INVESTIGATION OF THE MINORITY CARRIER LIFETIME REDUCTION DURING INDUSTRIAL DC-SPUTTERING OF METAL SEED LAYERS

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ABSTRACT: This works presents the first results of the investigation of the minority carrier lifetime reduction during industrial sputtering of metal seed layers for front side metallization of crystalline silicon solar cells with respect to the cathode performance and the exposure time. Furthermore a method to avoid the reduction of the effective lifetime during sputtering is demonstrated as well as the determination of the ion energy input with the retarding field analysis. All investigations were done by using a new pilot system for inline sputtering. Because of the deposition from below different concepts for substrate holders were used to minimize shadowing effects. Compared to previous investigations a possibility to avoid the lifetime reduction was determined. This underlines the possibility of sputtering for front side metallization.

1 INTRODUCTION

One possibility to achieve higher cell efficiencies is to transfer high efficiency cell concepts into industrial production. One of the key technologies for the metallization of these cell concepts features Physical Vapor Deposition (PVD) technologies instead of the standard screen printing of metal pastes for establishing either the complete metallization or a seed layer for subsequent electroplating. The PVD technology for the front side metallization of crystalline silicon solar cells is promising some advantages, like less shadowing and lower contact resistance, compared to screen printing techniques. Within a new pilot system from Applied Materials it is possible to sputter various metal layers with a high throughput. One possible negative effect of using the new inline sputtering technology for the front side metallization is a damage of the interface between the emitter and the passivation layer during the sputter deposition. Such degradation is known to be due to short wavelength radiation [1], [2].

2 PILOT SYSTEM SETUP

All experiments were performed using a new inline pilot system from Applied Materials. Two rotatable targets (Figure 1) of different materials in one process chamber allow sputtering two-layer systems of metal layers [3]. The system deposits metal layers in an inline system with high throughput and homogeneity.

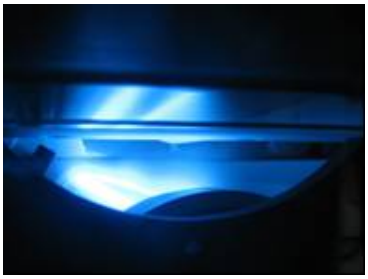

Figure 1: Picture of one target under process conditions**.**

To eliminate shading problems from detached metal chips, the deposition is from below. Shading effects and wrap-around of the substrates are avoided by optimized substrate holders.

3 INVESTIGATION OF THE MINORITY CARRIER LIFETIME REDUCTION

The investigation of the possible minority carrier lifetime reduction was separated in three different parts. The approach was to find out if there is any dependency of the used cathode performance, the exposure time of the substrates and the behavior when covering the surface with hot melt resist and photo resist. All experiments were performed with shiny etched p-type float zone silicon wafers ($\rho_{Si,Bulk}$ = 1 Ωcm, thickness t = 250 µm, area 125×125 mm²). The process flow is shown in Figure 2.

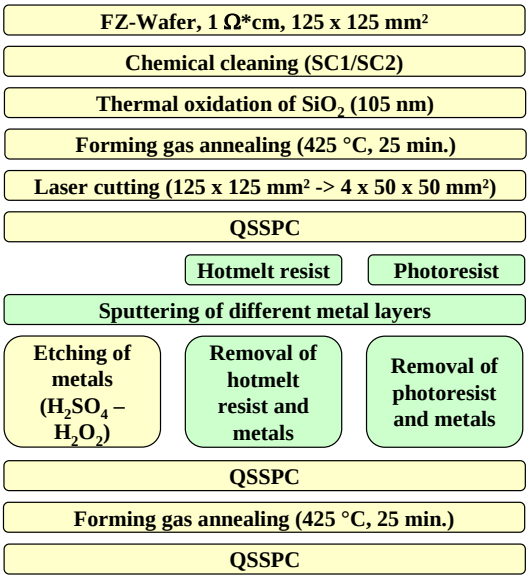

Figure 2: Process flow for investigation of lifetime reduction**.**

The initial lifetime is measured after the thermal oxidation of SiO_2 (thickness d = 105 nm) and the forming gas annealing step (at 425 °C for 25 min) by using the quasi-steady-state photoconductance (QSSPC) method [4]. A second lifetime measurement is performed after sputter deposition of titanium (directly on the passivation layer and on the hotmelt and photo resist) on both sides of the sample and a subsequent wet chemical removal of the metal layers respectively the removal of the resist and metal residues. The final lifetime measurement is done after the postannealing step under forming gas atmosphere (for 25 min at 425 °C).

3.1 Variation of the cathode performance

In the first part of the experiment different cathode performances (process I, II and III) of sputtered titanium layers were investigated. The pressure and the tray velocity were kept constant for all variations of the cathode performance. For every variation four samples of shiny etched float zone material were used. The results of the effective lifetime are shown in Figure 3.

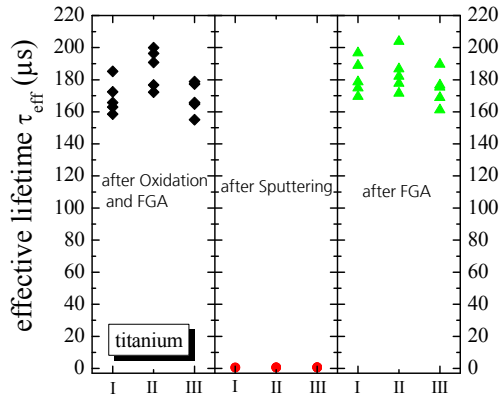

Figure 3: Results for different cathode performances (process I, II and III)**.**

It could be observed that for all cathode performances the lifetime dropped to very low values of approximately $\tau_{eff} = 1.5$ µs after the metal deposition and subsequent wet chemical removal of the metal layer. After the postannealing process in forming gas atmosphere (T =425 °C, t = 25 min) the minority carrier lifetime recovered again. Compared to the initial lifetime of process I, II and III the final value of the minority carrier lifetime seems to be the same. This leads to the conclusion that the damage of the interface is independently of the cathode performance and that the lifetime reduction (due to the sputtering) can be balanced with a subsequent annealing step.

3.2 Exposure time

To investigate a possible dependency of the process time, two different titanium layers ($t_1 = 30$ nm and $t_2 = 50$ nm) were deposited by using a constant cathode performance (process III and IV).

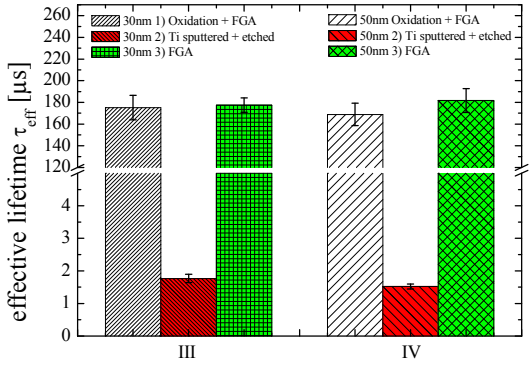

Figure 4: Results of the effective lifetime for different exposure times (process III and IV).

The results are shown in Figure 4. After the metal deposition, the effective lifetime drops for t_1 and t_2 to very low values of $\tau_{eff\,t1} = 1.75$ µs and $\tau_{eff\,t2} = 1.52$ µs, but recovered again with a post annealing process. The final minority carrier lifetime was determined to $\tau_{eff\,t1\_final} = (174 \pm 10)$ µs for a 30 nm thick titanium layer and $\tau_{eff\,t2\_final} = (181.7 \pm 11)$ µs for a 50 nm layer of sputtered titanium.

3.1 Using hotmelt and photo resist

The sputtering technology for front side metallization requires structuring methods to create the grid pattern. This means that for the wafer processing more than 90 % of the wafer will be covered by structuring resists. Therefore an investigation of the behavior during sputtering with hotmelt and photo resists was done. For every run five shiny etched float zone wafers with a thermally grown SiO_2 were covered on both sides with hotmelt resist and respectively with photo resist. Simultaneously samples without any resist were processed as a reference.

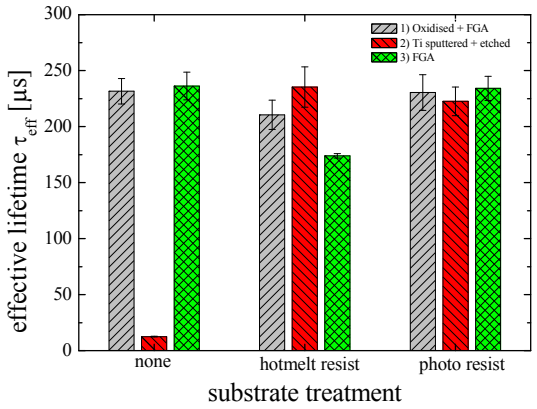

Figure 5: Results for covered samples**.**

In Figure 5 the results are shown. The determined effective lifetime τ_{eff} of the reference samples without any resist dropped after sputtering to $\tau_{eff} = 12$ µs and reached the initial value after a post annealing step ($\tau_{eff\_final} = [236 \pm 12]$ µs) again. For the samples covered with a hotmelt and a photo resist no reduction of the minority carrier lifetime was observed. The effective lifetime of hotmelt resist covered substrates remain constant or were even slightly increased ($\tau_{eff\_HR} = [235 \pm 18]$ µs). The effective lifetime after the annealing at the end of the process leads to a reduction again ($\tau_{eff\_final\_HR} = [173 \pm 2]$ µs), this corresponds to a relative change of $\Delta\tau_{eff\_HR} = 26$ % and could not be explained until now. The minority carrier lifetime of the substrates covered with photo resist remained constant after sputtering ($\tau_{eff\_PR} = [222 \pm 13]$ µs) and after FGA ($\tau_{eff\_final\_PR} = [234 \pm 11]$ µs). Although it was expected that the different resists are not able to absorb soft x-ray radiation, the minority carrier lifetime reduction could completely avoided.

4 RETARDING FIELD ANALYSIS (RFA)

To get a better understanding of the minority carrier lifetime reduction during sputtering, the impact of the

energy caused from ions from the sputter gas was determined by using the retarding field analysis.

4.1 Measurement setup

In a system (Figure 6) of two gratings (plasma and extraction grating) particles are extracted from the plasma [5]. The ion energy distribution can determined, if the extraction grating g2 has a negative potential compared to the plasma grating (respectively a positive potential for measuring the electron energy distribution).

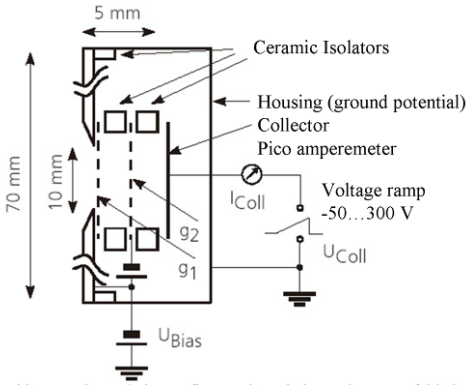

Figure 6: Schematic of the retarding field analyser [6]**.**

The plasma grating g1 with a grating constant of a = 32 µm and an optical transmission of T = 30 % is situated directly behind the faceplate with a diameter of D =10 mm. The front bezel and grating g1 can be operated floating or on a fixed potential. Independently of the internal wiring of the sensor it is proposed that g1 keeps an equipotential surface compared to the plasma. This is fulfilled as long as the grating constant a is small compared to the debye length λ_D [7] :

$$\lambda_D = \sqrt{\frac{\varepsilon_0 \, kT_e}{n_e e^2}} \qquad \text{(Eq. 1)}$$

In which T_e is the temperature of the electrons and n_e the electron density. For typical magnetron discharges (with $kT_e \approx 3$ eV and $n_e \approx 1{*}10^{-10}$ cm^{-3}), the debye length is approximately $\lambda_D \approx 130$ µm [8], so that the constraints with the used grating constant of a = 32 µm are fulfilled. Grating g2 (same construction as g1) is for the separation of the ions. To avoid that electrons reach the collector, g2 has a negative potential compared to the faceplate. Positive ions are accelerated due to the negative voltage at grating g1 and neutralized according to the optical transmission of g1. The remaining ions are slowed down by the positively biased collector, only the ions with sufficient kinetic energy reach the collector and thus contribute to the collector current I_{Coll}. By increasing the collector voltage U_{Coll} the ion current decreases, so that in the ideal case for high collector voltages the ion current will be zero.

4.2 Results

To determine the impact of impinging ions on the substrate a variation of the process pressure and the cathode performance was done. With the already described measurement principle the current density of the ions j_{ion} was measured [6]:

$$j_{ion}(E_{\min}) = e \int_{E_{\min}}^{\infty} n(E)\, v(E)\, dE \qquad \text{(Eq. 2)}$$

In which e is the elementary charge, n(E) is the ion density and v(E) the velocity.

In Figure 7 the results of the ion density are shown. The curves for a different pressure are shifted in y-direction for a better illustration.

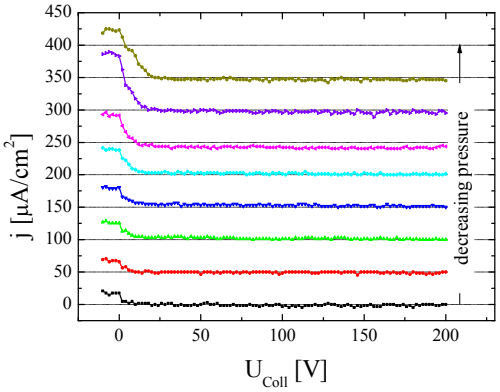

Figure 7: Results of the measurement for different pressure**.**

With the results from the measurement of the ion current density the ion energy distribution function was determined by the derivation of Eq. 2:

$$n(E) = -\frac{1}{e\, v(E)} \frac{dj_{Ion}}{dE} \qquad \text{(Eq. 3)}$$

Assuming that the ion energy is completely transferred into the crystal (simplified model) the energy input is calculated from:

$$(P/A) = \int_{E=0}^{\infty} \frac{dj_{Ion}}{dE} E \, dE \qquad \text{(Eq. 4)}$$

The process pressure was controlled by changing the flow rate of the argon. The cathode performance was kept constant at P = 5 kW for all different set points. The results of the ion energy input in dependency of the pressure are shown in Figure 8.

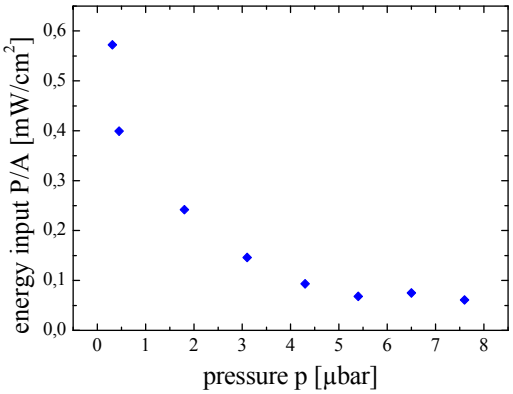

Figure 8**:** Results of the measurement for different pressure**.**

For low pressures the energy input P/A is highest. At p = 0.31 µbar the energy input was determined to

P/A = 0.57 mW/cm² and declined to P/A = 0.06 mW/cm² at p = 7.6 µbar at the highest investigated pressure. Compared to the results it seems to be that the energy input P/A is reciprocally proportional to the process pressure during sputtering. In the second part of the investigation the influence of different cathode performances was determined. At a constant pressure of approximately p = 0.45 µbar the power was increased from P_{min} = 3 kW to P_{max} = 20 kW.

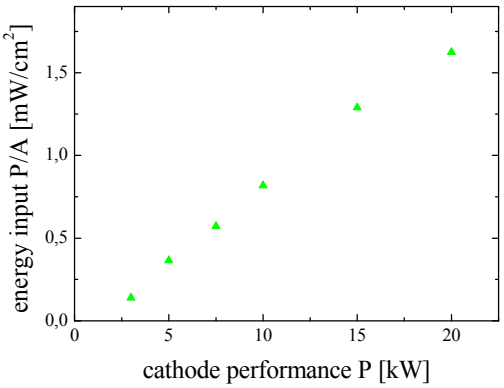

Figure 9: Results of the measurement for different cathode performances**.**

In Figure 9 it is visible that the energy input P/A is linear correlated to a changing cathode performance P in the investigated range. Compared to the results of the changing process pressure it seems to be that a changing cathode performance has a higher influence to the ion energy input ($P/A_{max\_\Delta P}$ = 1.62 mW/cm²).

5 CONCLUSION

The major objective of this work was to investigate the reduction of the minority carrier lifetime during sputtering of metal layers for front side metallization. Several different process conditions were investigated, to determine process dependent differences for the damage of the interface of silicon solar cells. The results for different cathode performances had shown that the effective lifetime decreases after sputtering to very low values of approximately τ_{eff} = 1.5 µs, but recovered again with a postannealing process in forming gas atmosphere to the initial values. Different exposure times (at a constant cathode performance) were investigated too and lead to the conclusion that no difference of the behavior during sputtering ($\tau_{eff\,t1}$ = 1.75 µs and $\tau_{eff\,t2}$ = 1.52 µs) could be observed. In part three of the experiment lifetime samples were covered with hotmelt or photo resist and were sputtered again. This was done; because of using the sputtering technology for front side metallization requires structuring methods to create the grid pattern (more than 90 % of the cell is covered by a resist during sputtering). The surprising result for hotmelt and photo resist was, that no visible reduction of the minority carrier lifetime could determined. Only the effect, that the effective lifetime (covered with hotmelt) was reduced for $\Delta\tau_{eff\_IJ}$ = 26 % could not explained. To get a better understanding of the minority carrier lifetime reduction the impact of the ion energy was determined by retarding field analysis. For low pressures at a constant cathode performance, the energy input of P/A = 0.57 mW/cm² was high, compared to higher pressures. In a second experiment the changing energy input P/A for different cathode performances was investigated. The result was a linear increase of the energy input P/A with increasing cathode performance. Together with the results of the determination of the minority carrier lifetime reduction during sputtering the ion energy input should not have a big influence on the interface for the investigated processes.
In terms of using the sputtering technology for front side metallization, the results of the covered lifetime samples supports the feasibility for industrial solar cell fabrication.

6 ACKNOWLEDGEMENT

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