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Citation for published version (APA):

DOI:
10.1063/1.1321793

Document status and date:
Published: 01/01/2000

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
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• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication
**In situ** single wavelength ellipsometry studies of high rate hydrogenated amorphous silicon growth using a remote expanding thermal plasma

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(Received 13 January 2000; accepted for publication 8 September 2000)

An in situ single wavelength HeNe rotating ellipsometry study of high rate (~80 Å s⁻¹) hydrogenated amorphous silicon (a-Si:H) deposition using an expanding thermal plasma is presented. An optical growth model is used to simulate the measured ellipsometric trajectories similar to models used for low rate a-Si:H growth in the literature. The in situ growth at high growth rates was studied as function of the substrate temperature. The refractive index n (at 632.8 nm) increases with increasing temperature corresponding to an increase in the density of the films. The in situ extinction coefficient k (at 632.8 nm) increases with increasing substrate temperature due to a smaller optical band gap and due to an increase in indirect absorption. It is shown that the ellipsometry setup in combination with optical modeling enables us to monitor the surface roughness evolution during deposition and to obtain the dynamic scaling exponent β for postinital growth. © 2000 American Institute of Physics. [S0021-8979(00)09123-4]

**INTRODUCTION**

Its opto-electronic properties makes hydrogenated amorphous silicon (a-Si:H) an excellent basis material for the large scale production of thin film solar cells and thin film transistors (TFTs). An increase in the a-Si:H growth rate can stimulate its application in thin film solar cells even more as a more competitive position in the energy market can be obtained. Beside the immediate applications of a-Si:H films, e.g., in the semiconductor and thin film solar cell industries, a lot of research has been performed to understand the fundamentals of a-Si:H growth.

One of the goals of the a-Si:H project at Eindhoven University of Technology (EUT) is to study the growth mechanism of a-Si:H at high growth rates (˃25 Å s⁻¹). To achieve this goal a systematic experimental approach of the following is needed: (1) plasma chemistry: which radicals and ions are created and arrive at the growth surface; (2) surface processes: how do the radicals and ions responsible for growth interact with the surface and (3) material quality: what physical features determine the defect densities and opto-electronic properties, etc. of the a-Si:H film grown. For exploration of these three topics a variety of in situ diagnostics and ex situ diagnostics is needed. To improve insight into the a-Si:H growth mechanism, it is required that correlations between results obtained from these three diagnostic parts be found.

In this article we will concentrate on the latter two diagnostic parts using in situ single wavelength rotating compensator ellipsometry, which is one of the few techniques capable of probing the growth surface without perturbing the growth processes. Over the past 20 years the ellipsometry technique has been used to improve understanding of the formation and properties of a-Si:H by conventional rf discharge, reactive sputtering processes and hot wire deposition.1–5 These studies were mainly concerned with the initial growth and showed that a-Si:H deposition starts by first nucleating in growing islands. It is proposed that differences in the initial growth, caused by the nature of the substrate and deposition conditions, may also be responsible for the final film properties. Depending on the desorption conditions and techniques this initial roughness is smoothened1 or increased during a-Si:H bulk growth.6

The expanding thermal plasma (ETP) deposition technique combines high growth rate (~100 Å s⁻¹) with good opto-electronic, solar grade properties.7–11 Here we present results obtained from a homebuilt single wavelength HeNe ellipsometry setup, which is suitable for monitoring in situ the high rate a-Si:H growth. An optical growth model is proposed to simulate the measured ellipsometric trajectories at these high growth rates. From this growth model the growth rate, the refractive bulk index nbulk and the extinction coefficient kbulk during growth are extracted. It is also demonstrated that the ellipsometer, although using single wavelength red light, provides sufficient sensitivity to probe the surface morphology. Results are presented as a function of the substrate temperature.

**EXPERIMENTAL SETUP**

In Fig. 1 the ETP deposition setup is presented. The plasma source is the cascaded arc, consisting of a cathode housing with three cathodes, eight cascaded plates and an anode plate with nozzle, all water cooled. An Ar/H₂ plasma is created in the 4 mm diam cylindrical arc channel by a dc voltage between cathodes and the anode plate, which is attached to the flange of the expansion vessel. Positioned 32 cm from the arc exit is a substrate holder which is tempera-
ture controlled up to 500 °C. A more detailed description of the desorption setup can be found in Ref. 7–11.

The results presented in this article are obtained by operating the arc at 45 A, 55 sccs Ar and 10 sccs H2 at a typical arc pressure of 0.5 bar.7–10 The atomic hydrogen rich plasma created expands in the vessel, which is at a typical pressure of 18 Pa. The results in this article correspond to SiH4 injection via an injection ring either 50 or 150 mm from the outlet of the arc. The electron temperature downstream of the arc is low (typically 0.3 eV) and the Ar+ and H+ densities are much smaller than the atomic H density for the above mentioned arc conditions. Consequently the silane is mainly dissociated by atomic hydrogen11 and the self-bias is minimal due to the low electron temperature and remote character of the plasma. Recent results show that under the conditions used, the plasma chemistry is dominated by the silyl radical (SiH3).12

### ROTATING COMPENSATOR ELLIPSOMETRY SETUP

The rotating compensator ellipsometry (RCE) setup used is similar to the rotating analyzer ellipsometry setup described by Azzam and Bashara,13 except in our setup the compensator is the rotating element. In Fig. 2 the homebuilt rotating compensator ellipsometry setup is depicted. The light source is a HeNe laser (632.8 nm) emitting polarized light (polarization ratio 500:1). The laser power is approximately 1 mW. A retarder is positioned behind the HeNe laser which turns the polarization from linear into circular. The next element is the polarizer and the analyzer (sheet polarizers, Melles Griot 03-FPG-001, open transmittance 0.20 and closed transmittance 10−4), which are mounted on stepping motors (OWIS, with accuracy of 0.005°, 200 steps/deg). During *in situ* measurements the polarizer and analyzer are kept on fixed positions. To determine the plane of incidence both sweep over an angle range of 11°. The element in between is the compensator, a quartz quarter wave plate which is coated with a nonpolarizing antireflection coating (R < 0.0075). The compensator rotates with constant frequency ω and is driven by an electromotor. The antireflection coating avoids internal reflections, which cause interference and give an additional 2ω signal variation. A lens is used to focus the beam onto the detector. The detector contains a photodiode (SGD-100A) and an amplification circuit (AD 524, gain ≲ 102).

The compensator axis is connected by means of a rubber hose to an encoder. The encoder generates one start pulse and 256 triggering pulses per revolution. After the detector signal is amplified, it is converted by a 12 bit analog-to-digital converter (ADC) (PCL 818 PC plug-in unit), triggered by the encoder, which makes the measurement insensitive to variations in rotation speed.

One compensator revolution takes approximately 30 ms. In the deposition setup described, typical growth rates are ~100 Å s−1, meaning that one to two data points (without averaging) per monolayer (ML) (~3 Å) growth can be obtained. At typical growth rates of 100 Å s−1, Ψ and Δ are determined over four revolutions. Bulk thickness changes of 4 ML can be detected, corresponding to approximately 12 Å. This sampling rate is sufficient to monitor high rate α-Si:H growth with enough thickness resolution.

### EXPERIMENTAL RESULTS

The RCE setup is used to monitor α-Si:H growth at 80 Å s−1 during deposition as a function of the substrate temperature. Using the growth model described below, the *in situ* values $n_{\text{bulk}}$ and $k_{\text{bulk}}$ and growth rate $r$ are determined from the measurements and compared to the measured *ex situ* values using infrared transmission (IR) and transmission reflection (TR) measurements. Finally, it will be shown that RCE measurements can be used to monitor the roughness evolution and that additional spectroscopic ellipsometry (SE) results will validate the roughness obtained by RCE measurements.

An example of a measured ellipsometry trajectory of a deposition at 80 Å s−1 is given in Fig. 3. Apart from ultrasonic cleaning in distilled water and ethanol no pretreatment was performed to remove the native oxide layer from the c-Si substrate. Before deposition the starting values of Ψ and Δ correspond to direct reflection of light on c-Si at 400 °C with a thin native oxide layer (10–20 Å) on top of it. Due to increasing α-Si:H bulk thickness the curves makes a clockwise-inward spiral, towards a convergence point, corresponding to the refractive index $n_{\text{bulk}}$ and extinction coefficient $k_{\text{bulk}}$ of the semi-infinite film.

In Fig. 3 simulation of the growth is also plotted using an optical model based upon homogeneous α-Si:H growth on...
a c-Si substrate with a thin oxide layer and on top of that an in time varying surface roughness. Within this model the angle of incidence, substrate refractive index \(n_{\text{sub}}\) substrate extinction coefficient \(k_{\text{sub}}\) and thickness of the oxide layer \(d_{\text{SiO}_2}\) are determined from the starting point. The \(n_{\text{sub}}\) and \(k_{\text{sub}}\) at 632.8 nm are temperature dependent which is included in the model. So for certain substrate temperature \(T_{\text{sub}}\) the substrate parameters \(n_{\text{sub}}\) and \(k_{\text{sub}}\) are fixed and the starting (\(\Psi, \Delta\)) value determines the angle of incidence and \(d_{\text{SiO}_2}\), since \(n_{\text{SiO}_2}(632.8 \text{ nm}) = 1.462\) (Refs. 20 and 21) and \(k_{\text{SiO}_2} = 0.000\) and both are considered to be temperature independent. In the literature it has frequently been shown, that by including extra overlayers in the optical growth model the ellipsometric fit of a-Si:H growth improves. This top layer can be regarded as the surface roughness and has a smaller refractive index than the bulk. The roughness is modeled by a top layer consisting of a certain volume fraction of voids. To restrict the number of free parameters, this fraction is assumed to be 50%, similar to that reported by Collins, and the refractive index \(n_{\text{top}}\) is calculated using the Bruggeman approximation to relate \(n_{\text{top}}\) and \(n_{\text{bulk}}\). So the top layer thickness \(d_{\text{top}}\) and \(n_{\text{top}}\) are exchangeable.

The measured trajectory is simulated piece by piece, with every successive trajectory piece having a different \(d_{\text{top}}\) value. Further improvement of the fit of the experimental data is achieved by including a small intermediate layer of 30–60 Å between the bulk and the oxide layer with a refractive index of 1.5–3. This layer enables us to simulate the small jump in the \(\Psi - \Delta\) trajectory after the starting point and corresponds to initial growth of an a-Si:H layer with larger void fraction than the bulk as a result of, most probably, nucleation dominated growth on c-Si. This intermediate film buried at the interface between the substrate and bulk film could correspond to an imperfect coalescence of the initial nuclei but an intermediate film of SiO2 and a-Si:H could also explain the observed interface film with lower refractive index. At high growth rate the used RCE setup collects only two to three data points for the initial growth phase, which is not enough to exclude the initial growth mechanism. Note that if the intermediate layer corresponds to imperfect coalescence of nuclei, this behavior evidently differs from observed nucleation at low growth rates.

As shown in Fig. 3 the simulation based on the optical model introduced is consistent with the measured ellipsometric trajectory. In the simulations the roughness and bulk thickness varied in time and \(n_{\text{sub}}\) and \(k_{\text{sub}}\) also vary slightly to improve the fit with the experiment. Other parameters are kept constant. The uniqueness of the fits is concluded from the fact that by taking, for example, a different value of \(n_{\text{sub}}\), the other three varying parameters show the same periodic fluctuations in time as the ellipsometric \(\Psi\) and \(\Delta\) values which are unphysical. From a large set of measurements and corresponding simulations at various deposition conditions, it is determined that the bulk refractive index varies during deposition \((\Delta n/n)_{\text{bulk}} \leq 0.02\) and the bulk extinction coefficient varies during deposition \((\Delta k/k)_{\text{bulk}} \leq 0.07\). From simulations we learned that the latter variation is larger because the \(k_{\text{bulk}}\) is more sensitive to the intermediate layer and surface roughness. The variation in \(n\) could correspond to changing void fractions with bulk thickness, similar to the work of Collins, who found a decreasing bulk void fraction with increasing film thickness. Next we will show that these variations in \(n_{\text{bulk}}\) and \(k_{\text{bulk}}\) are small enough to conclude that at the conditions used the bulk a-Si:H growth is homogeneous. As the \(n_{\text{bulk}}\) is constant within the measurement’s accuracy this would mean that no density gradient is present in the a-Si:H film apart from the intermediate layer and the surface roughness. The density of ETP a-Si:H films already has been measured using elastic recoil detection analysis (ERDA) and the following empirical relation between the atomic hydrogen density \(c_H\) and \(n_{\text{bulk}}(632.8 \text{ nm})\) was found: \(c_H = (3.22 - 0.66) 	imes n_{\text{bulk}} \times 10^{22}\) cm\(^{-3}\). Using the observed RCE accuracy \((\Delta n/n)_{\text{bulk}} \leq 0.02\) and assuming that the total density is constant during deposition the atomic hydrogen density does not change relatively more than \(\Delta c_H/c_H < 0.03\) during deposition.

Summarizing, we have shown that an optical growth model, based on homogeneous bulk growth and an in time evolving top layer corresponding to surface roughness, is also valid for high rate a-Si:H growth.

From the bulk thickness evolution the growth rate can easily be determined. In Fig. 4 the growth rate from RCE measurements are plotted versus the growth rate obtained from thickness measurements using \textit{ex situ} IR absorption on the films grown for various deposition conditions \((r = 2–500 \text{ Å s}^{-1})\). The IR measurement procedure used and interpretation of the measured IR spectra are presented elsewhere. The RCE growth shows a good correlation with the growth rate determined from the IR growth rate. For growth rates larger than 200 Å s\(^{-1}\) both diagnostics become less accurate. For growth rates smaller than 200 Å s\(^{-1}\), con-
ditions at which solar grade material is deposited, the proposed optical growth model is satisfactory in describing the optical growth. At higher growth rates ($\geq 200 \text{ Å s}^{-1}$) the RCE and IR results start to differ. These high growth rates are obtained at low hydrogen dilution plasma conditions at a substrate temperature of 100 °C, conditions in which films with a high void fraction are deposited. The model used to fit the IR spectra and the optical model used to fit the RCE data assumes homogeneous bulk growth and this may no longer be valid for film growth having a high volume void fraction. Another problem that can play a role is the obtained data assumes homogeneous bulk growth and this may no longer be valid for film growth having a high volume void fraction. Another problem is the obtained data assumes homogeneous bulk growth and this may no longer be valid for film growth having a high volume void fraction.

The measured refractive index at 632.8 nm versus the substrate temperature during deposition obtained from in situ measurements is fitted using the dielectric function model described by Ferlauto et al. The TR measurement was performed weeks later after an anneal of 30 min at 180 °C. The refractive index trend obtained from TR, SE and RCE measurements is consistent. The departure between, on the one hand, the TR and SE and, on the other hand, the RCE measurements is based upon the refractive index temperature dependence. From the RCE and TR data the $\alpha$-Si:H refractive index temperature dependence $\Delta n_{\alpha-\text{Si:H}}/(T_{\text{sub}} - T_0)$, where $T_0$ is the room temperature and $\Delta n_{\alpha-\text{Si:H}}$ is the change in refractive index between $T_{\text{sub}}$ and $T_0$, is determined and varies from a maximum value of $\Delta n_{\alpha-\text{Si:H}}/(T_{\text{sub}} - T_0) = (3.0 \pm 0.3) \times 10^{-3}$ K$^{-1}$ for films deposited at 250 °C to a minimum value of $\Delta n_{\alpha-\text{Si:H}}/(T_{\text{sub}} - T_0) = (7.0 \pm 0.7) \times 10^{-4}$ K$^{-1}$ for films deposited at 500 °C. This is a factor of 2–10 higher than for $c$-Si where $\Delta n_{c-\text{Si}}/\Delta T = 3.0 \times 10^{-4} - 4.4 \times 10^{-4}$ K$^{-1}$ and differs from pure $\alpha$-Si which shows a totally different temperature dependence of the optical constants: $\Delta n_{\alpha-\text{Si}}/\Delta T = -1.43 \times 10^{-4}$ K$^{-1}$ at 632.8 nm. The authors in the latter references explained this effect by the following refractive index behavior: $dn/dT = dn/dT$ (volume effect) + $dn/dT$ (electronic effect), where volume effects refer to thermal expansion and always causes a decrease of $n$ with temperature. This means that for our $\alpha$-Si:H films deposited at 250 °C the volume effect is smaller than the electronic effect as for $c$-Si:H films deposited at 500 °C the volume effect becomes relatively more important, but is still smaller than the electronic effect. This is in agreement with the fact that $\alpha$-Si:H films deposited at 500 °C have the lowest hydrogen content ($\sim 4\%$) and resemble $c$-Si the most.

In Fig. 6 $k_{\text{bulk}}$ obtained from RCE and ex situ TR and SE measurements at 632.8 nm versus the substrate temperature during deposition is plotted for depositions at an 80 Å s$^{-1}$ growth rate. The observed trend of increasing $k_{\text{bulk}}$ and increasing difference between RCE and TR measurements with temperature can be explained by two effects: one is based upon changing the intrinsic properties with substrate temperature and the second is absorption enhancement with temperature. First with increasing substrate temperature the hydrogen content decreases and as a result the band gap $E_{\text{Tauc}}$ is smaller. The HeNe photons have an energy of 1.95 eV, which is in the extended states of the $\alpha$-Si:H absorption spectrum. The smaller the band gap the higher the absorption.
thickness versus the bulk thickness on a c-Si substrate is plotted at three different substrate temperatures. Since the growth rate is constant during deposition, the horizontal axis can also be interpreted as a time axis by $d_{\text{bulk}} = r \times t$. Note that the $d_{\text{top}}$ has an accuracy of 0.1 Å, showing that the HeNe red light is suitable for probing the surface roughness with sufficient sensitivity.

At a bulk thickness of 500 Å the surface roughness is around 20–50 Å and, since the final roughness is 30–70 Å, this means that the roughness is mainly produced during initial growth, as also observed by others.\(^\text{1,3}\) The top layer time dependence in the initial phase ($d_{\text{bulk}} \leq 500$ Å) can be described by $d_{\text{top}} \sim t^\beta$\(^\text{33}\) where $\beta$ is the dynamic scaling exponent, equal to one half for random growth and smaller than one half if smoothening occurs during growth. At high growth rates (80 Å s\(^{-1}\)) $\beta$ varies from 0.3 to 0.7 for ETP deposition on c-Si,\(^\text{34}\) which corresponds to initial growth without smoothening processes. As mentioned earlier, at these high growth rates a bulk change of 4 ML can be detected with the RCE setup used, meaning that in the nucleation phase no evolution of a single ML can be detected. This makes it impossible to determine what kind of nucleation process occurs during initial growth at high growth rates.

After initial growth the roughness increases slightly, in agreement with Refs. 3, 6, and 34, and does not become smoother as it does in Ref. 1. Figure 8 also shows that the postinitial roughness evolution ($d_{\text{top}} > 500$ Å) can be modeled by $d_{\text{top}} \sim t^\beta$ (solid lines). The obtained dynamic scaling exponents are $\beta = 0.11$ at 250 °C, $\beta = 0.31$ at 300 °C, and $\beta = 0.18$ at 400 °C and are smaller than $\frac{1}{2}$, suggesting that a smoothening mechanism occurs during deposition. The values obtained are similar to the measured $\beta$ values using atomic force microscopy (AFM) and scanning tunneling microscopy (STM) at low a-Si:H growth rates (≤ 2 Å s\(^{-1}\)).\(^\text{35–38}\) As the dynamic scaling exponent correlates with the growth mechanism, there is an evident difference between initial growth and bulk growth. The $\beta$ values obtained suggest that $\beta$ shows a maximum at high growth conditions (70 Å s\(^{-1}\)) at a certain substrate temperature around 300 °C. As will be shown in a later paper, this maximum is a transition from the ballistic fractal growth model describing the roughness evolution at low temperatures, to solid on solid fractal growth at high temperatures, both including surface smoothening.\(^\text{39}\)

Figure 9 shows the surface roughness at a bulk thickness of 0.500 μm using two types of substrates, c-Si (RCE) and Corning 7059 (ex situ SE) and chrome (RCE), versus the substrate temperature. The RCE roughness results are compared with the results of ex situ SE measurements on six a-Si:H films deposited on Corning 7059 substrates under similar conditions to those presented in this article. The void fraction of the top layer in the simulation of the RCE and SE measurements is fixed at 0.50. The $d_{\text{top}}$ obtained from SE shows the same trend as the RCE results but the absolute values are consistently larger than the RCE (c-Si) ones and consistent with the RCE (chrome) results over the temperature range used except for the deposition at 400 °C. Notice that there are some experimental differences between the RCE and SE measurements, which could result in a slight
induced differences vanish in the postinitial roughness evolution of the substrate, meaning that at high growth rates nucleation does not depend strongly within the accuracy on the nature from the postinitial growth phase, which are smaller than 1 and the obtained dynamic scaling exponent which is the smallest for these substrate temperatures. The $k_{bulk}$ model used for high growth rate.

Furthermore, Fig. 9 shows that the roughness decreases with increasing temperature. The roughness at 0.50 µm does not depend strongly within the accuracy on the nature of the substrate, meaning that at high growth rates nucleation induced differences vanish in the postinitial roughness evolution. The fact that the surface becomes smoother at higher substrate temperatures again suggests that the substrate temperature surface smoothing process is thermally activated. The smoother the surface, the denser the film, as shown in Fig. 5, and the better the opto-electronic properties. A more profound description of the roughness evolution and dominating growth mechanisms as function of growth rate and substrate temperature will be presented elsewhere.

CONCLUSIONS

An optical model consisting of a substrate, native oxide layer, intermediate film, bulk film and roughness layer was presented to simulate the ellipsometric trajectories of high growth rate deposition of a-Si:H. The results show that at a growth rate of 80 Å s$^{-1}$ for $T_{sub}$ > 300 °C the material is more dense. This is in agreement with the obtained roughness, which is the smallest for these substrate temperatures. The decreasing roughness with increasing substrate temperature and the obtained dynamic scaling exponent $\beta$ determined from the postinitial growth phase, which are smaller than $\frac{1}{2}$, suggest that the smoothing process is thermally activated. The observed roughness on the c-Si substrate and chrome substrate does not differ significantly at bulk thickness of 0.50 µm.

We have shown that the in situ values of $n_{bulk}$ and $k_{bulk}$ obtained differ from values measured using TR at room temperature, so this temperature effect must be included in interpretation of the in situ measurements. The observed RCE $n_{bulk}$ temperature dependence at 632.8 nm for the high rate $a$-Si:H films deposited by the ETP technique differs from that for pure $a$-Si since the $k_{bulk}$ temperature dependence for $a$-Si:H films deposited at 250–500 °C is in the same order as that for $a$-Si.

ACKNOWLEDGMENTS

Students Iain Houston and Patricia Keijzers are thanked for their important contributions to this work. Tom Kiers and Bart Hovens are thanked for the construction and building of the RCE setup. Karine Letourneur is thanked for discussions about the ellipsometry technique. The skillful technical assistance of Ries va de Sande, Bertus Hüsken and Herman de Jong is gratefully acknowledged. Rene van Swaaij and Erik Jan Geluk of the Delft University of Technology are thanked for their assistance in the TR measurements. André Ferlauto and Dr. R. W. Collins are thanked for their assistance in the SE measurements. NOVEM, TDO, and FOM are acknowledged for their financial support.

26 The initial jump cannot be explained by a change in polarization due to a plasma induced surface charge which we could conclude from an ellipsometric measurement at small growth rates (~ 2 Å s$^{-1}$), in which the same initial jump for a longer time scale was observed, because a plasma induced surface charge should be present within 1 ms of starting the deposition.