Thin Solid Films xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Study on properties of Ga/F-co-doped ZnO thin films prepared using atomic layer deposition

Kyung-Mun Kang, Yue Wang, Minjae Kim, Hyung-Ho Park*

Department of Materials Science and Engineering, Yonsei University, 50 Yonseri-ro, Seodaemun-gu, Seoul 03722, Republic of Korea

ARTICLE INFO

Keywords:
Zinc oxide
Gallium
Fluor
Co-doping
Transparent conducting oxide
Atomic layer deposition

ABSTRACT

Zinc oxide (ZnO) thin films with co-doped Ga and F were deposited using atomic layer deposition. Structural, electrical, and optical properties of the ZnO thin films were analyzed for different F doping amounts under the condition that the Ga doping amount remained fixed. From the X-ray diffraction analysis results, it was confirmed that the preferred orientation changed from (002) to (100) with changing F amounts. The electrical properties, i.e., carrier concentration and mobility of these co-doped ZnO thin films improved with the F doping amount, resulting in a decrease in the electrical resistivity. The reason for this improved resistivity is that Ga and F atoms replace Zn and O in the lattice sites, respectively, despite a slight decrease in the mobility. An increase in the carrier concentration widened the optical bandgap of ZnO thin films by the Moss-Burstein effect.

1. Introduction

Transparent conductive oxides (TCOs) are transparent oxide semiconductors in the visible light range and are highly electronically controlled. TCOs, which have both transparency and conductivity, can be applied to optoelectronic devices such as organic light emitting diodes, photovoltaic devices, and flat panel displays [1–3]. Indium tin oxide (ITO) is most widely used transparent electrode material because of its high transparency and high electrical conductivity. However, there is a demand for an alternative to ITO due to its high price resulting from the limited resources and environmental problems. Among the potential TCO alternatives to ITO, ZnO is a promising n-type, semiconducting indium-free transparent conductive oxide with a high excitation coupling energy (60 meV) and direct wide bandgap (3.3 eV) [4]. However, the electron concentration of ZnO (10^{18}–10^{19} cm^{-3}) is lower than that of ITO (~10^{21} cm^{-3}). Therefore, many doping studies have been conducted to improve the electrical characteristics of ZnO thin films. Most studies have focused on increasing the number of effective carriers through impurity doping; however, thus far a maximum electron concentration of only 1.5×10^{21} cm^{-3} has been realized [5]. Single dopants such as In, Ga, Al, and F are commonly used in ZnO films and have been studied by several research groups [6–9]. However, the reported resistivity and mobility data are somewhat scattered and inconsistent. Furthermore, the physical and chemical properties of recently developed ZnO transparent conducting oxide thin films have not been optimized. Therefore, different composite ZnO-based materials have been studied to realize this objective [10,11]. For instance, double doping ZnO thin films using, for example, Ga/Al, Ga/N, Ga/B, and Ga/F have been carried out to improve the properties of the films [12–15]. Among the dopants, F ions restrict scattering of the conduction electrons by limiting the electronic permutation upon substitution at the O site. These F ions have a higher mobility than the cation dopant, thus reducing the resistivity of the films. In addition, F ion size is similar to that of O ions (F^-: 1.31 Å and O^{2-}: 1.38 Å), and thus, F ions have a high electron mobility without lattice distortion [9]. Various deposition methods such as the sol-gel method, chemical vapor deposition, sputtering, and atomic layer deposition (ALD) have been studied for the deposition of ZnO films [16–19]. Among these, ALD is a very advanced deposition technique capable of low-temperature deposition with high uniformity [20–23]. ALD is based on self-limiting chemistry and deposits the film by repetition of the source pulse and purge. Therefore, ALD is useful to realize low-temperature deposition, high step coverage, good uniformity, and control of film thickness by controlling the ALD cycles. Thus, films with excellent properties, such as those with a complex three-dimensional structure, can be obtained for use in electronic equipment, and can be used on a flexible substrate because of low-temperature deposition [24].

Therefore, in this study, we fabricated doped ZnO thin films with different F doping concentrations and fixed Ga concentrations. Then, we investigated the effect of co-doping on the structural, electrical, and optical properties of ZnO thin films and compared the properties with those of films doped with Ga only.

* Corresponding author.
E-mail address: hhpark@yonsei.ac.kr (H.-H. Park).

https://doi.org/10.1016/j.tsf.2018.02.030
Received 1 December 2017; Received in revised form 10 February 2018; Accepted 19 February 2018
0040-6090/ © 2018 Elsevier B.V. All rights reserved.

Please cite this article as: Kang, K.-M., Thin Solid Films (2018), https://doi.org/10.1016/j.tsf.2018.02.030

2. Experimental section

2.1. Fabrication of thin films using ALD

Ga-doped ZnO and Ga/F-co-doped ZnO thin films were deposited on Si and LCD glass (Eagle XG) substrates via ALD using a traveling-wave-type Lucida D100 system (NCD Technology, Inc. Korea) at 150 °C. Diethylzinc (DEZn, EGChem Co., Ltd., Korea) and trimethylgallium (TMGa, EGChem Co., Ltd., Korea) were used as the precursors for Zn and Ga, respectively, and deionized water (H_2O) was used as a reactant. The F source was prepared by mixing 50 mL H_2O and 0.5 mL diluted hydrogen fluoride (HF 48–51% diluted in H_2O) [9]. This solution was then stirred for 5 min in order to uniformly disperse HF in H_2O before the solution was put into a canister. DEZn, TMGa, hydrogen fluoride (HF/H_2O), and H_2O were delivered into the chamber with a N_2 carrier gas at a flow of 20 sccm at the respective pulse time.

For Ga doping into the ZnO matrix, the deposition generally consists of a combination of DEZn–H_2O cycles of ZnO and TMGa–H_2O cycles of Ga_2O_3 with the following sequence: DEZn pulse 0.1 s → N_2 purge 10 s → H_2O pulse 0.1 s → N_2 purge 10 s → TMGa pulse 0.1 s → N_2 purge 10 s → H_2O pulse 0.1 s → N_2 purge 10 s. Furthermore, the cycle ratio for the fabrication of ZnO:Ga films was fixed at 19:1 (19 ZnO:1 GaO cycles) in order to optimize the electrical resistivity (Fig. 1(a)). In order to incorporate the specific F doping content into Ga-doped ZnO films, H_2O and the F source (H_2O/HF) were alternately pulsed with a controlled Zn-O:Zn-O/F (x:y) ratio (Fig. 1(b–e)). The Ga doping concentration was fixed at 19:1 (19 ZnO: 1 GaO cycles) and the F doping concentration was varied from 4:1 to 0:1 in order to observe the change in the characteristics according to the F doping concentration while the Ga concentration was kept fixed (Fig. 1(b–e)). The samples were named according to the ALD deposition process (Fig. 1). For example, GZO (1:19) denotes Ga-doped ZnO with 1:19 (1 GaO: 19 ZnO cycles). In the case of Ga/F-co-doped ZnO, GFZO (1:4:15) represents Ga/F-co-doped ZnO with 1:4:15 (i.e., 1 GaO: 4 F-doped ZnO(FZO): 15 ZnO cycles). The composition of the GZO and Ga/F-co-doped ZnO thin films were determined by X-ray photoelectron spectroscopy (XPS: K-alpha, Thermo VG, U.K.) using Al Kα (1486.6 eV). The accelerating voltage and emission current of X-ray source were 15 kV and 20 mA, respectively. Avantage 3.25 was used for peak fitting software supplied by XPS manufacturer. The binding energies were corrected using the reference C 1 s peak at 284.5 eV [25]. A Shirley subtraction and Gaussian shape were used for background subtraction and peak fit analysis, respectively. During peak fit analysis of measured spectra, the parameters such as binding energy and FWHM were constrained refer to the published references [26–28]. The film composition is given in Table 1.

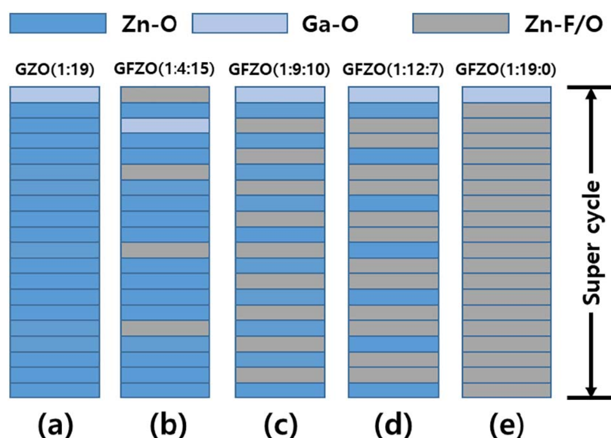

Fig. 1. Schematic diagram of the process sequence used to grow (a) Ga-doped ZnO, and (b–e) Ga/F-co-doped ZnO thin films with various F concentrations. The source pulse time and high purity N_2 purge time were fixed at 0.1 and 10 s, respectively.

2.2. Analysis of characteristics of the thin films

The crystal structure was analyzed by X-ray diffraction (XRD, D/MAX-2000, Rigaku) with CuKα_1 radiation (λ = 1.5416 Å). Scan was performed using theta/2theta (θ/2θ) method in the procedure of 0.05° step with a 4°/min scan speed. Room-temperature photoluminescence (PL) spectroscopy (Hitachi P7000) was conducted. The surface morphology of the Ga-doped ZnO and Ga/F-co-doped ZnO films were analyzed using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi) with an operating voltage of 15 kV. The electrical properties, including resistivity (r) and Hall coefficients (R_H), were obtained via the van der Pauw method at room temperature using a Hall Effect measurement system (Ecopia HMS3000). The optical transmittance spectra were obtained using an ultraviolet-visible-near infrared (UV–vis-NIR) spectrophotometer (V-570, JASCO) in the range of 200 to 1000 nm.

3. Results and discussions

3.1. XPS study

Table 1 shows the atomic contents of Zn, O, Ga, F, and C of the Ga-doped ZnO and Ga/F-co-doped ZnO thin films. The Ga doping concentration of Zn-O: Ga-O was fixed at 19: 1 as shown in Fig. 1. As seen in the Table 1, the Ga concentrations were similar in all the films. For the F doping concentration, the doping concentration was varied by adjusting as shown in Fig. 1(b)–(e). As a result, the F doping concentration also showed similar results as the previous study [9]. In the case of GFZO (1:4:15) film, the F doping concentration was not detected because it was below the detect limit of XPS. However, from the F doping concentration of other films and our previous studies, the F doping concentration is expected to be 0.2 at.%.

Fig. 2(a) shows the results of XPS analysis of Ga-doped ZnO and Ga/F-co-doped ZnO thin films in the Zn 2p region. As the doping amount of F increased, the shift of Zn 2p peak did not occur. Fig. 2(b) shows the XPS analysis in the O 1 s region. O_I, O_{II}, and O_{II} represent oxide lattice without oxygen vacancies, oxide lattice with oxygen vacancies, and hydroxide, respectively [29–31]. As can be seen from the Fig. 2(b), the peak intensities of the O_{II} and O_{II} portions decrease as the F doping amount increases. Particularly, the decreasing tendency of O_{II} is a result of the passivation effect of oxygen vacancy site due to F doping. Fig. 2(c) shows the XPS analysis of the Ga 2p region. The change of the doping amount of F did not affect the peak shift of Ga. Fig. 2(d) shows the results of Ga-doped ZnO and Ga/F co-doped ZnO thin films in the F 1 s region. It was confirmed that as the ratio of Zn-F/O in Zn-O: Zn-F/O increases, the amount of F doping increases.

3.2. Growth orientation

The crystal structures of Ga-doped ZnO and Ga/F-co-doped ZnO thin films were analyzed by XRD measurements. All diffraction peaks indicate a typical hexagonal wurtzite ZnO structure as shown in Fig. 3. The preferential growth plane orientation for the ZnO thin films changed from (002) to (100) according to F doping content. The preferential growth plane orientation of the thin film is determined by the surface energy of the crystal plane. Generally, the (002) plane has the lowest surface energy, so the thermodynamically supported growth orientation in the ZnO wurtzite structure is along this plane; in our case, the Ga-doped ZnO with the (002) preferred plane growth orientation agreed with it [32]. For all Ga/F-co-doped ZnO thin films, the growth plane orientation of (002) and (100) planes was obviously suppressed and promoted, respectively, and a new growth plane orientation of (110) with intensity comparable to that of (002) was observed.

A previous study reported the transformation from the (100) to the (002) growth plane orientation in ALD-prepared ZnO film using DEZn [33]; it was also found that the growth of (002) plan, which has the

Download English Version:

https://daneshyari.com/en/article/8032617

Download Persian Version:

https://daneshyari.com/article/8032617

Daneshyari.com