DEPOSITION OF HIGH-ELECTRON-MOBILITY TRANSPARENT CONDUCTING ALUMINUM-DOPED ZINC OXIDE THIN FILMS BY DC MAGNETRON SPUTTERING

Hoang Van Dung*, Nguyen Duy Khanh, Tran Cao Vinh

Laboratory of Advanced Materials – VNUHCM-University of Science, 227 Nguyen Van Cu, Ho Chi Minh City, Viet Nam.

*Email: hvdung@hcmus.edu.vn

Received: 6 September 2015; Accepted for publication: 26 October 2015

ABSTRACT

Transparent conducting Al-doped ZnO (AZO) thin films were deposited on glass substrates by DC magnetron sputtering from AZO ceramic target (0.75 %wt Al₂O₃) in gas mixture of (Ar + H₂) at different substrate temperatures. At value of 1.7 % of ratio of H₂ to (H₂+Ar) and at substrate temperature of 200 °C, electron mobility in obtained AZO films is 60.2 cm². V⁻¹.s⁻¹, which is much larger than 34.6 cm². V⁻¹.s⁻¹ of films fabricated in the same condition without H₂. AZO films also have a low resistivity of 2.53×10⁻⁴ Ω.cm, low sheet resistance of 2.5 Ω/□ and high average transmittance above 80 % in the wavelength range of 400 – 1100 nm.

Keywords: transparent conducting; AZO thin films; DC magnetron sputtering; high electron mobility.

1. INTRODUCTION

Transparent conducting oxide (TCO) thin films are widely used for opto-electronic device applications, such as solar cells, light emitting diodes, flat panel displays, and low emissivity windows [1 – 3]. At present, Indium tin oxide (ITO) thin films are popularly used as TCOs in opto-electronic devices. However, a shortage of indium may occur in the near future because of the limited nature of world indium reserves. Therefore, it is important to find other materials to replace indium. ZnO is one of the best choices because of its n-type wide bandgap and of its abundance in nature about ~10¹⁹ metric tons [4] led to the low prices. Undoped ZnO thin films have high transmittance in visible and near infrared wavelength regions, but the electrical resistivity is relatively high. For the TCO semiconductor films in general and ZnO films in particular, the resistivity is determined by the electron concentration and mobility through the expression:

\[
\frac{1}{\rho} = N\mu e
\]

where \(\rho\), \(N\), \(\mu\) and \(e\) are electrical resistivity, electron concentration, electron mobility and electron charge, respectively. For decreasing electrical resistivity, conventionally, aluminum (Al), gallium
Deposition of high-electron-mobility transparent conducting aluminum-doped Zinc oxide…

(Ga), indium (In), … were used as dopants in ZnO thin films with high content to increase electron concentration [5–8]. K. L. Chopra [9] had an expression for absorption as belows

\[
A = \frac{\lambda^2 e^3 N_d}{4 \pi^2 \varepsilon_0 c^3 n \mu} 
\]

(2)

where, \( A \) is absorbance in the visible and near-IR ranges, \( \lambda \) is wavelength of incident light, \( e \) is electron charge, \( N \) is electron concentration, \( d \) is film thickness, \( \varepsilon_0 \) is vacuum permittivity, \( c \) is speed of light, \( n \) is mean refractive index in these wavelength ranges, \( m^* \) is effective mass of electron. The expression shows that an increase in \( N \) will increase the absorption in visible and near-infrared regions. However, if the electron mobility are increased and electron concentration is not too large, the absorbance will decrease significantly.

Recently, first principle calculations have shown that hydrogen in ZnO acts as a shallow n-type donor and numerous articles proved this viewpoint [10–20]. Therefore, hydrogen has emerged as a dopant that increases electron concentration of ZnO thin films. In our study, we found that hydrogen played another role in ZnO thin films. Hydrogen reduced remarkably the scattering in ZnO thin films, so the electron mobility increased. We investigated the influence of hydrogen addition on the electrical and optical characteristics, especially the increasing electron mobility of aluminum-doped zinc oxide films with low Al dopant content.

2. EXPERIMENTAL PROCEDURES

ZnO thin films in this work were prepared by dc magnetron sputtering on glass substrates from AZO ceramic target (0.75 %wt Al₂O₃). The base chamber pressure was 6×10⁻⁶ torr using a turbo molecular pump for all depositions. The film thickness was 1 µm for all samples. The glass substrates were sequentially cleaned ultrasonically in dilute sodium hydroxide, acetone and de-ionized water. The distance between the target and substrate was 50 mm. The films were deposited in gas mixture of hydrogen and argon. In this study, ZnO:Al thin films were deposited at temperatures range from room temperature to 300 °C. At specific temperature, the hydrogen partial pressure ratio \([H_2/(H_2+Ar)]\) was changed from 0 % to 6.7 %.

The electrical properties of the films were determined by Hall effect measurement using Van der Pauw method at room temperature (HMS3000). The transmission spectra of the films in the wavelength range of 300–1100 nm were obtained from an UV–visible spectrophotometer (Jasco V530). The thickness of ZnO:Al thin films was determined using Dektak 6M surface profilometer and INFICON XTM/2 quartz crystal sensor. The crystalline structure of the films was identified by X-ray diffraction (XRD) using CuKα radiation. The surface morphologies of the films were analyzed using field emission scanning electron microscopy (FE-SEM; S4800 HITACHI) and atomic force microscope (AFM; Aligent 5500 SPM).

3. RESULTS AND DISCUSSION

3.1. The electrical properties

Figure 1 shows the electron concentration, electron mobility and resistivity of AZO films deposited at substrate temperature of 200 °C and electron mobility in AZO films deposited at different substrate temperatures between room temperature and 300 °C as a function of hydrogen partial pressure ratio. For the films deposited at 200 °C (Fig. 1a), as H₂ partial pressure
ratio increases from 0 to 1.7 %, the electron mobility increases from 34.6 to 60.2 cm²/Vs that is the highest electron mobility value obtained in this work. Besides, the electron concentration slightly increases from 2.5×10²⁰ to 4×10²⁰ cm⁻³ and resistivity decreases from 7.5 × 10⁻⁴ to 2.5 × 10⁻⁴ Ω.cm. With further increase in H₂ partial pressure ratio to 6.7 %, the electron mobility gradually decreases to 44 cm²/Vs because of an increase in impurity scattering of electrons. Consequently, the resistivity rise from 2.5×10⁻⁴ Ω.cm to 3×10⁻⁴ Ω.cm.

**Figure 1.** (a) Electron concentration, electron mobility and resistivity at substrate temperature of 200 °C and (b) electron mobility in AZO films deposited at various substrate temperatures as a function of H₂ partial pressure ratio.

Electron mobility of AZO films at various substrate temperatures in Fig. 1b dramatically increases by introducing a small amount of hydrogen gas during sputtering process. At hydrogen partial pressure ratio of 1.7 %, the electron mobility obtains the maximum value for all samples deposited at various substrate temperatures. The highest value of 60.2 cm²/Vs obtained at 200 °C. As H₂ partial pressure ratio further increases to 6.72 %, the electron mobility gradually decreases for all samples. In addition, as seen in Fig. 1b, the effect of hydrogen on electron mobility is more remarkable than that of substrate temperature.

**Figure 2.** Figure of merit (FOM) of AZO thin films deposited at substrate temperature of 200 °C as a function of hydrogen partial pressure ratio.
To quantitatively evaluate the performance of a transparent conductive film with different resistivity and transparency, Haacke proposed a figure of merit (FOM) defined by \[ \Phi_H = \frac{T}{R_S} \] (3)

where \( \Phi_H, T, R_S \) are figure of merit, transmittance in visible and near infrared range from 400 to 1100 nm and sheet resistance, respectively. Fig.2 shows FOM values of AZO thin films deposited at substrate temperature of 200 °C at different hydrogen partial pressure ratio. The highest FOM value of 4.44×10^{-2} \( \square/\Omega \) obtained in this paper, is higher than that of 1.17 ×10^{-2} \( \square/\Omega \) of ITO thin films prepared by sputtering [22].

In this present work, we proposed that hydrogen played two roles in improving electrical properties of AZO thin films. The first, hydrogen is considered as a shallow n-type donor to increase carrier concentration. In this case, the majority of hydrogen incorporation in polycrystalline ZnO films was attributed to hydrogen interstitials and a substantially smaller number of multicentre bonds at oxygen vacancies were formed [23]. The second, hydrogen passivate the broken bonds like “dangling bonds” in amorphous silicon, ionized impurities or defects at grain boundary to increase electron mobility.

3.2. The optical properties

The optical transmittances in the wavelength range of 300 – 1100 nm for the AZO films deposited with different H\(_2\) partial pressure ratio at substrate temperature of 200 °C are show in Fig. 3. The average transmittance of AZO films in the visible and near-infrared range (400–1100 nm) is approximately 80 % for samples with small H\(_2\) partial pressure ratio below 1.7 %. The absorption edge in the UV region shows a trend of blue shift with increase of H\(_2\) partial pressure ratio because of Burstein-Moss (BM) effects, which is caused by the excess electrons that fill up the lowest states of the conduction band thus increasing the value of optical band gap. Besides, the absorption in near infrared region becomes strong with further increase in hydrogen partial pressure ratio, indicating that the contributions of free electron absorption effect.

*Figure 3. The transmission spectra of AZO films deposited with different H\(_2\) partial pressure ratio at substrate temperature of 200 °C.*
3.3. The structural properties

![Figure 4](image-url)

Figure 4. The XRD patterns of AZO films deposited with different H$_2$ partial pressure ratio at substrate temperature of 200 °C.

Figure 4 shows the XRD patterns of the AZO films deposited at different H$_2$ partial pressure ratios. All the AZO films showed a (002) diffraction peak, which is an indication of the polycrystalline structure with a preferential orientation of the c-axis perpendicular to the substrate. The (002) plane in ZnO crystals has the lowest surface energy so that the continuous films tend to transform into the (002) orientation films in order to minimize the surface energy [24]. Figure 4 presents the decreasing trend of 2θ position of (002) peak from 34.55° to 34.31° with increase in H$_2$ partial pressure ratio. By comparing with the 2θ value of (002) diffraction peak for ZnO powder from the powder diffraction file (JCPDS#36-1451) (34.42°), it can be inferred that the tensile stress in the films tend to relax because of decrease in 2θ towards value of approximately 34.42° with increase in H$_2$ partial pressure ratio from 0 % to 1.7 %. With further increase in H$_2$ to 6.72 %, the AZO films tend to gradually transform from relaxation to compressive stress. The films prepared at H$_2$ partial pressure ratio
of 1.7% and at substrate temperature of 200 °C are least affected by compressive and tensile stress.

The data of Fig. 5 calculated from Fig. 4 show \( I_{002}/I_{\text{total}} \) ratio and grain size as a function of hydrogen partial pressure ratio. The \( I_{002}/I_{\text{total}} \) increase with adding hydrogen into the films whereas grain size decrease. From the X-ray diffraction data, we realize the etching effect of hydrogen on decreasing the grain size.

3.4. The surface morphology

Figure 6 shows the effects of hydrogen on surface morphology of AZO films deposited at substrate temperature of 200 °C. As mentioned above, the etching effect of hydrogen decrease the grain size of AZO films. Therefore, the Rms (root mean square) roughness value of AZO films deposited with hydrogen are smoother than that of films prepared without hydrogen, 12.94 nm and 11.54 nm, respectively.

![AFM images and Rms roughness value of AZO films](image)

Figure 6. AFM images and Rms roughness value of AZO films prepared at substrate temperature of 200 °C (a) without hydrogen and (b) with hydrogen partial pressure ratio of 1.7%.

4. CONCLUSION

AZO thin films with a high electron mobility and high transmittance in visible and near infrared regions were deposited by dc magnetron sputtering using a ZnO target mixed with 0.75 wt.% Al\(_2\)O\(_3\) in Ar +H\(_2\) ambient. All thin films exhibit a strong (002) c-axis oriented normal to the substrate. These results showed that H\(_2\) has a strong influence on the properties of AZO films, especially electron mobility with highest value of 60.2 cm\(^2\)/Vs at hydrogen partial pressure ratio of 1.7%. While the influence of substrate temperature is not significant for electrical properties of AZO films. Besides, the optical transmittance in visible and near infrared regions for films deposited with low hydrogen partial pressure ratio below 1.7% are approximately 80%. Therefore, it is suggested that the method presented in this study would be an effective way to prepare Al-doped ZnO films with good quality, especially high electron mobility that can be applied to device fabrication process with relative ease.

**Acknowledgements.** This research is funded by University of Science – Vietnam National Ho Chi Minh City (VNU-HCM) under grant number **TX2015-18-06**
REFERENCES


Deposition of high-electron-mobility transparent conducting aluminum-doped Zinc oxide…


TÓM TÁT

CHẾ TẠO MÀNG MỎNG DẪN ĐIỆN TRONG SUỐT OXIT KẼM PHA TẠP NHÔM CÓ ĐỘ LINH ĐỘNG ĐIỆN TƯ CAO BẰNG PHƯƠNG PHÁP PHÚN XẠ MAGNETRON DC

Hoàng Văn Dũng, Nguyễn Duy Khánh, Trần Cao Vinh

Phòng Thí nghiệm Vật liệu kỹ thuật cao – Đại học Khoa học tự nhiên,
Đại học Quốc gia TP. HCM, 227 Nguyễn Văn Cừ, Thành Phố Hồ Chí Minh

Email: hvduong@hcmus.edu.vn

Măng mỏng dẫn điện trong suốt oxit kẽm pha tạp nhôm (AZO) được lắng đọng trên đế thủy tinh bằng phương pháp phún xạ magnetron DC từ bia gồm AZO (0.75 % wt. Al₂O₃) trong hỗn hợp khí argon + hydrô tại các nhiệt độ đế khác nhau. Giá trị độ linh động điện tử màng AZO đạt được tại tỷ lệ áp suất riêng phần khí H₂ 1.7 % và nhiệt độ đế 200 ⁰C là 60.2 cm². V⁻¹.s⁻¹ cao hơn nhiều so với giá trị 34.6 cm². V⁻¹.s⁻¹ của màng được chế tạo ở cùng điều kiện mà không có pha tạp H₂. Cung với giá trị độ linh động điện tử cao màng mỏng AZO này còn đạt giá trị điện trở suất thấp là 2.53×10⁻³ Ω.cm, điện trở mặt 2.5 Ω/□ và độ truyền qua trung bình cao trong vùng khả kiến và vùng hồng ngoại gần (vùng bước sóng 400 – 1100 nm) trên 80 %.

Từ khóa: dẫn điện trong suốt, màng mỏng AZO, phún xạ magnetron DC, độ linh động điện tử cao.