Instabilities in reactive sputtering of ZnO:Al and reliable texture-etching solution for light trapping in silicon thin film solar cells

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Abstract

Texture etched zinc oxide is often used as transparent front contact for silicon thin film solar cells. Reactive sputtering is a potentially low-cost process. However, process stability, film uniformity, and reproducibility are challenges to be solved. Oscillations of the control signal and subsequent reaction of the plasma emission control with moving substrates from rotatable metallic targets cause fluctuations of aluminum doped zinc oxide (ZnO:Al) properties. Solutions to overcome such variations during the reactive sputtering process are discussed. However, effects on film properties, especially on etching behavior, cannot be totally removed. To achieve good light scattering properties for solar cell application ZnO:Al films are usually etched in dilute hydrochloric acid. An etch process based on hydrofluoric acid has been developed to tune the surface texture for a given ZnO:Al material. One feature of this process is the relaxed requirement on ZnO:Al film properties as the reactively sputtered ZnO:Al films do not necessarily possess optimized film structure for the HCl etch. Solar cells with optimized ZnO:Al front contacts achieved conversion efficiency well above 11 %.

Keywords: reactive sputtering, zinc oxide, etching thin film silicon, solar cells

1 Introduction
Aluminum doped zinc oxide (ZnO:Al), prepared by magnetron sputtering and surface textured by chemical etching, is a promising transparent conducting oxide (TCO) material for the use as front contact and light scattering source in amorphous and microcrystalline silicon thin film solar cells [1-5]. In view of an industrial process, high rate sputtering from cost effective metallic targets, specifically tube targets, was applied. The stabilization of the reactive process by plasma emission monitoring (PEM) [6] was studied with special focus on process dynamics and the influence of tube target rotation and carrier movement in an in-line sputtering system. During deposition, the operation point varies as tube targets rotate, substrate carrier moves and temperatures shift. These experimental findings and resulting effects on process and material properties will be described and discussed. To gain a deeper understanding of the relationship between the sputtering process and ZnO:Al film characteristics, we studied the material properties and the wet chemical etching behavior of ZnO:Al films on glass substrates. Finally we present results on a suitable etch process to create rough light scattering topography on ZnO:Al for the application as front contact in silicon thin film solar cells. Additionally, results on solar cells on these textured ZnO:Al films are reported.

2 Experimental Details

2.1 ZnO:Al sputter deposition

The ZnO:Al films were prepared in an in-line deposition system by VAAT (Dresden) for 30x30 cm² glass substrates. Figure 1 shows a sketch of the sputtering system. The system consists of two loading chambers and two process chambers. All chambers are equipped with back side heaters. Several processes are available: The left chamber contains a linear ion source for different surface treatments [7,8] and a rotatable dual magnetron (RDM). The right process chamber contains several planar cathodes for different excitation modes: RF, (pulsed) DC or AC. The left two cathodes are separated
by shields and are used for reference ZnO:Al films for front and back contacts from ZnO:Al2O3 target (99:1 w/w%) and silver target for solar cell preparation (dashed box in Figure 1) [5,9]. The double cathode on the right is specially designed for reactive sputtering. This and the RDM cathode are used for reactive sputtering throughout this work. All planar and tube target lengths are 750 mm. Metallic, planar or tube targets (Zn:Al 99.5:0.5 w/w%) were mounted on the double cathodes (see dotted boxes in Figure 1), which were operated by mid-frequency excitation at 40 kHz at a constant power of 4 kW and 14 kW, respectively. Oxygen gas flow was controlled via two-channel PEM of the 307 nm Zn line [6]. Substrate temperatures of 260-300 °C were applied to prepare ZnO:Al films with high mobility and low resistivity [10, 11]. The substrate temperature was measured prior to deposition by pyrometers. The deposition pressure was adjusted by choosing a constant Argon gas flow and specific position of butterfly valves in front of the turbo pumps. The substrate carrier consists of a metal frame that holds up to nine 10x10 cm² substrates for simultaneous onto several glass sheets. Wings on each side of the substrate prevent deposition onto the heaters, when the substrate has passed the cathode. Originally the wings of the carrier were covered by metal plates that were shielded from the heaters by another metal plate on the back side. However, unless otherwise specified experiments were performed with single glass plate instead of the two metal plates. To simulate industrial sputter machines with many cathodes, the substrate carrier moved back and forth in front of the cathode system. These dynamic depositions were carried out after pre-sputtering onto one wing.

2.2 ZnO:Al characteristics and solar cells

The depth profile of chemical composition was investigated by secondary ion mass spectroscopy. All values for Al film concentrations are given as Al/(Zn+Al) ratio as determined by CsMe⁺ ions. For light scattering purposes the ZnO:Al films were etched in diluted acids. Surface topography was imaged by scanning electron microscopy (SEM)
or atomic force microscopy (AFM). Single junction p-i-n microcrystalline silicon thin film solar cells (μc-Si:H) as well as amorphous silicon/microcrystalline silicon (a-Si:H /μc-Si:H) tandem solar cells were prepared using plasma enhanced chemical vapor deposition ZnO:Al / Ag double layers prepared in the above mentioned sputtering system served as a back reflector for all solar cells here. Solar cell J-V characteristics of 1x1 cm² cells were measured using a class A sun simulator under standard test conditions (AM1.5, 100 mW/cm² at 25ºC).

3 Results and Discussion

3.1 ZnO:Al sputter deposition

During sputtering of the metallic Zn:Al targets in reactive mode PEM intensity, gas flows, and generator voltage were monitored. In static mode we observed oscillations in process parameters as tube targets rotate. Exemplarily, rotating speed (left axis) and PEM intensity variation (right axis) are given as function of time in Figure 2 during pre-sputtering with constant oxygen flow (without active control) in the stable metallic mode. The oscillations of the process arise with the target rotation frequency. These oscillations are attributed to non-uniform target material, tube diameter or eccentric rotation of the tube targets. When increasing or decreasing the rotation speed, the process tends to get more oxidic or metallic, respectively, as seen at the peaks that arise immediately, when rotation speed is changed. This can be easily understood assuming a static tube there is equilibrium of oxidation and sputtering within the erosion zone on the target while the rest of the target is always fully oxidized. When the target starts to rotate, the oxidized zone of the target enters the erosion area and thus the operation point on the target immediately shifts towards oxide mode (low PEM intensity). At the same time, metal surface area leaving the erosion zone now is exposed to the
sputter atmosphere, getters the reactive gas and the process returns. Similar effects are also present on planar cathodes with moving magnets [12]. Of course, active process control by PEM is able to correct these oscillations. However, it is not clear, whether this should be done or not. Variations related to the operation point (oxidation state of the target) have to be corrected, but variations of the plasma emission intensity related to varying distance to the target surface should be neglected, as these are not related to the oxidation state. The best way to tackle these effects is the use of planar targets with fixed magnets that avoid these oscillations but lead to low target utilization. However, long term drifts over target lifetime might be even stronger due to the formation of erosion craters at the race track. A better solution could be the use of advanced PEM control to analyse not only the zinc but also oxygen emission [13].

During in-line deposition, substrate carriers move in front of the plasma and may disturb plasma conditions. Figure 3 exhibits the oxygen flow variation versus carrier position relative to the center of the planar double cathode. The substrate temperature during deposition from planar Zn:Al (0.5 wt%) targets was 300°C, sputter pressure about 0.9 Pa, and operation point was controlled in the transition mode close to metal mode (PEM 40%) [11]. Oxygen flow was actively controlled in order to keep PEM intensity constant within ±1 %. Three different carrier configurations were tested: standard carrier with metal wings which were shielded against heating from the back side by another metal, glass wings without shield, and mixed configuration. The metal wing is typically much cooler than glass due to the shield on the back facing the heater and the high heat capacity and conductivity that cause slow heating and fast spreading of energy impact from sputtering process. The carrier was moved at a constant speed of 0.5 m/min back and forth three times. After pre-sputtering on the right wing, the carrier moved and first, the hot substrate then the left wing approached cathode position. Two main cases are to be distinguished: metal and glass wings. Coming from the relatively cold metal wing (1,
dotted line) to the hot substrate, the temperature of the material in front of the cathode is drastically changed. As known from literature zinc desorbs from hot surfaces due to its low vapor pressure [14]. This means that the zinc deposited on the carrier evaporates from the hot glass leading to higher zinc content in the plasma as compared to the deposition on the cold metal wings that keep nearly all deposited zinc. PEM intensity increases, while the operation point of the target remains initially unchanged. As a result oxygen flow increases to keep PEM intensity constant. This effect is strongly suppressed in case of the glass wings (dashed line, right wing and solid line) since their temperature is quite close to substrate temperature and oxygen flow varies in the range of ±10 %.

Second order effects like energy impact from sputtering process and radiative cooling are also visible in the data. The energy impact during pre-sputtering with symmetric metal wings (dotted line) heats the right wing and thus the described effect for metal wings is less pronounced on the pre-sputtered one. The opposite effect on the glass wings with high oxygen flow when wings are in front of the cathode might be caused by the same reason. The wings are already coated with conductive ZnO:Al on the front, while the substrate is initially uncoated. Heating from the back side is similar for the substrate and the glass wing, but radiative cooling at the front is effectively suppressed by the low-e effect of the TCO. The wings, therefore, exhibit a temperature higher than the substrate. Apart from different materials and temperatures opposite to the cathodes, gas flows through slits or at the border of the carrier cause additional process perturbations. The corresponding range of target voltages taken during the experiments shown in Figure 3 reduced from 600-650 V (metal) via 550-680 V (mixed) to quite narrow voltage range of 550-570 V (glass). In all cases the lower voltage level is found at the center of the carrier position. After deposition the resulting sheet resistance of ZnO:Al in the center of the substrate varied from 4.5 Ω (metal wings) via 3.5 Ω (mixed)
to 2.9 Ω using glass wings. This means, that not only properties of the ZnO:Al coatings differ from one side to the other, but film properties even in the center of the substrate are strongly affected.

We tried to reduce operation point variations further by the adjustment of PEM control during a similar dynamic process as described in the previous section. Here tube targets and glass wings were used. Figure 4 shows fluctuations of discharge voltage and oxygen flow during the dynamic process. The legend indicates the tube target rotation frequency and PEM control speed. In previous studies, we adjusted the PID parameters of the PEM control to react quickly to process fluctuations in order to keep PEM intensity within a range of ±1 % (see Figure 3). These processes exhibit wide-spread discharge voltage and oxygen gas flow mainly due to variations with carrier position (Figure 4, stars and open triangles). The tube rotation speed does not change the spreading, but slightly increases the discharge voltage. If we now allow the PEM intensity to vary within a wider range by reducing the proportional parameter of the PID controller in order not to react on carrier movement, the process variation in terms of oxygen flow and target voltage is strongly suppressed (Figure 4, squares). This proves that PEM control should of course stabilize the process in the transition zone, but must not react on specific fluctuations e.g. by tube target rotation or carrier design.

3.2 ZnO:Al characteristics and solar cells

Examples of properties of ZnO:Al films prepared by dynamic reactive sputtering are given in this section. Figure 5 shows depth profiles of the aluminum content of ZnO:Al films prepared at different operation points. The carrier was equipped with glass wings and PEM parameters were adjusted to fast control leading to process variations as shown in Figure 3. At high PEM intensities (close to metallic mode) part of zinc cannot be oxidized and does not stick to the substrate at 300°C. Aluminum in contrast does not
evaporate at these temperatures thus Al is enriched in the films. According to the
previously described variations of the reactive process the amount of oxygen in the
plasma chamber varies and thus the amount of evaporated zinc varies as well. The
oscillations of the aluminum content in the films correspond to the number of passes in
front of the cathode. Oscillations of the operation point from the tube rotation cannot be
resolved in this measurement. For more oxidic operation points (lower PEM intensity)
the amplitude and level of Al content is reduced as less zinc evaporates at a higher
oxygen partial pressure. Similar variation of aluminum content has been observed by
other groups [15]. For comparison the aluminum level in the target is given as a dashed
line. Aluminum is enriched by up to a factor of 3. This sounds extremely high, but is well
in the range of values reported in literature [11,16].

During the etching step in dilute hydrochloric acid ZnO:Al rough surface structures
develop. These features can provide effective light scattering in thin film silicon solar
cells and modules. Figure 6 shows SEM images of two ZnO:Al films after etching in 0.5
w/w% HCl. The etch time was adjusted to reduce film thickness by about 150 nm. These
films were deposited using a Zn:Al target with 1 w/w% Aluminum. The same plasma
conditions were employed for both films, but the ZnO:Al film on the left slowly passed
the cathode once, while the other passed it four times. The carrier velocity was adjusted
to achieve the same effective deposition times. Electrical properties and thickness were
exactly the same which hints that the films had the same operation point. Upon etching
in diluted HCl both films developed craters of typical shape [3,5]. However, the craters
are more shallow for the left picture (single pass) and additional terraces with vertical
steps are etched into the ZnO:Al. The plateaus at the bottom show a topography similar
to that on the top of the ZnO:Al film. This behavior is explained by the multilayer system
that evolves during dynamic deposition. For similar sputter conditions, very etch
resistant ZnO:Al material was found at racetrack positions in static prints [17]. These etch resistant zones create an etch resistant layer in dynamically deposited ZnO:Al that forms the plateaus at the ground of each moon crater. The other ZnO:Al film (Figure 6, right) was deposited with four times higher carrier velocity, therefore each component layers are much thinner and their properties are blurred. From these results we see, that etching strongly depends on deposition conditions and is difficult to be controlled via sputtering conditions.

From previous work we know, that etching behavior of ZnO:Al is significantly modified by the sputtering process conditions like sputter pressure and substrate temperature [3,5] or the oxygen partial pressure [11,19], and thus the etching is also affected by process instabilities of the working point during dynamic sputtering as discussed in the previous sections. This turns out to be a drawback for adjustments of the ZnO:Al surface structure by the deposition conditions [3-5]. Thus we developed an etching process based on hydrofluoric acid (HF) to modify the surface structure for a given ZnO:Al material by varying the etching conditions instead of tuning the sputtering conditions. We prepared different ZnO:Al films that are known to develop different surface features of different lateral and vertical size upon etching with the standard HCl etch process [5,11]. These surface topographies are shown in Figure 7 (a-c). The SEM pictures (d-f) were taken after etching of the same ZnO:Al material in 1 w/w% HF for 60-120 seconds. Now all surface topographies reveal small etch pits with a similar density and the features are of similar size. Using a second etch step in HCl the small pits are widened and larger craters can be obtained (not shown here). A longer duration of the second etch step leads to larger and less craters [20]. This two-step etch process allows us to tune the surface features in size and shape. ZnO:Al films with excellent and uniform electrical and optical properties were etched with the etch process under various conditions. The
films were co-deposited in a single deposition run in the transition close to the metallic mode at high rates [20]. The standard [3] and optimized two-step etch process [20] are compared in Figure 8. The standard etch reveals only few large craters with only poor light scattering typical of compact ZnO:Al films [3]. The craters on the optimized textured ZnO:Al are regularly distributed over the surface. This uniform distribution of craters is a result of the first HF etch step that creates high crater density and uniform crater distribution. Of course the distribution depends on material properties, but as seen in Figure 7 (d-e) relatively uniform distribution is achieved for all ZnO:Al films. The shaping of craters by the second etch step in HCl is then determined by the already created attack points and can be performed more or less independent on ZnO:Al material properties. These ZnO:Al films were applied as front contact and source for light trapping in silicon thin film solar cells. The two-step etch process boosted the short circuit current density of 1.1µm thick single junction µc-Si solar cells from 19.1 mA/cm² for standard etch to 22.8 mA/cm². a-Si/µc-Si tandem solar cells prepared on the optimized ZnO:Al film achieved the excellent initial efficiency of 11.4 %. This value is in the same range as observed for a high quality low rate reference ZnO:Al etched only in HCl. In this specific experiment the co-deposited reference cell achieved only 11.1 % initial efficiency. The component cells were 320 nm and 1.1 µm thick.

4 Conclusion

We investigated the dynamics of the reactive sputtering process with special focus on rotating tube targets, carrier motion, and process parameters. To avoid perturbation of the sputter process several approaches have to be followed like improved uniformity of target manufacturing, substrate carrier design to avoid temperature variations in front of the cathode, as well as, careful selection of control parameters to stabilize the reactive sputtering process. The carrier design might be of less importance during real in-line
processing with continuous string of carriers rather than an oscillating carrier with wings. However, slits between carriers have to be avoided and carrier material should be carefully selected. Exemplarily, we showed typical ZnO:Al film properties arising from process perturbations. Finally, we investigated the etching behavior and pointed out its sensitivity to the material properties and deposition conditions. To be independent of these deposition conditions, we presented results of a HF based etch process that is able to optimize the etching behavior and the resulting surface topography for a given reactively sputtered ZnO:Al material. Tandem solar cells on optimized ZnO:Al front contacts with excellent light trapping properties achieved 11.4 % initial efficiency.

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References

Figure 1: Sketch of the vertical in-line sputtering system with two load chambers and two process chambers with different cathodes. The cathodes for reactive sputtering are framed by blue dotted lines.

Figure 2: Target rotating speed and PEM intensity during reactive sputtering from tube targets without active control.
Figure 3: Oxygen flow variation as function of position of the substrate carrier during dynamic sputtering from planar targets with different carrier design. The position corresponds to the center of the cathode system relative to the moving substrate carrier.

Figure 4: Discharge voltage versus oxygen flow data taken during dynamic deposition with moving carrier from tube targets. The spread of data represents the process variation. The target rotation speed and PEM control parameters were changed for the different experiments.
Figure 5: Aluminum concentration depth profile of ZnO:Al films deposited at different operation points in dynamic mode using planar targets with two glass wings. Target aluminium level is indicated by the dashed line.

Figure 6: SEM topography images taken after etching. Left ZnO film was prepared by passing one planar double cathode, the right one passed the same cathode 4 times. Carrier velocity was adjusted to a film thickness of about 800 nm in both cases.
Figure 7: SEM topography images taken after etching. The top row was etched in the standard etch process; bottom line was etched with a two-step etching process. The ZnO:Al films correspond to Jülich standard ZnO:Al (a, 40 sec HCl and d, 70 sec HF) [18], other films were prepared by reactive sputtering with moderate (b and e) and low oxygen partial pressure (c and f) [11]. These films were etched in HCl for 22 seconds (b, c) and in HF for 60 seconds (e, f), respectively.

Figure 8: AFM topography images taken after etching of ZnO:Al films. Both films are co-deposited with high rate reactive sputtering process. Left ZnO:Al film was etched in standard way, right with the HF based two-step process.