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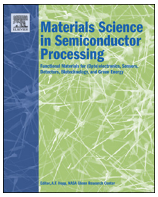

# Taguchi method-optimized sputter deposition of hydrogenated gallium-doped zinc oxide films in argon/hydrogen ambient

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ABSTRACT

Transparent conductive films of hydrogenated gallium-doped zinc oxide (HGZO) were deposited on glass under various deposition conditions (ratio of $H_2$ to Ar, RF power, sputtering pressure and time) by RF magnetron sputtering in $Ar+H_2$ ambient at room temperature (RT). In this work, the Taguchi method was used to find optimal deposition conditions and it was found that sputtering time and ratio of $H_2$ to Ar were significantly influencing parameters on figure of merit of HGZO films. For the HGZO film grown under the optimal condition, the highest figure of merit of $33.94 \times 10^{-3}\ \Omega^{-1}$, i.e. the lowest sheet resistance of 10.62 $\Omega$/sq ($\rho = 3.40 \times 10^{-4}\ \Omega$ cm) and high transmittance of 90.03% were obtained. In this case, hall mobility and carrier concentration are 8.87 $cm^2\ V^{-1}\ s^{-1}$ and $1.177 \times 10^{21}\ cm^{-3}$, respectively.

## 1. Introduction

Al or Ga doped ZnO (AZO, GZO) is one of the most promising transparent conductive oxides for various electronic devices such as solar cells, flat panel display, optoelectronic etc. [1,2]. An RF magnetron sputtering technique is the most commonly used method to deposit GZO owing to its more advantages such as high deposition rates, process stability and reliability, and preparation of high-quality thin films on large-scale substrates in comparison to the other methods [3]. For application of GZO films to devices such as organic solar cell and light emitting diodes (LEDs), it is necessary to prepare GZO films at low temperature such as room temperature (RT) [4,5]. However, it is difficult to obtain a film with both low resistivity and high transmittance at RT. Lately, first-principle calculations by Van de Walle have shown strong evidence that hydrogen acts as a source of n-type conductivity in ZnO [6]. Along with this theoretical result, some researchers have carried out experimental studies and reported that the resistivity of pure ZnO and metal doped ZnO films could be reduced by adding $H_2$ to sputtering gas during RF magnetron sputtering [7–12].

In the deposition process of HGZO films by RF magnetron sputtering at RT, many parameters, such as ratio of $H_2$ to Ar, RF power, sputtering pressure and sputtering time, play important roles in determining the characteristics of HGZO films. The effect of individual parameters on the characteristics and interrelationships between these parameters is very complex. To obtain optimal deposition condition, it is necessary to select an efficient analysis method. Some researchers have obtained optimal condition for GZO film by using the Taguchi design method [13–15].

In this paper, H was doped into GZO at RT to improve electrical and optical characteristics of the film and the

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Taguchi design method was implemented to optimize deposition parameters. The main objectives of this paper are to apply the Taguchi design method to the optimization of parameters for deposition of HGZO films by RF magnetron sputtering in Ar+$H_2$ ambient at RT and to investigate the structural, electrical and optical characteristics of HGZO films grown at the optimized conditions.

## 2. Experimental

Transparent conductive HGZO thin films were deposited on glass substrates by RF magnetron sputtering in Ar+$H_2$ ambient at RT. A disc of ceramic ZnO: 4 at% $Ga_2O_3$ (99.99% purity) was used as sputtering target. The target-to-substrate distance was 10.5 cm. Prior to deposition, the vacuum chamber was evacuated to a base pressure of $2 \times 10^{-3}$ Pa. High purity (99.999% purity) Ar and $H_2$ were introduced through a mass flow controller.

The crystal structure of the films was analyzed by X-ray diffraction (XRD) using an X'PertPRO system with a Cu Kα radiation ($\lambda$=0.1541 nm). The film thickness and the surface morphology were measured using field emission scanning electron microscopy (FE-SEM; HITACHIS-4800). Atomic force microscopy (AFM) was used to investigate the surface roughness of the film. Surface chemical state analysis was investigated by X-ray photoelectron spectroscopy (XPS; Thermo ESCALAB) using a 1486.6 eV Al Kα source. The electrical properties were analyzed by Bio-Rad HL5500 Hall measurements. The optical transmission spectra were measured with a UV 3600 spectrophotometer.

In the deposition process of HGZO films by RF magnetron sputtering at RT, many parameters play important roles in determining the characteristics of HGZO films. In detail, these parameters are the content of Ga, ratio of $H_2$:Ar, RF power, sputtering pressure, sputtering time and the distance between target and substrate. The content of 4% Ga was selected based on the previous study of our group on the GZO prepared by RF magnetron sputtering due to the best electrical and optical characteristics [16]. When the distance between target and substrate is in the range of 9–12 cm, the characteristics of the deposited film almost have no changes. So we selected the distance between target and substrate of 10.5 cm, the median between 9 cm and 12 cm. Therefore, except the content of Ga and the distance between target and substrate, four considerable deposition parameters, namely, ratio of $H_2$:Ar, RF power, sputtering pressure and sputtering time were selected in the current experiment. For each of deposition parameter, three levels were selected by a series of experiment to investigate the effects of individual parameters on the characteristics of transparent conductive HGZO films grown in Ar+$H_2$ ambient at RT before the current work. In the preliminary experiments, we have confirmed the value ranges of deposition parameters in which HGZO films have good electrical and optical characteristics. By analyzing the change of electrical and optical characteristics with value of deposition parameters, each parameter assigned three levels such as high, medium and low levels. The parameters and levels in the current experiment are presented in Table 1. The Taguchi experimental design, a $L_9$ ($3^4$) orthogonal array with four columns and nine rows, was implemented to investigate the effect of selected parameters [13,15]. When each of these parameters assigned three levels and a factorial experimental design was employed using each of these values, the number of permutations would be $3^4$=81. However, only nine experiments were required to study the entire parameter space by using the orthogonal array of $L_9$ type.

**Table 1**
Parameters and levels used in the current experiment.

| Symbol | Parameter | Level 1 | Level 2 | Level 3 |
|---|---|---|---|---|
| A | Ratio of $H_2$:Ar (%) | 3.2 | 5.3 | 7.2 |
| B | RF power (W) | 250 | 270 | 300 |
| C | Sputtering pressure (Pa) | 1.5 | 2.5 | 3.5 |
| D | Sputtering time (min) | 10 | 15 | 20 |

## 3. Results and discussion

### 3.1. Analysis of the S/N ratio and variance

In order to consider conductivity and transmittance of HGZO films simultaneously, we have applied a figure of merit, $\Phi_{TC}$, defined as $\Phi_{TC}=T^{10}/R_{sh}$, where $T$ is the average optical transmittance in the visible range and $R_{sh}$ is the sheet resistance [17].

The Taguchi method uses the S/N ratio to investigate the response variation, resulting in minimization of the quality characteristic variation [18,19]. According to the S/N ratio characteristics, S/N ratio can be defined as the-lower-the-better, the-higher-the-better, or the-nominal-the-better. Because the higher figure of merit is the better target value in the current work, S/N ratio is the-higher-the-better and defined as $S/N=-10\log\left[\frac{1}{n}\sum_{i=1}^{n}1/{y_i}^2\right]$, where $n$ is the replication number of the experiment and $y_i$ is results of experiments.

Table 2 indicates the experimental data on the figure of merit and the corresponding S/N ratio calculated by using the above equation. Each experiment was repeatedly performed twice. Based on Table 2, we calculated the mean S/N ratio for each level of the parameters and obtained optimal parameters.

The mean S/N ratio for each level of the parameters and obtained optimal parameter is shown in Table 3 and illustrated in Fig. 1. The greater S/N ratio implies that the figure of merit is higher. As a result, optimal parameters (conditions) are A2, B3, C3 and D2, i.e. 5.3% of ratio of $H_2$:Ar, 300 W of RF power, 3.50 Pa of sputtering pressure and 15 min of sputtering time.

In order to investigate which design parameters significantly affect the quality characteristic of HGZO films, the analysis of variance (ANOVA) was carried out. The ANOVA results for the figure of merit of HGZO films are presented in Table 4. The sputtering time and the ratio of $H_2$:Ar have a dominant effect on the figure of merit for HGZO deposited at RT as contribution of 58.42% and 32.60%, respectively. However, the RF power and sputtering pressure have no significant effect on the figure of merit for HGZO deposited at RT as contribution of 4.19% and 4.79%, respectively. Therefore, it is assumed that the