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Influence of deposition parameters and annealing treatment on the properties of GZO films grown using rf magnetron sputtering

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Abstract

In this study, transparent conductive films of gallium-doped zinc oxide (GZO) are deposited on soda–lime glass substrates, under varied coating conditions (rf power, sputtering pressure, substrate-to-target distance and deposition time), using radio frequency (rf) magnetron sputtering, at room temperature. The effect of the coating parameters on the structural, morphological, electrical and optical properties of GZO films was studied. This study uses a grey-based Taguchi method, to determine the parameters of the coating process for GZO films, by considering multiple performance characteristics. In the confirmation runs, with grey relational analysis, improvements of 14.1% in the deposition rate, 39.81% in electrical resistivity and 1.38% in visible range transmittance were noted. The influence of annealing treatment, in a vacuum, oxygen, and nitrogen gas atmospheres, at temperatures ranging from 130 to 190 °C, for a period of 1 h, was also investigated. GZO films annealed at 190 °C, in a vacuum, showed the lowest electrical resistivity, at 1.07×10^{-3} Ω-cm, with about 85% optical transmittance, in the visible region. It is likely that films grown at lower temperatures (190 °C) could be coated onto polymeric substrates, to produce flexible optoelectronic devices.

Keywords: GZO; Grey relational analysis; Annealing treatment; Electrical and optical properties

1. Introduction

Zinc oxide (ZnO) transparent conducting films have excellent electrical and optical properties and find uses in liquid crystal displays, gas sensors, solar cells, piezoelectric devices, various optoelectronic devices and surface acoustic wave (SAW) devices [1,2]. ZnO thin films have also found uses as a transparent conducting oxide (TCO) material, in solar cells based on Si and Cu (InGa) Se_2 [3]. The advantages of zinc oxide over ITO and SnO_2 films are its low material cost, non-toxicity, high crystallinity and stability in hydrogen plasma processes [4]. The addition of Group III metal dopants, such as Al, In and Ga, increases the electrical conductivity and transparency of ZnO films [5]. The incorporation of these elements into the ZnO lattice can stabilize the film, at high temperatures, and increase its electrical conductivity [6]. Of these dopants, Ga has several advantages, in that it is less reactive and more resistant to oxidation than Al [7]. The occurrence of defects is minimized, when ZnO is doped with Ga, since the radius of Ga^{3+} (0.062 nm) is closer to that of Zn^{2+} (0.060 nm) than that of Al^{3+} (0.053 nm) [8]. The diffraction patterns show that deposited Ga-doped ZnO films exhibit a hexagonal structure, which indicates that the Ga atoms substitute for Zn, in the hexagonal lattice [9], and Ga ions occupy the interstitial sites of ZnO, or segregate to the non-crystalline region in grain boundaries and form Ga–O bonds [10]. There are different growth techniques for ZnO films doped with Ga (GZO), but the common most fabrication techniques are sputtering [11], chemical vapor deposition [12], sol–gel techniques [13] and pulsed laser deposition [14]. This study analyzes the preparation of high quality Ga-doped zinc oxide (GZO) transparent conductive films, prepared on glass substrates, using rf magnetron sputtering, at room temperature. The influence of the coating parameters on the structural, morphological, electrical and optical properties of GZO films is also investigated.

The Taguchi method, which combines experimental design theory and the quality loss function concept, is used to design robust products and processes and has solved some confusing

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Table 1
Deposition parameters for GZO films, factors and levels.

Substrate	Soda–lime; thickness 1 mm
Target	97 wt.% ZnO, 3 wt.% Ga_2O_3; 99.995% purity
Gas	Argon (99.995%)
Base pressure	6.67×10^{-4} Pa
Substrate rotate vertical axis	10 rpm
Substrate temperature	Room temperature

Symbol	Process parameter	Level 1	Level 2	Level 3
A	rf power (W)	50	100	150
B	Sputtering pressure (Pa)	0.5	1	1.5
C	Substrate-to-target distance (cm)	8.5	9.5	10.5
D	Deposition time (min)	30	60	90

Table 2
L_9 (3^4) orthogonal array, with four columns and nine rows.

Experiment no.	Process parameter			
	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

problems in manufacturing [15]. This experiment uses four influential deposition parameters – rf power (A), sputtering pressure (B), substrate-to-target distance (C) and deposit time (D) – each of which is assigned high, medium and low levels, as shown in Table 1. In order to optimize the design of the deposition process for GZO films, this study uses a Taguchi L_9 (3^4) orthogonal array, with four columns and nine rows, as shown in Table 2. Then, based on grey relational analysis, optimization of the coating process parameters, with multiple qualities, for GZO films, is achieved [16]. In addition, there was also an investigation of the influence of annealing treatment, in a vacuum, oxygen and nitrogen gas atmospheres, at temperatures ranging from 130 to 190 °C, for a period of 1 h, on properties of GZO films.

2. Experimental details

GZO transparent conducting films were deposited on glass substrates, under various coating conditions, using rf magnetron sputtering, at room temperature, with a base pressure of 6.67×10^{-4} Pa. The commercially available hot-pressed and sintered target GZO (97 wt.% ZnO, 3 wt.% Ga_2O_3; 99.995% purity, Elecmat, USA) had a diameter of 50.8 mm and a thickness of 6 mm. The amount of Ga_2O_3 dopant in the ZnO powder varied, from 2 to 5% [16]. Ga_2O_3 of about 3 wt.% was chosen for this study. Before deposition, the glass substrates were ultrasonically cleaned in acetone, rinsed in deionized water and blow-dried with nitrogen. The magnetron sputtering system was microprocessor controlled.

2.1. Analysis of variance (ANOVA)

An analysis of variance (ANOVA) was performed, to evaluate the coating parameters that were statistically significant. Using the signal-to-noise (*S*/*N*) ratio and ANOVA analyses, the optimal combination of process parameters can be predicted [17]. A confirmation experiment was then conducted, to verify the optimal process parameters, obtained. An ANOVA and an F-test were used to analyze the experimental data:

$$S_m = \frac{\left(\sum \eta_i^2\right)}{9}, \qquad S_T = \sum \eta_i^2 - S_m \tag{1}$$

$$S_A = \frac{\left(\sum \eta_{Ai}^2\right)^2}{N} - S_m, \qquad S_E = S_T - \sum S_A \tag{2}$$

$$V_A = \frac{S_A}{f_A}, \qquad F_{Ao} = \frac{V_A}{V_E} \tag{3}$$

where S_T is the sum of squares, due to the total variation, S_m is the sum of squares, due to the means, S_A is the sum of squares, due to parameter A (A represents rf power, sputtering pressure, substrate-to-target, and deposit time, respectively), S_g is the sum of squares due to error, η_i is the η value of each experiment ($i = 1\ldots9$), η_{Ai} is the sum of the ith level of parameter A ($i = 1$, 2, 3), N is the repeating number of each level of parameter A, f_A is the degree of freedom of parameter A, V_A is the variance of parameter A and F_{Ao} is the F-test value for parameter A.

2.2. Grey relational analysis

Grey relational analysis can be used to effectively solve complicated interrelationships between multiple performance characteristics. The grey relational coefficient is [18]:

$$r(x_o(k), x_i(k)) = \frac{\min_i \min_k |x_0(k) - x_i(k)| + \zeta \max_i \max_k |x_0(k) - x_i(k)|}{|x_0(k) - x_i(k)| + \zeta \max_i \max_k |x_0(k) - x_i(k)|} \tag{4}$$

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 requirements. The coating parameters are of equal weighting, in this study, and therefore ζ is 0.5.

The grey relational grade is a weighting-sum of the grey relational coefficient. It is defined as [18]:

$$r(x_0, x_i) = \frac{1}{n}\sum_{k=1}^{n} r(r_0(k), x_i(k)) \tag{5}$$

where n is the number of performance characteristics.

Grey relational analysis, based on the grey system theory, can be used to effectively solve complicated interrelationships between multiple performance characteristics [19]. For grey