

行政院國家科學委員會專題研究計畫 成果報告

脈衝磁控濺鍍製備 TCO 薄膜及其表面粗化於薄膜太陽能電池

研究成果報告(精簡版)

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計畫主持人： 林義成

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☐ 期中進度報告

脈衝磁控濺鍍製備 TCO 薄膜及其表面粗化於薄膜太陽能電池

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計畫主持人：林義成 博士

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計畫參與人員：嚴文材 兼任助理

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行政院國家科學委員會專題研究計畫成果報告

脈衝磁控濺鍍製備 TCO 薄膜及其表面粗化於薄膜太陽能電池

Deposition and texturing of TCO thin films for thin film solar cells using pulsed DC magnetron Sputtering

計畫編號：NSC 98-2622-E-018-002-CC3

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主持人：林義成 教授 國立彰化師範大學機電工程學系

中文摘要

本研究計畫主要目的採用脈衝磁控濺鍍製備 AZO (ZnO:Al) 與 GZO(ZnO:Ga)薄膜，沈積於Soda-lime 玻璃基板上，並藉由化學濕式蝕刻進行薄膜表面粗化，於不同蝕刻時間下觀察薄膜對可見光之漫透射率與光電性質之影響。並透過調變濺鍍功率、工作壓力、脈衝頻率、薄膜厚度和基板溫度等參數來製備具最佳光電結構特性之 AZO 與 GZO 薄膜。其次，以 0.5%HCl、5%Oxalic acid 及 33%KOH三種不同的蝕刻液，調變蝕刻時間進行 AZO 與 GZO 薄膜表面粗化使其具有陷光結構；探討薄膜蝕刻後對電性、可見光的穿透及散射之影響。研究中利用薄膜測厚儀量測其薄膜厚度及沈積率、能量分散光譜儀量測成分含量、霍爾量測儀量測電阻率、載子濃度和載子遷移率、X 光繞射儀做薄膜結構性分析、X 光射線光電子能譜儀來觀察薄膜的表面元素的化學性質及成分比例、熱場發射掃描式電子顯微鏡與原子力顯微鏡量測設備進一步瞭解薄膜表面型態，利用光譜儀做光穿透率量測，並以可變角度多功能光學特性檢測系統做總透射率與鏡面透射率量測，藉此換算出漫透射率的光譜圖。研究 TCO 薄膜粗化之技術並應用於薄膜太陽能電池上，以期研發開可行之製程技術，盼能有效降低 TCO 薄膜粗化製程成本之比例。

關鍵字：AZO (ZnO:Al)、表面粗化、直流脈衝磁控濺鍍

Abstract

Transparent conducting thin films of ZnO:Al (Al-doped ZnO, AZO) were prepared via pulsed DC magnetron sputtering with good transparency and relatively lower resistivity. The AZO films with 800nm in thickness were deposited on soda-lime glass substrates keeping at 473K under 0.4Pa working pressure, 150W power, 100μs duty time, 5μs pulse reverse time, 10kHz pulse frequency and 95% duty cycle. The

as-deposited AZO thin films has resistivity of $6.39 \times 10^{-4} \Omega \text{cm}$ measured at room temperature with average visible optical transmittance, T_{total} of 81.9% under which the carrier concentration and mobility were $1.95 \times 10^{21} \text{cm}^{-3}$ and $5.02 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. The films were further etched in different aqueous solutions, 0.5%HCl, 5% Oxalic acid, 33%KOH, to conform light scattering properties. The resultant films etched in 0.5% HCl solution for 30 seconds exhibited high $T_{\text{total}}=78.4\%$ with haze value, $HT = 0.1$ and good electrical properties, $\rho=8.5 \times 10^{-4} \Omega \text{cm}$ while those etched in 5% oxalic acid for 150s had desirable $HT = 0.2$ and relatively low electrical resistivity, $\rho=7.9 \times 10^{-4} \Omega \text{cm}$. However, the visible transmittance, T_{total} was declined to 72.1%.

Keywords: Al-doped ZnO; Surface textured; Light trapping structure; Haze value; Pulsed DC magnetron sputtering.

1. Introduction

Transparent conducting oxides (TCOs) films are prerequisite for most photovoltaic applications and have been subjected to a very large number of investigations for several decades[1,2]. The most widely used and studied n-type TCOs are based on Zn, In, Sn and Cd owing to their superior optoelectronic properties, and especially, has widely applications in the front electrodes for most thin film solar cells [3-5]. Practically, Indium-Tin-Oxide (ITO) thin films are the widely used TCOs. Nevertheless, the limited Indium supply as well as the increasing price promotes the development of ITO alternatives [6]. Zinc oxide is a direct, wide bandgap($\sim 3.37 \text{ eV}$) semiconductor material with many promising properties for optoelectronics, electronics, spintronics and sensor applications[7]. It was shown that Al, Ga and In-doped ZnO films have great chemical stability and excellent electrical conductivity as well as visible transmittance which has made it one of

the most promising TCOs owing to its non-toxicity, less expensive, more resistant to defect, impurity doping, hydrogen plasma reduction[8] and can be deposited at lower temperature [9,10].

As a satisfactory front contact materials for photovoltaic applications, the TCOs films has to be highly conductive for good current transport to obtain low series resistance and highly transparent for the incident sunlight to reduce the absorption losses[11]. Moreover, an adapted surface topography for better light scattering and subsequent light trapping inside the silicon based solar cells is necessary. Surface textured TCO with light trapping structures can facilitate optical reflection, refraction, and scattering by a suitably rough surface to scatter the incident light [12,13]. The light scattering capability of the TCO front electrode depends on the dimensional features and surface morphology[14-16]. Polycrystalline ZnO films are readily etched in many acidic and alkaline solutions [7,14-18]. Up to now, there is no theoretical model to predict the wet-chemical etching behavior of polycrystalline AZO films as functions of processing parameters. However, a systematic approach to elucidate the properties of textured AZO films by different wet chemical solutions was quite rare. In this study, a comprehensive study for the surface textured Al-doped ZnO films by wet etching with three different mediums was illustrated. The influence of structural, electrical and optical properties of the resultant films as a function of texturing medium and time period was investigated to obtain the desirable front electrodes materials with good light-trapping properties for thin film silicon solar cells applications.

2. Experimental

All films were deposited onto soda-lime glass substrate by pulse DC magnetron sputtering using a ceramic AZO target 76mm in diameter, ZnO:Al₂O₃(2.0 wt.%). The sputtering chamber was pumped down to 6.65×10^{-6} Pa by cryogenic pump in which the AZO target was exposed to Ar plasma for 5min to clean the target surface. Since the optoelectronic properties of the films are very sensitive to the deposition conditions, the fine-tuned optimal parameters turned to be that: substrates temperature keeping at 473K, working distance between the target and the substrate was 5.5cm, pulse frequency 10kHz by modulating pulse sputter process parameters such as: power

150 W, working pressure 0.4Pa and duty cycle 95%, respectively. All of the films used in the following wet-chemical etch have identical deposition parameters, if without further notification. After baseline calibration, the deposition rate and thickness were determined by α -step (Kosaka laboratory Lt.d.ET3000). The films morphology was characterized by FE-SEM (JEOL JSM 7000F) and atomic force microscope (AFM, Q-Scope 350). X-ray diffraction (XRD, CuK α , $\lambda=1.54052\text{\AA}$, Shimadzu XD-6000) was used to analyze the crystalline structure of the deposited film. A typical θ -2 θ scan by Brag-Brentano geometry gives valuable information in both the crystallinity and grain size of the deposited thin films [13,14,17,18]. The intensity of XRD patterns has been normalized to the film thickness as the absorption depth of X-ray was considered. The electrical properties of the films were examined using Hall-effect measurements (ECOPIA HMS-2000). Only the films with lowest resistivity and optical transmittance greater than 78% in every batch were choose for further investigation. Quantitatively, the light scattering can be evaluated by the so-called haze value, i.e. the ratio of diffuse to total light transmission as defined by eq.(1).

$$\text{Haze} = T_{\text{diffuse}} / T_{\text{total}} \quad (1)$$

$$T_{\text{total}} = T_{\text{diffuse}} + T_{\text{specular}} \quad (2)$$

The total transmittance (T_{total}) and specular transmittance (T_{specular}) defined in eq.(2) was measured by the angle-adjustable and multifunctional optical characterization system (Hong-Ming MFS-630) with wavelength 400~800nm. Wet chemical etching experiments were conducted at 300K and compared separately in three different etching solutions: The etch time was: (1).0.5% HCl_{aq} for 15, 30, and 45s, (2). 5% oxalic acid (HOOC-COOH) solution for 75, 150 and 225s, and (3).33% KOH_{aq} for 45, 90 and 135s which corresponding to film thickness of 800(initial), 700, 600, 500 nm, respectively.

3. Results and Discussion

3-1 Etched in 0.5% HCl solution

We developed the surface morphology of AZO films which etched in 0.5% HCl_(aq.) at 300K with different etch time. Fig.1 shows the SEM images of the as-deposited films(a) and after different etching (b~d). The tilt angles for the

SEM observation are $\sim 40^\circ$ to the horizontal. The as-deposited film is quite smooth as a whole with typical root-mean-square roughness, δ_{rms} less than 3nm as measured by AFM. In addition, wet chemical etching in dilute hydrochloric acid leads to a rough surface with regularly distributed craters typically with lateral feature size of 200~300nm which was characteristic of the anisotropic etch behavior for all the etching time. In our system, the surface topography of AZO films etching in dilute hydrochloric acid is generally applicable by applying the Berginski's description [12] in which there is three different topography of textured-etched AZO as function of target alumina concentration(TAC) and substrate temperature (T_{sub}). The as-deposited AZO films in our study comprise a compact smooth topography with a small δ_{rms} value of 2.7nm. For those slightly texturing surfaces as shown in Fig.1b, a rough surface with a δ_{rms} value of 21.3nm is developed in Fig.2b. The topography of this film belongs to the type I surface by Berginski's definition. This result is somewhat contradict to what is predicted by Berginski under the condition of TAC=2% and $T_{\text{sub}}=200^\circ\text{C}$. On the contrary, for those etching for 30s, the textured films with a δ_{rms} value of 24.5nm belongs to the type II topography as shown in Fig.2c in which a rugged surface covering by craters with diameters around $1\mu\text{m}$ was appeared in Fig.1c. If the etching time exceeded 45s, larger craters with lateral diameters up to $1\mu\text{m}$ emerged in Fig. 1d. A more rugged surface with a root-mean-square roughness value of 30.8nm which belongs to the type III structure according to the Berginski's definition was evolved. During the etching process, the overall etch rate was about $6\sim 7\text{ nms}^{-1}$ which is similar to those prepared by reactive mid frequency magnetron sputtering under low plasma emission intensity [15]. The carrier concentration in Fig.3 decreased as the etching time increased. The mobility (μ) and carrier concentration (n) relationship derived in this study for textured AZO films etching in different aqueous solution all exhibit an tendency that the μ improved while the n decreased moderately by the etch time. The μ - n relationship is indicative that the conduction mechanism is different to those dominated by a typical grain boundary scattering [19]. In addition, the fact that n decreased moderately by the etch time as shown in Fig.3, 9 and 15 is reminiscent of an reasonable explanation that the

grain boundaries of textured AZO films were deteriorated by etching solution. There are more defect sites (area) throughout the whole boundaries. These defect sites could trap the charge carriers thus the concentration of electrons decreased. It is reasonable to predict that the decrease of carrier concentration might be correlated to the grain boundary defects by wet chemical etching. This could be further proved by the decrease in crystallinity by longer etch time, as shown in Fig.4. In contrast, the carrier mobility was at first elevated from 6.3 to $8.77\text{ cm}^2\text{VS}^{-1}$ owing to the depriving of the fragile surface structures by etching while the resultant films had robust and regular-packed columnar film structures. The prominent improvement in mobility might partly come from the reduced free carrier scattering by ionized impurities [9]. The net effect is that the resistivity slightly rose from $6.4\times 10^{-4}\Omega\text{cm}$ to $8.5\times 10^{-4}\Omega\text{cm}$ for the first 30s and raises dramatically to almost tenfold of its original value for etching 45s. In summary, the films etching in HCl solution destroys the films and subsequently, deteriorates the electrical conductivity substantially.

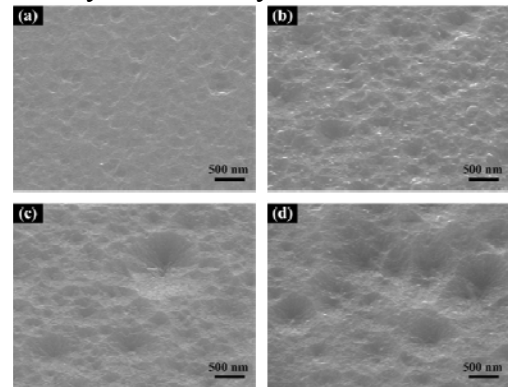


Fig 1. SEM micrographs of textured AZO films as function of etch time in 0.5% HCl solution. (a) as-deposition; (b) etched for 15 s; (c) etched for 30 s and (d) etched for 45 s.

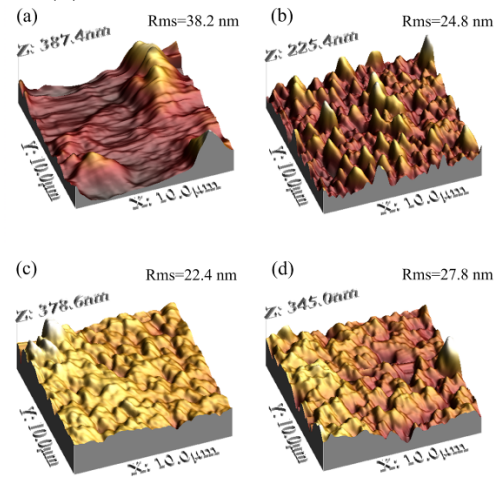


Fig 2. Surface morphology measurements of

textured AZO films as function of etch time in 0.5% HCl solution. (a) as-deposition; (b) etched for 15 s; (c) etched for 30 s and (d) etched for 45 s.

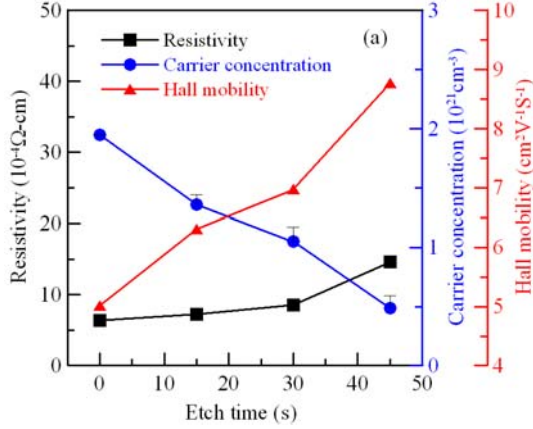


Fig 3. Electrical properties as function of etch time in 0.5% HCl solution.

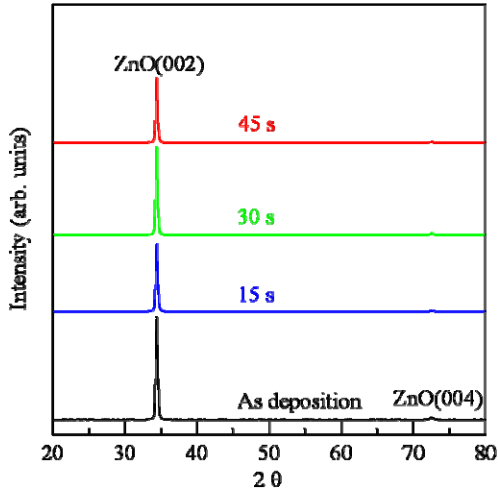


Fig 4. XRD patterns of AZO as function of etch time in 0.5% HCl solution.

Fig. 5 shows typical optical transmittance spectra of the texture-etched films at various etching time as function of wavelength. All the films exhibited apparent variation of transmittance as the result of interference phenomena were attributed to the uniform thickness of the textured films [1,10]. The spectral haze serves as an indicator for the light scattering properties of the texture etched ZnO:Al films as shown by Klutha et al.[20]. For amorphous silicon p-i-n solar cells co-depositing on smooth and texture etched ZnO coated glass substrates, those prepared on the textured ZnO exhibits an increase in short-circuit current density j_{sc} by 3.3mA/cm^2 as compared to those deposited on the smooth ZnO. This improvement is due to an effective light trapping in the long wavelength region. In our study, owing to the improvement of light-trapping effect, the $T_{diffuse}$ and H_T increased with time while the T_{total} decreased along with the etching time as some

compact structures has been destroyed by etching in HCl. The total transmittance (Fig.6) declined at first 15s after which the alteration in optical transmittance was meager until 30s. For prolonged etching over 45s, the T_{total} declined to 89% of its original value and both the total diffused transmittance ($T_{diffused}$) and total Haze(H_T) increased considerably which showed that the efficiently texturing effect by HCl could be achieved at very short period of time. Besides, the reduced free carrier absorption owing to the decrease of carrier concentration (Fig.3) didn't make significant improvement in optical transparency as those described elsewhere in which the total transmittance increase as the etch time increase because of the decrease in the film thickness[17]. In light of diffuse transmittance, the HCl etch indeed made no significant contribution at first 10s while for prolonged etching, the resultant moon surface like landscape with large craters and etch holes is responsible for the surge in diffuse transmittance as well as haze value. Kluth et al. [20] found that the sample textured with a haze value of 0.23 at 550nm wavelength light had a better short-circuit current density than the smooth AZO substrate. In this study, the sample etched in HCl_{aq} for 45s has maximum haze value of $H_T=0.28$. Nevertheless, at this time the resistivity was soared into $1.46 \times 10^{-3} \Omega\text{-cm}$ which was too high to be used. In contrast, a more reasonable value of 30s etching time was chooses to get the lower resistivity, $\rho = 8.54 \times 10^{-4} \Omega\text{-cm}$ with acceptable visible transmittance, $T_{total}=78.4\%$ and haze value, $H_T = 0.09$ as desirable front electrode material for thin films solar cell applications.

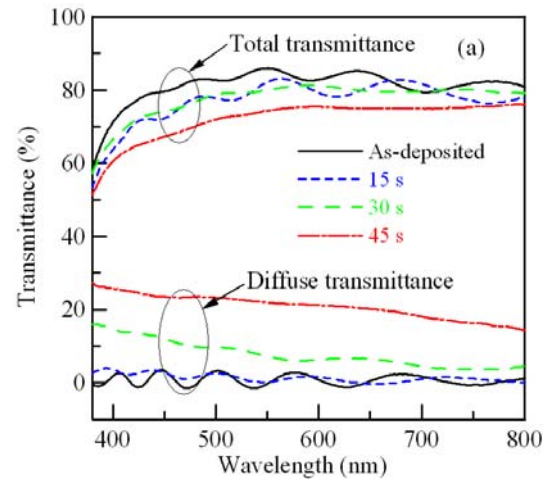


Fig 5. Transmittance spectra for AZO thin films as function of etch time in 0.5% HCl solution.

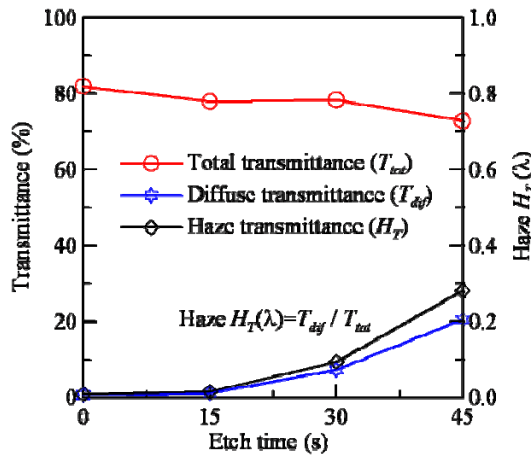


Fig 6. Optical properties of AZO thin films as function of etch time in 0.5% HCl solution.

3.2 Etched in 5% oxalic acid solution

Since the etching rate of AZO films in dilute HCl solution is comparatively fast, it adds some difficulty in fine tuning the textured surface morphology as well as preventing the over-etching problems. Accordingly, for better topographical control, a milder etching solution was prepared with 5% oxalic acid as the active reagent. The evolution of surface structures by various etching time (Fig.7) exhibits coarse and rugged surface morphology at first 75s which is characteristic microstructure for anisotropic etching. Further etching results in relatively smooth surface with large craters. Surface morphology by AFM measurements shown in Fig.8 indicated that δ_{rms} increases substantially at the start of the etching process. The overall film thickness was reduced at a rate of about 1.3nm s^{-1} . The carrier concentrations (Fig. 9) declined steadily at first 150s which is conjectured to be incurred by the dissipation of Al ions or the destruction of oxygen vacancies from the pristine films as indirectly supported by the fact that the Hall mobility, under identical circumstance, was increased by etching time owing to the reduced ionized impurity scattering at grain boundaries. Minami et al.[6,19] proposed the n - μ relationship for doped ZnO films prepared by different deposition method in which the abrupt mobility reduction accompanied by the increase in the carrier concentration. In our study, the n - μ relationship for textured AZO by oxalic acid solution are consistent with those described by above authors. Owing to milder stripping of the loosely-packed surface columnar structures, the decrease in carrier concentration is partly compensated by the improved mobility at the early stage of etching. The net effect is that the

resistivity was initially increased from $6.39 \times 10^{-4} \Omega\text{-cm}$ to its peak value for etching time of 75s, $8.15 \times 10^{-4} \Omega\text{-cm}$ after which the resistivity dramatically declines again. This could be further validated by the development of crystallinity upon etching. The ZnO (002) crystalline plane (Fig. 10) becomes meager at first 75s and subsequently, the preferential oriented diffraction intensified as an indication of the compact columnar structures now thriving. Finally, the overall crystallinity declined considerably for prolonged etching over 225s, as evidenced by SEM photograph in Fig.7, the topography of the remaining compact columnar structures was further destroyed severely by over etching.

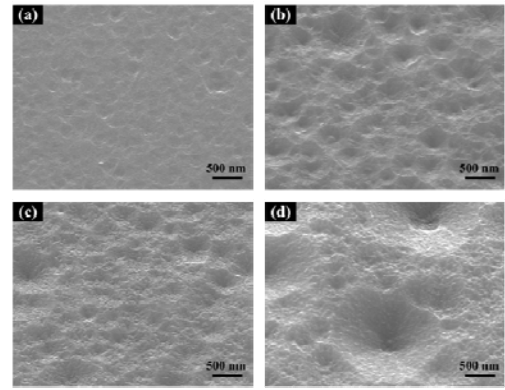


Fig 7. SEM micrographs of textured AZO films as function of etch time in 5% oxalic acid solution. (a) as-deposition; (b) etched for 75 s; (c) etched for 150 s and (d) etched for 225 s.

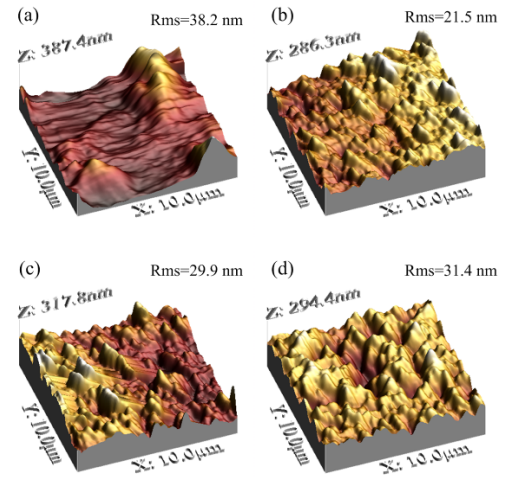


Fig 8. Surface morphology measurements of textured AZO films as function of etch time in 5% oxalic acid solution. (a) as-deposition; (b) etched for 75 s; (c) etched for 150 s and (d) etched for 225 s.

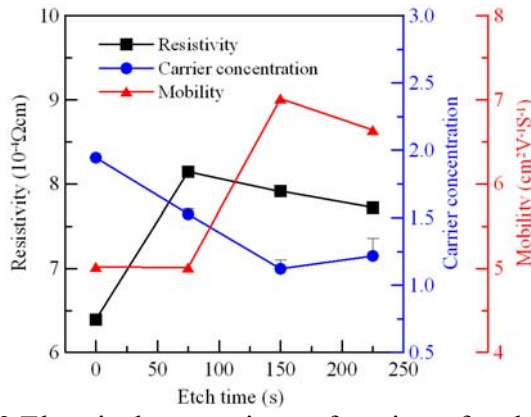


Fig 9. Electrical properties as function of etch time in 5% oxalic acid solution.

Typical optical transmittance spectra of the texture-etched AZO films in oxalic acid solution were depicted in Fig. 11. It is noteworthy that wavelength dependence is quite different to those etched by oxalic acid solution in that the total transmittance of the samples did exceed to those etched with shorter time, 150s. After some of the disorder loosely-packed overlayers had been removed, the total haze (H_T) owing to the intensified light-trapping was increased by etching (Fig. 12). At this point, T_{total} declined considerably with etch time. However, the improved light-trapping let the $T_{diffuse}$ and H_T increase accordingly which showed that a 5% oxalic acid solution was sufficed to texture the AZO surface efficiently. The reduction in visible transmittance is due to carrier scattering. In summary, the sample etched in oxalic acid solution for more than 150s has haze value greater than 0.23 while the resistivity was as low as $7.91 \times 10^{-4} \Omega\text{-cm}$ with visible transmittance of 72.1% which is acceptable as the front electrode material for thin films solar cell applications.

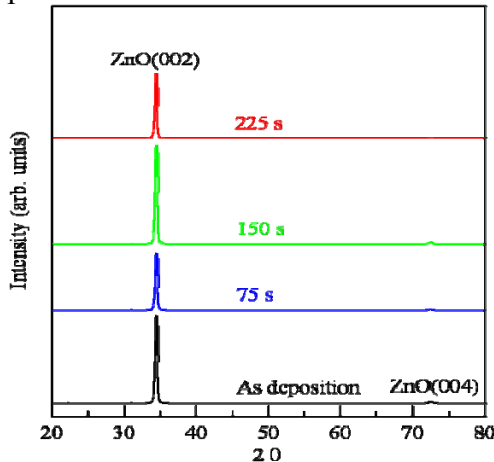


Fig 10. XRD patterns of AZO as function of etch time in 5% oxalic acid solution.

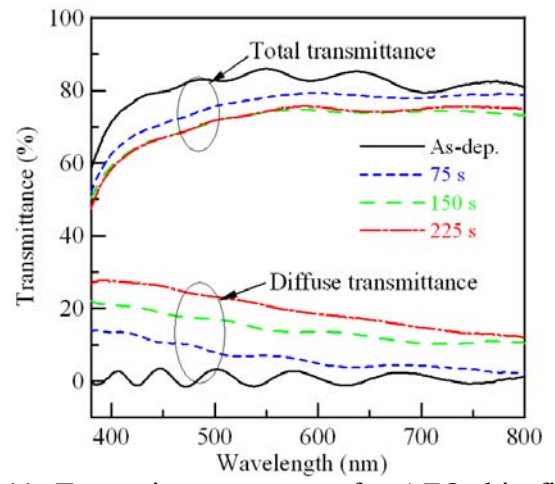


Fig 11. Transmittance spectra for AZO thin films as function of etch time in 5% oxalic acid solution

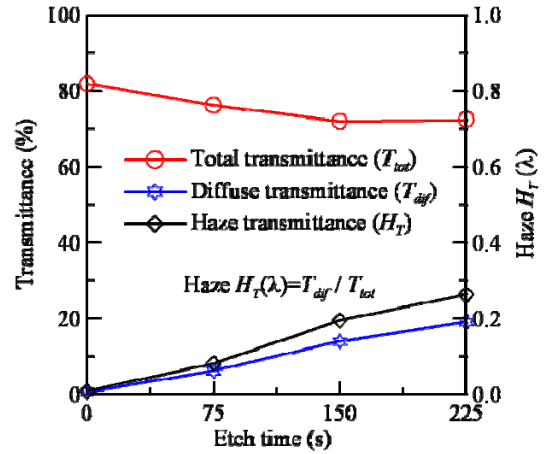


Fig 12. Optical properties of AZO thin films as function of etch time in 5% oxalic acid solution.

3.3 Etched in 33% KOH solution

The topography of polycrystalline ZnO has shown a strong dependence of etching behavior on the crystal planes and etchant solution [7]. Besides, the etch rate is governed by factors such as the formula of the etch solution, the composition and density of the films, processing time and temperature, etc. For comprehensive understanding of the etch behavior in etching solution with different chemical nature, a 33% KOH solution was chose for comparison with those textured in acidic medium. KOH solution attacks the AZO films surface randomly at certain points in which deep and steep holes are formed with rugged moon landscape-like surface appearance after etching for 45s as shown in Fig. 13. The AFM topography shown in Fig. 14 indicated that δ_{rms} increases steadily with the etch time. The etch rate in 33% KOH solution was far smaller than that in 0.5% HCl solution while slightly larger than that in 5% oxalic acid solution and estimated to be 2.3 nm s^{-1} . The carrier

concentration profile as function of etch duration (Fig. 15) is similar to those etched in oxalic acid solution. The carrier concentration drops steadily to $6.39 \times 10^{20} \text{ cm}^{-3}$ at first 90s based on similar reasons described above. After prolonged etching, the carrier concentration restored to $8.64 \times 10^{20} \text{ cm}^{-3}$ as could be explained by two factors: first, the microstructural evolution as shown in Fig.13(c),(d) revealed that the randomly dispersed craters reduced the grain boundary barrier height owing to the removal of loosely packed defect structures. Second, for doped ZnO, the dopant atoms were substitutionally incorporated at Zn sites in the ZnO lattice [7,19]. Consequently, the ionized impurity scattering dominated. The increase in carrier concentration could be rationalized by the reduced ionized impurity scattering centers by wet chemical etching.

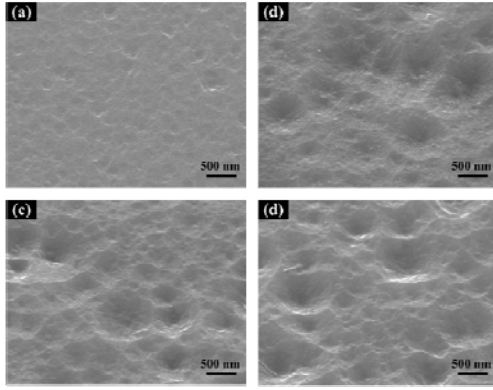


Fig 13. SEM micrographs of textured AZO films as function of etch time in 33% KOH solution. (a) as-deposition; (b) etched for 45 s; (c) etched for 90 s and (d) etched for 135 s.

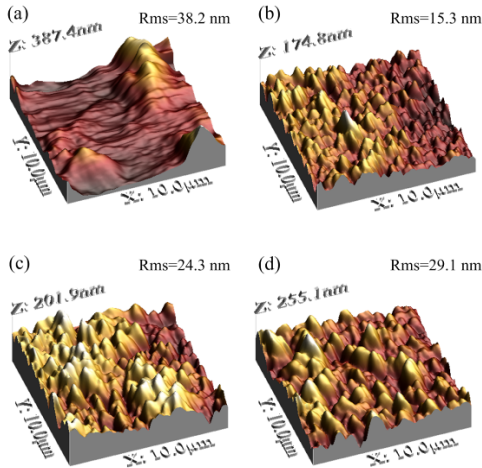


Fig 14. Surface morphology measurements of textured AZO films as function of etch time in 33% KOH solution. (a) as-deposition; (b) etched for 45 s; (c) etched for 90 s and (d) etched for 135 s.

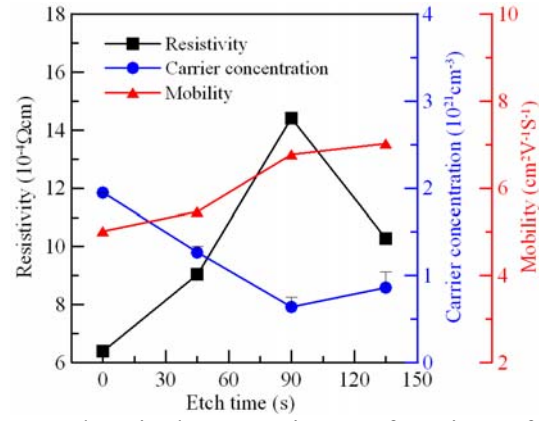


Fig 15. Electrical properties as function of etch time in 33% KOH solution.

Similarly, the revolution of c-axes preferred orientation crystallites resembles those textured in oxalic acid. As depicted in Fig.16, the intensity of (002) diffraction peak was weakened substantial at first 45s while recovered to about half of its original intensity for prolonged texturing. The position and the width of the diffraction peak seemed to be fixed without obvious fluctuation. This could be attributed mainly to the variation of crystallinity as the defect structures were deprived during the etching process.

The influence of etch time on optical transmittance (Fig.17) shown that the visible transparency was deteriorated with the increased etch duration. It is noteworthy that T_{total} was improved slightly from 73.2%(90s) to 74.1%(135s) as depicted in Fig.18. Besides, the T_{diffuse} increased considerable as the etching time over 45s which was an indication of effectively light-trapping. The increment in haze was meager at first 45s and increased steadily within 45~90s and fixed at $H_T=0.15$ thereafter. In summary, the film textured in KOH solution for 135s has larger haze, $H_T=0.15$ and visible transmittance, $T_{\text{total}}=74.1\%$ while the electrical properties were deteriorated considerably as the resistivity, ρ was declined to $1.0 \times 10^{-3} \Omega \cdot \text{cm}$.

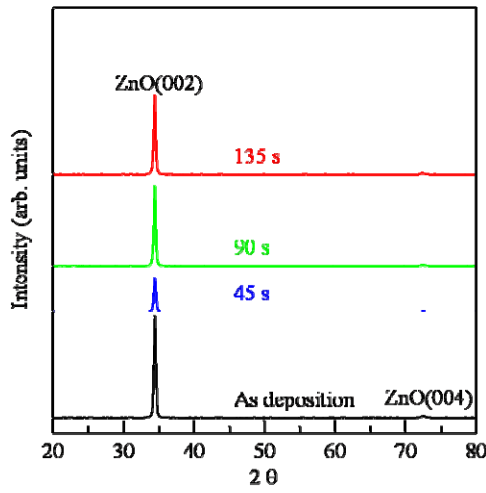


Fig 16. XRD patterns of AZO as function of etch time in 33% KOH solution.

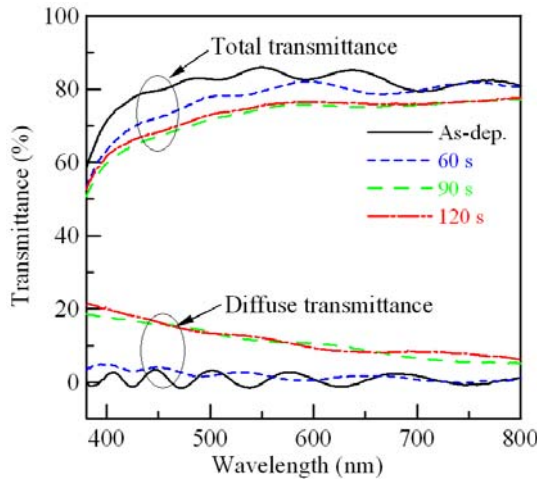


Fig 17. Transmittance spectra for AZO thin films as function of etch time in 33% KOH solution.

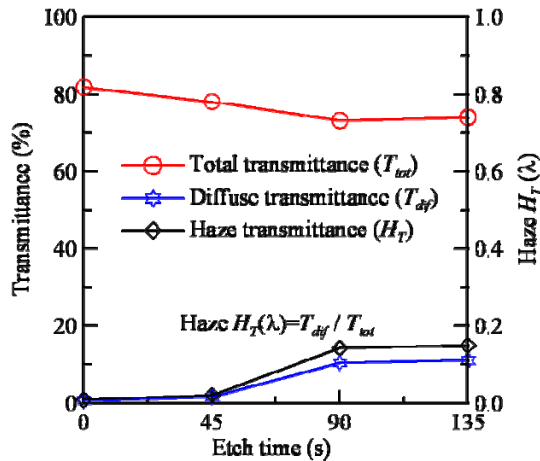


Fig 18. Optical properties of AZO thin films as function of etch time in 33% KOH solution.

4. Conclusions

In this study, pulsed DC magnetron sputtering was used to prepare AZO thin films on glass substrates. After the thin film was deposited, the wet etching process with 0.5 % HCl; 5 % Oxalic acid, and 33 % KOH solutions was conducted on the specimens to obtain the ideal

light trapping structure for thin film solar cells. The resultant films etched in 0.5% HCl solution for 30 seconds exhibited high $T_{\text{total}}=78.4\%$ with haze value, $H_T = 0.1$ and good electrical properties, $\rho=8.5 \times 10^{-4} \Omega\text{cm}$ while those etched in 5% oxalic acid for 150s had desirable $H_T = 0.23$ and relatively low electrical resistivity, $\rho=7.9 \times 10^{-4} \Omega\text{cm}$. However, the visible transmittance, T_{total} was declined to 72.1%.

5. References

- [1] K. L. Chopra, S. Major, D. K. Pandya, Thin Solid Films 102 (1983) 1
- [2] T. Minami, Semicond.Sci.Technol. 20 (2005) S35.
- [3] Y. C. Lin, J. Y. Li, and W. T. Yen, Appl. Surf. Sci., 254 (2008) 3262.
- [4] Y. C. Lin, S. J. Chang, Y. K. Su, T. Y. Tasi, C. S. Chang, S. C. Shei, C. W. Kuo, S.C. Chen, Solid state Electron, 47 (2003) 849.
- [5] Claes G. Granqvist, Sol. Energy Mater. Sol. Cells 91 (2007) 1529.
- [6] T. Minami, Thin Solid Films 516 (2008) 5822.
- [7] K. Ellmer, A. Klein, B. Rech, Transparent conductive zinc oxide, Springer, 2007
- [8] S. Major, S. Kumar, M. Bhatnagar and K. L. Chopra, Appl. Phys. Lett., 49 (1986) 394.
- [9] T. Minami, H. Sata, H. Nanto and S. Takata, Jpn. J. Appl. Phys., 24 (1985) L781.
- [10] J. Wienke, B. van der Zanden, M. Tijssen, M. Zeman, Sol. Energy Mater. Sol. Cells 92 (2008) 884.
- [11] M. Berginski, J. Hüpkes, W. Reetz, B. Rech, M. Wuttig, Thin Solid Films 516 (2008) 5836.
- [12] M. Berginski, J. Hupkes, M. Schulte, G. Schope, H. Stiebig, B. Rech, J. Appl. Phys., 101 (2007) 074903.
- [13] J. Hupkes, B. Rech, O. Kluth, T. Repmann, B. Zwaygardt, J. Muller, R. Drese, M. Wuttig, Sol. Energy Mater. Sol. Cells 90 (2006) 3054.
- [14] Y. C. Lin, Y. C. Jian, J. H. Jiang, Appl. Surf. Sci., 254 (2008) 2671.
- [15] S. Calnan, J. Hupkes, B. Rech, H. Siekmann, A.N. Tiwari, Thin Solid Films 516 (2008) 1242.
- [16] C. Agashe, O. Kluth, J. Hüpkes, U. Zastrow, B. Rech, M. Wuttig, J. Appl. Phys., 95 (2004) 1911.
- [17] J. Yoo, J. Lee, S. Kim, K. Yoon, I. J. Park, S.K. Dhungel, B. Karunakaran, D.

- [18] F. C. M. Van de pol F. R. Blom, TH. J. A. Popma, Thin Solid Films 204 (1991) 349.
- [19] T. Minami, H. Sato, K. Ohashi, T. Tomofuji, S. Takata, J. Cryst. Growth 117 (1992) 370.
- [20] O. Klutha, B. Rech, L. Houben, S. Wieder, G. Schöpe, C. Beneking, H. Wagner, A. Löffl, H.W. Schock, Thin Solid Films 351 (1999) 247.

【成果發表情形】

1. Wen-Tsai, Yen, Jia-Hong Ke, Hsin-Jung, Wang, Yi- Cheng, Lin, and Jung-Lung Chiang, 2009. 09 Influences on optoelectronic properties of damp heat ability of AZO and GZO for thin film solar cells, Advanced Materials Research, 79-82, pp 923-926.
2. W. T. Yen, Y. C. Lin^{*}, and J. H. Ke Surface textured ZnO:Al thin films by pulsed DC magnetron sputtering for thin film solar cells applications, Applied Surface Science, Accepted. 2101,8.

國科會補助專題研究計畫成果報告自評表

請就研究內容與原計畫相符程度、達成預期目標情況、研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）、是否適合在學術期刊發表或申請專利、主要發現或其他有關價值等，作一綜合評估。

1. 請就研究內容與原計畫相符程度、達成預期目標情況作一綜合評估

☒ 達成目標

☐ 未達成目標（請說明，以 100 字為限）

☐ 實驗失敗

☐ 因故實驗中斷

☐ 其他原因

說明：

本實驗利用脈衝直流磁控濺鍍的方式，於康寧 1737F 玻璃上濺鍍摻雜 Ga 及 Al 的 ZnO 薄膜，並利用改變功率、工作壓力、直流脈衝反轉時間，觀察 AZO、GZO 薄膜的光電、結構特性與抗化性的影響並歸納出下列幾項重點：

(1)本研究完成直流脈衝磁控濺鍍系統製備 AZO 與 GZO 薄膜之製程較佳參數。

(2)本研究透過製程實驗歸納出完整 AZO 與 GZO 薄膜光電性質。

(3)本研究透過實驗了解蝕刻製程對 AZO 與 GZO 薄膜光電性質的影響。

(4)本研究透過製程實驗找出最適用於非晶矽薄膜太陽能電池之蝕刻製程。

(5)提供合作公司後續之 TCO 薄膜蝕刻製程研發設計及改良之依據。

2. 研究成果在學術期刊發表或申請專利等情形：

論文：☒已發表 ☐未發表之文稿 ☐撰寫中 ☐無

專利：☐已獲得 ☒申請中 ☐無

技轉：☐已技轉 ☐洽談中 ☐無

其他：（以 100 字為限）

3. 請依學術成就、技術創新、社會影響等方面，評估研究成果之學術或應用價值（簡要敘述成果所代表之意義、價值、影響或進一步發展之可能性）（以 500 字為限）

在學術研究上，本計畫之研究成果已發表一篇期刊論文。本計畫所建立利用製程技術，除了提供本計劃執行外，亦將開放提供國內學術、產業界使用，並提供相關技術諮詢與服務，藉以提高國內太陽能光電之學術研究風氣與水準。此外，計畫主持人現今與國內綠色資源研究機構或產業界互動密切，將藉此本次計畫之執行整合師資專長，運用學術及研發資源落實學以致用，作為人才培育與技術支援之後盾，並協助產業升級與轉型，並協助技專校院發展特色，以具體實現技職教育使命。藉由參與產學合作計畫驗證理論，累積實務經驗，提升師生研究水準，協助產業發展，提高人力素質與就業競爭力，以提昇國內太陽能光電製程、設備、材料等研發之水準。

無研發成果推廣資料

本產學合作計畫研發成果及績效達成情形自評表

成果項目		本產學合作計畫 預估 研究成果及績效指標 (作為本計畫後續管考之參據)	計畫達成情形
技術移轉		預計技轉授權 0 項	完成技轉授權 0 項
專利	國內	預估 0 件	提出申請 0 件，獲得 0 件
	國外	預估 0 件	提出申請 0 件，獲得 0 件
人才培育		博士 0人，畢業任職於業界0人	博士 3人，畢業任職於業界1人
		碩士 0人，畢業任職於業界0人	碩士 4人，畢業任職於業界2人
		其他 0人，畢業任職於業界0人	其他 0人，畢業任職於業界0人
論文著作	國內	期刊論文 0 件	發表期刊論文 0 件
		研討會論文 0 件	發表研討會論文 0 件
		SCI論文 0 件	發表SCI論文 0 件
		專書 0 件	完成專書 0 件
		技術報告 0 件	完成技術報告 1 件
	國外	期刊論文 0 件	發表期刊論文 2 件
		學術論文 0 件	發表學術論文 0 件
		研討會論文 0 件	發表研討會論文 0 件
		SCI/SSCI論文 0 件	發表SCI/SSCI論文 2 件
		專書 0 件	完成專書 0 件
		技術報告 0 件	完成技術報告 0 件
其他協助產業發展之具體績效		新公司或衍生公司 0 家	設立新公司或衍生公司(名稱)：
<u>計畫產出成果簡述：請以文字敘述計畫非量化產出之技術應用具體效益。(限 600 字以內)</u>		本實驗利用脈衝直流磁控濺鍍的方式，於康寧 1737F 玻璃上濺鍍摻雜 Ga 及 Al 的 ZnO 薄膜，並利用改變功率、工作壓力、直流脈衝反轉時間，觀察 AZO、GZO 薄膜的光電、結構特性與抗化性的影響並歸納出下列幾項重點： (1)本研究完成直流脈衝磁控濺鍍系統製備 AZO 與 GZO 薄膜之製程較佳參數。 (2)本研究透過製程實驗歸納出完整 AZO 與 GZO 薄膜光電性質。 (3)本研究透過實驗了解蝕刻製程對 AZO 與 GZO 薄膜光電性質的影響。 (4)本研究透過製程實驗找出最適用於非晶矽薄膜太陽能電池之蝕刻製程。 (5)提供合作公司後續之 TCO 薄膜蝕刻製程研發設計及改良之依據。	