Regular Paper

J. Korean Inst. Electr. Electron. Mater. Eng.
Vol. 30, No. 5, pp. 307-311 May 2017
DOI: https://doi.org/10.4313/JKEM.2017.30.5.307
ISSN 1226-7945(Print), 2288-3258(Online)

In Situ Heat Treatment of ZnO:Al Thin Films Fabricated by RF Magnetron Sputtering

Deok Kyu Kim[a]

Advanced LED Technology Development Project, Samsung Electronics Co. Ltd., Yongin 17113, Korea

(Received February 26, 2017; Revised March 23, 2017; Accepted March 26, 2017)

Abstract: ZnO:Al thin films were deposited on glass substrate by RF magnetron sputtering followed by in situ heat treatment in the same chamber. Effects of in situ heat treatment on properties of ZnO:Al thin films were investigated in this study. As heat treatment temperature was increased, crystal quality was improved first and then it was deteriorated, surface roughness was decreased, and sheet resistance was also decreased. The decrease in sheet resistance was caused by increasing carrier concentration due to decreased surface roughness. The decrease in surface roughness resulted in increase of transmittance. Therefore, in situ heat treatment is an effective method for obtaining films with better electrical characteristics.

Keywords: ZnO:Al, RF magnetron sputtering, In situ heat treatment, Surface roughness

1. INTRODUCTION

According to the rapid progress in IT industry, the interests in transparent conductive oxide (TCO) due to the developments of optoelectronic such as organic light emitting diodes, solar cells, and light emitting diodes had been very intensive [1-3]. In general, indium tin oxide (ITO), which is most widely used, has low specific resistance, high transmittance within the visible area and high work function and then has very suitable characteristics as a TCO [4]. However, due to toxicity and high cost of In metal, the need to develop new material for transparent electrode is increasing [5]. Therefore, as an alternative ITO, ZnO:Al thin film has attracted much attention for many researchers. ZnO:Al has a very low specific resistance, high transmittance within the visible area, and because of a strong bonding of Zn-O, it is thermally and mechanically stable [6]. This characteristic makes it highly suitable for next generation transparent electrode material that could replace ITO. Recently, there are many active studies being performed to apply ZnO:Al thin film to TCO, fabricating the thin film using magnetron sputtering, atomic layer deposition, and pulsed laser deposition [7-9]. Among these methods, magnetron sputtering has been the most popular technique to deposit ZnO thin films. It was found that the properties of ZnO:Al films are strongly dependent upon the preparation conditions such as sputtering power, chamber pressure, and substrate temperature, in addition, heat treatment is also found to be an effective method to improve the properties [10-13]. There have been many previous studies on ex situ heat treatment but no previous reports showing the effects of in situ heat treatment on the properties of ZnO:Al thin films deposited by RF magnetron sputtering.

a. Corresponding author; dkkim@cju.ac.kr

Copyright ©2017 KIEEME. All rights reserved.
This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

In this study, the ZnO:Al thin film was deposited by

RF magnetron sputtering and then prepared by in situ heat treatment in the same chamber. The structures, the electrical and the optical characteristics of ZnO:Al thin films before and after in situ heat treatment were systematically analyzed.

2. METHOD FOR EXPERIMENT

Using ZnO target that is added with 2 wt% Al_2O_3, the ZnO:Al thin film was deposited by RF magnetron sputtering. The glass substrate (corning 1737) was used, and in order to remove impurities on the substrate, the acetone, methanol and distilled water were used for ultra-sonic cleaning, and it was performed for 10 minutes, respectively. The sputtering chamber was evacuated to 8.0×10^{-6} Torr before sputtering. During the film deposition, the ambient gas was the argon (40 sccm), and the working pressure was maintained at 15 mTorr. Prior to deposition, the target was pre-sputtered for 10 min in order to remove any contamination. The RF sputtering power was 150 W and the thickness of the ZnO:Al films was approximately 1 um. All the films were deposited at 500℃ during 1 hour. After deposition process, the samples were heat treated for 2 hours at 600℃ and 800℃ in the same chamber with Ar atmosphere. And then, natural cooling was performed.

The structural properties were analyzed with an X-ray diffraction (XRD, D/MAX III A) using a Cu Kα radiation. The surface morphology was investigated by atomic force microscopy (AFM, PUCOTECH). The electrical properties were measured at room temperature using a standard Hall measurement system (ECOPIA HMS-3000) in van der Pauw method. The optical properties were examined using a UV/VIS/NIR spectrophotometer (SHIMADZU, UV-2401PC).

3. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns of ZnO:Al thin film before and after in situ heat treatment. In case of the ZnO:Al thin film before heat treatment, two diffraction

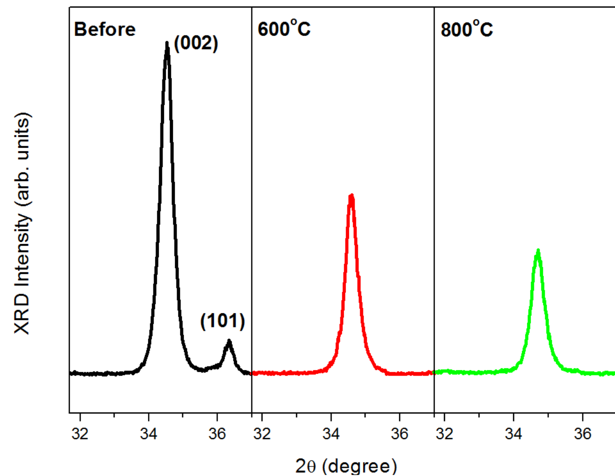

Fig. 1. XRD patterns of ZnO:Al thin films before and after in situ heat treatment at 600℃ and 800℃.

peaks were observed at 2θ position of 34.5° and 36.3° which were attributed to (002) and (101) planes of ZnO phase, respectively. A strong (002) peak of preferred orientation and relatively weak (101) peak was observed. This result showed the ZnO:Al thin films were polycrystalline and had a hexagonal structure. In case of the ZnO:Al films after heat treatment, the (101) peak disappeared by rearrange the atoms due to the heat energy. Also, the large difference between the intensity and full width at half maximum (FWHM) of the XRD peak of ZnO:Al thin film before and after heat treatment was verified. The intensity of XRD peak of ZnO:Al thin film before heat treatment was approximately 9,000 and the FWHM was measured to be 0.44°. The intensity for ZnO:Al thin film after 600℃ heat treatment showed peak of 5,500, which is reduction by 1.6 times of the ZnO:Al thin film before the heat treatment, and the FWHM was decreased by 0.42°. Also, the intensity for ZnO:Al thin film after 800℃ heat treatment was 4,500, which is a reduction by 2 times, compared to ZnO:Al thin film before the heat treatment, and FWHM was highest increase, at 0.48°. It is well known that FWHM is important factor judging the crystal quality. That is, the decrease in the FWHM after 600℃ heat treatment indicated a better crystal quality but the increase in the FWHM after 800℃ heat treatment showed a worse crystal quality. The result

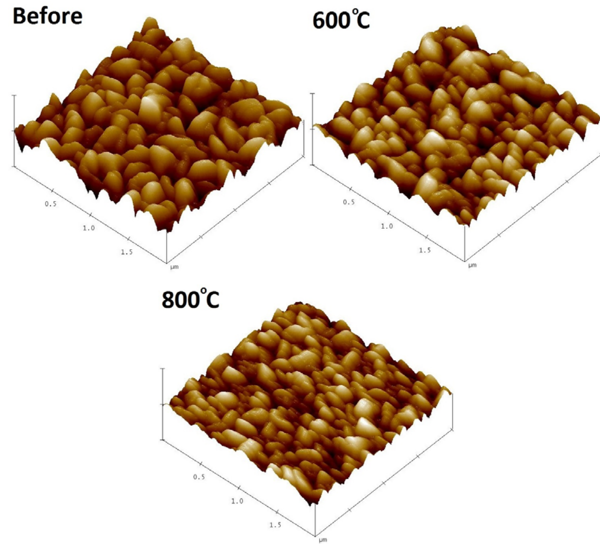

Fig. 2. AFM 3D images of ZnO:Al thin films before and after in situ heat treatment at 600℃ and 800℃.

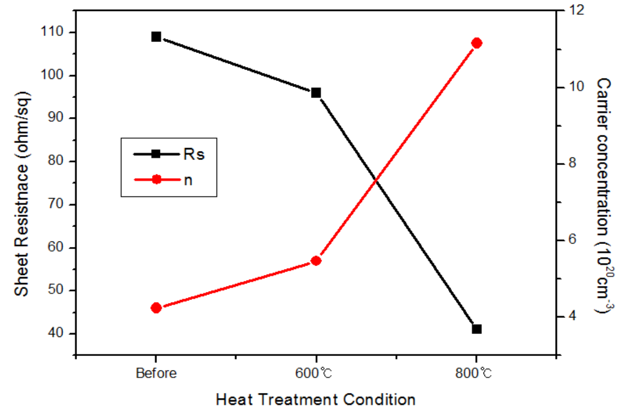

Fig. 3. Hall results of ZnO:Al thin films before and after in situ heat treatment at 600℃ and 800℃.

of 800℃ heat treatment is attributed to the severe detachment of surface atoms, leading to deteriorate the crystal quality. The average crystallite size was calculated using the Scherrer equation [14]:

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

where λ is the wavelength of X-ray radiation (1.5406 Å), B is the FWHM of the sample, and θ is the Bragg diffraction angle. As the heat treatment temperature increased, the average crystallite size first increased from 18.1 nm to 18.9 nm and then decreased to 16.6 nm. XRD results implied that microstructures of ZnO:Al thin film were influenced by heat treatment temperature.

Figure 2 is AFM 3D images of ZnO:Al thin film before and after in situ heat treatment. The image scale used for 3D surface analysis was set at 2×2 μm^2. As shown in the figure, the surface morphology of ZnO:Al film before heat treatment is found to be continuous, dense and hill- like surface textures. The surface roughness of ZnO:Al thin film before heat treatment was 27.7 nm and its crystal size was 206 nm. However, the surface roughness for ZnO:Al thin film after 600℃ heat treatment was 20.5 nm and its crystal size was 137 nm. Also, the surface roughness and the crystal size for ZnO:Al thin film after 800℃ heat treatment were 15.6 nm and 112 nm respectively. It can be seen that the surface roughness and the crystal size of ZnO:Al thin film after heat treatment is decreased rather than ZnO:Al thin film before heat treatment, thus indicating smoothness of the surface after heat treatment. These changes occurred owing to the thermal decomposition of the ZnO:Al thin film and the consequent desorption from the surface of the substrate [15].

In order to perform quantitative analysis for electrical properties, the Hall effects analysis was carried out. Figure 3 displays the Hall results of ZnO:Al thin film before and after in situ heat treatment. The sheet resistance and carrier concentration of ZnO:Al thin film before heat treatment were 109 Ω/□ and 4.2×10^{20} cm^{-3}, respectively. Also, the sheet resistance and carrier concentration of ZnO:Al thin film after 600℃ heat treatment were 96 Ω/□ and 5.5×10^{20} cm^{-3}, respectively. In particular, the sheet resistance and carrier concentration of ZnO:Al thin film after 800℃ heat treatment were 41 Ω/□ and 11.6×10^{20} cm^{-3}, respectively. From these Hall results, the best electric property is obtained in ZnO:Al thin film after 800℃ heat treatment. The reduction of sheet resistance for ZnO:Al thin film after heat treatment is due to increase in carrier concentration. Also, the increase in carrier concentration after heat treatment may be attributed to a decrease in surface

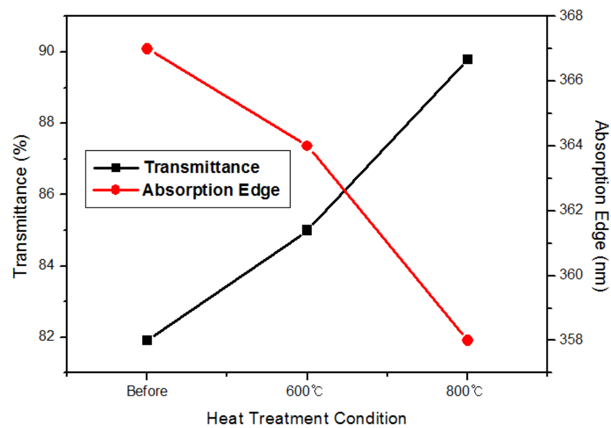

Fig. 4. Optical properties of ZnO:Al thin films before and after in situ heat treatment at 600℃ and 800℃.

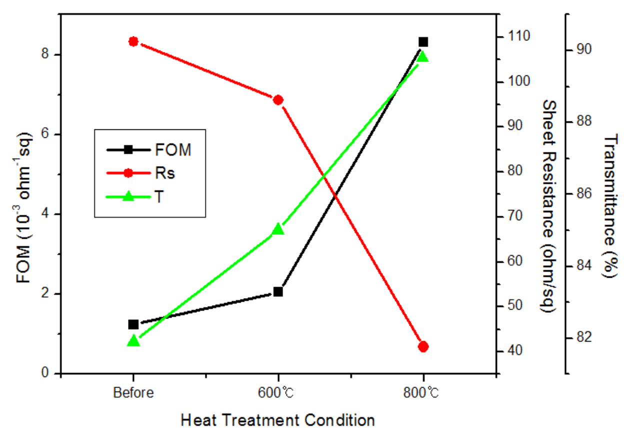

Fig. 5. FOM of ZnO:Al thin films before and after in situ heat treatment at 600℃ and 800℃.

roughness. The decrease in surface roughness decreases the number of absorption sites for oxygen causing resistivity to increase, resulting in decrease of the electrical resistivity. In general, oxygen adsorbed on the surface traps electrons and decreases carrier concentration [16]. That is, the in situ heat treatment minimizes the chemisorption of oxygen on the surface because of the heat treatment in the deposition chamber. Whereas, the ex situ heat treatment increases the possibility of chemisorption of oxygen on the surface because of the movement into the external chamber [17]. Therefore, we can conclude that the decrease in sheet resistance of ZnO:Al film after heat treatment can be contributed to the increase in the carrier concentration caused by the decrease in surface roughness. As a result, it confirmed that the most suitable temperature at which to apply heat treatment to obtain the best electrical characteristic is 800℃.

Figure 4 shows the optical properties of ZnO:Al thin film before and after in situ heat treatment. The average transmittance (T_a) of ZnO:Al thin film before heat treatment in the visible range (400~800 nm) was 82%. However, the T_a of ZnO:Al thin film after 600℃ heat treatment increased to 85%, which is 3% more than the T_a of ZnO:Al thin film before heat treatment. Especially, the T_a of after 800℃ heat treatment was approximately 90%. The increase of optical transmittance of ZnO:Al film with increasing heat treatment temperature can be due to the reduction of scattering and absorption of light caused by the decrease of surface roughness. Also, it can be seen that the absorption edge of the ZnO:Al film is observed below 380 nm, and a blue shift of the absorption edge occurs with increasing heat treatment temperature. This band gap broadening can be explained using the Burstein−Moss (BM) effect. According to BM effect, the increase in the Fermi level in the conduction band causes an increase in carrier concentration as wel las the expansion of the band gap energy [18].

Figure 5 shows the figure of merits (FOM) suggested by Haacke [19] a function of the RF power. It is defined as

$$\Phi = \frac{T_a^{\,10}}{Rs} \tag{2}$$

where T_a is the average transmittance in the visible range and Rs the sheet resistance of the film. Expressions are derived to predict the transparent electrode properties of material from its fundamental electrical and optical constants. In our case, the FOM was strongly dependent on sheet resistance because the change of FOM shows the same trend with that of sheet resistance. It is possible to observe a decrease in the figure of merit with increasing the heat treatment temperature. The highest value of FOM was 8.3×10^{-3} ohm^{-1}square for the ZnO:Al film after heat treatment at 800℃.

4. CONCLUSION

ZnO:Al thin films were deposited by RF magnetron sputtering and prepared by in situ heat treatment. It was found that the structural, electrical, and optical properties of the ZnO:Al films were affected by the in situ heat treatment temperature. The surface roughness is decreased and the sheet resistance is decreased as the heat treatment temperature is increased. The increment of sheet resistance was ascribed to the decrement of carrier concentration due to the reduction of the surface roughness. The in situ heat treatment is a major factor to determine the structural, electrical and optical of ZnO:Al films.

REFERENCES

[1] X. Jiang, F. L. Wong, M. K. Fung, and S. T. Lee, *Appl. Phys. Lett.,* **83**, 1875 (2003). [DOI: https://doi.org/10.1063/1.1605805]

[2] J. Muller, B. Rech, J. Springer, and M. Vanecek, *Solar Energy,* **77**, 917 (2004). [DOI: https://doi.org/10.1016/j.solener.2004.03.015]

[3] T. Minami, S. Takata, and T. Kakumu, *J. Vac. Sci. Technol. A,* **14**, 1689 (1996). [DOI: https://doi.org/10.1116/1.580320]

[4] T. Minami, T*hin Solid Films,* **516**, 5822 (2008). [DOI: https://doi.org/10.1016/j.tsf.2007.10.063]

[5] N. R. Armstrong, C. Carter, C. Donley, A. Simmonds, P. Lee, and M. Brumbach, *Thin Solid Films,* **445**, 342 (2003). [DOI: https://doi.org/10.1016/j.tsf.2003.08.067]

[6] M. Miyazaki, K. Sato, A. Mitsui, and H. Nishimura, *J. Non-Crystalline Solids,* **218**, 323 (1997). [DOI: https://doi.org/10.1016/S0022-3093(97)00241-X]

[7] A. Mosbah and M. S. Aida, *J. Alloys Compd.,* **515**, 149 (2012). [DOI: https://doi.org/10.1016/j.jallcom.2011.11.113]

[8] H. Kumarakuru, D. Cherns, and G. M. Fuge, *Surf. Coat. Technol.,* **205**, 5083 (2011). [DOI: https://doi.org/10.1016/j.surfcoat.2011.05.011]

[9] P. Baneerjee, W. J. Lee, K. R. Bae, S. B. Lee, and G. W. Rubloff, *J. Appl. Phys.,* **108**, 043504 (2010). [DOI: https://doi.org/10.1063/1.3466987]

[10] S. Y. Kuo, K. C. Liu, F. I Lai, J. F. Yang, W. C. Chen, M. Y. Hsieh, H. I. Lin, and W. T. Lin, *Microelectronics Reliability,* **50**, 730 (2010). [DOI: https://doi.org/10.1016/j.microrel.2010.01.042]

[11] C. H. Tseng, W. H. Wang, H. C. Chang, C. P. Chou, and C. Y. Hsu, *Vacuum,* **85**, 263 (2010). [DOI: https://doi.org/10.1016/j.vacuum.2010.06.006]

[12] A. I. Ali, A. H. Ammar, and A. Abdel Moez, *Superlattices Microstruct.,* **65**, 285 (2014). [DOI: https://doi.org/10.1016/j.spmi.2013.11.007]

[13] W. F. Yang, Z. Y. Wu, Z. G. Liu, A. S. Pang, Y. L. Tu, and Z. C. Feng, *Thin Solid Films,* **519**, 31 (2010). [DOI: https://doi.org/10.1016/j.tsf.2010.07.048]

[14] B. D. Cullity, *Elements of X-ray Diffraction* (Addison-Wesley Reading, Boston, 1978) p. 102.

[15] I. W. Kim, S. J. Doh, C. C. Kim, J. H. Je, J. Tashiro, and M. Yoshimoto, *Appl. Surf. Sci.,* **241**, 179 (2005). [DOI: https://doi.org/10.1016/j.apsusc.2004.09.087]

[16] Y. Igasaki and H. Saito, *Thin Solid Films,* **199**, 223 (1991). [DOI: https://doi.org/10.1016/0040-6090(91)90004-H]

[17] B. D. Ahn, S. H. Oh, C. H. Lee, G. H. Kim, H. J. Kim, and S. Y. Lee, *J. Cryst. Growth,* **309**, 128 (2007). [DOI: https://doi.org/10.1016/j.jcrysgro.2007.09.014]

[18] J. H. Oha, K. K. Kim, and T. Y. Seong, *Appl. Surf. Sci.,* **257**, 2731 (2011). [DOI: https://doi.org/10.1016/j.apsusc.2010.10.053]

[19] G. Haacke, *J. Appl. Phys.,* **47**, 4086 (1976). [DOI: https://doi.org/10.1063/1.323240]