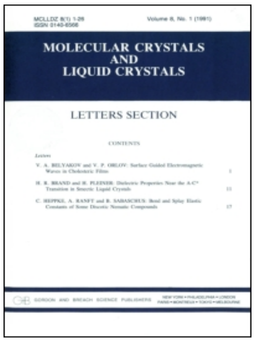

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Characterization of dopant density dependence on transmittance and resistance of ZnO films fabricated using spin-coating method

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ABSTRACT
We fabricated aluminum (Al) and gallium (Ga) co-doped ZnO films by wet-process and evaluated their sheet resistances and transmission spectra. It was found that the sheet resistance becomes minimum when the content ratios of Al and Ga are 0.02 at the annealing temperature of 550 degree. Moreover, we found that the sheet resistance can be improved by performing the spin-coating and annealing twice. In this case, the transmission probability in the visible light regime is more than 90%. This result is a simple method to fabricate fine transparence conductive ZnO films.

KEYWORDS
transparent conductive films; sol-gel; ZnO; doping mothod; sheet resistance

1. Introduction

Indium-tin-oxide (ITO) films are widely used as transparent conductive electrodes in electronics devices. However, the price of ITO has become more expensive because indium is a rare metal. Recently, the fabrication method of ZnO films has been energetically investigated for the application to transparent conductive films because of the low-price of Zinc [1–8]. Fine transparent conductive films of ZnO are usually fabricated by using sputtering method [3–5]. In addition, aluminum (Al) and/or gallium (Ga) atoms are doped in ZnO films to improve their conductivities [3–6]. Ga-doping and Al-doping can reduce sheet resistance values of ZnO films because of an increase of carrier concentration of ZnO films originating from the substitutional incorporation of Al^{3+} and Ga^{3+} ions at Zn^{2+} cation sites or incorporation of Al or Ga ions in interstitial positions [6]. On the contrary, wet-process is an effective candidate to realize the low-cost production of ZnO films because vacuum system is not necessary [6–8]. In this paper we have investigated to fabricate ZnO transparent conductive films by spin-coating method, in which Al and Ga are co-doped. In particular, we found that the sheet resistance can be decreased by performing the spin-coating and annealing twice.

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2. Experimental

2.1 Sample fabrication

To fabricate the precursor solution of ZnO, the mixture solution of $Zn(OAc)_2$, monoethanolamin (MEA) and 2-methoxyethanol was stirred at 50 degrees for 1 hour. Next, $[Al(NO_3)_3{\bullet}9H_2O]$ and $[Ga(NO_3)_3 \bullet nH_2O]$ were added to the mixture solution as an Al-dopant and Ga-dopant. Their content ratios against ZnO were changed from 0 to 0.03. Then, thin films of the precursor solution were fabricated on cleaned glass substrates using the spin-coating method. After that, they were annealed at 550 degree in an oven.

Their sheet resistances were evaluated using a 4 point probe measurement system SR-H1000C. Transmission spectra were measured using a spectrophotometer UV-2450 (Shimadzu). Surface roughnesses of the fabricated films was evaluated using an atomic force microscope (AFM).

Note that we evaluated the following two kinds of film fabrication methods,

(1) Spin-coating and annealing were performed once,
(2) Spin-coating and annealing were performed twice.

In the case of the second method, the sample was fabricated by preliminary spin-coating and annealing. Then, the sample was cooled to room temperature. After that, the second spin-coating was performed on the film. Then, the film was annealed again at 550 degree. The rotation speed of the first spin-coating was 2000 rpm, while that of the second spin-coating was changed from 1000 to 3000 rpm.

3. Results and discussion

3.1 Doping density dependence of sheet resistance

First, we evaluated the sheet resistances of the ZnO films fabricated by the single spin-coating of 2000 rpm and annealing at 550 degrees for 1 hour. The sheet resistances and the surface roughnesses of the ZnO films as a function of the Al and Ga doping densities are listed in table 1. It is very clear that the smallest sheet resistance of 6.4×10^6 Ω/□ was observed in the $Al_{0.02}Ga_{0.02}Zn_{0.96}O$ film. Thus, this doping density condition was fixed to fabricate other samples. To evaluate the annealing time dependence on the sheet resistance, we fabricated the sample annealed at 550 degree for 2 hours. In this case, however, the sheet resistance increased to be 1.0×10^7 Ω/□. This means that the longer annealing time does not improve the sheet resistance of ZnO films.

3.2 Effect of the second spin-coating and annealing on sheet resistance

To evaluate the effect of the second spin-coating and annealing on the sheet resistance and the surface roughness, we fabricated ZnO films by changing the rotation speed of the second

Table 1. The sheet resistance as a function of the content ratios of Al and Ga. The samples were fabricated by the single spin-coating of 2000 rpm and annealing at 550 degrees for 1 hour.

Sample	Ω/□□
$Al_{0.01}Ga_{0.01}Zn_{0.98}O$	3.1×10^7
$Al_{0.01}Ga_{0.02}Zn_{0.97}O$	7.1×10^7
$Al_{0.02}Ga_{0.01}Zn_{0.97}O$	2.4×10^8
$Al_{0.02}Ga_{0.02}Zn_{0.96}O$	6.4×10^6
$Al_{0.02}Ga_{0.03}Zn_{0.95}O$	5.5×10^7

spin-coating as listed in table 2. The first two samples were fabricated by the single spin-coating and annealing, which were already explained in the section of 3.1. The other six samples were fabricated by performing the spin-coating and annealing twice. The first annealing time was change as 10 minutes and 1 hour, while the second annealing times was fixed at 1 hour as listed in the left column. In addition, the rotation speed of the second spin-coating were changed from 1000 to 3000 as listed in the left column.

It is very clear that the sheet resistance becomes smaller in the samples of the first annealing time is 1 hour. In particular, the smallest sheet resistance of 1.2×10^6 Ω/□ was observed in the sample whose rotation speed of the second spin-coting is 1000 rpm. This is much smaller than that of the sample fabricated by the single spin-coating and annealing. Moreover, the result indicates that the annealing twice for 1 hour can obtain smaller sheet resistance than that fabricated by the single annealing for 2 hours. In the samples of the first annealing time of 10 minutes, the sheet resistances were not clearly improved. They revealed the sheet resistance on the order of 10^7 Ω/□. These results clearly demonstrate that the sheet resistance of ZnO films can be easily improved by performing the spin-coating and annealing twice. In addition, it exactly depends on the annealing time and the rotation speed of the spin-coating.

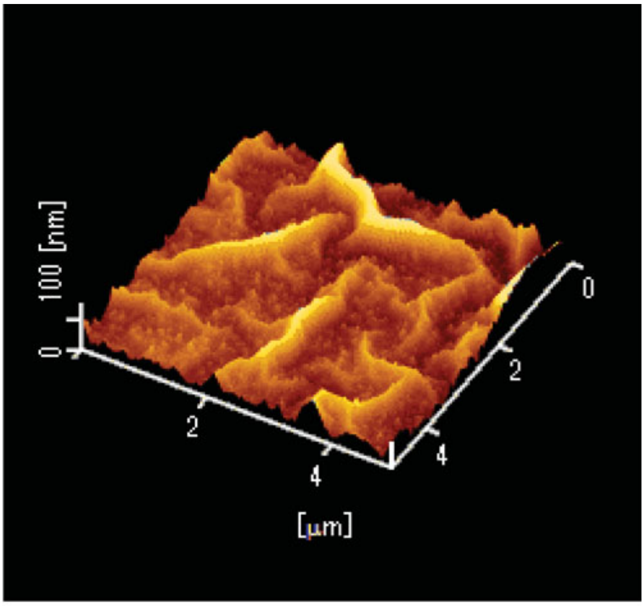
It is found from the relation between the sheet resistance and the surface roughness listed in table 2 that the sheet resistance does not depend on the surface roughness. Figure 1 shows AFM images of the samples. Fig. 1(a) is the sample surface fabricated by the single spin-coating and the annealing time is 1 hour, while Fig. 1(b) is the sample surface fabricated by the first and second annealing time is 1 hour and the rotation speed of the second spin-coating is 1000 rpm, in which the minimum sheet resistance was observed. Many mountains like figures of ZnO film were clearly observed in both sample surfaces.

3.3 Transmission properties

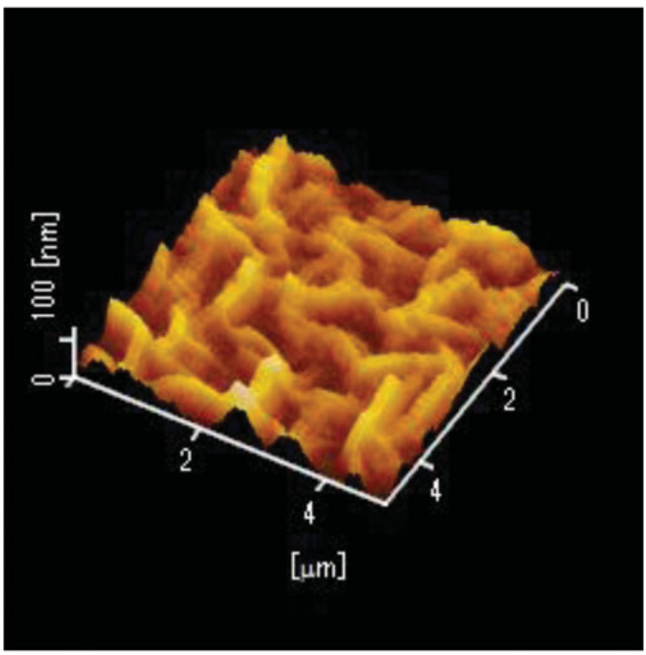
Figure 2 shows transmission spectra of the three samples fabricated by the first annealing time for 1 hour. In addition, the transmission spectrum of one sample fabricated by the single spin-coating and annealing is displayed. When the rotation speed of the second spin-coating is 1000 rpm, the transmission probability is more than 90% in the visible light regime. This is almost equal to that of the sample fabricated by the single spin-coating and annealing. This clearly demonstrates that the transmission probability is not deteriorated by the second spin-coating and annealing. However, if the rotation speed of the second spin-coating

Table 2. Effect of the second spin-coating and annealing on the sheet resistance and the surface roughness. The first two samples were fabricated by the single spin-coating and annealing. The time indicates the annealing time. The other six samples were fabricated by doing the spin-coating and annealing twice. In the left column, the first and second annealing times are listed. In addition, the rotation speed of the second spin-coating is listed.

Annealing time and rotation speed of second spin-coating	Ω/□□ surface roughness
1 h (single spin-coating)	6.4×10^6 24 nm
2 h (single spin-coating)	1.0×10^7 35 nm
1 h & 1 h, 1000 rpm	1.2×10^6 20 nm
1 h & 1 h, 2000 rpm	1.5×10^6 21 nm
1 h & 1 h, 3000 rpm	1.3×10^6 48 nm
10 min & 1 h 1000 rpm	1.2×10^7 13 nm
10 min & 1 h 2000 rpm	5.8×10^6 28 nm
10 min & 1 h 3000 rpm	1.1×10^7 16 nm



(a)



(b)

Figure 1. AFM images of the samples fabricated by (a) the single spin-coating and the annealing time is 1 hour (b) the first and second annealing time is 1 hour and the rotation speed of the second spin-coating is 1000 rpm, in which the minimum sheet resistance was observed.

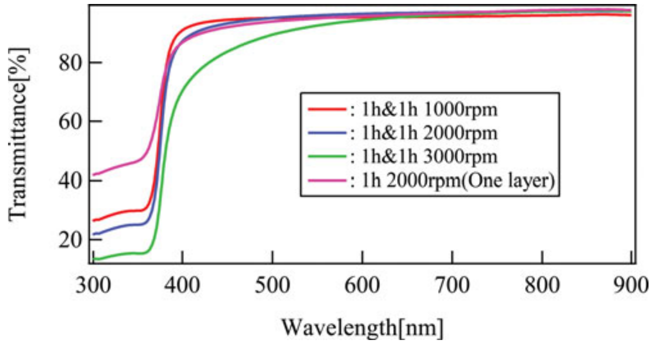


Figure 2. Transmission spectra of ZnO films of the three samples fabricated by the first annealing time for 1 hour. In addition, one sample fabricated by the single spin-coating and annealing.

is 3000 rpm, the transmission probability decreases especially around the shorter wavelength region as shown in Fig. 2(b). This is due to large Rayleigh scattering caused by the large surface roughness of 48 nm listed in table 2.

4. Conclusion

We have investigated the sheet resistance and transmittance of Al and Ga doped ZnO fabricated by wet-process. The best content ratios of Al and Ga were found to be $Al_{0.02}Ga_{0.02}Zn_{0.96}O$ in which the minimum sheet resistance was observed. In addition, it was found that the sheet resistance was easily improved by performing the spin-coating and annealing twice. In this case, the transmission probability in the visible light regime is more than 90%. This fabrication method is very useful to improve the sheet resistance of Al and Ga co-doped ZnO transparent conductive films.

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