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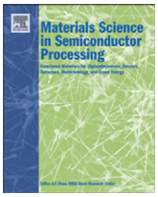

Structural and optical properties of (Al, K)-co-doped ZnO thin films deposited by a sol–gel technique

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ABSTRACT

Thin films of Al-doped ZnO (AZO) and (Al, K)-co-doped ZnO (AKZO) were synthesized by sol–gel spin coating and their structural and optical properties were investigated. All the films had a preferential orientation in which the *c*-axis was perpendicular to the substrate. The optical bandgap increased after Al doping, but decreased after K doping at a given Al doping concentration. UV emission and a broad visible emission band were observed in photoluminescence (PL) spectra. The intensity of both emission bands decreased after Al and K co-doping. PL excitation (PLE) spectra of the blue emission band indicate that the initial state is possibly the same for all the samples and a similar case occurs for the orange–red emission band. The green emission can be attributed to electronic transitions involving oxygen vacancies. A possible process for the orange–red emission of the thin films is radiative recombination of an electron trapped in a zinc interstitial defect with a hole deeply trapped in interstitial oxygen.

1. Introduction

With a direct wide bandgap (~3.37 eV) and large exciton binding energy (~60 meV), ZnO has attracted much attention for potential applications in optoelectronic devices such as transparent conductors, displays, and solar cells [1,2]. To improve the performance of ZnO-based optoelectronic devices, it is essential to grow high-quality ZnO films. The presence of intrinsic and extrinsic defects influences the quality of ZnO films. It is important to control these defects and investigate their effects on electrical and optical properties for ZnO-based devices. Luminescence can provide information on defects and relaxation pathways of excited states, and therefore provides an insight into the quality of ZnO films [3,4].

Extrinsic doping can modify the electron energy band structure and affect the crystalline quality and native point defects, and so it is considered an effective method for tuning the electrical, optical and magnetic properties of ZnO [5–7]. Al-doped ZnO (AZO) thin films have been extensively explored as transparent conducting films [8–10]. However, Al doping can reduce the crystalline quality of ZnO films and can change the defect environment, depending on whether Al atoms substitute for zinc atoms or occupy interstitial sites [9,10]. Group I elements are candidate acceptors for ZnO thin films. Co-doping with Al and a group I element has been used to improve dopant solubility, tailor the band structure of the matrix, and affect the formation or suppression of defects due to charge compensation [11,12]. In a previous study, (Al, Li)-co-doped ZnO thin films with an average transmittance of >85% in the visible range showed a broad

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yellowish-white emission band. The optical bandgap of the thin films decreased as the Li concentration increased for a fixed Al concentration of 0.5% [11]. (Al, Na)-co-doped ZnO thin films showed enhanced emission bands at 400–500 nm and improved transparency as the Na concentration increased [12]. Similar to Li and Na, K can be a candidate acceptor for ZnO by substituting for Zn sites. Some experimental results have revealed that K doping can change the electronic and optical properties of ZnO films [13–15]. However, few studies have investigated the optical properties of (Al, K)-co-doped ZnO thin films. Cost effectiveness is an important issue in the practical application of AZO thin films. Among the deposition methods available for AZO thin films, such as pulse laser deposition [9], sputtering [8,10], chemical vapor deposition [16] and sol–gel techniques [17], the sol–gel approach is attractive because of its simplicity, safety and low cost [18,19].

In the present study, AZO and (Al, K)-co-doped ZnO (AKZO) thin films were prepared on glass substrates using a sol–gel spin-coating process. The effects of the K doping concentration on the structural and optical properties of AKZO thin films were investigated. A possible mechanism responsible for the effects noted was elucidated.

2. Experimental procedure

ZnO, AZO and AKZO films were prepared by a sol–gel method using a spin-coating technique onto glass slide substrates. $Zn(CH_3COO)_2 \cdot 2H_2O$ was used as the starting precursor, aluminum nitrate nonahydrate $[Al(NO_3)_3 \cdot 9H_2O]$ and potassium acetate $[K(CH_3COO)_2]$ as Al and K dopant sources, 2-methoxy ethanol as the solvent, and monoethanolamine (MEA) as a stabilizer. The zinc ion concentration was 0.5 M and the molar ratio of MEA to zinc acetate was maintained at 1:1 to stabilize the solution against precipitation and produce a clear solution for coating. The resulting solution was stirred at 60 °C for 2 h until a clear homogeneous solution formed and was then aged for 48 h to obtain the optimal viscosity for spin-coating. For doped samples, the atomic [K]/[Zn] ratio in the precursor solution was adjusted to 0%, 1%, 2%, 6% and 10% and the atomic [Al]/[Zn] ratio was fixed at 1%. Glass slides were ultrasonically cleaned using acetone, ethanol and then distilled water and dried in air. The films were spin-coated at 3000 rpm for 30 s. After each layer was deposited, the substrate was heated in air at 300 °C for 10 min. The coating process was repeated 12 times. The films were finally annealed at 500 °C in air for 2 h and then cooled in the furnace to room temperature.

The surface topography and thickness of the films were examined using a JSOL/JSM-6700F field emission scanning electron microscope. The structural properties of the films were characterized using a Rigaku D/Max-3C system with Cu K_α radiation. The optical transmittance of the films was recorded on a UV-Vis spectrometer (Hitachi V4100) over the wavelength range 300–800 nm and the optical bandgap energy was calculated. Photoluminescence (PL) and PL excitation (PLE) spectra were measured on a HJYFL3-221-TCSPC spectrometer (Jobin-Yvon) using a xenon lamp as the excitation source. All measurements were carried out at room temperature.

3. Results and discussion

Fig. 1 shows in-plane SEM images of pure ZnO, AZO and AKZO thin films. Visual inspection reveals that the films have a nanometer crystalline size. Compared with pure ZnO, the microstructure of the AZO and AKZO thin films becomes increasingly finer and the crystalline size decreases. Moreover, the microstructure of AKZO films is not sensitive to K concentration in the range 0–10%. The results are consistent with previous reports for AZO films [20,21]. The pores in the film surface are partly generated by the coalescence of microvoids, which is related to decomposition of the precursor and evaporation of residual organics in the gel film [17]. The inset of Fig. 1 presents a typical cross-sectional view of a ZnO thin film, which shows a dense microstructure and no reaction with the substrate. The film thickness is approximately 450 nm.

Fig. 2 shows XRD patterns for pure ZnO, AZO and AKZO thin films. All XRD patterns reveal polycrystalline ZnO of a hexagonal wurtzite phase; no secondary phases were found within the XRD detection limits. The strong (0 0 2) diffraction peak indicates that all the films have a preferential orientation in which the *c*-axis is perpendicular to the substrate. The inset in Fig. 2a shows a magnification of the (0 0 2) diffraction peaks. Compared with pure ZnO, the intensity of (0 0 2) peak is lower for AZO and AKZO thin films, suggesting that Al doping can reduce the crystal quality. The (0 0 2) peak position shifts towards the high angle side for AZO film and then gradually shifts to the low angle side for AKZO films as the K concentration increases. This demonstrates that the lattice constant of ZnO changes on incorporation of Al or K atoms. According to the Bragg law, the *c*-axis constant can be calculated using the diffraction peak position for the (0 0 2) plane, as shown in the inset of Fig. 2b [21]. The *c*-axis constant is 0.52078 and 0.51932 nm for pure ZnO and AZO films, respectively. The value increases from 0.51932 to 0.52108 nm for AKZO films as the K concentration increases from 1% to 10%. It is clear that the *c*-axis constant decreases for the films on Al doping, indicating that incorporation of Al^{3+} ions (0.053 nm) to replace Zn^{2+} ions (0.072 nm) leads to shrinkage of the network and consequently decreases the unit cell parameters. For AKZO films with K doping at a low concentration (1%), the *c*-axis constant shows no obvious change, which may mean that K^+ ions (0.133 nm) are beneficial for incorporation of more Al atoms in the lattice sites because of mitigation of lattice strain for Al and K co-doping in ZnO. As the K concentration increases, the *c*-axis constant increases due to K^+ ion occupation of Zn sites.

Transmission spectra for pure ZnO, AZO and AKZO thin films are shown in Fig. 3a. The interference fringes indicate that the films have smooth surfaces and interfaces with the glass substrate. The average optical transparency was $>85\%$ in the visible region (400–700 nm) for all the films. Compared to pure ZnO film, the UV absorption edge is blue-shifted for AZO film, indicating broadening of the optical bandgap due to Al mono-doping. In general, a blue shift of the absorption edge in Al-doped ZnO films is associated with an increase in the concentration of carriers