

INVESTIGATION OF HYDROGEN DEPENDENT LONG-TIME THERMAL CHARACTERISTICS OF PECV-DEPOSITED INTRINSIC AMORPHOUS LAYERS OF DIFFERENT MORPHOLOGIES

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ABSTRACT: Hydrogenated intrinsic amorphous silicon ((i) a-Si:H) layers deposited on n-type crystalline silicon (c-Si) by plasma enhanced chemical vapour deposition (PECVD) are investigated during long-time thermal treatment (100 h at 200°C) with regard to the depth profile of hydrogen in the a-Si layer and its diffusion into the c-Si bulk. The morphology of the (i) a-Si:H is manipulated by the PECVD process parameters. A columnar and a non-columnar growth can be distinguished. Microscopic investigations are carried out by scanning electron microscopy (SEM). Minority carrier lifetime (τ_{eff}) measurements permit an evaluation of the surface passivation and thus the saturation of defects like dangling bonds at the (i) a-Si:H/c-Si interface. A non-columnar structure leads to a high stability of the passivation during thermal treatment of up to 100 h. In contrast a columnar structure of the amorphous silicon layer results in a better but less stable passivation of the c-Si wafer surface. Microvoids in the columnar layer are the reason for this behavior. Fourier transform infrared spectroscopy (FTIR) measurements confirm the formation of microvoids, i. e. a high concentration of Si-H₂ bonds. Investigating the changes in hydrogen depth profile by nuclear resonant reaction analysis (NRRA) reveals a higher loss in hydrogen concentration during thermal treatment of the (i) a-Si:H layers with columnar morphology. The hydrogen concentration profiles as measured by NRRA illustrate the dependency of passivation quality with time on the specific morphology of different amorphous layers.

Keywords: a-Si:H, hydrogen concentration profiles, NRRA, FTIR, Lifetime, SEM

1 INTRODUCTION

Silicon (Si) heterojunction solar cells using hydrogenated amorphous silicon (a-Si:H) in combination with crystalline silicon (c-Si) offers promising features like a high open-circuit voltage (Voc) and thus very high efficiencies [1]. To enhance this, an intrinsic interlayer (i) a-Si:H between the doped (p/n) a-Si:H layer and the wafer is favourable to reduce interface defect density [1].

Plasma-enhanced chemical vapour deposition (PECVD) is a common way to grow an a-Si:H layer on c-Si [2, 3]. Caused by formation of discontinuities like dangling bonds or voids, the (i) a-Si:H/c-Si interface is not defect-free. An enhancement of passivation quality can be achieved by a subsequent defect annealing step while the bonding structure is reorganized and mainly dangling bonds are passivated by hydrogen [2-6]. The mobility of hydrogen is related to temperature while too high temperatures deteriorate the passivation quality [2]. Therefore, common temperatures for the defect annealing step in PV applications are ~300°C [1, 2]. However, hydrogen diffusion in (i) a-Si:H already sets in at temperatures ~200°C [5, 6].

As mentioned in [4], hydrogen-rich microvoids created during deposition affect the long-time passivation quality of (i) a-Si:H. Hydrogen effuses from microvoids and saturates defects in its vicinity [4, 6].

However, a detailed comparison of the long-time performance of (i) a-Si:H layers of different morphologies with regard to surface passivation is still missing up to now.

Running such investigations, (i) a-Si:H layers of different morphologies are PECV-deposited and investigated during thermal treatment for a duration of up to 100 h. The annealing is carried out at 200°C to slow down hydrogen diffusion within and effusion from the (i) a-Si:H layer.

Points of interest of the characterisation are:

- Microscopic investigation and growth rates: scanning electron microscope (SEM)

- Passivation quality: effective minority carrier lifetime (τ_{eff}) measurements by quasi steady state photoconductance (QSSPC)
- Bonding structure: Fourier transform infrared spectroscopy (FTIR) Raman investigations
- Hydrogen concentration profiles: nuclear resonant reaction analysis (NRRA)

2 SAMPLE PREPARATION

Morphology and thus formation of microvoids can be influenced by the deposition parameters [5, 6]. The morphology of (i) a-Si:H deposited using only silane (Si-H₄), results in a non-columnar growth which leads to a random structure resembling a loose sphere packing (Fig. 1). In contrast, the presence of argon during PECV-deposition yields a columnar, chain-like structure of the amorphous layer [5]. This is mainly caused by different sticking coefficients of the process gas, well explained in [5].

A low sticking coefficient of the gas yields a high surface mobility. Atoms are able to interact with the surface before attaching to the growing layer in their final position. This growth process allows covering the c-Si wafer surface conformally. If the gas has a high sticking coefficient, the surface mobility is low. This leads to a self-shadowing effect at the surface [5, 7]. Therefore, incoming atoms connect directly to other ones sticking out of the growing surface. In this way a columnar structure will be formed. The chains of the columnar structure also form branches (Fig. 1).

While a layer of non-columnar morphology contains mainly defects like voids, a layer of columnar morphology contains mainly defects like microvoids. In this context microvoids are aligned vacancies embedded between the chains of the columnar structure and their branches.

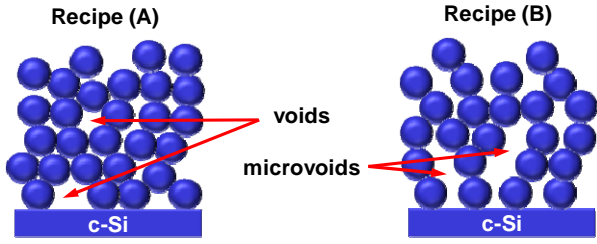


Figure 1: Illustration of different morphologies of a-Si:H according to [5] for adapted deposition conditions. Recipe (A) yields to a non-columnar structure containing voids and recipe (B) yields to a columnar structure containing microvoids.

Two different recipes are used in this study to deposit (i) a-Si:H layers of different structures. Recipe (A) is using only Si-H₄ and recipe (B) is composed of a Si-H₄/Ar mixture and additional hydrogen. The detailed parameters are listed in Tab. I.

For the experiments, phosphorous doped (n-type, 5-10 Ωcm, 250 μm, <100> oriented) chemically polished floatzone (FZ) silicon wafers (c-Si) are used. The native oxide is chemically removed in diluted hydrogen fluoride (HF) directly before (i) a-Si:H deposition. This deposition takes place in a PlasmaLab 100 direct plasma PECVD reactor from Oxford Instruments using the parameters listed in Tab. I.

Table I: PECVD parameters for the deposition of (i) a-Si:H layers of different morphologies.

Recipe	(A)	(B)
Si-H ₄	15 sccm	25 sccm
Ar	-	475 sccm
H ₂	-	25 sccm
rf power	50 W	10 W
Pressure	350 mTorr	1000 mTorr
Temperature	225°C	225°C
Time	5 min	5 min

Lower pressure and gas flow of recipe (A) yield to a higher mean free path length compared to recipe (B). Nevertheless, radio frequency (rf) power has to be increased to get stable plasma conditions for deposition.

3 EXPERIMENTS AND RESULTS

3.1 Microscopic investigation and growth rates

Thicknesses of PECV-deposited layers of different recipes (Tab. I) were determined by scanning electron microscopy (SEM), shown in Fig. 2.

During 5 min of deposition the layers grow up to 100 nm (recipe (A)) and 120 nm (recipe (B)). Based on the thicknesses, the different growth rates can be calculated. While layers deposited with recipe (A) grow at ~20 nm/min, recipe (B) leads to a 20% higher growth rate of ~24 nm/min.

This difference in growth rate is due to the respective morphology as well as hydrogen etching due to higher hydrogen content during deposition using recipe (A) [4, 5]. In more detail, the non-columnar a-Si:H of recipe (A) grows more slowly because silicon atoms have to find a place in the random structure, while for the columnar one (recipe (B)) silicon atoms only have to connect to a chain or a branch [5]. Furthermore, the proportionally higher content of hydrogen in recipe (A) leads to breaking up of weak Si-Si bonds during deposition. This additionally reduces the growth rate [4, 5].

SEM investigations are also carried out for microscopic comparison of the different layers.

As can be seen in Fig. 2 the non-columnar structure deposited using recipe (A) leads to a smooth surface of the cross section even difficult to distinguish from the c-Si bulk. However, the cross-section of the columnar structure shows a rough surface. Not the obvious big cracks are important in this aspect but rather the tiny fractures (red arrows).

These differently broken edges support the findings of the growth rate study taking into account references [5, 8], that recipe (A) generates non-columnar and recipe (B) columnar morphologies.

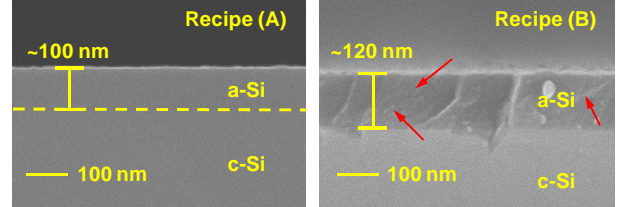


Figure 2: Cross-section surfaces of different PECV-deposited (i) a-Si:H layers. The roughness is an indicator for morphological differences in the growth of the layers. Also differences in the growth rate itself allow drawing a conclusion about the kind of morphology.

3.2 Passivation quality

The lifetime samples are placed on a hotplate at $200 \pm 2^\circ\text{C}$ in ambient air for thermal treatment. In order to track the degree of curing (and degradation afterwards), the effective minority carrier lifetime (τ_{eff}) of the samples is measured at room temperature via transient photo conductance decay (QSSPC, WCT 120, Sinton Instruments).

Results of τ_{eff} measurements at an injection level of $\Delta n = 1.0 \cdot 10^{15} \text{ cm}^{-3}$ are shown in Fig. 3.

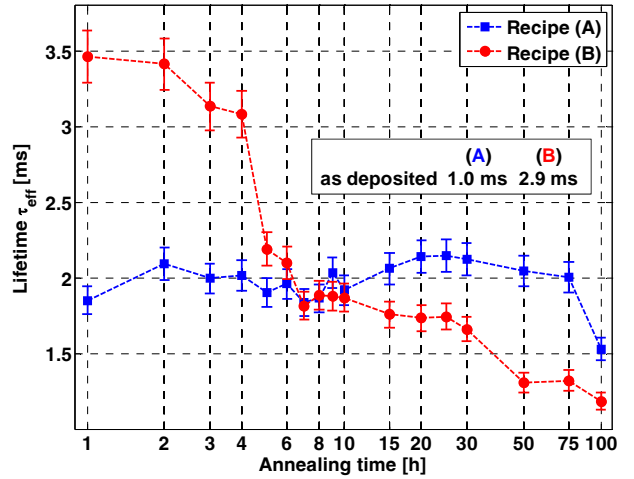


Figure 3: Evolution of τ_{eff} for long-time thermal treatment of PECV-deposited (i) a-Si:H layers of different morphologies. Lines are guides to the eye.

Minority carrier lifetimes of wafers passivated with (i) a-Si:H layers deposited by each of the recipes rises like expected [4] within the first time of thermal treatment to their respective maximum values (not shown in Fig. 3). Fig. 3 shows the further evolution of τ_{eff} for long-time annealing up to 100 h. Effective minority carrier lifetime of recipe (A) (blue squares) varies between 1.8 ms and 2.2 ms and decreases only after 75 h of thermal treatment. Passivation quality of recipe (B) (red circles) is much higher directly after deposition, also listed in Fig. 3. Furthermore, τ_{eff} of wafers passivated by (i) a-Si:H layers of recipe (B) (columnar)

decreases continuously showing the same lifetime as those of recipe (A) after 10 h of annealing and decreasing further down to ~ 1.2 ms after 100 h.

The different trends in τ_{eff} of c-Si wafers passivated by the two recipes could result from the different morphologies of the (i) a-Si:H layers. In both layers defects are saturated by hydrogen within the first time of thermal treatment [4]. It is conceivable that due to different morphologies generated by the different deposition parameters of the two recipes (A) and (B) curing and long-time behaviour is affected.

The random structure of the layer deposited using recipe (A) exhibits more defects like voids while the chain-like structure (recipe (B)) supports formation of defects like microvoids. Hydrogen embedded in the microvoids effuses during thermal treatment and saturates defects in the vicinity [4]. This yields high τ_{eff} values at the beginning of annealing. It can be expected that with time more and more hydrogen effuses along the chain parts, leaving unsaturated defects like dangling bonds. In contrast, the hydrogen contained in the layer deposited using recipe (A) has to diffuse through the random, non-columnar bonding structure. This hampers on the one hand side saturation of defects on the other hand effusion of hydrogen out of the layer is slowed down.

3.3 Bonding structure

To get further information of the hydrogen content, the bonding structure of the (i) a-Si:H layers is analysed by Fourier Transform Infrared spectroscopy (FTIR) using a Vertex 80 FTIR spectrometer from Bruker Optics. Evaluation of FTIR spectroscopy is carried out according to the method described in [9].

Discrimination between different types of silicon-hydrogen bonds is also provided by FTIR investigation. Monohydride (Si-H) bonds have a vibration mode at a wavenumber of 2000 cm^{-1} and polyhydride (Si-H₂) bonds at 2090 cm^{-1} [9, 10]. According to Pankove *et al.* a higher Si-H₂ content could indicate formation of hydrogen rich microvoids in the layer [6].

The measured Si-H₂ bond ratio (Tab. II) for the amorphous silicon layer deposited according to recipe (A) (non-columnar) is nearly 50%. In contrast, the Si-H₂ bond ratio measured at a columnar layer (recipe (B)) is significantly higher ($\sim 65\%$).

Table II: Comparison of Si-H₂ concentration referring to the total amount of silicon-hydrogen bonds (Si-H + Si-H₂) for long-time annealing.

Recipe	(A)	(B)
Si-H ₂	$\sim 50\%$	$\sim 65\%$
Si-H + Si-H ₂		

The converse argument of the values denoted in Tab. II is a higher amount of Si-H bonds in the non-columnar layer (recipe (A)). But according to Das *et al.* the passivation quality of amorphous silicon is only weakly dependent on the silicon-hydrogen bonding structure itself [11].

A correlation between the effective minority carrier lifetime and changes in total amount of silicon hydrogen bonds (Si-H + Si-H₂) during thermal treatment investigated by FTIR measurements is not obvious within measurement accuracy.

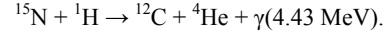
Complementary Raman investigations in accordance with [12] by using a "WITec alpha300" with a laser wavelength of 532 nm and a 50x zoom lens have shown that there is no indication of molecular hydrogen (H₂) inside the voids or microvoids. The specific hydrogen mode at a Raman shift of

$\sim 4160\text{ cm}^{-1}$ was not detectable within measurement accuracy. This suggests that all embedded hydrogen is connected in silicon-hydrogen bonds.

3.4 NRRA hydrogen concentration profiles

Investigating a hydrogen containing layer by ¹⁵N profiling technique yields hydrogen concentration profiles showing the depth dependent content of hydrogen [13].

The nuclear resonance reaction analysis (NRRA) called method is based on γ -rays arising from nuclear reaction of an accelerated nitrogen (¹⁵N) isotope reacting with a hydrogen atom to a carbon (¹²C) and a helium (⁴He) isotope [13]. The energy of the resonance reaction is 6.385 MeV and the energy of the yielded γ -rays is 4.43 MeV. However, the reaction equation according to [13] reads:



The depth of the measurement is related to the stopping energy of $\sim 1.3\text{ keV/nm}$ inside silicon. Hence a variation of the beam energy allows an excitation of the nuclear resonant reaction in a certain depth and the hydrogen profile can be measured. The final calculation of hydrogen concentration is carried out based on the atomic density of silicon of $\sim 5 \cdot 10^{22}\text{ atoms/cm}^3$ [14].

The presented measurements were carried out using a dynamitron tandem accelerator [15] located at the RUBION laboratories at the Ruhr- University of Bochum.

As shown in Fig. 2 thicknesses of the NRRA analyzed (i) a-Si:H layers were $\sim 100\text{ nm}$ for the non-columnar (recipe (A)) and $\sim 120\text{ nm}$ for the columnar (recipe (B)) layer.

The investigation displays that hydrogen concentrations for both recipes are quantitatively in the same range at around 12%...14%, Fig. 4. This is a little bit more than in the reference material BAM-S110 [16] which is used for calibration of the detector.

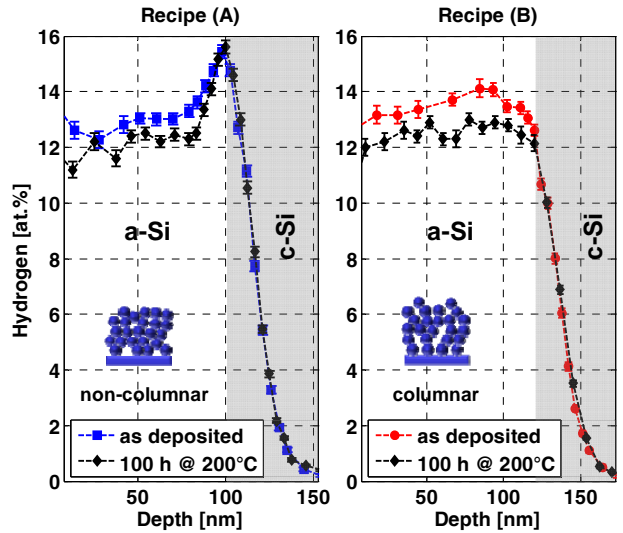


Figure 4: NRRA hydrogen concentration profiles of PECV-deposited (i) a-Si:H layers of different morphologies, measured directly after deposition and after 100 h of thermal treatment at 200°C. Lines are guides to the eye.

Furthermore, hydrogen depth profiles of (i) a-Si:H layers deposited by recipes (A) and (B) and their changes during annealing are quite different. Thermal treatment of a layer according to recipe (A) (Fig. 4, left) does not have large influence on the hydrogen profile. After 100 h of annealing at 200°C (black profile) the profile is not very different from the one measured directly after deposition (blue profile). In contrast, the decrease in hydrogen content of the layer

deposited with recipe (B) all over the layer is significantly higher (Fig. 4, right). As expected, hydrogen can effuse along silicon chains of the columnar morphology more easily (recipe (B)) than through the random, non-columnar structure deposited using recipe (A). The nearly constant hydrogen content in the layer according to recipe (A) and the hydrogen effusion out of recipe (B) sample correlates well with effective minority carrier lifetime measurements described in section 3.2. While hydrogen content remains stable, τ_{eff} remains constant too (recipe (A)). However, τ_{eff} decreases when hydrogen content decreases.

Another obviously inherent difference is the peak of the hydrogen content for recipe (A) directly at the interface while the content of hydrogen embedded in the columnar structure increases more slowly having its maximum in front of the interface.

The peak caused by recipe (A) could indicate a higher number of hydrogen containing voids in the beginning of the layer near the interface. Additionally, it should be mentioned that the peak is also stable during long-time thermal treatment. Brinkmann et al pointed out in [17] and even Gorgulla et al in [18] that there is a possibility of a significantly higher growth rate of a-Si:H layers at the beginning of PECV-deposition with parameters related to recipe (A). Silicon atoms locate earlier and void formation is supported in such a fast growing layer. At a later stage of deposition growth rate decreases and morphology becomes more compact. This leads to stable hydrogen content on a lower level.

Argon included in recipe (B) avoids such a significantly higher growth rate of a-Si:H in the beginning of deposition hence the obvious increase of hydrogen towards the interface is lower. Chains have to grow first before microvoids could arise and contain hydrogen on her part. However, at a later stage of growing branches arise and the microvoids became smaller Herby the amount of hydrogen embedded during deposition decreases.

4 DISCUSSION

Notable is that a much higher content of hydrogen directly at the (i) a-Si:H/c-Si interface of the non-columnar layer does not automatically yield better passivation than the non-columnar one (comparing Fig. 3 and 4). It must be assumed that the fast growing layer at the beginning of deposition (recipe (A)) supports not only the arising of voids but also of many defects like dangling bonds. Hydrogen will be mainly embedded in the voids and is not able to reach the defects. As can be seen in Fig. 3, hydrogen content at peak position does only decrease marginally during thermal treatment. This indicates that there is just a little hydrogen diffusion within and effusion from the peak area and only defects in the direct vicinity of the hydrogen get passivated. This compares on the one hand side to the stable passivation during thermal treatment. On the other hand it avoids better passivation of defects and due to this higher minority carrier lifetimes.

Compared to this the columnar layer itself is more permeable for the embedded hydrogen. Therefore defects could be better passivated at the beginning of thermal treatment. However, with ongoing treatment more and more hydrogen effuses out of the layer and passivation quality decreases.

5 CONCLUSIONS

Amorphous silicon layers of different morphologies (non-columnar and columnar) were PECV-deposited.

Their differences were investigated by SEM and FTIR characterization. SEM investigations have shown that different morphologies lead to differences in cross-section surfaces and the respective growth rate. FTIR measurements yield a significant higher Si-H₂ ratio of the columnar layer indicating formation of microvoids during deposition.

It could proven for the first time that there is a direct correlation in the long-time thermal characteristics between changes in passivation quality and the hydrogen depth profile according to the respective morphologies.

The effect of a fast growing, non-columnar layer at the (i) a-Si:H/c-Si interface on the amount of embedded hydrogen could be measured and its direct influence on passivation quality could be identified for the first time.

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