



E-MRS Spring Meeting 2015 Symposium C - Advanced inorganic materials and structures for photovoltaics

About nuclear resonant reaction analysis for hydrogen investigations in amorphous silicon

Sebastian Gerke^{a,*}, Hans-Werner Becker^b, Detlef Rogalla^b,
Giso Hahn^a, Reinhart Job^c, Barbara Terheiden^a

^aUniversity of Konstanz, Department of Physics, 78457 Konstanz, Germany

^bRUBION - Central Unit for Ion Beams and Radioisotopes, University of Bochum, Universitätsstraße 150, 44780 Bochum, Germany

^cMünster University of Applied Sciences, Department of Electrical Engineering and Computer Science, Stegerwaldstraße 39, 48565 Steinfurt, Germany

Abstract

Nuclear Resonant Reaction Analysis (NRRA) is a common method detecting the near-surface hydrogen distribution of a sample in a depth of up to a few microns. The mass density and related stopping power of a hydrogenated amorphous silicon (a-Si:H) layer depends on the hydrogen content. Correct hydrogen depth profiles are calculated considering the effective ion beam stopping cross-section as well as the related stopping power of the investigated film. The consideration of the local hydrogen concentration is important to avoid misinterpretations of the hydrogen distribution regarding profile depth. Therefore, stopping powers have to be considered carefully when interpreting hydrogen depth profiles especially of films that exhibit variations in hydrogen concentration. Moreover, further investigations like morphology dependent changes of the effective stopping-cross section are not possible without correctly calculated hydrogen depth profiles. Here the correct way is presented how to consider the embedded hydrogen of an a-Si:H layer when calculating absolute depth information of a NRRA measured hydrogen depth profile.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of The European Materials Research Society (E-MRS)

Keywords: a-Si; density; hydrogen depth profiling; NRRA; stopping cross-section; stopping power;

* Corresponding author. Tel.: +49-7531-88-2132; fax: +49-7531-88-3895.
E-mail address: sebastian.gerke@uni-konstanz.de

1. Introduction

Nuclear Resonant Reaction Analysis (NRRA) allows determining hydrogen depth profiles [1-4]. NRRA by using ^{15}N nitrogen isotopes, also known as ^{15}N profiling technique, is based on a nuclear reaction of ^{15}N isotopes (^{15}N) with hydrogen atoms in a matrix, e.g. crystalline silicon (c-Si) [5].

Several publications report the application of the ^{15}N technique to amorphous silicon (a-Si) and related amorphous layers like silicon nitride (SiN) [6-11]. The standard graphic account is to state the hydrogen content in relation to the energy of the ^{15}N ion beam [6, 10, 11]. Calculating absolute depth information has to consider the stopping power of the matrix (e.g. c-Si).

In literature it is mentioned that the hydrogen content in the matrix hardly affects the stopping power and could be neglected for calculating absolute depth values [12]. For a detailed investigation of a-Si:H/c-Si heterojunctions or multi-layer stacks this general statement needs to be precised. Rather an augmented hydrogen depth profiling is necessary to avoid misinterpretations by analyzing the hydrogen distribution at a-Si:H/c-Si interfaces or to determine the exact position of an interlayer in a multi-layer stack.

2. Sample preparation and experimental conditions

The here investigated (i) a-Si:H layers are plasma-enhanced chemical vapor deposited (PECVD) using a PlasmaLab 100 direct plasma reactor from Oxford Instruments. For the experiments phosphorous doped chemically polished float-zone (FZ) silicon wafers (c-Si) are used (n-type, $\sim 5 \Omega\text{cm}$). Native oxide on the surface of the c-Si wafers is chemically removed in diluted hydrogen fluoride (HF) directly before PECV-deposition [13].

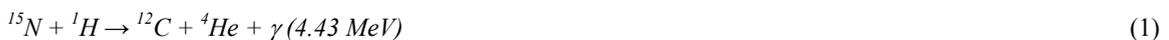
Hydrogen depth profiling by NRRA is performed for a columnar (i) a-Si:H single layer with homogenous hydrogen profile, as well as at an (i) a-Si:H multi-layer stack consisting of different hydrogenated layers. For the second case, a columnar layer is covered by a non-columnar layer providing a “nano-porous” fast grown base-layer with a higher hydrogen content. More information about the deposition parameters, the morphologies, the fast-grown-layer (FGL) and the multi-layer stack are given in Refs. [7, 8, 14].

The layer thickness of the (i) a-Si:H single layer is additionally determined by ellipsometry using a J. A. Woollam V-Vase 2000 ellipsometry unit [9].

2.1. Nuclear resonant reaction analysis

NRRA-analysis is performed at the RUBION laboratories at the RuhrUniversity in Bochum (Germany) using a Dynamitron tandem accelerator [15]. As mentioned, the here used profiling technique by NRRA is based on ^{15}N isotopes.

As described in Ref. [16], ^{15}N isotopes are accelerated towards the sample and react with hydrogen atoms. The nuclear reaction of a ^{15}N isotope and a proton results in a carbon (^{12}C) and a helium (^4He) isotope. In addition, a detectable γ -ray with energy of 4.43 MeV is emitted [4, 5, 16]. The full reaction equation reads:



Counting γ -rays of a sample and adjusting them to the background radiation 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 [17]. From this comparison the content of hydrogen atoms per cm^3 can be determined. Considering the atomic density of silicon of $\sim 5 \cdot 10^{22} \text{ atoms/cm}^3$ [18], the hydrogen concentration can be calculated [7-9].

Moreover, the reaction energy is an isolated and very narrow resonance at beam energy of 6.385 MeV [5]. An increase of the beam energy enables measuring a hydrogen depth profile. Accelerated ^{15}N isotopes slow down in the matrix achieving the resonant energy for nuclear reaction deeper in the sample. Knowing the stopping power of the matrix material, a hydrogen profile with absolute depth information can be deduced from the measurement [7].

3. Augmented hydrogen depth profiling

The relationship between the absolute depth of the nuclear reaction (d_{NRR}) and the energy of the ^{15}N ion beam (E_{ib}) is the stopping power (sp) of the matrix (eq. 2). Referred to literature, the stopping power of a matrix of pure silicon is 1.387 keV/nm [16].

$$d_{NRR} = \frac{E_{ib}}{sp} \tag{2}$$

If the matrix consists of other elements the stopping power could change. In case of hydrogen content in the matrix, it is mentioned in literature that the effect on stopping power can be neglected [11]. As mentioned in section one, this general statement is not applicable to the here investigated samples.

The stopping power itself depends on the atom density (ρ) and the effective stopping cross-section (scs_{eff}) of the matrix (e.g. c-Si) [1-3]

$$sp = \rho_{Si} \cdot scs_{eff} \tag{3}$$

The effective stopping cross-section results from the ratio between the stopping cross-section of all substances in the sample. For the here investigated (i) a-Si:H layers it can be assumed that hydrogen (N_{mH}) and the Si (N_{mSi}) are the only atoms in the layer. In this case N_{mSi} can be calculated as [8, 19]

$$N_{mSi} = 1 - \left(\frac{N_{c-Si}}{N_{mH}} \right) \tag{4}$$

considering the atomic density of c-Si $N_{c-Si} \approx 5 \cdot 10^{22}$ at./cm³. scs_{eff} (eq. 5) is calculated by weighing the measured hydrogen content in the matrix (N_{mH}) with scs of hydrogen ($scs_H = 60.9 \cdot 10^{-15}$ eV/(at./cm²)) and compare it with the scs of the Si-matrix ($scs_{mSi} = 279 \cdot 10^{-15}$ eV/(at./cm²)) [8, 20].

$$scs_{eff} = N_{mH} \cdot scs_H + N_{mSi} \cdot scs_{mSi} \tag{5}$$

Fig. 1 shows the calculated hydrogen-related changes in the stopping power and the atomic density of a silicon matrix in the range of 3...9% of hydrogen.

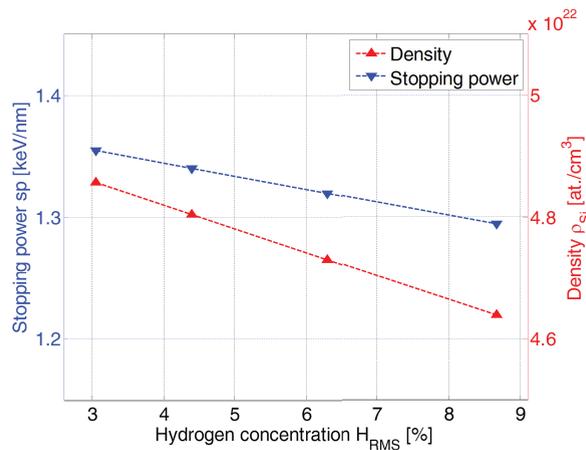


Fig. 1. Stopping power and atomic density of a silicon matrix as a function of the mean hydrogen concentration.

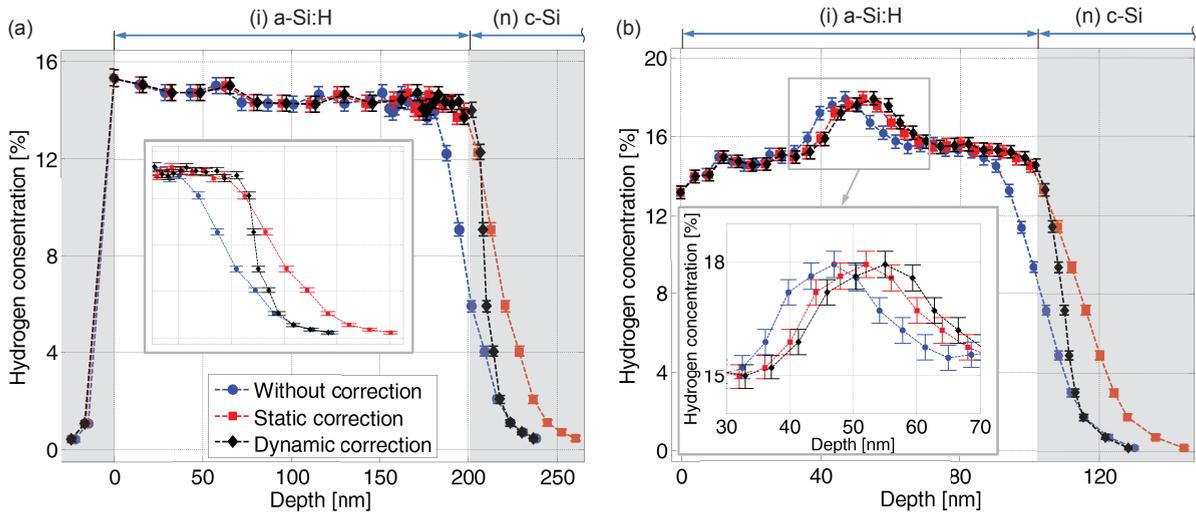


Fig. 2. Hydrogen depth profiles of an (i) a-Si:H single layer (a) and an (i) a-Si:H multi-layer stack (b). Depth information calculated from the stopping power without correction, with static correction and dynamic correction of the hydrogen content of the layers.

The hydrogen depth profiles with absolute depth information of an (i) a-Si layer (a) as well as of an (i) a-Si:H multi-layer stack (b) are shown in Fig. 2. The displayed graphs represent in each case (Fig. 2, a or b) the same NRR-measured data, but differ in the way the absolute depth of the nuclear reaction (d_{NRR}) is calculated.

The first profile (●) is calculated without considering any hydrogen content in the Si-matrix using $scs_{eff} = scs_{mSi}$ leading to $sp = sp_{Si} = 1.387$ keV/nm. Further Fig. 2 shows hydrogen depth profiles calculated with static (■) and dynamic (◆) correction of the hydrogen induced affect to scs_{eff} and related sp . While the static correction (■) considers the average hydrogen concentration of the samples

- single layer: $H_{RMS} = 11.1\% \rightarrow sp = 1.268$ keV/nm,
- multi-layer stack: $H_{RMS} = 12.8\% \rightarrow sp = 1.249$ keV/nm,

the dynamic correction considers the local hydrogen concentration in each measured data point and its influence to the stopping cross-section respectively to the related stopping power (eq. 1...5).

As can be seen in Fig. 2 (a and b) there are misinterpretations in the depth of the (i) a-Si:H/c-Si heterojunctions in the hydrogen depth profiles calculated without correction (●).

In more detail, starting with Fig. 2 (a), the thickness of the (i) a-Si:H single layer is ~ 201 nm determined by ellipsometry measurements. The underestimation of the hydrogen depth profile calculated without correction (●) is in this case ~ 20 nm.

The static correction (■) making use of the average hydrogen content ($H_{RMS} = 11.1\%$) for calculating scs_{eff} (eq. 5) and the related value of sp (eq. 3) leads to more precise a hydrogen depth profile with respect to layer thickness. Only a small deviation in thickness of the (i) a-Si:H layer of ~ 4 nm is left. The more significant disadvantage of this static correction is the overestimation of low hydrogen contents. As can be seen in Fig. 2 (a) there is a gap of about 18 nm in the transient region between the uncorrected (●) and the statically corrected graph (■). The transient region corresponds to the area between the (i) a-Si:H/c-Si interface and the c-Si bulk where the hydrogen concentration decreases.

Only the dynamic correction, considering the hydrogen concentration of each measured and displayed data point, allows to determine a correct profile (◆). The (i) a-Si:H/c-Si interface of the hydrogen depth profile (◆) based on a dynamic correction of sp can be specified to ~ 202 nm. Furthermore, it can be seen in the inset in Fig. 2 (a) that in the transient region the trend of the dynamic corrected profile (◆) converge to the uncorrected one (●) which shows that neglecting the hydrogen content for the determination of sp (eq. 3) is only appropriate for low hydrogen content.

In this context it should be mentioned that according to Fick's law the diffusion coefficient is i.a. a function of the concentration gradient [21]. For such investigations as discussed in Ref. [9] a dynamic consideration of the hydrogen concentration is mandatory to get true values.

The analysis of an (i) a-Si:H multi-layer stack (Fig. 2, b) shows the same results with respect to thickness of the stack and the true position of the heterojunction. Only the dynamically corrected hydrogen depth profile (◆) displays correct conditions in the transient region in the c-Si, behind the (i) a-Si:H/c-Si interface.

Moreover, the inlet in Fig. 2 (b) shows the hydrogen depth profile through the hydrogen rich fast-grown interlayer of the multi-layer stack. As can be seen the graphs diverge to each other. The difference in peak position of the uncorrected graph (●) and the dynamical corrected one (◆) is ~9 nm.

The static corrected graph (■) considers an average hydrogen content of $H_{RMS} = 12.8\%$. This yields, according to the equations above, a stopping power of $sp = 1.249$ keV/nm. However, the related stopping power to the hydrogen content of the interlayer of $H_{max} \approx 18\%$ is $sp = 1.195$ keV/nm. In consequence the static correction underestimates the hydrogen content and the related graph (■) deviates from the dynamically corrected one (◆) (inlet in Fig. 2, b).

4. Conclusions

NRR-analysed hydrogen depth profiles of a-Si:H layers can be displayed with absolute depth information. The calculation of the absolute depth should consider the hydrogen based influence to the stopping power of the film and the related ion beam stopping cross-section. A misinterpretation of the hydrogen content at the a-Si:H/c-Si heterojunction and its position can only be avoided by a dynamic consideration of the hydrogen concentration of each measured data point.

For the investigation of multi-layer stacks consisting of different hydrogenated a-Si:H layers, a dynamic correction of the hydrogen related stopping power is mandatory to get true depth information of the position of the fast-grown interlayer.

Acknowledgements

Part of this work was supported by the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (FKZ 0325581). The content is the responsibility of the authors.

References

- [1] Imbriani G, deBoer RJ, Best A, Couder M, Gervino G, Görres J, LeBlanc PJ, Leiste H, Lemut A, Stech E, Strieder F, Uberseder E, Wiescher M. Measurement of γ rays $^{15}\text{N}(p,\gamma)^{16}\text{O}$ cascade and $^{15}\text{N}(p,\alpha,\gamma)^{12}\text{C}$ reactions. *Phys Rev C* 2012;85:065810.
- [2] Rolfs C, Rodney WS. Proton capture by ^{15}N at stellar energies. *Nucl Phys A* 1974;235:450-94.
- [3] Wilde M, Fukutani K. Hydrogen detection near surfaces and shallow interfaces with resonant nuclear reaction analysis. *Surf Sci Rep* 2014;69:196-295.
- [4] Lanford WA. ^{15}N Hydrogen Profiling: Scientific Applications. *Nucl Instrum Methods* 1978;149:1-8.
- [5] Gall S. Admittanzspektroskopische Untersuchungen des a-Si:H/c-Si Heteroüberganges im Hinblick auf photovoltaische Anwendungen. PhD thesis Hahn-Meitner-Institut. Technical University of Berlin. Berlin; 1997.
- [6] Gerke S, Becker H-W, Rogalla D, Hahn G, Job R, Terheiden B. Investigation of hydrogen dependent long-time thermal characteristics of PECV-deposited intrinsic amorphous layers of different morphologies. In: *Proc 29th EU PVSEC, Amsterdam 2014*, p 9-12.
- [7] Gerke S, Becker H-W, Rogalla D, Hahn G, Job R, Terheiden B. Morphology and hydrogen in passivating amorphous silicon layers. *En Proc* 2015;accepted for publication.
- [8] Gerke S, Becker H-W, Rogalla D, Singer F, Brinkmann N, Fritz S, Hammud A, Keller P, Skorka D, Sommer D, Weiß C, Flege S, Hahn G, Job R, Terheiden B. Influence of post-hydrogenation upon electrical, optical and structural properties of hydrogen-less sputter deposited amorphous silicon. Submitted to *Thin Solid Films (TSF-S-15-00827)*, April 2015.
- [9] Joos S, Wilking S, Schiele Y, Herguth A, Heß U, Seren S, Terheiden B, Hahn G. Hydrogen in stacked dielectric layers. In: *Proc 28th EU PVSEC, Paris 2013*. p 1113-16.
- [10] Joos S, Schiele Y, Terheiden B, Becker H-W, Rogalla D, Hahn G. Fundamental studies of hydrogen at the silicon / silicon nitride interface. *En Proc* 2014;55:786-90.
- [11] Schatz G, Weidinger A. *Nukleare Festkörperphysik*, Vol. 293. B. G. Teubner, Stuttgart; 1997.
- [12] Gerke S, Hahn G, Job R, Terheiden B. Bias-plasma assisted RF magnetron sputter deposition of hydrogen-less amorphous silicon. Submitted to *En Proc*, May 2015.
- [13] Gerke S, Herguth A, Brinkmann N, Hahn G, Job R. Evaluation of capacitance-voltage spectroscopy by correlation with minority carrier lifetime measurements of PECVD-deposited intrinsic amorphous layers. In: *Proc. 28th EU PVSEC, Paris 2013*, p 2600-3.

- [14] Hanley PR, Cleland MR, Mason CF, Morganstern KH, Thompson CC. The Tandem Dynamitron. *IEEE T Nucl Sci* 1969;16:90-5.
- [15] Danesh P, Pantchev B, Antonova K, Liarokapis E, Schmidt B, Grambole D, Baran J. Hydrogen bonding and structural order in hydrogenated amorphous silicon prepared with hydrogen-diluted silane. *J Phys D Appl Phys* 2004;37:249-54.
- [16] Reinholz U, Weise H-P, Brzezinka K-W, Bremser W. Zertifizierungsbericht BAM-S110. Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin; 2004.
- [17] Fahrner WR, Mühlbauer M, Neitzert HC, Fisher D, Agarwala RP. Silicon Heterojunction Solar Cells. Trans Tech Publications, Zürich; 2006.
- [18] Ziegler JF. Handbook of Stopping Cross Sections for Energetic Ions in All Elements. Pergamon Press, New York; 1980.
- [19] Rudolph W, Bauer C, Brankoff K, Grambole D, Grötzschel R, Heiser C, Herrmann F. Plastic foils as primary hydrogen standards for nuclear reaction analysis. *Nucl Instrum Methodes B*1986;15:508-11.
- [20] Street RA, Cahn RW, Davis EA, Ward IM. Hydrogenated amorphous silicon. Cambridge University Press. Cambridge; 1991.
- [21] Becker H-W, Bahr M, Berheide M, Borucki L, Buschmann M, Rolfs C, Roters G, Schmidt S, Schulte WH, Mitchell GE, Schweitzer JS. Hydrogen depth profiling using ^{18}O ions. *Z Phys A* 1995;351:453-65.