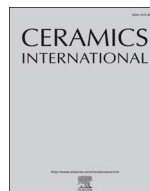




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# Investigation on the comparison of the structural, electrical and optical properties between ZCO:Na and ZCO:(Na, N) films synthesized by RF magnetron sputtering

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## ABSTRACT

Sodium doped ZnCdO (ZCO:Na) and sodium-nitrogen co-doped ZnCdO [ZCO:(Na, N)] films have been deposited on quartz substrates by radio frequency (RF) magnetron sputtering followed by a post-annealing treatment. The Hall-effect measurement results emphasized the importance of the dopant and annealing conditions in realizing p-type conversion. The ZCO:(Na, N) film annealed at 655 °C for 30 min (denoted sample F) showed optimal p-type conduction properties, which has the carrier concentration of  $7.84 \times 10^{18} \text{ cm}^{-3}$ . Compared to the best p-type conduction of the ZCO:Na film (sample C), sample F reveals an increased carrier concentration (up from  $10^{17}$  to  $10^{18} \text{ cm}^{-3}$ ) owing to the formation of  $\text{Na}_{\text{Zn}}$  and  $\text{N}_{\text{O}}$  dual acceptors. Furthermore, the XPS results revealed that sample F has a higher  $\text{Na}_{\text{Zn}}$  acceptor content than sample C. The ZCO:(Na, N) films exhibited better crystal quality compared to the ZCO:Na films based on comparison of the values of full width at half maximum and intensity. It was found that the band gap ( $E_{\text{g}}$ ) of all ZCO:Na and ZCO:(Na, N) films were smaller than that of pure ZnO due to Cd doping, and that the  $E_{\text{g}}$  increased with the increase of  $T_{\text{ann}}$ , which is ascribed to the fact that more Cd atoms were evaporated from the films at higher  $T_{\text{ann}}$ . In addition, the  $E_{\text{g}}$  of the ZCO:(Na, N) films (samples E-G) are generally larger than that of the ZCO:Na films (samples A-D). This is attributed to the incorporation of N in ZCO:(Na, N), as the  $\text{N}_{\text{O}}$  acceptor impedes the formation of  $\text{V}_{\text{O}}$  defects, resulting in a decrease in the formation of the  $\text{Cd}_{\text{Zn}}\text{-V}_{\text{O}}$  complex, which in turn decreased the Cd concentration.

## 1. Introduction

Among the various functional materials, zinc oxide (ZnO), which has a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, has been considered as a promising candidate for light emitting diodes (LEDs), laser diodes (LDs) in the ultraviolet (UV) region, photodetectors, and other optoelectronic devices [1,2]. The synthesis of p-type ZnO with preferable electrical properties would be the key to creating new opportunities for its applications in optoelectronic devices. Therefore, obtaining an efficient and reproducible p-type ZnO is an urgent issue that needs to be solved, and enormous efforts have been dedicated to fabricating p-type ZnO films [3–5]. Choosing an appropriate acceptor and doping method is pivotal in the preparation of p-type ZnO films. Among the various p-type dopants, Na is considered to generate a shallow acceptor level (170 meV) by the substitution of Na atoms in the Zn sites [6]. Practically, Yang et al. [7] have reported the reliable fabrication of Na-doped p-type ZnO films on quartz and glass substrates, indicating that Na is an

effective p-type dopant. However, attention should be paid to the fact that Na-doped ZnO films generally exhibit the relatively low carrier concentrations ( $10^{16}$ – $10^{17} \text{ cm}^{-3}$ ) [7,8]. Accordingly, a new path has been proposed that uses dual acceptor co-doping to enhance the carrier concentration of the film [9,10]. To date, several studies on the dual acceptor p-type ZnO have been reported, such as Li–N [11], K–N [12] and As–N [13] co-doping. Considering that N has the lowest p-orbital energy among group-V elements and the smallest ionic radius, it is also a suitable acceptor dopant for realizing p-type conversion [14]. Therefore, Na–N co-doping would be a promising method for obtaining p-type ZnO [9,15].

The fabrication of ZnO-related alloys is another important factor in the development of the ZnO-based optoelectronic device technologies. Alloying permits the modulation of band gap, and the subsequent preparation of barrier and quantum layers, which are basic components of hetero-junction devices, becomes possible. It has been reported that the band gap of ZnO can be tuned by alloying with Cd, which is regulated into 2.3–3.37 eV range through controlling Cd content in the

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films [16,17]. A tunable band gap suggests that ZnCdO-based materials may realize applications in areas such as LEDs (green, blue, and UV). Consequently, it is highly significant to achieve a favorable p-type ZnCdO (ZCO) to exploit the ZnO/ZCO quantum well or superlattice, which is the primary factor in ZnO-based LEDs and LDs devices [18,19]. In addition, because the valence-band maximum (VBM) of CdO is much higher than that of ZnO [20], the incorporation of Cd can lift the VBM, thereby reducing the ionization energy of the acceptor, which makes it favorable for p-type conduction [21]. However, reports focused on p-type ZCO have been scarce until now [8,22]. Z. Hua et al. [8] prepared a Na-doped p-type ZnCdO (ZCO:Na) film by magnetron sputtering, and the optimal p-type ZCO:Na exhibited a low carrier magnitude of  $\sim 10^{16} \text{ cm}^{-3}$  and relatively high resistivity of  $253 \Omega \text{ cm}$ . To date, there have been no reports on the preparation of a Na-N dual acceptors co-doped p-type ZCO. In the present work, we investigated p-type ZCO:Na and Na-N co-doped ZnCdO films [ZCO:(Na, N)] by radio frequency (RF) reactive magnetron sputtering followed by a post-annealing treatment. The electrical, structural, and optical properties of the ZCO:Na and ZCO:(Na, N) films are compared and discussed in detail.

## 2. Experimental section

The ZCO:Na and ZCO:(Na, N) films were prepared on quartz substrates by RF reactive magnetron sputtering followed by a post-annealing treatment. A ceramic target ( $\text{Zn}_{0.78}\text{Cd}_{0.2}\text{Na}_{0.02}\text{O}$ , denoting nominal components) was used in sputtering. The quartz substrates were sequentially rinsed at room temperature with trichloroethane ( $\text{C}_2\text{H}_3\text{Cl}_3$ ), acetone ( $\text{CH}_3\text{COCH}_3$ ), methanol ( $\text{CH}_3\text{OH}$ ) and de-ionized water for 15 min. Subsequently, they were cleaned by de-ionized water and blow-dried with nitrogen. The gas mixtures of Ar + O<sub>2</sub> (5N) for the ZCO:Na film and Ar + N<sub>2</sub> (5N) for the ZCO:(Na, N) film were introduced as the sputtering and reactive gas, and the work pressure was held at 1 Pa. The total mass flow rate of the working gas was 60 sccm. Both the Ar:O<sub>2</sub> and Ar:N<sub>2</sub> ratios were controlled at 1:2 through separate mass flow controllers. The sputtering power was 100 W and the deposition time was 60 min. During the sputtering process, the temperature of the substrate was maintained at 500 °C. After the fabrication of as-grown films, all samples were annealed under different conditions. The ZCO:Na films were annealed at temperatures ( $T_{\text{ann}}$ ) of 550 °C, 600 °C and 650 °C for 30 min in air. The ZCO:(Na, N) films were annealed at  $T_{\text{ann}}$  of 615 °C, 655 °C and 685 °C for 30 min in air.

The crystal structure of the films was determined by X-ray diffraction (XRD) using the Japan Rigaku D/max-ga X-ray diffractometer with  $\text{Cu}_{K\alpha}$  ( $\lambda = 0.15406 \text{ nm}$ ). The concentrations and chemical bonding states of the elements in the films were analyzed by X-ray photoelectron spectroscopy (XPS/ESCALAB MARK II, VG Inc.,) using an Al K $\alpha$  as radiation source. The electrical properties were analyzed with a Hall analyzer (Lake Shore 7600 Hall) at room temperature. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were measured using a JEM-2100 electron microscope. The room-temperature absorbance spectrum was measured using a UV-3101PC spectrophotometer.

**Table 1**

Electrical properties including resistivity ( $\rho$ ), carrier concentration ( $n$ ) and mobility ( $\mu$ ) of ZCO:Na and ZCO:(Na, N) films for different  $T_{\text{ann}}$ . The annealing conditions of the unannealed sample A have been denoted as  $T_{\text{ann}} = 20 \text{ }^\circ\text{C}$  and  $t_{\text{ann}} = 0 \text{ min}$ .

	Samples	$T_{\text{ann}}$ (°C)	$t_{\text{ann}}$ (min)	$\rho$ ( $\Omega \text{ cm}$ )	$n$ ( $\text{cm}^{-3}$ )	$\mu$ ( $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	Conduction type
ZCO:Na	A	20	0	$1.38 \times 10^3$	$5.47 \times 10^{12}$	768	n
	B	550	30	37.3	$2.47 \times 10^{17}$	0.757	n
	C	600	30	95.9	$2.98 \times 10^{17}$	0.225	p
	D	650	30	768	$3.94 \times 10^{14}$	22.7	p
ZCO:(Na,N)	E	615	30	7.3	$6.04 \times 10^{17}$	1.45	n
	F	655	30	30.9	$7.84 \times 10^{18}$	$2.68 \times 10^{-2}$	p
	G	685	30	316	$4.06 \times 10^{16}$	0.51	p/n

## 3. Results and discussion

Table 1 displays the electrical properties of ZCO:Na and ZCO:(Na, N) films which were annealed at different  $T_{\text{ann}}$ . It is worth noting that four contacts were placed at the corner area of the sample for avoiding the negative effect of inhomogeneities in carrier concentrations [23]. By using this method, the electrical measurements were performed several times to detect the reliability and repeatability of conduction type, and much the same results were obtained as expected. As summarized in Table 1, the as-grown ZCO:Na film (sample A) exhibits a poor n-type behavior with a low carrier concentration of  $5.47 \times 10^{12} \text{ cm}^{-3}$  and a high resistivity of  $1.38 \times 10^3 \Omega \text{ cm}$ , which is possibly due to the presence of numerous intrinsic defects. After annealing under 550 °C for 30 min (sample B), the electrical properties of ZCO:Na film were enhanced considerably, revealing a prominently superior n-type behavior with a carrier concentration of  $2.47 \times 10^{17} \text{ cm}^{-3}$  and a low resistivity of  $37.3 \Omega \text{ cm}$ . As the  $T_{\text{ann}}$  increased to 600 °C (sample C), preferable p-type characteristics were obtained, with a carrier concentration of  $2.98 \times 10^{17} \text{ cm}^{-3}$  and a mobility of  $0.225 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which can be understood by the following illustration. Fig. 1 displays the schematic diagram of the doping mechanism of Na and N in ZCO:Na and ZCO:(Na, N) films. It is observed from Fig. 1 that Na presents three characters including the  $\text{Na}_{\text{Zn}}$  acceptor,  $\text{Na}_i$  donor and electrically neutral complexes ( $\text{Na}_{\text{Zn}}\text{-Na}_i$ ,  $\text{Na}_{\text{Zn}}\text{-H}_i$ ). The  $\text{Na}_{\text{Zn}}\text{-Na}_i$  and  $\text{Na}_{\text{Zn}}\text{-H}_i$  complexes can be dissociated into  $\text{Na}_{\text{Zn}}$ ,  $\text{Na}_i$  and  $\text{H}_i$  under appropriate annealing conditions. For sample C, some  $\text{Na}_i$  (I),  $\text{Na}_i$  (II) and  $\text{H}_i$  donors have been evaporated after annealing; Meanwhile, new  $\text{Na}_{\text{Zn}}$  (III, IV) acceptors may be formed through the substitution of  $\text{Na}_i$  (I, II) for the Zn site. In addition, it has been reported that the formation energy of the  $\text{V}_o$  defect increases remarkably with the decrease in Cd concentration [24]. Therefore, the  $\text{V}_o$  content is reduced owing to the evaporation of Cd atoms during the annealing process, and then, it crippled the self-compensation effect [25]. Taking the three aspects mentioned above, it can be concluded that the content of the  $\text{Na}_{\text{Zn}}$  acceptor increased while the content of donors such as  $\text{Na}_i$ ,  $\text{H}_i$ , and  $\text{V}_o$  decreased after the annealing treatment, which facilitates the p-type conduction transformation (sample C). However, with further increase in  $T_{\text{ann}}$ , up to 650 °C (sample D), the p-type conduction properties were evidently impaired, and this sample possesses a lower carrier concentration of  $3.94 \times 10^{14} \text{ cm}^{-3}$  and higher resistivity of  $7.68 \times 10^2 \Omega \text{ cm}$ . Given the fact that the lattice energy of ZnO ( $3971 \text{ kJ mol}^{-1}$ ) is higher than that of  $\text{Na}_2\text{O}$  ( $2478 \text{ kJ mol}^{-1}$ ) [26]. Therefore, the deterioration of the electrical properties may be attributed to the tempestuous evaporation of the  $\text{Na}_{\text{Zn}}$  acceptor under the higher  $T_{\text{ann}}$ .

For the ZCO:(Na, N) film, it shows a superior n-type characteristic with a carrier concentration of  $6.04 \times 10^{17} \text{ cm}^{-3}$  and a low resistivity of  $7.3 \Omega \text{ cm}$  as the  $T_{\text{ann}}$  was set to 615 °C. When the  $T_{\text{ann}}$  increased from 615 °C to 685 °C, the film exhibits a conversion from n- (sample E) to p-type (sample F), and then to p/n vague type (sample G). The optimal p-type conduction for the ZCO:(Na, N) films is found in sample F, which has the highest carrier concentration of  $7.84 \times 10^{18} \text{ cm}^{-3}$  and a relatively lower resistivity of  $30.9 \Omega \text{ cm}$ . Compared to the best p-type conduction ZCO:Na film (sample C), the carrier concentration of sample

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