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Influence of ZnO buffer layer on AZO film properties by radio frequency magnetron sputtering

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Abstract

Transparent conductive films of Al-doped zinc oxide (AZO) were deposited on glass substrates under various ZnO buffer layer deposition conditions (radio frequency (r.f.) power, sputtering pressure, thickness, and annealing) using r.f. magnetron sputtering at room temperature. This work investigates the influence of ZnO buffer layer on structural, electrical, and optical properties of AZO films. The use of grey-based Taguchi method to determine the ZnO buffer layer deposition processing parameters by considering multiple performance characteristics has been reported. Findings show that the ZnO buffer layer improves the optoelectronic performances of AZO films. The AZO films deposited on the 150-nm thick ZnO buffer layer exhibit a very smooth surface with excellent optical properties. Highly *c*-axis-orientated AZO/ZnO/glass films were grown. Under the optimized ZnO buffer layer deposition conditions, the AZO films show lowest electrical resistivity of $6.75 \times 10^{-4}\ \Omega\,\text{cm}$, about 85% optical transmittance in the visible region, and the best surface roughness of $R_a = 0.933\,\text{nm}$.

Keywords: AZO; ZnO buffer layer; Grey relational analysis; Surface roughness

1. Introduction

Transparent conducting oxide (TCO) films with optical transmission more than 80% in the visible region and resistivity less than $10^{-3}\ \Omega\,\text{cm}$ are extensively used in transparent electrodes, solar cells,[1] optoelectronic devices, piezoelectric devices and surface acoustic wave devices.[2] Materials such as indium tin oxide (ITO), tin oxide (SnO_2) and zinc oxide (ZnO) films are well-known as typical transparent conductive films. Recently, ZnO conductive films show promise because of their low cost and high crystallinity.[3] Group III metal dopants, such as Al, In and Ga have been suitably added to increase the electrical conductivity and transparency of ZnO films.[4] Several deposition techniques have been used to grow AZO films, such as spray pyrolysis[5] and magnetron sputtering.[6] Studies show that AZO film properties are influenced by deposition parameters, such as substrate temperature, sputtering power, gas pressure, substrate-to-target distance and oxygen flow rate.[7,8] The ZnO films deposited on the *c*-plane sapphire have high carrier concentrations and show a rough surface morphology due to the large lattice mismatch and large difference in the thermal expansion coefficient between ZnO and sapphire.[9] In order to reduce the residual strain and structural defects, it is necessary to use suitable substrates. A variety of buffer layers have also been used as buffer layers in ZnO film growth, such as MgO,[10] SiC,[11] CaF_2,[12] and ZnS[13] to reduce residual strain and structural defects, and to improve the crystalline quality and optoelectronic performances of ZnO films. Moreover, the AZO films deposited on the proper thick AZO buffer layer exhibit the good structural and optical properties.[14]

This paper reports the preparation of high quality Al-doped zinc oxide (AZO) transparent conductive films prepared on glass substrates using ZnO buffer layer and radio frequency (r.f.) magnetron sputtering at room temperature. The grey relational analysis[15] is used to investigate multiple performance characteristics in the Taguchi method for the optimized deposition ZnO

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buffer layer process. The influence of ZnO buffer layer on the structural, electrical, optical and surface roughness properties of AZO films are investigated.

2. Experimental procedure

The AZO transparent conducting films and ZnO buffer layer were deposited on glass substrates by r.f. magnetron sputtering with a base pressure of 5.0×10^{-6} Torr. The AZO and ZnO targets (99.995% pure) were commercially available hot-pressed and sintered targets. All films were grown at room temperature with a water-cooled target. Before deposition, the glass substrates (Corning 1737F, 40 mm × 20 mm × 1.1 mm) were ultrasonically cleaned in acetone, rinsed in deionized water, and blow-dried with nitrogen. The film thickness was measured using a surface profilometer (α-step, AMBIOS XP-1). A field emission scanning electron microscope (SEM, JEOL, JSM-6500F) analyzed the surface morphologies and an atomic force microscope (AFM, PSIA-XE-100) obtained topographic images. The Rigaku-2000 X-ray diffraction (XRD) spectrometer analyzed the structural properties using Cu Kα radiation. The four-point probe method (Mitsubishi chemical MCP-T600) detected electrical resistivity. A UV–vis spectrophotometer carried out optical transmittance measurement in the 300–800-nm wavelength range.

The current work uses the Taguchi experimental design, an L_9 (3^4) orthogonal array with four columns and nine rows[16] to optimize the ZnO buffer layer (ZnO/glass) deposition process design. This experiment selects four major ZnO buffer layer deposition parameters, such as r.f. power, sputtering pressure, ZnO film thickness, and annealing temperature, each assigned high, medium, and low levels, as shown in Table 1.

This study conducted the preliminary experiments to determine the growth rate of ZnO buffer layer. The analysis of variance (ANOVA)[16] results for the ZnO growth rate, findings show that r.f. power is the major deposition parameter in the ZnO growth rate. The AZO films were grown (AZO/ZnO/glass) by maintaining the r.f. power to a constant value of 100 W, sputtering pressure of 5 mTorr, and AZO at a thickness of 700 nm. All samples were deposited with substrate rotation in order to have good surface morphology.

Table 1
Deposition parameters of ZnO buffer layer (ZnO/glass)

Substrate	Corning 1737F glass
Target	ZnO; 99.995% purity, 50.8 mm diameter
Gas	Argon (99.995%)
Base pressure	5.0×10^{-6} Torr
Substrate rotate vertical axis	10 rpm
Substrate-to-target distance	90 mm
Substrate temperature	Room temperature

	Level		
	1	2	3
(A) r.f. power (W)	50	100	150
(B) Sputtering pressure (mTorr)	1	5	10
(C) Thickness (nm)	50	150	300
(D) Post-annealing temperature (°C)	None	200	400

In the grey relational analysis, the experimental results of electrical resistivity and optical transmittance for AZO/ZnO/glass are first normalized in the range between 0 and 1 called the grey relational generating. The optimal combinations of the ZnO buffer layer deposition parameters are predictable with the grey relational analysis and statistical analysis of variance.

3. Results and discussion

3.1. Influence of ZnO deposition parameters on AZO film resistivity

The ANOVA results for the electrical resistivity of AZO grown on ZnO/glass and contribution ration of each parameter are shown in Table 2. The ZnO buffer layer sputtering power has a dominant effect on electrical resistivity, almost 62% contribution ratio. Fig. 1 shows the S/N response graph for the electrical resistivity of AZO grown on ZnO/glass. The AZO resistivity decreases with proper ZnO sputtering power. Fig. 2 shows the SEM micrographs of ZnO buffer layer with different r.f. powers. The crystallinity and crystallite size of ZnO buffer layer could be increased (see Fig. 2b) for proper sputtering power (100 W). The SEM micrographs of AZO films grown on ZnO/glass as shown in Fig. 3, the AZO crystallinity increases with proper ZnO sputtering power (Fig. 3b), and the electrical resistivity

Table 2
ANOVA results for electrical resistivity of AZO grown on ZnO/glass

Factor	Sum of square (*S*)	Degree of freedom (*F*)	Variance (*V*)	Contribution (*P* %)
A	547.5294	2	273.7647	62.107
B	48.8157	2	24.4078	5.537
C	250.2219	2	125.1109	28.383
D	35.0094	2	17.5047	3.971
Total	881.5764	8		100

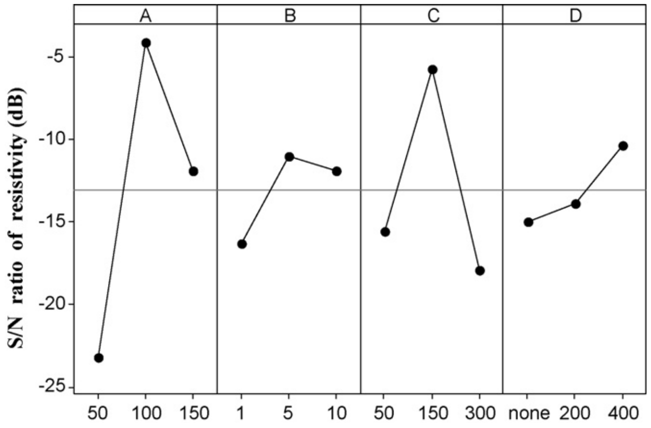

Fig. 1. S/N graph for electrical resistivity of AZO grown on ZnO/glass. *Note*: A, r.f. power; B, sputtering pressure; C, thickness; D, post-annealing temperature.

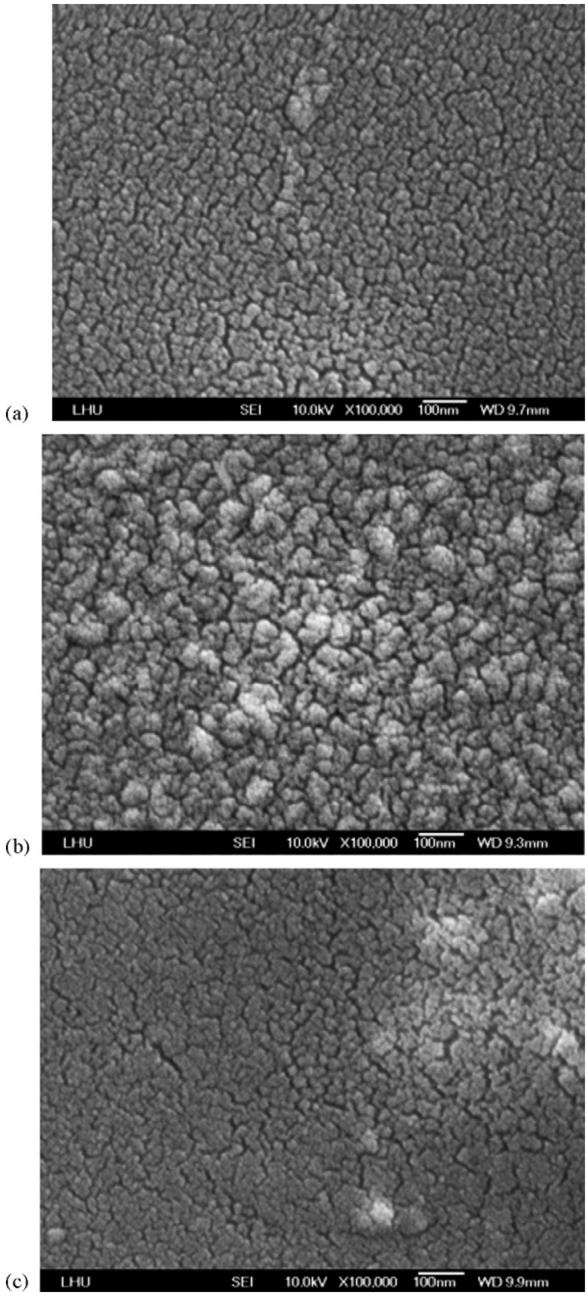

Fig. 2. SEM micrographs of ZnO buffer layer (ZnO/glass) with different r.f. powers: (a) 50 W, (b) 100 W, and (c) 150 W.

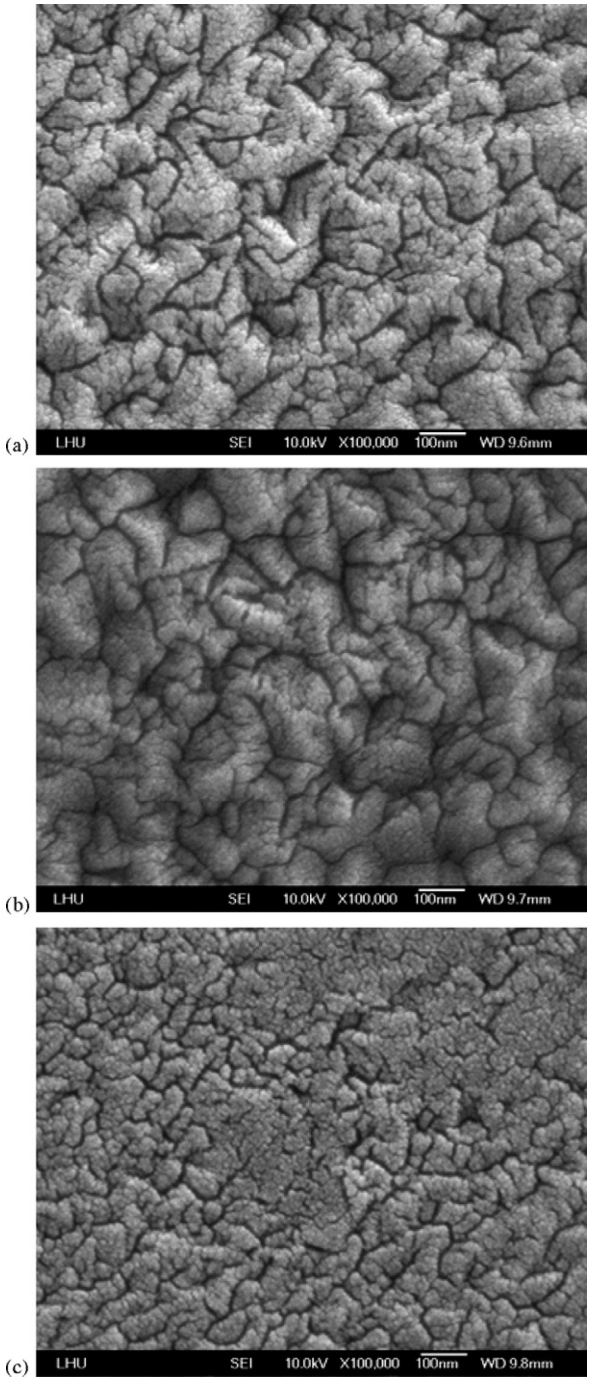

Fig. 3. SEM micrographs of AZO grown on ZnO/glass with different ZnO r.f. powers: (a) 50 W, (b) 100 W, and (c) 150 W.

of AZO/ZnO/glass film reduces. Additionally, the ZnO buffer layer thickness also influences the electrical resistivity by about 28% in contribution ratio. The grain size is calculated using Scherrer's equation. The crystallite sizes of AZO films with ZnO buffer layer thicknesses of 50, 150, and 300 nm, are calculated to be about 10.12, 15.39, and 10.57 nm, respectively, indicating that the crystallite size of AZO films increased with proper ZnO thickness (150 nm). This is also similar to the result of Wang et al.[14] The larger crystallite size results in lower grain boundary density, behaving as traps for free carriers and barriers for carrier transport. Therefore, increasing crystallite size can decrease the grain boundary scattering and increase the carrier lifetime, consequently leading to an increase in conductivity due to the increase in carrier concentration and Hall mobility,[17] and reduced electrical resistivity of AZO/ZnO/glass films.

3.2. *Influence of ZnO deposition parameters on AZO film transmittance*

Table 3 shows the ANOVA results for the transmittance of AZO film grown on ZnO/glass. The ZnO buffer layer thickness has a dominant transmittance effect, almost 36% in contribution ratio. Fig. 4 shows the S/N graph for the transmittance of

Table 3
ANOVA results for transmittance of AZO grown on ZnO/glass

Factor	Sum of square (*S*)	Degree of freedom (*F*)	Variance (*V*)	Contribution (*P* %)
A	0.0318	2	0.0159	5.664
B	0.1819	2	0.0909	32.346
C	0.2018	2	0.1009	35.819
D	0.1468	2	0.0734	26.098
Total	0.5624	8		100

AZO grown on ZnO/glass. Our findings reveal that the AZO transmittance increases with proper ZnO thickness. As shown in Fig. 5, the SEM micrographs of AZO deposited on different ZnO buffer layer thicknesses (50, 150, and 300 nm, respectively) indicate that the larger crystallite size of AZO with ZnO buffer thickness at 150 nm (Fig. 5b). Increasing crystallite size allows for the decrease in surface roughness of films,[18] and increasing AZO film transmittance, probably due to relatively low surface roughness, resulting in less light scattering.[14,19]

Additionally, the sputtering pressure of ZnO buffer layer also has some influence on transmittance, about 32% in contribution ratio. Fig. 6 shows the SEM micrographs of the ZnO buffer layer with different sputtering pressures. The resulting larger crystallite size with proper sputtering pressure (see Fig. 6b) corresponds to the experimental result of Lv et al.[17] The AZO film quality is strongly dependent on the ZnO buffer layer and the grain size in the AZO films has larger value. According to the Scherrer's equation, the grain size of AZO are estimated to be about 13.08, 17.81, and 9.27 nm, respectively, with different ZnO buffer sputtering pressure of 1, 5, and 10 mTorr. The ZnO buffer layer sputtering pressure of 5 mTorr is applied, increasing the AZO/ZnO/glass film transmittance.

3.3. Optimal ZnO buffer layer deposition parameters

The grey relational analysis can be used to effectively solve complicated interrelationships among multiple performance characteristics. The grey relational coefficient is[15]:

$$r(x_0(k), x_i(k)) = \frac{\min\limits_i \min\limits_k |x_0(k) - x_i(k)| + \zeta \max\limits_i \max\limits_k |x_0(k) - x_i(k)|}{|x_0(k) - x_i(k)| + \zeta \max\limits_i \max\limits_k |x_0(k) - x_i(k)|} \quad (1)$$

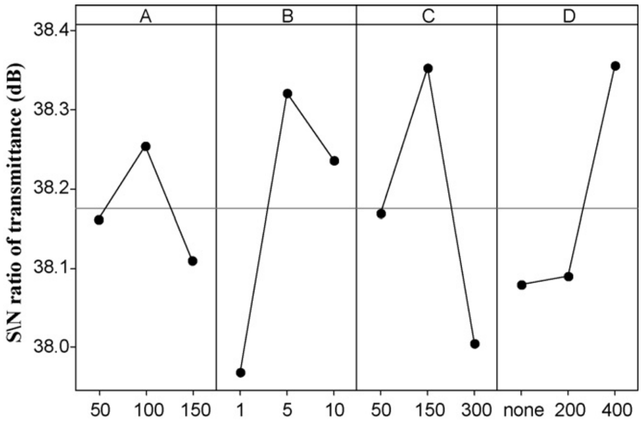

Fig. 4. S/N graph for transmittance of AZO grown on ZnO/glass. *Note*: A, r.f. power; B, sputtering pressure; C, thickness; D, post-annealing temperature.

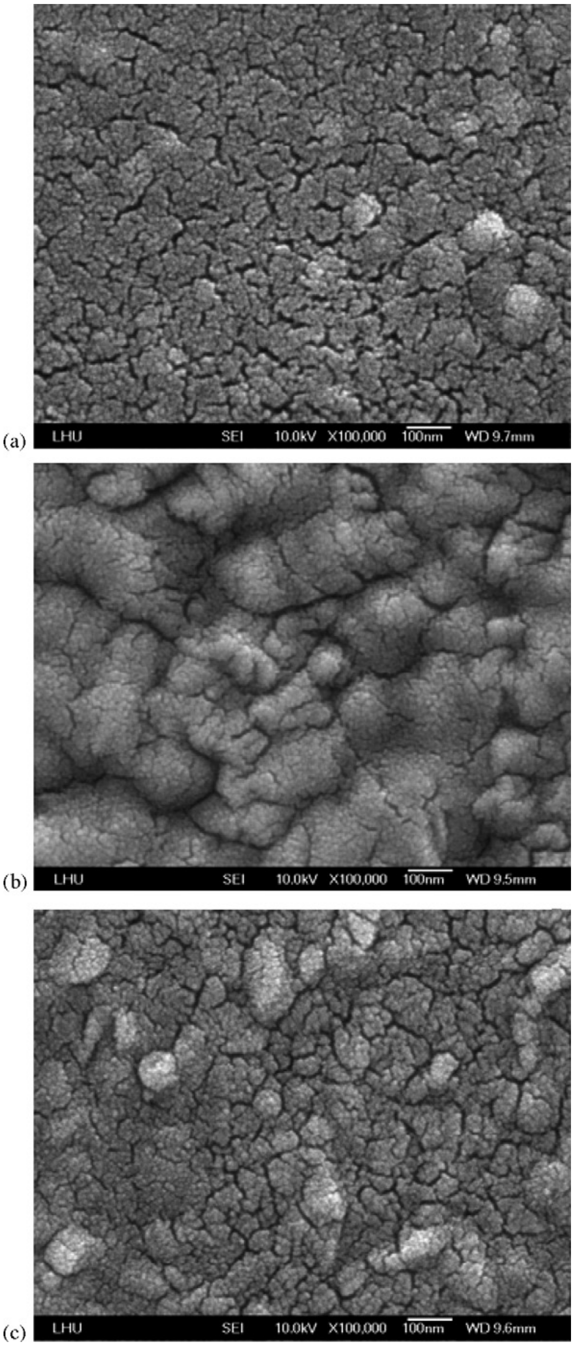

Fig. 5. SEM micrographs of AZO deposited on different ZnO buffer layer thicknesses: (a) 50 nm, (b) 150 nm, and (c) 300 nm.

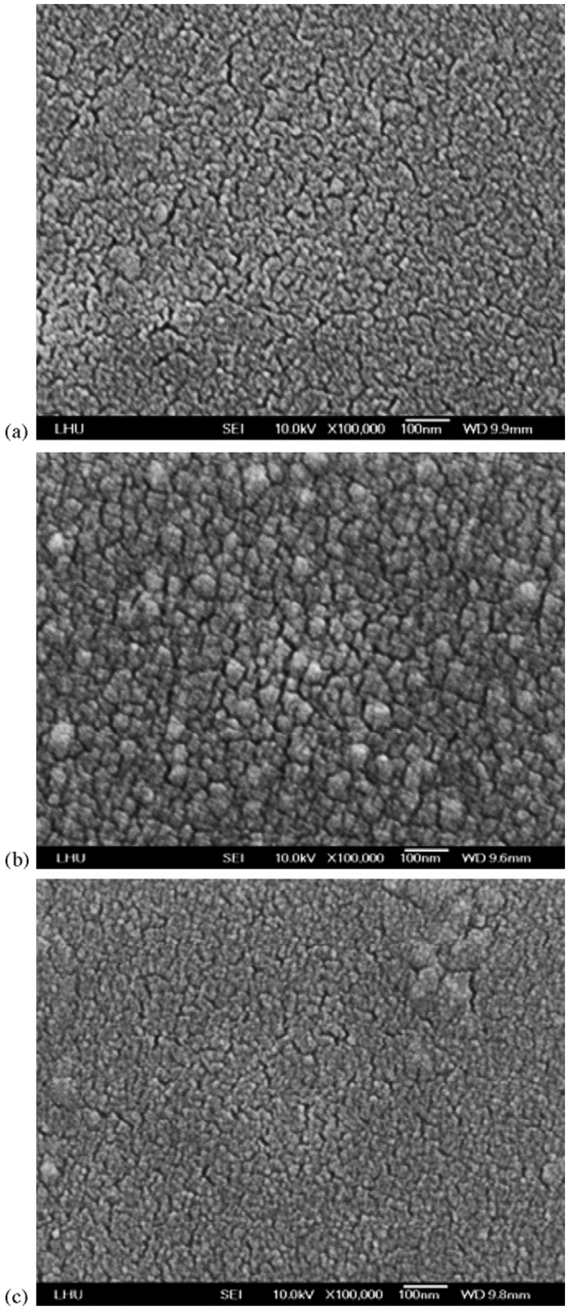

Fig. 6. SEM micrographs of ZnO buffer layer (ZnO/glass) with different sputtering pressure: (a) 1 mTorr, (b) 5 mTorr, and (c) 10 mTorr.

where $x_i(k)$ is the normalized value of the kth performance characteristic in the ith experiment and ζ is the distinguishing coefficient, $\zeta \in [0,1]$. The value of ζ can be adjusted according to actual system requirement. The coating parameters are of equal weighting in this paper, and therefore ζ is 0.5.

After the grey relational coefficient is derived, it is usual to take the average value of the grey relational coefficients as the grey relational degree. It is defined as[15]:

$$r(x_0, x_i) = \frac{1}{n}\sum_{k=1}^{n} r(r_0(k), x_i(k)) \tag{2}$$

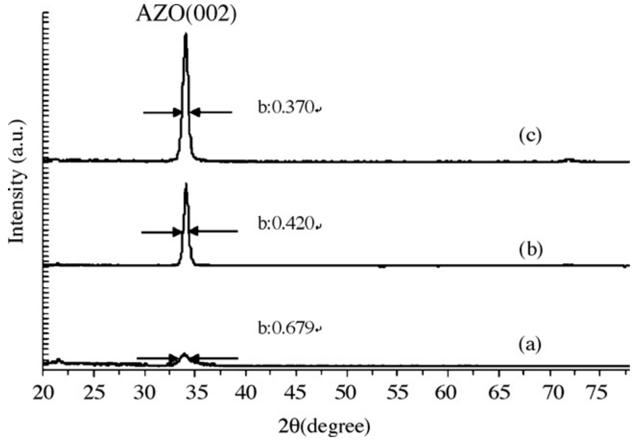

Fig. 7. XRD diffraction patterns of AZO films deposition with different deposition conditions: (a) no buffer layer, (b) orthogonal array parameters, and (c) grey theory prediction design (b: full width at half maximum, FWHM).

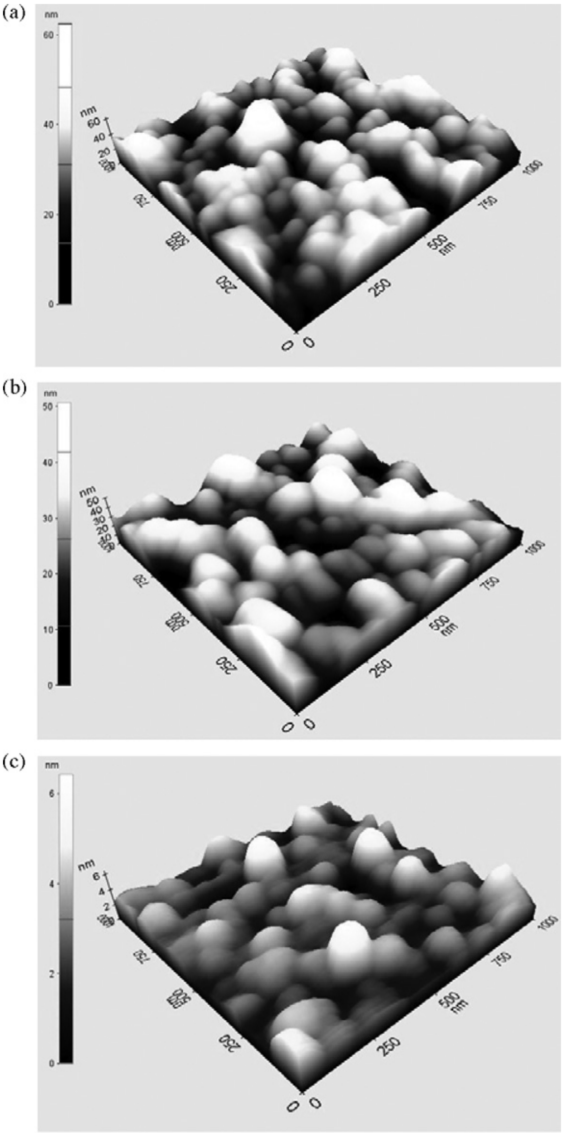

Fig. 8. The 3D AFM images of AZO films obtained with different deposition conditions: (a) no buffer layer, Ra=9nm, crystallite size=12.19 nm, (b) orthogonal array parameters, Ra=7.07nm, crystallite size=19.63 nm, and (c) grey theory prediction design, Ra=0.933nm, crystallite size= 22.26 nm.

where *n* is the number of performance characteristic. The grey relational grade shows the correlation between the reference sequence and the comparability sequence to be compared to. The evaluated grey relational grade fluctuates from 0 to 1 and equals one if these two sequences are identically coincident.

The gray relational grade for each experiment applying the L_9 (3^4) orthogonal array, higher gray relational grade indicates that the corresponding experimental result is closer to the ideal normalized value. Based on Eqs. (1) and (2), the multiple performance characteristics for the deposition of ZnO buffer layer with orthogonal array parameters (A2 B1 C2 D3), and optimal predicted coating process parameters (A2 B2 C2 D3) are obtained.

3.4. *Confirmation tests*

The confirmation test results for the multiple performance characteristics of AZO films. The electrical resistivity and optical transmittance of the AZO films grown on glass without ZnO buffer layer were $7.721 \times 10^{-3}\,\Omega\,\text{cm}$ and 80.48%, respectively. A comparison of the grey theory prediction design (AZO/ZnO, A2 B2 C2 D3/glass) with the orthogonal array parameters (AZO/ZnO, A2 B1 C2 D3/glass), indicating that the electrical resistivity of AZO reduces from 7.25×10^{-4} to $6.75 \times 10^{-4}\,\Omega\,\text{cm}$ and the optical transmittance improves from 83.25 to 84.78%, respectively.

Fig. 7 shows that when the grey theory prediction design (AZO/ZnO, A2 B2 C2 D3/glass) was applied, the peak intensity of (0 0 2) plane in the XRD patterns of AZO film had the highest value. The Scherrer's equation has been used to calculate the crystallite size. These results are consistent with 3D AFM images of AZO films shown in Fig. 8. As shown in the figure, the grey theory prediction design of AZO films revealed the smoothest surface and larger crystallite size (see Fig. 8c). A lower electrical resistivity for AZO has been obtained. Optical transmittance as a function of wavelength in the 350–800 nm range was measured as shown in Fig. 9, indicating that the average optical transmittance of the three experiment sets is higher than 80%. Transmittance in the grey theory prediction design was about 85%.

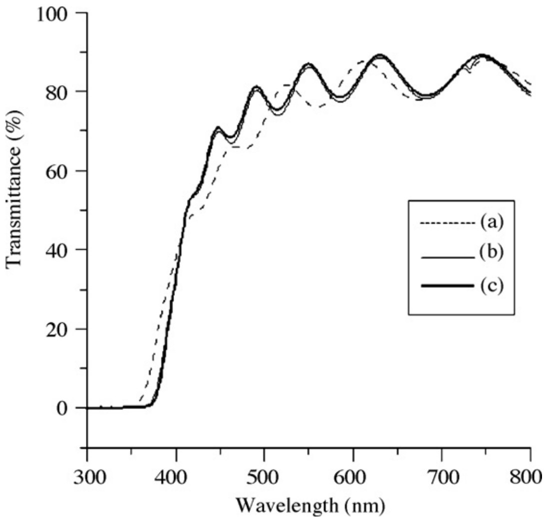

Fig. 9. Optical transmittance for AZO films with different ZnO deposition conditions: (a) no buffer layer, (b) orthogonal array parameters, and (c) grey theory prediction design.

4. Conclusions

This study applies the orthogonal array with grey relational analysis to optimize the AZO/ZnO/glass transparent conductive films. The effects of various deposition conditions of ZnO buffer layer on structure, surface roughness, and optoelectronic properties of AZO films were studied. The XRD analysis indicates that the AZO films were highly oriented along the *c*-axis, which is perpendicular to the substrate surface. The average crystallite size of AZO films was about 10–23 nm. ANOVA results indicate that ZnO sputtering power and ZnO thickness significantly affect the electrical resistivity and optical transmittance of AZO. The deposition conditions of ZnO buffer layer by applying grey theory prediction design show that the crystallinity and optical transmittance of AZO films increase, whereas the electrical resistivity decreases.

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