ANNEALING EFFECTS ON TITANIA DOPED ZINC OXIDE (ZnO:Ti) AND GALLIUM DOPED ZINC OXIDE (ZnO:Ga) THIN FILMS PREPARED BY DC MAGNETRON SPUTTERING

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MOTIVATION

Transparent conductive oxides (TCO) are used as transparent electrodes in thin film solar cells. Especially for CdTe solar cells, the successive production processes require high temperature stability for the TCO material. ZnO:Ti and ZnO:Ga thin layers can resist temperatures up to 600°C while having a smooth surface and good electrical and optical properties.

Layers of zinc oxide doped with titania or gallium oxide were deposited on glass substrates using magnetron sputtering from a single planar cathode (length of 750 mm). The thin film properties were investigated and compared to aluminum doped zinc oxide (ZnO:Al) thin films.

The sputtering power was set to the upper load limit of the targets to deposit thick layers with a deposition rate of more than 100 nm × m/min. Additionally, the thin films were annealed at high temperatures of up to 600°C in vacuum or ambient air.

Depending on the sputtering parameters and the annealing treatment the resulting resistivity was less than 300 µΩcm for ZnO:Ga and less than 1000 µΩcm for ZnO:Ti with a high transmission in the visible spectral range. In contrast to ZnO:Al layers, the electrical properties of ZnO:Ga and ZnO:Ti thin films do not deteriorate at high annealing temperatures.

EXPERIMENTAL SETUP

Doped zinc oxide thin films were sputtered in the vertical in-line sputtering plant ILA 750 using planar ceramic targets with the size of 750 mm × 120 mm. The different dopants used are listed in table I. The glass substrates were coated dynamically with a constant transport system velocity. The resulting thin film thickness was approximately 1000 nm.

The sputtering pressure was set to 3 µbar or 9 µbar. The sputtering power was 10 kW, which is a relatively high power density for the planar targets used. The substrate temperature before sputtering was varied from room temperature (RT) up to 350°C.

An oven with circulating air was used for annealing in ambient air. The samples are heated up to the set temperature in approximately 10 min. After that time the temperature is constant (figure 1 and 2). The annealing in vacuum was carried out in a high vacuum chamber with a two-sided radiation heater. Comparable to the annealing in air, the substrates are heated up in less than 10 min and kept at constant temperature for 20 min.

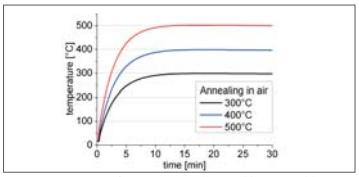

Figure 1: Annealing in air for 30min at 300°C (I), 400°C (II) and 500°C (V)

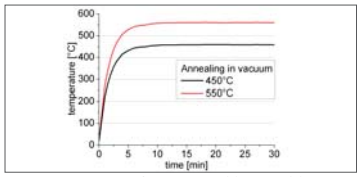

Figure 2: Annealing in vacuum for 30min at 450°C (III) and 550°C (IV)

target	dopant	concentration
A	TiO_2	3wt%
B	Ga_2O_3	3wt%
C	Ga_2O_3	2wt%
D	Al_2O_3	2wt%
E	Al_2O_3	1wt%
F	Al_2O_3	1wt%*

Table I: doped zinc oxide targets
*target F contains additional dopants

annealing	ambience	T (time) [°C]
A1	air	300 (30 min)
A2	air	400 (30 min)
V1	vacuum	450 (30 min)
V2	vacuum	550 (30 min)
A3	air	500 (30 min)

Table II: annealing of the doped zinc oxide thin films

EXPERIMENTAL DETAILS AND RESULTS

BEFORE ANNEALING:

- lowest thin film resistivity with ZnO:Ga (target B): 360 µΩcm due to a high free carrier density
- high thin film resistivity of ZnO:Ti (target A): 2500 µΩcm (low carrier density and mobility)
- properties dependent on the dopant concentration in the target (compare target B/C and D/E/F)

ANNEALING IN VACUUM

- free carrier density decreases when annealing at higher temperature (annealing V2)
- free carrier mobility increases for all thin films
- lowest thin film resistivity with ZnO:Ga (target B): 270 µΩcm (annealing V1)
- resisitvity of ZnO:Ti more than halved when annealing in vacuum (940 µΩcm)

ANNEALING IN AIR

- free carrier density decreases when annealing at higher temperature (annealing A2)
- thin films are not stable when annealing
  - → time dependant diffusion and oxidation processes
- ZnO:Al: increase of the resistivity due to decrease of the free carrier mobility
  - → grain boundary effect
- ZnO:Ga and ZnO:Ti: increasing free carrier mobility
  - → no or less effect of grain boundaries
  - → decreasing thin film resistivity
- ZnO:Al can be "stabilized" when adding certain additional elements in the target
  - → almost constant free carrier density and mobility when annealing

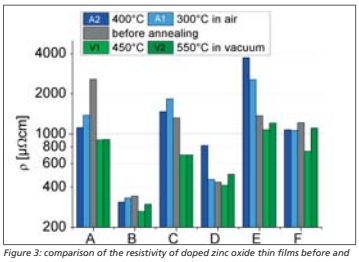

Figure 3: comparison of the resistivity of doped zinc oxide thin films before and after annealing

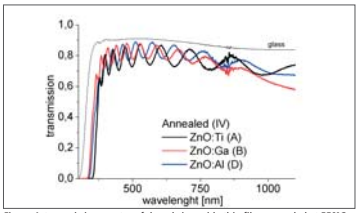

Figure 4: transmission spectra of doped zinc oxide thin films annealed at 550°C in vacuum

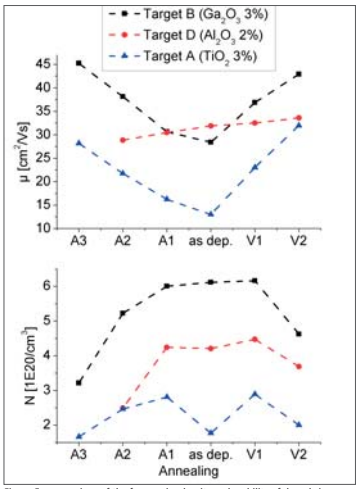

Figure 5: comparison of the free carrier density and mobility of doped zinc oxide thin films before and after annealing after annealing

	A2 (air 400°C)			as.dep			V2 (vakuum 550°C)		
	ρ [µΩcm]	N [10^{20}/cm³]	µ [cm²/Vs]	ρ [µΩcm]	N [10^{20}/cm³]	µ [cm²/Vs]	ρ [µΩcm]	N [10^{20}/cm³]	µ [cm²/Vs]
A	1150	2.5	21.8	2930	1.8	13.0	970	2.0	32.0
B	315	5.2	38.1	360	6.1	28.4	310	4.6	42.9
C	1500	2.5	16.6	1180	3.1	17.2	755	2.5	32.5
D	860	2.5	28.9	465	4.2	31.9	510	3.7	33.6
E	4070	1.6	9.4	1450	1.8	23.8	1130	2.4	23.1
F	1120	2.0	28.2	1180	2.0	26.5	1310	1.7	26.9

SUMMARY

Different doped zinc oxide targets were sputtered on glass substrates with an inline sputter plant. The thin films were annealed in vacuum and ambient air respectively. It could be shown, that ZnO:Ti and ZnO:Ga thin films can be annealed in air up to 500°C without deterioration of the resistivity. All doped zinc oxide thin films had a good resistivity after annealing in vacuum. The absorption was about 3% for the 1000 nm thick films.

The doped zinc oxide films are most promising for solar cells, due to its low absorption, low cost and smooth surface. Further investigations on ZnO:Ti and the stabilized ZnO:Al with different doping concentrations are planned.

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ACKNOWLEDGEMENT

THIS PROJECT WAS FUNDED BY THE EU AND THE FREE STATE OF SAXONY: 14274/2473

Freistaat Sachsen
Staatsministerium für Wissenschaft und Kunst

SAB Sächsische AufbauBank

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solarfabrik 2020