Novel *in situ* and real-time optical probes to detect (surface) defect states of a-Si:H

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**ABSTRACT**

This paper describes two novel optical diagnostics that were recently introduced to the field of Si-based thin films, in particular for probing defect states present in the bulk and at the surface of a-Si:H films. It is expected that these diagnostics, when applied *in situ* or real time during film growth, can provide new insights into the a-Si:H film properties as well as into the fundamental surface processes during growth. The first method is cavity ringdown spectroscopy (CRDS). From *ex situ* measurements on a-Si:H thin films, it is shown that this method is very powerful for measuring *absolute* defect-related absorptions at subgap energies *without* the need for a calibration procedure, even for films as thin as 4 nm. It is also shown that the method can be used for measuring rare-earth dopants – here Er$^{3+}$ in silicon-rich oxide – to the extent that issues about absorption cross-sections can be resolved by using thin samples instead of waveguides. Furthermore, the *in situ* application of the method for thin films is discussed by presenting the evanescent-wave cavity ringdown (EW-CRDS) technique. The second method is spectroscopic second harmonic generation (SHG). It has been found that this non-linear optical technique yields a photon energy dependent signal for as-deposited a-Si:H films and that this signal has a contribution from a-Si:H surface states. From a comparison with c-Si surface science studies, the possible origin of the signal from surface Si dangling bonds and strained Si-Si bonds is discussed. The application of SHG during real-time film growth is also presented.

**INTRODUCTION**

The performance of Si-based thin film devices is largely determined by their interface properties with defects such as Si dangling bonds and Si-Si strained bonds playing a key role. But also during the growth process of these films from plasma or hot-wire activated radicals, the role of dangling bonds and strained bonds appears to be essential as they are considered active sites for radical adsorption.

Figure 1 shows a schematic representation of a-Si:H growth from SiH$_3$ radicals. In the growth process different aspects can be distinguished that need to be investigated in order to come to a full understanding of film formation: (i) the key radical precursor(s); (ii) the surface reaction and sticking probability of the growth precursors; (iii) the surface hydride composition and surface hydrogen coverage; (iv) the surface active sites and their density; (v) the radical surface reactions such as adsorption, abstraction, and insertion; and (vi) surface diffusion mechanisms. Almost all these aspects have been investigated in relative detail. There have been numerous reports on measurements of radical gas phase densities, and there have been several studies of the surface reactivity of the radicals [1,2]. Real-time (spectroscopic) ellipsometry [3,4,5,6,7] and infrared spectroscopy [4,8,9,10,11] have been particular powerful for studying surface roughness evolution processes (and consequently surface diffusion mechanisms) and the
Figure 1. Schematic representation of a-Si:H surface and incoming SiH₃ radical. The different aspects of the growth process that need to be investigated to come to an understanding of the film growth mechanism are indicated.

surface silicon hydride composition of a-Si:H, respectively. However, experimental studies with respect to the detection of dangling bonds and strained bonds have not been readily available, although it has been predicted from molecular dynamics simulations and \textit{ab initio} calculations that these defect sites play a key role for SiH₃ radical adsorption [12]. So far only Yamasaki and co-workers have been able to detect Si dangling bonds during film growth by \textit{in situ} electron spin resonance [13].

From the above, it is clear that there is a need for more \textit{in situ} diagnostic techniques that are able to measure (surface) dangling bonds and strained bonds in a-Si:H. Such techniques are preferentially all-optical (\textit{i.e.}, photon-in – photon-out) due to their non-intrusive character and their \textit{in situ} applicability under relatively normal process conditions. In this paper, we present two techniques that are completely new to the field of a-Si:H. The first technique is cavity ringdown spectroscopy, originally a gas phase absorption method, and the second technique is second harmonic generation, a technique that has a long tradition in (c-Si) surface science. In recent years, we have been working on the implementation of these two techniques to find out what they can tell us about a-Si:H. The abovementioned application has been kept in mind throughout the work, but in the first stage of the research some feasibility studies (\textit{e.g.}, \textit{ex situ} studies on thin films) have been carried out which already have led to some interesting spin-off results. Currently, the research is focused on the implementation of both methods in \textit{in situ} and real time studies. In the remainder of this paper, a description of the techniques will be given followed by a brief presentation of some of the “highlights” of the work so far, including references to more detailed reports in the literature.

**CAVITY RINGDOWN SPECTROSCOPY ON THIN FILMS**

**Introduction and experimental**

Cavity ringdown spectroscopy (CRDS) is an ultra-sensitive absorption technique which, since its invention in the late 80s, has found many applications, mostly in trace gas analyses and the
detection of reactive species in plasmas and flames [14]. The method relies on the measurement of the rate of loss of a light pulse confined in a high-quality optical cavity. Such a stable optical cavity is typically formed by two plano-concave mirrors with high reflectivities. After coupling in a short (laser) light pulse through one of the mirrors, the light intensity in the cavity decays exponentially in time with characteristic time $\tau$ depending on the roundtrip time of the cavity $t_r$ and the sum of the cavity losses $L$:

$$\tau = \frac{t_r}{\sum L_i}.$$  \hspace{1cm} (1)

This so-called ringdown time $\tau$ can be measured by monitoring the small fraction of light transmitted through one of the mirrors. For an “empty” cavity, the cavity losses are called intrinsic losses $L_0$ and for a basic cavity these are equal to the reflectivity losses of the mirrors $\sum L_i = L_0 = L_{mirror} = 1-R$. However, when an absorbing medium is introduced into the cavity, the cavity loss will be enhanced by absorption losses, $\sum L_i = L_0 + L_{abs}$, such that the ringdown time will be shorter than for the “empty” cavity. By measuring both the ringdown time $\tau_{ref}$ for an empty cavity (reference) and the ringdown time $\tau_{abs}$ for the cavity with absorbing medium, the absorption losses $L_{abs}$ can be determined:

$$L_{abs} = \alpha d = t_r \left( \frac{1}{\tau_{ref}} - \frac{1}{\tau_{abs}} \right).$$  \hspace{1cm} (2)

In this equation $L_{abs}$ is represented by the product of the absorption coefficient $\alpha$ and the absorption path length $d$ (valid for a homogeneous $\alpha$ over length $d$). This method leads to an ultrahigh sensitivity with the minimal detectable absorption loss given by $L_{abs,min} = L_0(\Delta\tau/\tau)$, with $(\Delta\tau/\tau)$ the accuracy in the ringdown time. The advantage in sensitivity over conventional absorption spectroscopy results basically from (i) the intrinsic insensitivity to light source intensity fluctuations, and (ii) the extremely long effective path lengths due to multipassing in the cavity. In the past, we have exploited the method to measure (low-density) radicals in plasmas such as used for the deposition of amorphous and microcrystalline silicon and silicon nitride films [2,15].

In recent years there have been several reports of extending the CRDS method to condensed phase samples, e.g., to measure absorption by thin films or by adsorbates on a surface, mostly by using intercavity elements [16,17,18]. We have explored the application of CRDS to determine directly (i.e., without calibration) absolute absorption values and number densities of defects in thin films. These films are deposited on a substrate which is placed inside the cavity with the substrate perpendicular to the optical axis as shown in Fig. 2. The absorption loss in the thin film is now calculated by using a cavity with a “clean” substrate as a reference measurement. The intrinsic loss of the cavity for this reference measurement is given by $L_0 = L_{mirror} + L_{substrate}$, with the losses by the substrate $L_{substrate}$ comprising of absorption losses in the substrate and possible scattering losses induced by the substrate. We have shown that scattering losses can be neglected for substrates and films with typical surface roughness values (< few nanometers). Moreover, we have verified that Eq. (1) remains valid for a cavity with a sample (substrate with film) placed perpendicular to the optical axis of the cavity as long as the reflectivity of the sample and the absorption losses of the sample are not too high. These conditions are usually fulfilled [19].
Figure 2. Cavity ringdown setup for measuring weak absorption by defects or dopants in thin films. The cavity consists of 2 plano-concave mirrors with radii of curvature of -100 cm which are placed 40 cm apart. Different sets of mirrors, each with a typical reflectivity $R > 0.9997$ at its center wavelength have been chosen to cover the photon energy range of 0.7 – 1.8 eV. Tunable laser radiation (typical bandwidth 10 cm$^{-1}$) produced by a combination of an optical parametric oscillator (OPO) and a seeded Nd:YAG laser is used to excite the cavity without the use of mode-matching optics. Only a very small fraction of light is coupled into the cavity (typically <3 µJ per pulse). The ringdown signal is detected by either a photomultiplier or infrared diode and the transients are processed separately before averaging the ringdown times. Typical ringdown transients are shown in the inset on a semi-logarithmic plot. The cavity is covered by a N$_2$ purge box during the measurements to avoid influence of water absorption peak in the wavelength range of interest. The minimal substrate size is 1 cm$^2$ and good film uniformity is desired over this area.

To achieve a high sensitivity, it is necessary to minimize $L_{\text{substrate}}$ meaning that it is necessary to use substrates with a high optical quality and with low absorption losses for the photon energy range of interest. Figure 3 shows the losses for a fused silica substrate, typical of those used for our experiments. Absorption peaks due to vibrational overtone and combination modes of SiO$_4$ and OH in the substrate are clearly visible and these severely limit the sensitivity of the method for particular photon energies. On the other hand, in regions with low $L_{\text{substrate}}$ values a minimal detectable absorption can be reached of $L_{\text{abs,min}} = 10^6$ for single-shot and $5 \times 10^{-8}$ for a typical value of 400 averages. This is an unprecedented accuracy for absorption spectroscopy on thin films.

Figure 3. The optical loss $L_{\text{substrate}}$ induced by the 2-mm thick fused-silica substrate when placed inside the linear cavity. The absorption peaks observed are related to vibrational overtone and combination modes of SiO$_4$ and OH present in the substrate material.
CRDS for subgap absorption spectroscopy on a-Si:H

Si dangling bonds form midgap states between the valence and conduction bands of a-Si:H. Dangling bonds can therefore be measured in the photon-energy range 0.7 – 1.5 eV by probing transitions between valence band and midgap states and between midgap states and conduction band states. The subgap absorption spectroscopy techniques of photothermal deflection spectroscopy (PDS) and constant photocurrent method (CPM) are very powerful in this respect, but their limitation is that they measure the absorption values indirectly and that they generally require calibration, especially when measuring very thin films.

CRDS, as a direct and absolute absorption technique, was therefore applied on a 1031 nm thick a-Si:H film (roughness < 1.2 nm) deposited on a fused silica substrate (cf. Fig. 3). The inset of Fig. 4 shows the absorption losses in the film which clearly reveal interference fringes. These fringes arise from constructive and destructive interference in the film leading to enhanced/reduced optical loss in the film. Correction for these interference effects can take place by calculating the electric field distribution in the film for the photon energy range of interest using a procedure [19,20] similar to the one in Ref. [21]. This correction is also important for very thin films as in these films the electric field can be altered by interference as well. Figure 4 gives the absorption coefficient obtained after the correction and shows that the CRDS data have a very good signal-to-noise ratio. The data also overlap perfectly with the results obtained by transmission-reflection (T-R) spectroscopy, a technique which also yields absolute absorption values similar to CRDS. The absolute scale on the PDS data, however, is obtained by linking the PDS and T-R results at an energy of 1.65 eV. For low photon energies the PDS data corroborate the CRDS data.

Due to the high-sensitivity of the technique the absorption losses in relatively thin films can easily be measured as shown in Fig. 5. This figure gives the absolute absorption coefficient as calculated from \( L_{\text{abs}} \) (after correction for interference effects) and by dividing by the film thickness. The absorption coefficient increases with decreasing film thickness due to the fact that the thinner films are dominated by the dangling bonds in the defect-rich surface/interface layer [21]. However, the lowest \( L_{\text{abs}} \) value of \( 2 \times 10^{-5} \) is obtained for the 4 nm thick film with an excel-
lent signal-to-noise ratio. This clearly illustrates that CRDS is an ultra-sensitive alternative for PDS and CPM. More details are given in Refs. [19,22].

**Measuring rare-earth dopants by CRDS: Er$^{3+}$ in silicon-rich oxide**

The broad applicability of the CRDS technique for measuring absorption in films has also been illustrated by experiments in the field of rare-earth doped Si materials for photonic applications. Er$^{3+}$ ions embedded in silicon-rich oxide (SRO) play an important role in optical amplifiers for waveguide applications in which Si nanoclusters present in the material lead to a broadband sensitization effect [23]. Knowledge about the optical absorption cross section of the 1.5 µm $^4$I_{15/2} $\rightarrow$ $^4$I_{13/2} transition of Er$^{3+}$ ions embedded in Si-rich oxide has been pivotal but so far this cross-section could only be estimated indirectly using waveguides [24]. Therefore CRDS measurements on this material have been set up in collaboration with the AMOLF Institute.

High-purity fused silica (Suprasil 300) has been implanted by Er (2.3 at.%) and Si (10 at.% excess Si) leading to SRO after thermal anneal (800 °C). The optical loss induced by the Er$^{3+}$ has been measured by the setup in Fig. 2 yielding typical spectra as shown in Fig. 6. The Er$^{3+}$ absorption peak is clearly visible and by taking into account the background optical losses (possibly due to scattering), a peak cross-section of $(8 \pm 2) \times 10^{-21}$ cm$^2$ at 1536 nm was calculated directly from the data. Most important is that the interpretation of this experiment on a thin film is straightforward and has resolved an important issue in the field. For more details see Ref. [25].

**Evanescent-wave CRDS for real-time monitoring a-Si:H film growth**

Compared to PDS and CPM, the advantage of CRDS is that it is an all-optical method which makes it possible to implement the technique in a vacuum reactor for *in situ* studies. Application of a linear cavity is not straightforward under such conditions but instead a folded cavity can be used. Such a folded cavity is an optical resonator that employs ultrahigh-reflectivity mirrors and a total internal reflection surface. The evanescent-wave emanating from this surface can be used to measure adsorbates and even thin films by means of the evanescent-wave CRDS method. A monolithic folded cavity as designed at NIST is shown in Fig. 7 [26]. The figure shows also a picture of a folded cavity with an unfolded cavity length of 2 cm and a radius of curvature of 9 cm. These parameters are different from those of the folded cavities used so far (e.g., used for the detection of adsorbed chloroethylenes [27]) and provide a higher sensitivity.

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**Figure 6.** Absorption losses induced by Er$^{3+}$ ions embedded in silicon-rich oxide (SRO) as measured by CRDS. The Er$^{3+}$ absorption feature centered at 1536 nm can clearly be distinguished while the baseline losses (dashed line) can possibly be attributed to scattering losses induced by the SRO.
Although EW-CRDS has not been used yet to monitor a-Si:H film growth the folded cavities have been designed and tested. To enable Si dangling bond detection, mirror coatings with a center wavelength of 1205 nm were chosen. The bulk losses of the fused silica were estimated as $<5 \times 10^{-6}$ and after aligning the cavity it was found that the intrinsic loss of the cavity was $\sim 2 \times 10^{-5}$ and being limited by the mirrors (cf. Fig. 8). This implies that $L_{abs, min} = 10^{-7}$ for single-shot detection which is an extremely high sensitivity for an (in situ) absorption technique. The high sensitivity can already be observed in Fig. 8 in which some very small and highly-polarized absorption peaks are present related to vibrational combination modes of surface hydroxyls [28].

**SPECTROSCOPIC SECOND HARMONIC GENERATION**

**Introduction and experimental**

Second harmonic generation (SHG) is a nonlinear optical technique in which a laser beam with frequency $\omega$ incident on a surface generates light at the double frequency $2\omega$. Or in terms of electric fields, an electric field with frequency $\omega$ incident on a surface induces a polarization

$$\vec{P}(2\omega) = \varepsilon_0 \chi^{(2)} : \vec{E}(\omega)\vec{E}(\omega)$$

(3)

**Figure 8.** Intrinsic losses for a clean folded cavity for $s$- and $p$-polarization which were detected simultaneously. The number of averages is 75.
oscillating with a frequency component at $2\omega$. $\chi^{(2)}$ is a third-rank tensor that represents the second order nonlinear susceptibility. Within the electric dipole approximation, it follows from parity considerations that $\chi^{(2)} = 0$ in the bulk of media with inversion symmetry (such as c-Si and a-Si:H) while $\chi^{(2)} \neq 0$ at surfaces and interfaces where the symmetry is broken [29,30]. This makes SHG a surface- and interface-sensitive technique. Furthermore, the SHG signal is resonantly enhanced whenever $\omega$ or $2\omega$ coincides with an optical transition from an initially occupied state to an initially unoccupied state. Such a transition can for example be an electronic or vibrational transition of species adsorbed at the surface. Information about the surface properties can also be obtained by probing the different elements of the tensor $\chi^{(2)}$, i.e., by measuring the SHG signal for different combinations of the polarization states of the incoming and outgoing beams.

The power of SHG has been exploited in surface science studies of c-Si [31]: for c-Si resonant optical transitions in the visible and near-infrared arise from the presence of surface states in the band gap of the Si. These surface states originate from Si dangling bonds and strained Si-Si bonds that are polarized. Figure 9 shows the SHG signal as obtained for a Si(111)-(7×7) surface [32] revealing basically two resonances: the resonance between 1.0-1.5 eV has been attributed to Si dangling bond states (yielding a single- and two-photon resonance in this region) [33] whereas at ~1.7 eV a strained-induced resonance is observed which is due to a two-photon transition at ~3.4 eV [33,34]. These assignments are based on several experiments and calculations in the literature with the most important proof being: (i) the fact that the resonance due to dangling bonds disappears when the surface is dosed with O$_2$ which is known to quench dangling bond surface states on c-Si [31,32]; and (ii) the fact that the strain-induced resonance shows close resemblance with the 3.4 eV direct bandgap transition ($E_0'/E_1$ critical point transition) observed in the linear susceptibility of c-Si [34].

A setup for SHG experiments on Si thin films is given in Fig. 10, which shows the implementation of the optical setup in a UHV reactor [35] such that in situ and real time measurements after and during film growth can be carried out. The SHG signal $I(2\omega)$ is measured at exactly twice the fundamental photon energy $\omega$ and is proportional to:

$$I(2\omega) \propto |\chi^{(2)}|^2 I^2(\omega)$$

with $I(\omega)$ the intensity of the fundamental radiation. Whether the signal measured is really SHG

Figure 9. SHG signal from a Si(111)-(7×7) surface as a function of fundamental probe and SH photon energy [32].
or not can be verified by checking the quadratic dependence of $I(2\omega)$ on the laser power. It also needs to be ensured that no SHG signal is generated by other components in the laser beam path. Due to the nonlinear character it is also very important that the laser intensity on the substrate is kept constant during a spectroscopic scan and that the laser intensity is sufficiently low to avoid damage to the sample.

For amorphous films, an “isotropic” SHG signal is expected as described by $\infty m$-symmetry which means that the SHG signal shows maxima for three polarization configurations (for $p$-in – $p$-out, $s$-in – $p$-out, and mix-in – $s$-out, with mix representing a combination of 50% $p$ and 50% $s$) and zero signal for at least two polarization combinations (for $p$-in – $s$-out and $s$-in – $s$-out). Furthermore, the SHG signal should show no changes when the sample is rotated around its axis and should give zero signal for normal angle of incidence of the fundamental radiation. Furthermore, for thin films a SHG signal can originate both from the surface and buried interface of the film and surface sensitivity can only be proven by “modifying” the surface, e.g., by quenching of surface states (such as dosing silicon films with O$_2$, etc.).

**Spectroscopic and real-time SHG**

The first SHG experiments were carried out *ex situ* on rf plasma deposited a-Si:H films to investigate whether a-Si:H would yield any SHG signal. A SHG signal was detected for very thin a-Si:H films on fused silica substrates and from the polarization and rotational dependence shown in Fig. 11 it was concluded that the signal was isotropic as also expected for an amorphous film. The SHG signal showed also a distinct spectral dependence and by probing the film from the surface side and buried interface side it was concluded that the SHG signal was generated from both the surface and buried interface of the films [36].

![Figure 10. SHG setup implemented in an UHV reactor for *in situ* and real-time experiments on thin films. The laser (same as in Fig. 2) is directed onto the sample (35º angle of incidence) and the SHG signal is detected by photon counting using a photomultiplier and gated electronics. The polarization states of the fundamental and SHG radiation can be varied and filters and a monochromator are used to filter radiation at the SHG photon energy out of the fundamental radiation and vice versa. The intensity of the laser radiation is attenuated to avoid damage to the sample. A reference channel with SHG produced on GaAs is used to monitor the stability of the laser.](image-url)
To obtain insight into the microscopic origin of the SHG signal, SHG experiments were carried out in situ on hot-wire CVD deposited a-Si:H such that a possible influence of native oxide can be excluded. Figure 12 shows the spectral dependence of the SHG signal obtained for a 9 nm thick a-Si:H film deposited on fused silica. Spectral features are clearly observed and although identification of “resonances” in SHG signals is far from trivial, two resonant features can possibly be distinguished: one between 1.0 and 1.3 eV and one from 1.3 eV up to higher energies but with a center around 1.6 eV. Because the SHG signal of this 9 nm thick film can originate from the surface and the buried interface, the film was exposed to O₂ to investigate surface sensitivity. The spectral scan after O₂ dosing, also shown in Fig. 12, shows some clear differences from that of the as-deposited film revealing that the SHG technique is able to measure surface states of the a-Si:H. Especially the region between 1.0 and 1.3 eV is affected by the O₂ dosing while the region for energies >1.3 eV shows less change. On the basis of these and other observations, speculation on the microscopic origin of the SHG signal of a-Si:H is possible. For a full and detailed discussion also involving more experimental data we refer to Ref. [37], but here we give just our hypothesis with the main arguments: (i) the resonance between 1.0 and 1.3 eV is expected to originate from surface dangling bonds because the SHG signal is quenched by O₂ similar to the case of c-Si while also the photon energy range is similar; (ii) the resonance around 1.6 eV is expected to originate from strained Si-Si bonds in the surface and interface region using the same argument as is used for c-Si, i.e., the resonance resembles with the peak in the linear susceptibility of a-Si:H.

SHG is also very well suited for real-time measurements for example during film growth. Figure 13 shows the SHG signal for a photon energy of 1.2 eV as recorded during hot-wire CVD of an a-Si:H film up to a film thickness of 405 nm. Interference fringes in the SHG signal are clearly observed, and important information can be extracted from the fringes as can be attributed to several interference effects: interference of the fundamental radiation in the film, interference of the SHG radiation in the film for both the SHG created at the surface (in transmission) and at the buried interface (in reflection), and interference between the different contributions (surface/interface) to the SHG signal itself. These last two contributions disappear when going to thicker films (>150 nm) as the SHG radiation is effectively absorbed in the a-Si:H. These results show clearly the potential of the SHG technique for monitoring a-Si:H film growth. Reference [37] provides additional details.
Figure 12. *In situ* SHG spectra for the polarization combination $p_{\text{in}} - p_{\text{out}}$ for an as-deposited 9 nm thick $a$-Si:H film and for the film after exposure to $O_2$ ($8 \times 10^{-5}$ Torr, 300 s).

Figure 13. Real-time SHG signal ($p_{\text{in}} - p_{\text{out}}$ polarization configuration) at a photon energy of 1.2 eV as measured during $a$-Si:H deposition by hot-wire CVD.

ACKNOWLEDGMENTS

The authors acknowledge the following people for their important contributions: M. Nesládek (Limburgs Universitair Centrum) for the PDS measurements; H. Mertens and Prof. A. Polman (Center for Nanophotonics, FOM-Institute AMOLF) for the collaboration on the Er-doped Si-rich oxide experiments; Dr. A.C.R. Pipino (NIST) for the collaboration on the EW-CRDS technique; B. Hoex and dr. R. Engeln (Eindhoven Univ. of Technology) for the experiments and discussions; and M.J.F. van de Sande, J.F.C. Jansen, A.B.M. Hüsken, and H.M.M. de Jong for their skilful technical assistance. This work was supported by the Netherlands Foundation for Fundamental Research on Matter (FOM). The research of W.K. has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences (KNAW).

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