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# Replacing NRA by fast GD-OES measurements as input to a model based prediction of hydrogen diffusion in a-Si

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**Abstract**

In order to predict hydrogen diffusion in hydrogenated amorphous silicon (a-Si:H) layers, Gerke *et al.*[1] proposed a model which requires just one nuclear resonant reaction analysis (NRA) and one Fourier transform infrared spectroscopy (FT-IR) as input. This contribution presents the possibility to substitute this single NRA measurement by a calibrated glow discharge optical emission spectroscopy (GD-OES) measurement. In the hydrogen concentration range of 2-30 at% relevant for a-Si:H layers there are currently no commercial calibration standards available, leading to the necessity of laboratory standards. Hydrogen depth profiles of a-Si:H layers exhibit plateaus of constant hydrogen concentration in a range large enough to qualify them as calibration standards. Therefore, six plasma enhanced physical vapor deposited (PECVD) a-Si:H layers with different hydrogen concentrations were prepared as laboratory standards. The absolute hydrogen concentration was determined using the NRA technique and the layer thickness was determined with a focused ion beam (FIB) in a scanning electron microscope (SEM). These results enabled a calibration of the GD-OES setup for a-Si:H, which successfully reproduced the NRA measurements of Gerke *et al.* [1].

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## 1. Introduction

Hydrogenated amorphous silicon (a-Si:H) is frequently used in photovoltaics, especially as thin layer. Since hydrogen has a significant impact on the electronic and optical properties of such layers, a fundamental understanding of the hydrogen diffusion processes is required, including the measurement of hydrogen depth profiles. A widely used method to determine precise depth profiles is the nuclear reaction analysis (NRA) [2]. Since it is hardly accessible and costly, huge efforts are necessary to measure hydrogen depth profiles of a series of samples. To reduce these efforts Gerke *et al.* proposed a model based prediction of the diffusion of hydrogen in post-hydrogenated a-Si:H [1]. With this model it is possible to predict the hydrogen depth profiles of layers exposed to post-hydrogenation processes of different durations with just one single NRA measurement and one Fourier transform infrared spectroscopy (FT-IR) measurement. In this contribution the glow discharge optical emission spectroscopy (GD-OES) [3] is introduced to replace even this single NRA measurement in the sense of further minimizing the efforts. GD-OES is a fast and cost effective technique for obtaining depth profiles of hydrogen in a-Si.

The basis of the model proposed by Gerke *et al.* [1] is the assumption, that the hydrogen diffusion in a-Si can be described according to Fick's law by a complementary error function [4]:

$$H_x(x_l) = H_i + (H_s - H_i) \cdot erfc\left(\frac{x_l}{2\cdot\sqrt{D_H \cdot t_t}}\right) \tag{1}$$

Except for the depth of the calculated hydrogen concentration $x_l$ and the treatment duration $t_t$, the other parameters are determined using the results of the NRA and FT-IR measurements. The parameters are namely $H_i$ the hydrogen concentration at the interface of a-Si and the bulk material, $H_s$ the hydrogen concentration at the surface and $D_H$ the diffusion coefficient. A consideration of a possibly initial hydrogen concentration $H_0$ prior to the post-hydrogenation treatment leads to a more accurate prediction of the hydrogen depth profiles. Fig. 1 presents several NRA measured hydrogen depth profiles and the corresponding calculated depth profiles using the model prediction (for experimental details see [1]).

## 2. GD-OES

### *2.1. Measurement principle*

The GD-OES technique determines depth profiles of the elemental composition by applying a glow discharge argon plasma to the sample surface. The argon ions sputter the atoms of the surface which are then excited in the plasma and emit a characteristic spectrum. The intensities of this characteristic light carry information about the initial elemental composition which is determined by a comparison with the light intensities of certified calibration standards. The resulting composition and the corresponding densities of the pure elemental solids are then used to transform the sputter process duration into depth information [3]. For the atmospheric elements, *i.e.* hydrogen, nitrogen and oxygen, this procedure is not possible, because they are gaseous at room temperature and so no density of the elemental solid is available. The depth information has to be determined individually for each sample type containing these elements.

In fact, once the GD-OES device is calibrated, it has powerful advantages. The most important advantage is the very short measurement duration, typically in the range of 10-100 s for layers up to several µm thickness, depending on the chosen plasma conditions. Also these plasma conditions are highly reproducible and hence a reliable comparison with the intensities of the calibration samples is possible. A resolution down to 100 ppm is achievable, depending on the chosen emission line and specific detector setup. In principle it is possible to achieve depth resolution in the order of 1 nm. But this depth resolution is limited by the specific detector setup and the shape of the crater sputtered into the sample, which in turn is defined by the plasma conditions. The shape of the crater as well as the crater bottom roughness may reduce depth resolution with increasing measurement duration or at interfaces of two materials with different sputter rates.

### 2.2. Calibration procedure

Since GD-OES is a relative measurement technique, it requires a suitable calibration for every single element of interest. The hydrogen content in a-Si:H usually varies in the range of 2-30 at% [5] and therefore also calibration samples in this range must be provided. Certified calibration samples that are commercially available show very low hydrogen concentrations (*e.g.* [6]). An exception is the standard BAM-S110 with a hydrogen concentration of 11.9 at% [7]. However, this standard is currently not available on the market. Therefore, laboratory standards are necessary. One possibility for such standards are a-Si:H layers with a plateau of constant hydrogen concentration as usually achieved with plasma enhanced chemical vapor deposition (PECVD) devices. The hydrogen content can then be determined by NRA or alternatively by SIMS (secondary ion mass spectrometry) or ERDA (elastic recoil detection analysis).

A common GD-OES calibration procedure is the so called multi matrix calibration. It allows to include calibration standards with different matrices as it considers the individual sputter rates $S$ of every calibration sample and links them to a reference sputter rate, commonly to the sputter rate of pure iron. This measure is then called $q$, the relative sputter rate (RSR) [3]:

$$q = \frac{S}{S_{Fe}} = \frac{\rho \cdot \Delta z}{\rho_{Fe} \cdot \Delta z_{Fe}} \cdot \frac{\Delta t}{\Delta t_{Fe}} \tag{2}$$

The elemental concentration of the individual calibration sample is multiplied by $q$, resulting in virtual concentrations which are in general different from the real concentration and in some cases even larger than 1. A final normalization transforms these virtual concentrations into the real concentrations.

For the actual calibration in this contribution, three non-a-Si:H calibration samples are included, two titanium samples with low hydrogen content and silicon content below the detection limit of the GD-OES setup, namely IARM 178D and IARM 271A [6], and a p-doped silicon float zone (FZ) wafer (1 Ωcm). The IARM samples serve as low concentration values for the hydrogen and zero point for the silicon calibration, the silicon FZ wafer serves as zero point for the hydrogen calibration.

## 3. Experimental

### 3.1. Laboratory standards preparation

The a-Si:H layers were PECV deposited with a columnar morphology on chemically polished silicon FZ wafers (p-type) by a direct plasma reactor PlasmaLab 100 from Oxford Instruments with a mixture of silane ($SiH_4$), Ar and $H_2$. The flux ratios of $R_H = 0.5$ and $R_{Ar} = 0.95$, with $R_x = R_x/(R_x+R_{SiH4})$, were kept constant for all depositions. Different hydrogen concentrations were achieved by varying the sample deposition temperature from 100 °C to 400 °C, since a higher temperature leads to a stronger effusion of the hydrogen during the deposition. Increasing the sample temperature also increases the growth rate of the layer and so the final thickness, since the deposition duration was kept constant at 1500 s. A reason for this behavior might be a larger probability to dissociate silane near the sample surface, which increases the growth rate [4].

### 3.2. Hydrogen profile measurements

The employed GD-OES setup was the GDA 750 HR from Spectruma Analytik GmbH equipped with a spectrometer in Paschen-Runge arrangement and photomultiplier detectors at the positions on a Rowland-circle corresponding to the wavelengths of 121.567 nm for hydrogen and 288.158 nm for silicon. The device was operated in pulsed mode to minimize the heat load on the sample surface and thus avoid hydrogen diffusion during the sputter process. The power supply was chosen to be RF, since the a-Si:H layers' low conductivity prevents a stable DC plasma. The plasma parameters were optimized on silicon FZ material to a preferably low sputter rate and a stable plasma, resulting in an applied power of 5 W and a plasma pressure of 9 hPa. Afterwards the pulse parameters were

optimized aiming at high intensities of the emitted characteristic light of silicon, resulting in a pulse frequency of 1 kHz and a pulse duration of 100 µs.

Fig. 1 presents the GD-OES raw data and the absolute NRA hydrogen profiles of the a-Si:H layers. The decrease of the hydrogen concentration and the increase of the layer thickness with increasing sample temperature are clearly visible in the profiles of both techniques. Each layer shows an almost flat profile enabling the determination of an average value. For the GD-OES profiles at each sample temperature the weighted mean of two measurements was determined. The average values extracted from both techniques are shown in Table 1.

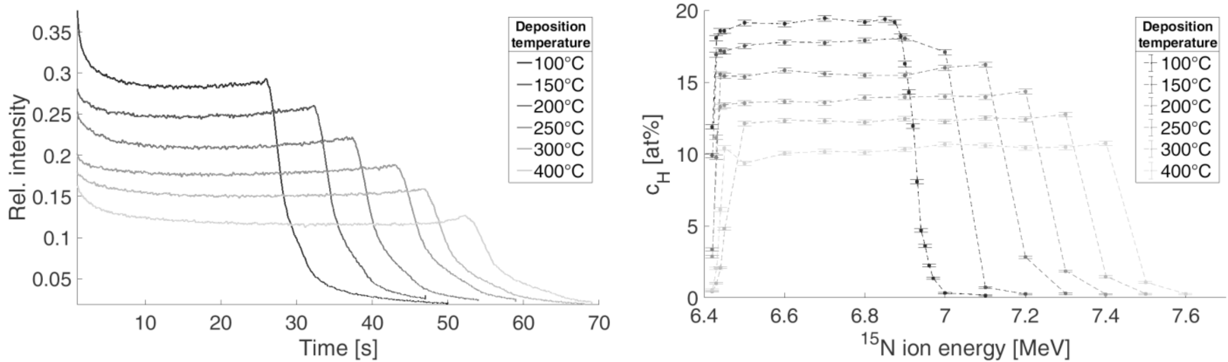


Fig. 1. Hydrogen profiles of the a-Si:H samples determined by GD-OES (left, raw data, intensity relative to argon intensity at 415.2 nm) and NRA (right, absolute data, dotted lines as guide for the eye only).

Table 1. Average values extracted from the GD-OES and NRA profiles presented in Fig. 1 and corresponding standard deviations. The average values extracted from the GD-OES profiles were calculated from the weighted mean of two measurements.

| Rel. hydrogen intensities (GD-OES) | $C_H$ [at%] (NRA) |
|---|---|
| 0.278 ± 0.007 | 19.22 ± 0.08 |
| 0.251 ± 0.006 | 17.67 ± 0.08 |
| 0.214 ± 0.006 | 15.61 ± 0.07 |
| 0.180 ± 0.005 | 13.77 ± 0.07 |
| 0.153 ± 0.005 | 12.27 ± 0.07 |
| 0.117 ± 0.04 | 10.10 ± 0.06 |

### *3.3. Sputter rate measurements*

As mentioned above, in the case of hydrogen the depth information cannot be derived from the elemental composition and the density of the pure solid. Alternatively, since the whole calibration is meant for a-Si:H layers only, the sputter rate can be determined from the laboratory standards as function of the hydrogen content. Expressing this hydrogen content dependent sputter rate in nm/s, it just has to be multiplied with each time step in the GD-OES profile to receive the depth information. For obtaining this sputter rate, and also for determination of the RSRs, the thickness $\Delta z_{a\text{-}Si}$ of the a-Si:H layers needs to be known. It was determined from a focused ion beam (FIB) cut cross section of the layer using a Zeiss Neon 40 ESB electron microscope. The values for $\Delta t$ were extracted directly from the GD-OES profiles in Fig. 1, since the interface between a-Si:H layer and substrate is clearly visible.

A multi matrix calibration always requires the RSRs (Eq. 2) of all calibration samples and consequently also the sputter rate of pure iron. For the IARM samples, the silicon FZ and a certified pure iron sample (EZRM 098-1 [8]) GD-OES craters were sputtered with the optimized plasma parameters described above for $\Delta t$ = 200 s. Afterwards the depth of the crater $\Delta z$ was determined with an average of three line scans through the center of each crater using

a mechanical profilometer. For the determination of the density $\rho$ of each material it was possible to simply weigh and measure the volume of the samples, since all of them are cylindrical, except the silicon FZ wafer, whose density is well known.

## 4. Results

### 4.1. Relative sputter rates

The characteristic light intensity of silicon as generated by the GD-OES measurements was equally high for all a-Si:H layers, independent of the hydrogen concentration (Fig. 3). This suggests that the atomic density of the silicon in the layers stays constant and the hydrogen is located in microvoids formed by the silicon atoms without any influence on the amorphous network. This means that the density in g/cm$^3$ can be calculated by simply adding the weight of the hydrogen to that of the silicon atoms:

$$\rho_{a-Si:H} = (n_{a-Si} \cdot m_{Si} + c_H \cdot n_{a-Si} \cdot m_H) \tag{3}$$

with $n_{a\text{-}Si} = 4.9 \cdot 10^{22}$ cm$^{-3}$ the atomic density of amorphous silicon [9] and $c_H$ the results of the NRA measurements (Table 1). Table 2 summarizes all results for the sputter rate determination, including the final RSRs calculated according to Eq. 2.

Table 2. Summary of all quantities necessary for the determination of the RSRs according to Eq. 2.

| Sample temperature / Sample Name | Crater depth Δz [µm] (Profilometer) | Layer thickness $\Delta z_{a\text{-}Si}$ [nm] (FIB - SEM) | Sputter duration Δt [s] (GD-OES) | Density ρ [g/cm$^3$] | **RSR q** |
|---|---|---|---|---|---|
| 100 °C | / | 43 | 24.5 | 2.301 | **0.209** |
| 150 °C | / | 526 | 31 | 2.300 | **0.199** |
| 200 °C | / | 608 | 38 | 2.298 | **0.187** |
| 250 °C | / | 683 | 42 | 2.296 | **0.190** |
| 300 °C | / | 724 | 44.5 | 2.295 | **0.190** |
| 400 °C | / | 778 | 51 | 2.293 | **0.178** |
| IARM 178D | 2.826 | / | 200 | 4.534 | **0.326** |
| IARM 271A | 2.814 | / | 200 | 4.410 | **0.316** |
| Silicon FZ | 2.693 | / | 200 | 2.332 | **0.160** |
| EZRM-098-1 | 3.941 | | 200 | 9.966 | **1** |

From the layer thicknesses and sputter durations the sputter rate in nm/s of the a-Si:H samples is directly accessible. Combined with the results of the NRA measurements for $c_H$, the hydrogen concentration dependent sputter rate for the a-Si:H layers was determined as presented in Fig. 2. The equation of the fit was then used to determine the sputter rate for each time step of the GD-OES raw profile, dependent on the corresponding calculated hydrogen concentration during this time step (see Sec. 4.3).

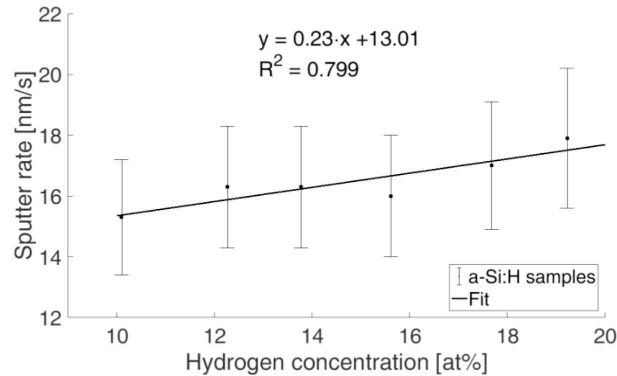


Fig. 2. Hydrogen concentration dependent sputter rate of the a-Si:H layers.

### 4.2. Calibration curves

Fig. 3 shows the calibration curves for hydrogen and silicon, while the measured characteristic light intensities (Table 1) are plotted against the virtual concentrations $c{\cdot}q$ with the RSRs from Table 2. The $R^2$ values of the linear fits close to one suggest a successful fitting procedure. However, there are two important points to mention. First, the positive intersection of the fit with the x-axis accounts for the dark current of the detectors which may indeed be very different because of the individual detector's dark current value and the spectral background at the characteristic wavelength. Second, the silicon characteristic light intensities of all a-Si:H samples is equal, as mentioned above. This behavior was useful to determine the densities of the a-Si:H layers (see Sec. 4.1, Eq. 3), but for the calibration curve it causes an underestimation (overestimation) of the silicon concentration for lower (higher) hydrogen content, and consequently an overestimation (underestimation) of the hydrogen concentration.

At this point it should be mentioned, that one could also omit the rather complex multi matrix calibration and just consider the a-Si:H samples. In this absence of the virtual concentration normalization there would be no need for a silicon calibration, since $c_{Si} = 1\text{-}c_H$. The above explained under- and overestimations would be avoided. But a fit through the data of the a-Si:H samples only leads to a positive intersection of the fit with the y-axis at 3.6 at%, which is unphysical. This calibration would result in a non-zero hydrogen concentration in the total absence of any detector signal.

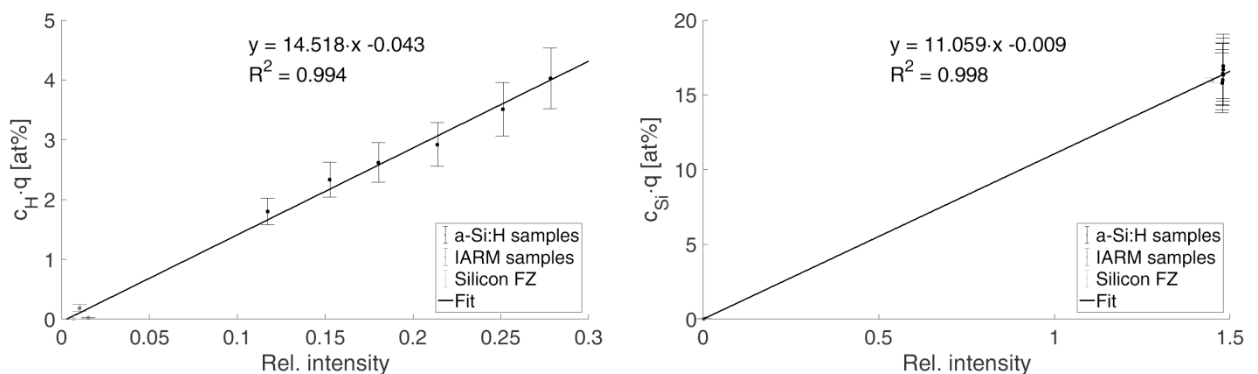


Fig. 3. Calibration curves of hydrogen (left) and silicon (right) with virtual concentrations c·q.

### 4.3. Test of the calibration

Calibrated GD-OES depth profiles of unknown a-Si:H samples can now be determined as follows:

a) The calibration equations from Fig. 3 are used to transform the measured relative intensities $I_H$ and $I_{Si}$ in virtual concentrations $q \cdot c_H$ and $q \cdot c_{Si}$.
b) Both virtual concentrations are normalized to obtain the real concentrations $c_H$ and $c_{Si}$.
c) The depth information is received by multiplying each time step $\Delta t$ from the raw profile with the sputter rate calculated by the fit parameters in Fig. 2 and $c_H$ from step b).

The accuracy of the calibration was evaluated investigating two of the original samples used by Gerke *et al.* [1], namely "3 min/nm Post-Hydro." and "100 min/nm Post-Hydro." 29 months after the original NRA measurements were performed. For the GD-OES measurements, the optimized plasma parameters (Sec. 3.2) were used and the procedure above described was applied to receive the hydrogen depth profiles. The NRA measurements are the original data from Gerke *et al.* [1], except for the depth information. The depth was recalculated using the fit parameters from the hydrogen concentration dependent NRA stopping power of the $^{15}$N ions determined for the a-Si:H layers in this contribution (Fig. 4).

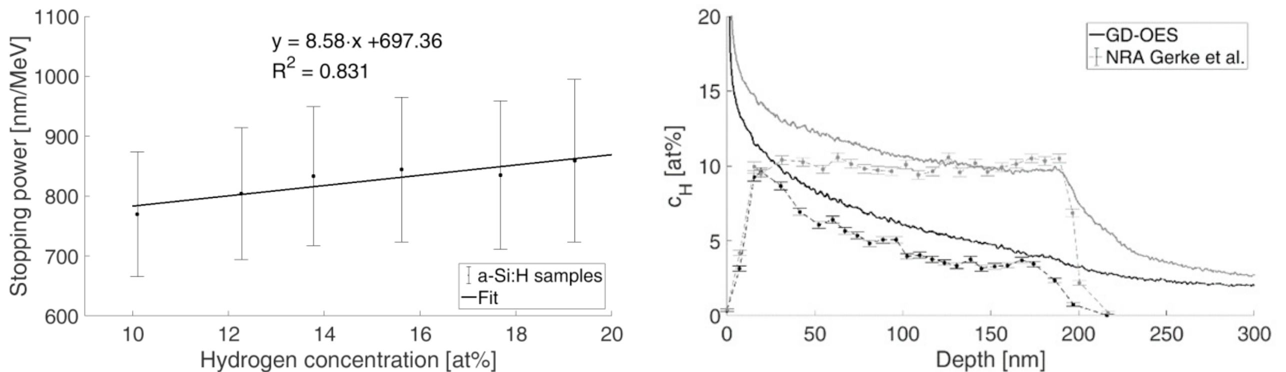


Fig. 4. Left: hydrogen concentration dependent NRA stopping powers of the a-Si:H layers. Right: depth profiles of the original samples by Gerke *et al.* [1]. Black: 3 min/nm Post-Hydro., grey: 100 min/nm Post-Hydro. Dotted lines as guide for the eye only.

The final hydrogen depth profiles of both techniques are presented in Fig. 4 and show an overall agreement. The most striking deviations appear in the first few nm, where the hydrogen concentration from GD-OES exceeds 20 at%. Such large hydrogen signals are typical for GD-OES measurements and are attributed to atmospheric impurities inside the GD plasma. For the lower hydrogen concentrations there is a clear overestimation, which is caused by the constant silicon intensities for all a-Si:H samples as described in Sec. 4.2. Another effect which might additionally contribute to the differences of the GD-OES and NRA profiles is the fact that there are no calibration points in the range of 0.5 at% $< c_H <$ 10 at% for hydrogen and 0.1 at% $< c_{Si} <$ 80 at% for silicon.

## 5. Conclusion

In this contribution a successful GD-OES multi matrix calibration for hydrogen and silicon in a-Si:H layers was presented. A comparison with independently prepared and NRA measured samples revealed an overall agreement with a slight overestimation of the hydrogen concentration using GD-OES. Since this deviation is only small, the replacement of the NRA depth profile measurement by a GD-OES measurement as input for the hydrogen diffusion model proposed by Gerke *et al.* [1] can be justified. The agreement of both techniques is expected to improve by an optimization of the GD plasma purity and by adding calibration points between 0.5 at% $< c_H <$ 10 at%.

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