CHIN. PHYS. LETT. Vol. 29, No. 3 (2012) 038103

Optical and Mechanical Properties of Transparent Conductive Al-Doped ZnO Films Deposited by the Sputtering Method *

ZHU Yun(竺云)**, WANG Yue(王越), WAN Peng-Fei(宛鹏菲), LI Hong-Yu(李洪玉), WANG Shou-Yu(王守宇)

College of Physics and Electronic Information Science, Tianjin Normal University, Tianjin 300387

(Received 8 October 2011)

Al-doped ZnO transparent conductive oxide thin films (AZO) are prepared by the magnetron sputtering method. The structural, optical and mechanical properties of the AZO films are studied systematically. The average haze of the AZO sample is increased from 0.34% to 23.6% through wet etching treatment between 380 and 1100 nm, and the etched AZO sample has a higher average transmittance of about 82.3% in infrared wavelength range from 760 to 1100 nm due to the reduction of absorption by carriers. The average hardness and elastic modulus of the as-deposited AZO films, as determined using the nanoindentation technique, are approximately 10.2 GPa and 130 GPa, respectively. The critical fracture load related to the adhesion strength is about 91 mN. The optimized optical and electrical properties and referable mechanical data indicate that AZO films have good prospects for commercial applications.

PACS: 81.15.Cd, 68.35.Gy DOI: 10.1088/0256-307X/29/3/038103

Transparent conducting oxide (TCO) thin films have been widely used in photovoltaic devices,[1] liquid crystal displays,[2,3] sensors[4] and organic light emitting diodes.[5] The demand for large-area, high-quality solar cells requires that the transparent electrode films have high optical transparency (more than 80%) in the visible spectrum range, high electrical conductivity (about $10^3\,\Omega^{-1}\mathrm{cm}^{-1}$ or more)[6] and good mechanical properties. Among all of the TCO materials, zinc oxide (ZnO) thin films doped with group Ⅲ elements such as aluminum, boron, gallium, and indium,[7−10] or group Ⅶ elements such as fluorine[11,12] have attracted a great deal of interest because of their excellent electrical and optical properties, lower cost, nontoxicity, etc. Al-doped ZnO (AZO) is one of the most widely studied n-type ZnO films. In recent years, deposition methods,[13,14] deposition conditions,[15] and optical and electrical properties of AZO films[15,16] have been investigated in detail. However, reports about the mechanical properties of doped zinc oxide thin films are relatively lacking. Mechanical properties such as hardness or adhesion of TCO thin films are very important in order to guarantee the large-area and durability required for various types of commercial applications. Especially for photovoltaic modules, a tough front contact layer and good adhesion between the layers are needed to ensure more than twenty years service life. The study of mechanical properties may be far-reaching for designing multi-layer TCO thin films, developing micro-scale or nano-scale technology, and fabricating TCO thin films on flexible substrates.

From the previous research results,[15] we have learnt that the fabrication conditions, such as substrate temperature, sputtering power, sputtering pressure (argon pressure), target-to-substrate distance and so on could have a great influence on the optical and electrical properties of AZO films. As the front and back contact layers in solar cells, a rough surface of TCO film has always been used as the light trap to guarantee good light absorption.[17] In this study, we prepare AZO thin films by dc magnetron sputtering under optimized conditions. Then the as-deposited films are roughened by a wet chemical etching process. Next, we systematically measure the optical, electrical, structural and mechanical properties of the films. The measurement of the mechanical properties is focused on the hardness, elastic modulus, and scratch scan by using the nano-indentation technique. It is expected that an AZO film with high electrical conductivity, high optical transparency, appropriate hardness and good adhesion will be obtained in this work.

AZO thin films were prepared on super-white float glass (thickness 3.2 mm, Shandong Jin Jing Technology Co., Ltd., China) at a substrate temperature of 280℃ by dc magnetron sputtering. The Ar pressure was 1.1 Pa and Ar gas flow rate was 15 sccm during sputtering. The purity of the AZO target (ZnO doped with 2wt% Al_2O_3, Polema Co., Ltd.) is 99.999%. Prior to the deposition of AZO films, a 70-nm SiO_2 buffer layer was deposited directly on the glass substrate to prevent the inexhaustible ions diffusing from glass to the TCO film,[18] and the buffer layer also could improve the crystalline quality and adhesive

*Supported by the National Natural Science Foundation of China under Grant No 51001081, the Introduction of Talent Foundation of Tianjin Normal University under Grant No 5RL075, and the Science and Technology Development Fund Planning Project of Tianjin Colleges and Universities under Grant No 20081101.

**Email: wdxyzy@mail.tjnu.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

ability of the TCO films.[19] The as-deposited AZO films used in this study have thicknesses ranging from 700 nm to 1100 nm. In order to achieve a light trapping structure, the deposited AZO films were subsequently roughened by wet chemical etching in hydrochloride acid (0.5%). The etching times were chosen to be 60 s and 80 s, respectively.

An x-ray diffraction (XRD) apparatus (Rigaku powder diffractometer) was employed to reveal the crystallographic structures of the samples using Cu Kα radiation. The surface morphology of the films was analyzed by using an atomic force microscope (AFM, Digital Instruments D3000, USA). The hardness and the elastic modulus of the film were measured by using a nanoindentation system (Nano Indenter XP, MTS Cooperation, USA) with the continuous stiffness measurement (CSM) method. A three-sided pyramidal Berkovich indenter tip with a half angle of 65.38° was used for the indentation. Sheet resistance, concentration, and mobility were measured using Hall effect measurement system (HMS-2000, ECOPIA). The optical transmission of the films was examined with a spectrophotometer (Lambda 750, Perkin Elmer Inc., USA).

Since the sheet resistance is directly connected with the conductivity, the sheet resistance has been measured firstly to examine the as-deposited AZO films. It is indicated that the sheet resistance of 820 nm and 1100 nm AZO films are 6.4 Ω/sq and 4.2 Ω/sq, respectively. Both of them are lower than 10 Ω/sq, which is the basic requirement for TCO films used in solar cells.[6] Considering the manufacturing cost and the uniformity in the research, AZO film with a thickness of 820 nm has been selected as a typical sample in the following discussions.

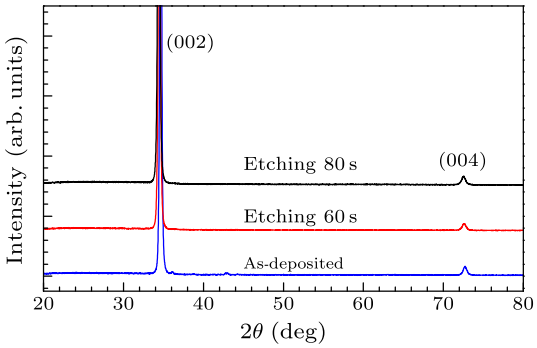

Fig. 1. XRD spectra of AZO films in the as-deposited state and after etching for 60 s and 80 s.

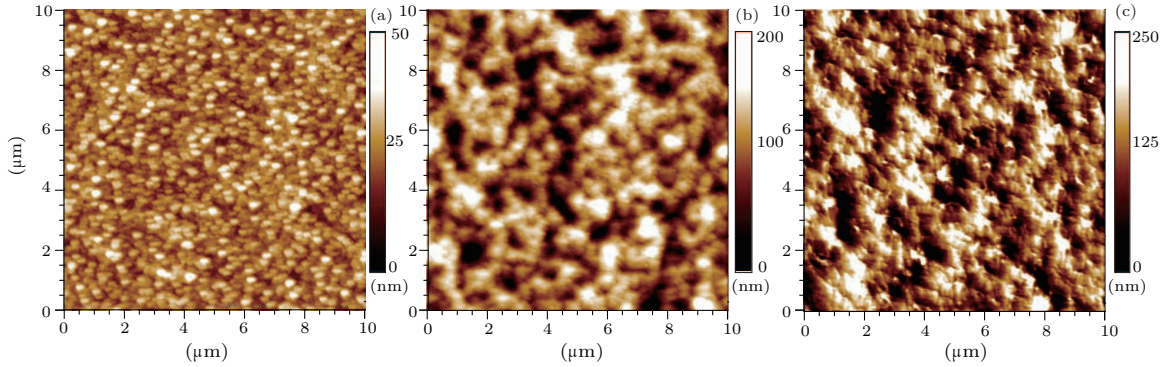

Fig. 2. The atomic force microscope (AFM) images of (a) the as-deposited, (b) etching 60 s, and (c) etching 80 s AZO films.

Figure 1 shows the XRD spectra of the AZO film. The XRD scan of the as-deposited AZO film gives a strong peak at 34.4° and a tiny peak at 72.6°, which corresponds to the (002) and (004) reflection of ZnO, respectively. There is no evidence of an Al_2O_3 phase due to the very low content. The strong peak at 34.4° indicates that (002) orientation is dominant in the polycrystalline structure. Since ZnO is hexagonal close-packed structure, the domination of the (002) orientation means that the c-axis of the grains is perpendicular to the substrate surface. This causes a smooth mirror surface of AZO films and very weak light absorption.[20] In fact, the haze of the as-deposited AZO film was measured to be 0.34% from 380 to 1100 nm, which is far lower than the haze requirement for commercial purposes. In order to obtain a light trapping structure, a post-ething process is applied to the AZO films. After etching 60 s and 80 s, in the wavelength range between 380 and 1100 nm, the haze reached 15.2% and 23.6%, respectively. From Fig. 1, the XRD curves show no changes following the etching process. It seems that the etching process has little effect on the structure of AZO films. From the Scherrer equation, the size of ZnO grains is calculated to be about 28 nm.

An AFM was used to image the surface of the samples. The surface morphologies of the as-deposited, 60 s etched, and 80 s etched AZO films are shown in Figs. 2(a), 2(b), and 2(c), respectively. As can be seen, the as-deposited film has a homogenous particle distribution. The average grain diameter is about 25 nm, which is consistent with the XRD results. Af-

ter the etching process, the surface becomes rougher. Figure 2(c) indicates that some sag structures, about 1 μm × 1 μm, appear on the surface. These sag structures, also called gratings, are conducive to light absorption.[21] That is why the haze can be improved from 15.2% to 23.6% with the etching time increasing from 60 s to 80 s.

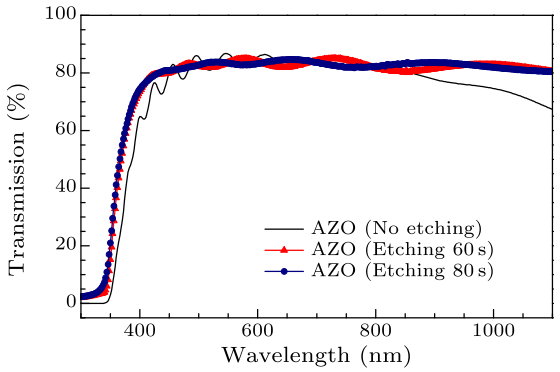

Fig. 3. Optical transmittance spectra of the AZO samples. Samples have been etched for 60 s and 80 s.

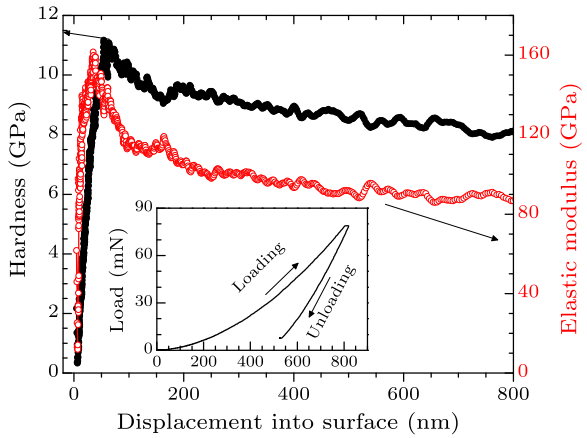

Fig. 4. Hardness and elastic modulus of the as-deposited AZO film. The inset shows the load-displacement curve.

Optical properties have been characterized by measuring the optical transmittance and reflection from 300 to 1100 nm. Figure 3 shows the optical transmittance spectra of the AZO samples, including the glass substrate, the SiO_2 buffer layer and the AZO film. The as-deposited AZO film shows the oscillation transmittance curve due to the smooth mirror surface, and the average transmittance can reach 83.2% in the visible spectrum range from 450 to 800 nm, which coincides with the reported data.[14,22] However, the average transmittance is only 76.5% in the infrared wavelength range from 760 to 1100 nm. Along with the etching process, the oscillation phenomenon disappears gradually because of the rough surface; meanwhile a higher transmittance is obtained. Especially in the infrared wavelength range from 760 to 1100 nm, the average transmittance reaches about 82.3%, which is caused by the reduction of carrier absorption in the etched samples. The increased average transmittance makes it more favorable to expand photovoltaic application in the range from visible to infrared wavelength. The concentration, resistivity, and mobility of as-deposited AZO film have been measured to be $3.9 \times 10^{20}\,\mathrm{cm}^{-3}$, $5.2 \times 10^{-4}\,\Omega\cdot\mathrm{cm}$ and $31\,\mathrm{cm}^2/\mathrm{V}\cdot\mathrm{s}$, respectively. After etching for 60 s and 80 s, the film thicknesses decrease to 645 nm and 580 nm. We can calculate the sheet resistance to be $8.1\,\Omega/\mathrm{sq}$ and $9\,\Omega/\mathrm{sq}$, accordingly. It seems that the AZO film treated using the corrosion procedure has high optical transparency without sacrificing good conductivity.

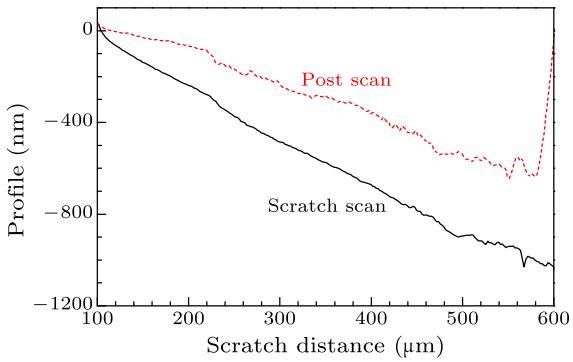

Fig. 5. Surface profiles of the scratch scan and post scan on the as-deposited AZO film.

Figure 4 shows the hardness and elastic modulus of the as-deposited AZO film as a function of indentation depth using the continuous stiffness measurement (CSM) technique. The load-displacement curves of the film are illustrated in the inset, and the typical indentation behavior of the oxide ceramic materials is observed. Over one hundred measurements have been performed and these curves are reproducible, which indicates that the film is homogenous. The degree of elastic recovery is defined as $R = (d_{\max} - d_{\mathrm{res}})/d_{\max}$, where $d_{\max}$ and d_{res} are the displacement at the maximum load and the residual displacement after unloading, respectively.[23] As shown in the inset picture, $d_{\max}$ and d_{res} of the AZO film are about 800 and 500 nm, thus the elastic recovery is calculated to be 37.5%, much higher than the metal films. In order to avoid the substrate effect, the indentation depth should be less than one-tenth of the film thickness.[24] Since the CSM technique can reveal the elastic modulus and hardness of the film as the function of indentation penetration depth, there will be a range in which the influence of the substrate on the elastic modulus and hardness can be ignored. In our experiments, the results show that such a region is within an indentation depth of 40–120 nm. Figure 4 clearly shows that the hardness and elastic modulus decrease gradually as the indentation penetrates through the film over this region. With the depth of indentation increasing, the measured hardness and elastic modulus of

the AZO films gradually approaches that of the glass substrate. The average hardness and elastic modulus determined by nanoindentation within the displacement range of 40–120 nm are approximately 10.2 GPa and 130 GPa, respectively. These results show similar a hardness and elastic modulus to that of indium zinc oxide (IZO) films, and are higher than that of indium tin oxide (ITO) films reported by Zeng *et al.*[25] Although the films were fabricated by using different processes and equipments have different properties, it has been reported that hardness and elastic modulus depend strongly on the amount of grain boundary area.[26,27] That is, for the samples composed of similar elements, the grain size effect is particularly important. For nanocrystalline materials, the hardness has been given by two modes, the Hall-Petch and the G. B. Sliding equations, separated by the critical grain size. In consideration of the maximum hardness at the critical point, further investigations will be focused on the critical grain size and the mechanisms related to hardness.

Figure 5 shows the scratch scan and post-scan surface profiles on the as-deposited AZO film. The postscan curve is always above the scratch-scan curve due to plastic recovery after scratching. It is known that adhesion fails when the scratch scan profile starts to become rougher or shows an abrupt increase point in the scanning process. The failure may be due to crack initiation, propagation and accumulation of fragments. The normal load corresponding to this point is the critical fracture load L_c of the coating, characterizing the adhesion strength of the coating films. As can be seen from Fig. 5, the scratch scan profile exhibits firstly a smooth linear curve, and then a slight abrupt change is observed at the 290 nm scratch depth, the corresponding $L_c = 91$ mN. A good adhesion between the layers is one of the most important factors to ensure product performance and a long service life. An appropriate buffer layer can play a role to improve the adhesive ability of TCO films.

In summary, Al-doped ZnO films have been fabricated by using the sputtering method. The AFM and XRD results indicate that the etched AZO films have a rough surface and the same structure as the as-deposited films. The hazes of the etched AZO films with the corrosion times 60 s and 80 s reach 15.2% and 23.6% between 380 and 1100 nm, respectively. The sheet resistances are calculated to be 8.1 Ω/sq and 9 Ω/sq, accordingly. The etched AZO samples have higher average transmittances, about 82.3% in the infrared wavelength range from 760 to 1100 nm. The elastic recovery, average hardness and elastic modulus of as-deposited AZO films determined by nanoindentation are approximately 37.5%, 10.2 GPa and 130 GPa, respectively. The critical fracture load related to adhesion strength is about 91 mN. It shows that an AZO film with high electrical conductivity, high optical transparency, appropriate hardness and good adhesion has been obtained in this work.

References

[1] Beyer W, Hüpkes J and Stiebig H 2007 *Thin Solid Films* **516** 147
[2] Lee B H, Kim I G, Cho S W and Lee S H 1997 *Thin Solid Films* **302** 25
[3] Kim S I, Cho S H, Choi S R, Oh M C, Jang J H and Song P K 2009 *Thin Solid Films* **517** 4061
[4] Zhang J, Hu J Q, Zhu F, Gong H and O'Shea S J 2002 *Sens. Actuat.* B *Chem.* **87** 159
[5] Low B L, Zhu F, Zhang K and Chua S J 2002 *Appl. Phys. Lett.* **80** 4659
[6] Minami T 2005 *Semicond. Sci. Technol.* **20** S35
[7] Liu X D, Jiang E Y and Li Z Q 2007 *J. Appl. Phys.* **102** 073708
[8] Agura H, Suzuki A, Matsushita T, Aoki T and Okuda M 2003 *Thin Solid Films* **445** 263
[9] Liu Z F, Shan F K, Li Y X, Shin B C and Yu Y S 2003 *J. Cryst. Growth* **259** 130
[10] Kim D H, Cho N G, Kim H G and Choi W Y 2007 *J. Electrochem. Soc.* **154** H939
[11] Olvera M de la L, Maldonado A and Asomoza R 2002 *Sol. Energy Mater. Sol. Cells* **73** 425
[12] Lee C H and Lin L Y 1996 *Appl. Surf. Sci.* **92** 163
[13] Sahu D R, Lin S Y and Huang J L 2007 *Sol. Energy Mater. Sol. Cells* **91** 851
[14] Yim K and Lee C 2006 *Cryst. Res. Technol.* **41** 1198
[15] Kim S M, Rim Y S, Keum M J and Kim K H 2009 *J. Electroceram.* **23** 341
[16] Jeong W J, Kim S K and Park G C 2006 *Thin Solid Films* **506-507** 180
[17] Springer J, Poruba A, Vanecek M, Fay S, Feitknecht L, Wyrsch N, Meier J, Shah A, Repmann T, Kluth O, Stiebig H and Rech B 2001 *Proceedings 17th European Photovoltaic Solar Energy Conference Munich* (Munich, Germany 22–26 October 2001) p 2830
[18] Meng Y, Yang X L, Chen H X, Shen J, Jiang Y M, Zhang Z J and Hua Z Y 2002 *J. Vac. Sci. Technol.* A **20** 288
[19] Hsu C Y and Tsang C H 2008 *Sol. Energy Mater. Sol. Cells* **92** 530
[20] Lee J H, Chou C Y, Bi Z X, Tsai C F and Wang H Y 2009 *Nanotechnology* **20** 395704
[21] Lin A and Phillips J 2008 *Sol. Energy Mater. Sol. Cells* **92** 1689
[22] Fang G J, Li D J and Yao B L 2003 *Vacuum* **68** 363
[23] Chen W, Gong H and Zeng K Y 2006 *J. Vac. Sci. Technol.* A **24** 537
[24] Buckle H, Westbrook J H and Conrad H 1971 *The Science of Hardness Testing and Its Research Applications* (ASTM, Philadelphia) p 263
[25] Zeng K Y, Zhu F R, Hu J Q, Shen L, Zhang K R and Gong H 2003 *Thin Solid Films* **443** 60
[26] Deng X Y, Wang X H, Gui Z L, Li L T and Chen I W 2008 *J. Electroceram.* **21** 238
[27] Malygin G A 2007 *Phys. Solid State* **49** 1013