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Advanced properties of Al-doped ZnO films with a seed layer approach for industrial thin film photovoltaic application

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ABSTRACT

Currently sputtered Al-doped ZnO films are transferred to industry for the application in thin film silicon solar modules. These films are known to easily form light trapping structures upon etching which are necessary for absorbers with low absorbance such as μc-Si. Up to now the best structures for high efficiency thin film silicon solar cells were obtained by low rate radio frequency (r.f.) sputtering of ceramic targets. However, for industrial application a high rate process is essential. Therefore a seed layer approach was developed to increase the deposition rate while keeping the desired etch morphology and electrical properties.
Aluminum doped ZnO films were deposited dynamically by direct current (d.c.) magnetron sputtering from a ceramic ZnO:Al_2O_3 target (1 wt.%) onto an additional seed layer prepared by r.f. sputtering. ZnO:Al films were investigated with respect to their optical and electrical properties as well as the morphology created after etching for a-Si/μc-Si solar cells. Additionally atomic force microscopy, scanning electron microscopy, X-ray diffraction and Hall measurements were performed, comparing purely r.f. or d.c. sputtered films with d.c. sputtered films on seed layers.
With the seed layer approach it was possible to deposit ZnO:Al films with a visual transmittance of 83.5%, resistivity of 295 μΩ cm, electron mobility of 48.9 cm^2/Vs and electron density of $4.3 \cdot 10^{20}$ cm^{-3} from a ceramic target at 330 °C. Etch morphologies with 1 μm lateral structure size were achieved.

1. Introduction

In thin film photovoltaics transparent conducting oxides (TCO) are used as front electrodes [1–4]. Using aluminum doped zinc oxide (ZnO:Al) as a front electrode for thin film silicon solar cells offers a number of advantages. In addition to good transparency and conductivity as well as good stability in hydrogen plasma [5,6], ZnO:Al can be easily textured after deposition. This can be achieved by the wet chemical approach introduced by Kluth et al. [7], which leads to various etch morphologies depending on the preparation method used for the samples [8,9] and the etching parameters themselves [10,11].

Optimized etch morphologies of approximately 1 μm lateral structure size can be obtained when sputtering ZnO:Al by radio frequency (r.f.) with low rate from a ceramic target followed by etching in diluted hydrochloric acid [3,7]. These films show a high polycrystalline quality as confirmed by X-ray diffraction (XRD) measurements, as well as low resistivity and high electron mobility. However, low power densities are required to deposit high-quality films by r.f. sputtering, which lead to low deposition rates. This paper focuses on a seed layer approach to obtain ZnO:Al films of comparable quality at higher deposition rates [12–16]. Therefore a thin r.f. sputtered seed layer is used for improved nucleation of a thick direct current (d.c.) sputtered film that is deposited subsequently. The resulting properties are very promising and are demonstrated in this paper.

2. Experimental details

R.f. sputtered ZnO:Al seed layers were prepared dynamically on Corning Eagle XG substrates with a deposition rate of 10.2 nm m/min. This is nearly twice as high as the standard r.f. sputtering process. The ZnO:Al was sputtered from ceramic ZnO:Al_2O_3 (1 wt.%) targets. The seed layer thickness was varied between 26 nm and 387 nm. In a next step, a ZnO:Al film was deposited on top, but now with d.c. excitation at a higher deposition rate of 18.9 nm m/min. The total film thickness was kept at approximately 1 μm. The detailed process parameters can be found in Table 1.

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Table 1
Process parameters for deposition of ZnO:Al sputtering deposition by r.f. and d.c. on glass substrates.

Process	Dynamical deposition by r.f. and d.c. magnetron sputtering from ceramic ZnO:Al_2O_3 targets in the in-line facility Leybold A700V. Heated substrates.			
General information	Base pressure	p_0	<0.5 mPa at room temperature <1 mPa at T_S ~ 310 °C	
	Cathode		Leybold PK 750, 88 × 750 mm^2	
	Generators		Advanced Energy Pinnacle$^+$, Solvix Magic DC-Generator, AE r.f. generator Cesar 1350	
	Target substrate distance	d_{ST}	90 mm	
	Target area		750 × 88 mm^2	
	Target material		ZnO:1 wt.% Al_2O_3	
	Substrate		Corning Eagle XG 100 × 100 mm^2	
Process parameters	Ar flow	q(Ar)	2 × 98 sccm, purity 4.8	
	O_2 flow	$q(O_2)$	2 × 2 sccm, mixed gas (1:10, O_2:Ar)	
	Total pressure	p_{tot}	400 mPa	
	Substrate temperature	T_S	320–330 °C	
	Discharge power	P	2500 W	
			r.f.	d.c.
	Carrier velocity	v_c	6.6 mm/s, varying number of oscillations	9 mm/s, varying number of oscillations
	Dyn. deposition rate	a_D	~10.2 nm m/min	~18.9 nm m/min
	Seed layer thickness	d_{SL}	26, 77, 155, 387 nm	
	Total film thickness	d_{ges}	~800…1000 nm	

First the substrate temperature was determined to obtain optimized etch structures for a purely r.f. magnetron sputtered ZnO:Al film. In the next step the r.f. seed layer thickness was decreased as described in Table 2. Also a purely d.c. sputtered film was deposited for comparison and the impact of a vacuum break between seed layer deposition and d.c. ZnO:Al deposition was examined.

The as deposited samples were characterized optically with transmittance and reflectance measurements in the spectral range from 250 to 2500 nm using a double beam spectrophotometer (Varian Cary-5). Hall measurements were performed in van der Pauw configuration in air at room temperature and with a sample size of 1 × 1 cm^2. The crystalline structure and quality were measured with XRD scans in Bragg Brentano geometry with a Philips X'Pert Pro MRD using the Cu K_α radiation at a wavelength λ of 0.154056 nm. Here an X'Celerator CCD line array detector was used in scanning mode. The beam spot on the sample had a line profile with the size of 10 mm × 40 μm. Beside a Phi-scan, also rocking curves were measured. The samples were examined in movement direction (0°) and perpendicular to it (90°).

All samples were etched in 0.5 wt.% hydrochloric acid (HCl) and approximately 150 nm of the films was removed. The etch rate was about 3.5 nm/s and was determined by Dektak measurements. These measurements have a larger error bar for small etch craters, because the profilometer tip cannot enter the crater in total. Thus the height is overestimated.

The etched samples were observed with scanning electron microscopy (SEM, type LEO 1530) and atomic force microscopy (AFM, type Nanoscope). The AFM scans were used for statistical evaluation of rms roughness and lateral structure size ξ which can be extracted from the autocorrelation function G(R). ξ is the radius R for which the curvature of G(R) is maximal. Information about G(R) is given in [17,18].

The angular-dependent light scattering was measured with a small integrating sphere circling around the sample and collecting the scattered light in transmittance. The light hit the samples perpendicular from the coated side. The measurement is called ARS (angular-resolved light scattering). For further details see [19].

A retarding field analyzer cup (RFA) was used to determine the energy and flux of Ar ions bombarding the sample for d.c. and r.f. sputtering processes [20,21].

Table 2
Overview of depositions and experiments.

Sample	Number of oscillations		Approx. seed layer thickness [nm]	Total film thickness [nm]	Vacuum break
	r.f.	d.c.			
Sample A	30	0	875	875	No
Sample B	15	15	387	992	No
Sample C	6	24	155	1037	No
Sample D	3	27	77	1001	No
Sample E	1	29	26	1041	No
Sample F	0	24	0	771	No
Sample G	1	24	26	849	Yes
Sample H	6	24	155	999	Yes

3. Results and discussion

3.1. R.f. and d.c. sputtered ZnO:Al films

The deposition conditions for r.f. ZnO:Al films with optimized etch morphology were used for all subsequent seed layer depositions. The etch morphology obtained for such an r.f. film is shown in Fig. 1. The large lateral structure sizes around 1.1 μm are favorable for light scattering in a-Si:H/μc-Si:H tandem solar cells.

The etch morphology of the purely d.c. sputtered film with the same deposition conditions as the r.f. film is shown in Fig. 2. In both cases 150 nm were etched off the original film according to the measurements by profilometer, which has a larger error for small craters because of the tip radius. In the d.c. case only small feature sizes around 430 nm were obtained.

While the r.f. film was deposited with a dynamical deposition rate of 10.2 nm m/min, the d.c. film was deposited significantly faster with 18.9 nm m/min. In the literature the r.f. sputtering rate for similar films is often even smaller than the rate used here (three times lower than the d.c. rate).

The optical properties of the as deposited r.f. and d.c. films are similar and the visual transmittance (folded with the sensitivity of a human eye) is 83.1 and 84%, respectively. The folded reflectivity is 13.3 and 12% and the visual absorption is 3.6 and 4%.

The electrical properties are also similar, but the d.c. film is slightly better. The resistivity ρ of the r.f. film is with 583 μΩ cm a bit higher than 472 μΩ cm for the d.c. film. The charge carrier density N_e is $3.4 \cdot 10^{20}$ cm^{-3} and $4.3 \cdot 10^{20}$ cm^{-3}, while the electron mobility μ is 31.5 cm^2/Vs and 30.9 cm^2/Vs for r.f. and d.c., respectively.

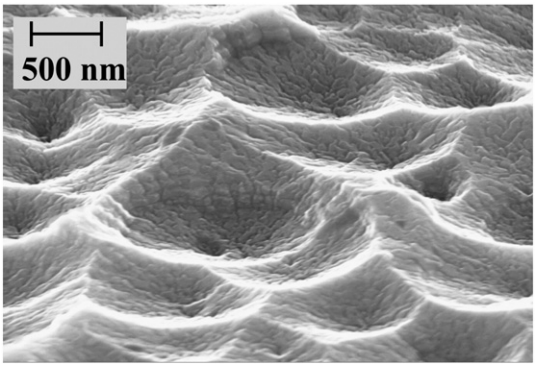

Fig. 1. SEM picture of a purely r.f. sputtered ZnO:Al film etched in 0.5% HCl in 30.000 magnification seen under 60°.