Electrical and Optical Properties in Transparent Conducting Oxides: Effect of Ultra Violet Irradiation

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ABSTRACT

A design of experiments was applied in order to investigate the effect of processing variables in UV irradiation on the electrical/optical properties in indium-zinc oxide thin films, The processing variables, equivalently input variables are listed as UV irradiation time, oxygen flow rate, and chamber pressure. The statistical significance of Ultra Violet (UV) treatment was confirmed using a paired-t test. The full factorial 2^3 design was employed to determine significant main and interaction effects in UV irradiation process. The chamber pressure and the interaction between UV irradiation time and O_2 flow rate were found to be statistically significant at the significance level of 0.1. Furthermore, the optimized approach was proposed in achieving the improved conductivity after UV irradiation.

Key words : Indium-zinc oxides, UV irradiation, Electrical/Optical Properties, Design of experiments

1. INTRODUCTION

Indium zinc oxide (IZO) is an n-type wide-band gap semiconductor as one of the transparent conducting oxides (TCOs). TCOs have been expanded as electrodes to flat-panel displays, solar cells, touch screens, etc, due to the unique features: high electrical conductivity and excellent transparency in visible regime[1,2]. Most of TCOs are constructed based on the bixbyte of In_2O_3 or the wurtzite structure of ZnO[3]. In indium oxide-based transparent conducting oxides, the high resistivity of indium oxides was modified to highly-conducting states through the incorporation of tin oxide, zinc oxides, and the co-doping of tin and zinc oxides[4-7]. Transparent conducting oxides are fabricated through electron beam evaporation, RF and DC magnetron sputtering, etc[8-14]. The status of transparent oxide conducting films determines critically characteristics in organic light-emitting diodes (OLEDs), in terms of resistance and surface states. The beneficial surface state of the transparent conducting oxides increases the luminance feature in OLEDs and leads to longer lifetime in conjunction with the luminance characteristics.

With the aim to improve the device performance in OLEDs, the current work places emphases on the UV irradiation on the transparent conducting oxides, specifically the IZO thin films deposited on glass substrates at room temperature. The electrical and optical properties were investigated using Hall effect measurements and UV-Vis. transmittance measurements. In particular, an statistical approach was applied in order to confirm the effectiveness of UV irradiation processing in TCOs and to identify the effect of the processing variables and the associated interactions on the electrical/optical properties in transparent conducting oxides. Furthermore, the relevant experimental data were analyzed in terms of a statistical design of experiments (DOE). The optimized approach is suggested in UV irradiation on the transparent conducting oxides.

2. EXPERIMENTAL PROCEDURE

Indium-zinc oxide thin films were prepared using DC magnetron sputtering. A 4" IZO target (99.99% In_2O_3:ZnO=9:1, High Purity Chemical Co. Ltd.

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Japan) was used in depositing the IZO thin films. The initial deposition rates exhibited dissimilar trends depending on the processing conditions. The initial deposition rate was controlled to the identical thickness in indium-zinc oxide thin films, 1000Å. The detailed information is summarized in Table 1. The electrical characteristics were made using Hall measurements (HL5500, Bio-Rad, U.S.A): the corresponding conductivity, charge mobility, and concentration of charge carriers were measured in numerical formats. In order to evaluate the effectiveness of UV irradiation and to perform and analyze a design of experiments, the statistical data were analyzed using a commercially available software (Minitab, Mintab Inc. State College, PA, USA). The experimental order was randomized to eliminate the effect of uncontrollable variables as can be seen in Table 1.

Table 1. Experimental Conditions for DOE in UV irradiation on IZO thin films.

Run Number	Irradiation Time [min]	O_2/Ar Ratio [sccm]	Chamber Pressure [mtorr]
1	10	30	2
2	5	0	2
3	5	30	5
4	5	30	2
5	7.5	15	3
6	7.5	15	3
7	7.5	15	3
8	5	0	5
9	10	0	2
10	10	0	5
11	10	30	5

3. RESULTS AND DISCUSSION

Due to the low deposition temperature, at room temperature, the IZO thin films are attributed to the amorphous state[15-17]. Compared to that deposited at high temperature, the electrical resistance is lower. The similar trend is found in ITO-based materials[18]. However, the indium zinc oxide thin film shows high degrees of transmittance in visible light regime, as shown in Fig. 1. The high transmittance is a unique feature, in oxide thin films. In the ultraviolet regime, the transmittance is low, in other words, the absorption is significantly high. The UV irradiation does not change the optical transmittance in TCOs.

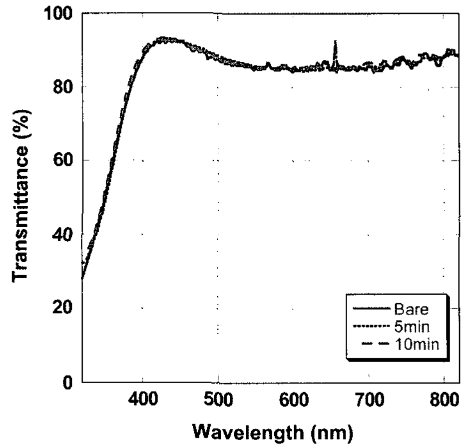

Fig. 1. Transmittance before and after UV-irradiation on *IZO thin films.*

Based on the information in Table 2, the UV irradiation process was evaluated in terms of the paired 't-test' which determines to allow the statistical significance of the UV irradiation in the electrical properties in transparent conducting oxides: the t-test was evaluated before and after UV irradiation processing applied to the identical specimens. The statistical analysis indicates highly low P-value, rigorously nearly zero. The P-value is much lower than a specified alpha error, or type I error, which is the significance level, 0.05. Furthermore, the calculated t-value is -10.87 which is much larger than the usual limit, approximately 3. The low P-value proves that the UV irradiation improves the electrical resistance, decreasing the sheet resistance significantly. The estimated interval in electrical resistivity is located between -1.0×10^{-4} and -6.8×10^{-5} with the confidence level of 95%. The UV irradiation decreases the electrical resistivity of the amorphous IZO thin films compared to those untreated using UV irradiation.

The full 2^3 factorial design allows the relative significance in primary effects and multi-factor interactions: in this work, the highest multi-interaction factor is a three-factor interaction. The current system can be described as the following equation

$$Y = B_0 + \beta_A X_A + \beta_B X_B + \beta_C X_C + \beta_{AB} X_A X_B + \beta_{AC} X_A X_C + \beta_{BC} X_B X_C + \beta_{ABC} X_A X_B X_C \quad (1)$$

where Y is the output (the change in resistivity) and X_A, X_B, and X_C are the experimental input conditions (i.e., high and low values in UV irradiation time, oxygen flow rate, and chamber pressure), β_0 is the constant, β_A, β_B, and β_C, are the constant with respect to the main effect, β_{AB}, β_{AC} and β_{BC} are the coefficients of the 2-factor interactions, and β_{ABC} is the coefficient

Table 2. Experimental Results before and after UV irradiation on IZO thin films: resistivity and mobility.

Run Number	r(Before) [$\times 10^{-4}\Omega\cdot cm$]	r(After) [$\times 10^{-4}\Omega\cdot cm$]	M(Before) [$cm^2/V\cdot s$]	M(After) [$cm^2/V\cdot s$]
1	4.46	3.92	9.84	6.82
2	4.41	3.90	9.82	11.20
3	4.51	3.61	10.40	11.00
4	4.69	3.84	9.12	11.00
5	4.98	4.06	10.08	9.79
6	4.89	4.19	10.60	13.90
7	4.80	3.94	9.03	11.80
8	4.78	3.95	10.30	12.90
9	4.83	3.88	9.84	13.80
10	4.82	3.56	9.10	14.40
11	4.76	3.77	10.90	15.60

Table 3. Experimental Results before and after UV irradiation on IZO thin films: concentration and transmittance.

Run Number	C(Before) [$\times 10^{20} cm^{-3}$]	C(After) [$\times 10^{20} cm^{-3}$]	Transmittance (550nm)[%]
1	1.42	2.34	85.83
2	1.26	1.43	83.19
3	1.81	1.57	87.08
4	1.36	1.41	85.81
5	1.98	1.57	84.29
6	0.94	1.07	84.12
7	1.26	1.35	85.76
8	1.18	1.22	83.71
9	1.03	1.17	84.97
10	1.02	1.22	86.24
11	0.91	1.06	85.80

of three-factor interactions.

The statistical results on the 11 runs are summarized in Tables 2 and 3. The corresponding Pareto Plot and normal distribution plot are shown in Figs. 3 and 4 respectively, where the significance level is limited to 0.1, i.e., α=0.1. A majority of the primary effects and two-factor interactions form a scattered distribution around the linear line: the effects and interactions lead to an random error with the average value of zero, indicating that the contributions are negligible. The corresponding factors and interactions form the normal distribution: the variation in the factors and interactions, does not change the electrical resistance of the indium-zinc oxide thin films upon irradiating the TCO thin films under UV lights. As seen in Figs. 3 and 4, one main effect and one interaction deviate from the above-mentioned normal distribution. The main effect of a processing variable,

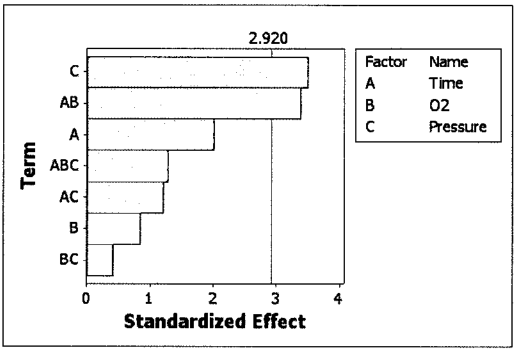

Fig. 2. Pareto charts of the standardized effects and interactions. (The output response is the change in resistivity before and after UV treatment).

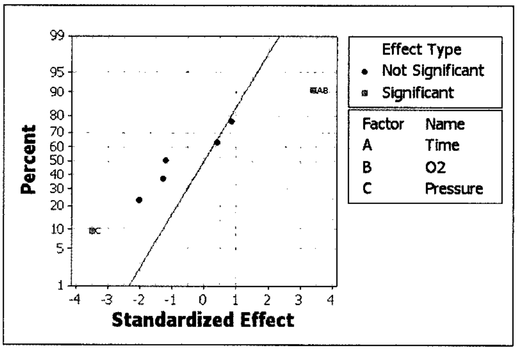

Fig. 3. Normal plot of main effects and interactions. (The output response is the change in resistivity before and after UV treatment).

chamber pressure, does not contribute to the normal distribution. The chamber pressure is estimated to change the sheet resistance in the statistically significant manner in the current work. Only the interaction between the UV irradiation time and oxygen flow rate affects the resistivity change after UV irradiation with the positive value of the interactions. The low values in time and oxygen flow rate or the high values in the two variables lead to the increase in resistivity after UV irradiation.

As shown in Fig. 5, the effect of the main effects is shown: i) the longer the irradiation time, the smaller the resistivity, ii) the higher the oxygen flow rate, the higher the resistivity, and iii) the higher pressure, the smaller resistivity. In the main effect plot of pressure, the slope is highly steep: the other two main effects does not contribute to the improvement in conductivity in IZO thin films. The higher chamber pressure leads to the decreased in sheet resistance in ITO thin films. The flow rate of O_2 increase the sheet resistance. However, the effect is minimal in TCO characteristics, based on the relative comparisons along main effects.

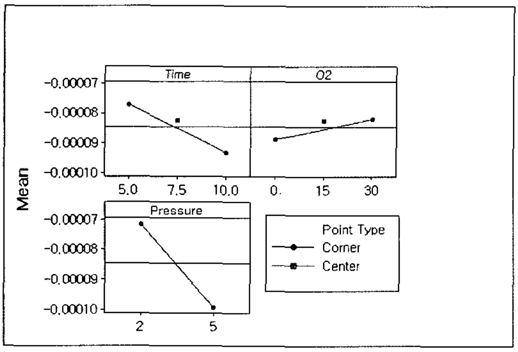

Fig. 4. Main effect plots of the processing variables where the output response is the change in resistivity before and after UV treatment.

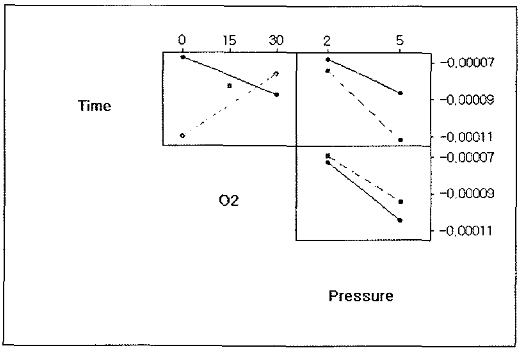

Fig. 5. Interaction effect plots of the processing variables where the output response is the change in resistivity before and after UV treatment.

The interaction effects are shown in Fig. 5. The interaction between the UV irradiation time and O_2 flow rate is statistically significant. The interaction between oxygen flow rate and pressure is not significant. The interaction between the UV irradiation time and pressure is not significant. Unlike the effects analysis performed in the above sections, the dissimilar slope in two states guarantees the dominant role of the interaction which affects the resistivity change in IZO thin films.

The pseudo-center points allow the calculation of the P-value and the presence of the curvature at the center points between the experimental values. The small P-value in the contributions of the center points the presence of a certain curvature in the output response surface around the center points located amid two experimental values in input values, i.e., high and low values in time, flow rate, and pressure.

The properties of indium tin oxide thin films vary depending on deposition temperature, working pressure, RF power, etc. The statistical analysis leads to a proposed model equation. The UV processing is simplified in terms of experimental conditions to the following:

$$\Delta\rho = \beta_0 + + \beta_C X_C + \beta_{AB} X_A X_B$$
$$= -8.5\times10^{-5} - 1.4\times10^{-5}\times X_C + 1.4\times10^{-5} X_A X_B \quad (2)$$

In order to decrease the electrical resistivity, the following conditions should be satisfied: i) the chamber pressure should be high and ii) the UV irradiation time should be short if the oxygen flow rate is high or the UV irradiation time should be long if the oxygen flow rate is low.

In summary, the statistical approach was successfully employed in oder to monitor the effect of UV irradiation on the electrical properties in transparent conducting oxide thin films in terms of processing variables. Furthermore, the additional step can be derived from the statistical DOE.

4. CONCLUSIONS

The statistical design and analysis of experiments were applied in order to understand the effect of the processing variables, UV irradiation on the electrical/optical properties in transparent conducting IZO thin films. The UV treatment decreases the electrical resistivity in indium-zinc oxide thin films. From the analysis of main effects and interactions, the most significant main factor was found as a chamber pressure and the interaction between UV irradiation time and oxygen flow rate is dominant. The higher the chamber pressure, the lower the resistance. The UV irradiation time should be short if the oxygen flow rate is high or the UV irradiation time should be long if the oxygen flow rate is slow in order to achieve the lower resistivity after UV irradiation

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