Electrical and Optical Properties of Transition Metal-Doped ZnO Films Deposited Using DC and RF Magnetron Sputtering

Scott Campbell, Kyle Fischbach
SCI Engineered Materials, Inc.; Columbus, Ohio, USA
Minh Le
Applied Materials Inc., Santa Clara, California, USA

INTRODUCTION

Transparent conductive oxides (TCO's) are essential materials in a variety of applications such as flat panel displays, thin film photovoltaic thin film solar cells and light emitting diodes. Currently indium tin oxide (ITO) is the TCO of choice due to its relatively low resistivity, relatively high transparency in the visible spectrum, and environmental stability. However, due to the relative scarcity of indium, ITO is too expensive for some applications such as thin film solar cells. During the past decade, there has been a considerable amount of work on alternative TCO materials such as doped-ZnO and doped SnO2. For thin film solar cell applications F-doped SnO2 is currently being used on glass substrate based designs, but Al and Ga doped-ZnO is gaining more interest in designs that use polymer substrates as well as glass substrates. Previous work [1-5] has reported the properties of Al and Ga-doped ZnO films as well as ZnO doped with other transition metals and several promising compositions were presented [1-4]. The purpose of the present work is to provide a survey of the electrical and optical properties of transition metal-doped ZnO as well as and investigation of the doping level of promising compositions with the goal of identifying dopants that may warrant further study as TCO's for solar cell and other applications.

EXPERIMENTAL

Sputtering targets were fabricated d using the following method. A pressing powder was prepared by mixing oxides of the dopant metal with ZnO in water containing an organic binder then spray drying the resultant slurry to obtain a free flowing powder. The pressing powder was formed into a near net pre-form using cold isostatic pressing (CIP). The pre-forms were sintered at temperatures above 1300oC for more than 4 hours to obtain a dense ceramic. The ceramic was diamond ground to obtain the final dimensions. Target sizes of 5.0 cm in diameter by 4.5 mm in thickness were used for screening tests and targets 10.2 cm in diameter and 4.5 mm thick were used for optimization. Both size targets were bonded to a copper backing plates using indium solder.

Films were deposited on 2.54 cm square fused quartz substrates using an Anatech Hummer 8.3 sputtering system. Films were deposited at 250W DC for the 5.0 cm diameter targets and 500W DC for the 10.2 cm targets in 7 mtorr of pure Ar on unheated substrates. Both soda-lime-silica glass and fused quartz substrates were used. Deposition times were selected to yield films 750 nm thick.

Film thickness was measured using a Dektak 6M stylus profiler. Film resistivity was measured using a Jandel 4-point probe and a Keithly model 6220 current source, model 2182

nanovoltmeter, and model 6485 picoammeter. Optical transmission was measured using an Hitachi U-4100 spectrophotometer in the range of 300-2600 nm. Hall effect was measured using an HL55WIN Hall System.

As a reference, a section of soda-lime-silica glass coated with fluorinated tin oxide obtained from Guardian Industries was characterized using the equipment listed above.

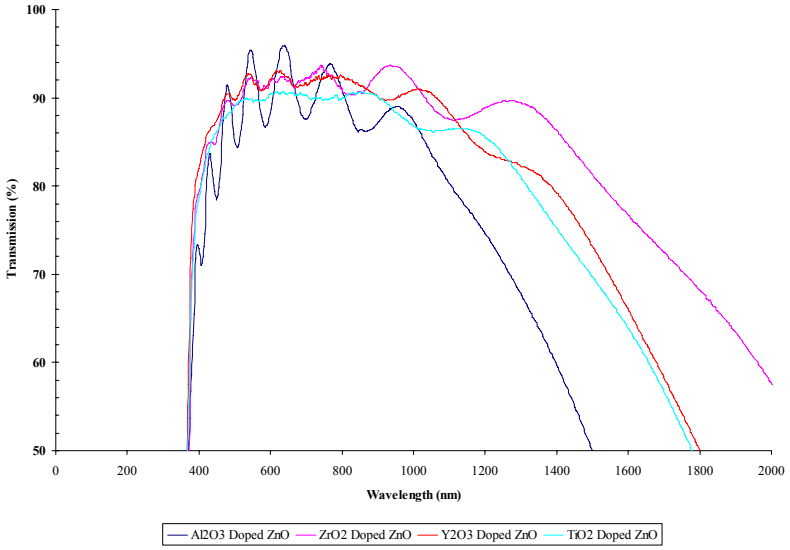
RESULTS AND DISCUSSION

The results of screening test measurements are summarized in Table 1. The transmission results for Al2O3, ZrO2, Y2O3, and TiO2-doped ZnO Films are presented in Figure 1.

Table 1: Summary of Doped-ZnO Film Data

Dopant	ρ (mΩ-cm)	%T > 90% (nm)	% T > 80% (nm)
Pure	6.00	532-1496	426-2232
TiO_2	0.49	540-860	400-1320
V_2O_5	0.64	990-1100	410-1370
Cr_2O_3	1.74	750-1330	450-2250
MnO	2.16	550-1580	490-1970
CoO	1.48	680-1150	430-1850
NiO	2.98	760-1700	500-2410
CuO	20.50	750-1330	450-2250
ZrO_2	0.51	490-1060	400-1550
Y_2O_3	0.65	496-1056	390-1378
Al_2O_3	0.39	460-880	380-980
F-SnO_2	0.44	790-840	490-1200

Figure 1: Transmission vs Wavelength
Doped ZnO Films (Doping Level = 1.0 wt%)



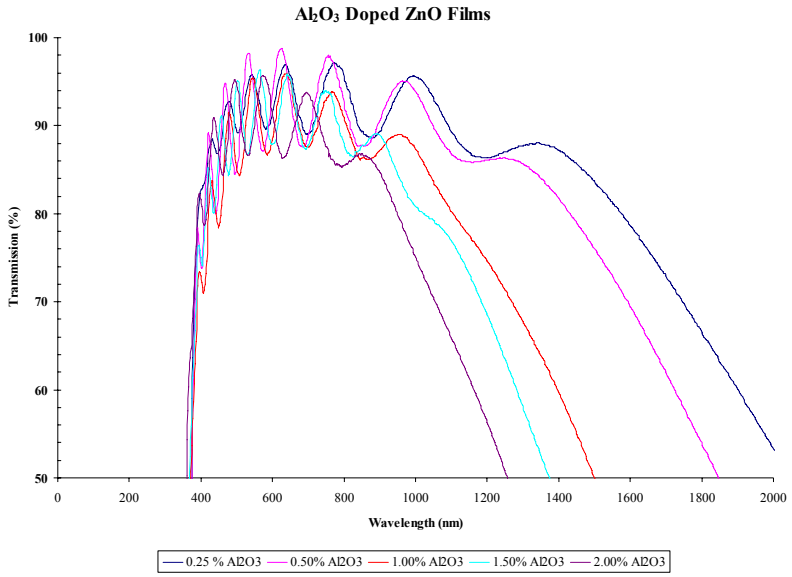
For screening tests, the dopant levels were set at 1 weight percent. As can be seen in the table, there are several dopants in addition to Al2O3 that yield ZnO films of comparable performance to F-doped SnO2 films. ZnO doped with TiO2 yields a film with a resistivity of 0.49 mΩ-cm and slightly better optical transmission than both Al2O3 doped ZnO and F-doped SnO2. ZrO2-doped ZnO films exhibited only a slightly higher resistivity of 0.51 mΩ-cm again with an even better optical transmission. Although the resistivity of the V2O5 doped and Y2O3 doped films are somewhat higher they too are interesting due to their wider optical transmission range.

Based on these results, optimization runs were performed using the Al2O3, TiO2, and ZrO2 dopants at doping levels ranging from 0.125 weight percent to 2.00 weight percent. The transmission results for Al2O3-doped ZnO films are presented in Figure 2 and all results are summarized in Table 2.

Table 2: Summary of Dopant Level Evaluations

Dopant (wt%)	ρ (mΩ-cm)	%T > 90% (nm)	% T > 80% (nm)
Al_2O_3 (0.125)	0.95	500-1170	390-1750
Al_2O_3 (0.25)	0.62	480-980	390-1450
Al_2O_3 (0.50)	0.43	480-890	380-1130
Al_2O_3 (1.00)	0.39	460-880	380-980
Al_2O_3 (2.00)	0.40	480-820	390-900
TiO_2 (0.25)	0.65	500-1060	400-1490
TiO_2 (0.50)	0.68	540-960	410-1380
TiO_2 (1.00)	0.49	540-860	400-1320
ZrO_2 (0.25)	1.06	500-1450	400-1670
ZrO_2 (1.00)	0.51	490-1060	400-1550
ZrO_2 (2.00)	0.60	450-822	380-1050

Fig. 2: Transmission vs Wavelength



As can be seen in Table 2, the dopant amount has a profound effect on the electrical and optical properties of doped ZnO films. As one might expect, the resistivity of Al-doped ZnO films decreases with increasing dopant amount and the effect appears to plateau at the 0.5 weight percent level. The effect on the optical transmission was greater with the transmission range decreasing significantly with increasing dopant amount as shown in Figure 2 for Al2O3-doped ZnO films. Similar behavior was observed as dopant amounts were increased in both Zr and Ti doped ZnO films.

The results of Hall Effect measurements on films deposited on fused quartz substrates are summarized in Table 3.

Table 3: Hall Effect Measurements of Doped ZnO Films

Dopant (wt%)	Mobility (cm^2/V-s)	Concentration ($10^{20}/cm^3$)
Al_2O_3 (0.25)	36.8	1.83
Al_2O_3 (0.50)	29.3	2.82
Al_2O_3 (1.00)	22.5	5.03
Al_2O_3 (1.50)	20.4	4.71
Al_2O_3 (2.00)	15.2	5.13
TiO_2 (1.00)	27.1	2.40
Y_2O_3 (1.00)	32.9	2.28
ZrO_2 (2.00)	22.0	4.37

As can be seen in Table 3, both dopant type and amount has an effect on mobility and carrier concentration. For Al-doped ZnO, the mobility decreases with increasing Al content as the carrier concentrations increases up to 1% doping then levels off. This observation is consistent with what was observed in the resistivity and transmission results presented in Table 2. The Ti and Y doped ZnO films had higher mobilities than the Al doped film at the same concentration level with significantly lower carrier concentrations. The Hall Effect results of the 2% ZrO2-doped film were similar to those of the 1% Al2O3-doped film thought the ZrO2 -doped film had a slightly higher resistivity but slightly better optical transmission range.

CONCLUSIONS

The results of this study have shown that ZnO films doped with Al, Zr, Ti, and Y show promise as substitutes for both ITO and F-doped SnO2 transparent conductive oxides in photovoltaic solar cell and other applications requiring TCOs. The electrical and optical properties of these films are equivalent or slightly better than F-doped SnO2 and can be applied using DC magnetron sputtering at room temperature. Significant improvements in properties may be obtained by depositing films at higher temperatures or post annealing as has been noted in previous studies. In addition, the properties of Al-doped ZnO films are known to degrade in humid conditions and this degradation may be avoided by using the other dopants as has been noted in previous work on Ga-doped ZnO films [6].

ZrO_2, TiO_2, and Y_2O_3 dopants are as easily incorporated into ceramic targets as Al_2O_3 and can be manufactured using the same production equipment thus providing a wider range of material choices for TCO applications. As a result, future work will concentrate on further optimizing the properties of these doped ZnO films and evaluating the effect of environmental conditions on their properties.

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