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Towards a Fast Determination of the Hydrogen Concentration in Thin Passivating a-Si:H Layers Using GD-OES

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Abstract. In this contribution, the measurement of the hydrogen concentration in thin passivating amorphous silicon (a-Si:H) layers using Glow Discharge Optical Emission Spectroscopy (GD-OES) is suggested. Usually GD-OES hydrogen measurements suffer from additional signals from atmospheric contaminations, especially from H_2O desorbed on the surfaces of such thin layers. This issue is addressed by the deposition of a hydrogen-free copper buffer layer on top, which provides a delay between sputtering the sample surface and the a-Si:H layer itself. Thus the signals from the atmospheric contaminations and from the a-Si:H layer itself are separated. The contamination-free hydrogen signals of the thin a-Si:H layers are eventually calibrated to average hydrogen concentrations.

INTRODUCTION

Surface passivation is a critical issue in silicon solar cell preparation and continuously investigated. A frequently used method is the chemical vapour deposition of a thin intrinsic a-Si:H layer with a thickness of several nanometers, especially relevant for high efficiency heterojunction solar cells. The underlying passivating mechanism is commonly described as chemical passivation through hydrogen with its capability of saturating the dangling silicon bonds [1]. For an even deeper understanding of this mechanism, the determination of the hydrogen concentration c_H in such thin a-Si:H layers is crucial.

Common methods to determine the hydrogen concentration in a-Si:H are Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Reaction Analysis (NRA), Elastic Recoil Detection Analysis (ERDA) or Secondary Ion Mass Spectroscopy (SIMS). The first method requires a sufficiently thick layer to obtain a significant absorption, causing undesired complications to the analysis of thin layers. The latter three methods may suffer from accessibility since they require either a particle accelerator or an ion gun, both large and costly devices.

In this contribution, a first step towards a fast and accessible measurement of the hydrogen concentration in thin passivating a-Si:H layers is presented using GD-OES, a technique for measuring compositional depth profiles [2]. A proof-of-principle for measurements of the hydrogen concentration in a-Si:H layers with a thickness of roughly 100-500 nm was independently given before [3,4].

However, in the context of thin a-Si:H layers, the issue that GD-OES measurements suffer from atmospheric contaminations at the beginning of each measurement, is more relevant compared to thicker layers. These contaminations mostly originate from the sample surface as well as from the anodes inner surface since the measurement chamber is exposed to ambient air during sample exchange. In particular, the hydrogen signal from desorbed H_2O consequently superimposes the signal from the layer. To avoid this effect, a hydrogen-free copper buffer layer is deposited onto the a-Si:H layer by magnetron sputtering. The measurement through this buffer layer causes a delay between sputtering the sample surface and the a-Si:H layer and hence the signal from the atmospheric

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contaminations is separated from the signal of the layer itself. This leads to a contamination-free signal originating exclusively from the hydrogen in the thin a-Si:H layer.

MATERIALS AND METHODS

Thin a-Si:H layers with a thickness of around 10 nm were plasma-enhanced chemical vapour deposited (PECVD) on 250 µm thick boron-doped Si FZ material of an area of 5x5 cm^2 (2-3 Ωcm, (100)-oriented) with a commercial tool (PlasmaLab 100 from Oxford Instruments) at a radiofrequency of 13.56 MHz with prior removal of the native oxide by a dip in diluted hydrofluoric acid immediately before each deposition. The substrate temperature during deposition was varied from 100–250 °C to obtain different hydrogen concentrations in the layers. Simultaneously, the deposition duration was adjusted to obtain similar layer thicknesses as the deposition rate increases with higher substrate temperatures [5]. At each substrate temperature several samples were deposited to obtain sufficiently large statistics. Each deposition was initiated by a plasma ignition step, after which the power was reduced. All the other parameters were kept constant over the whole deposition process including the ignition step. In a last step, the hydrogen-free copper buffer layer with a thickness of roughly 500 nm was deposited on top of the a-Si:H layer using magnetron sputtering with an RF power of 200 W and an Ar-plasma at 2 mTorr.

TABLE 1. PECVD parameters used for the a-Si:H depositions. Square brackets indicate the corresponding gas fluxes.

Parameter	Values
Substrate temperature	100-250 °C
Deposition duration	20-30 s
$R_{H2}=[H_2]/([H_2]+[SiH_4])$	50%
$R_{Ar}=[Ar]/([Ar]+[SiH_4])$	95%

The a-Si:H layer thicknesses were determined prior to the copper buffer layer deposition using a Vertical VASE Rotating analyser ellipsometer (J.A. Woollam Co., Inc.) in a spectral range of 270-1000 nm. A Tauc-Lorentz oscillator was employed to model the a-Si:H layer with an additional native oxide layer on top.

The GD-OES measurements of the hydrogen content in the a-Si:H layers were performed with a GDA 750 HR (Spectruma Analytik GmbH) equipped with a spectrometer in Paschen-Runge arrangement. For the hydrogen measurements a photomultiplier detector is installed at the position corresponding to the light wavelength of 121.567 nm. All measurements were performed with a radiofrequency power supply with 13.56 MHz at 5 W in a pulsed mode with pulse lengths of 200 µs and a pulse frequency of 1 kHz. The plasma pressure was regulated to a value of 5 mbar. Details on the hydrogen detection using GD-OES can be found in [2,3].

As mentioned above, GD-OES hydrogen measurements suffer from atmospheric contaminations which one can overcome with an additional hydrogen-free buffer layer on top of the layer of interest. The principle of this technique is presented in Fig. 1. Without a buffer layer (Fig. 1, left), the hydrogen signal from the thin a-Si:H layer is superimposed by the signal from the atmospheric contaminations. With a buffer layer (Fig. 1, right), the signal of the a-Si:H layer itself and the signal of the atmospheric contaminations are clearly separated. The former appears as a clear peak, while the latter appears as an exponential decrease similar to the case without a buffer layer, but consequently with lower intensity.

However, the exponential decrease of the hydrogen signal in the first seconds differs from one measurement to another and hence it has to be corrected for each measurement individually. To do so, a two term exponential fit between 2-20 s with exclusion of the peak was performed, as indicated in Fig. 2. The resulting fit function represents the signal from the atmospheric contaminations plus a general background. Subtraction of this fit function reveals the pure hydrogen signal from the a-Si:H layer as a peak (Fig. 2).

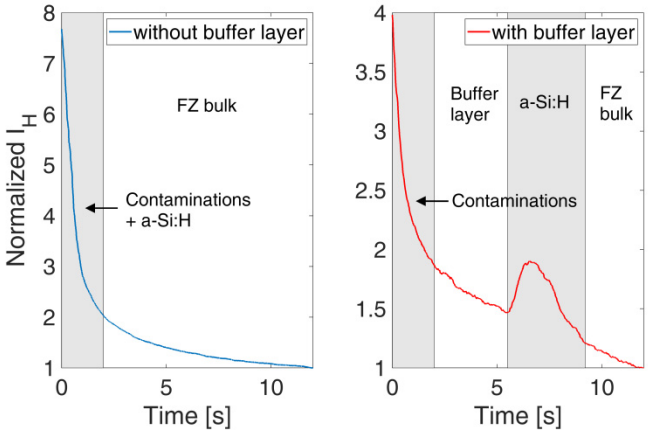

FIGURE 1. Principle of the hydrogen free Cu buffer layer. The GD-OES hydrogen intensity I_H is normalized to the last data point in the plot and plotted against the sputter duration. Left: Without buffer layer, the signal of the atmospheric contaminations superimposes the signal from the a-Si:H layer. Right: With buffer layer, the signal of the a-Si:H layer is clearly separated from the signal of the atmospheric contaminations.

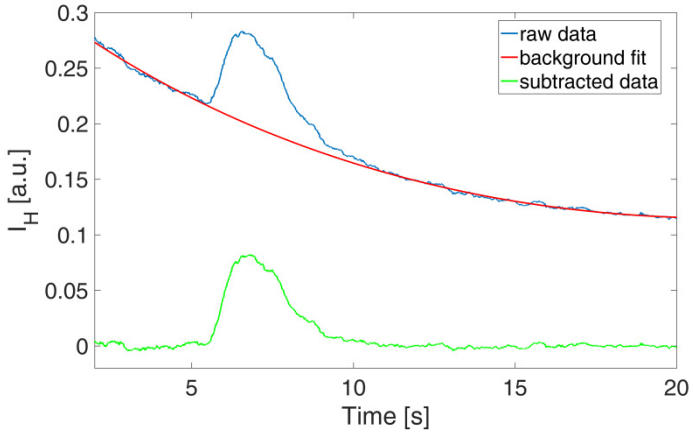

FIGURE 2. GD-OES hydrogen measurement of a thin a-Si:H layer deposited at a substrate temperature of 100 °C with a hydrogen-free Cu buffer layer on top (raw data), plotted as hydrogen intensity I_H against the sputter duration. The atmospheric contaminations and a general background are fitted by a two term exponential fit (background fit). Subtraction of the fit function from the raw data reveals the pure signal from the a-Si:H layer (subtracted data).

In the low intensity regime, the GD-OES signal is typically a linear function of the number of sputtered atoms [2]. This implies that the integral under the peak in the GD-OES measurement of the a-Si:H layer is proportional to the total number of sputtered hydrogen atoms from this layer, i.e. to the average concentration c_H of this layer. Consequently, it is possible to calibrate such integrals to absolute hydrogen concentrations. In this study, the NRA measurements in [3] were used as reference measurements and to correct also for different layer thicknesses, the quantity ξ was defined to perform the calibration:

$$\xi = \frac{\int I_{H,sub}(t)dt}{d} \tag{1}$$

with $I_{H,sub}$ the GD-OES hydrogen signal corrected by subtraction of the fit function and d the a-Si:H layer thickness. As such, ξ describes qualitatively the average number of hydrogen atoms per area. Especially its calibration is independent of the a-Si:H layer thickness.

RESULTS AND DISCUSSION

Table 2 presents the a-Si:H layer thicknesses determined by spectral ellipsometry as described in the previous section. The substrate temperature during deposition was varied to yield different hydrogen concentrations and as the deposition rate increases with higher substrate temperatures, the deposition duration was adjusted to receive a constant layer thickness of around 10 nm. However, there is a trend for thicker layers with higher substrate temperatures. Such a trend is unexpected since the adjustment of the deposition duration should have produced a uniform distribution around 10 nm. Rather, the trend is attributed to the ignition step where a compensation of a higher growth rate with increasing substrate temperature was not considered, since the duration was kept constant over all depositions.

TABLE 2. a-Si:H layer thicknesses determined by spectral ellipsometry on each sample. The error corresponds to the standard deviation of the number of samples indicated in the last column.

Substrate Temperature [°C]	Deposition Duration [s] (without ignition)	a-Si:H Layer Thickness [nm]	# Samples / # GD-OES Measurements
100	30	9.8 ± 0.2	3 / 9
150	26	10.1 ± 0.2	2 / 6
200	23	10.4 ± 0.1	3 / 9
250	20	10.4 ± 0.2	3 / 9

On each sample three GD-OES measurements were performed as indicated in Table 2 and for each resulting profile the quantity ξ was extracted following the procedure described in the previous section. Since the a-Si:H layer deposition parameters in this study were chosen to match the parameters of the NRA analyzed layers in [3], a calibration is possible. Figure 3 shows the resulting linear calibration fit. The errors in c_H originate from the NRA measurements and the errors in ξ correspond to the standard deviations over all ξ values from GD-OES measurements of layers deposited at equal substrate temperatures as depicted in Table 2.

The linear calibration fit matches within the errors of ξ and so a linear relationship between ξ and c_H is concluded, at least in the hydrogen concentration range of ~13-20 at%. From the fit equation in Fig. 3 the cross section with the y-axis is determined to 10 at%, which corresponds to $\xi = 0$ and hence no peak in the GD-OES measurement. Following this observation, the resolution limit of this method is located around 10 at%. The typical optimum substrate temperature for passivating a-Si:H layers is ~200-250°C, which is included in this calibration. Following this calibration, such passivating a-Si:H layers presumably yield hydrogen concentrations in the range of 14-16 at%.

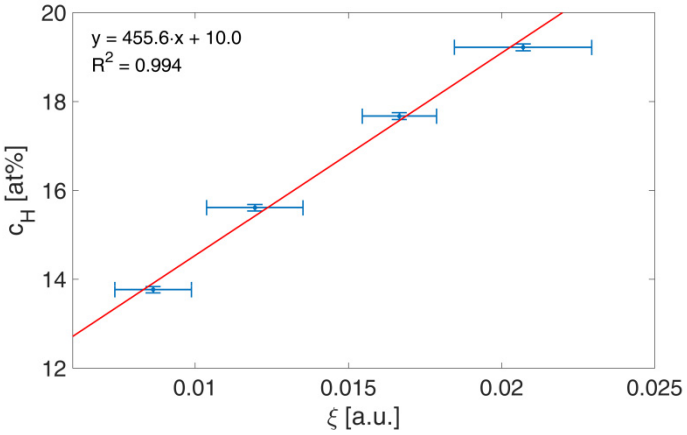

FIGURE 3. Calibration of ξ with the NRA measurements of [3]. The errors originate from the NRA measurements and from the standard deviations of the ξ values of the layers deposited at equal substrate temperatures.

CONCLUSION

A ~500 nm thick Cu buffer layer on top of a thin a-Si:H layer successfully separates the GD-OES hydrogen signals from the atmospheric contaminations and from the a-Si:H layer itself. Thus, a calibration of these GD-OES measurements of thin passivating a-Si:H layers to average hydrogen concentrations c_H is possible, at least in the range of 13-20 at%. The usage of the quantity ξ causes this calibration to be independent of the layer thickness. Further investigations have to be carried out regarding the applicability to thin a-Si:H layers deposited under a wider CVD parameter variation and regarding a potential damage of the a-Si:H layer during the deposition of the Cu buffer layer.

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