Preparation and Characterization of ZnO and (Zn,Mg)O films doped with Al

Haruki Ryoken¹,², Isao Sakaguchi¹, Takeshi Ohgaki¹, Yutaka Adachi¹, Naoki Ohashi¹
Tadashi Takenaka³ and Hajime Haneda¹,²

¹Advanced Materials Laboratory, National Institute for Materials Science,
1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
Phone: +81-29-860-4665 E-mail: OHASHI.Naoki@nims.go.jp
²Department of Applied Science for Electronics & Materials, Kyushu University,
6-1 kasugakoen, kasuga, fukuoka 816-8580, Japan
³Department of Science and Technology, Tokyo University of Science,
2641 Yamazaki, Noda, Chiba 278-0022, Japan

I. Introduction

Zinc Oxide (ZnO) films are attracting material for many possible applications, such as transparent electrodes[1], transparent field effect transistors (TFETs)[2], and UV photodetectors[3]. On the use of ZnO based films for these applications, controlling of both optical and electronic properties are required. For example, precise controlling of band-gap and complete passivation of deep levels are required for practical applications.

It is well-known that addition of MgO into ZnO causes expansion of bandgap of MgO. In fact, exciton confinement effect was confirmed in a quantum well structures of ZnO/(Zn,Mg)O multilayers.[4] Thus, the use of (Zn,Mg)O alloy extends the possible applications of ZnO related materials. For example, electron doped (Zn,Mg)O is likely appropriate for transparent electrodes for UV emitters and detectors.

In the present study, we investigate electric and optical properties of electron doped ZnO and (Zn,Mg)O. Particularly, we prepared Al-doped ZnO and (Zn,Mg)O by pulse laser deposition (PLD) method to evaluate the growth condition dependence of electric and optical properties.

2. Experimental Procedures

The films were prepared by a PLD method. We used polycrystalline oxide targets prepared by a conventional ceramics technique and the nominal concentrations of the targets were x=0.0-0.001 and y=0.0-0.15 in (Zn1-x-yMgyAlx)O. We choose two kinds of substrates; they are sapphire single crystals with well polished (11-20) face and ZnO single crystals with well polished c-face. Pressure in the PLD chamber was kept at 1.5 x 10⁻⁵ torr during the deposition by introducing oxygen gas. In order to investigate charge compensation phenomena, we compared the films grown in oxygen gas ambient with those deposited under oxygen radical irradiation. The oxygen radicals were generated by using r.f. discharge plasma source equipped with the PLD chamber. A pulsed laser beam of the fourth harmonic generation of Nd:YAG laser was used for abrasion and substrate temperature was set to 400-600°C.

The crystallinity of the samples were characterized by x-ray diffraction technique (XRD) and transmission electron microscope (TEM). Electric properties were evaluated by measuring Hall effect using a four prove Van der Pauw configuration. Optical properties were characterized by measuring transmittance, photoluminescence (PL) and cathodoluminescence (CL) spectra. Particularly, CL spectra were measured within temperature range of 20-300K.

In order to elucidate the concentration of defects in the obtained films, solid state diffusion behavior was investigated. We evaluated cation and anion diffusion coefficients by using Co and ¹⁸O as tracer elements, respectively, and measuring depth profile of tracer concentration after thermal treatment to induce solid state diffusion. The elemental distribution was analyzed by using secondary ion mass spectroscopy using primary ion beam of Cs⁺ or O₂⁻.

3. Results and Discussion

Figure 1 shows growth condition dependence of lattice parameters of undoped and Al-doped ZnO films. Here, nominal concentration of Al was set to 1% of Zn. There was a general tendency that c₀ parameter decreased with increasing growth temperature. For the undoped samples, c₀-value was not affected by radical irradiation and was close to the bulk value except for the films grown at 400°C. In contrast, significant reduction of c₀-value by radical irradiation was confirmed in Al-doped films. These results indicate that the strong oxidation
activity of radicals caused change in charge compensation mechanism in the doped ZnO films.

Figure 1  Lattice parameter $c_0$ of undoped and Al-doped ZnO films deposited on sapphire substrate. Open and closed symbol denote the films deposited without or with oxygen radical irradiation.

The similar results were obtained in (Zn,Mg)O system. Figure 2 shows reciprocal space mapping of 114 diffraction of (Zn$_{0.85}$Mg$_{0.15}$)O films doped with 0.1 mol% Al grown on c-face ZnO substrate. It was clearly shown that the lower growth temperature causes elongation of $c_0$ parameter of Al-doped (Zn,Mg)O films. In contrast, lattice parameter of undoped (Zn,Mg)O films was insensitive to the variation of growth conditions.

Figure 2  Reciprocal space mapping of 114 diffraction of Al-doped (Zn,Mg)O films grown on c-face ZnO substrate at (A) 600°C and (B) at 400°C.

Thus, it is obvious that doping with Al resulted in enhanced sensitivity of the film properties on growth conditions. This enhanced growth condition dependence in Al-doped films is likely originated in formation of defects for charge compensation. For example, formation of zinc vacancy is expected in Al-doped ZnO as described by Eq. 1 using Kroger and Vink notation:

$$\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^{2+} + 3\text{O}^{2-} + \text{V}_{\text{Zn}}^{\text{Zn}}$$  (1)

Figure 3 shows temperature variation of Co diffusion constants in ZnO and Al-doped (Zn,Mg)O films grown on sapphire with or without radical irradiation. It is obviously shown that radical irradiation causes change in diffusion coefficient. This result indicates that concentration and/or structure of defects are changed high oxidation activity of the radicals as well as formation of defect for charge compensation.

Figure 3  Diffusion constants of Co in ZnO and Al-doped (Zn,Mg)O films.

4. Summary

Charge compensation phenomena in Al-doped ZnO and (Zn,Mg)O was investigated. Due to limited space in this abstract, we cannot mention about detail in electric and optical properties of these films. Strong correlation between lattice parameters and electric and optical properties was confirmed, indicating that formation of defects for charge compensation give rise to drastic change in electric and optical properties.

References