Optimization of the electrical properties of magnetron sputtered aluminum-doped zinc oxide films for opto-electronic applications

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Abstract

Magnetron sputtered ZnO:Al films are promising candidates as front electrode in a variety of opto-electronic devices. Here we report on efforts to obtain highly conductive and transparent ZnO:Al films using different deposition conditions for RF, DC and MF (mid frequency) sputtering. Investigations were made to see the effect of target doping concentration (TDC), film thickness, sputter pressure and deposition temperature. RF sputtering from ceramic targets yields low resistivities between 3-5 x 10^{-4} Ωcm for target doping concentrations between 4 % to 0.5 %. With decreasing TDC to 0.5 % carrier mobilities up to 44 cm^2/Vs were obtained, accompanied by the extension of the region of high transmission to the near infrared, due to a reduction in free carrier absorption and corresponding shift in plasma wavelength. DC and MF sputtering from metallic targets yielded similar low resistivities at deposition rates up to 200 nm/min. An analysis of mobility (μ) data of all films as function of the corresponding carrier densities (N) showed that the μ-N values obtained in this study are in vicinity to the limits suggested in the literature.

1. Introduction

Transparent conducting oxides (TCOs) possess a wide range of applications in a variety of opto-electronic devices like flat panel displays [1] or thin film solar cells [2-3]. Most TCOs are based on SnO_2, In_2O_3, ZnO and their mixed compounds and are deposited by different physical and chemical techniques [4-5]. Sputtered ZnO films are especially attractive since they promise lower cost than ITO films and higher conductivities and transparencies than SnO_2 based TCO films. ZnO is used as standard front contact in CIS thin film solar cells [3] and is investigated as an alternative TCO material for silicon thin film solar cells [2,6]. The unique combination of electro-optical properties of TCOs, namely a simultaneous occurrence of high visible transparency and high electrical conductivity can be controlled through the material parameters like dielectric constant ε, effective mass m*, carrier concentration N and mobility μ [4,5,7], where the experimentally controllable parameters are N and μ. TCOs with high carrier mobility are desired for many applications either simply to reduce the sheet resistance or to avoid free carrier absorption in the near infrared range. E. g. in thin film solar cells based on CIS or μc-Si, high optical transparency is required for the wavelength range between 400 nm and 1100 nm.

This paper addresses the electrical and optical properties of ZnO:Al films prepared using different sputtering techniques and process parameters. The first part treats the relationship between sputter conditions and resulting film properties in the case of RF magnetron sputtered ZnO:Al films. We investigated the influence of target doping concentration, film thickness, sputter pressure and deposition temperature on the electrical properties. The role of the deposition pressure as one decisive process parameter was studied for all applied deposition techniques, i.e. RF, DC sputtering from ceramic and metallic targets in stationary mode and reactive MF sputtering in dynamic mode. The mobility data of all films are analysed as function of the corresponding carrier densities and compared to recent literature. Finally, the interdependence of electrical and optical properties is shown for representative films.

2. Experimental

RF and DC sputtered ZnO:Al films were deposited in stationary mode on 10x10 cm^2 Corning 1737 glass substrates in a high vacuum sputtering system (Lesker Inc. USA, 6” diameter cathode) with a base pressure of ~ 1×10^{-7} Torr. The doping concentration of the ZnO:Al films was varied by using targets with different Al_2O_3/ZnO or Al/Zn weight ratios (referred in the following text as target doping concentration, TDC) for ceramic and metallic targets, respectively. Other deposition parameters and their range of variation are given in Table 1. The MF films were deposited in an Inline sputter system (VISS 300, supplied by Ardenne Anlagentechnik) with linear double magnetron cathodes using Zn:Al metallic targets. These depositions were made in dynamic mode. Process stabilization was done using plasma emission monitoring.

Film thickness was measured with a thickness profiler. For electrical characterization the room temperature Hall measurements were performed with a Keithley 920 Hall set-up. Transmission was measured with a Perkin Ellmer spectrometer in the wavelength range 0.3 – 2.0 μm.

Table 1
Range of deposition parameters for RF and DC sputtering from ceramic targets as well as DC sputtering from metallic targets.

Sputter mode	RF	DC	DC (reactive)
Target	$ZnO:Al_2O_3$	$ZnO:Al_2O_3$	Zn:Al
TDC (wt%)	0.5 - 4	2	2
Power (W)	225	250	350-390
T_S(°C)	100 - 330	150, 270	270
Pressure (μbar)	0.5 - 40	0.4 - 40	0.7 - 106
$O_2/(Ar + O_2)$ (%)	0,014	0	0 – 20

3. Results and discussion

3.1 Influence of target doping concentration (TDC) and film thickness on electrical properties of RF sputtered films

Our previous efforts to optimize RF sputtered ZnO:Al films for their application in silicon thin film solar cells were performed at the constant TDC of 2 % [8,9,10,11]. Highly transparent films with low resistivity (< 4×10^{-4} Ωcm) were obtained at low sputtering pressures. The specific resistance ρ is a direct result of concentration N and mobility μ of free carriers in the films. While the carrier concentration strongly depends on the doping level, the mobility is mainly influenced by grain boundary scattering, lattice defects and impurity scattering introduced by Al dopants [12]. To address these aspects, in a first series of experiments we studied the effect of the TDC on the resistivity of RF sputtered films as a function of film thickness. ZnO:Al films with thicknesses between 70 nm and 1400 nm were deposited by increasing the deposition time from 3.5 to 45 min at a fixed substrate temperature of 100°C and a pressure of 2.66 μbar. The TDC were 0.5 %, 1 %, 2 % or 4 %. Further deposition conditions are described in Table 1. Fig. 1 shows the transport parameters ρ, N and μ for these films. The lowest resistivity (Fig. 1a) is found for 2 % TDC for all film thicknesses. In this case resistivity values below 4×10^{-4} Ωcm are already achieved at thicknesses below 400 nm. For lower doped films the resistivity increases with reduced TDC. Moreover, the minimum resistivity for these films is obtained at higher film thicknesses. In case of 0.5 % TDC, ρ continuously decreases with increasing film thickness and even at thicknesses up to 1400 nm no saturation of the resistivity is observed. Note that the highest TDC of 4 % leads to only moderate conductivity which is mainly due to the low mobility. Even the carrier concentration has not increased as one would expect from the higher TDC. For TDC of 0.5 %, 1 % and 2 %, comparable thick films (> 800 nm) show the expected variation of the electrical properties. The carrier concentration N depends almost linearly on TDC (see Fig. 1b). Here almost no effect of film thickness was observed. The corresponding mobilities improve with decreasing TDC, which can mainly be attributed to a reduction of ionized impurity scattering as discussed in 3.3. However, the increase of mobility with increasing film thickness already saturates at lower film thickness in the case of 2 % TDC as compared to 0.5 % TDC. A maximum mobility of ~ 36 cm^2/Vs was achieved for film thicknesses above 1 µm in the latter case.

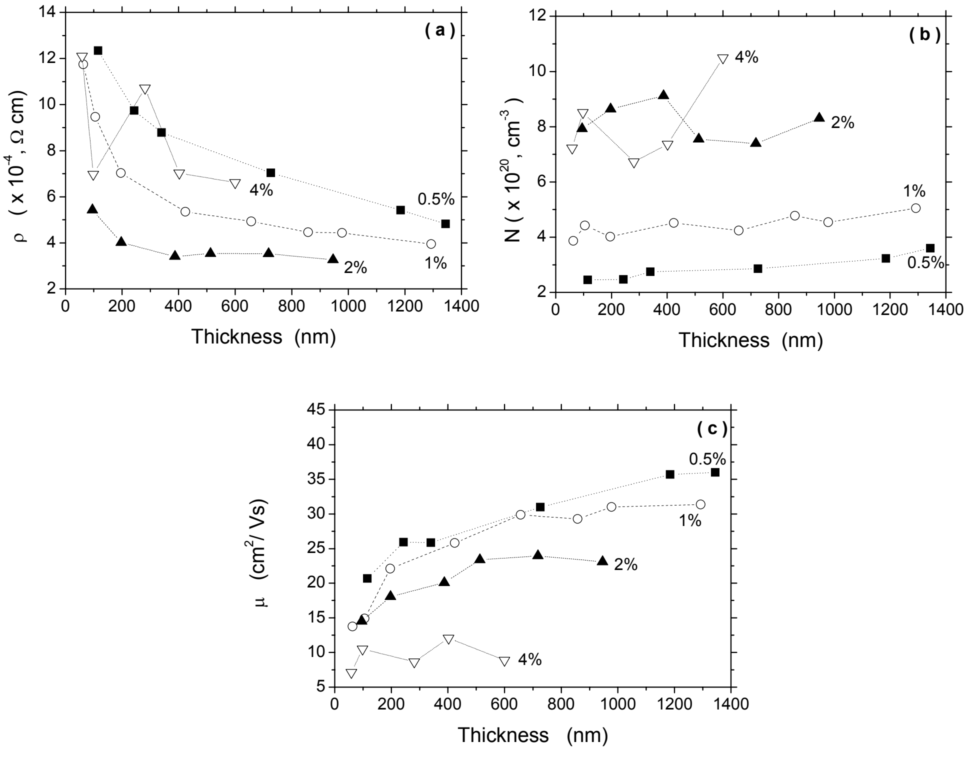

Fig. 1. Electronic transport parameters specific resistance ρ, carrier concentration N and carrier mobility μ of differently doped RF sputtered ZnO:Al films as a function of film thickness.

The inferior properties of the 4 % films can be understood by anticipating the effects of heavy Al incorporation into the films. As suggested by Hartnagel et al. [12] and Aktaruzzaman et al. [13], the heavy incorporation of Al probably leads to the formation of aluminum oxide or Al-suboxide, which will in turn affect the inclusion of electrically active dopants as well as will affect the mobility following the structural changes through the presence of Al-O species.

From the experimental data presented in this section we conclude that in case of RF sputtering from ceramic target, μ can be improved by lowering the TDC to 0.5 %. Thus still low resistivities are maintained. However, the lowest resistivities were obtained at 2 % TDC, governed by the high carrier concentration. At low doping levels the electrical film properties remarkably improve with increasing film thickness, which can be mainly attributed to the increase in carrier mobility. By a further optimization of substrate temperature and sputter pressure, mobilities up to 44 cm^2/Vs ($\rho = 3.7 \times 10^{-4}$ Ωcm) could be obtained for a TDC of 0.5 % (see section 3.4 for optical properties and further discussion).

3.2 The role of sputter pressure for RF, DC and MF sputtering

Former studies of our group on RF and reactively DC sputtered ZnO:Al films have shown that irrespective of the sputter technique the sputter pressure has a remarkable influence on the structural and electrical film properties [8,9, 10,11]. Moreover, the different structural properties can be utilized to produce different surface textures by wet chemical etching with excellent light scattering properties for silicon thin film solar cells [6,8,9,11]. The relationship between the sputter conditions and the structural properties and surface morphology after etching, is discussed in detail in a related paper [14]. The effect of sputter pressure on the electrical properties of ZnO:Al films deposited in RF and DC mode is presented in the following. Additionally, the results for films prepared on 30x30 cm^2 substrates with MF sputtering from metallic Zn:Al targets in dynamic mode are included. Fig. 2 gives ρ, N and μ as a function of the deposition pressure. The results are as follows: Irrespective of the sputtering technique and deposition temperature, the sputter pressure plays a key role in deciding the electrical properties. The resistivity is low for low sputter pressure and increases if a certain pressure is exceeded. This effect is compensated to some extent when the deposition temperature is raised. This is very prominently observed for the RF sputtered films. In this case, at 150°C the resistivity increases already beyond a sputter pressure of 2.66 µbar, whereas for RF films deposited at 270°C low resistive films can be obtained at higher pressures up to 13 µbar. For the DC films sputtered from a ceramic target (non-reactive case) at a deposition temperature of 150°C, sputter pressures even up to 26 µbar can be used to obtain low resistivity. There is only a slight extension of the pressure window for films with low resistivity when the temperature is raised to 270°C in this case. In the MF sputter mode a sputter pressure as high as 43 µbar could be still used for depositing highly conductive films.

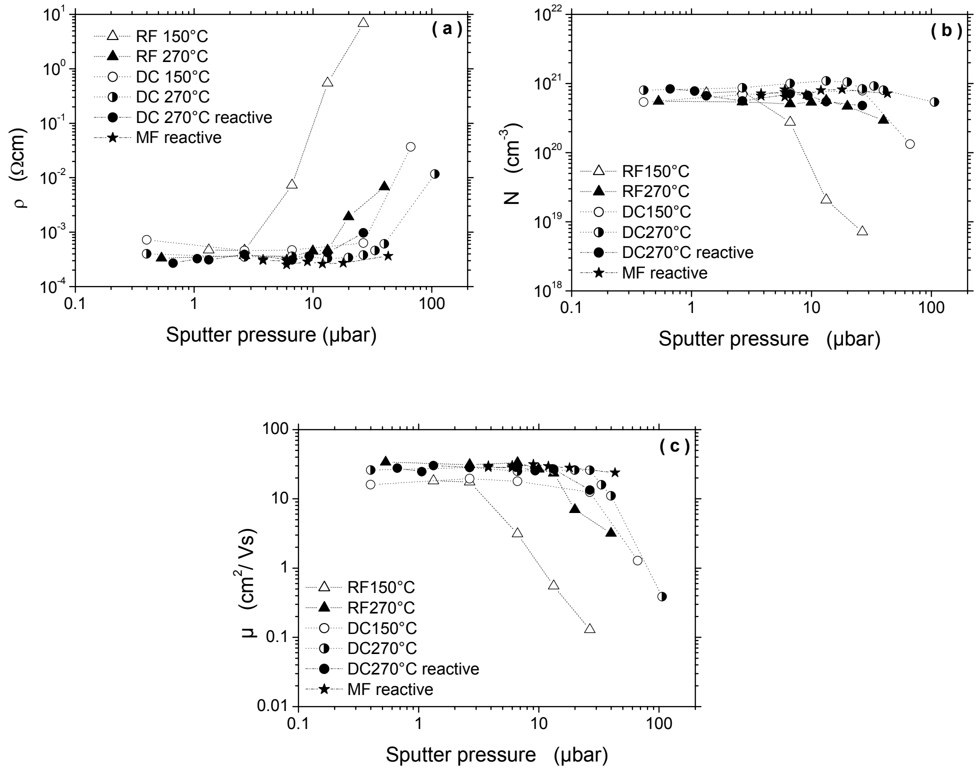

Fig. 2. Pressure dependence of electronic transport parameters resistivity ρ, carrier concentration N and carrier mobility μ for RF, DC and MF sputtered films (ceramic and metallic targets).

The pressure dependence of N is shown in Fig. 2b. For RF films deposited at 150°C a considerable drop in N is observed at sputter pressures higher than 2.66 μbar. This sensitivity of N to pressure changes lowers as one goes for higher substrate temperature (see RF 270°C) and to DC and MF sputter deposition mode.

The pressure dependence of mobility is viewed in Fig. 2c. At higher substrate temperatures the decrease in mobility is observed at higher pressure values. The MF sputtered films (calculated stationary deposition rates between 200 and 250 nm/min) exhibit almost no change in μ up to a sputter pressure of 43 μbar.

A comparison of Figs. 2a, 2b and 2c shows that except for the low temperature (150°C) RF sputtered films, the increase in resistivity with increasing deposition pressure is mainly governed by the pressure dependence of μ. The decrease in mobility with increasing deposition pressure can be mainly attributed to a less compact film structure as discussed in a related paper [14]. In the case of RF films sputtered at 150°C both N and μ were reduced significantly at higher pressures, thereby leading to further increase in ρ by 2 orders of magnitude more as compared to other cases. For these films a low amount of oxygen was added during sputtering (see Table 1). Since the Ar/O_2 flux was constant the oxygen partial pressure increases for higher sputter pressures due to the reduced pumping speed. The presence of oxygen in combination with the low compactness found for the RF film sputtered at low T_S and high pressures can lead to a change in oxygen incorporation into the film through the grain boundaries, which will consequently cause a decrease in both, mobility and carrier concentration [16].

3.3 Relationship between carrier density and mobility

Increasing the carrier mobility is a key issue for the improvement of opto-electronic film properties of TCOs. For a deeper discussion of the electrical properties of ZnO:Al films prepared using different process parameters and sputter techniques, we plotted the mobility as a function of the carrier concentration in Fig. 3.

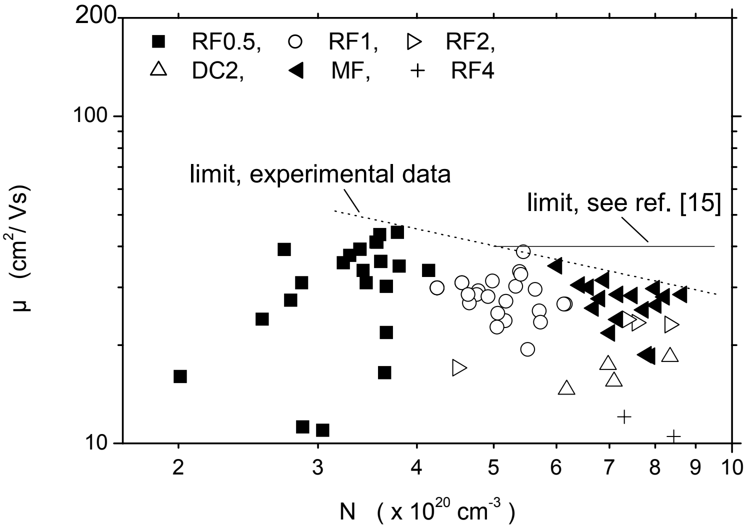

Fig. 3. Carrier mobility μ versus carrier concentration N (μ-N) dependence for films deposited using different sputter techniques and conditions.

Only films with a thickness above 500 nm were included to reduce the limitation on the mobility due to the thickness effect as discussed in section 3.1. Ellmer [15] suggested a limit of $\mu \sim 40$ cm^2/Vs for $N > 5x10^{20}$ cm^{-3} for TCO films. This limit is also marked in the figure by a compact line. Corresponding to diverse deposition conditions including the target doping concentration, the carrier concentration of these films lies in a range of 2 - 9 $x10^{20}$ cm^{-3}. With increasing N the maximum mobility shows a drop from 44 cm^2/Vs for RF 0.5 % films to 38 cm^2/Vs and 23 cm^2/Vs for RF 1 % and RF 2 % films, respectively. The DC and MF films show limiting μ values of ~ 18 cm^2/Vs and 35 cm^2/Vs which are very similar to the best RF values for a given N.

The comparison with recent literature data shows that the maximum mobility values obtained in our work are in close vicinity to the limiting values given by Ellmer [15] and Minami [16] for sputtered ZnO films. The almost linear decrease of maximum mobility with increasing N clearly indicates that irrespective of the deposition technique and conditions of deposition, a ‘practical’ limit of μ exists for a given range of N.

The μ-N relationship for TCOs has been discussed for example by Bellingham et al. [17] Minami [16] and Ellmer [15]. Bellingham et al. calculated the resistivity limit as function of the carrier concentration and compared it with experimental data obtained for different TCOs. They found that the μ-N values follow a linear trend for carrier concentrations in the range of 10^{19}- 10^{21} cm^{-3} and concluded that ionized impurity scattering is the limiting factor for the lowest achievable resistivities. The same was reported by Minami et al. for intrinsic and Al doped ZnO films and carrier concentrations of 10^{20}- 10^{21} cm^{-3} and by Ellmer et al. for $N > 10^{20}$. The linear decrease of maximum mobility observed for N= 4-9×10^{20} cm^{-3} in Fig 3 is consistent with these results. Therefore we conclude that ionized impurity scattering limits the mobility in the present ZnO:Al films, deposited by different sputtering techniques and with diverse deposition conditions.

3.4 Optical properties

A comparison of the transmittance of electrically best quality films (for ρ, N and μ see Table 2) deposited using RF and MF techniques is given in Fig. 4, showing the effect of target doping concentration and deposition temperature on the total transmittance. All films exhibit high optical transmittance in the visible wavelength range up to 800 nm wavelength. As demonstrated by the RF sputtered films from targets with TDC equal to 2 % (film RFC), a high visible transparency can also be achieved at a reasonable low substrate temperature of 100°C. The MF sputtered film shows a comparable transparency. The transmittance - particularly in the near infrared wavelength range strongly improves by lowering the TDC from 2 % (film RFC) down to 0.5 % (film RFA). This is a consequence of low free carrier absorption owing to the reduced carrier concentration in this film. However, the resistivity increases by a factor of 2. By increasing the deposition temperature to 330°C (film RFB), the resistivity decreases to 4.3×10^{-4} Ωcm, while still an excellent NIR transparency is maintained.

Table 2

Target composition, total pressure, thickness d, deposition rate and electrical properties of the films shown in Fig. 4.

Film	Target composition	Total Pressure	Thickness d	Deposition Rate	Resistivity ρ	Carr. Conc. N	Mobility μ
	TDC (wt.%)	(μbar)	(nm)	(nm/min)	10^{-4} (Ωcm)	10^{20} (cm^{-3})	(cm^2/ Vs)
RFA	0.5	2.66	726	33	7.04	2.86	30.98
RFB	0.5	2.66	640	29.1	4.26	3.55	41.3
RFC	2	2.66	718	23.9	3.54	7.37	23.95
MF	1	6	826	200	2.53	8.64	28.53

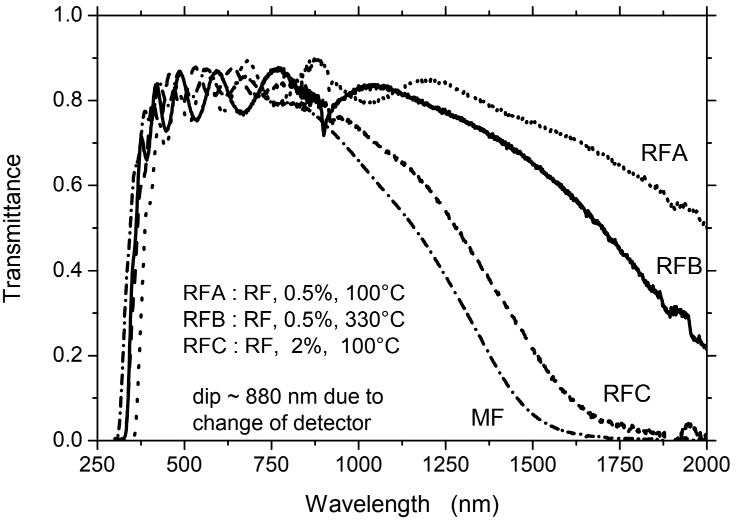

Fig. 4. Spectral transmittance of RF and MF films with low electrical resistivity.

4. Conclusions

Focus of this study was to investigate and improve the electrical and optical properties of sputtered ZnO:Al films. For RF sputtered films the effect of target doping concentration, film thickness and sputter pressure were found to be of prime importance to tailor the trade off between optical and electrical film properties. For the lowest target doping concentration of 0.5 % the mobility could be increased up to 44 cm^2/Vs while maintaining the electrical resistivity as low as $3.7\text{x}10^{-4}$ Ωcm. This consequently improved the wavelength discrimination of optical properties, along with the reduction in free carrier absorption and plasma frequency. This work was partly extended for DC and MF sputtering to compare the best quality films. From an analysis of the μ and N values of all sputtered films we conclude that μ is limited by ionized impurity scattering in the range of high carrier concentration. The target doping concentration for ZnO:Al sputter deposition can be applied as major parameter to govern the electronic transport parameters as well as the optical properties. This work confirms that high quality ZnO:Al films can be obtained using RF, DC as well as MF sputtering techniques.

Acknowledgements

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