Characterization of F- and Al-codoped ZnO Transparent Conducting Thin Film prepared by Sol-Gel Spin Coating Method

Gil Mo Nam and Myoung Seok Kwon[†]

Department of Materials Science and Engineering, University of Seoul, Seoul 02504, Korea

(Received February 3, 2016; Revised March 11, March 28, 2016; Accepted March 29, 2016)

ABSTRACT

ZnO thin film co-doped with F and Al was prepared on a glass substrate via simple non-alkoxide sol-gel spin coating. For a fixed F concentration, the addition of Al co-dopant was shown to reduce the resistivity mainly due to an increase in electrical carrier density compared with ZnO doped with F only, especially after the second post-heat-treatment in a reducing environment. There was no effective positive contribution to the reduction in resistivity due to the mobility enhancement by the addition of Al co-dopant. Optical transmittance of the ZnO thin film co-doped with F and Al in the visible light domain was shown to be higher than that of the ZnO thin film doped with F only.

Key words : Sol-gel, ZnO, Co-doping, Transparent conducting film, Spin-coating

1. Introduction

Main interest item for the present study among various applications of doped ZnO thin films is the application of transparent conducting thin films in the flat panel display area. For flat panel display panels such as flat display panel and touch screen panel, etc. use of the transparent conducting films is essential, and the latter have been mass-produced thus far with emphasis on ITO thin film containing In.^{1,2)} From the aspect of next-generation fundamental studies, transparent conducting oxide films for substitution of ITO have been widely studied, which do not contain the In element subjected to unstable supply and great price variations. Such transparent conducting thin films essentially require a low resistivity and a high optical transmittance in the visible light band.¹⁻³⁾

The method widely studied as a preparation method for doped ZnO thin films is a physical vapor deposition (PVD) method such as sputtering.²⁻³⁾ In comparison with this, the sol-gel method⁴⁻⁷⁾ has advantages as a fundamental study method for the search of material systems, although its resistivity characteristics are rather poor. Namely, the advantageous features include that manufacturing equipment is inexpensive and simple, not only host composition but also types and contents of the added doping elements can be flexibly varied, and material synthesis begins in a homogeneous solution state at a molecular level. The follow-up crystallization heat treatment to finally obtain a crystallized thin film is also possible at a relatively low tempera-

ture. Additional advantages include the fact that thin films can be formed on diversified substrates including a glass substrate.⁴⁻⁷⁾

In the studies on preparation of doped ZnO thin films by the sol-gel method, Al, Ga, In, etc. are being studied as doping elements.⁴⁻⁷⁾ As a thin-film coating method onto substrates, the method of dip coating or spin coating is being adopted. In the previous articles by the present authors, studies on spin coating of ZnO thin films by the sol-gel method have been reported, where the results concerning single dopants such as Ga, Al, and F, etc. were reported in order.⁸⁻¹⁰⁾ To form the doped ZnO thin films for application of a transparent conducting thin film, other study groups employed metal alkoxides. Unlike the latter, the present study group has adopted a zinc acetic compound which is easy to handle and of a low cost as the sol-gel precursor for Zn. Ga and Al as a doping element were aimed at substitution of Zn ions,^{8,9)} while F doping was used for substitution of O ions.¹⁰⁾

The purpose of this article is to prepare ZnO thin films on glass substrates by co-doping of a small amount of Al along with F doping of an optimum concentration obtained in the previous study¹⁰⁾ as the basis, and to evaluate the characteristics thereof. Namely, after fixing the F doping content to be constant, microstructures along with changes in electrical and optical properties in the thin film were evaluated following preparation of ZnO thin films with a variation in the added amounts of Al as a co-doping element.

2. Experimental Procedure

ZnO thin films co-doped with F and Al by sol-gel spin coating were prepared on glass substrates. The present study experiments were performed on the basis of the sol-gel spin

[†]Corresponding author : Myoung Seok Kwon
E-mail : mskwon@uos.ac.kr
Tel : +82-2-6490-2411 Fax : +82-2-6490-2404

coating method reported by the present authors in the previous articles.⁸⁻¹⁰ As the sol for ZnO thin film coating, zinc acetate dihydrate ($\text{Zn}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$) was selected as a starting material. The zinc acetate compound is a supply source for ZnO as a type of compounds, and has advantages of being stable at room temperature and of having a low cost. Also, 2-methoxyethanol with a high boiling point was selected as the solvent so that volatilization occurred slowly during spin coating as well as heat treatment process and compatibility of thin films was realized. Since solubility of the zinc acetate compound used as a solute in the 2-methoxyethanol as a solvent is basically low, an adding method for the molar ratio to Zn acetate to be 1 : 1 was employed by using monoethanolamine (MEA) as a stabilizing agent. As the starting materials for F and Al used as dopants, ammonium fluoride and aluminium nitrate enneahydrate were selected.

After mixing 2-methoxyethanol and MEA at room temperature, the mixture was agitated on a hot plate at about 70°C for 90 minutes, and zinc acetate dihydrate was added to obtain 0.75 M. As the co-dopants, ammonium fluoride and ammonium nitrate were added to the mixed solution. After the final sol solution with preparation completed is aged for 48 h, the doped ZnO thin films were prepared on glass substrates using a spin coater.

As a substrate for formation of the thin film, substrates with 250 Å of SiO_2 vapor deposited onto soda lime glass were used. The SiO_2 glass substrates were ultrasonically cleaned in distilled water to remove organics and foreign objects from the surface. Then, dust on the substrates was blown off by using a nitrogen gun, followed by drying at 80°C for 30 minutes. The sol solution prepared earlier was dripped onto the substrate for wetting for 10 seconds, and rotated at a speed of 3000 rpm for 30 seconds. From the coated thin films, organic solvent remaining on thin films was removed through pre-heat-treatment in air atmosphere at 350°C for 10 minutes. To obtain thin films of a sufficient thickness, the above processes were repeated for a few times. Finally, for realization of crystallization in ZnO thin films, the 1st post-heat-treatment was performed in the air atmosphere at 500 ~ 600°C. The subsequent 2nd post-heat-treatment was performed in the hydrogen reduction atmosphere (5% H_2 -95% N_2) to induce electrical activation and property improvement for the doped ZnO thin films.

By using X-ray diffraction (XRD, D8 Advanced X-ray, Bruker Axs), crystallinity and preferred orientation, etc. of the doped ZnO thin films were investigated. Surface shapes and particle sizes of the doped ZnO thin films were observed by using Field Emission Scanning Electron Microscope (FE-SEM, S-4300, Hitachi, Japan). Electrical properties of the doped ZnO thin films were measured by using Hall Effect measurement System (HMS - 3000, Ecopia). Electrical properties such as resistivity, carrier concentration, Hall mobility, etc. were measured and extracted. And, for optical properties evaluation as a transparent conducting thin film for flat panel display, optical transmittance in the visible

light domain of 400 ~ 800 nm in wavelength was measured by using UV-visible spectrometer (UV-3150, Shimadzu, Japan).

3. Results and Discussion

The present authors have reported the results of preparation by sol-gel method with addition of F as the single dopant to improve electrical conductivity and material property characteristics of ZnO in the previous study.¹⁰ In the current study, experiments were conducted while the added concentrations of a small amount of Al were varied with the doping composition of F fixed at 2.0 at. % which showed the most excellent electrical properties in the previous study.

Figure 1 shows the results of XRD pattern for the ZnO thin films co-doped with 2.0 at. % of F and 0 ~ 0.8 at.% of Al. The thin films were samples with the 2nd post heat treatment in the hydrogen reduction atmosphere (5% H_2 - 95% N_2) at 450°C for 30 minutes after the 1st post heat treatment in the air atmosphere at 500°C for 1 h. For comparison of diffraction results, the results for the ZnO thin films with no doping of F and Al are listed alongside. The ZnO thin films without a dopant and the doped thin films commonly exhibit diffraction peaks corresponding to (002) face of the hexagonal ZnO crystal structure. The result is implied where the ZnO thin film is preferentially oriented along the (002) face or the c-axis direction. Peak intensity distribution

Fig. 1. XRD patterns of the co-doped ZnO films (F 0 or 2 at.% + Al 0 ~ 0.8 at.%).

for the thin film samples doped with F only and the co-doped thin film samples did not show a large difference. In the samples with addition of 0.8 at.% of Al as a co-doping element, the peak intensity was somewhat reduced, and the weak peaks of (100) face and (101) face were observed.

Within the experimental composition range of the present study, the undoped ZnO thin films, the ZnO thin films doped with F only, and the ZnO thin films co-doped with F and Al are considered to show the preferred orientation mainly along c-axis. In addition, when the concentrations of co-doped Al were increased, it was shown that such preferred orientation could be reduced.

Figure 2 shows the measured results of resistivity for the co-doped ZnO thin films where Al concentrations were varied between 0 at.% ~ 0.8 at.% after F concentration was maintained to be constant at 2 at.%. The thin films were prepared by the 1st post heat treatment in the air atmosphere at 500°C for 1 h, followed by the 2nd post heat treatment in the hydrogen reduction atmosphere (5% H₂-95% N₂) at 450°C for 30 minutes.

According to the previous study results by the authors,¹⁰⁾ the reduction effect of resistivity by the 2nd heat treatment in the reducing atmosphere was not observed as compared with the results after the 1st post heat treatment in the air atmosphere, in the case of ZnO thin films doped with F only. On the contrary, the result of an increase in resistivity was exhibited after the 2nd post heat treatment in the reducing atmosphere.¹⁰⁾ In addition, the resistivity when F doping concentration was 2 at.% was reported to be minimized commonly for both the measured values of resistivity after the 1st post heat treatment and the results after the 2nd post heat treatment.¹⁰⁾ The minimum resistivity figure after the 1st post heat treatment was 5.62 Ω·cm.¹⁰⁾

As shown in Fig. 2, the thin films doped with 2 at.% of F and those doped with 0.5 at.% of Al showed a resistivity value of 7.4×10^{-2} Ω cm which was the minimum value after the 2nd post heat treatment in the reducing atmosphere. Therefore, as compared with the previous study result by the authors for the ZnO thin films doped with 2 at.% of F

only, the improved characteristics were obtained where the resistivity was reduced by about 2 orders of magnitude. The thin films co-doped with F and Al showed the lowest resistivity characteristics when 0.5 at.% of Al was added under the condition where F concentration was constant at 2 at.%. Also, it represents the result of improvement by 1 order of magnitude compared with the resistivity value as the previous study result⁹⁾ where only Al was doped.

According to this experimental result, the result could be observed where the co-doping method with addition of Al and F induced a change in electrical properties for thin films unlike the cases of single doping with an individual element only. Also, the result of a marked reduction in resistivity values was obtained upon the 2nd post heat treatment in the hydrogen reduction atmosphere (5% H₂-95% N₂) after co-doping with F and Al, as compared with only the 1st post heat treatment in the air atmosphere.

Figure 3 shows a graph for carrier concentrations and Hall mobilities of the ZnO thin films prepared with a change in the doped amounts of Al while the doped amount of F was maintained to be constant at 2 at.%. The thin films were prepared through the 1st post heat treatment in the air atmosphere at 500°C for 1 h, followed by the 2nd post heat treatment in the hydrogen reduction atmosphere (5% H₂-95% N₂) at 450°C for 30 minutes. For the composition where the co-doped amount of Al showing the minimum resistivity in Fig. 2 as the previous resistivity result was made to be 0.5 at.%, the carrier concentration and the mobility showed the values of 5.59×10^{19} cm⁻³ and 1.12 cm²/V·s, respectively. The carrier concentration for the sample where doped amounts of Al were varied with the amount of F fixed at 2 at.% showed the lowest figure when Al was not doped, and showed the maximum value of 7.37×10^{19} cm⁻³ when 0.25 at.% of Al was added. Afterward, the carrier concentration was not increased further even if the added concentrations of Al were increased, rather showing the result of a slight reduction. When Al was not added after F was fixed at 2 at.%, Hall mobility showed the maximum value of 6.61 cm²/V·s, while the minimum value was observed when

Fig. 2. Resistivity of the co-doped ZnO films (F 2 at.% + Al 0 ~ 0.8 at.%).

Fig. 3. Carrier concentration and mobility of the co-doped ZnO films (F 2 at.% + Al 0 ~ 0.8 at.%).

0.25 at.% of Al was added. When the added amounts of Al were more than 0.25 at.%, the mobility was increased again as the Al concentrations were increased. When Al is co-doped with the F concentration being fixed, the carrier concentrations were increased by about 2 orders of magnitude. Carrier concentrations did not show a tendency of being correspondingly increased as the Al concentrations were increased when Al existed as a co-doping element. Carrier concentrations rather showed the result of being reduced when the concentrations of the co-dopant Al continued to be increased. Also, under the condition where the carrier concentration showed the maximum value, the mobility exhibited the minimum figure, and showed an increase as the carrier concentrations were reduced. As a result of adding Al as a co-dopant with the F concentration maintained to be constant, the overall tendency was an increase in the carrier concentrations by about 2 orders of magnitude with addition of a small amount of Al, while the increasing effect of mobilities are considered not to exist. In the case of mobility, it rather showed the result of reduced figures as the digit number of the carrier concentration was increased. Consequently, the macroscopic reduction of resistivity (improvement of electrical conductivity) shown earlier in Fig. 2 is considered to be most largely dependent on the increase in carrier concentrations induced by addition of the co-dopant Al to the fixed F concentration.

Figure 4 shows the FE-SEM pictures of shapes of thin film surfaces observed for the undoped ZnO thin films, the thin films doped with 2 at.% of F only, the thin films doped with 0.5 at.% of Al only, and the thin films doped with 2 at.% of F and co-doped with 0.5 at.% of Al. The thin films were subjected to the 1st post heat treatment in the air atmosphere at 500°C for 1 h, followed by the 2nd post heat treatment in the hydrogen reduction atmosphere (5% H_2 - 95% N_2) at 450°C for 30 minutes. Surface shapes for the undoped ZnO thin films and the thin films with 2 at.% of F added were observed not to have a large difference. In contrast, particle sizes can be observed to be remarkably reduced in the thin

films with addition of 0.5 at.% of Al only. Crystal sizes of thin films with co-doping of 2 at.% of F and 0.5 at.% of Al are considered to be between the crystal size of the thin films with single doping of F only and that of the thin films with single doping of Al only. Relatively fewer pores were observed for the co-doped thin films as compared with the undoped films and the films having single doping of F only.

Figure 5 shows a graph for optical transmittance in the visible light domain (400 ~ 800 nm) of the ZnO thin films prepared by doping with a given concentration of F and varying concentrations of the co-doped Al. The thin films prepared by sol-gel method were subjected to the 1st post heat treatment in the air atmosphere at 500°C for 1 h, followed by the hydrogen reduction heat treatment in the hydrogen reduction atmosphere (5% H_2 – 95% N_2) at 450°C for 30 minutes. Thickness of the thin films co-doped with 2 at.% of F and 0.25 at.% of Al was 295 nm, and an excellent optical transmittance of about 96% was exhibited. Thickness range for the ZnO thin films co-doped with F and Al was 290 ~ 320 nm, and an optical transmittance of about 92 ~ 96% was observed in the visible light domain. Also, within the concentration variation range of the present experiments the ZnO thin films with additional co-doping of Al showed rather the improved results in optical transmittance across the entire range in comparison with the thin films with single doping of F only.

Therefore, in the doped ZnO thin films based on F, interesting results could be obtained where Al added as a co-doping element contributed to the improvement of optical transmittance. Based on the XRD diffraction results of Fig. 1, the results could also be observed where the preferred orientation observed with a continued increase in the contents of added Al began to be reduced. Macroscopic aspect of resistivity as well as the variation aspects of microscopic carrier concentration and mobility which were observed when the contents of added Al continued to be increased at a given F concentration are considered to suggest that the domain of optimum doping concentration exists within a given range.

Fig. 4. FE-SEM micrographs of the surface of the co-doped ZnO films (F 0 or 2 at.% + Al 0.5 at.%).

Fig. 5. Optical transmittance of the co-doped ZnO films (F 2.0 at.% + Al : 0.25, 0.5, 0.8 at.% of F).

In the aspect of particle sizes for the polycrystalline ZnO thin films obtained by the sol-gel method, the particle sizes of the undoped ZnO thin films and the ZnO thin films with single doping of F only tended to be larger than those of the thin films with single doping of Al only, and hence the particle sizes upon additional co-doping of a small amount of Al with F as the base could be observed to be larger in comparison with those for the polycrystals doped with Al only.

4. Conclusions

As compared with material properties of the ZnO thin films with single doping of F only, the ZnO thin films co-doped with F and Al showed the results of reduction in resistivity by 2 orders of magnitude after undergoing the 2nd post heat treatment process in a reducing atmosphere. When the added amounts of Al are varied while the F concentration is fixed to be constant, the concentration range for Al addition minimizing resistivity is considered to exist, and the factors determining such macroscopic change in the resistivity are considered to mainly originate from the increase in carrier concentrations as a result of Al addition. In contrast, the reduction effect of resistivity due to an increase in mobilities is considered not to exist even if Al is added at a constant F concentration. In comparison with the ZnO thin films with single doping of F only, the ZnO thin films with co-doping of F and Al exhibited rather an improvement of optical transmittance in the visible light domain. Meanwhile, it has been observed that the crystallinity and the preferred orientation of the thin films as well as the particle sizes and the compactness of the polycrystals were affected according to the presence status and the contents of doped F and Al.

Acknowledgments

This work was supported by the 2013 sabbatical year research grant of the University of Seoul.

REFERENCES

1. T. Minami, "New n-type Transparent Conducting Oxides," *MRS Bull.*, **25** [8] 38-44 (2000).
2. D. C. Plain, H. Y. Yeom, and B. Yaglioglu, "Transparent Conducting Oxide Materials and Technology," pp. 79-98 in *Flexible Flat Panel Displays* Edited by G. P. Crawford, John Wiley & Sons, Ltd, Singapore, 2005
3. G. J. Exarhos and X.-D. Zhou, "Discovery-Based Design of Transparent Conducting Oxide Films," *Thin Solid Films*, **515** [18] 7025-52 (2007).
4. Y.-S. Kim and W.-P. Tai, "Electrical and Optical Properties of Al-doped ZnO Thin Films by Sol-Gel Process," *Appl. Surf. Sci.*, **253** [11] 4911-16 (2007)
5. A. Kurz, K. Brakecha, J. Puetz, and M. A. Aegerter, "Strategies for Novel Transparent Conducting Sol-Gel Oxide Coatings," *Thin Solid Films*, **502** [1-2] 212-18 (2006).
6. S. Mridha and D. Basak, "Effect of Thickness on the Structural, Electrical and Optical Properties of ZnO Films," *Mater. Res. Bull.*, **42** [5] 875-82 (2007).
7. C.-S. Hong, H.-H. Park, J. Moon, and H. H. Park, "Effects of Metal (Al, Ga, and In)-Dopants and/or Ag-Nanoparticles on the Optical and Electrical Properties of ZnO Thin Films," *Thin Solid Films*, **515** [3] 957-60 (2006).
8. G. M. Nam and M. S. Kwon, "Transparent Conducting Ga-doped ZnO Thin Film for Flat-Panel Displays with a Sol-Gel Spin Coating," *J. Inf. Disp.*, **9** [3] 8-11 (2008).
9. G. M. Nam and M. S. Kwon, "Al-Doped ZnO via Sol-Gel Spin-Coating as a Transparent Conducting Thin Film," *J. Inf. Disp.*, **10** [1] 24-7 (2009).
10. G. M. Nam and M. S. Kwon, "F-Doped ZnO by Sol-Gel Spin-Coating as a Transparent Conducting Thin Film," *Electron. Mater. Lett.*, **7** [2] 127-31 (2011).