Transparent Conductive Oxides for Display Applications

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Keywords : Al-doped zinc oxide, magnetron sputtering, fine patterning

Abstract

We report on our material and process research on ZnO:Al films and on our investigations on wet chemical etching using a variety of etching solutions. We achieve resistivity as low as 750 µΩcm for ZnO:Al films with film thickness of 140 nm. Etching with phosphorous acid allows for accurate fine patterning of the ZnO:Al films on glass substrates.

1. Introduction

Transparent conductive oxide films are key components for all types of flat panel displays. State of the art are ITO films deposited by magnetron sputtering. ITO films are grown either in the amorphous state, when fine patterning is necessary, or in the crystalline state, when optimum conductivity is necessary. The high cost level for ITO and rising demand for In in the field of CIGS thin film photovoltaics define strong demands for development of alternative In free TCO materials for display applications.

Transparent and conductive ZnO:Al is an alternative cost effective TCO material which is used as front contact in a-Si:H / µc-Si:H and CIGS thin film photovoltaics. The demands of thin film PV differ considerably from the FPD industry. Films with high thickness in the order of 500-1000 nm are used in photovoltaics. Light scattering and IR transparency is necessary for the a-Si:H/µc-Si:H thin film PV while soft growth PVD without plasma damage and chemical stability are most crucial for CIGS thin film photovoltaics.

Some typical demands on resistivity and optical properties of TCO films for FPD application are summarized in Tab. 1. The thickness of TCO films on glass is usually defined by the need for high optical transmittance in the visible range. For borosilicate glass substrates (n@550 nm ≈ 1.53) and ZnO:Al films with high carrier density ($n_e \approx 8 \times 10^{20}$ cm^{-3}) and therefore n@550 nm ≈ 1.8, this ends up with film thicknesses of ~140 nm or ~280 nm. In this thickness range, the carrier mobility exhibits strong dependence on film thickness.

TABLE 1. Typical demands on TCO films for flat panel display.

Display	d [nm]	ρ [µΩcm]	R_{Sh} [Ω]	T@550 nm [%]
LCD-TFT	90-110	< 210	< 25	> 88
LCD-CF	150 ± 20	210	14	> 85
OLED	150 ± 10	210	14 – 50	> 86
PDP	150	150	10	> 80
TP	15 ± 5	600 ± 150	400	> 90

It is therefore important to optimize the growth conditions towards high mobility at small film thickness, as described in section 3.1 and 3.2. The second and even more relevant issue is the need for fine patterning. ZnO:Al films can be etched using a large variety of etchant. For precise fine patterning, however, it is important to investigate into the details of the etching procedures as described in section 3.3.

2. Experimental

The ZnO:Al films examined in this work have been deposited by reactive MF magnetron sputtering (RMFMS) from metallic Zn:Al targets using the vertical in-line coater Leybold A700V at Fraunhofer IST. The coater was equipped with two PK750 cathodes with zinc targets containing 1.5 wt. %

aluminum. The two targets were driven as a dual magnetron at a frequency of 40 kHz by an Advanced Energy PEII MF generator. In order to obtain both conductive and transparent films operation in transition mode is required. A closed loop control adjusting discharge power was used to stabilize oxygen partial pressure measured by a λ-sensor at constant oxygen flow. Details on the process can be found in [1, 2, 3].

Optical properties were determined by measuring optical transmittance and reflection from 250 to 2500 nm (Varian Cary-5) and spectroscopic ellipsometry at variable angle (VASE) from 250 to 850 nm (Sentech SE 850). Sheet resistance was measured with a four point probe. We used standard photo lithography and wet chemical etching for fine patterning of the ZnO:Al films. A variety of etching agents has been utilized.

3. Results

3.1 Film deposition

The process parameters used for sputter deposition of ZnO:Al films are summarized in Table 2. As a starting point, we used the ZnO:Al process developed for a-Si:H thin film photovoltaics [12]. The carrier speed has been adopted for deposition of 140 nm thick coatings. A three fold gas inlet was used for reactive gas distribution. The reactive gas partial pressure was monitored using three l-sensors (top / center / bottom) and a proper reactive gas flow distribution has been adjusted according to [4]. Soda-lime glass and borosilicate glass Schott AF45 with thickness of 1.1 mm has been used as substrate material. Prior to the deposition, the substrates have been cleaned using our standardized cleaning procedure for optical films on glass.

3.2 Film properties

The dependence of film resistivity and visual light transmittance τ_V on oxygen partial pressure is shown in Fig. 1 for substrate temperature of $T_S = 180$ and 200 °C. Resistivity of $\rho < 350\ \mu\Omega$cm is achieved for $p(O_2) = 13 \ldots 16$ mPa. At 200 °C temperature, the light transmittance is constant and the resistivity increases at small reactive gas pressure.

This effect is due to desorption of Zn when insufficient oxygen is available. This is in contrast to 180 °C substrate temperature where the increase of oxygen partial pressure gives rise to an increase in transmittance. At that temperatures, the Zn desorption is less prominent. Therefore, substoichiometric and thus absorbing films are grown at small reactive partial pressure.

TABLE 2. Deposition parameters used for MF reactive magnetron sputtering of ZnO:Al films.

Process	• Dynamic deposition using the vertical in-line coater Leybold A700V at Fraunhofer IST. • Reactive MF (40 kHz) magnetron sputtering from metallic Zn:Al targets (RMFMS). • Transition mode process control at constant gas flow using the control of discharge power as function of oxygen partial pressure measured by λ-sensors: $P = f(p(O_2))$ • Heated substrates		
System parameters	module		M4
	base pressure	p_0	$< 5 \times 10^{-6}$ mbar
	cathode		Leybold PK 750, TwinMag arrangement
	generator		Advanced Energy PEII, sinusoidal plasma excitation
	target-substrate-distance	d_{ST}	90 mm
	target area		$2 \times 750 \times 88$ mm^2
	target materials		Zn:0.5-1.5 wt. % Al, 4N
Process parameter	Ar-flow	q(Ar)	2 x 40 sccm, purity: 4.8
	O_2-flow	$q(O_2)$	100 sccm, purity: 4.8
	total pressure	p_{tot}	≈ 100 mPa
	reactive gas partial pressure	$p(O_2)$	12 … 17 mPa
	discharge power	P	4900 … 5200 W
	substrates		Float glass and AF 45 $100 \times 100 \times 1.1$ mm^3 $50 \times 50 \times 1.1$ mm^3
	substrate temperature	T_S	180 - 200 °C
	carrier speed	v_C	9.0 mm/s
	film thickness	d	~140 nm up to 800 nm
	deposition rate	a_D	60 … 80 nm m/min

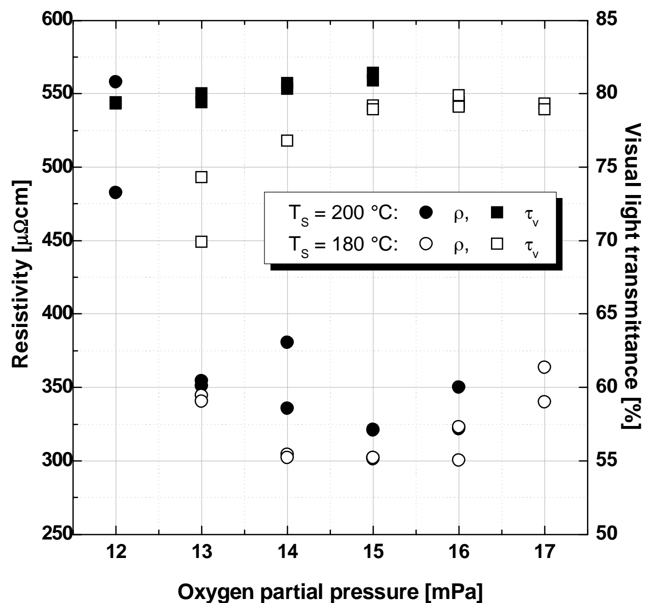

Fig. 1. Dependence of the resistivity and visual light transmittance on oxygen partial pressure for ZnO:Al films on soda lime glass deposited at different substrate temperature (film thickness ~800nm).

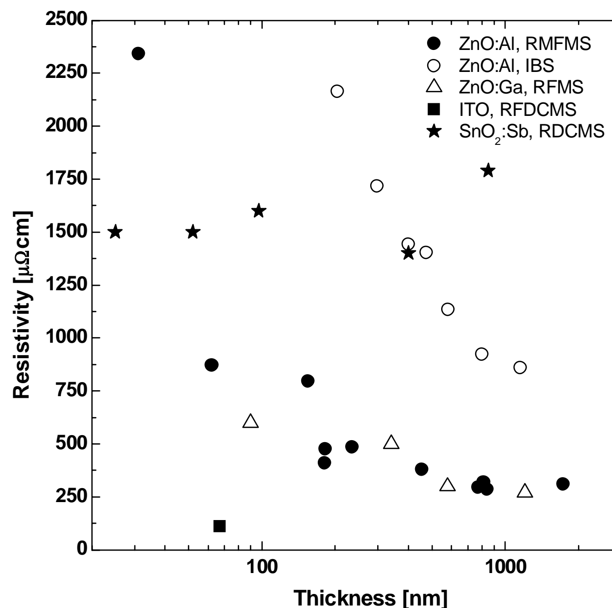

Fig. 2. Dependence of the resistivity of TCO films on film thickness for various materials and deposition processes. ZnO:Al RMFMS: This work, T_S = 200 °C. ZnO:Al ion beam sputtering (IBS): [5], $T_S \approx$ 250 °C. ZnO:Ga RFMS: [6], T_S = RT. SnO_2:Sb, ITO: [7], T_S = 300 °C.

The dependence of TCO film resistivity on film thickness is shown in Fig. 2 for different TCO materials. ZnO:Al films deposited by ion beam sputtering [5] and ZnO:Ga films deposited RF magnetron sputtering from ceramic target [6] are shown for comparison. Date for SnO_2:Sb by reactive DC magnetron sputtering and for ITO by RF superimposed DC magnetron sputtering is also shown [7]. In contrast to SnO_2:Sb, ZnO:X films exhibit a strong dependence of resistivity on film thickness. This effect is attributed to the increase of carrier mobility when the film thickness is increased. However, at 150 nm film thickness, a resistivity of $\rho \approx 800$ µΩcm is achieved for films made by RMFMS. This is similar to RF deposition of ZnO:Ga. ZnO:Al films made by IBS exhibit higher resistivity of $\rho > 2000$ µΩcm at that film thickness. ITO films by RFDCMS exhibit two dimensional growth and resistivity of films with only 67 nm thickness is already close to the theoretical limit.

The transmittance spectrum of a low resistivity ZnO:Al film on glass is shown in Fig. 3 in comparison to ITO at 67 nm thickness. A maximum transmittance of 90.0 % is achieved for ZnO:Al on glass with sheet resistivity of R_{Sh} = 44 Ω, corresponding to ρ = 750 µΩcm.

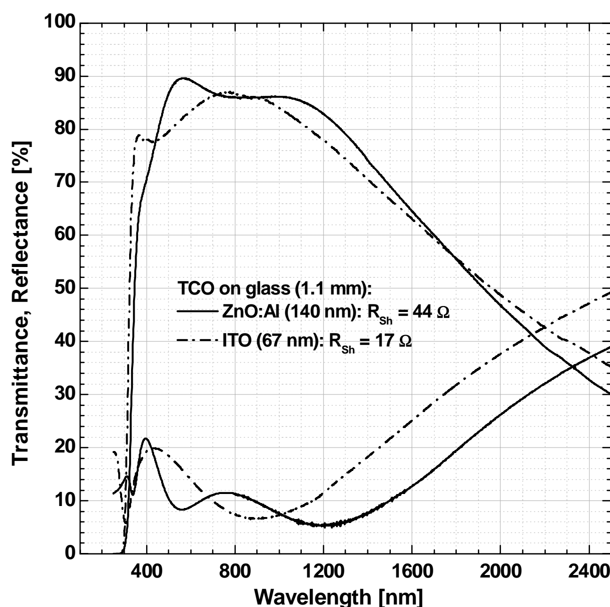

Fig. 3. Optical transmittance of Glass / ZnO:Al (140 nm) on glass by reactive MF magnetron sputtering and Glass / ITO (67 nm) by RF/DC magnetron sputtering.

3.4 Fine patterning

The lack of proper techniques for fine patterning of ZnO based TCO films is one of the main obstructions which hinder the substitution of ITO by ZnO:X. This is due to several problems:

(1st) The severe dependence of the etching rate on crystal surfaces: Sputtered ZnO films grow polycrystalline. The sputtered films exhibit usually textured growth where the c-axis of the wurtzite phase ZnO films is oriented perpendicular to the substrate. However, etching experiments in 25 % nitric acid at room temperature reveal that the etching rate of the different crystal planes differs by a factor of 50. An etching rate of 32 Å/s has been measured for the Zn terminated surfaces while 330 Å/s was found for the O-terminated surfaces. Perpendicular to this direction, the etching rate is 1520 Å/s [8].

(2nd) The Al doping and the corresponding segregation of Al_2O_3 at the grain boundaries: The doping efficiency of TCO defined as the fraction of carrier density obtained from Hall measurements and dopant concentration obtained from electron probe microanalysis is in the order of 100 % for ITO films while 50-70 % is reached at Fraunhofer IST for ZnO:Al films depending on the growth conditions [9]. This is due to the fact that Al_2O_3 segregation is favored by thermodynamics in respect to incorporation of Al^{3+} und Zn^{2+} sites. Therefore, regions with small etch rate are observed at the grain boundaries ending up with crater-like structures where the grain is etched and where the grain boundary is a residue.

The ability to fine tune the etching morphology of ZnO films using the process parameters such as total pressure, deposition temperature, oxygen partial pressure and Al content is the key for the optimization of light scattering to enhance the efficiency of a-Si:H / µc-Si:H thin films solar cells [11, 12].

Several concepts for fine patterning of ZnO are described in the literature. Chang et al. reports on reactive plasma etching in $SiCl_4$ and on wet chemical etching in diluted HCl (< 0.4 %) and in NH_4Cl, respectively [13]. The experiments reveal under cutting of the edges which can be prevented using O_2 plasma pretreatment.

The pattering of ZnO single crystals using acetic acid (CH_3COOH) and hydrochloric acid is reported by Takahashi et al. [14]. The experiments using acetic acid reveal a suppression of the unwanted anisotropy of the etching compared to hydrochloric acid.

Vellekoop et al. [15] compare different methods for fine pattering of ZnO. Proper results in terms of etch rate and robustness of the process and also for the ability of metallization using Al have been obtained for phosphoric acid and acetic acid.

Based on this knowledge, we investigated into the ability of fine pattering of ZnO:Al films deposited on borosilicate glass Schott AF 45 (50 x 50 x 1.1 mm3) with film thickness of 140 nm by reactive AC magnetron sputtering. The films were patterned using conventional photo lithography and etched using the etching solutions described in Table 3.

TABLE 3. Etching solutions used for fine patterning of ZnO:Al.

Nr.	Etching solution
1	HCl (0.005 %), 20 °C
2	NaOH (0.1-1.0 %), 20 °C
3	Oxalic acid (0.05 %), 20 °C
4	EDTA - ethylenediamine tetraacetic acid (0.1-1.0 %), 20 °C
5	H_3PO_4 (85 %) : HNO_3 (65 %) = 20 : 1;
	there from 50-100 µl/l, 20 °C
6	HCl (32 %) : H_2O : HNO_3 (65 % ig) = 20 : 200 : 3;
	there from 1 ml/l, 20 °C
7	H_3PO_4 (85 % ig) : acetic acid (96 % ig) : H_2O = 1 : 1 : 30;
	there from 100 ml/l, 20 °C
8	6 g NH_4Cl + 4 ml NH_4OH + 30 ml H_2O
	there from 10 ml/l, 20 °C
9	12 g/l NH_4Cl + 8 ml/l NH_4OH, 20 °C
10	1 g/l citric acid, 20 °C

Proper etching performance (no under etching, homogenous etching at reasonable etch rate) has been achieved for etch solutions Nr. 3 (diluted oxalic acid), Nr. 1 (diluted hydrochloric acid) and Nr. 5 and Nr. 7 (diluted phosphoric acid and acetic acid and HNO_3, respectively). As and example, Fig. 4 shows the micrographs of ZnO:Al films patterned using oxalic acid.

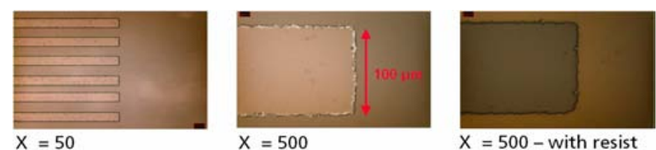

Fig. 4. Micrographs of Glass / ZnO:Al (140 nm) patterned by wet chemical etching using 0.05 % oxalic acid ($H_2C_2O_4$) for 2 min at 20 °C.

The micrographs reveal no under etching of the edges. The ragged profile is due to a non ideal patterning of the photo resist. For further investigation of the etching performance, we used a photo mask which with more precise and finer structures. Fig. 5 shows the results for phosphoric acid. The techniques allows for the formation of pixel electrodes with proper shape of the edges as well as for precise patterning of conducting paths to a width of 1 µm.

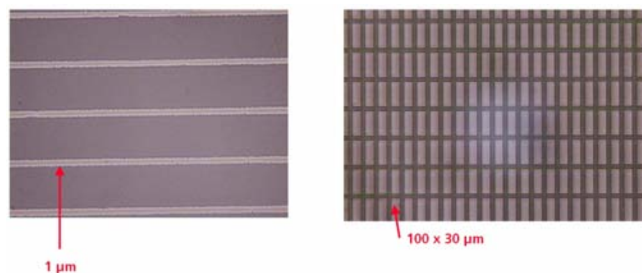

Fig. 5. SEM micrographs of Glass / ZnO:Al (140 nm) patterned by wet chemical etching for 5min at 20 °C using diluted phosphoric acid.

To summarize, we have shown that the wet chemical etching techniques can be adopted for the fine pattering of ZnO:Al films. Proper performance in terms of etch rate and robustness of the process has been achieved. We think homogenous etching of ZnO:Al can be achieved for those etchant, where large cations are formed and where the etch process is therefore limited by the diffusion in the boundary layer and not by surface reaction kinetics.

4. Summary

ZnO:Al films deposited by RMFMS opens up new possibilities for application as transparent electrodes in FPD. The patterning problems can be solved using appropriate wet or plasma etching procedures. Further impact can be expected from LCD applications where improved switching characteristics have been reported using ZnO:Al compared to those using ITO [16].

Acknowledgements

The authors would like to thank S. Biehl, A. Dietz and G. Klumpp for fine pattering of the films. We also gratefully acknowledge financial support by the German Federal Ministry under grant NMT/03X2503/B.

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