태양전지용 ZnO:Al 투명 전도막 제작

탁 성주[1], 강 민구[2], 김 동환[3]

Preparation of ZnO:Al transparent conductive films for solar cell

Sung Ju Tark, Mingu Kang and Donghwan Kim

Key words : ZnO(Zinc Oxide), solar cell(태양전지), rf magnetron sputtering(rf 마그네트론 스퍼터링)

Abstract : Highly transparent ZnO films with low resistivity for thin film solar cell applications were fabricated at low temperature by rf magnetron sputtering. Al-doped ZnO films were deposited on glass substrates at a substrate temperature of 200 ℃. electrical and optical properties of the ZnO:Al films were investigated in terms of the reparation conditions. The transmittance of the ZnO:Al films in the visible range is 90 %. The lowest resistivity of the ZnO:Al films is about 5.7×10^{-4} Ω cm at the Al content of 2.5 wt% with the film thickness of 500 nm. After deposition, the smooth surface of ZnO:Al films were etched in diluted HCl (0.5%) to investigate the variation of electrical and surface morphology properties due to an textured surface.

1. Introduction

Transparent conductive ZnO films have been investigated in recent years because of their good electrical and optical properties, in combination with their large band-gap, abundance in nature and absence of toxicity. The properties exhibited by ZnO thin films depend on the non-stoichiometry of the films, resulting from the presence of oxygen vacancies and interstitial zinc[1]. The electrical and optical properties ZnO are generally dependent on deposition techniques[2] and post-annealing conditions[3], because these properties change significantly with the absorption of oxygen that occurs during these processes.

Recently we have reported that sputtered ZnO:Al films prepared under adapted deposition conditions can be textured by wet chemical etching in diluted hydrochloric acid. We present a more detailed investigation of the interrelation between the structural properties of initial film and the resulting morphology of etched film in an accompanying paper. For films with an appropriate structure the duration of the etching process controls the surface texture.

In this report, we describe the effect of sputtering parameters on the structural, electrical and optical properties of ZnO:Al thin films. Moreover, we will show promising results demonstrating an improved light trapping due to the textured surface formed by an etching technique.

2. Experimental procedure

1) 책임 저자의 소속
E-mail : solar@korea.ac.kr
Tel : (02)3290-3713 Fax : (02)928-3584
2) 저자2의 소속
E-mail : solar@korea.ac.kr
Tel : (02)3290-3713 Fax : (02)928-3584
3) 저자3의 소속
E-mail : solar@korea.ac.kr
Tel : (02)3290-3713 Fax : (02)928-3584

The ZnO:Al thin films were deposited on glass (Corning 2947) substrates using a rf magnetron sputtering system. 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 X 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 rf sputtering power was varied from 100 to 250 W. Discharge has been done in a mixing gas of Ar and O_2. As the main working gas, Ar gas was used. Then O_2 gas was added. The ratio of the gas flow rate [O_2(Ar/O_2)], which is called 'O_2 gas flow ratio' hereafter, with a constant total pressure of 1 mTorr was varied. ZnO:Al thin films were deposited on the substrates at a room temperature or 200 ℃.

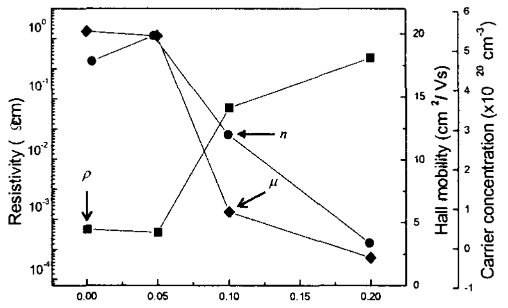
Depending on their structural properties these films develop a textured surface during etching in diluted HCl solutions (0.5 %, HCl/H_2O). The electrical properties were measured using the van der Pauw Hall method. Optical transmission spectra were measured in the wavelength range from 250 to 800 nm. The film thickness was measured by a stylus surface profiler (Dektak ST, Veeco Instruments Inc.).

3. Results and discussion

3.1 Electrical properties

Figure 1 gives the O_2 gas flow ratio dependence of the resistivity, carrier concentration and hall mobility for the ZnO:Al thin films. All effective measurements shows that the ZnO:Al thin films are degenerate doped n-type semiconductor. It can be seen that as the O_2 gas flow ratio increases from 0 to 0.2, both carrier concentrations and hall mobility decreases from 5.37$10^{20}$ to 1.46$10^{20}$ cm^{-3} and 20.19 to 2.2 cm^2 V^{-1} s^{-1}, respectively, whereas resulting the resistivity of the films increases from 6.53$10^{-4}$ to 1.95$10^{-1}$ cm. The highest value of the resistivity of ZnO:Al thin films is approximately 5.86 cm at O_2 gas flow ratio 0.05. The resistivity of ZnO:Al thin films increased rapidly between O gas flow ratio 0.1 and 0.2, because the oxygen voids in the thin films aresubstituted for oxygen atoms and the additional oxygen atoms in the films effectively function as carrier traps [4].

Fig. 1. O_2 gas flow ratio dependence of Resistivity, Hall mobility and Carrier concentration of ZnO:Al thin film.



3.2 Optical properties

Figure 2 show the variation of optical transmittance of the ZnO:Al thin films deposited at various rf power, respectively. The average transmittance in the visible range is measured to be about 90.7 %, enough for a transparent conductive electrode. The optical transmittance of these films is not influenced by rf power. It means that, ZnO:Al thin films provides an excellent UV shielding.

Fig. 2. Optical transmission spectra for the ZnO:Al thin films with various rf powers.

3.3 Surface-textured ZnO:Al

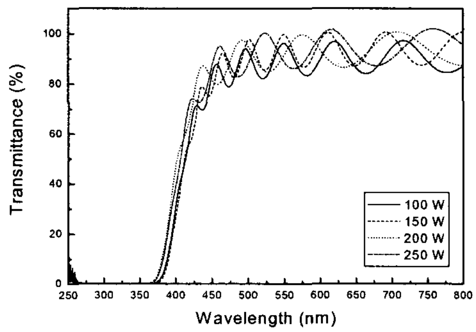
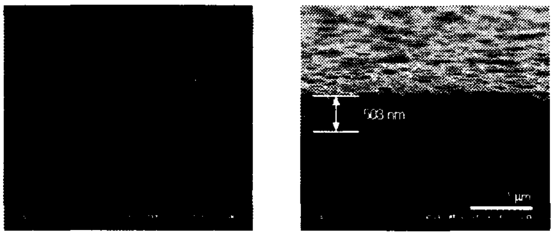
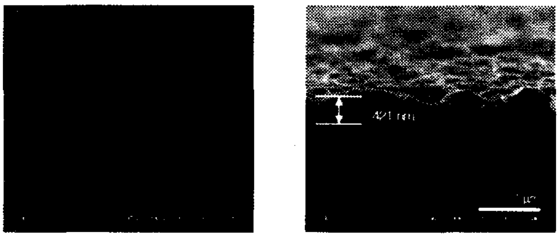


Figure 3 (a) shows the SEM (scanning electron microscopy) image of a ZnO:Al film deposited at an rf power of 200W, working pressure of 1 mTorr and at a substrate temperature of 200 ℃. The image reveals the smooth nature of the as-grown ZnO:Al film. Etching of these films results in distinctly different surfaces. As-grown ZnO:Al were subjected to a 0.5 % diluted HCl etching. The SEM image of the film etched for 8 sec is shown in the Figure 3 (b). Particularly striking is fact that the averages feature sizes of

ZnO:Al thin films are significantly smaller than that of etched ZnO:Al (root mean square roughness δ_{rms}=80 ~ 120), whereas the structure perform quite similar when applied in solar cell.



(a)



(b)

Fig. 3. SEM image of two typical surface of (a) ZnO:Al and (b) texture-etched ZnO:Al thin film.

Figure 4 shows the transmittance of the ZnO:Al thin films deposited at an rf power of 200 W and at different etching time ranging from 0 to 20 sec. From the spectrum, we can observe the decrease of the transmittance with increase in etching time.In order to study the effect of etching time on the optical properties of the films, a typical film deposited at an rf power 200 W and substrate temperature of 200℃ with 1 mTorr working pressure was chosen. The variation in the total transmittance, the diffuse transmittance and also the haze parameter are studied as a function of etching time (Figure 5). It is observed that both the total and diffuse transmittance increase with the increase in the etching time, which is attributed to the decrease in the film thickness.

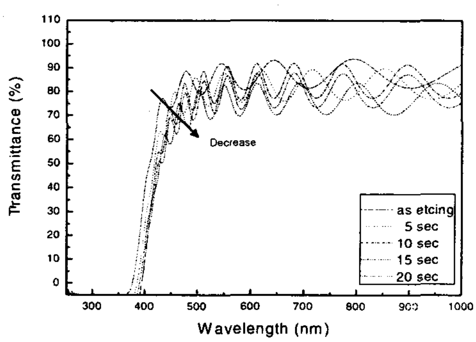


Fig. 4. Optical transmission spectra of the surface textured AZO films with various etching time.

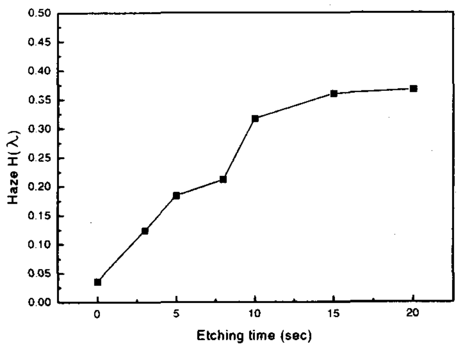


Fig. 5. Change of Haze spectra(b) of AZO films prepared with different etching time.

Figure 6 gives the etching time dependence of the resistivity and rms roughness for the ZnO:Al films. As the etching time increases from 0 to 20 sec, RMS roughness increases from 27 to 438 nm. The lowest value of the resistivity of ZnO:Al films was approximately 5.7$10^{-4}$ cm . In addition to the AFM studies, the SEM morphological studies on the films show the denser and compact film structure which will be useful for effective light-trapping in thin film silicon solar cells.

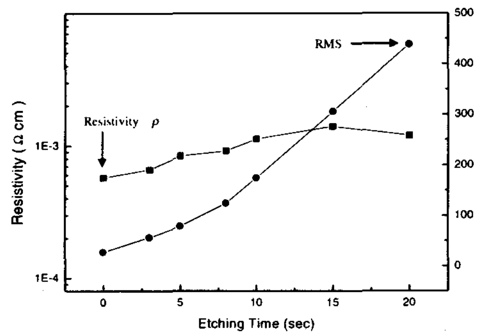


Fig. 6. Change of resistivity and RMS value of AZO films prepared with different etching time.

4. Conclusions

ZnO:Al thin films were deposited on glass substrate by rf magnetron sputtering. The obtained films were polycrystalline with the hexagonal structure and had a preferred orientation with the c-axis perpendicular to the substrates. The average transmittance for prepared sample was over 90.7 % in the visible range and the lowest resistivity was 5.71cm. Moreover, the surface morphology of films exhibits a more dense and compact film structure with effective light trapping to apply the solar cell.

References

[1] S. Major, K.L. Chopra, 1998, "Indium-doped zinc oxide films as transparent electrodes for solar cells", Sol. Energy Mater. Vol. 17, p 319.

[2] K. Ellmer, 2000, "Magnetron sputtering of transparent conductive zinc oxide: relation between the sputtering parameters and the electronic properties",J. Phys. D: Appl. Phys. Vol. 33, R17.

[3] A. Malik, A. Seco, R. Nunes, E. Fortunato, R. Martins, 1997, "Spray-Deposited Metal Oxide Films with Various Properties for Micro- and Optoelectronic Applications: Growth and Characterization", Mater.Res. Soc. Symp. 471, 47.

[4] T. Minami, H. Nanto and S. Takata, 1985, "Optical Properties of Aluminum Doped Zinc Oxide Thin Films Prepared by RF Magnetron Sputtering", Jpn. J. Appl. Phys. 24, L605.