

CHANGES IN PASSIVATION QUALITY OF PECVD-DEPOSITED HYDROGENATED AMORPHOUS SILICON LAYERS USED IN SOLAR CELLS DUE TO SPUTTER DEPOSITION OF TCOs

Daniel Skorka, Nils Brinkmann, Angelika Gorgulla, Giso Hahn, Barbara Terheiden
University of Konstanz, Department of Physics, 78457 Konstanz, Germany

ABSTRACT: The decrease in passivation quality of films of a-Si:H manufactured using plasma-enhanced chemical vapor deposition (PECVD) after exposure to a sputtering process for deposition of a transparent conducting oxide (TCO), which is inevitable for the production of front heterojunction solar cells, is investigated. This so-called sputtering damage is determined in terms of minority carrier lifetimes. We show that sputtering typically causes a decrease of effective carrier lifetimes by a factor of five and that almost complete recovery is possible by short low temperature annealing. The magnitude of this decrease shows no dependence on pressure during sputtering or power applied to the sputtering plasma. However, a strong dependence on a-Si:H film thickness is observed, with thinner films showing a much higher decrease of effective lifetimes. Modeling of lifetimes using the Olibet model is performed. We conclude that a Staebler-Wronski-like defect formation caused by photons in the deep UV range or bombardment by high energy electrons is responsible for the sputter damage.

Keywords: a-Si:H, Heterojunction, TCO Transparent Conducting Oxides, Passivation

1 INTRODUCTION

The heterojunction solar cell concept, which employs stacked films composed of an intrinsic hydrogenated amorphous silicon (a-Si:H) passivation and a doped a-Si:H emitter layer featuring front side contacts by transparent conducting oxides (TCOs) has already proven its high efficiency potential (24.7%) [1]. In order to reach the highest possible solar cell efficiencies, one of the most important factors is a strong reduction of charge carrier recombination at the wafer surface [2]. Recombination directly lowers open circuit voltages and therefore solar cell efficiency. As the silicon wafers used for producing solar cells become thinner, the influence of the surface in relation to the bulk volume increases. Thin films of hydrogenated amorphous silicon, typically deposited by PECVD, have long been shown to be an excellent choice in solving this problem [3].

However, the very poor conductivity of an a-Si:H emitter requires the use of full area contacts to avoid strong serial resistance losses. In the case of front side contacts, as is the case for standard heterojunction solar cells, these need to be both transparent and highly conductive. Therefore, TCOs are employed, with aluminum doped zinc oxide (ZnO:Al) being one possibility. Formation of TCOs is usually carried out by sputtering, a low temperature process in which highly energetic ions eject mainly neutral material from a target which then deposits on the substrate. However, besides the desired target material, ions from the sputtering gas, electrons and radiation are also incident on the substrate. The passivation quality of a-Si:H films decreases strongly when subjected to such an environment.

In this work, we aim to establish a correlation between the various parameters controlling the sputtering process, and the sputtering damage associated with them.

2 EXPERIMENTAL PROCEDURE

We used RCA [4] cleaned crystalline floatzone silicon wafers with a resistivity of 2 Ω cm, boron p-type doping and a thickness of 250 μ m. a-Si:H films were deposited on both sides of the wafer using a commercial PECVD reactor (Plasmalab100, Oxford Instruments).

The nominal film thicknesses of the deposited a-Si:H films were 15 nm, 25 nm and 35 nm, respectively. Samples were subsequently annealed for 2 min at 200°C on a hot plate in ambient air in order to activate the passivation layer.

The samples were then sputter coated with ZnO:Al layers on both sides in an AJA Orion system (using RF magnetron sputtering) under different conditions at room temperature. Parameters varied were deposition pressure and plasma power. Deposition time was kept constant. After coating, the zinc oxide layers were removed by diluted hydrochloric acid (approx 0.5% by vol.). Finally, all samples were annealed at 300°C in incremental steps until maximum recovered lifetime was measured.

Further samples were processed the same way, but were covered with 1mm thick slides of quartz glass (transparency > 60% at a wavelength of 180 nm) during sputtering such that no particles could reach the sample surface during sputtering. The reasoning behind this was to specifically test for the effects of UV radiation.

Finally, additional samples were processed the same way, but omitting the sputtering step. This was done to measure the influence of etching with diluted hydrochloric acid on minority carrier lifetimes.

Lifetimes were measured by transient photo conductance (tPC, [6]) using a Sinton WCT-120. Measurements were carried out on all samples after deposition, after first annealing, after etching and after each incremental anneal step.

Curves of excess carrier density versus incident light intensity were fitted using the Olibet model [6] in order to determine the defect densities N_s and fixed charge densities Q_s at the interface.

Four samples were processed for each sputter process, and the lifetime values were averaged.

3 RESULTS AND DISCUSSION

Investigation of the influence of etching with diluted hydrochloric acid shows no significant detrimental effect, effective lifetime before and after etching were 2.1 ms and 1.9 ms, respectively.

All samples used in this investigation showed lifetimes of less than 0.9 ms directly after PECVD of

a-Si:H. After a first annealing step (2 min @ 200°C) samples reached lifetime values of about 2 ms. The respective value for each sample after first annealing will hereafter be called the reference lifetime. After sputtering and etching, lifetimes drop to less than 0.6 ms for all samples. During subsequent annealing steps (up to 2 min), lifetime rises sharply to a maximum and decreases slowly due to the outdiffusion of hydrogen during prolonged annealing. This maximum lifetime will be called the recovered lifetime. For most samples this recovered lifetime reaches at least 90% of the reference value. Fig. 1 shows the typical behavior of τ_{eff} , N_s and Q_s during the course of these processing steps. The lifetime drops sharply from the reference value of 2.0 ms to 0.4 ms after sputtering and etching, and finally recovers to a value of 1.8 ms. Interface defect density N_s rises from $2.3 \cdot 10^8 \text{ cm}^{-2}$ to $1.5 \cdot 10^9 \text{ cm}^{-2}$ and decreases down to $1.9 \cdot 10^8 \text{ cm}^{-2}$.

3.1 Influence of sputter parameters

Samples were coated at different pressures and with different values for plasma power, see Table I.

For each sputter recipe, four samples were processed, with the graphs showing averages of the four samples and standard deviations as error bars. In addition, both τ_{eff} and N_s are plotted relative to their reference value after first annealing.

It is found that the decrease in lifetime is independent of sputter pressure, with all samples showing very similar behavior, as can be seen in Fig. 2: The mean values at each step for each pressure lie within less than one standard deviation from each other. In all cases, τ_{eff} drops to 0.2 times the reference value after sputtering and recovers to about 90% of the reference value after second annealing. N_s rises to 7 times the starting value after sputtering, but finally settles on slightly less than the reference value. Not plotted is Q_s , which remains almost constant between steps (compare Fig. 1).

Table I: Parameters used in five different recipes for sputtering Al-doped zinc oxide films. All other parameters, e.g. oxygen flow and coating time are kept constant for all samples.

	R1	R2	R3	R4	R5
Pressure (mTorr)	1.5	2.5	3.5	2.5	2.5
Power (Watt)	550	550	550	350	750

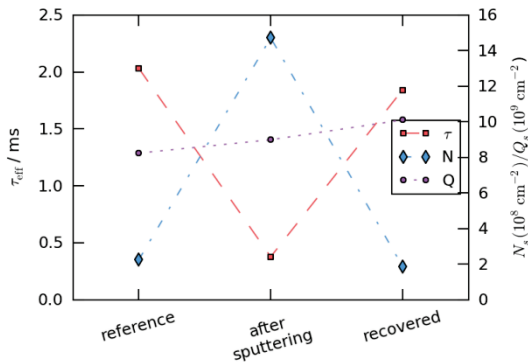


Figure 1: Typical evolution of τ_{eff} , N_s and Q_s for a sample during processing. Sample shown had a 25 nm (nominal) film of a-Si:H and was subjected to Recipe R2.

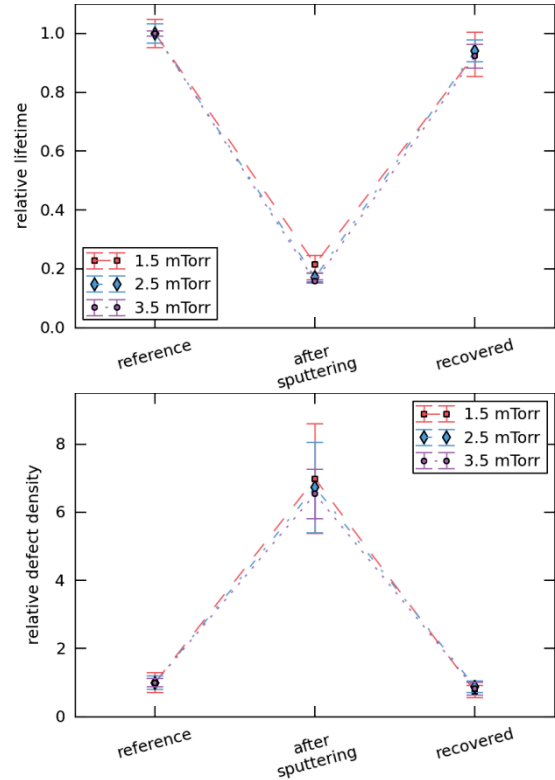


Figure 2: Evolution of measured lifetime (top) and fitted interface defect densities (bottom) for three different sputtering pressures, with every plotted point representing the average value and standard deviation of four samples.

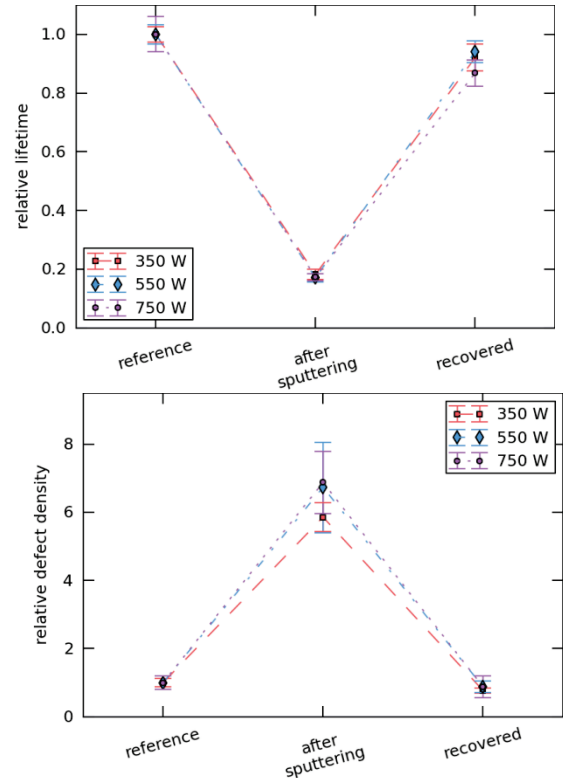


Figure 3: Evolution of measured lifetimes (top) and fitted defect densities (bottom) for three different sputtering powers, with every plotted point representing the average value and standard deviation of four samples.

Similarly, no dependence was found for variations in power coupled into the plasma, see Fig. 3. Again, lifetime and N_s are clearly correlated and show a very similar behavior compared to Fig. 2. While the Olibet model allows for the density of fixed charges in the heterointerface to vary, such variation was not found for any of the samples. Instead, Q_s shows only small changes, with a mean across all samples of $9 \cdot 10^9 \text{ cm}^{-2}$.

All samples used for this part of the investigation have a nominal a-Si:H thickness of 25 nm.

3.2 Influence of a-Si:H thickness

In order to investigate the influence of a-Si:H thickness, samples with nominal 15 nm (resp. 35 nm) film thickness were deposited and processed the same way. Sputtering conditions used were a pressure of 2.5 mTorr and power of 550 W (i.e. combination R2 from Tab. 1).

The thickness of the a-Si:H film is found to have a strong impact on the behavior of lifetime and thus on interface defect density, see Fig. 4.

Here, the lifetime after sputtering of the 15 nm layer drops to 9% of the reference value, in contrast to 17% for 25 nm and 28% for 35 nm. Almost complete recovery of lifetimes to the value reached before sputtering can again be seen.

Defect densities again correlate well with lifetime. Specifically, for the thinnest layer N_s rises to 11.6 times the starting value after sputtering and drops slightly below that on recovery.

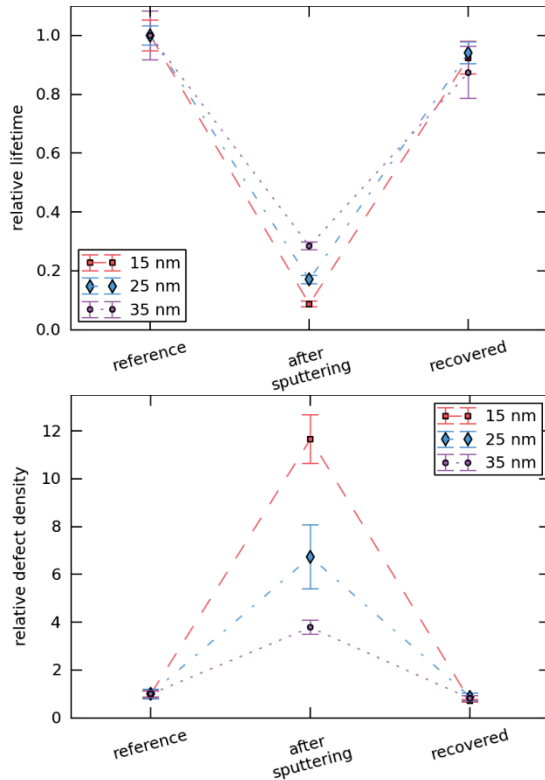


Figure 4: Evolution of measured lifetime (top) and fitted interface defect densities (bottom) for three different a-Si:H layer thicknesses, with every plotted point representing the average value and standard deviation of four samples.

For 25 nm, a rise to 6.7 times the reference value is found, and for 35 nm, defect density after sputtering increases to just 3.8 times the initial value. Again, Q_s stays almost constant, with a mean of $8 \cdot 10^{19} \text{ cm}^{-2}$.

3.3 Influence of UV radiation

To test specifically for the effects of UV radiation, four samples with nominal 25 nm a-Si:H film thickness were deposited and processed as the other samples. However, during sputtering (using recipe R2) the samples were covered with a 1 mm thick slide of quartz glass having a transparency of $>60\%$ at 180 nm (6.9 eV). The glass did not contact the samples, but was placed a few millimetres above them. In this way, any highly energetic particles were prevented from impacting on the surface, while still allowing UV radiation (with the exception of very deep UV) to impinge on the a-Si:H film.

The samples show a drop in effective lifetimes to about 0.75 times the reference value after sputtering, and almost complete recovery (to 90% of reference) on annealing, see Fig. 5. This drop is much smaller than for any of the other samples. Defect densities show very small changes compared to the large changes seen in uncovered samples (compare Fig. 5 to Fig. 1-4). The density of fixed charges Q_s also shows very little change, with no clear trend, as is the case for all other samples. It is thus found that photons with energies of less than 6.9 eV cause very little, if any, sputtering damage.

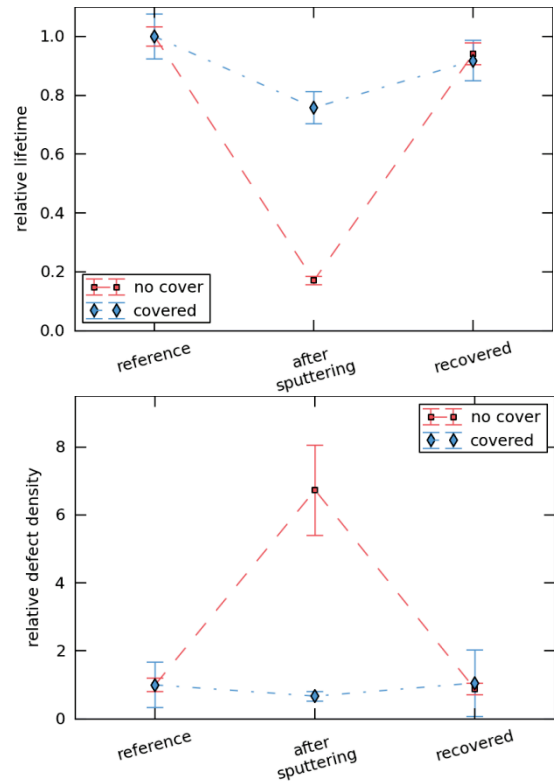


Figure 5: Evolution of measured lifetime (top) and fitted interface defect densities (bottom) for samples without and with covering by a quartz glass slide, with every plotted point representing the average value and standard deviation of four samples.

3.4 Origin of sputtering damage

As damage clearly depends on layer thickness, the effect is most likely caused by bombardment of the exposed a-Si:H surface that penetrates to the interface

between the amorphous and crystalline layers. Incident on the samples are ions, neutral particles, electrons and radiation. Fast neutral particles, created by sputtering or from ions by charge exchange, have energies of less than 30 eV [7]. Ions incident on the substrate surface have similar energies [8]. These energies are not high enough to facilitate penetration. In addition, reference [8] shows that ion energy depends on pressure, whereas ion flux density depends on plasma power. Therefore, variations in either should affect the sputter damage if ions are responsible. We therefore conclude that ions and neutral particles are not responsible for the occurrence of sputtering damage.

In contrast, electrons can reach the substrate after ejection from the target, where they are accelerated by the self-bias voltage, which was on the order of 100 V in this investigation. This energy is high enough to easily penetrate the a-Si:H layer and thus to cause damage at the a-Si:H/c-Si interface. Highly energetic radiation emitted from the plasma could also penetrate this far and could cause a Staebler-Wronski-like defect-formation at the heterointerface [9]. However, this radiation has to be deep UV or X-rays, with energies greater than 6.9 eV, as show in section 3.3.

Our findings are corroborated by B. Demareux et al., who obtained very similar results with respect to the sputter deposition of ITO [10].

We therefore conclude that the decrease of minority carrier lifetime during the sputtering process can be attributed to defect formation at the heterointerface and is most likely caused by highly energetic electrons and/or photons.

4 CONCLUSION

The influence of different sputter parameters and a-Si:H film thicknesses on minority carrier lifetime and interface defect density on surface passivation quality were studied. Within the investigated range, sputtering damage was found to be independent of sputtering parameters except for film thickness, where a clear relationship between thickness and damage was found: Thinner layers are damaged more severely than thicker layers, but recovery is possible independent of thickness.

We conclude that the sputter damage is likely due to electron and/or highly energetic photon induced formation of defects at the a-Si:H/c-Si interface.

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