Critical concentration of Zinc in amorphous silicon solar cells

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Abstract
Transparent conductive oxide (TCO) contacts based on zinc oxide (ZnO) are often used in thin film silicon solar cells and ZnO has a lower contamination potential compared to Tin Oxide or Indium-Tin Oxide. However, in this paper the adverse effects of zinc contamination on solar cell performance in large area systems when using non-optimal processes are demonstrated. Controlled contamination experiments were performed; optical emission spectroscopy allowed us to study the Zn release dynamic; secondary ions mass spectroscopy measurements allowed us to determine the Zn contamination threshold level in a-Si:H solar cells of $10^{18}$ at/cm$^3$. Higher Zn concentrations lead to loss of cell performance in the initial state and increased light induced degradation compared to cells with lower contamination. Additionally, a simple approach for Zn contamination removal is presented.

1. Introduction

Thin-film silicon solar cells based on hydrogenated amorphous silicon (a-Si:H) are usually deposited by Plasma-enhanced chemical vapor deposition (PECVD) on a Transparent Conductive Oxide (TCO) front contact. The most commonly used TCOs are Fluorine-doped Tin Oxide (FTO), and Zinc Oxide (ZnO, either Al-doped or B-doped) due to their the good light scattering properties and transparency [1,2], in some cases Indium-doped Tin Oxide (ITO) may be used too. During cell deposition, especially at the initial stage, the TCO surface is exposed to hydrogen radicals which may reduce the oxides to the metals. Literature indicates that ZnO is more resistant to hydrogen plasma and reduction than FTO or ITO [3–6]. No specific studies on Zn contamination in a-Si:H were found, however Zn contamination has been investigated in crystalline silicon revealing that Zn forms deep acceptor levels and other trap levels [7,8].

Recent literature investigated contamination in a-Si:H, especially the influence of oxygen and nitrogen on solar cell performance. Critical impurities concentrations were determined to be approximately between $2\times10^{19}$ at/cm$^3$ and $10^{20}$ at/cm$^3$ for oxygen and $4\times10^{18}$ at/cm$^3$ for nitrogen [9,10]. These results are similar to earlier studies on light induced degradation indicating a threshold for oxygen and nitrogen impurities of approximately $10^{19}$ at/cm$^3$ [11]. Fluorine contamination was observed to impair performance of solar cells in production systems starting at concentrations between $10^{18}$ at/cm$^3$ and $10^{17}$ at/cm$^3$ [12].

Usually a microcrystalline silicon contact layer is used to achieve a good electrical contact between ZnO and a-Si:H cell [13]. Several attempts were made to implement such a layer in large area systems, however the resulting cell performance was always systematically poorer compared to cells prepared without a microcrystalline silicon contact layer. An alternative contacting method based only on amorphous silicon was found [14,15] to avoid this issue at the cost of lower transparency and consequent power loss. The origin of poor cell performance was eventually found to be Zn contamination. The effects of Zn contamination were then studied more in depth by performing on-purpose contamination leading to the results presented in this publication, additionally from the results of this study further improvement of the ZnO/a-Si:H interface could be made [15].

2. Material and methods

To study the effect of Zn contamination in a-Si:H solar cells experiments were performed by depositing a reference solar cell, then contaminating the deposition system by using a high dilution SiH$_4$/H$_2$ plasma suitable for depositing an μc-Si layer and then depositing several solar cells using the same recipe as the reference cell. Measuring cell performance and Zn concentration in a set of similar experiments allowed to correlate Zn concentration with cell parameters. Large area (Gen5, 1.43 m$^2$) low pressure chemical vapor deposition (LPCVD) and PECVD systems were used to prepare a-Si:
H cells as described elsewhere [16,17]. TCO front contacts had 27% haze at 600 nm and the i-layer thickness was 220 nm. All cells used for experiments use an a-Si:H contact p-layer deposited using a 1:1:0.5 gas flow ratio of SiH₄:H₂:TMG (2% in H₂), 0.022 W/cm² VHF power density at 40 MHz, 0.5 mbar process pressure and 200 °C substrate temperature [16]. The complete cell deposition was performed in one single chamber as in industrial production lines. Both 1 cm² and laminated submodules with 10 series-connected cells and 37.87 cm² active area were used for this study. Each point plotted corresponds to the average of 64 cells or 3 submodules distributed on the glass surface to minimize random scattering effects. A Si wafer piece (single side polished, n-doped, ≈ 1 cm², coated with 40 nm a-Si:H:P) was positioned at the center of each glass substrate before each PECVD cell deposition run and later used as sample for Secondary Ions Mass Spectroscopy (SIMS) measurements. The n-type a-Si:H coating helps to reduce artefacts at the interface between crystalline Si and hydrogenated amorphous Si thus improving the measurement accuracy at the start of deposition.

Flat samples are necessary for SIMS measurements: the ZnO roughness is comparable with the total a-Si:H cell thickness and such a strong roughness would completely destroy the depth information. The comparatively small SIMS sample surface compared to the glass surface leads to deposition conditions very close to the real device under study, however an underestimation of the Zn content at the very beginning of deposition on ZnO cannot be excluded. Conversely, a direct SIMS measurement on TCO-coated glasses would not determine the trace Zn content in a-Si:H at the interface with ZnO due to the roughness and due to the abrupt change in concentration. More information on SIMS calibration and measurement conditions can be found elsewhere [18]. Although the Zn concentration varies at different positions on the glass, the center position was identified to be representative of the whole glass.

Zn contamination was generated deliberately by exposing ZnO-coated glasses to a high dilution microcrystalline silicon (μc-Si) plasma deposition regime \( \text{R} = [\text{H}_2]/[\text{SiH}_4]=250, 0.1 \text{ W/cm}^2, 2 \text{ mbar} \) for 30 s at 200 °C substrate temperature; these glasses were not used for cell depositions but only for contaminating the deposition system. Optical Emission Spectroscopy (OES) of the plasma was performed using an Ocean Optics S2000 spectrometer, full plasma emission spectra in the range between 344 nm and 1000 nm were recorded with a time resolution of 0.1 s and the Zn emission lines at 472.21 nm, \( (3d^{10}4s^25p^3) \text{P}^0, -3d^{10}4s^25s^2 \text{S}^2 \), \( 481.05 \text{ nm} \ (3d^{10}4s^55p^34p^3 \text{P}^3 - 3d^{10}4s^25s^2 \text{S}^2 \ ), \( 636.23 \text{ nm} \ (3d^{10}4s^24p^34p_2 - 3d^{10}4s^25s^2 \text{D}^0 \) [19] were further analyzed.

Fourier-transform photocurrent spectroscopy (FTPS) measurements were done connecting the sample through a current amplifier (Stanford Research SR570) as an external detector to a Thermo-Scientific Nicolet 8700 FTIR spectrometer. To cope with the large dynamic range the spectrum was split into 3 bands, the first band was measured without filter, the second band was measured through a red/blue color filter and the third band was measured through a Si wafer with antireflective coating. The sample spectra were referenced to the lamp spectrum measured with the internal deuterated triglycine sulfate (DTGS) detector. The corrected partial spectra measured with the filters were then scaled to get a single overlapping curve [20].

More information on current–voltage (IV) measurements, external quantum efficiency (EQE) measurements and light induced degradation procedure can be found elsewhere [16,21].

3. Results and discussion

To study the effect of Zn contamination in a-Si:H solar cells experiments were performed exposing ZnO-coated glasses deliberately to contamination using a high dilution SiH₄:H₂ plasma suitable for depositing a μc-Si layer. Reference cells prepared after Zn contamination and without μc-Si layer were affected by a significant reduction of fill factor (FF) from ≈ 73% to ≈ 60% and of open-circuit voltage \( V_{oc} \) from ≈ 880 mV to ≈ 840 mV leading to a reduction of initial conversion efficiency from ≈ 10.4% to ≈ 8.4%. A sequence of nominally identical cells deposited afterwards showed a gradual recovery of performance until the original reference performance was achieved. The evolution of the fill factor after a deliberate Zn contamination in an exemplary sequence of cells is shown in Fig. 1 together with the average i-layer Zn contamination. A systematic measurement of the Zn content by SIMS on several samples during performance recovery allowed to determine the effect of Zn content on cell performance. Fig. 2 shows the conversion efficiency, the FF and the \( V_{oc} \) as a function of the average i-layer Zn concentration determined by SIMS in 15 independent runs. Conversion efficiency, FF and \( V_{oc} \) start to decrease when the Zn concentration is larger than 10¹⁸ at/cm².

Zn contamination SIMS profiles of both the least contaminated and the most contaminated run are shown in Fig. 3 together with the cell parameters of a single representative cell from each run. In the SIMS profiles it was possible to identify three features. First, at a depth of less than 100 nm a n-SiOₓ layer, then in the middle the i-layer and buffer, and finally at depths greater than 250 nm, the p-layer at the start of deposition on ZnO with a Zn concentration peak. Slight thickness differences between both samples were related to coating thickness non-uniformities, therefore the profiles were shifted in depth to obtain an overlap at beginning of the deposition (that is, the p-layer). The SIMS profiles indicate a strong Zn release and incorporation at the beginning of deposition when the ZnO surface is exposed to the plasma. By comparing the SIMS profiles of Carbon and Zn (data not shown), it is possible to determine that the Zn peak is limited to the SiC:H p-layer in regular cells with low contamination (e.g. cells using only an a-Si:H contact layer). However, the peak Zn level in the p-layer does not correlate with performance loss. An almost constant Zn level is then present across the i-layer and the average i-layer contamination correlates with cell performance as shown in Fig. 2. The run to run decrease of Zn contamination in the i-layer of a series of depositions as shown in Fig. 1 suggests that Zn contamination is mediated by internal surfaces of the reactor acting as Zn storage and releasing Zn at a constant rate. The almost constant...

![Graph showing Zn contamination and Fill Factor](image-url)
Zn level in lowly contaminated i-layers highlights that a-Si:H contact layers allow to avoid Zn contamination. At the end of deposition, the n-SiOx layer incorporates again more Zn probably due to the presence of carbon from CO2 used as an oxygen source. The effect of Carbon on Zn incorporation is discussed later, separate experiments (data not shown) with water vapor ruled out an effect of oxygen on Zn incorporation.

For better understanding of the effect of Zn contamination the external quantum efficiency (EQE) of the representative cells mentioned in Fig. 3 were measured. EQE measurements were performed both at a reverse voltage of −1 V and near to the operating point at 0.7 V; results are shown in Fig. 4 together with the corresponding IV curves. In the inset the corresponding IV curves, IV results are reported in Fig. 2.

In the case of strong Zn contamination the EQE at the operating point clearly shows a large loss of charge collection efficiency across the whole spectrum compared to the reference cell. However, at −1 V the contaminated cell shows a slightly higher EQE in the short wavelengths below 500 nm leading to a 0.1 mA/cm² higher short-circuit current. This effect was not further studied but a slight reduction of the p-layer deposition rate leading to a thinner p-layer than in the reference cells was suspected.

Further study of the effect of Zn contamination was performed by FTPS measurement of cells with three contamination levels: highest, intermediate and lowest. The absorption curves measured are shown in Fig. 5 and the Urbach energy extracted from the absorption curves is shown in the inset. The Urbach energy, which reflects the degree of order in the film, correlates linearly with the
logarithm of Zn-contamination level. From the experimental points it was determined that an order of magnitude Zn contamination increase leads to an increase of the Urbach energy by 8.7 meV. Therefore the presence of Zn in the film is directly correlated with an increase of the structural disorder. Given the Zn atom size (atomic number 30 in comparison to 14 for Si) the result is not surprising. Distortion in the Si lattice is very likely inducing an additional number of Si dangling bonds and increases the instability of electronic properties (e.g. reducing free hole lifetime through recombination) to illumination with direct implications to the performance of solar cells. Additionally, the acceptor character of Zn in silicon enhances the detrimental effect of Zn in a-Si:H and explains the poor EQE signal near operating conditions shown in Fig. 4. This supposition is supported by the absorption curves in Fig. 5 indicating that contaminated samples have a higher absorption mainly around 1.4 eV compared to the least contaminated sample. If the bandgap energy of intrinsic a-Si:H of 1.70 eV is considered together with the well-known fact that the absorption tail originates from transitions from valence band tail to the conduction band, it can be concluded that the additional absorption for the contaminated sample is due to the absorption on an acceptor level located about 0.30 eV above the valence band mobility edge. This acceptor-level energy corresponds well with the levels reported by Stolz et al. on a Zn double acceptor level located at 0.252 eV (Zn\(^{0/-}\)) or 0.317 eV when the Poole–Frenkel effect is considered [7].

To fully assess the effect of Zn contamination to a-Si:H solar cells an additional series of laminated submodules with varying Zn contamination was prepared and exposed to light soaking to study the performance degradation induced by light exposure. The relative conversion efficiency degradation after 1000 h of light soaking at 1 sun is shown in Fig. 6. With increasing Zn contamination above \(10^{18}\) at/cm\(^2\) light induced degradation increases from approximately 20% for reference cells to more than 24% driven by higher short circuit current degradation and higher fill factor degradation. It can be speculated that in the case of higher Zn contamination, the more disordered material promotes the recombination which takes place also through dangling bonds will increase too. This second recombination mechanism is enhanced due to both an increased number of trapped holes in the band tail and a reduction in the average difference in energies between these trapped holes and the dangling bonds energy levels in the middle of the gap. Hence during light soaking more and more trapped holes in the band tail recombine and because of this the trapping rate of free holes from valence band to localized states in the valence band tail increases. This has a direct consequence on the concentration of free holes in the valence band and thus on photocurrent, which is diminished. The FF degradation could be explained either simply by the enhanced dangling bonds assisted band-to-band recombination, or by the photocurrent degradation at the maximum power point (MPP) through the same mechanism described above enhanced due to a weaker electric field at MPP. Therefore Zn contamination leads to a loss of initial performance and to an increase of light induced degradation.

It has been reported that Zn acceptor states in crystalline silicon may be passivated by hydrogen [7] similarly a passivation effect can be expected in a-Si:H too and possibly the passivation is impaired by light soaking. A more fundamental understanding of Zn contamination is however beyond the scope of this study.

To better understand the mechanism of Zn contamination time resolved OES measurements were performed during the first few seconds after igniting the plasma process used for producing Zn contamination. In the inset of Fig. 7 the OES spectrum 1 s after plasma ignition on a ZnO coated substrate at 200 °C is compared with an OES measurement at equal conditions but in an empty deposition chamber: three Zn emission lines at 472 nm, 481 nm, and 636 nm are clearly visible beside the background SiH\(_4\)-H\(_2\) emission spectrum. Further analysis will be focused on the line at 481 nm, although similar results were observed on the weaker lines too.

A typical time evolution of the OES Zn signal at 481 nm on a glass coated with ZnO and heated to 200 °C is shown in Fig. 7. Within less than 10 s the emission peak disappeared and the Zn emission signal approached the detection limit of our equipment. Based on additional experiments, it was determined that the ZnO surface was not yet covered with Si when the Zn signal disappeared from the OES spectrum. It was concluded that only a comparatively small amount of Zn was released from the ZnO surface upon exposure to a reducing plasma suggesting a self-limiting mechanism.

OES measurements allow a direct and quick comparison of different deposition processes assuming a negligible contribution from the background contamination. As an example of its
application, the emission at the standard substrate temperature of 200 °C and at a reduced substrate temperature of 30 °C are shown; operating at a lower substrate temperature reduced the emission peak intensity to about one half although the same PECVD process was used. Similar results were obtained by reducing the applied RF power by a factor 4 (data not shown).

The OES peak intensity was correlated with the p-layer Zn concentration peak measured by SIMS (data not shown). However, a full quantitative scaling OES vs SIMS was not possible for two reasons: (a) limited intensity-sensitivity of the spectrometer; (b) intrinsic limitation of the OES as a tool for quantitative measurements in the absence of a rate equations model [22]. Nevertheless OES was proven to be both a valuable tool for monitoring the contamination state of the PECVD reactor and a useful method for understanding the mechanisms of Zn contamination.

Combining SIMS and OES measurements, the Zn profile can be explained as a combination of Zn release upon the ignition of a hydrogen-rich plasma on ZnO and Zn release from internal surfaces of the deposition chamber not coated with silicon. A hydrogen-rich plasma will probably reduce a small amount of ZnO to metallic Zn which can then sublime and glow in the plasma as shown by OES. Possible formation of metallic Zn on ZnO surfaces was mentioned in the past [4] although it was not directly observed. A reduction process induced by hydrogen plasma has been documented for ITO and FTO leading to the formation of a metallic Sn or In layer on the TCO surface [4–6], similarly incorporation of Sn and In in a-Si:H was also observed [3].

It is further speculated that a fraction of the metallic Zn is sublimated. A part of the sublimated Zn is directly incorporated into the p-layer and a part is stored on internal surfaces slightly colder than the substrate. During the i-layer deposition in the same chamber a continuous amount of Zn is sublimating from the storage locations and becomes incorporated in the layer. The almost constant Zn level across the i-layer indicates a slow depletion compared to the amount of available Zn. Working at a lower substrate temperature of 30 °C would reduce the vapor pressure and less Zn would be present in the plasma explaining the observed lower Zn peak in OES compared with 200 °C.

Considering the major effect of Zn contamination on a-Si:H cell performance it is important to develop a method for controlling accidental Zn contamination due to improper processing. To this purpose a simple approach is presented based on the deposition of Carbon-rich layers alternation with intrinsic a-Si:H layers. An example of the Zn concentration in such a layer stack is shown in Fig. 8. Layers containing carbon are able to release a larger amount of Zn from the deposition system than intrinsic layers and the peak Zn concentration is quickly reduced. Enhanced Zn incorporation when using Carbon-rich gas mixtures may be related to the formation of volatile organometallic compounds as discussed in the context of ZnO etching [23]. Depositing a series of similar stacks on bare glass allows to quickly restore the cell performance after an accidental reactor contamination.

Contamination of i-layers can be completely avoided by depositing the p-layer and the i-layer in separate deposition chambers: additional results not shown indicated that Zn contamination in the p-layer does not correlate with cell performance. In general, considering that Zn contamination is not widely discussed in a-Si:H literature, the issue is probably more pronounced in large area single chamber deposition systems than in research systems. Assuming that Zn cross contamination is mediated by the internal reactor surfaces, a system having a comparable size of substrate (e.g. ZnO) and deposition chamber like an industrial systems would be more sensitive to Zn contamination than a research system were usually small substrates are coated in a much larger deposition chamber.

4. Conclusions

In conclusion, it was shown that Zn contamination is a critical aspect to be considered for large area thin film silicon production. Zn contamination above 10^{10} at/cm^3 caused a loss of initial FF and Voc, additionally light-induced degradation was increased. FTPS measurements indicate that Zn contamination increases the Urbach energy and introduces additional absorption possibly related to a Zn acceptor level. Solar cells deposited on ZnO may be affected by Zn contamination and therefore a hidden efficiency potential may lie in carefully controlling Zn contamination. Future industrial production systems should be designed to avoid this topic altogether, possibly by adopting a multi-chamber approach. Alternatively strategies to reduce Zn release at the beginning of deposition should be developed. Possible approaches include optimization of the surface temperature and optimization of the applied RF power for the first few seconds of depositions. To this purpose, OES is a promising technique for quickly studying Zn release by different processes under consideration.

Bibliography

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Acknowledgments

Support by the pilotline team in Trübbach, and proofreading by Heather Booth are gratefully acknowledged. Sukanta Biswas, Steve Smith and the team at EAG Group supported us with useful discussion on SIMS measurements.
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