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

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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 (NRRA) 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 NRRA 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 NRRA analysis. A model based prediction of hydrogen depth profiles based on a single NRRA 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 NRRA 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 frequency 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 NRRA [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 Ω cm, 250 μm, (100) 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 °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) 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 layer related to the thickness (d_{film}) the effective absorption coefficient (α_{eff}) can be obtained by FTIR measurements, Eqs. (1) and (2) [11]:

\[ A_{film} = A_{total} - A_{carrier/substrate}, \]  
\[ α_{eff} = \frac{A_{film}}{d_{film} \cdot \log_{10} e}. \]

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 bonds, according to Eq. (4) [11]:

\[ I_{ω} = \int α(ω) dω, \]  
\[ N_{H} = c_{2000} \cdot I_{2000} + c_{2090} \cdot I_{2090}. \]

The coefficients are: c_{2000} = 9 × 10^{19} cm⁻² for Si–H bonds and c_{2090} = 2.2 × 10^{20} cm⁻² for Si–H₂ bonds.

Hydrogen bond structures of RFS-deposited 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]:

\[ ^{15}\text{N} + ^{1}\text{H} \rightarrow ^{12}\text{C} + ^{4}\text{He} + γ(4.43 \text{ MeV}). \]

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 cm³ can be determined. Considering the atomic density of silicon of ~5 × 10²² atoms/cm³ [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 bonds are formed. The hydrogen can leave these Si–H bonds, move and reform in new Si–H bonds. This ongoing process leads to a continuous motion of hydrogen within the a-Si. The more the defects are saturated 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 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 bonds.

Figure 1 shows the total hydrogen concentration (\text{F}_{\text{H}}(t)) 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):

\[ \text{F}_{\text{H}}(t) = g \cdot \ln(t) + b, \]
The overall hydrogen concentration \( H \) increases gradually with time \( t \) 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]:

\[
H_s(x_i) = H_i \cdot \text{erfc} \left( \frac{x_i}{2 \sqrt{D_H \cdot t_i}} \right).
\]

The parameters of Eq. (7) are the depth dependent hydrogen concentration \( (H_s) \), the hydrogen concentration at the surface of the a-Si film \( (H_s) \), the depth of the calculated hydrogen concentration \( (x_i) \), the diffusion coefficient of hydrogen within the a-Si \( (D_H) \) and the time of treatment \( (t_i) \). In this context \( t_i \) 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]:

\[
H_s(x_i) = H_i + (H_s - H_i) \cdot \text{erfc} \left( \frac{x_i}{2 \sqrt{D_H \cdot t_i}} \right).
\]

### 3.2 Model based prediction

Only two of the parameters of Eq. (8) are \textit{a priori} known \( (x_i, b_H) \). The other parameters have to be determined by the model for estimating hydrogen depth profiles.

### 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 RFSD 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 \( (e.g. t_i = 400 \text{ min}/\text{nm}) \) 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

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**Figure 1** Evaluation of the total hydrogen concentration \( (\bullet) \) 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 \( H_i \).

**Figure 2** Process flow-chart of the model based estimation of hydrogen depth profiles as well as required experimental inputs.
The amount of hydrogen in the layer increases [3, 4]. The gradients required parameters can then be directly read from the measured profile. The fusion coefficient can be calculated using Eq. (8). The measured by NRRA. Based on this profile the specific diffusion coefficient can be extrapolated, Fig. 1.

Figure 3 visualizes the prediction of further DH values for several post-hydrogenation timespans, based on experimental determined by NRRA. Further, Fig. 4 shows the respective model based predictions of the hydrogen concentration at the a-Si/c-Si interface (H0), Eq. (10):

\[
D_H \ln(t_i) + b_0 = D_H(t_i). \tag{9}
\]

To determine the offset value \( b_0 \) one single hydrogen depth profile of a post-hydrogenated a-Si layer has to be measured by NRRA. 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 \( g_0 \) and \( g_D \). The gradient of the diffusion coefficient \( g_0 \) can be deduced from the gradient of the hydrogen concentration \( g_D \), Eq. (10):

\[
g_D = -\ln(g_0). \tag{10}
\]

Figure 3 visualizes the prediction of further \( D_H \) values \( \bullet \) 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 \( g_0 \) further values of \( H_i \) can be extrapolated, Fig. 1. The needed offset value \( b_0 \) can be experimentally determined based on the one measured hydrogen depth profile \( H_i = H_0 \), Fig. 1.

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 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 NRRA. 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 trap limited diffusion process will be trapped by unsaturated defects. The defects will also trap the built-in hydrogen, resulting 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 \( h_0 \) 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 \( (H) \), Section 3.6. Therefore, \( H_0 \) has to be considered \( (b_H = H_1 - H_0) \) by extrapolating \( H \) to the point \( H_{H_0} = 0 \).

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

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