

Annealing to achieve lower resistivity in Ga-doped ZnO epitaxial films  
grown from low-temperature aqueous solution

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## **Abstract**

Various annealing conditions were examined for enhancing the electrical conductivity of gallium-doped ZnO (ZnO:Ga) epitaxial films grown from a low-temperature aqueous solution. The resistivity of the films decreased with increasing annealing temperature, accompanying increases in both the carrier concentration and mobility. However, the improvement obtained from 0.5 h of annealing was limited because the films spalled when the temperature exceeded  $\sim 300$  °C. The temperature at which spalling of the films occurred depended on the annealing atmosphere, and it was lower in 5% $H_2$ -Ar than in air or vacuum. Thermal desorption spectroscopy showed that the cause of spalling was expulsion of  $H_2O$  vapor from the interior of the film, indicating that water molecules or hydroxides were incorporated into the crystal during film growth. Analysis of the variations in electrical properties with increasing annealing duration revealed that the electrical properties were quickly improved upon heating before the film spalled. Thus, by limiting the annealing duration to  $\leq 20$  s, annealing could be performed at a temperature as high as 580 °C without spalling of the film, which yielded the lowest resistivity of  $4.7 \times 10^{-4} \Omega \text{ cm}$ . The annealed film exhibited transmittance as high as  $>75\%$  in the visible spectrum.

## **Keywords**

Semiconductors; Thin films; Annealing; Heat treatment; Electrical properties

## 1. Introduction

Zinc oxide (ZnO), a transparent semiconductor, has potential applications in many fields including solar cells, sensors, light-emitting diodes (LEDs), and lasers [1, 2]. Although vapor-phase deposition techniques such as sputtering and pulsed-laser deposition have been extensively used for the growth of high-quality ZnO films, low-temperature aqueous fabrication methods have recently attracted more attention owing to their capability to produce large-area films at minimal cost and with low environmental impact. These aqueous-solution methods can produce not only polycrystalline films but also epitaxial ZnO films [3, 4]. Preparation of highly conductive ( $7 \times 10^{-4} \Omega \text{ cm}$ ) ZnO epitaxial films doped with group III elements has also been demonstrated [5-7]. Practical applications of such films as current-spreading layers [8] or as the n-type layer in GaN-based LEDs [9] have been studied. Further improvement in the quality of such films is still needed, however, to further apply aqueous-synthesized ZnO films in other areas.

Post-fabrication thermal annealing is a useful approach to enhance the electrical properties of ZnO-based films. Indeed, the resistivity of films prepared by the aqueous-solution methods can be significantly reduced by annealing [5-7], and it is expected that the film properties can be further improved by optimizing the annealing conditions. There is, however, only a limited number of studies on the annealing of aqueous-synthesized ZnO epitaxial films, although annealing for films prepared by vapor-phase processes have been intensively studied [10-14]. Meanwhile, Richardson et al. pointed out that annealing of epitaxial ZnO films deposited from a low-temperature aqueous solution could have detrimental effects on their optoelectrical properties because the aqueous-grown crystals involve hydroxide that is expelled as water vapor by heating, leaving pores in the film [15]. As the incorporation of hydroxide is unique to films grown from aqueous solutions, it is necessary to optimize the annealing conditions especially for such films.

In this study, we examined the effects of various annealing conditions including temperature, atmosphere, and time on the electrical properties of epitaxial Ga-doped ZnO (ZnO:Ga) films grown from an aqueous solution. A critical problem was that the films were fractured when they were annealed at high temperatures. Analysis of variations in the electrical properties with annealing duration revealed that rapid thermal annealing was effective for producing a low-resistivity film without fracturing; transparent films with a low resistivity of the order of  $10^{-4} \Omega \text{ cm}$  were obtained.

## 2. Experimental Section

ZnO:Ga films were prepared from an aqueous solution using a flow reactor. The details of the deposition procedure using the flow reactor are described elsewhere [7]. An A-plane single crystal sapphire ( $5 \times 7 \times 0.43 \text{ mm}$ ) was used as the substrate. To ensure adhesion of the ZnO:Ga film that would be deposited later, an epitaxial ZnO seed layer with a thickness of  $\sim 10 \text{ nm}$  was formed in advance on the substrate by magnetron sputtering. The sputtering was performed at a substrate temperature of  $500 \text{ }^\circ\text{C}$ , and Ar and  $\text{O}_2$  partial pressures of 1.3 and 0.3 Pa, respectively. The substrate was heated with a heating element, and its temperature was controlled with a thermostat (Chino, KP1000C). The chamber for the sputtering was first pumped to a base pressure of  $<4 \times 10^{-4} \text{ Pa}$ , and then,  $\text{O}_2$  gas was flowed into the chamber so that the pressure would be 0.3 Pa. Subsequently, Ar was introduced so that the total pressure would be 1.6 Pa. The orientation relationship between the seed layer and the substrate was  $[0001] \text{ ZnO} // [1\bar{1}20] \text{ sapphire}$  and  $[2\bar{1}\bar{1}0] \text{ ZnO} // [0001] \text{ sapphire}$  [16]. The reaction solution was prepared by dissolving an excess amount of ZnO powder in an aqueous solution containing 0.90–0.98 M  $\text{NH}_3$ , 0.02–0.10 M  $\text{NH}_4\text{NO}_3$ , 3 mM sodium citrate tribasic dehydrate, and 5–8 mM  $\text{GaCl}_3$ . The pH of the solution was adjusted

to be 10.9–11.2 by controlling the concentration of  $\text{NH}_4\text{NO}_3$ , while the total ammonia concentration in the solution was kept at 1.0 M. In this pH range, ZnO:Ga films with a smooth surface could be obtained. The ZnO:Ga film was formed on the ZnO-seeded substrate by heating the substrate to 80 °C at a rate of 4 °C  $\text{min}^{-1}$  and then maintaining this temperature for 6 h under a constant flow of the solution at a rate of 90  $\mu\text{L min}^{-1}$  in the reactor. The Ga content and the thickness of the obtained ZnO:Ga films were in the ranges of 2.7–3.5 at.% and 1.4–1.8  $\mu\text{m}$ , which were determined by energy-dispersive X-ray spectroscopy (EDX; INCAxact, Oxford Instruments) and observation of the films' cross sections with a scanning electron microscope (SEM; JSM-6510LV, JEOL), respectively.

Annealing of the ZnO:Ga films in air was carried out in a box-type electric furnace (KBF848N1, Koyo Thermo Systems Co. Ltd.), and in vacuum or under a 5% $\text{H}_2$ –Ar atmosphere in an electric furnace (ARF-50K, Asahi Rika Seisakusho Co., Ltd) with a quartz tube (inner diameter: 46 mm; length: 700 mm). The vacuum with a pressure of  $\sim 6 \times 10^{-4}$  Pa was maintained by a diffusion pump (DPF-200, ULVAC). The gas mixture of 5% $\text{H}_2$ –Ar was flowed into the tube at a rate of 200  $\text{mL min}^{-1}$  during the 5% $\text{H}_2$ –Ar annealing. The annealing in each atmosphere was carried out by heating the ZnO:Ga films from room temperature to a given temperature at a rate of 2.5 °C  $\text{min}^{-1}$ , holding at the temperature for 0.5 h, and slow cooling in the furnace. Rapid thermal annealing (RTA) was carried out by quickly inserting the ZnO:Ga film into the center of the tubular furnace that was preheated at 580 °C, holding it in the furnace for 2–90 s, and then removing the film from the furnace. This process is referred to as RTA at 580 °C in this paper, although the temperature of the film could not reach 580 °C when the annealing duration was short.

X-ray diffraction (XRD) patterns and pole figures of the produced films were obtained using an X-ray diffractometer (X'pertPRO-MPD, PANalytical) with Cu  $K_\alpha$  radiation. The electrical

resistivity, carrier concentration, and mobility of the films were measured with a resistivity/Hall-measurement system (ResiTest 8300, Toyo Corporation) using the van der Pauw method. Thermal desorption spectroscopy was carried out by heating the as-grown ZnO:Ga film in a vacuum chamber at a rate of 2.5 °C min<sup>-1</sup> and analyzing the gas species escaping from the film with a quadrupole mass spectrometer. The optical transmittance of the film was measured by a spectrophotometer (UV-2450, Shimadzu).

### 3. Results

A typical XRD pattern and a pole figure of a ZnO:Ga film prepared from an aqueous solution are shown in Fig. 1. The epitaxial growth of the single-phase ZnO:Ga film was confirmed by the  $\theta$ - $2\theta$  scan showing only the diffraction peaks of ZnO (002) and ZnO (004), and the ZnO {101} pole figure revealing a clear six-fold symmetric pattern of the diffraction peaks at a tilt angle of  $\psi = \sim 60^\circ$ .

To examine the effects of the annealing temperature, the ZnO:Ga films were annealed in air for 0.5 h at various temperatures ranging from 200 to 400 °C. The transparent appearance of the films was not changed by annealing at temperatures below 350 °C, whereas the film that was annealed at 400 °C turned opaque and fragments of the film were also scattered around the substrate. SEM observation confirmed that the surface of the films annealed at temperatures below 350 °C was as smooth as that before annealing (Fig. 2(a)). In contrast, spalling spots were observed on the opaque film that was annealed at 400 °C (Fig. 2(b)). As will be discussed later, the spalling was caused by evaporation of water from the film.

Figure 3 shows the electrical properties of ZnO:Ga films before and after annealing at various temperatures. While the resistivity of the as-grown film was of the order of 10<sup>-1</sup> Ω cm, it dropped

by two orders of magnitude after annealing at 200 °C and continued to gradually decrease with increasing temperature, reaching  $1.5 \times 10^{-3} \Omega \text{ cm}$  at 350 °C. However, further increase in the temperature to 400 °C increased the resistivity because of spalling of the film. Both the carrier concentration and mobility increased with increasing annealing temperature up to 350 °C, contributing to the decrease in resistivity in this temperature range.

Annealing experiments in different atmospheres—air, vacuum, and 5% $\text{H}_2$ -Ar—revealed that the temperature at which the film fractured depended on the atmosphere. As described above, the film was intact up to 350 °C but spalled at 400 °C in air, while it fractured at a lower temperature of 350 °C in vacuum and at 300 °C in 5% $\text{H}_2$ -Ar. The lowering of the fracture temperature in vacuum should be caused by acceleration of the evaporation of water from the film. In 5% $\text{H}_2$ -Ar, a small additional amount of water vapor can be generated by the following reaction:  $\text{ZnO} + \text{H}_2 \rightarrow \text{Zn} + \text{H}_2\text{O}$  [17], which should be responsible for the lowering of the fracture temperature.

Table 1 compares the electrical properties of the films annealed in the different atmospheres. The annealing temperature selected for each atmosphere was close to the highest temperature at which film fracture would not occur, i.e., 350 °C in air, 300 °C in vacuum, and 250 °C in 5% $\text{H}_2$ -Ar. Table 1 shows that the differences between the electrical properties were quite small. When the values for the film annealed in 5% $\text{H}_2$ -Ar were compared to those for the film annealed at the same temperature (250 °C) in air (Fig. 3), the former were slightly better, but the differences were still small, showing that the change of the atmosphere did not create a great impact on the electrical properties. This is probably because the concentration of Ga atom is much higher than that of the intrinsic defects such as oxygen vacancy, which would be introduced through the annealing.

Thermal desorption spectroscopy (TDS) was conducted on the ZnO:Ga film to explore the cause of spalling of the film during annealing. The most prominent signal was detected at  $m/z = 18$ ,

which corresponds to H<sub>2</sub>O. Figure 4 displays the TDS signal of H<sub>2</sub>O as a function of temperature, showing that an immense evolution of H<sub>2</sub>O started at 305 °C and peaked at 335 °C. The temperatures at which the evolution of H<sub>2</sub>O was detected are close to the temperature at which the film was spalling during the annealing in vacuum, indicating that the expulsion of H<sub>2</sub>O vapor from the film caused the spalling of the film. Since the film was grown in an aqueous solution, it is not surprising that hydroxide ions were incorporated in the as-grown ZnO:Ga crystal as substitutes for oxygen in the ZnO lattice [15]. As the film was heated, the hydroxide was expelled from the crystal in the form of water vapor and the film spalled under the pressure of the water vapor. Because the origin of the water vapor should be the hydroxide ions incorporated in the ZnO:Ga crystal, the expulsion of water vapor occurs at the higher temperature than the dehydration of pure Zn(OH)<sub>2</sub> (110–140 °C [18]). The lattice and thermal expansion mismatches between the film and the substrate may also cause the spalling of the film. However, the influence of the water expulsion should be more predominant, because the film spalled at different temperatures depending on the atmosphere.

In the mass spectrum (inset of Fig. 4), the second largest signal (except for the signals at  $m/z = 16$  and  $17$  due to the fragments of H<sub>2</sub>O) is located at  $m/z = 44$ , which corresponds to CO<sub>2</sub>. The detection of CO<sub>2</sub> indicates that the citrate contained in the growth solution was incorporated in the film [19]. The citrate was necessary to enhance the lateral growth of the ZnO:Ga crystals and to form a smooth film surface thereafter [3]. As is the case for the H<sub>2</sub>O signal, the CO<sub>2</sub> signal reaches a peak at around 330 °C, suggesting that the citrate was trapped inside the film, not only on the surface, and it was released by spalling of the film. Judging from the signal intensities, the content of citrate in the film should be much smaller than that of hydroxide.



From the results shown in Fig. 3, it is expected that as long as film spalling could be avoided, a lower resistivity could be obtained by annealing at a higher temperature. Therefore, the effects of short-term annealing, so called rapid thermal annealing (RTA), at a high temperature were examined, with a view to achieving a lower resistivity in a short time before the film spalled. RTA was carried out at 580 °C in a 5%H<sub>2</sub>-Ar atmosphere for 2–90 s. The film remained transparent for the initial 60 s, but it turned opaque after 90 s of RTA, indicating that the film spalled at some point between 60 and 90 s.

The variation in electrical properties of the film is shown in Fig. 5. The resistivity rapidly decreased within 5 s and then gradually increased with the elapse of the annealing time after 20 s. At the annealing time of 20 s, the minimum resistivity of  $4.7 \times 10^{-4} \Omega \text{ cm}$  was obtained, which is the best result for films grown from aqueous solutions [7] and is comparable to the values of those prepared by much costlier vapor-phase processes. The drastic decrease in the resistivity was due to the increases in both carrier concentration and the mobility, which reached  $4.4 \times 10^{20} \text{ cm}^{-3}$  and  $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively, at 20 s. The carrier concentration gradually decreased after 20 s, while the mobility started to decrease at 40 s and dropped substantially at 90 s owing to spalling of the film.

One might assume that the increase in mobility resulted from improvement in the crystallinity of the film. However, the crystallinity was actually degraded by annealing, as indicated by the broadening of the ZnO (002) XRD peak width with increasing annealing time (Fig. 6), although the epitaxial nature was preserved. The diffraction peaks are so sharp that the peaks caused by  $K\alpha_1$  and  $K\alpha_2$  rays could be observed separately until 40 s, but this peak separation disappeared after 60 s because of the broadening of the peaks. Variations in the peak position with annealing time was also observed, indicating that the lattice expanded in the *c*-direction for the initial 40 s of annealing;

the lattice shrank after 60 s (inset of Fig. 6). The structural degradation accompanying the lattice expansion should be related to the excess hydroxide that would be expelled from the crystal as water vapor during the annealing process. By the stress of the hydroxide moving out of the crystal, the lattice should be expanded. The subsequent lattice shrinkage should have been the result of this release.

Optical transmittance spectra of the films after RTA (Fig. 7) show that the films exhibited an absorption edge at ~360 nm, which corresponds to the bandgap of ~3.4 eV, and high transmittance of >75% in the visible light range if they had undergone less than 60 s of RTA, whereas the film that was subjected to 90 s of RTA exhibited low transmittance of <30% because of the damage by the water expulsion. The films after RTA for up to 60 s exhibited the absorption edge at the shorter wavelength than as-grown film. This blue-shift is attributable to the increase in the carrier concentration, i.e. Burstein-Moss effect [20]. However, the red-shift observed after RTA for 90 s cannot be fully explained by the opposite mechanism as the decrease in the carrier concentration is relatively small. The reason for the red-shift remains unclear.

#### **4. Discussion**

In ZnO:Ga crystals, Ga is the dominant electron donor. However, compared with the Ga content in ZnO:Ga films ( $\sim 3\% \approx 10^{21} \text{ cm}^{-3}$ ), the carrier concentration of the as-grown film ( $\sim 10^{19} \text{ cm}^{-3}$ ) was too low. This suggests that most of the Ga atoms in the as-grown film either existed in an electronically inactive form (e.g., located at interstitial sites instead of the substitutional Zn atom sites) or were counteracted by defects or impurities. The former idea of Ga being in a neutral form is, however, inconsistent with the mobility improvement (Figs. 3 and 5) because if the annealing merely activated the Ga atoms, the mobility must have decreased since the ionized Ga atoms would

have scattered more electrons. Therefore, a more plausible explanation is that along with ionized Ga atoms, compensating acceptors existed in the as-grown film, and the elimination or passivation of the compensating acceptors was responsible for both the increases in carrier concentration and mobility after annealing: as the compensating species must be negatively charged, their elimination should have reduced electron scattering, leading to the enhancement of the mobility.

Considering that ZnO:Ga films prepared by vapor-phase processes are usually highly conductive without annealing [12, 21-23], an unintentional impurity unique to the films grown from aqueous solutions, i.e., hydroxide, is suspected to have played a significant role in the transition of the electrical properties. Hydroxide substituting for oxygen in ZnO, which can also be regarded as a hydrogen interstitial, is predicted to act as a shallow donor [15, 24]. However, it can be assumed that most of the hydroxide existed in an electronically inactive or compensating form in the as-grown film, as it should when the system is far from the equilibrium state. Upon annealing, the hydroxide i.e., hydrogen and oxygen atoms, should have moved toward stable positions in the ZnO:Ga crystal, forming the predicted shallow-donor state. Hydrogen has been known to be a common impurity that is unintentionally incorporated in ZnO during various synthesis processes, and it contributes to the n-type conductivity not only by acting as shallow donors [24, 25] but also by passivating ionized compensating acceptors [26]. Hence, the increases in the carrier concentration and mobility by annealing can be explained by the hypothesis that the hydroxide ions existed in a compensating form in the as-grown film and they were activated to act as shallow donors by heating.

The content of hydroxide ions in the ZnO:Ga film was obviously higher than its equilibrium value at an elevated temperature, and, therefore, they were expelled in the form of water vapor. The evaporation of water from inside the film involved a long-range mass transfer. Compared to

this evaporation, the activation of the hydroxide should occur in a shorter period of time, because it should not involve a long-range mass-transfer.

During RTA, even before the film fractures, the evaporation of water must proceed, and thereby, the content of the activated hydroxide in the film must gradually decrease. This could be the reason for the gradual decrease in the carrier concentration after 40 s of RTA. The decrease in the concentration of the activated hydroxide could also bring about an increase in the mobility because it should decrease the ionized impurity scattering. However, along with the expulsion of the hydroxide, the degradation of the ZnO:Ga crystal lattice occurred during RTA, which should decrease the mobility. The fact that the mobility maximized at 40 s of RTA should be resulted by the combination of these two effects.

The citrate in the ZnO:Ga film may have also had an influence on the conductivity. Wagata et al. reported that the conductivity of citrate-containing ZnO films prepared by the spin-spraying method was improved by an ultraviolet treatment, owing to the formation of shallow donors by photocatalytic decomposition of citrate in the film [27]. The same donors should have been formed by thermal decomposition of citrate in the ZnO:Ga film. However, as expected from the TDS measurement (Fig. 4), the concentration of such donors must have been much smaller than that of hydrogen originating from the hydroxide. Therefore, the impact of the citrate would have been minor in the films of this study.

## **5. Conclusions**

The effects of various annealing conditions on the electrical properties of the ZnO:Ga epitaxial films prepared from an aqueous solution were examined. For the film subjected to 0.5 h of conventional annealing, both the carrier concentration and mobility increased with increasing

annealing temperature up to a critical temperature where the film spalled. The spalling temperature depended on the annealing atmosphere; the film fractured at a lower temperature in 5%H<sub>2</sub>-Ar (300 °C) than in air (400 °C) and in vacuum (350 °C). However, the change of the atmosphere did not create significant differences in the electrical properties of the films. TDS measurement revealed that spalling of the film was caused by expulsion of water vapor from the film, indicating that hydroxide was incorporated in the crystal during the film's growth. RTA was found to be effective because the conductivity was quickly enhanced before the film fractured. When the film was subjected to RTA at 580 °C for 20 s, the lowest resistivity of  $4.7 \times 10^{-4} \Omega \text{ cm}$  was achieved, which corresponds to a carrier concentration of  $4.4 \times 10^{20} \text{ cm}^{-3}$  and mobility of  $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The films subjected to RTA for  $\leq 60$  s exhibited high transmittance of  $>75\%$  in the visible spectrum. These results demonstrate that films with high electrical conductivity and transparency can be produced by the low-temperature aqueous solution method and subsequent RTA, and they indicate that this fabrication process has great potential for application in low-cost production of various optoelectrical devices.

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## References

- [1] L. Schmidt-Mende, J.L. MacManus-Driscoll, ZnO - nanostructures, defects, and devices, *Materials Today*, 10 (2007) 40-48.
- [2] K. Ravichandran, N.J. Begum, S. Snega, B. Sakthivel, Properties of Sprayed Aluminum-Doped Zinc Oxide Films A Review, *Materials and Manufacturing Processes*, 31 (2016) 1411-1423.
- [3] D. Andeen, J.H. Kim, F.F. Lange, G.K.L. Goh, S. Tripathy, Lateral epitaxial overgrowth of ZnO in water at 90 degrees C, *Advanced Functional Materials*, 16 (2006) 799-804.
- [4] T. Hamada, A. Ito, E. Fujii, D. Chu, K. Kato, Y. Masuda, Preparation of single-crystalline ZnO films on ZnO-buffered a-plane sapphire by chemical bath deposition, *J Cryst Growth*, 311 (2009) 3687-3691.
- [5] H.Q. Le, S.K. Lim, G.K.L. Goh, S.J. Chua, J. Ong, Optical and Electrical Properties of Ga-Doped ZnO Single Crystalline Films Grown on MgAl<sub>2</sub>O<sub>4</sub>(111) by Low Temperature Hydrothermal Synthesis, *J Electrochem Soc*, 157 (2010) H796-H800.
- [6] H.Q. Le, S.J. Chua, Gallium and indium co-doping of epitaxial zinc oxide thin films grown in water at 90 degrees C, *J Phys D Appl Phys*, 44 (2011) 8.
- [7] M. Miyake, H. Fukui, T. Doi, T. Hirato, Preparation of low-resistivity Ga-doped ZnO epitaxial films from aqueous solution using flow reactor, *J Electrochem Soc*, 161 (2014) D725-D729.
- [8] A.H. Reading, J.J. Richardson, C.-C. Pan, S. Nakamura, S.P. DenBaars, High efficiency white LEDs with single-crystal ZnO current spreading layers deposited by aqueous solution epitaxy, *Optics Express*, 20 (2012) A13-A19.
- [9] H.Q. Le, S.K. Lim, G.K.L. Goh, S.J. Chua, N.S.S. Ang, W. Liu, Solution epitaxy of gallium-doped ZnO on p-GaN for heterojunction light-emitting diodes, *Applied Physics B*, 100 (2010) 705-710.
- [10] H. Tong, Z.H. Deng, Z.G. Liu, C.G. Huang, J.Q. Huang, H. Lan, C. Wang, Y.G. Cao, Effects of post-annealing on structural, optical and electrical properties of Al-doped ZnO thin films, *Appl Surf Sci*, 257 (2011) 4906-4911.
- [11] W.T. Yen, Y.C. Lin, P.C. Yao, J.H. Ke, Y.L. Chen, Effect of post-annealing on the optoelectronic properties of ZnO:Ga films prepared by pulsed direct current magnetron sputtering, *Thin Solid Films*, 518 (2010) 3882-3885.
- [12] J.H. Kim, B. Du Ahn, C.H. Lee, K.A. Jeon, H.S. Kang, S.Y. Lee, Effect of rapid thermal annealing on electrical and optical properties of Ga doped ZnO thin films prepared at room temperature, *Journal of Applied Physics*, 100 (2006) 113515.
- [13] K. Zhu, Y. Yang, T.F. Wei, R.Q. Tan, P. Cui, W.J. Song, K.L. Choy, Effects of post-rapid thermal annealing on structural, electrical and optical properties of hydrogenated aluminum doped zinc oxide thin films, *J Mater Sci-Mater El*, 24 (2013) 3844-3849.
- [14] P.W. Wang, Y.Y. Chen, J.C. Hsu, C.Y. Wang, Structural, optical and electrical properties of aluminum doped ZnO films annealed in air and hydrogen atmosphere, *Journal of Non-Crystalline Solids*, 383 (2014) 131-136.
- [15] J.J. Richardson, G.K.L. Goh, H.Q. Le, L.-L. Liew, F.F. Lange, S.P. DenBaars, Thermally Induced Pore Formation in Epitaxial ZnO Films Grown from Low Temperature Aqueous Solution, *Cryst Growth Des*, 11 (2011) 3558-3563.
- [16] P. Kuppusami, G. Vollweiler, D. Rafaja, K. Ellmer, Epitaxial growth of aluminium-doped zinc oxide films by magnetron sputtering on (001), (110), and (012) oriented sapphire substrates, *Appl Phys a-Mater*, 80 (2005) 183-186.

- [17] Y. Natsume, H. Sakata, Electrical conductivity and optical properties of ZnO films annealed in hydrogen atmosphere after chemical vapor deposition, *J Mater Sci-Mater El*, 12 (2001) 87-92.
- [18] S.V. Nistor, D. Ghica, M. Stefan, I. Vlaicu, J.N. Barascu, C. Bartha, Magnetic defects in crystalline Zn(OH)(2) and nanocrystalline ZnO resulting from its thermal decomposition, *J Alloy Compd*, 548 (2013) 222-227.
- [19] H. Wagata, N. Ohashi, T. Taniguchi, K.I. Katsumata, K. Okada, N. Matsushita, Control of the Microstructure and Crystalline Orientation of ZnO Films on a Seed-free Glass Substrate by Using a Spin-Spray Method, *Cryst Growth Des*, 10 (2010) 4968-4975.
- [20] Z.C. Jin, I. Hamberg, C.G. Granqvist, Optical-Properties of Sputter-Deposited ZnO-Al Thin-Films, *Journal of Applied Physics*, 64 (1988) 5117-5131.
- [21] S.W. Shin, G.L. Agawane, I.Y. Kim, Y.B. Kwon, I.O. Jung, M.G. Gang, A.V. Moholkar, J.H. Moon, J.H. Kim, J.Y. Lee, Low temperature epitaxial growth and characterization of Ga-doped ZnO thin films on Al<sub>2</sub>O<sub>3</sub> (0001) substrates prepared with different buffer layers, *Appl Surf Sci*, 258 (2012) 5073-5079.
- [22] J.L. Zhao, X.W. Sun, H. Ryu, Y.B. Moon, Thermally stable transparent conducting and highly infrared reflective Ga-doped ZnO thin films by metal organic chemical vapor deposition, *Optical Materials*, 33 (2011) 768-772.
- [23] H. Makino, Y. Sato, N. Yamamoto, T. Yamamoto, Changes in electrical and optical properties of polycrystalline Ga-doped ZnO thin films due to thermal desorption of zinc, *Thin Solid Films*, 520 (2011) 1407-1410.
- [24] C.G. Van de Walle, Hydrogen as a cause of doping in zinc oxide, *Physical Review Letters*, 85 (2000) 1012-1015.
- [25] A. Janotti, C.G. Van de Walle, Hydrogen multicentre bonds, *Nat Mater*, 6 (2007) 44-47.
- [26] Z. Zhang, D.C. Look, R. Schifano, K.M. Johansen, B.G. Svensson, L.J. Brillson, Process dependence of H passivation and doping in H-implanted ZnO, *J Phys D Appl Phys*, 46 (2013) 055107.
- [27] H. Wagata, N. Ohashi, K.-i. Katsumata, H. Segawa, Y. Wada, H. Yoshikawa, S. Ueda, K. Okada, N. Matsushita, An aqueous solution process and subsequent UV treatment for highly transparent conductive ZnO films, *J Mater Chem*, 22 (2012) 20706-20712.



## Figure captions

**Fig. 1** Typical XRD  $\theta$ - $2\theta$  scan of a ZnO:Ga film prepared from an aqueous solution in this study. The  $2\theta$  range of from 36.3 to 39.0° was not scanned to avoid the intense reflection from the sapphire substrate entering the counter. The inset shows a ZnO (101) pole figure of the film.

**Fig. 2** Surface SEM images of ZnO:Ga films (3.5% Ga) after annealing at (a) 350 °C and (b) 400 °C in air for 0.5 h.

**Fig. 3** Resistivity, carrier concentration, and mobility of ZnO:Ga film (3.5% Ga) before and after annealing at various temperatures in air for 0.5 h.

**Fig. 4** Thermal desorption spectra of ZnO:Ga film. The inset shows the mass spectrum at 335 °C.

**Fig. 5** Electrical properties of ZnO:Ga films (2.7% Ga) before and after RTA at 580 °C in 5%H<sub>2</sub>-Ar atmosphere for various durations.

**Fig. 6** Enlarged XRD patterns showing ZnO (002) diffraction peaks of ZnO:Ga films (2.7% Ga) before and after RTA at 580 °C in 5%H<sub>2</sub>-Ar atmosphere for various annealing durations. The inset shows the lattice constant of *c*-axis of the ZnO:Ga crystal, calculated from the peak position.

**Fig. 7** Transmittance spectra of ZnO:Ga films (2.7% Ga) before and after RTA at 580 °C for 2, 60, and 90 s.