

Model based prediction of the trap limited diffusion of hydrogen in post-hydrogenated amorphous silicon

Sebastian Gerke^{*1}, Hans-Werner Becker², Detlef Rogalla², Reinhart Job³, and Barbara Terheiden¹

¹ Department of Physics, University of Konstanz, 78457 Konstanz, Germany

² RUBION – Central Unit for Ion Beams and Radioisotopes, University of Bochum, 44780 Bochum, Germany

³ Department of Electrical Engineering and Computer Science, Münster University of Applied Sciences, 48565 Steinfurt, Germany

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* Corresponding author: e-mail sebastian.gerke@uni-konstanz.de, Phone: +49 753 188 213 2, Fax: +49 753 188 389 5

The diffusion of hydrogen within an hydrogenated amorphous silicon (a-Si:H) layer is based on a trap limited process. Therefore, the diffusion becomes a self-limiting process with a decreasing diffusion velocity for increasing hydrogen content. In consequence, there is a strong demand for accurate experimental determination of the hydrogen distribution. Nuclear resonant reaction analysis (NRRRA) offers the possibility of a non-destructive measurement of the hydrogen distribution in condensed matter like a-Si:H thin films. However, the availability of a particle accelerator for NRR-analysis is limited and the related costs are high. In comparison, Fourier transform infrared spectroscopy (FTIR) is also a common method to determine the total hydrogen content of

an a-Si:H layer. FTIR spectrometers are practical table-top units but lack spatial resolution. In this study, an approach is discussed that greatly reduces the need for complex and expensive NRR-analysis. A model based prediction of hydrogen depth profiles based on a single NRRRA measurement and further FTIR measurements enables to investigate the trap limited hydrogen diffusion within a-Si:H. The model is validated by hydrogen diffusion experiments during the post-hydrogenation of hydrogen-free sputtered a-Si. The model based prediction of hydrogen depth profiles in a-Si:H allows more precise design of experiments, prevents misinterpretations, avoids unnecessary NRRRA measurements and thus saves time and expense.

1 Introduction Hydrogenated a-Si:H is a widely used material, especially for photovoltaics (PV) [1]. For example, an intrinsic a-Si:H layer in 'hetero junction with intrinsic thin layer' (HIT) silicon solar cells enables cell efficiencies of more than 25% [2]. The standard deposition process for a-Si:H is plasma enhanced chemical vapor deposition (PECVD) using hydrogen containing silane gas (SiH₄) [3]. The hydrogen concentration gradient between an a-Si:H layer and a crystalline silicon (c-Si) carrier substrate would not allow to investigate the migration of hydrogen, as the hydrogen concentration within the c-Si bulk would be below the quantification limit. Therefore, performing special hydrogen diffusion experiments for a better understanding of the hydrogen related influences on PV thin films requires a hydrogen drain layer [4–6]. Such a hydrogen-free a-Si layer can be processed by radio fre-

quency magnetron sputter deposition (RFSD) [7, 8]. The RFSD technology uses a solid target consisting solely of the material intended to be deposited, making the deposition of hydrogen-free a-Si possible [8]. To investigate the hydrogen diffusion in the a-Si layer and its influence on structural, electrical and optical characteristics, the initially hydrogen-free grown a-Si is hydrogenated in a subsequent post-hydrogenation step [4, 7]. This hydrogenation is carried out using a hydrogen remote plasma [9]. The distribution of hydrogen as well as the related ongoing trap limited diffusion process is investigated by the measurement of hydrogen depth profiles by NRRRA [10].

The most important advantage of the proposed model is the possibility to investigate the hydrogen diffusion *in situ* as well as to predict hydrogen depth profiles. Normally separate hydrogen depth profiles have to be measured for

each period of post-hydrogenation. However, the parametric model based estimation takes advantage of material characteristics and allows predicting any number of hydrogen depth profiles.

2 Experimental details

2.1 Sample preparation Hydrogen-free intrinsic (i) a-Si layers were RFS-deposited at a pressure of 2 mTorr using only Ar as process gas. RFS-deposition took place in an “AJA ATC 2200” RF magnetron sputtering system. For the experiments phosphorous doped (n-type), chemically polished float-zone (FZ) silicon wafers (c-Si) were used ($5 \Omega \text{ cm}$, $250 \mu\text{m}$, $\langle 100 \rangle$ oriented). Native oxide at the surface of the c-Si wafers was chemically removed in diluted hydrogen fluoride solution (HF, 5%, 30 s) directly before RFS-deposition of 170 nm thick intrinsic a-Si. Determination of the a-Si layer thickness was carried out by spectral ellipsometry measurements by a “J. A. Woollam V-Vase 2000” ellipsometry unit.

Several initially hydrogen-free samples were hydrogenated after the deposition in a post-hydrogenation process using a microwave induced hydrogen remote plasma (MIRHP) reactor at a process temperature of $370 \text{ }^\circ\text{C}$ and a chamber pressure of 1000 mTorr [9]. The diffusion based hydrogen concentration in a certain depth depends on the thickness of the a-Si film. In order to compare the hydrogenation process of different a-Si layer thicknesses (e.g. in related studies [4, 7]), the duration (t_i) of the post-hydrogenation treatment is normalized to the layer thickness.

2.2 Fourier transform infrared spectroscopy

FTIR-spectroscopy enables to determine the total hydrogen concentration without detailed spatial resolving information within the a-Si:H film. Based on the absorption intensity (A_{film}) of the a-Si:H related to the film thickness (d_{film}) the effective absorption coefficient (α_{eff}) can be obtained by FTIR measurements, Eqs. (1) and (2) [11]:

$$A_{\text{film}} = A_{\text{total}} - A_{\text{carrier substrate}} \quad (1)$$

$$\alpha_{\text{eff}} = \frac{A_{\text{film}}}{d_{\text{film}} \cdot \log_{10} e} \quad (2)$$

As mentioned in [12], it is recommended to obtain a baseline correction of the FTIR data, i.e. subtracting the Drude term, before calculating α_{eff} .

The intensity (I_ω) of an interesting bandwidth of wavenumbers (ω) can be calculated by integrating, Eq. (3) [12]. Langford et al. described a method and gave coefficients to calculate the Si–H (2000 cm^{-1}) and Si–H₂ (2090 cm^{-1}) bond densities and therefore the sum (N_{H}) of these Si–H_x bonds, according to Eq. (4) [11]:

$$I_\omega = \int \frac{\alpha(\omega)}{\omega} d\omega \quad (3)$$

$$N_{\text{H}} = c_{2000} \cdot I_{2000} + c_{2090} \cdot I_{2090} \quad (4)$$

The coefficients are: $c_{2000} = 9 \times 10^{19} \text{ cm}^{-2}$ for Si–H bonds and $c_{2090} = 2.2 \times 10^{20} \text{ cm}^{-2}$ for Si–H₂ bonds.

Hydrogen bond structures of RFSD a-Si layers were analyzed in the described way by using a “Bruker Vertex 80” spectrometer.

2.3 Nuclear resonant reaction analysis Several publications have discussed hydrogen depth profiles within a-Si:H layers as measured by NRRA [3, 4, 13]. NRRA-analyses in this study were carried out using the Dynamitron tandem accelerator [9] located at the central unit for ion beams and radioisotopes at the University of Bochum.

NRRA, also known as ¹⁵N profiling technique, is based on the nuclear reaction of a nitrogen isotope (¹⁵N) with a hydrogen atom. An accelerated ¹⁵N isotope reacts with a hydrogen atom to a carbon (¹²C) and a helium (⁴He) isotope. This reaction also emits a detectable γ -ray at an energy of 4.43 MeV, Eq. (5) [14]:



Counting γ -rays from a sample under beam irradiation leads to a quantitative value which can be compared to γ -rays of a known (i) a-Si:H standard like the certified reference material BAM-S110 [15].

From this comparison the content of hydrogen atoms per cm^3 can be determined. Considering the atomic density of silicon of $\sim 5 \times 10^{22} \text{ atoms/cm}^3$ [3], the hydrogen concentration can be calculated. Moreover, the reaction energy is an isolated and very narrow resonance at a beam energy of 6.385 MeV [15]. Assuming a stopping power of the a-Si:H layer of 1.38 keV/nm [13], a correspondingly higher beam energy enables measuring a hydrogen depth profile.

3 Model details

3.1 Hydrogenation and diffusion The hydrogenation of the a-Si during the post-hydrogenation process is based on diffusion. The diffusion itself takes place by the trap limited diffusion mechanism, an interplay of hydrogen and defects like dangling bonds [3, 16]. Defects trap hydrogen and Si–H_x bonds are formed. The hydrogen can leave these Si–H_x bonds, move and reform in new Si–H_x bonds. This ongoing process leads to a continuous motion of hydrogen within the a-Si. The more the defects are unsaturated the more the hydrogen can diffuse within the a-Si layer [3, 16].

In an a-Si:H layer most of the hydrogen is trapped in Si–H_x bonds and hardly any interstitial hydrogen exists [3, 4]. This is important because it denotes that an increase of the overall hydrogen concentration is directly correlated to an increase in the quantity of Si–H_x bonds.

Figure 1 shows the total hydrogen concentration (●) of several post-hydrogenated samples. As can be seen, the total hydrogen concentration rises with post-hydrogenation time. The amount of hydrogen in the a-Si:H layer was found to increase linearly with the logarithm of the post-hydrogenation time, as given in the empirical Eq. (6):

$$\text{Fit}_{\text{Si-H}}(t_i) = g_{\text{H}} \cdot \ln(t_i) + b_{\text{H}} \quad (6)$$

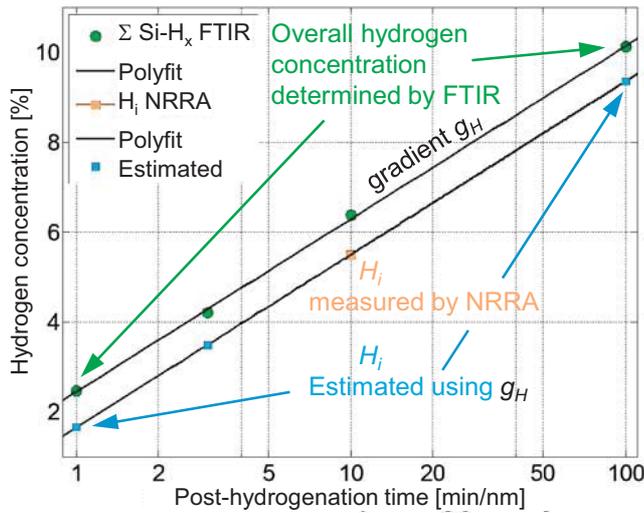


Figure 1 Evaluation of the total hydrogen concentration (●) after different durations of post-hydrogenation (determined by FTIR) as well as the estimated evolution of the hydrogen concentration at the a-Si/c-Si interface H_i (■).

The overall hydrogen concentration (●) increases gradually with time t_t according to the gradient g_H . The offset (b_H) represents an initial hydrogen contamination (H_0) of the a-Si and can be disregarded ($b_H = 0$) for hydrogen-free RFS-deposited a-Si.

The model to predict hydrogen depth profiles is based on a relationship between the total hydrogen concentration in the a-Si and the hydrogen diffusion profile within the film.

The process of hydrogen diffusion within the a-Si layer can be described by a complementary error function, Eq. (7) [3]:

$$H_x(x_1) = H_s \cdot \operatorname{erfc}\left(\frac{x_1}{2 \cdot \sqrt{D_H \cdot t_t}}\right). \quad (7)$$

The parameters of Eq. (7) are the depth dependent hydrogen concentration (H_x), the hydrogen concentration at the surface of the a-Si film (H_s), the depth of the calculated hydrogen concentration (x_1), the diffusion coefficient of hydrogen within the a-Si (D_H) and the time of treatment (t_t). In this context t_t is the duration of the remote plasma post-hydrogenation process.

For thin films with a layer thickness less than the diffusion length, the accumulation of hydrogen in the layer has to be taken into account. Based on Fick's second law the different hydrogen concentration at the surface (H_s) of the film and the a-Si/c-Si interface (H_i) can be considered, Eq. (8) [3]:

$$H_x(x_1) = H_i + (H_s - H_i) \cdot \operatorname{erfc}\left(\frac{x_1}{2 \cdot \sqrt{D_H \cdot t_t}}\right). \quad (8)$$

3.2 Model based prediction Only two of the parameters of Eq. (8) are *a priori* known (x_1 , t_t). The other parameters have to be determined by the model for estimat-

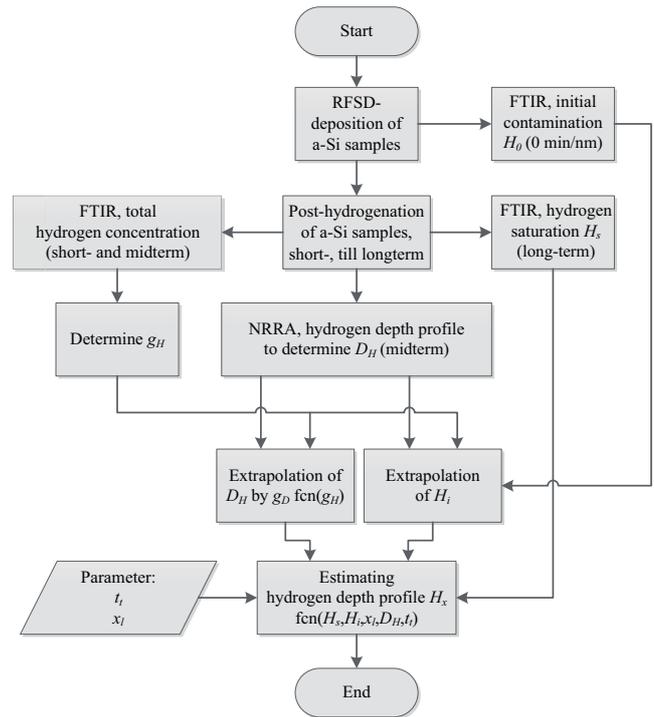


Figure 2 Process flow-chart of the model based estimation of hydrogen depth profiles as well as required experimental inputs.

ing hydrogen depth profiles. Figure 2 depicts the process flow-chart of the model based estimation of hydrogen depth profiles as well as of the experimentally determined quantities required as initial inputs for the model.

Several different samples need to be prepared by RFS-deposition and post-hydrogenated. Determining the total hydrogen concentration by FTIR and measuring at least one hydrogen depth profile by NRA enables to determine the required input parameters for the model, which then enables to predict any number of hydrogen depth profiles for each timespan of post-hydrogenation.

3.3 Initial hydrogen concentration H_0 Humidity in the air causes adherence of hydrogen to the c-Si substrate as well as to the RFS sample carrier. Therefore, hydrogen enters the deposition chamber of the sputter reactor during the sample transfer. Due to this, an initial hydrogen contamination of the a-Si is possible. A first FTIR measurement directly after the deposition determines the total initial built-in concentration (H_0) of hydrogen in the a-Si film.

3.4 Surface hydrogen concentration H_s The hydrogen depth profile of a sample after very long post-hydrogenation (e.g. $t_t = 400$ min/nm) becomes flat [4]. The total hydrogen concentration of a constant hydrogen depth profile is then equal to the a-Si surface concentration H_s .

3.5 Diffusion coefficient D_H The diffusion coefficient (D_H) of hydrogen in a-Si is not constant. Due to the

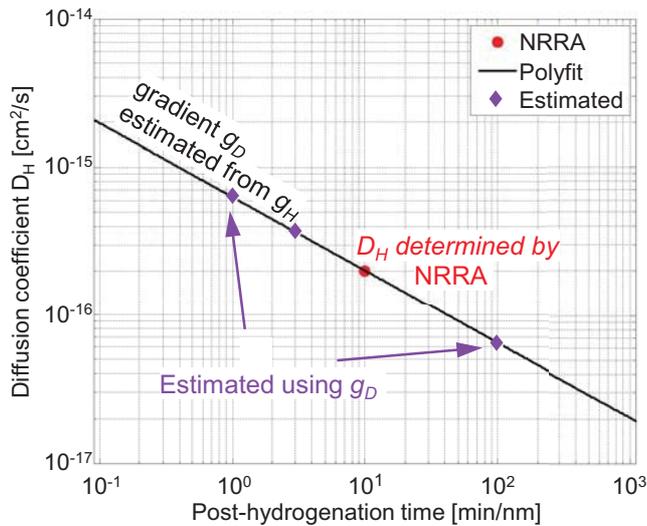


Figure 3 Estimated evolution (\blacklozenge) of the diffusion coefficient D_H based on the gradient g_D and one experimental determined D_H start value (\bullet).

trap limited diffusion mechanism D_H decreases as the total amount of hydrogen in the layer increases [3, 4].

Similar to Eq. (6), the evolution of D_H during post-hydrogenation can be mathematically described by Eq. (9):

$$\text{Fit}_{D_H}(t_i) = g_D \cdot \ln(t_i) + b_D, \quad b_D \equiv D_H(t_i). \quad (9)$$

To determine the offset value b_D one single hydrogen depth profile of a post-hydrogenated a-Si layer has to be measured by NRA. Based on this profile the specific diffusion coefficient can be calculated using Eq. (8). The required parameters can then be directly read from the measured profile.

The correlation between Eqs. (6) and (9) is given by the gradients g_H and g_D . The gradient of the diffusion coefficient (g_D) can be deduced from the gradient of the hydrogen concentration (g_H), Eq. (10):

$$g_D = -\log(g_H). \quad (10)$$

Figure 3 visualizes the prediction of further D_H values (\blacklozenge) for several post-hydrogenation timespans, based on extrapolation from Eqs. (9) and (10).

3.6 Interface hydrogen concentration H_i The hydrogen concentration at the a-Si/c-Si interface (H_i) increases during the post-hydrogenation step in parallel to the total hydrogen concentration. Therefore, based on Eq. (6) and the gradient g_H further values of H_i can be extrapolated, Fig. 1 (\blacksquare). The needed offset value (b_H) can be experimentally determined based on the one measured hydrogen depth profile ($b_H = H_i$), Fig. 1 (\blacksquare).

4 Validation The samples for model validation were prepared by RFS-deposition and post-hydrogenated for $t_i = 1, 3, 10$ and 100 min/nm as described in Section 2. The built-in hydrogen concentration of the a-Si determined by

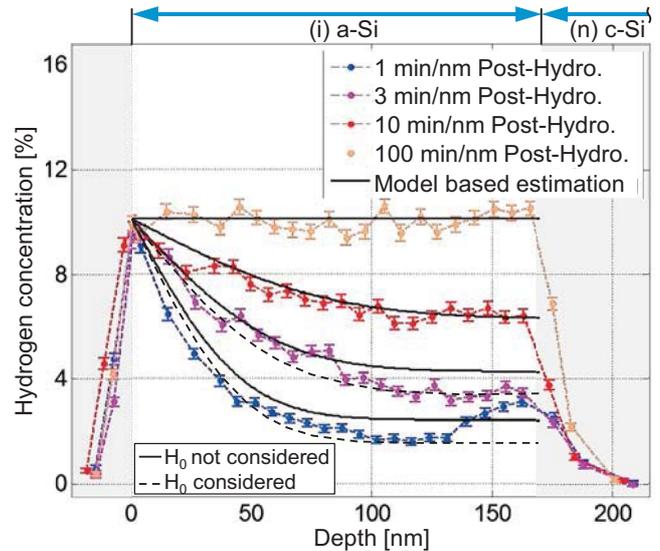


Figure 4 NRA measured hydrogen depth profiles and their respective related model based predictions (—). The dashed lines (--) represent additional estimations which take the built-in hydrogen concentration H_0 into account.

FTIR prior to post-hydrogenation is $H_0 = 0.9\%$ (Section 2.2).

Figure 4 shows the hydrogen depth profiles of the model validation samples measured by NRA. Further, Fig. 4 shows the respective model based predictions of the related hydrogen depth profiles (—), calculated by disregarding H_0 .

As can be seen, the predicted hydrogen depth profiles (—) are in excellent agreement with the measured hydrogen profiles of 10 min/nm and 100 min/nm post-hydrogenated samples and in acceptable agreement with the 3 min/nm post-hydrogenated one. However, the predicted profile of the 1 min/nm post-hydrogenated sample deviates from the measured profile (\bullet).

The hydrogen depth profile itself (\bullet) shows an obvious increase of hydrogen near the a-Si/c-Si interface indicating the built-in of hydrogen which has entered the reactor chamber during the sample transfer process. As the amount of inadvertent hydrogen in the chamber decreases during the deposition process, the content of built-in hydrogen in the growing a-Si layer also decreases.

The built-in hydrogen starts to diffuse during the post-hydrogenation process at 370°C and affects the trap limited diffusion process. Initially, not only hydrogen which diffuses into the a-Si during the post-hydrogenation process will be trapped by unsaturated defects. The defects will also trap the built-in hydrogen, results in a co-diffusion process. This co-diffusion lowers the total hydrogen diffusion velocity, as traps are already occupied. As a consequence the model overestimates the hydrogen concentration. This can be seen in Fig. 4 for most of the predicted profile of the 1 min/nm post-hydrogenated sample as well as for the depth between 80–170 nm of the 3 min/nm post hydrogenated sample (\bullet).

The built-in hydrogen spreads within the a-Si layer during post-hydrogenation and the process of co-diffusion mitigates. As a consequence, the trap limited diffusion process is lowered and long-time post-hydrogenated samples are not affected by the co-diffusion of built-in hydrogen, Fig. 4.

In order to accurately predict hydrogen depth profiles in a-Si after short post-hydrogenation times, the initial built-in hydrogen concentration has to be taken into account. As discussed in Section 3.1, the offset value b_H of Eq. (6) is affected by H_0 . Moreover, Eq. (6) is used to estimate further values of the hydrogen concentration at the a-Si/c-Si interface (H_i), Section 3.6. Therefore, H_0 has to be considered ($b_H = H_i - H_0$) by extrapolating H_i to the point $H_i|_{H_i=0}$.

Considering H_0 yields a more precise prediction of the hydrogen depth profile of the 1 min/nm post-hydrogenated a-Si film, Fig. 4 (---). Moreover, the predicted profile of the 3 min/nm post-hydrogenated a-Si layer becomes more accurate in the depth from 80–170 nm.

5 Simplification Deviation between the experiment and the model based prediction of hydrogen depth profiles is due to non-uniform distribution of the initial built-in hydrogen H_0 . A modification of the RFSD process leading to truly hydrogen-free a-Si could allow the omission of the FTIR measurement of H_0 . Such samples can be achieved by thorough drying before RFS-deposition of a-Si.

Based on Fig. 1, it can be deduced that the gradient g_H can be determined from the hydrogen concentrations of only two different long-time post-hydrogenated sample. One of these can be calculated from one NRRA-measured hydrogen depth profile. The second concentration can be determined by FTIR spectroscopy. Therefore, it is possible to reduce the measurement efforts to a minimum of only one NRRA and one FTIR measurement.

6 Conclusions For a model based prediction of hydrogen depth profiles in trap limited afflicted amorphous silicon, an approach using the general diffusion equation is sufficient. While the depth profile of diffused hydrogen can be described by a complementary error function, the required parameters still have to be estimated. The model presented and validated herein allows to determine the *a priori* missing parameters and to predict any number of hydrogen depth profiles. The model may be simplified to allow reducing the experimental effort to just one NRRA measured hydrogen depth profile and one FTIR measurement.

The proposed model for the prediction of hydrogen depth profiles allows a more accurate design of experi-

ments, prevents misinterpretations, avoids unnecessary measurements of hydrogen depth profile and thus saves time and costs.

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