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Characteristics of the electromagnetic interference shielding effectiveness of Al-doped ZnO thin films deposited by atomic layer deposition

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ABSTRACT

The structural, optical, and electrical properties of Al-doped ZnO (ZnO:Al) thin films deposited by atomic layer deposition (ALD) with a modified precursor pulse sequence were investigated to evaluate the electromagnetic interference shielding effectiveness (EMI-SE). A Zn–Al–O precursor exposure sequence was used in a modified ALD procedure to result in better distribution of Al^{3+} ions in the ZnO matrix with the aim of reducing the formation of complete nano-laminated structures that may form in the typical alternating ZnO and Al_2O_3 deposition procedure. The ALD dopant concentration of the ZnO:Al films was varied by adjusting the dopant deposition intervals of the ZnO:Zn—Al—O precursor pulse cycle ratios among 24:1, 19:1, 14:1, and 9:1. The lowest obtained resistivity and average transmittance in the visible region (380-780 nm) were $5.876 \times 10^{-4}\ \Omega$ cm (carrier concentration of 6.02×10^{20} cm^{-3} and Hall mobility of 17.65 cm^2/V s) and 85.93% in the 131 nm thick ZnO:Al(19:1) film, respectively. The average value of the EMI-SE in the range of 30 MHz to 1.5 GHz increased from 1.1 dB for the 121 nm thick undoped ZnO film to 6.5 dB for the 131 nm thick ZnO:Al(19:1) film.

1. Introduction

Zinc oxide (ZnO) has been actively explored as a promising alternative material to indium tin oxide (ITO), which has drawbacks such as the exhaustion of natural indium sources and its toxicity. ZnO, which is an n-type, wide band gap transparent oxide semiconductor (3.27 eV at room temperature) possessing a high exciton binding energy of 60 meV [1], has recently attracted attention for applications involving transparent electrodes in solar cells and transparent thin film transistors because it is non-toxic, inexpensive, highly abundant, and stable in hydrogen plasma, compared to ITO [2]. However, due to the low conductivity of ZnO compared to ITO, doping with trivalent metal cations (Group III elements; B, Al, and Ga) has been investigated while focusing on regulating the doping levels [3]. Because group III elements generally have same valencies but smaller ionic sizes than the host Zn^{2+} cation, it is theoretically explained that extrinsic dopants substitute into host Zn sites and provide an extra electron. Among cation-doped ZnO films, Al-doped ZnO (ZnO:Al) has been intensively investigated in recent years. Agura et al. reported the lowest resistivity of $8.5 \times 10^{-5}\ \Omega$ cm with extremely high carrier concentration of 1.5×10^{21} cm^{-3} for ZnO:Al films deposited by pulsed laser deposition (PLD) [4]. Moreover, many research groups reported the electrical properties of ZnO:Al films in order to apply to electronic devices due to high carrier concentration of ZnO:Al films [5–8].

Several techniques are used for the fabrication of ZnO thin films including sol–gel, spray pyrolysis, sputtering, e-beam evaporation, chemical vapor deposition, and atomic layer deposition (ALD) methods [9]. In particular, ALD technique is a thin film growth method by a self-limiting surface chemistry composed with repeating process of pulse and purge with precursors, and also keeping the source materials separately during whole depositing process. Therefore, ALD can allow low temperature growth, better step coverage (high-aspect-ratio), good uniformity, and controllability of the film thickness by controlling the number of ALD cycles. Moreover, separate dosing of the precursors prevents gas phase reactions, which allows the use of highly reactive precursors and provides sufficient time for each reaction step to reach completion. These excellent properties allow the deposition of electronic devices with a complex 3D structure and processing at relatively low temperatures, facilitating the use of flexible substrates [10].

The introduction of an optimum amount of Al to the ZnO matrix results in a marked increase of the electrical conductivity while the optical properties remain excellent with a slight increase of

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Table 1
Sample identification (I.D.), DEZ/H2O (DH):DEZ/TMA/H2O (DTH) cycle ratio, number of ZnO monolayers (*N*) during one super cycle, film thicknesses measured by SEM, and Al atomic contents of the ZnO:Al films obtained by EDS.

I.D.	DH:DTH cycle ratio	*N*	Total number of super cycles	Thickness (nm) (via SEM)	at.% Al (via EDS)
ZnO	–	667	–	121	0
R_{24}	DH 24:DTH 1	24	32	132	1.7
R_{19}	DH 19:DTH 1	19	40	131	2.1
R_{14}	DH 14:DTH 1	14	53	126	2.9
R_9	DH 9:DTH 1	9	80	130	4.7

transmittance due to the band gap widening effect [11]. In ZnO:Al films formed using ALD, most researchers typically use ZnO/Al_2O_3 nano-laminated structures for doping Al^{3+} ions into the ZnO matrix [12]. In ZnO:Al films deposited by this conventional process, however, it is very difficult to uniformly distribute the Al dopant into the ZnO matrix by ALD due to the huge gap between the numbers of ZnO and Al_2O_3 cycles. To address this problem, we demonstrated an effective ALD procedure for uniform dopant distribution in our previous work [13]. Therein, a uniform dopant distribution was confirmed by secondary ion mass spectrometry using an O^{2-} ion source, while the chemical bonding state of Al dopant in ZnO matrix was analyzed by photoemission spectroscopy.

With an increase in the use of mobile electronic devices, the level of interest in electromagnetic interference (EMI) shielding has grown in recent years. EMI shielding materials are commonly used with metals, metal powder, metal-fiber filled plastics, and metal-reinforced polymers [14–16]. In the case of metals, however, there are some limitations such as corrosion susceptibility, long processing time, high cost of equipment for production, and also the difficulty of deposition on transparent electronic devices. In the case of polymer composite materials, they are weakly resistant to moisture and have mechanical strength issues although many limitations of metal-related materials can be overcome. However, due to the lack of EMI shielding applications of transparent conducting oxides (TCOs), less attention has so far been paid to EMI shielding properties of TCO films even though they have many merits compared with metals and polymer materials. Therefore, in this study, undoped ZnO and ZnO:Al films were investigated to apply in transparent EMI shielding materials as an alternative to metal and polymer composites because it has adequate transparency and conducting properties for reflection and absorption of EMI radiation. Furthermore, a modified precursor pulse sequence was adopted and the properties of ZnO:Al thin films with varying compositions deposited using this sequence were determined for applications in transparent EMI shielding materials used in mobile electric devices.

2. Experimental details

Undoped ZnO and ZnO:Al thin films were deposited on Si(1 0 0) wafers and glass (Fusion 1737) substrates via ALD using a traveling wave type Lucida D100 system (NCD Technology, Inc., Korea) at a deposition temperature of 250 °C and a working pressure of 3–3.3 Torr. Diethylzinc (DEZ, Hansol Chemical Co., Ltd., Korea) and trimethylaluminum (TMA, Hansol Chemical Co., Ltd., Korea) were used as the precursors for Zn and Al, respectively, and deionized water (H_2O) was used as a reactant. DEZ and TMA were delivered into the chamber with a high purity N_2 (99.999%) carrier gas flow of 20 sccm (standard cubic centimeters per minute). The ZnO films were typically deposited by DEZ-H_2O cycles with following sequence: DEZ pulse 0.1 s → N_2 purge 10 s → H_2O pulse 0.1 s → N_2 purge 10 s. For Al-doping into the ZnO matrix, most of the deposition is ordinarily composed with the combination of the DEZ-H_2O cycles of ZnO and TMA-H_2O cycles of Al_2O_3 with following conventional sequence: TMA pulse 0.1 s → N_2 purge 10 s → H_2O pulse 0.1 s → N_2 purge 10 s. To avoid the formation of ZnO:Al films by a ZnO/Al_2O_3 nanolaminate structure and improve uniform dopant contribution, we conducted modified sequence for fabrication of ZnO:Al films in this work: DEZ pulse 0.1 s → N_2 purge 10 s → TMA pulse 0.1 s → N_2 purge 10 s → H_2O pulse 0.1 s → N_2 purge 10 s. The details of the fabrication method and operating conditions of the conventional and modified ZnO:Al thin films are provided in our previous publication [13]. For the deposition of ZnO:Al films, various numbers of ZnO ALD cycles (*N*) and one modified Zn—Al—O ALD cycle were repeatedly carried out for a total of 800 ALD cycles (except for the R_{14} samples, which had 795 ALD cycles). This allowed us to manipulate the doping concentration (Table 1).

The phase and crystallinity of the films were monitored by X-ray diffraction (XRD; Rigaku Ultima IV) with Cu Kα radiation (λ = 1.5418 Å). The electrical properties of the films were measured using the van der Pauw method at room temperature using a Hall effect measurement system (Ecopia HMS3000). The electrical parameters were measured by the direct current (I_{DC} = 10–1 mA) four probe method in a magnetic field strength of up to 0.57 T. Scanning electron microscopy (SEM; JEOL, JSM 7001F) was used to observe the morphologies of the ALD-grown thin films and to measure the final thicknesses of the films via cross-sectional images. Energy dispersive spectroscopy (EDS) was used to quantify the Al content in the ZnO:Al thin films. Optical transmittance measurements were conducted using an ultraviolet-visible-near infrared (UV-vis-NIR) spectrophotometer (V-570, JASCO). The EMI shielding effectiveness (SE) was tested by the ASTM (American Society for Testing and Materials) D4953-99 method, which is commonly used for the measurement of the EMI-SE as a global standard. By using ASTM D4953-99, the EMI-SE of the films was measured using a Network Analyzer 4396B (Agilent Technologies) with a flanged circular coaxial transmission line holder. The measured frequencies ranged from 30 MHz to 1.5 GHz. Fig. 1 shows the dimensions of the specimens and ALD-deposited samples used in measuring the EMI-SE of the films where Fig. 1(a) and (b) show a reference sample and load sample, respectively. The EMI-SE values in terms of decibels (dB) were calculated using the following equation,

$$\text{EMI-SE (dB)} = 10 \log \left(\frac{P_{out}}{P_{in}} \right) \quad (1)$$

where dB is the unit of the power ratio, typically used to specify shielding effectiveness, P_{out} is the output power (Watts), and P_{in} is the input power (Watts) [17].

3. Results and discussion

To confirm the deposition rates of the ALD-ZnO:Al thin films, the film growth behaviors of individual ZnO and Al_2O_3 films were investigated. The thicknesses of the undoped ZnO and ZnO:Al films are given in Table 1 which remained relatively constant as a function of the number of ALD cycles in the range of 121–132 nm, indicating the self-limiting conditions for ALD growth. The film growth rates of the Al_2O_3, ZnO, and ZnO:Al(R_{19}) films were 1.2 Å/cycle, 1.8 Å/cycle, and 1.6 Å/cycle, respectively. These growth rates of the ALD-grown materials are in the range of other results,