

# Conductivity study of nitrogen-doped calcium zinc oxide prepared by spray pyrolysis



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## ARTICLE INFO

### Article history:

Received 23 September 2015

Accepted 26 October 2015

Available online 28 October 2015

### Keywords:

Nanocrystalline materials

Calcium zinc oxide

Spray pyrolysis

Electrical properties

Thin films

## ABSTRACT

In this study, the spray pyrolysis method was used to prepare unintentionally doped and nitrogen-doped calcium zinc oxide films by using zinc acetate, calcium nitrate precursor, and ammonium acetate precursor. Morphological and structural analyses were conducted using scanning electron microscopy and X-ray diffraction. The results indicated that film grain size decreased as the nitrogen doping was increased. Both calcium oxide and zinc oxide structures were identified in the unintentionally doped calcium zinc oxide. When nitrogen doping was introduced, the film mainly exhibited a zinc oxide structure with preferred (002) and (101) orientations. The concentration and mobility were investigated using a Hall measurement system. P-type films with a mobility and concentration of  $10.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $2.8 \times 10^{17} \text{ cm}^{-3}$ , respectively, were obtained. Moreover, according to a temperature-dependent conductivity analysis, an acceptor state with activation energy 0.266 eV dominated the p-type conduction for the unintentionally doped calcium zinc oxide. By contrast, a grain boundary with a barrier height of 0.274–0.292 eV dominated the hole conduction for the nitrogen-doped calcium zinc oxide films.

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## 1. Introduction

Zinc oxide (ZnO)-based materials have attracted significant attention in recent years. Numerous electronic [1–3] and optoelectronic [4–6] devices that are based on these materials have been studied. In optoelectronic device applications, a window layer with a higher bandgap is generally required for reducing unwanted optical absorptions. Therefore, group II materials such as Be, Mg, and Cd have been incorporated into ZnO films for enhancing bandgaps [7–9]. Researchers have recently incorporated Ca into ZnO to form CaZnO films [10,11], which showed high potential to satisfy high bandgap requirements. Moreover, dopants were introduced to enhance the film conductivity. Group-III (aluminum (Al) [12], gallium (Ga) [13], and indium (In) [14]) atoms are well known to be used as n-type doping dopants in previous studies. Furthermore, a study reported that an N-doped ZnO demonstrated the ability to achieve efficient p-type concentration [15]. However, few studies have been examined on the conductivity behavior of N-doped CaZnO films.

Numerous film deposition techniques have been used in fabricating ZnO-based materials [16–19]. Among such techniques, the

spray pyrolysis method [20] is one of the most attractive because it is applicable in large areas without high vacuum requirements.

Although CaZnO thin film properties have been reported, research on the various conductivities of spray-pyrolyzed CaZnO thin films as a function of temperature is limited. Therefore, in the current study, we prepared CaZnO films with and without N doping by using the spray pyrolysis method. The crystalline and electrical properties of the films were analyzed and the conductive behavior of the films was realized. Temperature-dependent conductivity analyses were then used to determine the activation energy and barrier height quantities for different species.

## 2. Materials and methods

Zinc acetate (0.2 mol/L), calcium nitrate, and ammonium acetate were used as the precursors in the deposition of ZnO, CaZnO, and N-doped CaZnO films. The atomic ratio of Ca/Zn was maintained at 2.5%. For N doping, the atomic ratios of N/Zn were controlled to 0.3 (CaZnO:N(0.3)) and 1 (CaZnO:N(1)). Unintentionally doped ZnO (u-ZnO) and CaZnO (u-CaZnO) films were also prepared. Furthermore, n-(111) Si with a resistivity of 1–5  $\Omega \text{ cm}$  was used as the substrate. To obtain the results of the optical transmission measurement, glass substrates (Corning 1737) were used. The deposition temperature was maintained at 450 °C.

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The surface morphology of the film was studied by using scanning electron microscopy (SEM, HITACHI S-4300N), and the crystalline structure was obtained using X-ray diffraction (XRD, Bruker D8). Next, 10 K photoluminescence (PL) measurements were conducted using an HR2000+ system equipped with a He-Cd (325 nm) laser and cryostat. The conductivity was obtained by applying a van der Pauw four-point method using a KEITHLEY 2400 multimeter. Moreover, a temperature-controlled stage was used for the temperature-dependent conductivity measurement. The carrier type, concentration, and mobility were obtained using a Hall measurement system with a magnetic field strength of 0.42 T.

### 3. Results and discussion

Fig. 1 shows the transmission spectra of the u-ZnO and u-CaZnO thin films. Through a linear extrapolation, the cutoff wavelengths of the u-ZnO and u-CaZnO films were observed at approximately 372 (3.33) and 369 nm (3.36 eV). A blue shift of the cut-off wavelength was observed, indicating the effect of calcium incorporation; previous studies have reported [10,21] that the bandgap of calcium oxide was wider than that of zinc oxide [10,11].

Fig. 2(a)–(d) illustrates the surface morphologies characterized by SEM for the u-ZnO, u-CaZnO and, CaZnO:N(0.3), and CaZnO:N(1) films, respectively. For the u-ZnO film, the surface exhibited a petal-like morphology. A granular structure was observed for the u-CaZnO film. The surface morphology of the N-doped CaZnO film was different. The CaZnO:N(1) film demonstrated a grain structure with a fine surface structure.

Fig. 3(a) depicts the XRD patterns of the u-ZnO, u-CaZnO, CaZnO:N(0.3), and CaZnO:N(1) films. The peaks for the u-ZnO film were located at approximately 34.46°, 36.28°, and 47.62° are referred to as ZnO (002), (101), and (102) planes, respectively. The peaks for the u-CaZnO film were located at approximately 26° and 28.5°, respectively, can be referred to as CaO and/or Ca-related structures [22]. Thus, the Ca-related phase was separated from ZnO for the u-CaZnO film. A slight distortion of the (002) peak for u-CaZnO was also observed at approximately 34.48°. For the CaZnO:N(0.3) and CaZnO:N(1) films, peaks located at nearly 26–30° were broadened, and the films showed primary (002) and (101) peaks. Therefore, the full-width at half-maximum (FWHM) values of the peaks of these CaZnO films were broader than those of the u-CaZnO films. Fig. 3(b) shows the FWHM values of the (002) peak for these films. According to Scherrer's formula, the average grain size  $D$  for the film can be calculated as follows [23]:

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

where  $\theta$  is the Bragg diffraction angle,  $\lambda$  is the incident radiation wavelength, and  $\beta$  is the FWHM of the diffraction ray. Fig. 3(b) also illustrates the grain size estimated from the (002) peak in the XRD pattern. The grain size decreased with the introduction of calcium nitrate for the u-CaZnO film and ammonium acetate for the CaZnO:N films.

Table 1 shows the carrier concentration, conduction type, and mobility and resistivity of the CaZnO films. For the u-ZnO film, an n-type conduction with a concentration of  $2.8 \times 10^{18} \text{ cm}^{-3}$  was observed. Because the conduction band edge of n-Si/n-ZnO is relatively flat, electrons can more easily pass between n-Si and n-ZnO [24]. The measured n-type concentration may result from the combination of electrons from ZnO with Si. For the u-CaZnO film, a p-type conduction with a low concentration  $2.7 \times 10^{16} \text{ cm}^{-3}$  was observed. The origin of low p-type concentration was attributable to the incorporation of the calcium and N content from calcium nitrate or other deep-level states [25]. Furthermore, the p-type concentration increased with increasing the amount of ammonium acetate.

Fig. 4 depicts the 10 K PL spectra of the films. For the u-ZnO film, peaks were observed at 368 (3.37) and 372 nm (3.33 eV) and were attributed to the near band edge (NBE) emission and bound neutral donors ( $D^0X$ ), respectively [26,27]. Furthermore, other peaks were observed at 380 (3.26) and 388 nm (3.19 eV); they may be attributable to the phonon replica of  $D^0X$ . A small broadened signal was observed at approximately 500 nm; it may be attributable to oxygen-antisite, ionized oxygen vacancy, and zinc vacancy [28,29]. For the u-CaZnO film, enhanced NBE peaks and a broadened signal stabilized at nearly 500 nm were observed. For the CaZnO:N(0.3) and the CaZnO:N(1) films, broadened NBE peaks with a shoulder at approximately 366 nm were observed. Because of the broadening of the  $D^0X$  peaks at 372 nm, certain state variation can be expected for the CaZnO:N(0.3) and CaZnO:N(1) films. A signal was also observed at approximately 382 nm (3.25 eV). Because this peak occurred in only the N-doped CaZnO films, it may be attributable to the N-related states. However, more effort is required to definitively distinguish this peak. A broadened signal was also observed at approximately 500 nm. Thus, a certain deep-level defect was generated for the CaZnO:N films [29].

To further understand the conduction mechanism of the CaZnO films, the temperature-dependent conductivity measurement was applied (Fig. 5). Conductivity increased with increasing measurement temperature.

For the semiconductor film comprising a grain structure, a large amount of surface trapping states formed in the boundary region. Carriers were trapped and the band was distorted, resulting in the formation of a depletion around the grain boundary [30,31]. To evaluate the carrier transport behavior, the Debye length ( $L_D$ ) was calculated as follows [31]:

$$L_D = \left( \frac{\epsilon \epsilon_0 kT}{q^2 p} \right)^{1/2} \quad (2)$$

where  $\epsilon$  is the specific dielectric constant,  $\epsilon_0$  is the dielectric constant in vacuum,  $k$  is the Boltzmann constant, and  $p$  is the hole concentration. The  $L_D$  values derived for the u-CaZnO, CaZnO:N(0.3), and CaZnO:N(1) films were 21.4, 12.5, and 6.7 nm, respectively. The average grain size  $D$  was compared with  $2L_D$  parameters for these films and the comparison results revealed that  $D < 2L_D$  for the u-CaZnO film. Thus, the band became flat through each grain and the barriers across the grain boundary were neglected [30]. In this case, the conductivity was dominated by the activation of the doping level. The electrical conductivity  $\sigma$  as a function of

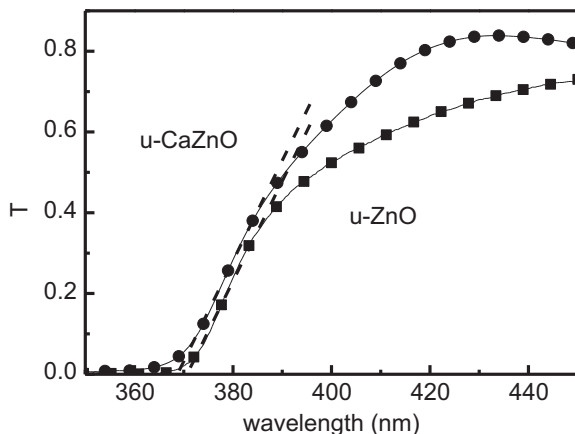


Fig. 1. Transmission spectra of the u-ZnO and u-CaZnO films.

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