# In-situ study by Spectroscopic Ellipsometry of ETP-CVD a-Si:H

M. A. Wank, R. A. C. M. M. van Swaaij, and M. C. M. van de Sanden

*Abstract*—**We report on in-situ analysis of hydrogenated amorphous silicon (a-Si:H) deposited with the ETP-CVD method utilizing spectroscopic ellipsometry. The procedure to analyze the ellipsometry data is described in detail. The steps necessary to determine the dielectric function of the substrate and the bulk film are presented and fits of the dynamic data obtained in-situ during deposition for different temperatures are discussed. We observe similar trends for all substrate temperatures, but at different magnitudes. The lower the substrate temperature, the larger the final surface roughness layer thickness. Compared to other deposition methods, we obtain rougher surfaces at comparable temperatures. A continuous increase in surface roughness during the whole deposition is observed with a decreasing slope. Nucleation and smoothening could not be observed, contrary to other deposition methods, which is attributed to the significantly higher growth rates in our study. Finally, the measured dielectric function of a-Si:H is fit with two different parameterizations and the quality of the fits are compared both visually and utilizing the means square error (MSE). Cody-Lorentz delivers a better fit for dense material deposited at 300°C, at lower temperatures both Cody-Lorentz and Tauc-Lorentz parameterization deliver similar results.**

*Index Terms*—**ETP-CVD, hydrogenated amorphous silicon, spectroscopic ellipsometry**

## I. INTRODUCTION

In recent years Spectroscopic Ellipsometry (SE) has become a very popular method for thin-film analysis. Main advantage of SE is its non-destructive and non-invasive nature; hence the sample is not affected by the measurement in any way and can be reused for further studies. Furthermore it can be used in-situ, e.g., during fabrication or manipulation of the sample, and modifications of physical properties can be monitored in real-time. Multilayer-structures can be analyzed very accurately, providing information on:

- the depth profile of a multilayer structure
- the thickness, dielectric functions and composition of individual layers
- estimates of volume fractions of amorphous and crystalline material in each layer
- the presence of interlayers
- the presence of contaminant overlayers, like oxidized surface layers
- the thickness of a surface roughness layer
- the determination of the void volume fraction in a film utilizing the Bruggeman effective medium approximation
- the analysis of layers containing two materials with different dielectric functions, including volume fractions, also as a function of film thickness (graded layers)

A good overview of the development of spectroscopic ellipsometry was published by Vedam [1]. The first to apply ellipsometry as a tool to analyze thin films was Paul Drude in 1888 [2], who also derived the equations still in use today for the analysis of the data. It took until 1975 when Aspnes and Studna [3] were able to reduce the measurement time of a set of ellipsometric data for one wavelength by automating the previously manual process. Thus ellipsometric measurement could now be conveniently applied to a whole range of the visible electromagnetic spectrum, thus called spectroscopic ellipsometry. While their method still required consecutive measurements for each wavelength, parallel measurement of all wavelengths was the next breakthrough and also the starting point of spectroscopic ellipsometry as a broadly applied method. Parallel measurement was first introduced by Mueller and Farmer [4] and later refined by Kim, Collins and Vedam [5] in the early 1990s. The measurement time for a full spectrum was reduced to a few seconds, which enabled the application as Real-Time Spectroscopic Ellipsometry (RTSE). Nowadays RTSE can perform scans of the full visible electromagnetic spectrum; additionally, it can be extended into the IR or UV wavelengths, with measurement times in the millisecond range for a full scan.

Results of in-situ RTSE on thin-film growth of sputtered amorphous silicon (a-Si) were analyzed for the first time by An et al. [6]. It was successfully demonstrated that RTSE is capable of quantitatively analyzing the initial growth phase of

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thin films. A transition from nucleation to bulk film growth could be observed at a film thickness of 13 Å. Shortly afterwards, RTSE was also applied in studies of hydrogenated amorphous silicon (a-Si:H) grown by PECVD [7].

An important step in the optimization of a-Si:H thin films for solar-cell application was the development of phase diagrams by Collins et al. [8] for the evolution of Si:H from the amorphous to the microcrystalline phase as a function of hydrogen dilution. RTSE was used to monitor the roughness development of the films in situ and allowed to determine the transition from pure amorphous film growth to a parallel amorphous and microcrystalline Si:H growth (mixed-phase growth). A strong increase in roughness indicates the start of this transition, whereas a subsequent smoothening indicates the transition from mixed-phase growth to pure microcrystalline growth. An important result was that a-Si:H with the best opto-electronic properties can be obtained at the highest hydrogen dilution that still yields amorphous Si:H with the necessary thickness (~ 500 nm for the intrinsic layer thickness in a solar cell), so-called protocrystalline a-Si:H.

Recently, also thin a-Si:H films grown by Hot-Wire (HW) CVD are being investigated by RTSE. Levi et al. [9] were able to reveal a 100-200 Å thick zone at the substrate interface with a constant hydrogen concentration independent of deposition temperature which could not be resolved by SIMS, thus demonstrating the sensitivity of RTSE even for very thin layers. In another article [10] they developed a phase diagram similar to Collins et al. [8] to determine the transition from a-Si:H to μc-Si:H as a function of hydrogen dilution for HW-CVD. Kessels at al. [11] applied RTSE to study surface processes and especially thermally activated surface diffusion of a-Si:H deposited by HW-CVD a-Si:H, focusing on the initial growth phase. Additionally they observed similar smoothening and roughening trends like Collins et al. [8] for PECVD a-Si:H.

The deposition method utilized for the work presented here is called ETP-CVD and will be discussed in detail in the experimental section below. So far RTSE has not been used for in-situ studies of a-Si:H films grown by ETP-CVD. However, single-wavelength ellipsometry has been applied by Smets et al. [12], [13]. It could be observed that thin a-Si:H films grown by ETP-CVD show a decrease in surface roughness with increasing deposition temperature. Furthermore, rougher surfaces are obtained compared to films grown by PECVD or HW-CVD at similar deposition temperatures. The presence of a thermally activated smoothening process was suggested, based on analysis of the dynamic scaling exponent, β [13]. However, even fast single-wavelength ellipsometry was not able to resolve the initial growth phase of the films where smoothening was observed for other deposition methods, due to the high growth rates of > 3 nm/s which can be obtained with ETP-CVD.

In this paper we report on an RTSE study of a-Si:H thin films deposited with the ETP-CVD technique. The results of the roughness layer thickness development will be compared to RTSE studies on different deposition methods reported in the literature, as well as single-wavelength SE studies carried out on ETP-CVD material. Additionally, we will compare two parameterization models for the dielectric function of a-Si:H.

## II. Experimental

The deposition method utilized for the work presented in this paper is called expanding thermal plasma chemical vapor deposition (ETP-CVD). This method has been developed in the group Plasma and Materials Processing of the Eindhoven University of Technology. High deposition rates of up to 10 nm/s for a-Si:H thin films have been demonstrated, compared to growth rates of ~ 0.1-0.2 nm/s obtained with conventional RF-PECVD methods [14]. A schematic representation of the reactor is shown in Fig. 1.

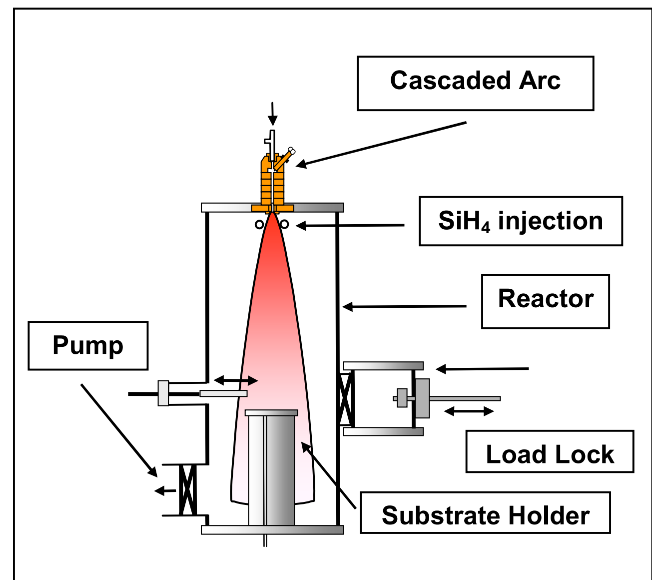


Fig. 1: Schematic drawing of the ETP-CVD reactor. The plasma is created in the arc and expands into the reactor due to the lower pressure.

An Ar-$H_2$ plasma is created in the arc, where the gases are injected into a 2.5-mm diameter tube surrounded by six isolated copper plates. A DC-discharge is sustained between three cathodes and the grounded copper plate located at the end of the arc. While the arc operates at pressures of 0.2 to 0.5 bar, a pressure of about 0.2 mbar is maintained in the reaction chamber by two stacked root blowers during depositions. Due to the large pressure difference, the plasma expands supersonically into the reactor. After a stationary shock a few centimeters after the nozzle, the plasma continues to expand subsonically.

The precursor gas $SiH_4$ is injected into the plasma beam via an injection ring located a few centimeters below the nozzle. $SiH_4$ reacts with the atomic hydrogen created in the Ar-$H_2$ plasma, abstracting one hydrogen atom from the silane molecule, forming silyl–radicals ($SiH_3$), the dominant growth radical responsible for 90% of the film growth [15]. The distance between the injection ring where the $SiH_4$ is injected

and the substrate holder is 43 cm.

For all depositions reported here, identical gas flows were used: 570 sccm Ar and 190 sccm $H_2$ in the arc, 150 sccm $H_2$ in the nozzle, and 200 sccm $SiH_4$ in the injection ring. The current in the arc is 40 A. The substrate temperature was varied between 150 and 300°C and the deposition time was 5 minutes. The reactor pressure was around 0.15 mbar and the deposition rate around 1.1 nm/s for all depositions, thus obtaining films with a thickness of about 300 nm. The films have been deposited on c-Si wafers (prime wafer, 500-550 µm, 2 nm native oxide).

Our RTSE measurements were performed using a J. A. Woollam Co., Inc M-2000F rotating compensator spectroscopic ellipsometer. The measurement setup and data acquisition were controlled using WVASE 3.486 provided by J. A. Woollam Co., Inc. Spectra were collected from 250 nm to 1000 nm in 470 separate channels. The angle of incidence was about 68° and the light beam passed through non-strain free windows, so a window effect had to be included in the data analysis. For all in-situ experiments 8 measurements were averaged, resulting in a time resolution of about 1.8 s. For the fitting of our experimental data we used EASE 2.3 by J. A. Woollam Co., Inc.

The actual data obtained in an RTSE measurement is the change of the polarization state of the incident light beam, defined by the ellipsometric angles $\Psi$ and $\Delta$ as a function of wavelength. These polarization angles by themselves do not give any information about the sample structure. A fitting procedure is required to deduce physical information like layer thickness and dielectric function. Depending on the sample structure, a single or multilayer model must be created, in our case consisting of a substrate (crystalline silicon wafer) with a thin bulk film (a-Si:H) and a roughness layer, modeled by a mixture of 50% film / 50% voids, following the Bruggeman effective medium approach (EMA) [21]. In the final fitting, the only fitted parameters are the bulk film thickness, $d_f$, and the thickness of the surface roughness layer, $d_s$.

In our RTSE data analysis we follow a procedure similar to the one established by Van den Oever et al. [16]. The first step is to determine the dielectric function of the substrate. We follow the pseudo-substrate approach and determine the dielectric function numerically from the RTSE data directly before the deposition by numerical inversion [17]. The dielectric function of the substrate is thus obtained at the same temperature at which the deposition is carried out, thereby excluding analysis problems due to the temperature dependence of the dielectric function of the substrate.

The dielectric function of the deposited film can be modeled by parameterized models, for example Cody-Lorentz or Tauc-Lorentz models [18]. However, this requires initial assumptions for the starting values of the parameters, so one must already have a good idea of the dielectric function of the material. Additionally, it introduces additional fitting parameters. The approach taken in this work does not require any parameterization of the dielectric function. Instead a tabulated, Kramers-Kronig consistent version of the dielectric function is fitted via a global regression analysis using around 8 spectra of the in-situ measurement equally distributed over the deposition time, excluding only the initial 200 Å where material with properties different from the bulk film material is deposited [16]. The fit of the dielectric function is repeated until a minimum in the mean square error (MSE) is reached. Utilizing many spectra stretched over the whole deposition time ensures a good representation of the bulk dielectric function. An initial, tabulated version is required as a starting point for the fitting procedure, as well as the dielectric function of the substrate obtained in the previous step. Surface roughness is implemented using the EMA with 50% voids.

Once the dielectric functions have been extracted, the dynamic fit of the in-situ data can be carried out. The only parameters in this final, dynamic fit are $d_f$ and $d_s$, of which the latter can be related to the roughness found by AFM measurements ($d_{rms}$) via a correlation found by Koh et al. [19]:

$$d_s = 1.5\, d_{rms} + 4\ \text{Å} \qquad (1)$$

Additionally, the dielectric function of the bulk thin film can be fitted separately with parameterized models like Cody- or Tauc-Lorentz to determine acceptable parameters that can be used for future fittings or additional analysis.

## III. Results & Discussion

An example of results obtained from in situ data obtained during a deposition at 300°C substrate temperature can be seen in Fig. 2. In the figure, the development of the film thickness and the surface roughness layer thickness is shown versus the deposition time. The time axis does not start at zero since the first minutes of the measurement are required for background measurements, the actual deposition starts after 4 minutes and 25 s for the example shown here.

The thickness (solid triangles) increases linearly with time, as is expected when the deposition conditions and growth flux are constant. The roughness (empty squares), however, shows a continuous non-linear increase during the whole deposition, with a maximum of the roughness increase (i.e., the time derivative of $d_s$) at the beginning of the deposition. Towards the end of the measurement time the roughness increase seems to be constant around 2.3 Å/s

Within the first minute of deposition the roughness increases to $d_s$ = 32 Å, at a total film thickness $d_f$ = 500 Å. In the remaining 4 minutes of the deposition, the roughness increase to a final value of 50 Å at a final thickness of 3000 Å. Thus the total roughness is mainly produced during the initial phase of the deposition, which has been observed before [13].

Initial nucleation and smoothening could not be observed in these results, as was reported previously for a-Si:H deposited by PECVD [7], [8] or HW-CVD [11]. This is presumably related to the difference in growth rate: while our samples were grown at 1 nm/s, these studies used growth rates below

1 Å/s. The question is whether an initial smoothening occurs, but can not be resolved in time by our RTSE setup, or if this initial smoothening indeed does not occur at these higher growth rates. However, also Smets et al. [13] did not observe smoothening during the initial growth phase using much faster single-wavelength ellipsometry. Their growth rates were slightly higher than in our study (3-5 nm/s), but their time resolution of 30 ms was 2 orders of magnitude faster than our RTSE resolution and resulted in a thickness resolution of 6Å. It can thus be assumed that a smoothening after a very quick nucleation phase at these high growth rates does not occur.

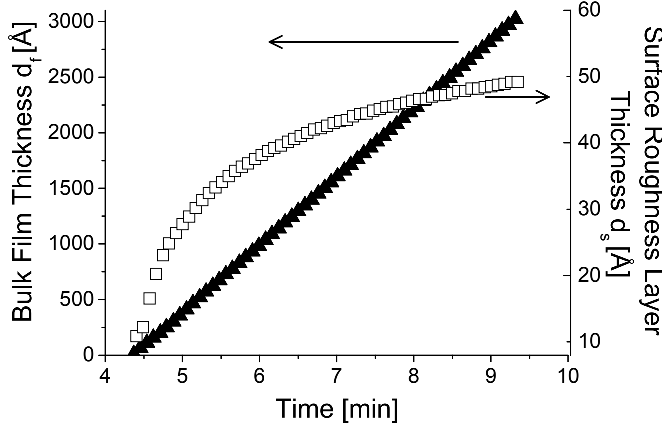


Fig. 2: Plot of the surface roughness layer thickness (open squares) and the bulk film thickness (filled triangles) versus deposition time.

Comparing the obtained roughness at the end of deposition, ETP-CVD material is significantly rougher than PECVD-material, which usually has roughness of around 20 Å for a wide range of deposition temperatures [8]. Also HW-CVD material gives roughness values similar to PECVD at temperatures above 150°C, with a strong increase in roughness at lower temperatures [11]. For both HW-CVD and PECVD, it was observed that the roughness is strongly related to the hydrogen dilution and much higher roughness values can be obtained at deviations from the optimum dilution [8], [13], already before growth of μc-Si:H sets in.

The development of the surface roughness layer thickness versus bulk film layer thickness for 3 different substrate temperatures can be seen in Fig. 3. The final roughness layer thickness, $d_s$, of the films at the end of the deposition clearly depends on substrate temperature. The values are very similar to the results obtained by Smets et al. [13], who measured 39Å surface roughness layer at a bulk film thickness of 3000Å and a substrate temperature of 300°C, where we measure 41 Å. As can be seen in Fig. 3, the lower the substrate temperature during deposition, the thicker the obtained surface roughness layer at the end of deposition.

Above bulk film thicknesses $d_f > 2000$ Å, the roughening development for all 3 deposition depends on the substrate temperature, with roughening slopes of around 0.003, 0.005 and 0.007 Å/Å for 300°C, 200°C and 150°C, respectively. The majority of final surface roughness $d_s$ is created in the first half of the deposition, below $d_f < 2000$ Å. From Fig. 3 it can be seen that all three samples have a similar roughness development in the beginning of the deposition, with a rather large roughness increase. The higher the substrate temperature, the earlier the roughness increase reduces until it settles at a constant increase in roughness described earlier. Additionally, depositions at 150°C and at 200°C show a feature at a film thickness of around 500 Å, where the slope suddenly increases again. This “kink” in the plot can not be observed at 300°C.

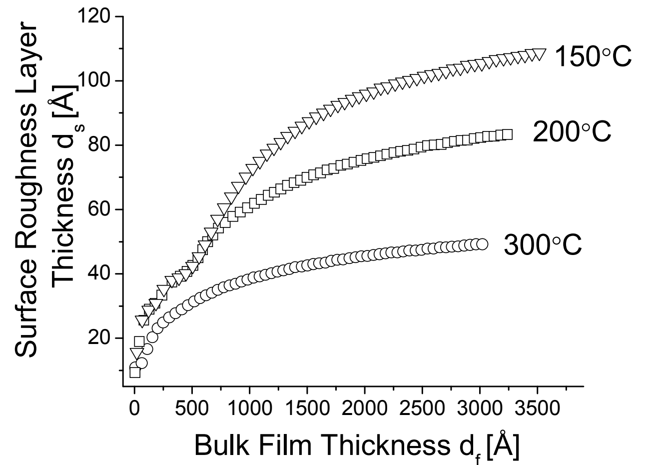


Fig.3: Surface roughness layer thickness $d_s$ versus the bulk film thickness $d_f$ for 3 depositions at 150°C, 200°C and 300°C.

As mentioned earlier, the dielectric function of thin films can be modeled by parameterized models, such as Cody-Lorentz or Tauc-Lorentz. Both models have been used to fit the dielectric functions of the films obtained during the three depositions described above. An example can be seen in Fig. 4, where both Cody-Lorentz and Tauc-Lorentz have been used for the sample deposited at 300°C. An overview over the obtained parameters as well as the MSE can be seen in Table 1.

Both models can describe the dielectric function obtained at 300°C very well, as can be seen in Fig. 4, with a slightly better fit obtained for the Cody-Lorentz model. Especially at the peak around 410 nm and at longer wavelengths the Tauc-Lorentz fit deviates slightly from the experimental data. This observation is confirmed by the MSE from Table 1, which is lower for the Cody-Lorentz (0.017) than for Tauc-Lorentz model (0.031) at 300°C. It has been reported previously that better fits are obtained when using Cody-Lorentz parameterization [16].

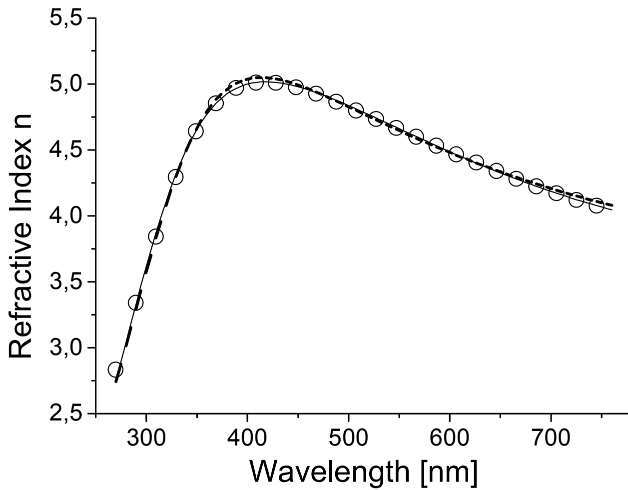


Fig.4: Refractive index obtained from a sample deposited at 300°C (open circles), a fit of the data with the Cody-Lorentz parameterization (solid line) and the Tauc-Lorentz parameterization (dashed line).

For depositions at 200°C and 150°C the fits are very similar for both models (not shown in the figure), as are the values for MSE in the table. A-Si:H thin films deposited with ETP-CVD usually require a temperature above 300°C to give dense material with solar-grade properties, while below this temperature the void-fraction in the film increases with decreasing deposition temperature [20]. Thus the choice between the two different parameterizations is only important for fits of solar-grade material.

Tauc-Lorentz

| Sample | 300°C | 200°C | 150°C |
|---|---|---|---|
| A [eV] | 180.425 | 184.424 | 179.357 |
| Br [eV] | 2.459 | 2.402 | 2.626 |
| $E_0$ [eV] | 3.734 | 3.941 | 4.042 |
| $E_g$ [eV] | 1.433 | 1.717 | 1.853 |
| MSE | 0.031 | 0.022 | 0.013 |

Cody-Lorentz

| Sample | 300°C | 200°C | 150°C |
|---|---|---|---|
| A [eV] | 93.235 | 104.917 | 110.134 |
| Br [eV] | 2.643 | 2.591 | 2.817 |
| $E_0$ [eV] | 3.886 | 3.991 | 4.04 |
| $E_g$ [eV] | 1.465 | 1.628 | 1.73 |
| $E_p$ [eV] | 1.242 | 1.901 | 2.258 |
| MSE | 0.017 | 0.02 | 0.012 |

Table 1: Parameter values obtained for fits of 3 different samples for both Cody-Lorentz and Tauc-Lorentz parameterizations as well as the obtained MSE.

## IV. CONCLUSION

Our approach of analyzing RTSE data has been explained in detail, resulting in the dielectric function of both the substrate and the bulk thin film which can be used to fit the in-situ data obtained during deposition. The change of surface roughness layer thickness versus deposition time has been discussed and compared to similar data obtained for other deposition methods, PECVD and HW-CVD. ETP-CVD material in general has a thicker surface roughness layer thickness at similar deposition temperatures and bulk film layer thicknesses. Additionally, nucleation and initial smoothening could not be observed which is attributed to the higher growth rates obtained with the ETP technique compared to other deposition techniques. It is concluded that smoothening after a very quick nucleation at these high growth rates does not occur. It was found that, for a deposition of solar-grade material at 300°C, the majority of the final surface roughness layer thickness is created in the initial phase of the deposition until a bulk film thickness of about 500Å. The extracted dielectric function of a-Si:H hast been fitted with both the Cody-Lorentz and the Tauc-Lorentz parameterization. Cody-Lorentz gives better fits at dense material obtained at 300°C while similar fit qualities were obtained at lower substrate temperatures.


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