Unambiguous determination of Fourier-transform infrared spectroscopy proportionality factors: The case of silicon nitride

V. Verlaan,* C. H. M. van der Werf, W. M. Arnoldbik, H. D. Goldbach, and R. E. I. Schropp

Utrecht University, Faculty of Science, Department of Physics and Astronomy, Surfaces, Interfaces and Devices, NL-3508 TA Utrecht, The Netherlands

Fourier-transform infrared spectroscopy (FTIR) analysis is a widely used tool for the analysis of bonded hydrogen in hydrogenated silicon nitride (SiN_x:H). However, the proportionality factors between the integrated absorbance and bond densities, necessary for accurate hydrogen quantification, are still under discussion. The evolution of the total hydrogen concentration in thermally stable SiN_x:H during an anneal, as determined by FTIR, using previously reported proportionality factors [E. Bustarret *et al.*, Phys. Rev. B **77**, 925 (1998); W. A. Lanford and M. J. Rand, J. Appl. Phys. **49**, 2473 (1978)] appears to be inconsistent with the hydrogen concentration evolution as determined by elastic recoil detection (ERD) analysis. The differences indicate invalid proportionality factors for our samples. Since annealing experiments of thermally stable SiN_x:H offer a set of samples that differ only in N-H and Si-H bond densities, recalibration of these factors can be achieved by fitting the anneal time-dependent FTIR data to the evolution curves of the hydrogen concentration as detected with ERD. In this way a fully *experimental* calibration tool for the N-H and Si-H FTIR proportionality factors is obtained for individual, thermally stable, alloy films with multiple configurations of hydrogen bonds. Calibration was applied to SiN_x:H films in the range $1.09 < x < 1.35$, deposited at high deposition rate using the hot-wire (HW) chemical vapor deposition (CVD) technique. Each film was cut into 25 samples, which were annealed for different durations at 800 °C in N_2 and investigated using FTIR and ERD analysis. ERD measurements show that for the HWCVD SiN_x:H, no detectable change in N/Si ratio or mass density occurs during an anneal. The thermal stability of the samples is also confirmed by FTIR measurements, where the sensitive Si-H peak position shows negligible shift during the anneal treatment. Calibration of FTIR proportionality factors for these samples shows that both proportionality factors change with the composition of the deposited films, and that they differ from reported values.

PACS number(s): 33.20.Ea, 33.15.Fm

I. INTRODUCTION

Hydrogenated silicon nitride (SiN_x:H) is a widely used material with many technological applications. We investigated SiN_x:H for its use as a top layer on multicrystalline Si (mc-Si) solar cells where it simultaneously acts as an antireflection coating (ARC) and induces bulk and surface passivation of the mc-Si wafers.[1,2] These mc-Si solar cells dominate the present commercial photovoltaic market[3] whereby the SiN_x:H coating plays an important role in the enhancement of mc-Si solar cell performance. Apart from the proper optical properties, such as a high and tunable refractive index and low extinction coefficient, also good passivating properties of the SiN_x:H are very important. During a short anneal treatment, hydrogen is released from the SiN_x:H bulk and diffuses into the wafer, inducing bulk passivation.

Because the hydrogen incorporated in the SiN_x matrix plays such an important role in device physics, much effort has been devoted to gain knowledge on the behavior of hydrogen within SiN_x:H.[4–12] Hydrogen in SiN_x:H is mainly bonded as N-H and Si-H and a standard and quick technique for quantification of the hydrogen bonding configurations is Fourier-transform infrared spectroscopy (FTIR). With FTIR it is possible to determine the density of nonsymmetric bonds in the hydrogenated SiN_x matrix. A typical FTIR spectrum for SiN_x:H can be seen in Fig. 1. For the study of hydrogen the N-H vibration at 3340 cm^{-1} and the Si-H vibration around 2200 cm^{-1} are the most important.[13] In general, the

hydrogen bond density $[X\text{-}H]$, defined as the number of bonds per unit volume, can be determined by[14]

$$[X-H] = A_{(X-H)} \int \frac{\alpha(\omega)}{\omega} d\omega = A_{(X-H)} I. \quad (1)$$

Here, $\alpha(\omega)$ is the absorption coefficient at frequency ω, $A_{(X-H)}$ is the proportionality factor (also called proportional-
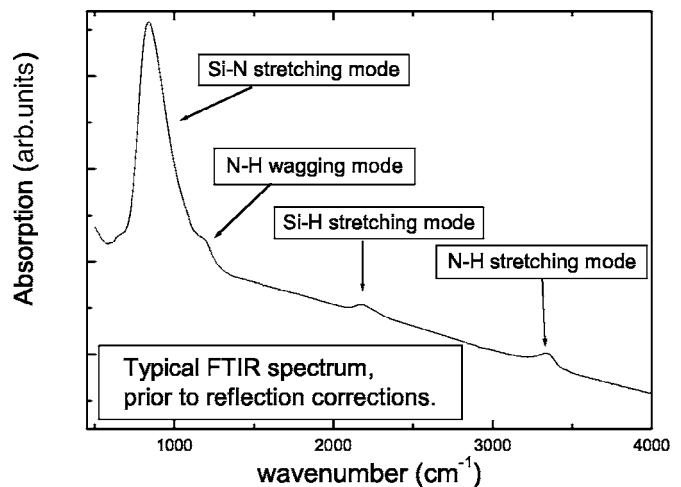

FIG. 1. Typical FTIR absorption spectrum with an indication to the most important peak. In this spectrum no correction for coherent and incoherent reflections are made.

ity constant), and I is the integrated absorption. The presence of NH_2 can be neglected in our films since the integrated absorption of the $N-H_2$ peak at 1550 cm^{-1} is less then 0.5% of that of the N-H integrated absorption. Also, the presence of significant amounts of $Si-H_2$ and $Si-H_3$ bonds is unlikely since our Si-H peaks are narrow and symmetrical.

As a result, the total hydrogen concentration can be determined as

$$[H] = \frac{H}{Si+N+H} = \frac{[Si-H]+[N-H]}{[Si]+[N]+[Si-H]+[N-H]}, \quad (2)$$

where H, Si, and N are the total number of atoms and [Si] and [N] denote the densities (atoms per unit volume). Because the density of Si and N per unit volume cannot be obtained directly from FTIR, these values are normally estimated from the Si-N bond density,[15] determined from the refractive index,[16,17] or calculated with the mass density.[6] In this paper, more reliable elastic recoil detection (ERD) data are used for this purpose. The major challenge that remains for determining reliable hydrogen concentrations with FTIR is to obtain trustworthy FTIR proportionality factors for the hydrogen bonds.

The main bottleneck in determining the FTIR proportionality factors for materials where hydrogen is distributed over multiple types of hydrogen bonds, is that direct one-to-one calibration with the hydrogen concentration from other methods is impossible. Consequently, the calibration of proportionality factors for silicon nitride is not as unambiguous as for *a*-Si:H, where all hydrogen is bonded in the Si-H bond configuration only and direct calibration can be performed readily.[18–21] In alloys the hydrogen is distributed over multiple types of bonding configurations, which thus far always necessitated assumptions to obtain the respective hydrogen proportionality factors.

In SiN_x:H, another challenge in the determination of the hydrogen proportionality factors is the large difference in electron negativity between N and Si influencing the strength of the hydrogen bonds for each type of back bonding, which is manifested by the large Si-H peak shift in the IR absorption spectrum.[16,17,22,23] This change in bond strength is also expected to change the oscillator strength and thereby the proportionality factor of the hydrogen bonds.[17] From silicon oxynitride research, it is known that not only the Si-H but also the N-H proportionality factor changes with differences in back bonding.[24] However, since it is expected that no N-N bonds are present in SiN_x:H, differences in primary back bonding for the N-H bonds can be excluded.

The first widely accepted values for the SiN_x:H hydrogen proportionality factors were obtained by Lanford and Rand.[25] They are still commonly used today. The authors used a collection of SiN_x:H samples with different compositions to derive one general value for the ratio of the cross sections of Si-H and N-H bonds. Using this ratio, it is possible to derive single-valued FTIR proportionality factors, under the assumption that they are identical for all as-deposited compositions. Whereas the procedure used by Lanford and Rand is an elegant one, their values do not account for the presence of different types of back bonding and therefore the assumption of invariable proportionality factors for all SiN_x:H com-

positions is questionable. Bustarret *et al.*[26] tried to overcome this shortcoming by assuming that the N-H bond density is proportional to the Si-N bond density. In addition, they took into account the differences in Si-H back-bonding configurations by determining the peak positions for each type of back bonding and ascribed different proportionality factors to each of them. Still, the two papers share the assumption of a fixed N-H proportionality factor for all SiN_x:H compositions.

In this paper we present a fully experimental method for the determination of the FTIR proportionality factors (N-H and Si-H) by calibrating them with the help of absolute concentrations from ERD analysis as a function of anneal treatment of the films. With this calibration procedure we do not make any assumptions about proportionality factors in SiN_x:H as a function of x. The only boundary condition is that H in Si-H and N-H bonds adds up to the total hydrogen concentration as derived by ERD. Because no assumptions are made about the investigated material, this calibration method is also applicable to comparable alloys such as $SiGe_x$:H, SiO_x:H, SiC_x:H, and even nonsilicon-containing alloys, as long as the matrix withstands an annealing treatment and the H disappears gradually from the material during the anneal. We calibrated the FTIR proportionality factors for a range of SiN_x:H films and show that both the Si-H and N-H proportionality factors change with the composition of hot-wire (HW) chemical vapor deposition (CVD) SiN_x:H.

II. EXPERIMENTAL DETAILS

SiN_x:H films were deposited on highly resistive monocrystalline Si wafers using the HWCVD technique, also known as hot filament (HF)-CVD or Cat-CVD. With this deposition method, the source gases are catalytically decomposed with very high efficiency[27] at heated wires only, and therefore no plasma is needed. This has the benefit that the substrate does not incur damage caused by ion bombardment. Moreover, this deposition technique reaches high deposition rates (up to 7 nm/s) for dense transparent films,[28–30] and the HWCVD technology can be applied on a large area.[31] The four-filament hot-wire reactor is part of an ultrahigh vacuum multichamber system (PASTA).[32] Pure silane (SiH_4) and ammonia (NH_3) were used as source gasses, which were catalytically decomposed on tantalum filaments at a temperature of 2100 °C. No hydrogen dilution was used. The substrate was heated by radiation from the filaments only and reached a temperature of about 450 °C. A shutter is located between the sample and the wires to control the growth and to let the substrates thermally equilibrate before the start of the deposition.

To investigate the hydrogen concentration for different compositions of SiN_x:H during an anneal treatment, films with different flow ratios were deposited and cut into 25 samples of 1×1 cm^2 from a homogeneous part of the films. Each of the 25 samples was annealed for a different time, between 0 and 600 s, whereby multiple samples were prepared using the shortest anneal durations to obtain reliable results also in the region where the fastest decrease in hydrogen concentrations occurs. The anneal experiments were performed with a rapid thermal process (RTP) furnace at
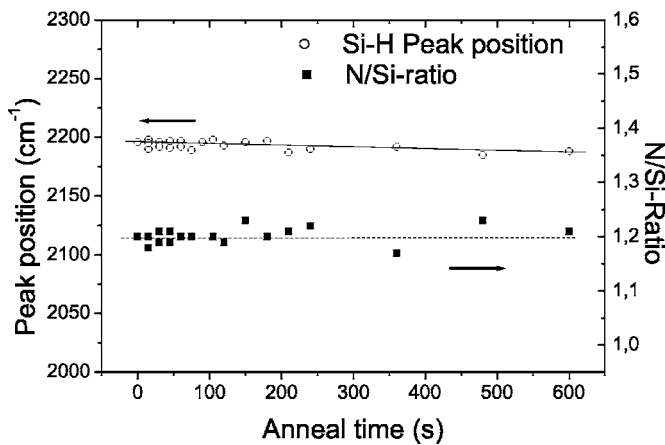
FIG. 2. The N/Si ratio and the Si-H peak position during annealing, showing negligible small changes. As the mass density also remains unchanged during annealing, it is safe to assume an invariable set of proportionality factors.

800 °C in a N_2 atmosphere. Apart from the anneal times, all samples experienced an extra anneal time due to short ramp-up and ramp-down periods. On all samples FTIR and ERD analyses were performed. Since the heavy ions (56 MeV Cu^{9+}) that are employed in ERD are expected to break many bonds,[33] the nondestructive FTIR measurements were performed prior to the ERD measurements. FTIR was used for determination of the hydrogen bond densities, whereby the H_2O and CO_2 signals were eliminated by intensive dry N_2 purging during the FTIR measurements. The raw FTIR spectra were corrected for incoherent and coherent reflections.[34,35] Correction for substrate absorption was achieved by subtraction of the measured absorption from a bare part of the same substrate. For comparison, values for the N-H and Si-H bond densities were initially determined using the proportionality factors from Lanford and Rand.[25] ERD analysis[36] was used to establish the densities of Si, N, and H per unit area from which, in combination with ellipsometry data, the mass density could be derived.

III. RESULTS

The ERD analysis shows that the SiN_x:H films have the intentionally different N/Si ratios of 1.09, 1.20, 1.24, and 1.35, and that each composition is uniform in the growth direction. The compositional inhomogeneity over the wafer area used for these experiments was less then 3%. The N/Si ratios remain constant during annealing, as do the mass densities of the films. The oxygen content was less then 0.5 at. % and is mainly located at the surface, as a result of postdeposition surface oxidation. Also, the Si-H peak position, which is sensitive to changes in the back-bonding configurations, shifts by only a negligible 6 cm^{-1} over the total anneal duration. As an example, the structural properties during an anneal are plotted in Fig. 2 for a film with a N/Si ratio of 1.20.

In Fig. 3 the bond densities for each of the samples are presented during an anneal by making use of the proportionality factors as published by Lanford and Rand.[25] For the

as-deposited samples, it appeared that for N-rich films the hydrogen is mainly bound to the nitrogen atoms and only a very small amount is bound to silicon. By incorporating more Si in the silicon nitride, the amount of N-H bonds decreases and the amount of Si-H bonds increases with a "crossover" around N/Si=1.20, as is also reported earlier for SiN_x:H depositions for different deposition techniques.[17,22,26,30] During the anneal treatment for each material, a decrease in the N-H bond density can be observed, whereby the N-H decrease is faster for more Si-rich materials. The three slightly Si-rich films show an increase in Si-H bond density during the anneal, which can be explained by a hydrogen transfer from N-H to Si-H bonds.

The total hydrogen concentration from FTIR as determined using Lanford and Rand's proportionality factors[25] reveals large inconsistencies when compared to the results from the ERD analysis. In Fig. 4 the total hydrogen concentrations as determined by the two techniques are compared for each film. A deviation of up to 2 at. % occurs in the H concentration as determined by the two techniques. It is remarkable that the FTIR hydrogen concentration is smaller than the ERD hydrogen for the N/Si=1.09 sample, while it is larger for the other samples. Moreover, while ERD analysis reveals the expected continuously decreasing hydrogen concentration, the hydrogen concentration as determined by FTIR, using Lanford and Rand's constants, shows a very unlikely *increase*.

IV. DISCUSSION

One possible explanation for the increase in the bonded hydrogen concentration upon annealing as observed with FTIR is the presence of as-deposited molecular hydrogen in the samples. This molecular hydrogen, not visible in FTIR, could dissociate during an anneal and thereby act as hydrogen source for the FTIR measurements. However, NMR measurements performed at the University of Utah on our HWCVD deposited SiN_x:H show that only a negligible amount of 0.1% of the hydrogen is present in molecular form in as-deposited samples. The presence of as-deposited H_2 would also be in conflict with the *higher* concentrations obtained by FTIR analysis than by the ERD analysis. We can thus rule out that the presence of as-deposited molecular H_2 causes the observed discrepancies between the two techniques.

This leads to the conclusion that the FTIR proportionality factors of Lanford and Rand are unsuitable. Of course, proportionality factors reported for individual samples may accidentally result in correct hydrogen concentrations. The unsuitability of the reported factors is revealed here, with discrepancies appearing as a result of an annealing treatment.

Because all structural properties remain stable during the anneal, it is justified to assume that the back bonding and internal structure of the SiN_x matrixes are unaltered during the anneal treatment and thus the FTIR proportionality factors are unaffected at any stage during the anneal treatment. The FTIR and ERD hydrogen concentration from a set of samples containing identical internal structure but different hydrogen distributions thus offers multiple independent
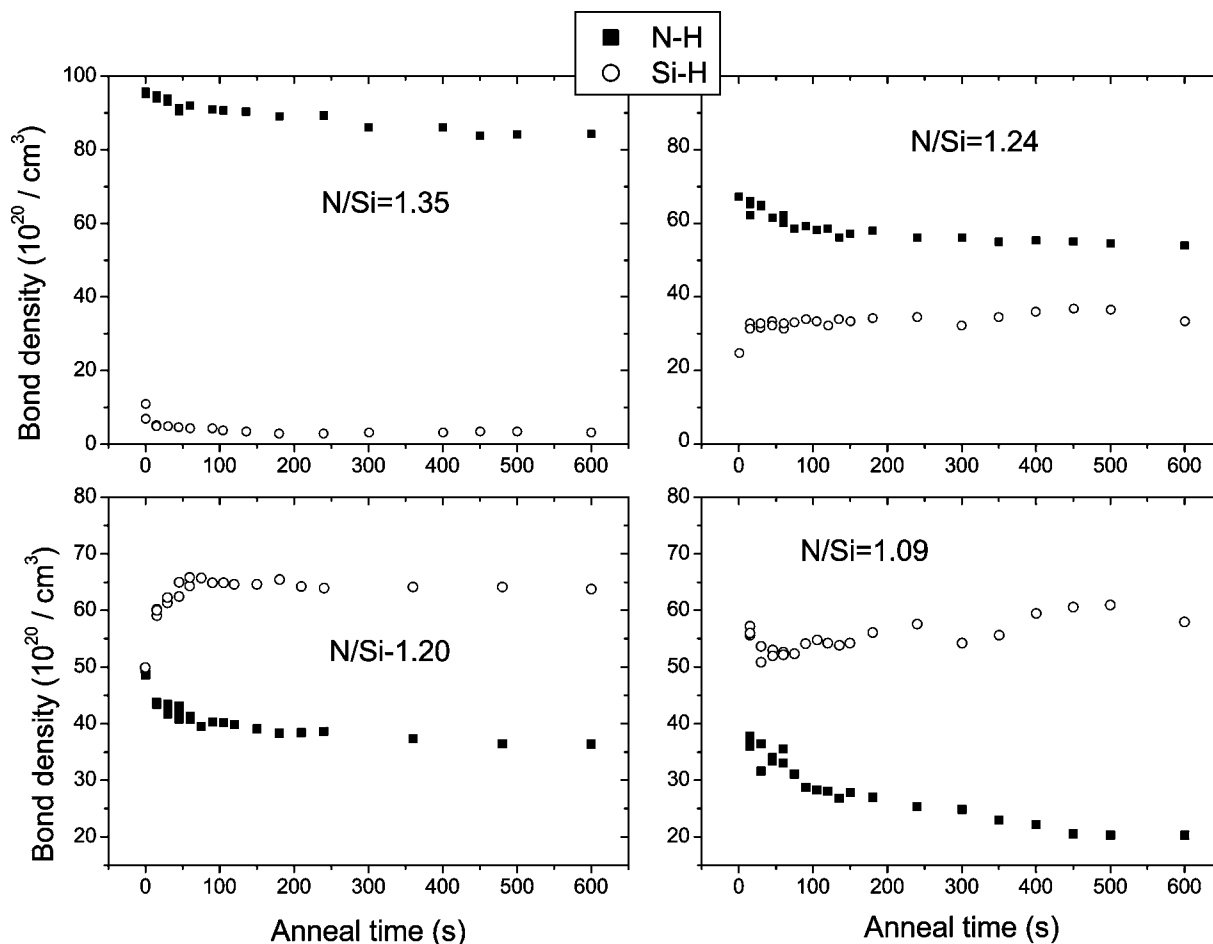
FIG. 3. Hydrogen bond densities with FTIR proportionality factors as reported by Lanford and Rand (Ref. 25), for different compositions of silicon nitride.

equations, which allows us to solve the two unique proportionality factors applicable to that material. Therefore, we are able to determine the correct FTIR proportionality factors for each film individually, by fitting the evolution of the total hydrogen concentration from FTIR to that determined by ERD analysis. The presented comparison between the hydrogen concentrations from FTIR and ERD during annealing thus offers a simple and fully experimental tool for independent calibration of the two FTIR proportionality factors without the need for assumptions. From the results in Fig. 5 it can be concluded that it is possible to match the hydrogen concentrations from FTIR and ERD by only varying the proportionality factors for the hydrogen bonds. Because both FTIR bond densities and the ERD atom concentrations are originally determined per unit area and only afterwards converted to volume densities by dividing by the thickness, this proportionality factor calibration method is independent of the accuracy of the thickness determination used.

The legitimacy of the calibrated values for the proportionality factors were confirmed by measuring FTIR on the different annealed samples with N/Si=1.20 a second time, this time *after* the ERD measurements were performed. When we determined the changes in the FTIR spectra arising from the heavy ion bombardment during the ERD measurement, an observed increase in N-H bond density at the expense of the

Si-H bond density seemingly leads to a decrease in the total H content by as much as 2.5% when Lanford and Rand's proportionality factors are used. The fact that the total FTIR hydrogen content does not change if we use the newly calibrated proportionality factors, in agreement with the invariable H content as determined from ERD itself, is a strong confirmation that our method for calibration of the FTIR proportionality factors is correct.

Although we applied this hydrogen proportionality factor calibration method to hot-wire deposited SiN_x:H, the presented method is not limited to this material only. No assumptions are made about the material or the proportionality factors themselves, and therefore the method can also be applied to other materials in which the hydrogen is bonded in multiple configurations provided that the matrix is thermally stable. The only restriction for the materials to enable the calibration of the proportionality factors using this method is that the ratio of the densities of the two types of bonding configurations shows a change.

The presented calibration method was applied to SiN_x:H samples with different compositions $(1.09 < x < 1.35)$. The results of the calibration technique are summarized in Table I together with compositional properties of the investigated films. The direct consequences of the newly calibrated values
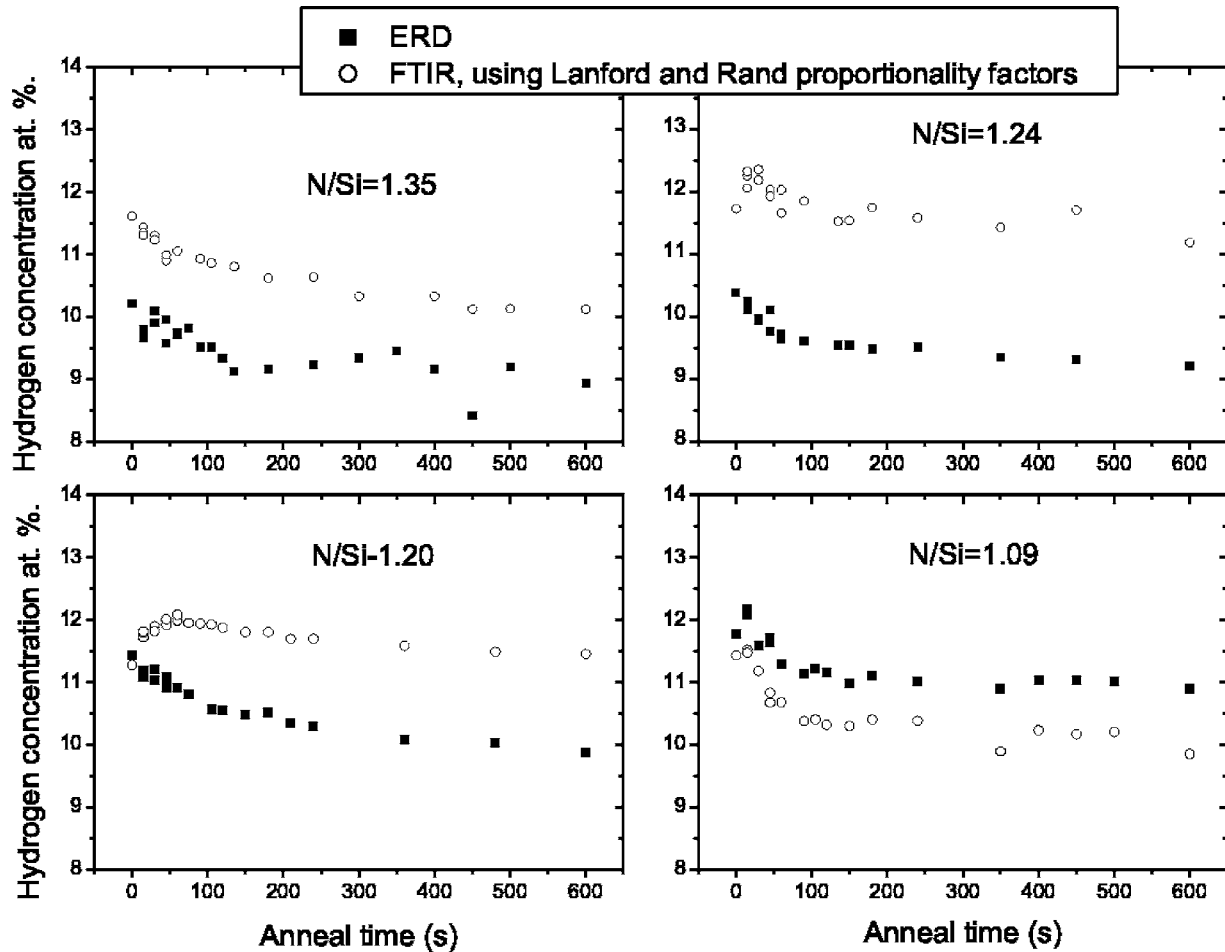
FIG. 4. Hydrogen concentrations as determined with FTIR using proportionality factors as reported by Lanford and Rand (Ref. 25), and ERD.

for the constants for the hydrogen bonding configurations can be seen by comparing Figs. 3 and 6. Interestingly, the two samples with comparable N/Si ratios, 1.20 and 1.24, have similar bond densities and trends during anneal, despite the fact that they have different proportionality factors. Even more interesting is that for the material with N/Si=1.20 the hydrogen bonding changes with the newly calibrated proportionality constants from predominantly silicon bonded to predominantly nitrogen bonded.

When comparing the present FTIR proportionality factors with the values as reported in literature distinct differences emerge. The first important difference is that the value for the N-H constant does vary with the composition of the SiN$_x$:H films. Both Lanford and Rand[25] and Bustarret *et al.*[26] *assume* a *fixed* value for the proportionality factor of 2.8×10^{20} cm^{-2} and 1.2×10^{20} cm^{-2}, respectively. Our calibrations show that this value can differ by almost a factor of 6 with the reported values and by a factor 2 over the investigated compositions.

For the Si-H proportionality factors, comparison of the calibrated proportionality factors with reported values is more complex since Bustarret *et al.* already accounted for a change in proportionality factors with different primary back bonding and, consequently, for the composition of the deposited films. They reported values between 0.7×10^{20} cm^{-2} and

4.0×10^{20} cm^{-2} depending on the peak position of the Si-H mode. Lanford and Rand reported an invariable value of 1.4×10^{20} cm^{-2}. Again, some of the calibrated proportionality factors in this work differ considerably from the reported values. While keeping in mind the specific Si-H peak positions of the samples, also these newly calibrated proportionality factors differ up to a factor of 6 from the reported proportionality factors. We note, however, that both referenced papers made the assumption of one single N-H proportionality factor for all compositions. This assumption itself directly influences their Si-H proportionality factors.

In the following we explain why such large differences in proportionality factors with earlier reported data are feasible. Due to the large differences in the electron negativity between N and Si, the electron distribution changes for different back-bonding configurations of the hydrogenated host atom. Most likely, different back-bonding configurations of the hydrogenated host atom cause changes in the FTIR proportionality factors. Because no N-N bonds are present in silicon nitride no different back bonding for the N-H configuration is possible, which is also in agreement with experiments, where no N-H peak shift is observed for different types of silicon nitride compositions. Since our calibration shows that the FTIR proportionality factor for N-H does
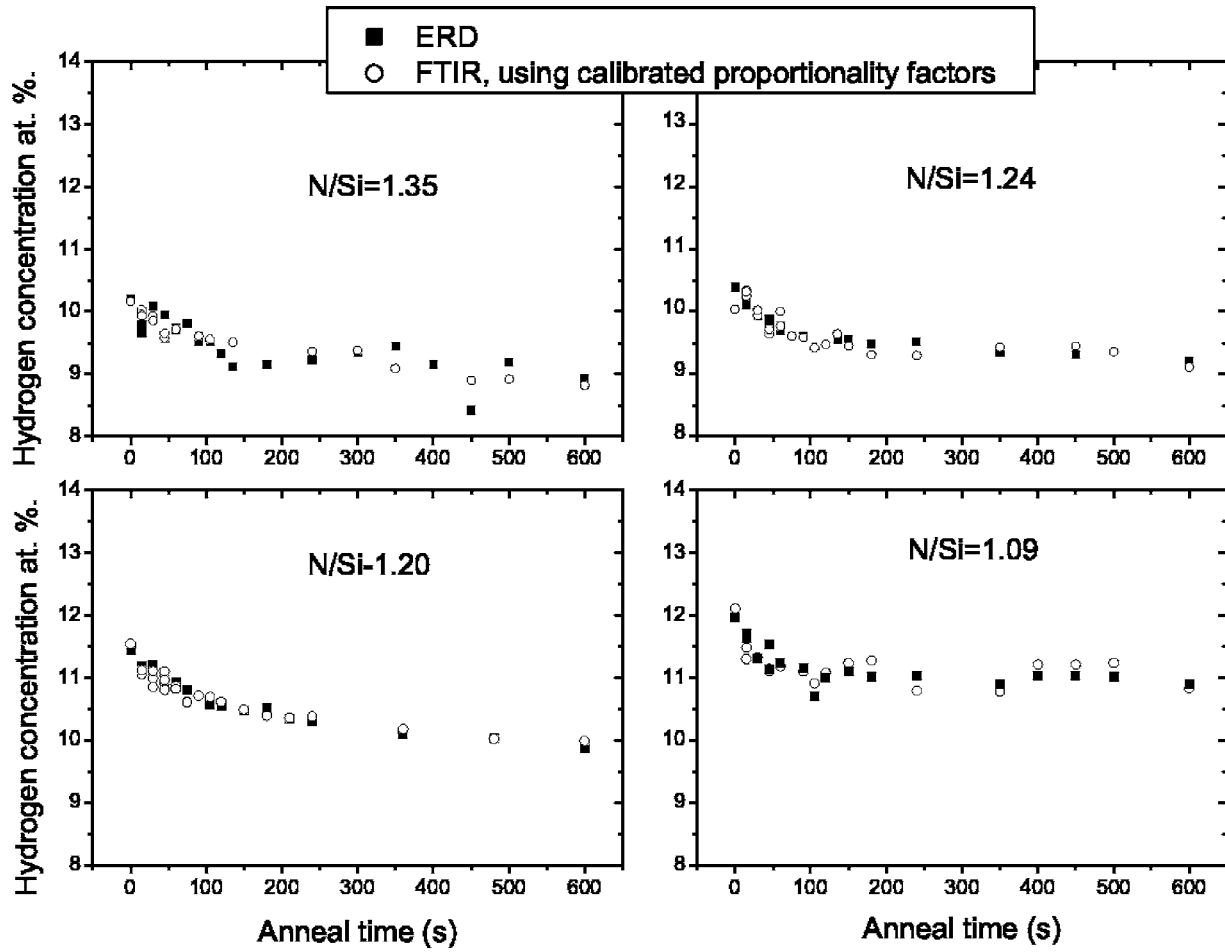
FIG. 5. Comparison of hydrogen concentration as determined with FTIR, with calibrated proportionality constants and ERD analysis.

change with composition, which cannot be caused by differences in primary back-bonding configurations, the observed changes in this FTIR proportionality factor with composition can be explained by changes in the total environment of the hydrogen bond including the mass density and secondary back bondings.

In this respect, Hasegawa *et al.*[37] made an interesting statement by claiming that the change in proportionality factors of the Si-H configuration is solely dependent on the physical environment and not on the back-bonding configuration. They used for their determination of the proportion-

ality factor, the modified random-bonding (MRB) model,[38] whereby the proportionality factor is described by

$$A_{\text{Si-H}} = \frac{cn\mu\omega}{2\pi^2 e^{*2}}, \tag{3}$$

where c is the speed of light, n the refractive index, μ is the reduced mass, and e^* is the effective charge. They therefore reported the value of the Si-H proportionality factor to be linearly dependent on the refractive index n as

$$A_{\text{Si-H}} = 2.58 \times 10^{19} n. \tag{4}$$

TABLE I. Calibrated FTIR proportionality factors for different SiN$_x$ compositions compared with reported values.

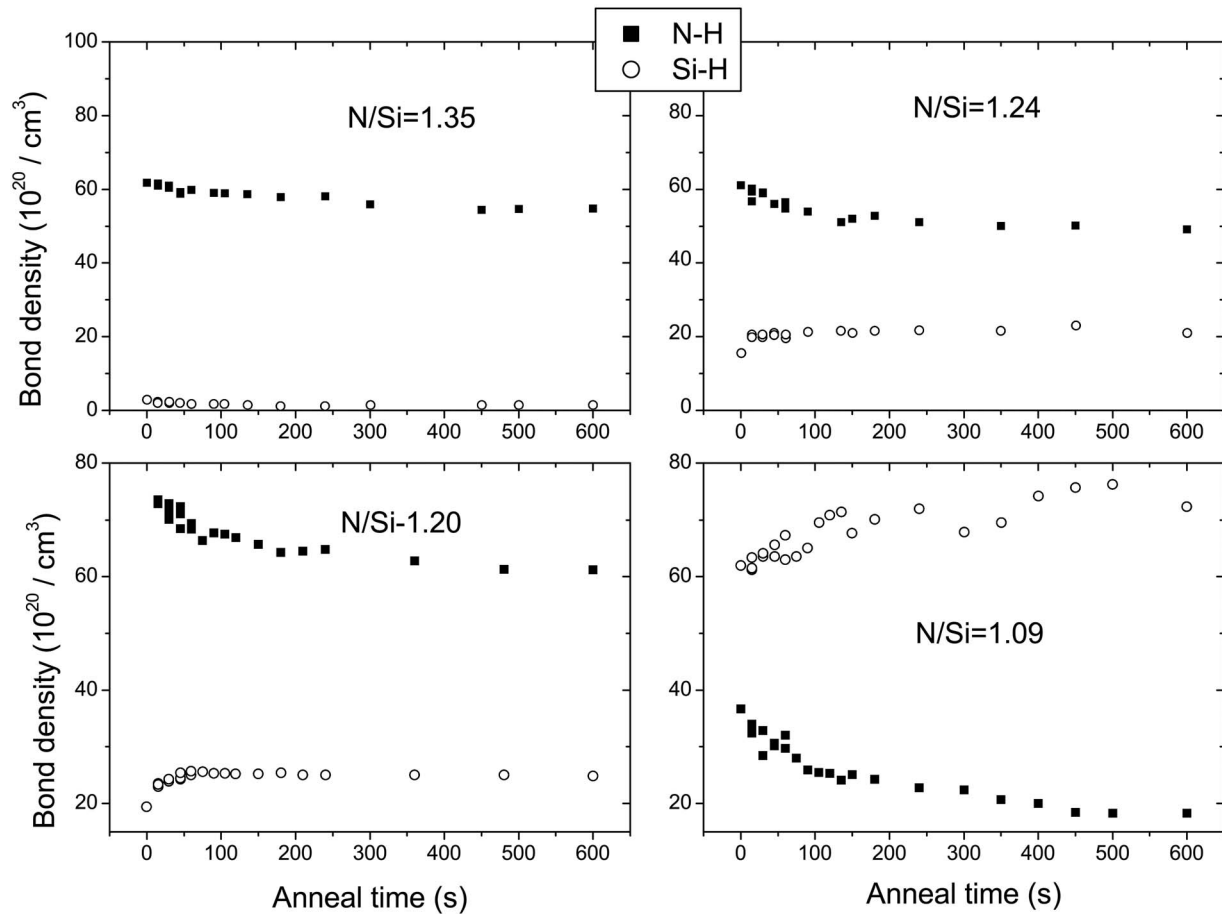| N/Si	ρ (g/cm^3)	This work		Ref. 26		Ref. 25		Ref. 37
		Si-H 10^{19} (cm^{-2})	N-H 10^{19} (cm^{-2})	Si-H 10^{19} (cm^{-2})	N-H 10^{19} (cm^{-2})	Si-H 10^{19} (cm^{-2})	N-H 10^{19} (cm^{-2})	Si-H 10^{19} (cm^{-2})
1.35	2.03	12±2	18±1	20	12	14	28	4.8
1.24	2.62	10±1	25±2	~28	12	14	28	5.0
1.20	2.93	5.5±0.5	47±2	~30	12	14	28	5.2
1.09	2.71	16±2	25±3	~36	12	14	28	5.5

FIG. 6. Hydrogen bond densities with calibrated FTIR proportionality factors for different compositions of silicon nitride.

Although our values are not exactly equal to these values, of all reported values for the Si-H proportionality factors these are closest to our calibrated proportionality factors. It is known that many other properties influence the IR absorbance of the hydrogen bonds. For instance, it is known that in a-Si:H the bond density of the Si-H configuration itself has influence on the Si-H proportionality factor,[39] causing a nonlinear relation between the integrated absorption and the bond density. Furthermore, it has been shown that the activation energy for N-H bond breaking varies for different types of materials,[40–42] which is an indication that the bond structure of N-H changes. Taking all this into account, it is clear that the proportionality factors are influenced by the total environment of the hydrogen bonds.

V. CONCLUSIONS

The evolution of the hydrogen concentrations for a range of compositionally different silicon-nitride films upon annealing is determined by ERD and FTIR analysis. When using the FTIR proportionality factors as reported by Lanford and Rand, the trends determined by these analysis techniques are inconsistent with each other. The annealing experiments have been utilized to offer a set of samples, which differ only

in N-H and Si-H bond densities; thus, the ERD and FTIR results form a set of multiple independent equations allowing us to solve the hydrogen FTIR proportionality factors appropriate for each composition. As a result, a fully experimental calibration method is obtained for the N-H and Si-H FTIR proportionality factors.

Because no assumptions are made about the material or proportionality factors themselves, the presented calibration method is not restricted to SiN_x:H only, and is also applicable to similar hydrogenated alloys having a rigid matrix structure. Calibration was performed on a range of SiN_x:H samples with different compositions and shows that both proportionality factors are dependent on the composition of the layer, and differ from reported values.

*Electronic mail: V.Verlaan@phys.uu.nl

[1] A. G. Aberle, Sol. Energy Mater. Sol. Cells **65**, 239 (2001).

[2] W. Soppe, H. Rieffe, and A. Weeber, Prog. Photovoltaics **13**, 551 (2005).

[3] G. P. Willeke, in *Proceedings of the 19th Photovoltaic Solar Energy Conference*, Paris, 2004 (WIP-Munich, Munchen, Germany, 2004).

[4] M. T. K. Soh, N. Savvides, C. A. Musca, M. P. Martyniuk, and L. Faraone, J. Appl. Phys. **97**, 93714 (2005).

[5] F. L. Martinez, I. Martil, G. Gonzalez-Diaz, B. Selle, and I. Sieber, J. Non-Cryst. Solids **523**, 227 (1998).

[6] G. Morello, J. Non-Cryst. Solids **187**, 308 (1995).

[7] M. Maede and H. Nakamura, J. Appl. Phys. **58**, 484 (1985).

[8] J. Hong, W. M. M. Kessels, W. Soppe, A. Weeber, W. M. Arnoldbik, and M. C. M. van der Sanden, J. Vac. Sci. Technol. B **21**, 2123 (2003).

[9] J. K. Holt, D. G. Goodwin, A. M. Gabor, F. Jiang, M. Stavola, and H. A. Atwater, Thin Solid Films **430**, 37 (2003).

[10] C. Boehme and G. Lucovsky, J. Appl. Phys. **88**, 6055 (2000).

[11] F. Jiang, M. Stavola, A. Rothatgi, D. Kim, J. K. Holt, H. Atwater, and J. Kalejs, Appl. Phys. Lett. **83**, 931 (2003).

[12] W. M. Arnoldbik, C. H. M. Marée, A. J. H. Maas, M. J. van den Boogaard, F. H. P. M. Habraken, and A. E. T. Kuiper, Phys. Rev. B **48**, 5444 (1993).

[13] A. Morimoto, Y. Tsujimura, M. Kumeda, and T. Shimizu, Jpn. J. Appl. Phys., Part 1 **24**, 1394 (1985).

[14] M. Cardona, Phys. Status Solidi B **118**, 463 (1983).

[15] A. W. Weeber, H. C. Rieffe, I. G. Romijn, W. C. Sinke, and W. J. Soppe, in *IEEE Photovoltaic Specialists Conference*, Florida, 2005.

[16] H. Mackel and R. Ludemann, J. Appl. Phys. **92**, 2602 (2002).

[17] F. Giorgis, F. Giuliani, C. F. Pirri, E. Tresso, C. Summonte, R. Rizzoli, R. Galloni, A. Desalvo, and P. Rava, Philos. Mag. B **77**, 925 (1998).

[18] A. A. Langford, M. L. Fleet, B. P. Nelson, W. A. Lanford, and N. Maley, Phys. Rev. B **45**, 13367 (1992).

[19] N. Maley, A. Myers, D. Pinarbasi, D. Leet, J. R. Abelson, and J. A. Thornton, J. Vac. Sci. Technol. A **7**, 1267 (1989).

[20] J. D. Ouwens and R. E. I. Schropp, Phys. Rev. B **54**, 17759 (1996).

[21] W. Beyer, Sol. Energy Mater. Sol. Cells **78**, 235 (2003).

[22] A. H. Mahan, A. C. Dillon, L. M. Gedvilas, D. L. Williamson, and J. D. Perkins, J. Appl. Phys. **94**, 2360 (2003).

[23] W. M. M. Kessels, J. Hong, F. J. H. van Assche, J. D. Moschner, T. Lauinger, W. J. Soppe, A. W. Weeber, D. C. Schram, and M. C. M. van de Sanden, J. Vac. Sci. Technol. A **20**, 1704 (2002).

[24] C. M. M. Denisse, J. F. M. Janssen, F. H. P. M. Habraken, and W. F. van der Weg, Appl. Phys. Lett. **52**, 1308 (1988).

[25] W. A. Lanford and M. J. Rand, J. Appl. Phys. **49**, 2473 (1978).

[26] E. Bustarret, M. Bensouda, M. C. Habrard, J. C. Bruyere, S. Poulin, and S. C. Gujrathi, Phys. Rev. B **38**, 8171 (1998).

[27] H. Umemoto, T. Morimoto, M. Yamawaki, Y. Masuda, A. Masuda, and H. Matsumura, Thin Solid Films **430**, 24 (2003).

[28] V. Verlaan, Z. S. Houweling, C. H. M. van der Werf, H. D. Goldbach, and R. E. I. Schropp, in MRS Symposia Proceedings No. 910 (Materials Research Society, Warrendale, PA, to be published).

[29] J. D. Moschner, J. Schmidt, and R. Hezel, in *Proceedings of the 19th Photovoltaic Solar Energy Conference*, Paris, 2004 (WIP-Munich, Munchen, Germany, 2004).

[30] C. H. M. van der Werf, H. D. Goldbach, J. Loffler, A. Scarfo, A. M. C. Kylner, B. Stannowski, W. M. Arnoldbik, A. Weeber, H. Rieffe, W. J. Soppe, J. K. Rath, and R. E. I. Schropp, Thin Solid Films **501**, 51 (2006).

[31] A. Lederman, U. Weber, C. Mukherjee, and B. Schroeder, Thin Solid Films **395**, 61 (2001).

[32] R. E. I. Schropp, K. F. Feenstra, E. C. Molenbroek, H. Meiling, and J. K. Rath, Philos. Mag. B **76**, 309 (1997).

[33] A. M. Brockhoff, W. M. Arnoldbik, and F. H. P. M. Habraken, Nucl. Instrum. Methods Phys. Res. B **190**, 226 (2002).

[34] M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phys. Rev. B **16**, 3556 (1977).

[35] N. Maley, Phys. Rev. B **46**, 2078 (1992).

[36] W. M. Arnoldbik and F. H. P. M. Habraken, Rep. Prog. Phys. **56**, 859 (1993).

[37] S. Hasegawa, L. He, Y. Amano, and T. Inokuma, Phys. Rev. B **48**, 5315 (1993).

[38] S. Hasegawa, M. Matuura, H. Anbutsu, and Y. Kurata, Philos. Mag. B **56**, 633 (1987).

[39] W. Beyer and M. S. Abo Ghazala, Mater. Res. Soc. Symp. Proc. **507**, 601 (1998).

[40] M. Maeda and I. Umezu, J. Appl. Phys. **70**, 2745 (1991).

[41] L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals* (Cornell University Press, Ithaca, NY, 1969).

[42] Z. Yin and F. W. Smith, J. Vac. Sci. Technol. A **9**, 972 (1991).