Research Article

Optimization of the Cathode Arc Plasma Deposition Processing Parameters of ZnO Film Using the Grey-Relational Taguchi Method

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We deposited undoped ZnO films on the glass substrate at a low temperature ($<70^{\circ}\text{C}$) using cathode arc plasma deposition (CAPD) and the grey-relational Taguchi method was used to determine the processing parameters of ZnO thin films. The Taguchi method with an L9 orthogonal array, signal-to-noise (S/N) ratio, and analysis of variance (ANOVA) is employed to investigate the performances in the deposition operations. The effect and optimization of deposition parameters, comprising the $\text{Ar}:\text{O}_2$ gas flow ratio of 1:6, 1:8, and 1:10, the arc current of 50 A, 60 A, and 70 A, and the deposition time of 5 min, 10 min, and 15 min, on the electrical resistivity and optical transmittance of the ZnO films are studied. The results indicate that, by using the grey-relational Taguchi method, the optical transmittance of ZnO thin films increases from 88.17% to 88.82% and the electrical resistivity decreases from $5.12 \times 10^{-3} \Omega\text{-cm}$ to $4.38 \times 10^{-3} \Omega\text{-cm}$, respectively.

1. Introduction

Zinc oxide (ZnO) has gained a great interest in research due to wide and direct band gap (3.3 eV) and excellent optoelectronic properties, which are desirable for optoelectronic devices such as photodetectors, solar cells, light emission diodes, gas sensor, varistors, and ultraviolet laser diodes [1]. And ZnO thin films also obtain a processing advantage of thermal stability, which does not suffer from dislocation degradation during operation. Moreover, pure or doped ZnO thin films have been considered as good candidates to be transparent conductive oxide (TCO) materials because of their good optical transmittance, low electrical resistivity, and low-cost fabrication [2–9].

Highly transparent and conducting ZnO films have been deposited by several different methods, including chemical vapor deposition (CVD) [2], thermal oxidation [3], radio frequency (RF) magnetron sputtering [4], pulsed laser deposition [5], electron beam evaporation [6], spray pyrolysis [7], electrodeposition [8], and the cathodic arc plasma deposition

(CAPD) [9–14]. Most of the mentioned deposition methods need a high substrate temperature or *in situ* annealing process ($>300^{\circ}\text{C}$) to obtain desired optical and/or electrical properties. However, in order to avoid reactive and elemental diffusion of different layers and to protect substrates having thermal stress, low temperature deposition is preferred in some processes. It is, thus, a challenge to deposit high quality ZnO thin films with desired optical and/or electrical properties at a low temperature. Among various deposition methods, CAPD technique has many advantages, including high deposition rate, convenient *in situ* doping using an overlying plasma, and the readily adjustable deposition parameters, such as substrate temperature, arc current, gas flow rate, and deposition time [9–12].

The Taguchi method [15–17] uses many ideas from the statistical experimental design for evaluating and implementing improvements in products, processes, and equipment. The Taguchi method is used to study a large number of design variables with a small number of experiments. The better level combinations of design variables are decided by the

FIGURE 1: The XRD patterns of the of the ZnO films on glass substrates for the L9 orthogonal array from experiments number 1~9.

orthogonal arrays and signal-to-noise (S/N) ratios. In 1982, grey analysis was first proposed by Deng to fulfill the crucial mathematical criteria for dealing with poor, incomplete, and uncertain systems [18]. Grey analysis can effectively recommend a method of optimizing the complicated inter-relationships among multiple performance characteristics [19]. In grey system theory, the grey-relational analysis is a measurement method to analyze the relationship between sequences using less data and multifactor, which is considered more helpful to the statistical regression analysis. There are few papers concerning the examination on properties of ZnO thin films by using grey-relational Taguchi method [20–22]. However, there is no related research concerning grey-relational Taguchi method to design the processing parameters for depositing ZnO thin films by using CAPD.

In this paper, we deposited undoped ZnO thin films on the glass substrate at a low temperature ($<70^\circ\text{C}$) using cathode arc plasma deposition, and the grey-relational Taguchi method was used to determine the optimal processing parameters including the gas flow ratio, the arc current, and the deposition time. By using the grey-relational Taguchi method, the experimental results confirm that the optical transmittance of ZnO thin films increases from 88.17% to 88.82% and the electrical resistivity decreases from $5.12 \times 10^{-3} \Omega\text{-cm}$ to $4.38 \times 10^{-3} \Omega\text{-cm}$, respectively. Namely, the Grey analysis is actually an effectively optimizing method of the multiprocessing parameters for depositing ZnO thin films by using CAPD.

2. Experimental Method and Optimization Approach

ZnO films were deposited onto the glass substrate in a CAPD system. Metallic Zn with a diameter of 100 mm and a purity of 99.99% as a cathode target was held in an alumina ceramic tube and O_2 gas with a high purity of 99.99% was used as the reactant gas. Before deposition, glass substrates were

TABLE 1: Deposition parameters of ZnO films factors and levels using cathode arc plasma deposition (CAPD).

Substrate	glass		
Target	Zinc: 99.99% purity 100 mm diameter		
Base pressure	7×10^{-4} torr		
Substrate-to-target distance	21 cm		
Substrate rotation	2 r.p.m		
Substrate temperature	Room temperature		
	Level		
	1	2	3
A: gas flow ratio ($\text{Ar}:\text{O}_2$)	1:6	1:10	1:8
B: arc current (A)	50	60	70
C: deposition time (min)	5	10	15

washed by alcohol and then ultrasonically cleaned in alcohol for 10 min. In the depositions of ZnO films, base pressure was kept at 3×10^{-4} torr. Substrate rotation of 2 r.p.m. and substrate-anode electrode distance of approximately 21 cm remained constant during the deposition work. Without extra heating, the depositions of ZnO films were performed at room temperature.

The ZnO films with different thicknesses were confirmed by the measurement of Alpha-Step (α -step, Kosaka Laboratory Ltd. ET-4000). X-ray diffraction system (XRD, BRUKER D8 ADVANCE) equipped with $\text{CuK}\alpha$ radiation of average wavelength $1.5406 \text{ \AA}$ was used to specify the existent phases and the orientation of ZnO thin films. X-ray patterns were taken with 2θ between 20° and 60° and a scan speed of $4.5^\circ/\text{min}$. UV-VIS spectrometer (Thermo Evolution 300) was used to measure the optical properties of ZnO films in the wavelength range of 300–800 nm. The standard four-point probe method was used for room-temperature sheet resistance of the films.

The L9 orthogonal array was selected in this paper. There are three factors in the ZnO deposition processing, which are the $\text{Ar}:\text{O}_2$ gas flow ratio of 1:6, 1:8, and 1:10, the arc current of 50 A, 60 A, and 70 A, and the deposition time of 5, 10, and 15 min. Each experiment was repeated two times in this study. Table 1 shows factor and level setting in ZnO deposition parameters.

2.1. Analysis of the S/N Ratio. Taguchi method was used to execute the experiment, employing a generic signal-to-noise (S/N) ratio to quantify the present variation. Depending on the particular type of characteristics, S/N ratios may be defined as “the lower the better” or “the higher the better.” The S/N ratios were calculated using the following equations [12].

The lower the better is as follows:

$$\frac{S}{N} = -10 \times \log \left(\frac{1}{n} \sum_{i=1}^n y_i^2 \right); \quad (1)$$

FIGURE 2: The optical transmittance of the deposited ZnO thin films as a function of wavelength; (a) experiments number 1~5 and (b) experiments number 6~9.

FIGURE 3: The optical energy gaps of the ZnO thin films; (a) experiments number 1~5 and (b) experiments number 6~9.

the lower the better is as follows:

$$\frac{S}{N} = -10 \times \log \left(\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right), \quad (2)$$

where n is the number of experiment and y is the experimental data; the S/N ratio is expressed on a decibel scale (dB). The mean S/N ratio for each level of the parameters is summarized and obtained as the S/N response graph used

to analyze the S/N ratio of each experimental parameter. Then, we can obtain the best level combination of deposition parameters.

2.2. Analysis of Variance (ANOVA). The purpose of the analysis of variance (ANOVA) is to investigate which design parameters significantly affect the quality characteristic. This is accomplished by separating the total variability of the S/N ratios, which is measured by the sum of the squared

TABLE 2: Grain size of ZnO thin films for the L9 orthogonal array from experiments 1~9.

Experiment number	Control factors			Grain size (nm)
	A	B	C	
1	1	1	1	19.17
2	2	2	2	21.08
3	3	3	3	21.08
4	1	2	3	21.62
5	2	3	1	19.61
6	3	1	2	18.74
7	1	3	2	19.16
8	2	1	3	20.57
9	3	2	1	21.62

deviations from the total mean S/N ratio. The analysis of variance and the contribution of each design parameter are obtained by following equation:

$$\begin{aligned}
 S_m &= \frac{(\sum \eta_i)^2}{N}, & S_T &= \sum \eta_i^2 - S_m, \\
 S_A &= \frac{\sum \eta_{Ai}^2}{n}, \\
 V_A &= \frac{S_A}{f_A}, \\
 C_A &= \frac{S_A}{S_T} \times 100\%,
 \end{aligned} \tag{3}$$

where S_m is the sum of squares due to the means, S_T is the sum of squares due to the total variation, S_A is the sum of squares due to parameter A, f_A is the degree of freedom of parameter A, V_A is the variance of parameter A, and C_A is the contribution of each design parameter.

2.3. Grey-Relational Analysis. Grey-relational analysis can be used to effectively solve complicated interrelationships among multiple performance characteristics. The grey-relational coefficient is [18]

$$\begin{aligned}
 r(x_0(k), x_i(k)) &= \left(\min_i \min_k |x_0(k) - x_i(k)| + \zeta \max_i \max_k |x_0(k) - x_i(k)| \right) \\
 &\times \left(|x_0(k) - x_i(k)| + \zeta \max_i \max_k |x_0(k) - x_i(k)| \right)^{-1}.
 \end{aligned} \tag{4}$$

Grey-relational analysis can be used to effectively solve complicated interrelationships among multiple performances, where $x_i(k)$ is the normalized value of the k th performance characteristic in the i th experiment and ζ is the distinguishing coefficient, $\zeta \in [0, 1]$. The value of ζ can

be adjusted according to the practical system requirement. Transmittance and resistivity are equally weighted in this paper; therefore, ζ is 0.5.

The grey-relational grade is a weighting-sum of the grey-relational coefficient. It is defined as follows [19]:

$$r(x_0, x_i) = \frac{1}{n} \sum_{k=1}^n r(x_0(k), x_i(k)), \tag{5}$$

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

3. Results and Discussions

Figure 1 shows the XRD patterns of the ZnO films on glass substrates for the L9 orthogonal array from experiments number 1~9. For all as-grown films, (0 0 2) diffraction peaks at around 34.2° and (1 0 3) diffraction peaks at around 62.4° appear in the diffractogram, indicating that the films reveal a polycrystalline hexagonal wurtzite crystal structure ($a = 3.249$, $c = 5.206$ Å). Moreover, except for experiment number 3, all of ZnO thin films present that the diffraction intensity of the (0 0 2) direction is much stronger than that of the (1 0 3) direction, indicating that the structure of the ZnO thin films is preponderantly consist of columnar grains standing perpendicular to the substrate. The average grain size (D) of the ZnO films is determined by applying the Scherrer equation to the full width at half maximum (FWHM) of the (0 0 2) peaks, as given by [23]

$$D = \frac{0.9\lambda}{\omega \cos \theta}, \tag{6}$$

where ω is the calibrated FWHM of the selected diffraction line in radians, θ is the Bragg angle, and λ is the X-ray wavelength (0.15406 nm). Table 2 shows grain size of deposited ZnO thin films for the L9 orthogonal array from experiments number 1~9.

Figure 2 shows the optical transmittance of the deposited ZnO thin films as a function of wavelength. From the measured optical transmittance of the deposited ZnO thin films, the average transmittance can be obtained [24]. Moreover, the variation of the absorption coefficient α with the photon energy $h\nu$ can be given as [25]

$$(\alpha h\nu)^2 = B(h\nu - E_g), \tag{7}$$

where α was estimated from the transmittance data and B is a constant depending on the materials' properties. By plotting $(\alpha h\nu)^2$ as a function of $h\nu$ and extrapolating to $\alpha = 0$ from the linear region of "Tauc" plots, the optical energy gaps of the ZnO thin films can be obtained. As shown in Figure 3, the optical energy gaps of the ZnO thin films are in the range of 3.15~3.2 eV, indicating that undoped ZnO films were successfully deposited on the glass substrate at a low

TABLE 3: Experimental results for the transmittance and resistivity of the deposited ZnO films on glass substrate.

Experiment number	Control factors			Transmittance (%)			Resistivity ($10^{-3} \Omega\text{-cm}$)		
	A	B	C	Y1	Y2	Mean value	Y1	Y2	Mean value
1	1	1	1	87.57	86.73	87.15	5.56	4.59	5.51
2	2	2	2	83.17	82.47	82.82	6.19	5.71	5.95
3	3	3	3	77.71	77.43	77.57	2.99	2.79	2.89
4	1	2	3	78.14	77.66	77.90	6.75	5.97	6.36
5	2	3	1	81.25	79.61	80.43	7.25	5.99	6.62
6	3	1	2	84.98	84.82	84.90	6.13	5.93	6.03
7	1	3	2	77.96	77.34	77.65	5.46	5.23	5.35
8	2	1	3	80.39	80.17	80.28	4.32	4.28	4.30
9	3	2	1	88.17	87.23	87.70	5.66	5.12	5.39

TABLE 4: Grey-relational grade and S/N ratio.

Experiment number	Control factors			Grey-relational grade	S/N (dB)
	A	B	C		
1	1	1	1	0.6589	-3.62
2	2	2	2	0.4440	-7.05
3	3	3	3	0.6667	-3.52
4	1	2	3	0.3452	-9.24
5	2	3	1	0.3720	-8.59
6	3	1	2	0.5083	-5.88
7	1	3	2	0.3832	-8.33
8	2	1	3	0.4876	-6.24
9	3	2	1	0.7137	-2.93

TABLE 5: S/N response for grey-relational grade.

Parameters	Mean S/N ratio (dB)			Optimal parameters
	Level 1	Level 2	Level 3	
A: gas flow ratio (Ar:O ₂)	-7.06	-7.29	-4.11	A3
B: arc current	-5.25	-6.41	-6.81	B1
C: deposition time	-5.05	-7.09	-6.33	C1

TABLE 6: Results of confirmation test for multiple performance characteristics of ZnO thin films.

Resistivity	Transmittance
Experiment number 9 (A3 B2 C1)	
$5.12 \times 10^{-3} \Omega\text{-cm}$	88.17%
Grey-relational prediction design (A3 B1 C1)	
$4.38 \times 10^{-3} \Omega\text{-cm}$	88.82%

temperature ($<70^\circ\text{C}$) by using cathodic arc plasma deposition in this experiment.

Table 3 shows the experimental results for the transmittance and resistivity of the deposited ZnO thin films on glass using CAPD. Table 4 shows the grey-relational grade for each experiment by using (4) and (5) and its S/N ratio by using (1). The results indicate that number 9 experiment has the

highest grey-relational grade. The larger the grey-relational grade is, the better the multiple performance characteristics will be. Table 5 shows S/N response for grey-relational grade. As shown, the optimal parameters are the gas flow ratio (Ar:O₂) of 1:10, arc current of 50 A, and deposition time of 5 min. Hence, the optimal parameter level was selected to accomplish the proof experiment. Experiment number 9 has the best Grey-relational grade, indicating that it has superior multiple performance characteristics compared with another eight experiments. Table 6 shows the result of comparison between the grey-relational prediction design (A3 B1 C1) and orthogonal array experiment number 9 (A3 B2 C1). The result indicates that the resistivity decreases from $5.12 \times 10^{-3} \Omega\text{-cm}$ to $4.38 \times 10^{-3} \Omega\text{-cm}$ and transmittance increases from 88.17% to 88.82%. Table 7 shows the ANOVA results of grey-relational grade for ZnO thin films. For this study, the gas flow rate is the most influential processing parameter. However, the arc current and the deposition time should not be ignored.

4. Conclusions

In summary, undoped ZnO films were successfully deposited on the glass substrate at a low temperature ($<70^\circ\text{C}$) by using cathodic arc plasma deposition. The grey-relational Taguchi method successfully predicted the optimal processing parameters including the Ar:O₂ gas flow ratio, the arc current and the deposition time for multiple performance, the transmittance, and the resistivity of the ZnO films. The result of the confirmed experiment (A3 B1 C1) showed that the transmittance increases from 88.17% to 88.82% and the resistivity decreases from $5.12 \times 10^{-3} \Omega\text{-cm}$ to $4.38 \times 10^{-3} \Omega\text{-cm}$, indicating that the result of final confirmed experiments could be certainly improved.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

TABLE 7: ANOVA results of grey-relational grade for ZnO thin films.

Parameters	Degree of freedom (F)	Sum of square (S)	Variance (V)	Contribution (%)
A: gas flow ratio (Ar : O ₂)	2	18.92	9.46	65
B: arc current	2	3.97	1.99	13
C: deposition time	2	6.38	3.19	22
Total		29.27		100

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