한국신·재생에너지학회 2006년도 춘계학술대회논문집 pp.162~165

H_2/Ar 분위기에서 제조한 투명전극용 ZnO:Al 박막의 특성

탁 성주[1], 이정섭[2], 김원목[3], 김 동환[4]

Characteristics of ZnO:Al Thin Films for TCO Prepared by RF Magnetron Sputtering in H_2/Ar Atmosphere

Sung Ju Tark, Jeong-Seop Lee, Won Mok Kim and Donghwan Kim

Key words : ZnO(Zinc Oxide), TCO (투명전극), rf magnetron sputtering(rf 마그네트론 스퍼터링) H_2 atmosphere (수소분위기)

Abstract : AZO (ZnO:Al) were fabricated by RF magnetron sputtering in H_2/Ar (5 % H_2) atmosphere, and structural, electrical and optical properties were investigated. The substrate temperatures were varied at RT, 100 ℃, 150 ℃ and 200 ℃. The resistivity of the films grown in H_2/Ar(5 % H_2) were reduced from $7.67\times 10^{-4}\ \Omega\cdot cm$ to $5.95 \times 10^{-4}\ \Omega\cdot cm$ comparing that Ar (100 %) and the transmittance of the ZnO:Al films in the visible range was 85 %.

1. Introduction

Zinc oxide films (ZnO) have been studied with a focus on applications to sensors, transparent electrodes in display, heat mirrors and transparent conductive oxide (TCO) coatings for solar cell [1-5]. ZnO is a wide optical band gap material with wurtzite crystal structure, which exhibits a change in conductivity with the doping of Al, Ga or In. Because of their chemical stability, the ZnO films, particularly, aluminum-doped films, are more useful in the fabrication of thin film solar cells compared to Sn-doped In_2O_3 (ITO) [6]. Among the known TCO materials ITO has most extensively been used as it yields excellent electrical properties, can be processed easily and deposition methods are well known. However ITO is a rather expensive metal and the ever increasing demand for the material caused by the large growth of the market for FPDs has caused prices to rice further over the last 2 years. This has cause an increased effort to improve material properties and production processes for other TCO materials. The properties of zinc oxide as TCO material have been extensively studied[7]. The most promising doping materials are Ga and Al. Al-doped ZnO films have been produced by a variety of deposition techniques, including sol-gel coating, ion plating, spray pyrolisis, chemical vapour deposition (CVD), pulsed laser ablation and magnetron sputtering.

The essential parameters which decide the film properties prepared by sputtering technique are the substrate temperature and the amount of hydrogen. Although many reports are available on the preparations of ZnO:Al films using sputtering, we desired to examine the influence of the above stated parameters on the properties of these films.

In this work, we prepared aluminum-doped zinc oxide films (ZnO:Al) by rf magnetron sputtering in H_2/Ar (5 % H_2) atmosphere and investigated the mutual dependence of electrical, optical and structural properties of the films.

1) 고려대학교 신소재공학과
E-mail : solar@korea.ac.kr
Tel : (02)3290-3713 Fax : (02)928-3584
2) 고려대학교 신소재공학과
E-mail : tarkwind@korea.ac.kr
Tel : (02)928-8466 Fax : (02)928-3584
3) 한국과학기술연구원 박막재료 연구센터
E-mail : wmkim@kist.re.kr
Tel : 02)958-5384 Fax : (02)928-3584
4) 고려대학교 신소재공학과
E-mail : solar@korea.ac.kr
Tel : (02)3290-3713 Fax : (02)928-3584

2. Experimental procedure

The ZnO:Al thin films were deposited on glass (Corning 2947) substrates using a rf magnetron sputtering in H_2/Ar atmosphere. The sputtering targets used in this experiment were specifically designed using high-purity of zinc oxide (99.99%) and aluminum hydroxide (99.99%) powders. The sputtering system was pumped down to 1×10^{-6} Torr using a turbo molecular pump. The glass substrates were ultrasonically cleaned in de-ionized water, acetone, alcohol and de-ionized water, sequentially, and finally dried with nitrogen gas. The substrates were heated in the temperature range of RT ~ 200 ? and also were rotated using a motor in order to get uniform ZnO:Al films. During the film growth, the total amount of argon and hydrogen was maintained at 20 sccm (5 % H_2). The electrical properties were measured using the van der Pauw Hall method. Optical transmission spectra were measured in the wavelength range from 250 to 800 nm. The film thickness was measured by a stylus surface profiler (Dektak ST, Veeco Instruments Inc.). And crystallinity of ZnO:Al films was investigated by X-ray diffraction using a CuK_{α}source.

3. Results and discussion

The most important parameters required for the application of ZnO:Al film as a transparent conductor are its low electrical resistivity and high optical transmittance(7). Hence, emphasis was given in this study to prepare highly transparent and low resistive films.

X-ray diffraction patterns of the ZnO:Al films deposited in H_2/Ar (5 % H_2) atmosphere at different substrate temperature (RT ~ 200℃) are shown in Fig. 1.

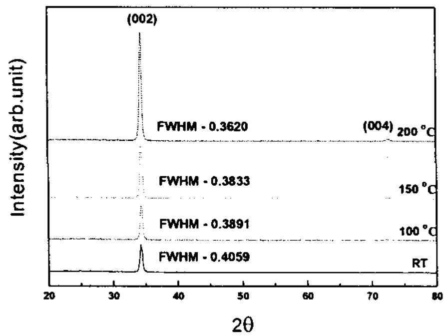


Fig. 1. XRD pattern of AZO thin films as a function of temperature.

All the films are found to have the hexagonal wurtzite structure. A prominent (002) peak indicates that the crystallite structure of the films is oriented with their c-axis perpendicular to the substrate plane(8). But H_2 addition in substrate room temperature slightly weaken the relative intensity of c-axis (002) peak. As rising temperature, c-axis (002) peak markedly weakened and (103) peak is highly enhanced. We observed improved surface roughness of the ZnO:Al films, because hydrogen enhanced (103) orientation.

A significant drop in resistivity is observed if hydrogen is added to the sputtering gas. Fig. 2.shows the resistivity of the ZnO:Al films sputtered in H_2/Ar (5 % H_2) atmosphere. We observe a drop of up to 22 % in resistivity from 7.67×10^{-4} $\Omega \cdot cm$ at room temperature to 5.95×10^{-4} $\Omega \cdot cm$ at 150℃. Except ZnO, all other semiconductors, interstitial hydrogen has been found to act as an amphoteric impurity(9). In p-type material, hydrogen incorporates as H^+ (a donor), and in n-type material as H^- (an acceptor), always counteracting the prevailing conductivity of the material. This amphoteric behavior precludes hydrogen from acting as a dopant. In ZnO, however, hydrogen occurs exclusively in the positive charge state. It always acts as a donor(10). From this reason the hydrogen plays an important role in n-type conduction as a donor(11).

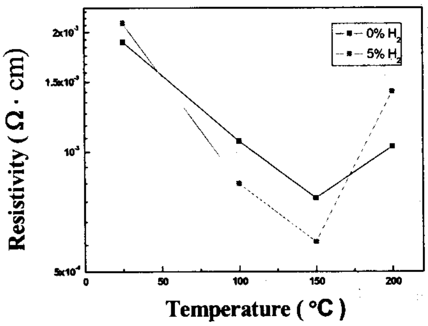


Fig. 2. Variation of the resistance of Ar (100 %) and H_2/Ar (5 % H_2) with the temperature.

Fig.3 gives the substrate temperature dependence of carrier concentration and hall mobility for the ZnO:Al thin films. All of these measurements show that the ZnO:Al thin films are degenerate doped n-type semiconductors. It can be seen that as the substrate temperature increases from 0 to 0.2, the carrier concentration and hall mobility decrease from -4.9 × 10^{20} cm^{-3} to -9.4 × 10^{20} cm^{-3} and 8 $cm^2V^{-1}s^{-1}$ to 13 $cm^2V^{-1}s^{-1}$

Fig. 4 show the variations of the optical transmittance of the ZnO:Al thin films with the H_2-flow, respectively. The average transmittance in the visible range is measured to be about 85 %, which is sufficient for a transparent conductive electrode. The optical transmittance of these films is not influenced by the H_2-flow.

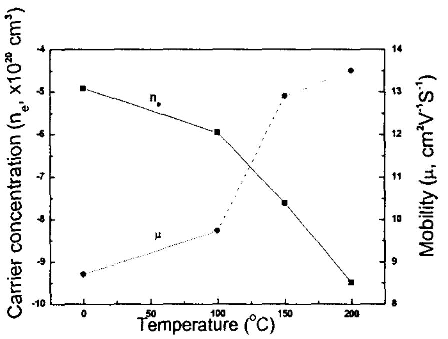


Fig. 3. Hall mobility and carrier concentration of AZO thin films as a function of temperature.

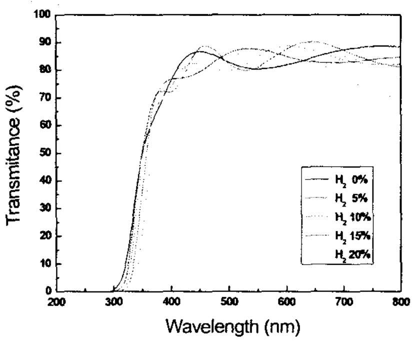
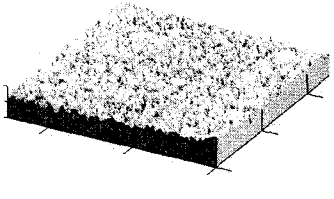
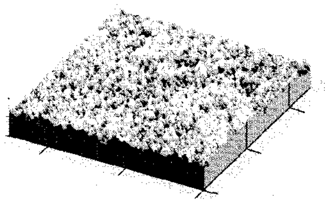


Fig. 4. Transmittance of AZO thin films as a function of H_2-flow.

ZnO:Al thin films have become attractive for solar cell. To be used for solar cell front electrode, RMS roughness of ZnO:Al should be more over 100 Å. Fig. 5 shows the RMS roughness of ZnO:Al. When substrate temperature is 150℃, RMS roughness is increased from 35.78 Å to 111.83 Å by in growing H_2/Ar (5 % H_2) atmosphere(12-13). The reason is that hydrogen enhanced (103) orientation.



(a)



(b)

Fig. 5. AFM images of (a) Ar (100 %), (b) H_2/Ar (5 % H_2).

4. Conclusions

ZnO:Al thin films were deposited on glass substrates at different substrate temperature in H_2/Ar (5 % H_2) atmosphere by rf magnetron sputtering. The electrical, optical and structural properties of the films were studied as a function of substrate temperature during deposition from the viewpoint of their application as transparent electrodes. As we can see in XRD diffraction pattern, we can find H_2 addition in substrate room temperature slightly weaken the relative intensity of c-axis (002) peak. And adding H_2 make the (103) peak highly enhanced. It affects the surface roughness. Highly transparent (T > 85%) ZnO: Al with excellent electrical resistivity 5.95×10^{-4} $\Omega\cdot cm$ could be deposited at a temperature of 150 ℃. And these parameters are comparable to that of ITO films. AFM image clearly shows the surface roughness of the films with the increase of substrate temperature.

References

[1] I. Stambolova, K. Konstantinov, S. Vassilev, P. Peshev, Ts. Tsacheva,Mater. Chem. Phys. 63, p104, 2000.

[2] M. Chen, Z.L. Pei, C. Sun, J. Gong, R.F. Huang, L.S.Wen, Mater. Sci. Eng., B, Solid-State Mater. Adv. Technol. 85, p212, 2001.

[3] Y.R. Ryu, S. Zhu, D.C. Look, J.M. Wrobel, H.M. Jeong, H.W. White,J. Cryst. Growth, 216, p330, 2000.

[4] M.A. Martinez, J. Herero, M.T. Gutierez, Sol. Energy Mater. Sol.Cells, 45, p75, 1997.

[5] K.T.R. Reddy, H. Gopalaswamy, P.J. Reddy, R.W. Miles, J. Crystal.Growth, 210, p516, 2000.

[6] C.G. Granqvist, Thin Solid Films, 193, p730, 1990.

[7] K. Ellmer, J. Phys. D: Appl. Phys., 34, p3097,2001.
[8] M. Yoshino, Wilson, W. Wenes, A. Yamada, M. Konagi, K. Takahasi, Jpn. J. Appl. Phys., 32, p726, 1993.
[9] K. Ellmer, R. Cebulla, R. Wendt, Thin Solid Films, 317, p413, 1998.
[10] Hydrogen in Semiconductors, Semiconductors and Semimetals, edited by J. I. Pankove and N. M. Johnson (Academic Press, Boston), 34. 1991.
[11] Chris G. Van de Walle, The American Physical Society, 85, No. 5, 2000.
[12] Seung Yeop Myong, Koeng Su Lim, Applied Physics Letters, Vol.82, No.18
[13] S.J. Baik, J.H. Jang, C.H. Lee, W.Y. Cho, K.S. Lim, Appl. Phys. Lett. 70, p3516, 1997.
[14] Seung Yeop Myong, Koeng Su Lim, Applied Physics Letters, Vol.82, No.18