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Microstructure and optoelectronic properties of Cu–Li codoped ZnO film: Role of Cu_{Zn} and Li_i defects

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ABSTRACT

Wurtzite Cu–Li codoped ZnO (Cu–Li:ZnO) films with Cu concentrations of 0–3 at.% were grown by sol–gel method. The conductivity, band gap and transparency of the Cu–Li:ZnO films decrease with increasing the Cu concentration due to the substitution of Cu for the Zn sites (Cu_{Zn}) and the interstitial Li atoms (Li_i). The Cu_{Zn} defects generate a fully occupied impurity band above the valance band maximum (VBM), resulting in an upward shift of the VBM and a decrease of the band gap. The Cu_{Zn} acceptors can compensate for the Li_i donors and further form complex self-compensation defects [$Cu_{Zn} + Zn_i$]. The carrier mobility of the Cu–Li:ZnO film is about 2–5 orders of magnitude lower than that of the intrinsic one due to the grain boundary and surface scattering.

1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor with direct band gap of 3.37 eV and a large exciton binding energy of 60 meV. It attracts an increasing interest owing to promising applications in optoelectronics and ultraviolet light emitters [1,2]. Much efforts have been made to obtain better ZnO-based materials by doping, such as increasing the conductivity using Al [3], tuning the band gap with Mg [4], promoting dilute magnetic semiconductivity by Co and Mn [5], and achieving p-type ZnO by Li–N and In–N codoping [6–8], respectively.

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Among the dopants studied, Li is effective in modifying the microstructure, ferroelectricity and optoelectrical properties. Previous studies showed that Li prefers to occupy the interstitial position (Li_i) acting as the donor, rather than the znic site (Li_{Zn}) acting as the acceptor [9]. Lin et al. [10] observed that the changes of the Li incorporation-induced strain along *c*-axis are closely related to the concentration ratio of Li_i to Li_{Zn} in the films. By codoping Li with Mg or Al, ZnO films show enhanced electrical and optical properties due to form acceptor levels [11,12]. Cu, possessing a similar electronic structure and small size mismatch with Zn [13], can act as an acceptor when it substitutes for Zn sublattice of ZnO and has +1 valence (denoted as Cu_{Zn}^{+1}) [14]. Ferhat et al. [15] found that the band gap narrowing in the Cu doped ZnO is principally due to the strong p–d mixing of the O and the Cu in the substitutional sites. Ghosh et al. [16] discovered that, with increasing Cu doping ratio, the sol–gel ZnO film transparency decreases while the resistivity increases.

Codoping may induce more intriguing changes in the crystal lattice and better characteristics because of the combined effects of the dopants. Ghosh et al. [17] reported that, in the 0.1% Cu and Li (from 2% to 7%) codoped ZnO films, Li-related complex defect forms and acts as nonradiative path for luminescence. Zou et al. [18] observed both room temperature ferroelectric and ferromagnetic behaviors in single phase Cu–Li:ZnO films. However, few studies have focused on how the Cu doping ratios affect the phase, morphology, electrical and optical properties of Cu–Li:ZnO films, where the dopants may form defects of Li_i and Cu_{Zn}.

In this work, Cu–Li:ZnO films were fabricated using the sol–gel method and effects of the Li_i and Cu_{Zn} defects on the film microstructure and optoelectrical properties were experimentally and theoretically investigated.

2. Experimental

Zinc acetate-2-hydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), ethanol, and Diethanola-mine (DEA) were used as the starting precursor, solvent, and sol stabilizer respectively and all chemicals were of analytical grade. $Zn(CH_3COO)_2{\cdot}2H_2O$ was dissolved in ethanol to obtain a 0.8 M solution of ZnO precursor followed by a thorough mixing at 60 °C for 1 h. LiCl and $CuCl_2{\cdot}2H_2O$ were then added with stirring for another 1 h under the same conditions. The concentration of LiCl was fixed at 3 at.% and the concentrations of $CuCl_2{\cdot}2H_2O$ were selected as 0.15, 0.3, 0.6, 1.5 and 3 at.%. The solutions were finally aged at room temperature for 24 h. After that, the undoped and Cu–Li:ZnO films with ~120 nm thick were deposited using sol–gel spin-coating at 3000 rpm for 30 s on clean Si(100), ITO and glass slides. It was followed by annealing at 550 °C in a muffle furnace for 2 h with the heating rate of 5 °C/min. The films on silicon were used for the X-ray diffraction (XRD) and the scanning electron microscopy (SEM) analysis, while the samples on ITO and glass were prepared for electrical and optical characterizations, respectively. To examine the particle size and crystallinity, the transmission electron microscopy (TEM) samples were prepared by the following procedures [19]. First, 5 ml ZnO sol–gel was dropped into a clean crucible and calcined at 550 °C for 2 h under the same conditions as that of the films. Second, the dried powder was thoroughly grinded in a clean mortar. The as-obtained particles were then ultrasonically dispersed in pure ethanol before dipped onto the TEM copper grid. The XRD analyze was performed with a X′ Pert Pro using Cu Kα radiation with a wavelength of 0.154056 nm. SEM was carried out on a SSX-550. TEM and electron diffraction patterns were recorded with a TECNAI G220. Current-voltage (*I–V*) curves were measured using a LK2005A potentialstat with device structure of GaIn/ZnO film/ITO. The transmittance was characterized using a UV759S UV–vis spectrometer.

3. Results and discussion

3.1. Crystalline phase

Fig. 1 shows the XRD patterns of the ZnO, Li:ZnO and Cu–Li:ZnO films with different Cu doping concentrations. All the films exhibit a hexagonal wurtzite ZnO structure and no impurities related to Cu, Li or their oxides are detected [20,21]. Table 1 summarizes the lattice parameters *a* and *c*, grain size, and relative intensity of the (002) and (101) peaks, respectively. Unlike the undoped film, the Li:ZnO