HIGH RATE SPUTTERING OF ZNO:AL FROM ROTATING CATHODES AS FRONT CONTACT IN SILICON THIN FILM SOLAR CELLS

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ABSTRACT: Aluminium doped zinc oxide (ZnO:Al) thin films were deposited by mid-frequency magnetron sputtering method from rotatable dual magnetrons at different substrate temperatures, working pressure and discharge power on Corning glass substrates. The ceramic zinc oxide targets are doped with 0.5 wt% aluminium oxide. Highly transparent films with low resistivity below 4×10^{-4} Ω·cm were obtained at deposition rates up to 110 nm·m/min. The ZnO:Al films were texture-etched in diluted hydrochloric acid before they were applied as front contacts in silicon thin-film solar cells. For films deposited at low deposition rate the etched films show a surface with regularly distributed large craters and a root mean square roughness of around 140 nm. Microcrystalline silicon solar cells with 8.5% conversion efficiency were prepared on these films. The high rate ZnO:Al films exhibit reduced light scattering after etching. Nevertheless a conversion efficiency of 7.5% was achieved on these substrates.

Keywords: ZnO, Magnetron Sputtering, High Deposition Rate

1 INTRODUCTION

Besides the often used indium tin oxide (ITO) and fluorine doped tin oxide (SnO_2:F), aluminium doped zinc oxide (ZnO:Al) is regarded as a reliable high quality alternative as transparent conductive electrode material – which can be incorporated in thin-film solar cells based on silicon, chalcopyrites or cadmium telluride (CdTe) as well as other optoelectronic devices like light emitting diodes and flat panel displays.

Doped zinc oxide thin films can be fabricated by several methods like magnetron sputtering [1], low pressure chemical vapour deposition (LPCVD) [2], sol-gel method [3, 4] or pulsed laser deposition (PLD) [5]. In terms of an industrial production, sputtering and LPCVD are most promising since both result in highly conductive films and allow coating on large area.

These films exhibit high transparency and excellent conductivity. For silicon thin-film solar cells another factor is even more important: a textured surface, which leads to the so-called "light-trapping" effect. Light trapping is beneficial for the performance of silicon thin-film solar cells, since it leads to a significant improvement of the photocurrent [6].

ZnO films with a textured surface can be achieved e.g. by a deposition process, which directly leads to the desired film topography [2, 7] or by a post-deposition wet-chemical etching step in diluted acid of sputter deposited films [6]. Both methods have proven to provide textured ZnO:Al films which enable effective light-trapping in thin-film silicon solar cells [2, 6].

This study addresses the preparation of ZnO:Al films by sputtering from rotatable dual magnetrons (RDM) with high deposition rates exceeding 100 nm·m/min. The use of tube targets offers a better target utilization as compared to planar targets. Furthermore, it promises constant film properties over the whole target life time, since no race track formation is observed.

2 EXPERIMENTAL

All ZnO:Al films were prepared on 1.1 mm thick glass substrates (Corning Eagle 2000) in a vertical in-line sputtering system (VISS 300 by "Von Ardenne Anlagentechnik" VAAT, Dresden, Germany). The system is equipped with two rotatable ceramic targets doped with 0.5 wt% Al_2O_3. The cathode length of 75 cm allows homogeneous deposition on a substrate area of at least 30 × 30 cm². Mid-frequency (MF) sputtering mode with an excitation frequency of 40 kHz was used. The substrates were heated for at least one hour up to a maximum substrate temperature of 350°C. The substrate temperature was determined by pyrometer prior to the deposition. The process chamber was evacuated to a base pressure of less than 8×10^{-7} mbar. Pure argon was used as sputtering gas. During the deposition process the carrier passes the targets at constant speed several times to simulate an in-line process with several cathodes. The speed and number cycles were adjusted until the desired film thickness of 800-900 nm is reached. More details concerning the sputtering process can be found in [8] or [9]. In order to achieve a textured surface a wet chemical etching step is carried out by dipping the samples into diluted hydrochloric acid (0.5% HCl). The etching time was 50 s.

The electrical properties of the as-deposited films were investigated by van der Pauw Hall effect measurements. Optical transmission and reflection of textured thin films were carried out using a dual beam spectrometer with an integrating sphere (Perkin Elmer Lambda 19). The topography of etched ZnO:Al films was evaluated by scanning electron microscopy (SEM). The root mean square (rms) roughness was calculated from atomic force microscopy (AFM) data.

Selected texture-etched ZnO:Al films were applied as front contact in single junction microcrystalline silicon p-i-n solar cells prepared by plasma enhanced chemical vapour deposition (PECVD) with an intrinsic layer thickness of around 1.1 µm and an active cell area of 1 cm². Details of silicon deposition and cell preparation are described elsewhere [10]. A ZnO/Ag double layer served as back reflector.

Solar cell J/V characteristics were measured using a sun simulator at standard test conditions (AM1.5, 100 mW/cm² at 25°C).

3 RESULTS

3.1 Influence of substrate temperature on ZnO:Al films

Two series of samples were prepared at 4 kW and 14 kW discharge power, respectively. The substrate temperature was varied between 250°C and 350°C. Note, that the working pressure and Argon gas flow of the 4 kW series were 20 µbar and 100 sccm, respectively, while for the 14 kW series they were 20 µbar and 200 sccm. The resistivity as a function of the substrate temperature of both series is illustrated in Figure 1. It can be seen that the resistivity decreases with increasing substrate temperature. The results of the Hall effect measurements show that the mobility increases with elevated substrate temperature. The carrier concentration shows a maximum at around 300°C (not shown, see [8]). This trend for magnetron sputtered ZnO:Al films is well known [11, 12]. It is generally explained by an improved grain structure and healing of defects of the polycrystalline ZnO:Al.

These results demonstrate again that high temperatures are necessary to deposit low resistive ZnO:Al films.

3.2 Influence of discharge power on ZnO:Al films

In Figure 1 it can also be seen that the 4 kW series has slightly higher resistivities than the 14 kW series. The reason for this lies in the fact that the 4 kW series was deposited at lower Ar gas flow. Previously it has been shown, that increasing Argon gas flow leads to a reduced resistivity [9]. There it is argued that a higher argon gas flow reduces the influence of the background pressure.

In Figure 2 (top) it can clearly be seen, that the resistivity of the films increases with increasing discharge power if all other deposition parameters are kept constant. In fact, here it increases only slightly from less than 3.4×10^{-4} Ω·cm at 2 kW to 4.1×10^{-4} Ω·cm at 14 kW.

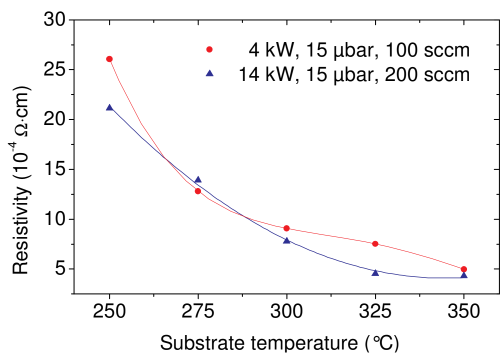

Figure 1: Resistivity for two series of ZnO:Al thin films deposited at different conditions as a function of substrate temperature. All lines are guides for the eye.

Note that the working pressure was 15 µbar, the Argon gas flow was 200 sccm and the substrate temperature was 350°C. The corresponding Hall data (not shown, see [9]) reveal, that this behaviour originates from a decrease of mobility as well as carrier concentration. In [13] the decrease of Hall mobility of films deposited at higher deposition rate is attributed to more intrinsic stress in the thin films.

The motivation to use higher discharge power lies in the possibility to increase the deposition rate. Figure 2 (bottom) discovers that the deposition rate increases linearly from about 15 nm·m/min at 2 kW discharge power up to 110 nm·m/min at 14 kW. Thus, the normalized deposition rate approximately amounts to 7.5 nm·m/(min·kW). The linear trend promises, that even higher deposition rates should be possible by a further increase of the discharge power. Note that 14 kW is the actual power maximum of our sputtering system – which is limited by the attached generators and the targets. Even higher rates are feasible for reactive sputtering [14]. Finally, it has to be pointed out, that even at high deposition rates conductivity is sufficient for use as front electrode in silicon based solar cells. Also the optical transmission of all samples is higher than 80% in the visible spectral range and the absorption loss is below 5% (not shown).

Figure 2 (bottom) also depicts the etch rate of the thin films in diluted HCl. It decreases from 4.5 nm/s to about 1.75 nm/s for films deposited at 2 kW and 14 kW, respectively. This behaviour is generally attributed to more compact ZnO:Al films deposited at higher

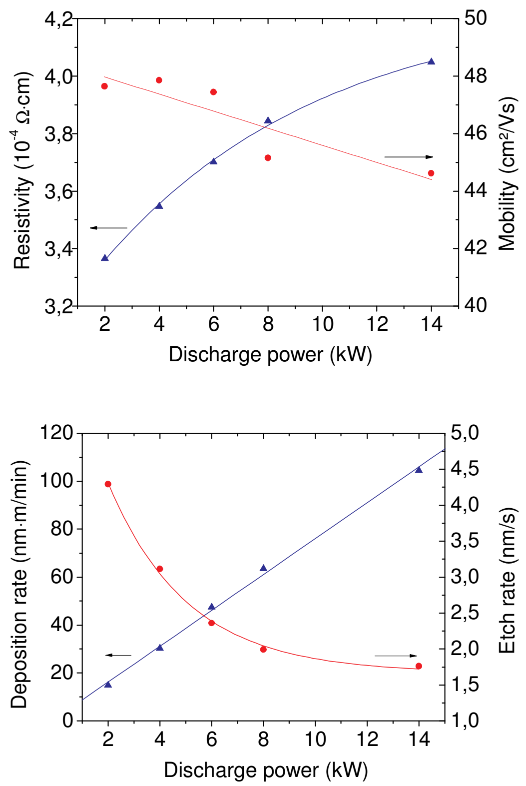

Figure 2: (top) Resistivity and (bottom) deposition rate and etch rate of as a function of discharge power. All lines are guides for the eye.

discharge power. Higher compactness is believed to slow down the wet-chemical etching process [15].

3.3 Influence of working pressure on ZnO:Al films

A working pressure variation was carried out at 2 kW and 14 kW discharge power while substrate temperature and argon gas flow were kept constant at 350°C and 200 sccm. Figure 3 (top) depicts the pressure dependency of the resistivity. It shows a minimum at 15 µbar (3.4×10^{-4} Ω·cm) and 20 µbar (3.7×10^{-4} Ω·cm) for the 2 kW and 14 kW series, respectively. The fact that in the whole range of working pressure the resistivity of the samples deposited at 2 kW, confirms the results of the investigations on the influence of the discharge power.

Figure 3 (bottom) illustrates that these observations are mainly caused by the variation of the Hall mobility, whereas the carrier concentration of the films (not shown here) is almost constant for all samples. The decrease of the mobility towards lower pressures is often explained by the influence of high energetic oxygen ions [13]. The decrease of mobility for higher working pressures can be explained by higher porosity of the films**.**

3.4 Texture etched films

Figure 4 shows the SEM images of two selected films after wet-chemical etching. For the sample deposited at low deposition rate (top) the surface is covered with deep and wide crates with the feature sizes of ~350 nm in depth and 1~2 µm in diameter. The rms roughness of this film is around 138 nm (AFM image not shown here). The surface topography of the 14 kW sample (bottom) shows

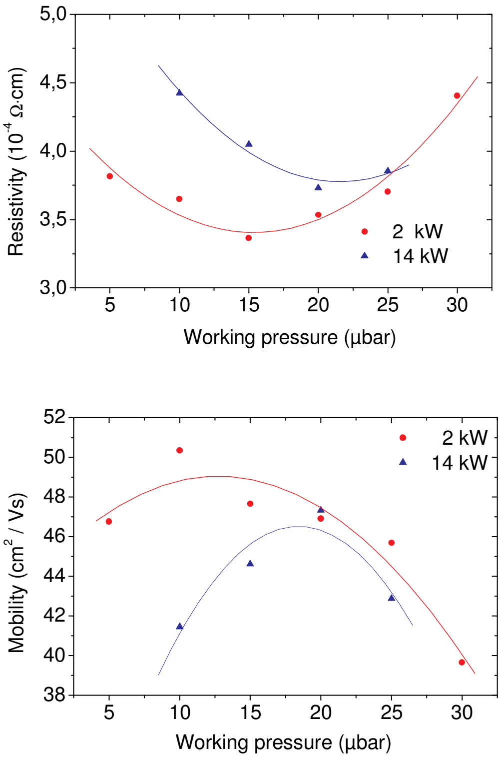

Figure 3: Electrical properties of ZnO:Al thin films deposited at low and high discharge power as a function of working pressure: (top) resistivity, (bottom) Hall mobility. All lines are guides for the eye.

a rather flat texture with only a few randomly distributed craters. The rms roughness of this surface is only 78 nm. These are the highest values for the pressure series at 2 kW and 14 kW discharge power, respectively. Note that upon longer etching –especially of the high power films– the rms roughness can be increased slightly, however this also leads to holes in the ZnO:Al film which reach the glass.

4 DISCUSSION

On most films of the two pressure series microcrystalline silicon solar cells were prepared. For the 2 kW and 14 kW series the best cell efficiencies were achieved for films deposited at a working pressure of 10 µbar and 20 µbar, respectively. In both cases the substrate temperature was 350°C and an Argon gas flow of 200 sccm was used.

The J(V) characteristics measured under AM1.5 illumination of these cells are shown in Figure 5. For sample deposited at 2 kW, an efficiency of 8.5% is obtained. This value is an outstanding result and it marks the progress of the works with the rotating targets [8]. The fill factor, open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) of this solar cell are 71.4%, 0.519 V and 22.9 mA/cm^2, respectively.

The solar cells fabricated on the samples deposited at 14 kW show lower efficiency of 7.5%. This is mainly caused by the smaller J_{sc} of 20.2 mA/cm^2, while the fill factor (72,1%) and V_{oc} (0,514 V) are comparable to the cell on low rate ZnO:Al film.

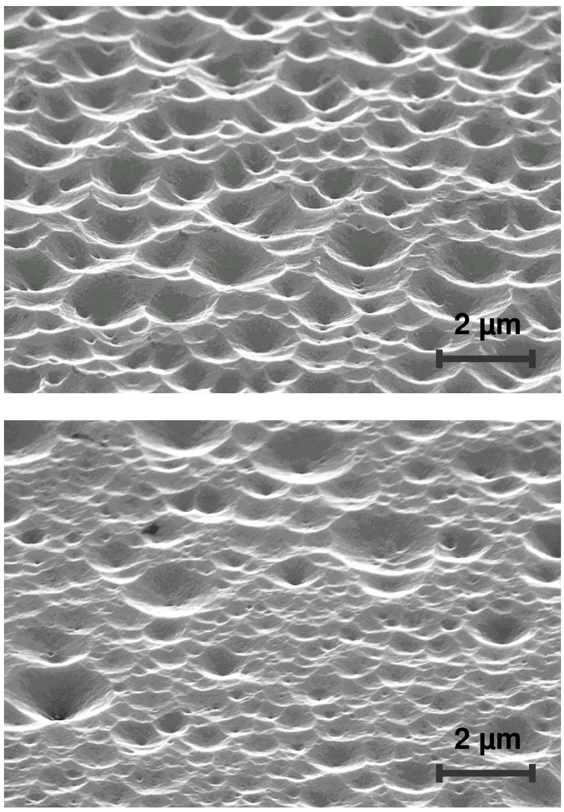

Figure 4: SEM images of selected samples. Deposition conditions: (top) 2 kW, 200 sccm, 10 µbar. (bottom) 14 kW, 200 sccm, 20 µbar.

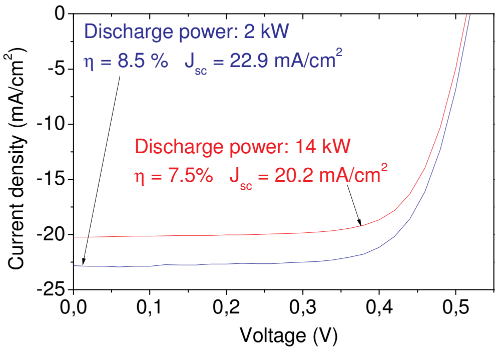

Figure 5: J-V curves of the optimize samples deposited at low and high discharge power.

Up to now, the correlation between surface texture of the substrate and photocurrent of a solar cell is not fully understood and still under discussion [16]. However, in this particular case we attribute the reduced photocurrent to the fact that the high rate films show a limited light trapping ability. This is caused by the flatter texture with fewer craters of the high rate films after etching.

The almost unchanged fill factor and V_{oc} imply that the crystalline volume fraction of the silicon layers on low and high rate substrates does not vary significantly. Furthermore, the evaluation of the J-V curves shows that the sheet resistance of the films after etching is small and does not lead to significant ohmic losses in the front contact.

Finally, it has to be pointed out that the 7.5% conversion efficiency marks a good value for 1.1 µm thick µc-Si:H solar cells on ZnO:Al films deposited at rates of 110 nm·m/min.

Future works address the improvement of the of high rate ZnO:Al films in terms of a better surface texture for improved light trapping.

5 CONCLUSION

The influence of substrate temperature, discharge power and working pressure on sputter deposited ZnO:Al films from dual rotatable targets with MF excitation was investigated. ZnO:Al thin films with resistivity of 3.4×10^{-4} Ω·cm and 3.7×10^{-4} Ω·cm have been obtained for samples deposited at deposition rates of 15 nm·m/min and 110 nm·m/min, respectively.

Selected wet chemically etched films deposited at low discharge power show regular deep and large craters while for films deposited at high power the film surfaces are more flat with fewer craters due to the higher compactness of the film.

Surface textured ZnO:Al films deposited at low and high deposition rate were successfully applied as front contact in p-i-n microcrystalline silicon solar cells and initial efficiencies of 8.5% and 7.5% were obtained, respectively.

5 ACKNOWLEDGEMENT

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References

[1] B. Szyszka, Thin Solid Films 351 (1999) 164.

[2] S. Fay, L. Feitknecht, R. Schlüchter, U. Kroll, E. Vallat-Sauvain, A. Shah. Sol. Energy. Mater. Sol. Cells 90 (2006) 2960.

[3] M. J. Alam and D. C. Cameron. J. Vac. Sci. Technol. A. 19 (2001) 1642.

[4] W. Tang and D. C. Cameron. Thin Solid Films 238 (1994) 83.

[5] Jong-Pil Kim, Sang-A Lee, Jong Seong Bae, Sung-Kyun Park, Ung-Chan Choi, Chae- Ryong Cho.Thin Solid Films 516 (2008) 5223.

[6] B. Rech, T. Repmann, V. M. N. van den Donker, M. Berginski, T. Kilper, J. Hüpkes, S. Calnan, H. Stiebig, S. Wieder. Thin Solid Film 511-512 (2006) 548.

[7] A.E. Delahoy, S. Guo, A. Patel, and J. Cambridge Delahoy, Proceedings of the 22nd EU PVSEC, Milan, Italy, (2007).

[8] E. Bunte, J. Hüpkes, H. Zhu, M. Berginski, H. Siekmann, W. Appenzeller, B. Rech, Proceedings of the 22nd EU PVSEC, Milan, Italy (2007).

[9] H. Zhu, E. Bunte, J. Hüpkes, H. Siekmann, S. M. Huang, Proceeding of the 7th ICCG (2008) 6-16.

[10] T. Repmann, W. Appenzeller, T. Roschek, B. Rech, O. Kluth, J. Müller, W. Psyk, R. Geyer, P. Lechner, Proceedings of the 17th EU PVSEC, Munich, Germany (2001).

[11] C. Agashe, O. Kluth, J. Hüpkes, U. Zastrow, B. Rech, M. Wuttig, Journal of Applied Physics 95 (2004) 1911.

[12] M. Berginski, J. Hüpkes, M. Schulte, G. Schöpe, H. Stiebig, B. Rech, M. Wuttig, Journal of Applied Physics 101 (2007), 1911.

[13] I. Petrov, V. Orlinov, A. Misiuk. Thin Solid Films 120 (1984) 55.

[14] J. Hüpkes, M. Berginski, V. Sittinger, F. Ruske, B. Rech, H. Siekmann, J. Kirchhoff, B. Zwaygardt, Proceedings of the 21st EU PVSEC, Dresden, Germany (2006).

[15] O. Kluth, G. Schöpe, J. Hüpkes, C. Agashe, J. Müller, B. Rech, Thin Solid Films 442 (2003) 80.

[16] P. Lechner, R. Geyer, H. Schade, B. Rech, O. Kluth, H. Stiebig, Proceedings of the 19th EU PVSEC, Paris, France (2004).