CHARACTERIZATION OF ZnO:Al DEPOSITED BY CO-SPUTTERING FOR TRANSPARENT CONDUCTIVE ELECTRODES

NGUYEN TRAN THUAT, BUI BAO THOA, THAN THI CUC, NGUYEN MINH HIEU, HOANG NGOC LAM HUONG, AND BUI VAN DIEP
Nano and Energy Center, VNU University of Science, 334 Nguyen Trai, Thanh Xuan District, Hanoi, Vietnam

HOANG CHI HIEU
Faculty of Physics, VNU University of Science, 334 Nguyen Trai, Thanh Xuan District, Hanoi, Vietnam

E-mail: thuatnt@vnu.edu.vn

Abstract. *Aluminum doped zinc oxide was prepared by magnetron sputtering methods at room temperature using a ZnO ceramic target doped 2%wt by Al_2O_3. The optical transmittance of the films is higher than 80% in the visible range. A direct bandgap type was reached by controlling deposition conditions; the bandgap value was in the range between 3.2 eV and 4.2 eV. Good electrical and optical properties were obtained for the films deposited by an appropriate co-sputtering of ZnO and Al targets. These films with a resistivity, about $1.3 \times 10^{-2} \Omega.cm$, and a transmittance, higher than 80%, can be applicable for transparent conducting electrodes.*

Keywords: AZO thin film, co-sputtering method, resistivity, transmittance .

I. INTRODUCTION

Transparent conductive oxides (TCOs) have been extensively studied because they are essential elements for optoelectronic applications such as thin film solar cells [1], flat-panel displays [2] and light emitting diodes [3, 4]... For these applications, the average optical transmittance is up to 80% in the visible range. At the presence, the commonly used TCO material is indium tint oxide (ITO), and there are growing concerns are due to its toxicity, high cost and the limited availability of the element indium [5].

Aluminum doped zinc oxide (ZnO:Al or AZO) thin films are attracted a lot of intentions in the research community due to the optical properties having a sharp ultra violet(UV) cut-off. Highly transparent AZO thin films in the visible range even exhibit the low conductivity varying from 9.8×10^{-2} Ωcm to 1.5×10^{-4} Ωcm. Furthermore, because of their chemical stability and their adhesion to the substrate, AZO films are more useful in the fabrication of thin-film solar cells. Several deposition techniques are used to grow ZnO:Al thin films, including chemical vapour

deposition (CVD) [6], spray pyrolysis [7], pulsed laser deposition (PLD) [8], pulsed magnetron sputtering [9] and conventional magnetron sputtering [10–12]. Compared to other techniques, conventional magnetron sputtering showed many advantages, such as large area smoothly thin film and relatively high growth rate.

It was reported that the conductivity of AZO films could be mostly controlled by Al concentration, which was easily adjusted by sputtering power set and time. Alnajjar confirmed that the ratio of mixture between ZnO and Al_2O_3 about 98:2 ensured good electrical properties [9]. Other studies showed that the AZO resistivity was the lowest when the Al concentration was different from 2% of weight. In this paper, a complete experimental optical and electrical study of AZO thin films is presented for applications in low cost oxide semiconductor based solar cells.

II. EXPERIMENTS

In this study, AZO thin films were deposited on silicon and corning substrates by using various sputtering techniques. Commercial 2-inch of diameter AZO (2% weight of Al_2O_3) and Al targets are used. The oxide target is fabricated by pressing at high temperature the corresponding oxide thin powder. Four series of AZO thin films were fabricated by magnetron sputtering with: (i) only the AZO target, (ii) the AZO and the Al target under an oxygen reactive plasma, (iii) the AZO and the Al target with multiple 2-minute duration of the direct current (DC) sputter power and with/without post annealing. For the latter series, each 2min of duration of DC sputter power was distributed equally during the whole process. All of the samples were deposited on a Syskey 2-DC and 2-radio frequency (RF) magnetron gun system. The optical properties of all the thin films were characterized on a spectroscopic ellipsometer, SmartSE Horiba-Jobin Yvon and on an ultra violet visible near infrared (UV-VIS-NIR) spectrometer, Jasco V670. The sheet resistance of thin films was measured on a four-point prober, Jandel RM3000. The thicknesses of the films were characterized also on a stylus profiler, Bruker Dektak XT system.

Table 1. The sputter conditions of various AZO thin films series

Deposition parameters	AZO series	Oxygen reactive AZO series	AZO with more aluminum series
Target	AZO	AZO Al	
RF power	30 to 90W	90 W at AZO target	
DC power	N/A	90W at Al	45W at Al target
Time	1h	30 min	1h for RF Multiple of 2-minute duration for DC
Base pressure	$< 5 \times 10^{-6}$Torr		
Sputter pressure	9.10^{-3} Torr		
Ar flow rate	20 sccm		
O2 flow rate	N/A	1 to 2 sccm	N/A
Substrate	Silicon and corning glass		
Target-substrate distance	10cm		
Post deposition annealing			500^oC, under 5.10^{-2}Torr of 5% H_2 in Ar

III. RESULTS AND DISCUSSION

Fig. 1 shows the dependence of AZO thin films deposition rate as function of the RF power. The thickness of the films is deduced by spectroscopic ellipsometer adjustment by using the mixture of ZnO (98% of weight) and Al_2O_3(2% of weight) materials provided by the DeltaPsi2 software. The details of the adjustments are not shown here; only the thickness of the main layer is used for calculating the deposition rate. From Fig. 1, one can easily sees that when the RF sputter power increases from 30W to 90W, the deposition rate increases from about 15 Å/min to about 35 Å/min.
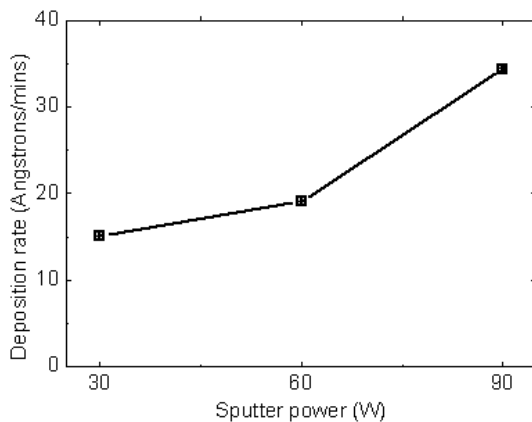
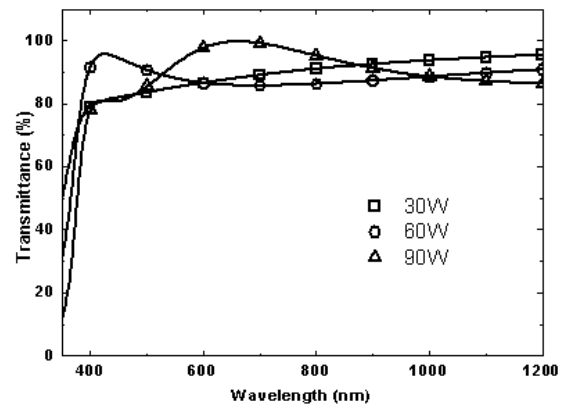**Fig. 1.** The RF-power dependence of the deposition rate of AZO thin films

Fig. 2. Transmittance spectra of AZO thin films vs. RF powers

Fig. 2 shows the transmission spectra of AZO thin films deposited at different RF sputter power. The average transmittance of these films is generally higher than 80%, thus showing its good transparent properties for the range of wavelength higher than 400nm. One can see the peak feature of the spectra. However these peaks correspond to the interference effect of the light.

In order to deduce the band gap of the AZO thin films, the absorption coefficient of the films is calculated from the transmittance spectra with thickness provided by spectroscopic ellipsometer. Fig. 3 shows the dependence of $(\alpha h\nu)^2$ curves versus photon energy. At higher photon energy, the linear feature is observed, giving the way to extrapolate the Tauc band gap of the AZO thin films [13]. The extrapolation indicates that the direct band gap value is between 3.2 eV and 3.3eV which corresponds to the transparent window showed at Fig. 2.

The synthesis of AZO is further studied by more complicated reactive co-sputter techniques. An additional Al target is used and a small quantity of oxygen gas is introduced with Ar for the reactive sputtering process. At this experiment, the RF power is kept fixed at 90W on the AZO target; the DC power on the Al target is also fixed at 60W. For this series, only oxygen flow rate is changed from 5% to 10% of the total gas flow rate, which is constant at 20 sccm. Fig. 4 shows the deposition rate of AZO thin films as function of the oxygen flow rate ratio. We can see that the deposition rate decreases slightly, from 75 Å/min to about 50 Å/min as the oxygen flow rate increases. These deposition rates are generally higher than those when only the AZO target is used. This is the direct result of the reactive sputtering process on the additional Al target.
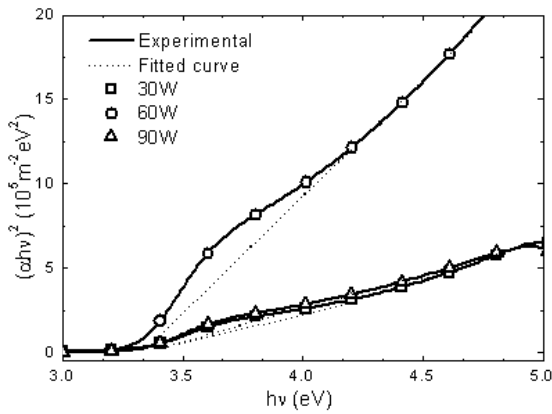
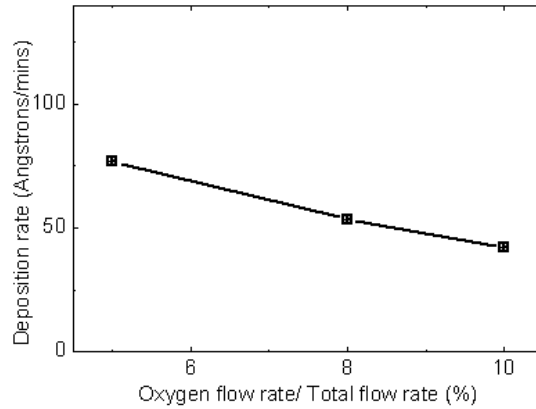**Fig. 3.** The $(\alpha h\nu)^2$ curves vs. the photon energy for AZO/glass thin film.

Fig. 4. The deposition rate of the oxygen reactive AZO series with different oxygen flow rate ratio

Fig. 5 shows the transmission spectra of thin films obtained by the oxygen reactive co-sputter method with different oxygen flow rate ratio. It can be seen clearly that the overall transmission of these thin films is higher than 90%. These films are in fact more transparent than thin films obtained by sputtering only the AZO target (showed by Fig. 2). By adding more Al and under the oxygen reactive plasma, the films exhibit more enhancements of the transparent effect, which may give the drawback of the conductive properties.
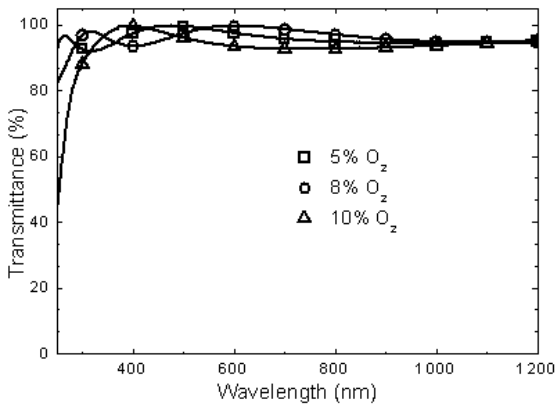

Fig. 5. The transmittance spectra of oxygen reactive co-sputtered AZO thin films at different oxygen flow rate ratio
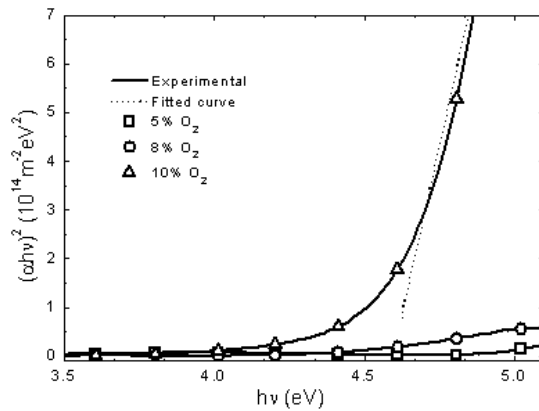
Fig. 6. The extrapolation of bandgap of oxygen reactive co-sputtered AZO thin films

Fig. 6 show the $(\alpha h\nu)^2$ curves versus photon energy of the films obtained by the oxygen reactive co-sputtering method. From the linear fit of the curves, the bandgap is then extrapolated. It is found that this band gap varies from about 4.3 to 4.5 eV.

In order to enhance the conductive properties of AZO thin films, aluminum was added by using another co-sputtering method. For this series of experiment, the RF power on the AZO target is kept constant at 90W, only Ar is used for reducing the oxidation effect during the sputtering. The DC power on the Al target is ignited during a limited numbers of 2 min duration for 1h of sputtering time. 4 min condition corresponds to 2 times the DC power is ignited during 2 min each, equally distributed during 1 hour. 6 min corresponds to 3 times the DC power is on during 2 min. The more time DC power on Al target is ignited, the more aluminum is added to the films.

The conductive effect of the obtained films is further enhanced by the annealing process just after sputtering, at 500^oC under 5×10^{-2}Torr of 5% hydrogen in Ar gas mixture. The presence of the hydrogen is supposed to passivate dangling bonds of the films, thus giving a raise to the conductivity. Fig. 7 shows the deposition rate of AZO thin film as function of the DC sputter time on the Al target. One can see that this value stays relatively stable, at about 25 Å/min to 30 Å/min as the DC power time increases from 0 to 6 min. The thicknesses of these films are in fact confirmed by the measurement on a stylus profilometer.
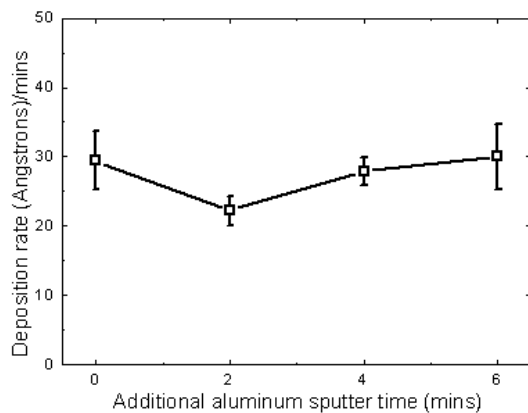
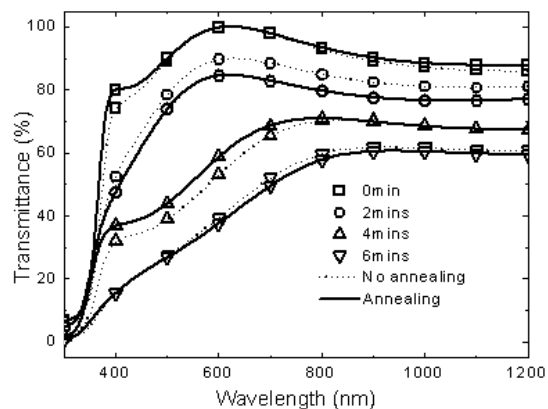**Fig. 7.** The deposition rate of AZO vs. aluminum co-sputtering time

Fig. 8. The transmittance spectra of AZO deposited at different aluminum co-sputtering time

Fig. 8 shows the transmittance of the AZO thin films obtained by co-sputtering method with added aluminum. Once can see that the more DC sputter time on the Al target, the films exhibit less transparent properties. Also annealed thin films have less significance effects on the transmission spectra. Fig. 9 show the $(\alpha h \nu)^2$ curves versus photon energy of the AZO in dependence of Al sputtering time. With the linear fit at higher photon energy, we can extrapolate the direct band gap of these films. This value is at the range between 3.2 eV and 3.4 eV, which is clearly smaller than that value of thin films deposited under the oxygen reactive sputtering condition.

The effect of the annealing process on the sheet resistance of AZO thin films doped more aluminum is showed on Fig. 10. For the film with no added aluminum, which is corresponded to the 0 min of the DC sputter time, the sheet resistance could be hardly measured. But for the films annealed under the hydrogen atmosphere this value is about 6 kΩ/o. As the DC sputter time on the

Al target increases, the value of sheet resistance decreases. And the annealed films always exhibit smaller sheet resistance.
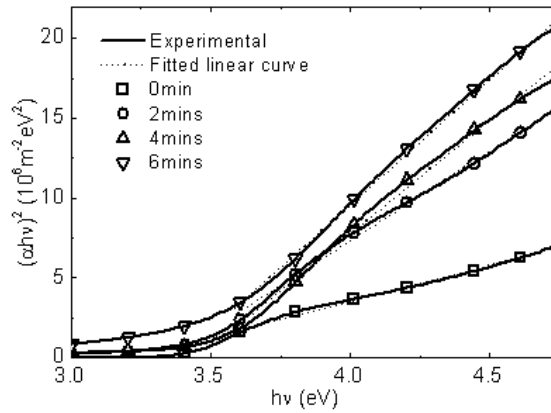

Fig. 9. The extrapolation of optical bandgap of AZO vs aluminum co-sputtering time

Fig. 11 shows the calculated resistivity of the AZO thin films with added aluminum by the co-sputtering method. As the DC sputter time on the Al target increases more, the resistivity of AZO films greatly decreases from $10^{-1}\Omega$.cm to about $10^{-2}\Omega$.cm. By putting together the transmittance spectra and the resistivity of the AZO thin films, one can see that with 2 min of the DC sputter time, the film possesses optimum properties: a good conductance, with the resistivity about $1.3\times10^{-2}\Omega$.cm, and a good transparency, with the transmission higher than 80%. This condition can be used for further studies and shows highly potential applications in thin film solar cell as transparent conductive oxide layers.
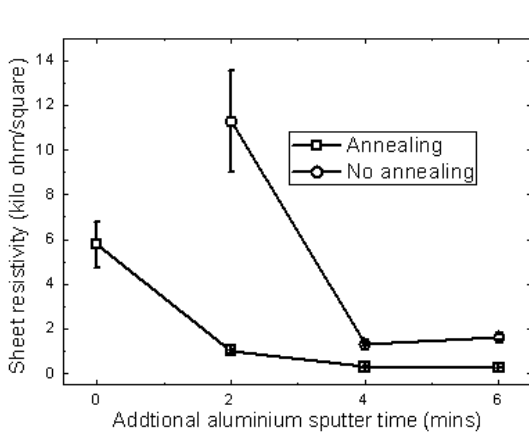

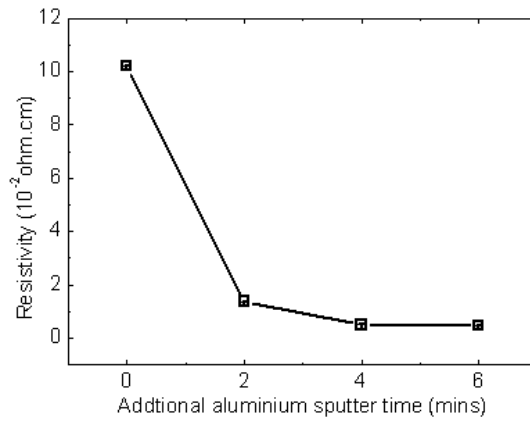**Fig. 10.** The effect of annealing on the sheet resistance of AZO thin films

Fig. 11. The dependence of resistivity as function of aluminum co-sputtering time

IV. CONCLUSION

A study on the sputtering conditions affecting to the properties of AZO thin films is presented; started by a simple sputtering method on single AZO target, then followed by a complicated oxygen reactive co-sputtering and added aluminum co-sputtering during limited numbers of time. The AZO thin films showed high transparency properties for oxygen reactive co-sputter series but very low conductivity. The AZO thin films have optimized TCO properties for the condition of 2 min of the DC sputter time on the Al target followed by annealing under a hydrogen atmosphere. At these conditions, a transmittance higher than 80% for the wavelength range from 400 nm to 1200 nm, and a resistivity of $1.3 \times 10^{-2} \Omega.cm$ were obtained. These AZO thin films serving as a n-type TCO layer may be suggested to applications in the low-cost semiconducting oxide based solar cells.

ACKNOWLEDGEMENTS

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