

# Quantitative determination of hydrogen concentration in silicon nitride dielectric films on silicon wafers using FTIR spectroscopy

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## Introduction

There has been a renewed interest in the research and development of silicon nitride ( $\text{SiN}_x\text{:H}$ ) films due to their excellent physical, mechanical, and optoelectronic properties. Silicon nitride films are widely used in the automotive, aerospace and medical devices industry as device passivation layers, interlayer insulators, and gate dielectric in modern semiconductor processes.<sup>1-3</sup> For  $\text{SiN}_x\text{:H}$  films prepared by plasma-enhanced chemical vapor deposition (PECVD), the degree of bonded hydrogen incorporation is an important characteristic.<sup>4-5</sup> Total hydrogen content, for example, affects film processing such as the etch rate.<sup>1</sup> The Si-H/N-H ratio, on the other hand, is a predictor of the refractive index (RI) and film stress of these films.<sup>2</sup> For example, an elevation from the stoichiometric ratio of 0.75 ( $\text{Si}_3\text{N}_4$ ) results in an increased RI as well as a less tensile (more compressive) stress.<sup>4</sup>

The nuclear resonance analysis-Rutherford backscattering spectroscopy (NRA-RBS) and secondary ion mass spectrometry (SIMS) are two classic techniques to analyze composition of solid surfaces and thin films. Both techniques are extremely sensitive but destructive; hence, not suited in a production environment where samples need to be analyzed in every deposition cycle. To that end, Fourier transform infrared spectroscopy (FTIR) readily lends itself for process monitoring in semiconductor fabrications due to its non-destructive measurements. FTIR is a fast, precise and reliable analytical technique widely used for the characterization of dielectric films in semiconductor wafer processing.

N-H and Si-H have unique IR absorption bands at  $3350\text{ cm}^{-1}$  (N-H stretching) and  $2170\text{ cm}^{-1}$  (Si-H stretching) regions, respectively. These spectral features are the basis for ensuing quantitative analysis on hydrogen concentration in  $\text{SiN}_x\text{:H}$  films, expressed in bond density ( $[\text{X-H}]$ ) or atomic % hydrogen (*at.% H*). This technical note provides a brief overview of the Lanford and Rand method for computing hydrogen concentration in  $\text{SiN}_x\text{:H}$  films based on FTIR measurements. Considerations in FTIR measurements and their implications on quantitative analysis are also discussed. A general discussion on partial least squares (PLS) approach for hydrogen analysis is also included.



Thermo Scientific™ Nicolet™ iS50 FTIR  
Spectrometer

## Sampling methods

Transmission is the most widely used FTIR sampling technique for thin film analysis on semiconductor substrates, especially for those films of thicknesses above 1000 Å, and analyses where non-contact measurements are required. Various wafer holder accessories, including Harrick variable angle transmission accessory<sup>5</sup> and Pike MappIR/MAP300 accessory,<sup>6</sup> can be used to place wafers into the beam path. For thinner films and analyses that require higher sensitivity, grazing angle attenuated total reflectance (GATR) offers a considerable advantage over transmission. Figure 1 shows the FTIR spectra of a 1000 Å silicon nitride film using transmission and two different ATR accessories with the Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer. The spectra obtained with the VariGATR™ and the WafIR accessories show a 4.6- and 40-fold increase, respectively, in signal intensity of the 2170 cm<sup>-1</sup> band (Si-H stretching) over the one using transmission. However, the GATR technique is largely a destructive method as the measurements require intimate contact between the sample and the Ge ATR crystal. The WafIR technique offers a significant improvement over the VariGATR sampling by minimizing the contact to only two pin-points of the wafer sample, but its

application is limited to the double-side polished (DSP) silicon wafer samples. A detailed account on the principle of the WafIR accessory will be published elsewhere. Note that the presence of non IR-transparent metal layers underneath the silicon nitride films will also limit the use of WafIR sampling and transmission.

With respect to quantitative analysis, it is important to note that GATR measurements do not follow a simple linear relationship between absorbance and thickness because of the limited penetration depth of the Ge crystal. Caution should therefore be exercised when interpreting experimental results.

Figure 2 shows the absorbance vs. thickness plots of four silicon nitride films on silicon wafers, with thicknesses ranging from 500 to 5000 Å. As expected, transmission shows a linear relationship between film thickness and absorbance. The measurements using VariGATR and WafIR accessories, on the other hand, exhibit a clear deviation from the linear relationship above 2000 Å. However, for the really thin films under ~2000 Å, the absorbance vs. thickness relationship is sufficiently linear for quantitative analysis while leveraging the great advantage in sensitivity of the grazing angle ATR technique.

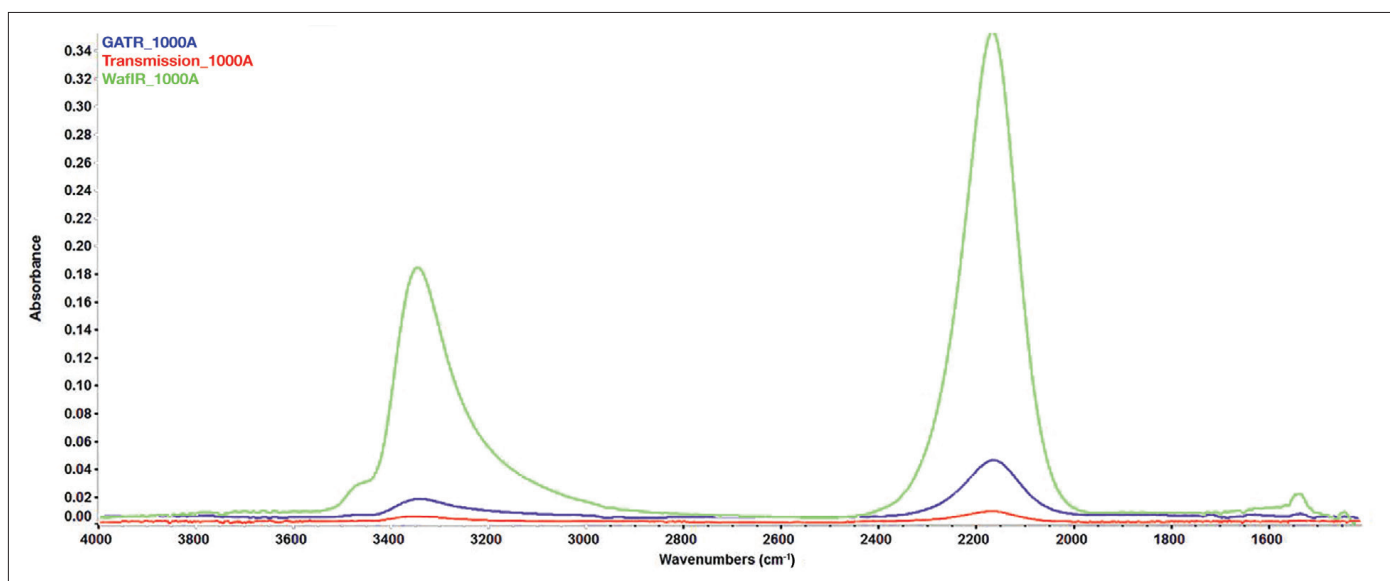


Figure 1. FTIR spectra of a 1000 Å SiN<sub>x</sub> film using transmission (red), GATR (blue), and WafIR (green) sampling methods. A VariGATR Germanium ATR accessory at an angle of 62.5° was used for the grazing angle measurements. For all measurements 256 scans were collected at a resolution of 4 cm<sup>-1</sup> in a nitrogen purged Nicolet iS50 FTIR Spectrometer.

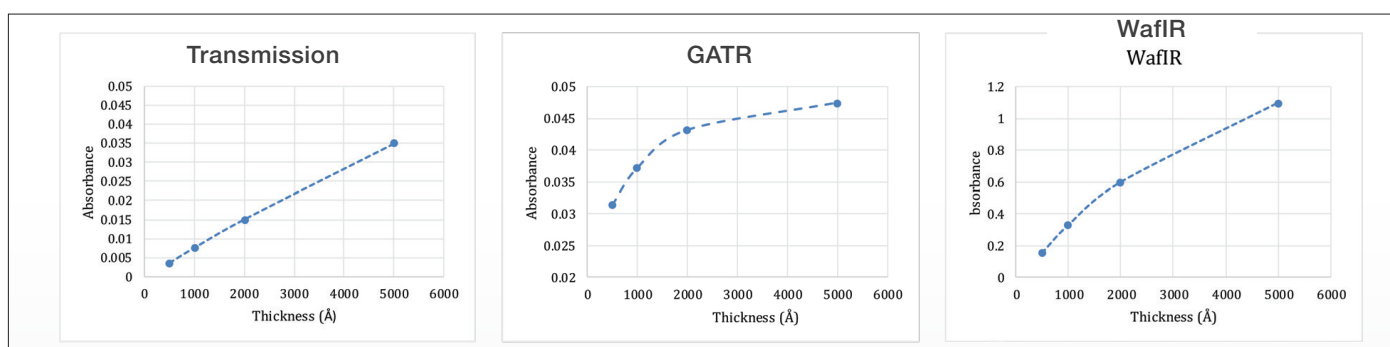


Figure 2. Absorbance vs. film thickness using three sampling techniques: transmission, grazing angle ATR using a VariGATR accessory, and multi-bounce ATR using a WafIR accessory.

In summary, transmission FTIR remains the method of choice for thick films and quantitative analysis due to its simplicity and wide range of linearity. GATR FTIR analysis with different accessories excels in sensitivity and ultra-thin film analysis, but with limitations in its applicability and a limited linearity range in quantitative analysis.

### Lanford and Rand method for quantitative determination of hydrogen concentration

The Lanford and Rand method<sup>7</sup> allows the determination of bond densities, and thus hydrogen concentration from FTIR measurements. By correlating the hydrogen content determined by NRA-RBS, absorption on a series of SiN<sub>x</sub>:H samples with different compositions, the IR absorption cross sections of Si-H and N-H bonds and the proportionality factor between N-H and Si-H were derived. While the assumption that proportionality factors are identical for all as-deposited compositions is controversial, the Lanford and Rand method remains one of the most widely used analytical methods for hydrogen analysis in silicon nitride films.

Equations 1 and 2 show the calculation of N-H and Si-H bond densities in atoms/cm<sup>3</sup>, where  $\sigma$  denotes the IR absorption cross section for different hydrogen bonds. Based on the Lanford and Rand method,  $\sigma_{N-H}$  is  $5.3 \times 10^{-18}$  and  $\sigma_{Si-H}$  is  $7.4 \times 10^{-18}$ . With a reasonably symmetrical band, the product of the absorbance and the full bandwidth at half height (FWHH) is a good approximation to the peak area. For N-H and Si-H, the FWHHs are approximately 110 cm<sup>-1</sup> and 130 cm<sup>-1</sup>, respectively. The film thicknesses are often measured by ellipsometry.

To compute the hydrogen concentration in at.% H, film density is also required, as shown in Equations 3 and 4. In which, [Si] and [N] denote the densities in atoms per unit volume. Because the density of Si and N cannot be obtained directly from FTIR measurements, these values are often estimated from the Si-N bond density, determined from the refractive index or calculated with the mass density.

#### Equation 1

$$[N - H] \text{ in } \frac{\text{atoms}}{\text{cm}^3} = \frac{\text{Peak area}_{3350 \text{ cm}^{-1}}}{\sigma_{N-H} \times \text{Film Thickness}} = \frac{\text{Peak height} \times 110 \times 10^8}{\text{Thickness} \times 5.3 \times 10^{-18}}$$

#### Equation 2

$$[Si - H] \text{ in } \frac{\text{atoms}}{\text{cm}^3} = \frac{\text{Peak area}_{2160 \text{ cm}^{-1}}}{\sigma_{Si-H} \times \text{Film Thickness}} = \frac{\text{Peak height} \times 130 \times 10^8}{\text{Thickness} \times 7.4 \times 10^{-18}}$$

#### Equation 3

$$\text{at. \% H in N - H} = \frac{[N-H]}{[Si] + [N] + [Si-H] + [N-H]} = \frac{\frac{\text{Peak height} \times 110 \times 10^8}{\text{Thickness} \times 5.3 \times 10^{-18}}}{3.0054 \times 10^{22} \times \text{Film Density} + [N-H] + [Si-H]} \times 100$$

#### Equation 4

$$\text{at. \% H in Si - H} = \frac{[Si-H]}{[Si] + [N] + [Si-H] + [N-H]} = \frac{\frac{\text{Peak height} \times 130 \times 10^8}{\text{Thickness} \times 7.4 \times 10^{-18}}}{3.0054 \times 10^{22} \times \text{Film Density} + [N-H] + [Si-H]} \times 100$$

As can be seen in Equations 1–4, the only variable in the Lanford and Rand model that is associated with FTIR measurements is the respective peak heights of the N-H and Si-H bands. To ensure accuracy, baseline correction is often required prior to the computation to remove the baseline artifacts arising from the internal reflections within the film (Figures 3 and 4).

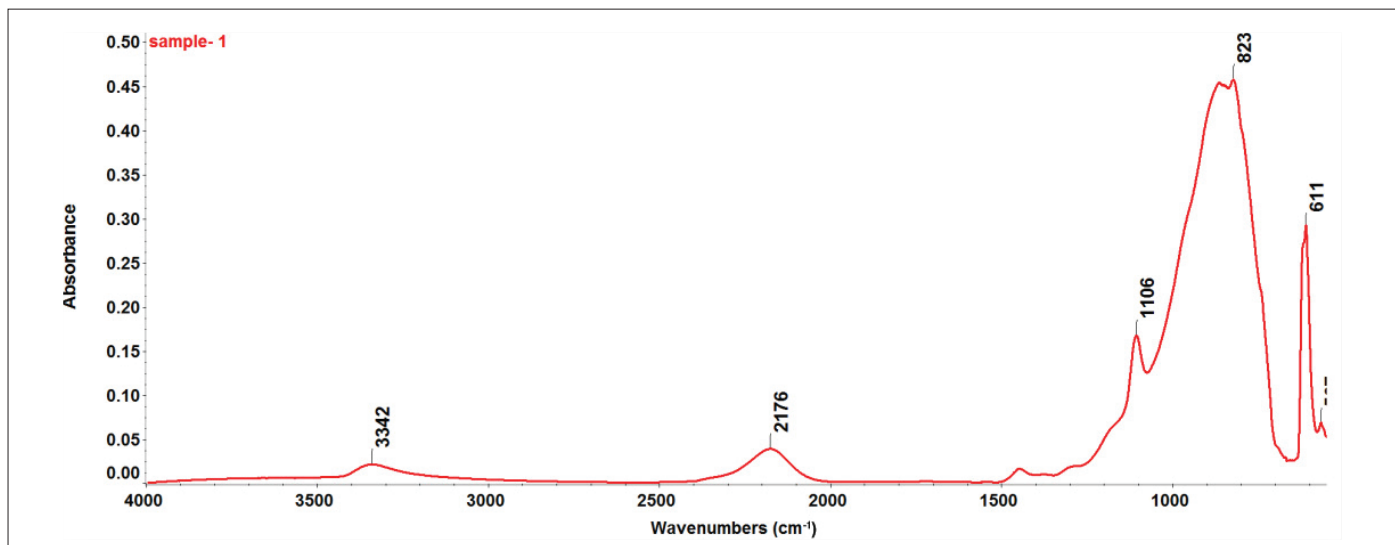


Figure 3. Transmission FTIR spectrum of a silicon nitride film on silicon wafer.

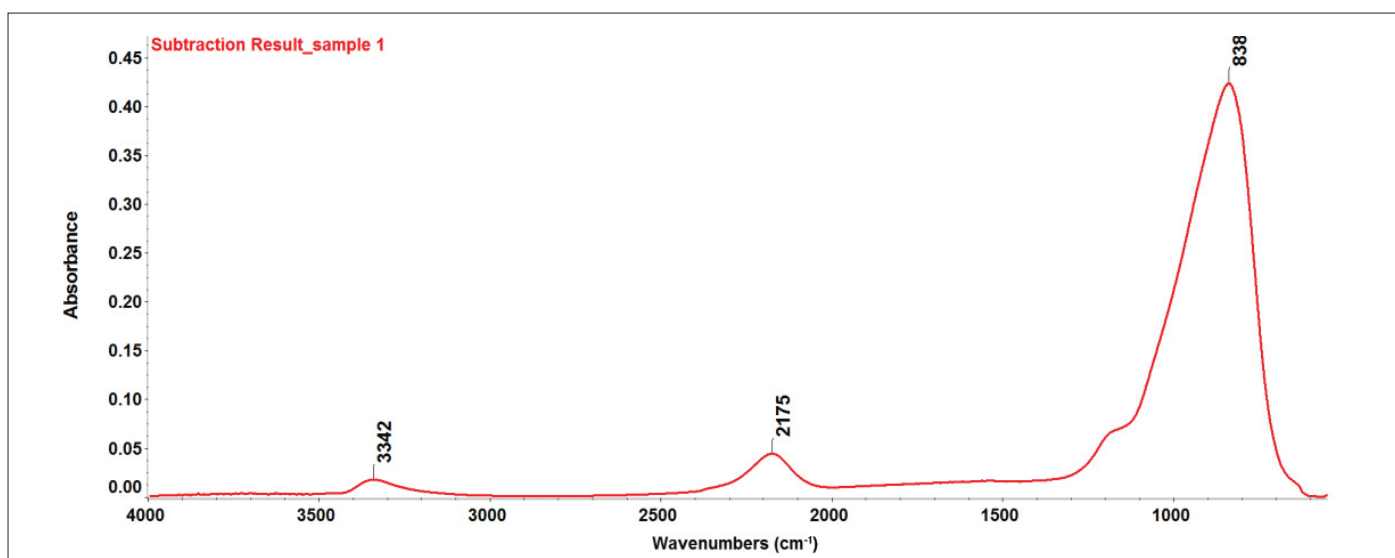


Figure 4. Processed spectrum after baseline correction and subtraction.

A series of silicon nitride films on silicon wafers with thickness ranging from 2990 to 5150 Å were measured by transmission FTIR spectroscopy, followed by the calculation based on the Lanford and Rand equations. Resulting *at.%* H values were compared with those obtained from the NRA-RBS measurements and summarized in Figure 5. In general, the difference % between the two methods are within  $\pm 5\%$  with one exception, where the *at.%* H (N-H) of sample 5 from the Lanford and Rand method is 7.5% lower than that from the RBS method. Note that there is no discernible correlation between difference % and film thickness, suggesting no systematic bias. The source of deviation includes internal reflections in FTIR measurements, non-conformity and difference in wafer substrates.

### Comments on PLS modeling for hydrogen determination

Recently various groups have recommended the partial least squares (PLS) approach for evaluating N-H and Si-H content in Si-N films.<sup>8</sup> Several factors should be taken into account when developing a PLS model. First, the wafer type of the calibration set should be the same as those to be analyzed to ensure the applicability of the PLS model. Secondly, wafers should have low variability, and the backside finish and resistivity need to be controlled to attain the precision typically required in the analysis. Thirdly, the hydrogen concentration and thickness range of the calibration set should bracket those of the samples such that the analysis can provide insight to process deviation.

Finally, the hydrogen concentrations of Si-H and N-H in the calibration set should be independent from each other, which can be accomplished by adjusting the flow rates of the  $\text{NH}_3$  and  $\text{SiH}_4$  reactants independently. While the PLS modeling is a more vigorous and often more accurate approach to quantitatively determine the hydrogen concentration, a prerequisite of the PLS modeling is that the hydrogen concentration of the calibration set needs to be predetermined by other techniques like NRA-RBS or SIMS, which can be time consuming.

### Summary

In this technical note, characterization of  $\text{SiN}_x\text{H}$  films on silicon wafers by FTIR spectroscopy is described. Three sampling techniques are discussed. Transmission is the method of choice for thick films ( $> 1000 \text{ \AA}$ ) and has a wide range of linearity in quantitative analysis. Grazing angle ATR offers a considerable advantage in sensitivity for thin films, but with a limited linearity range ( $< 2000 \text{ \AA}$ ). WaFIR analysis is a new approach for obtaining highly enhanced spectra from thin films. With respect to hydrogen concentration determination in hydrogenated silicon nitride films, the Lanford and Rand model, based on FTIR transmission spectroscopy, is simple and straightforward. Albeit flawed in its assumption that proportionality factors are identical for all as-deposited compositions, the *at.%* H results of a series of films in this study using the Lanford and Rand model show good agreement with the NRA-RBS methods. PLS calibration model approach is appropriate for wafer sets, where various internal reflection issues cause major deviation from the Lanford and Rand model.

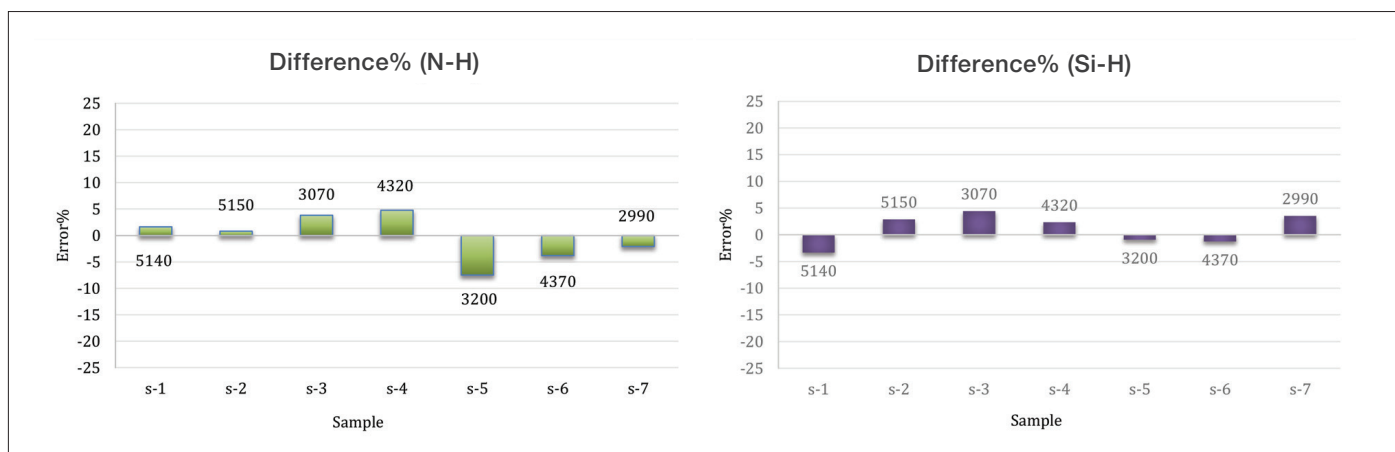


Figure 5. Comparison in *at.%* H values obtained from the Lanford and Rand method and the NRA-RBS method. The numbers inside the figures denote the thickness of the sample in Å.

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