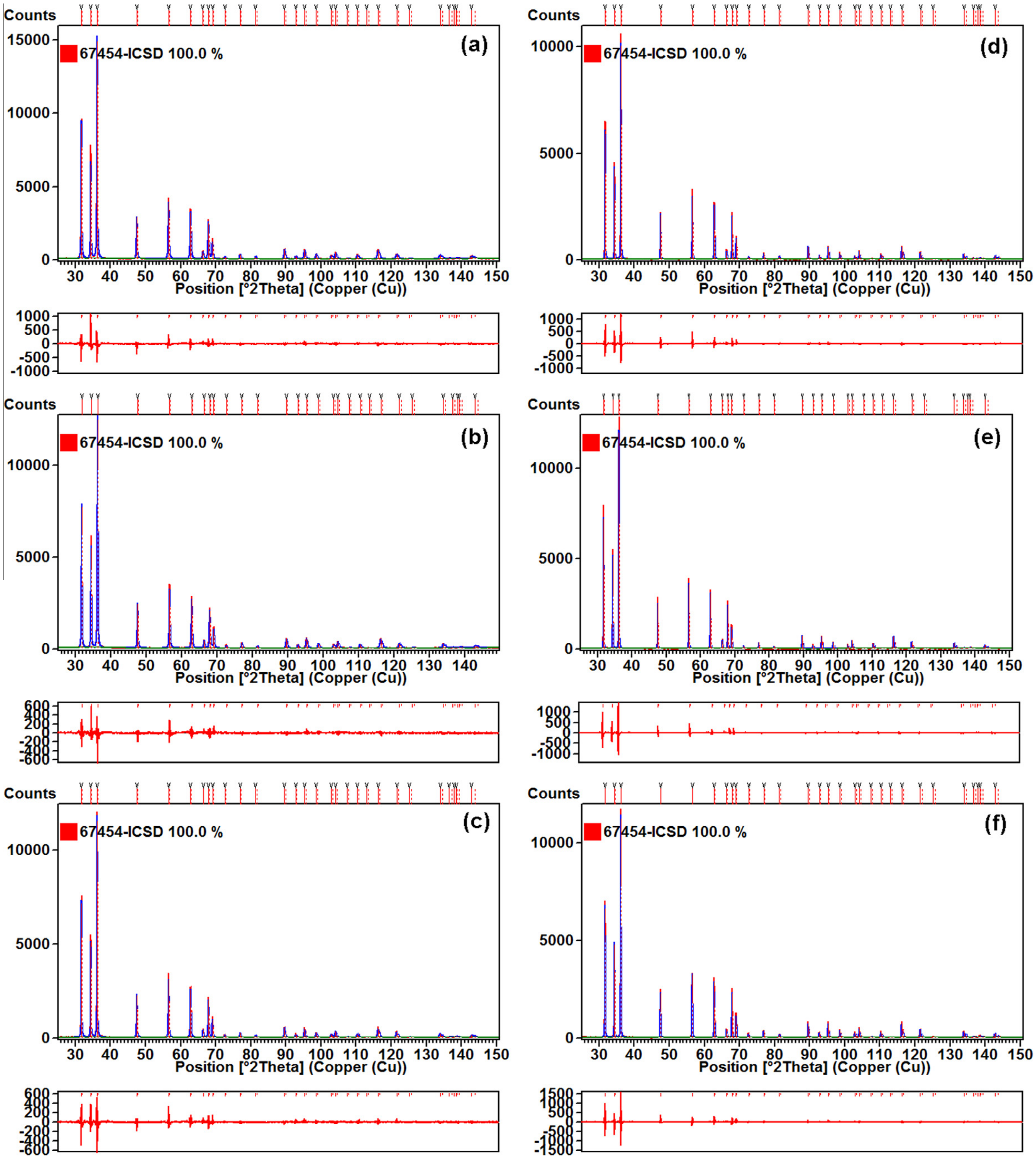

Fig. 1. Rietveld refinements of XRD patterns for (a) Z400 (b) Z500 (c) Z600 (d) Z700 (e) Z800 (f) Z1200 samples.