Application Note: 50640

FT-IR Measurement of Interstitial Oxygen and Substitutional Carbon in Silicon Wafers

Ross Boyle, Thermo Fisher Scientific, Madison, WI, USA

Key Words

- **BPSG**
- **Classic Least Squares (CLS)**
- **Dielectric Films**
- **FT-IR ECO**
- **K-matrix**
- **Partial Least Squares (PSL)**
- **PSG**
- **Semiconductor Metrology**

Introduction

Most silicon wafers used in the production of semiconductors are cut from single crystals grown by the Czochlarski (CZ) method. During the growth process, oxygen and carbon are introduced into the molten silicon to varying degrees from the quartz crucible and the graphite heaters. As the ingot is pulled from the melt and the silicon solidifies, these impurities become incorporated into the crystal lattice. Because the carbon atoms occupy sites normally taken by silicon atoms in the lattice structure, this type of impurity is classified as substitutional. In addition, the oxygen atoms can find positions within the lattice structure between the silicon atoms, forming what are called interstitial impurities.

Different levels of interstitial oxygen (O_i) in the silicon have been correlated with varying effects, both physical and electrical. The need to control these effects leads to the need for monitoring the concentration of O_i [O_i] in the wafers used to fabricate devices. Although no direct effects of the substitutional carbon (C_s) have been proven, many experiments suggest that Cs affects the way the O_i behaves when silicon is heated, such as in typical silicon-processing temperature cycles.

The O_i is present in a gas/solid solution, which can undergo changes when heated. Oxygen is dissolved in molten silicon above the melting point (1,410 °C). As the silicon cools to ambient temperature, the oxygen becomes trapped at concentrations too high for a stable solution at this temperature, creating a super-saturated state. There is then a tendency for the Oi to precipitate out of the silicon as SiO_x when heated to temperatures that allow the oxygen some mobility. Substitutional carbon may form the centers for these precipitates to begin accumulating. As the oxygen comes out of solution, it can form electrically active defects that affect the characteristics of the devices fabricated on these wafers. Certain types of oxygen precipitates have been theorized to “getter” heavy metal impurities. In drawing these impurities away from the device regions of the wafer, a “denuded zone” can be formed that has superior qualities for device construction.

Historically, a number of techniques have been used to monitor [O_i] and the concentration of C_s [C_s] in bulk silicon. These include gas fusion analysis, mass spectrometry, charged particle analysis and neutron activation analysis, all of which are destructive, costly and time consuming. Because they are all methods that detect the elemental carbon and oxygen, they are non-specific and can be in error if carbon or oxygen is present in any other form.

The chemical nodes formed between silicon and these impurities can also be analyzed using infrared spectroscopy, which has none of the disadvantages noted above and is very specific to the [O_i] and [C_s] in silicon.

Infrared Analysis of [O_i] and [C_s] in Silicon

Silicon atoms form bonds with the carbon atoms (Si-C) and oxygen atoms (Si-O-Si) in the lattice structure. Infrared spectrometry uses light of wavelengths (2-25 µm) to irradiate the sample. Silicon is transparent to these wavelengths, and as the light passes through the sample, chemical bonds in resonance with a wavelength can absorb a portion of the light. The amount of light absorbed is proportional to the concentration of atoms forming the bond, and thus is measured and used to quantitate the concentration. In infrared spectroscopy, it is more convenient to represent the wavelengths as frequencies with the units cm^{-1} (frequency = 1/wavelength). In these units, the O_i absorption is centered at 1107 cm^{-1}, and the C_s absorption is centered at 605 cm^{-1} (Figure 1).

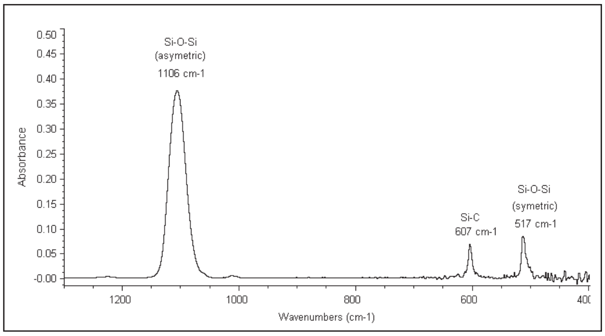

Figure 1: Spectrum showing the O_i and C_s absorptions in silicon. The spectrum of a float zone (FZ) reference has been removed to facilitate the viewing of the baselines around the peaks of interest.

The silicon crystal also gives rise to some unique absorptions in this region for the lattice bonds (Si-Si). These have been well characterized by studying the spectra of FZ silicon. FZ silicon is silicon that has been purified to remove (or greatly reduce) the Oi and Cs impurities. These absorbances can be used to determine the thickness of the sample (Figure 2).

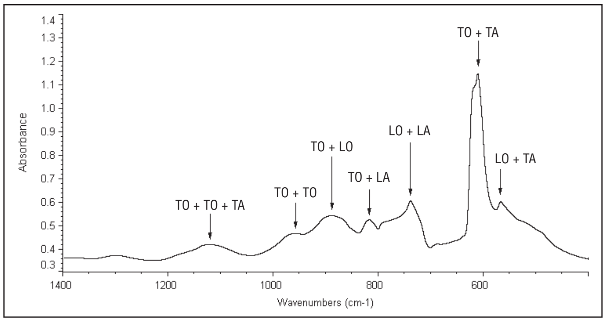

Figure 2: Spectrum of a FZ silicon reference. The labeled features are attributed to the different lattice vibrations in silicon. TA = transverse acoustic, TO = transverse optic, LA = longitudinal acoustic and LO = longitudinal optic

The FZ refining method is performed by passing the ingot through a furnace having different temperature regions. This silicon is heated to near melt in one of these regions, and the zones are moved along the ingot to "sweep" the now mobile impurities to one end of the crystal. This process is repeated a number of times to improve the purity of the silicon. The vacuum float zone (VFZ) method performs the process in a vacuum to aid in the removal of gaseous impurities. In both methods, the more passes performed, the lower the concentrations of the impurities.

An FZ silicon reference is needed because the Cs absorption occurs at the same locations as those of the strongest absorption from the silicon lattice (Figure 3). The TO + TA phonon (sometimes referred to as the "two phonon band") of silicon is centered at 630 cm^{-1} and makes the measurement difficult because of the lower signal-to-noise ratio in this region of the spectrum and the relatively low concentrations of carbon present. A phonon present in the oxygen region (TO + TO + TA or "three phonon band") at 1118 cm^{-1} is much less intense. This absorption imparts a non-linear baseline below the O$_i$ peak and is removed by the use of the FZ silicon reference (Figure 4).

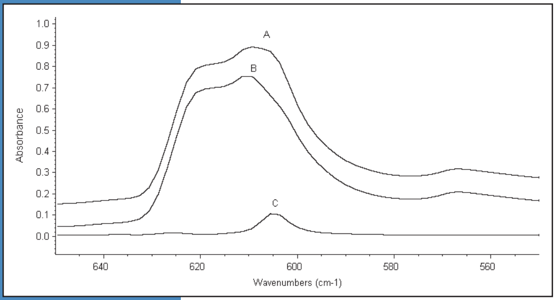

Figure 3: Spectra of silicon showing the region of the Cs carbon feature: A) CZ silicon with 1 ppmA carbon; B) FZ silicon with undetectable amounts of carbon; C) Difference spectrum showing the carbon absorption without the interfering silicon phonon absorption.

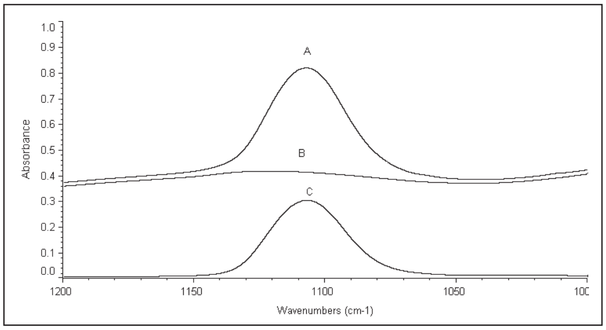

Figure 4: Spectra of silicon in the region where the absorption due to O$_i$ occurs: A) CZ silicon with 30 ppmA carbon; B) FZ silicon with an undetectable amount of oxygen; C) Difference spectrum showing the absorption due to oxygen without the silicon phonon interference.

Beer's Law expresses the relationship between concentration, sample thickness and absorption as follows:

$$A = a \bullet b \bullet c$$

where:

A = the measured absorbance
a = the absorptivity of a particular bond
b = the thickness of the sample
c = the concentration of the impurity

This equation shows that a linear relationship exists between concentration and absorbance (Figure 5) for a known thickness. Assuming that the impurity levels are negligible, the concentration of silicon is considered to be unity, allowing the phonon bands to be used to calculate the thickness (Figure 6).

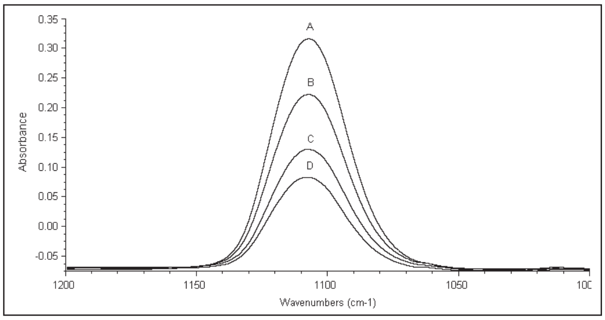

Figure 5: Spectra of the O$_i$ peak at various concentration levels: A) 40 ppmA; B) 30 ppmA; C) 20 ppmA; D) 15 ppmA. All levels are expressed in ASTM-79 concentrations

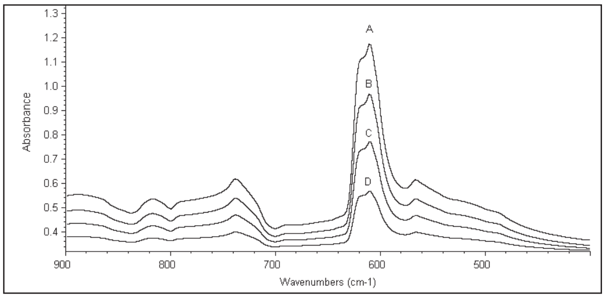

Figure 6: Spectra from silicon samples of various thicknesses: A) 2.00 mm; B) 1.50 mm; C) 1.00 mm; D) 0.50 mm

The following American Standard Test Methods (ASTM) documents address these analyses:

ASTM Designation F120 – Infrared Absorption Analysis of Impurities in Single Crystal Semiconductor Materials

ASTM Designation F121 – Interstitial Atomic Oxygen Content of Silicon by Infrared Absorption

ASTM Designation F123 – Substitutional Atomic Carbon Content of Silicon by Infrared Absorption

ASTM Designation F951 – Test Method for Determination of Radial Interstitial Oxygen

ASTM Designation F1188 – Test Method for Interstitial Atomic Oxygen Content of Silicon by Infrared Absorption

ASTM Designation F1189 – Test Method for Using Computer-Assisted Infrared Spectrophotometry to Measure the Interstitial Oxygen Content of Silicon Slices Polished on Both Sides

ASTM Designation F1391 – Test Method for Substitutional Atomic Carbon Content by Infrared Absorption

These documents are geared to the analysis of a specifically defined sample. The definition of the sample is a 2 mm-thick wafer, which has a resistivity greater than 10 Ω-cm and is lapped to a mirror finish on both sides (double-side polished). These limitations are partially due to the types of infrared instruments available at the time the original analyses were optimized. The modern Fourier transform infrared (FT-IR) spectrometers have much better performance specifications allowing the analyses to be performed on production wafers. Combined with the use of advanced mathematical algorithms, this process yields rapid and reproducible results on standard wafers (Table 1). Careful implementation of the quantitative approach is required to be assured that the published calibration constants are still valid for the non-ideal sample case. By implementing a step-wise procedure that mimics the individual steps described in the ASTM methods, Thermo Scientific Nicolet™ ECO™ software can be shown to comply with these published procedures, while removing all the operator-related errors by automating many of the required steps in the methods.

ANALYSIS	PRECISION	TIME
Oxygen [Oi]	±0.1 ppmA	30 sec.
Carbon [Cs]	±0.2 ppmA	100 sec.

Table 1: Reproducibility of Determinations

The need for 2-mm double-side polished samples has been overcome. However, there is still a need to control the resistivity to a level above 1 Ω-cm because the portion of the silicon spectrum used to calculate thickness and carbon becomes opaque to infrared radiation much below this value. Interstitial oxygen can still be determined at lower resistivity levels, but the thickness must be measured externally to the system and entered at the time of analysis. Due to the location of the C_s absorption, carbon determinations are not usually possible in low-resistivity samples.

Calculation & Calibration

The ASTM methods call for the sample spectrum to be acquired relative to an FZ silicon reference. The spectrum of FZ silicon contains all the absorbances of the silicon lattice, allowing them to be removed from the sample spectrum. Baselines are then fit into the resulting spectrum below the peaks, and the quantitative amounts are calculated from the Beer's Law relationship shown above.

The O_i concentration of FZ silicon is undetectable by infrared spectrometry, but the concentrations of C_s are still high enough in many types of FZ silicon that the determination of this impurity in standard samples is affected. The analysis of many samples with varying low levels (below 1 ppmA) of C_s can be used to extrapolate to the point of undetectable levels. This yields an enhanced spectrum of FZ silicon that can be used to analyze any sample of CZ silicon without erroneous results. The Thermo Scientific Oxygen & Carbon analysis package incorporates this enhanced FZ silicon reference, allowing for lower levels of carbon to be determined than is possible with commercially available FZ silicon samples.

In the computerized determination, each of the component concentrations and the thickness are calculated using least squares methods referenced to the calibration spectra used in generating the model. Each component concentration and thickness are analyzed independently using integrated absorbances over frequency intervals in the spectrum. The calculation can be further refined to a specific level of resistivity and backside damage by factoring in a sample spectrum of a representative CZ wafer of known thickness and impurity concentrations. References, interferences and baselines are known before the sample spectrum is acquired, so most of the time-consuming mathematics is pre-calculated. At the time of data collection, only the sum of the products of the integrated sample absorbances must be preformed, yielding a rapid analysis.

Further calibration of this technique to agree with an "accepted" alternate type of analysis is performed by applying a leveling correction to any or all of the results calculated by the algorithm. Only the final calculated concentrations are reported.

An additional benefit from the least squares evaluation of the O_i is the ability to extract the Oi information from the data in the presence of precipitated oxygen in the sample. This offers a new capability to monitor the change in $[O_i]$ in the sample after it has been annealed to force precipitation and formation of the denuded zone. This change in $[O_i]$ can be used to estimate the amount of precipitated oxygen in the sample. Normal peak height determinations outlined in the ASTM procedures cannot be used to accurately predict the $[O_i]$ after precipitation due to the overlap of the absorption bands associated with these different Si-O species.

Calculation of the $[O_i]$ is accomplished by multiplying the normalized absorbance by a conversion coefficient. Several conversion coefficients are currently in use, including DIN or "new ASTM", "old ASTM" and JEIDA. Because of the diversity of values, it is desirable to identify the one used when reporting the $[O_i]$. Our software suite offers all the standard conversions listed above and a user configurable conversion to meet any future changes in this analysis.

Conclusion

The use of Fourier transform infrared spectrometry for the determination of $[O_i]$ and $[C_s]$ levels in silicon is rapid, precise, non-destructive, non-contact and relatively inexpensive. With ECO application-specific software tailored for customer operation, these determinations can be performed with little knowledge of the theory of the instrument involved. Wafers of varying resistivities, backside damages and thickness can be easily analyzed. This affords the device engineers and operators in the fabrication lines a powerful technique to aid them in the production of semiconductor devices without the need for the spectroscopy "expert" to perform the analysis.

Bibliography

1. Kaiser (W.), Keck (P. H.), Lange (C. F.). *Phys. Rev.*, 1956, 101, 1264.
2. Kaiser (W.), Keck (P. H.). J. *Appl. Phys.*, 1957, 28, 882.
3. Kaiser (W.), Fisch (W.), Reiss (H.). *Phys. Rev.*, 1958, 112, 1546.
4. Baker (J. A.). *Solid-State Electronics*, 1970, 13, 1431.
5. Corbett (J. W.), Watkins (G. D.). *Phys. Rev.*, 1961, 121, 1001.
6. Corbett (J. W.), Chrenko (R. M.). *Phys. Rev.*, 1961, 121, 1015.
7. Bean (A. R.), Newman (R. C.), Smith (R. S.). *J. Phys. Chem. Solids*, 1970, 31, 739.
8. Aggarwal (R. L.), Fisher (P.), Mourzine (V.). *Phys. Rev.*, 1965, 138 A, 882.
9. Pajot (B.). *Solid-State Electronics*, 1969, 12, 923.
10. Graff (K.), Grallath (E.), Ades (S.), Goldback (G.), Tolg (G.). *Solid-State Electronics*, 1973, 16, 887.
11. Johnson (F. A.). *Proc. Phys. Soc.*, 1959, 73, 265.
12. Hrostowski (H. J.), Adler (B. J.). *J. Chem. Phys.*, 1960, 33, 980.
13. Schumann (P. A.), Keewan (W. A.), Tong (A. H.), Gegnwarth (H. H.), Schneider (P. C.). *J. Electro-chem. Soc.*, 1971, 118, 145.
14. Newman (R. C.), Willis (J. B.). *J. Phys. Chem. Solids*, 1965, 26, 373.
15. Baker (J. A.). *J. Appl. Phys.*, 1968, 39, 4365.
16. Nozaki (T.), Yatsurugi (Y.), Akiyama (N.). *J. Electro-chem. Soc.*, 1970, 117, 1566.
17. Kagel (R. O.), Baker (J. A.). *Appl. Spectrosc.*, 1974, 28, 65.
18. Hrostowski (H. J.), Kaiser (R. H.). *Phys. Rev.*, 1957, 107, 966.
19. Pajot (B.), Deltour (J. P.). *Infrared Phys.*, 1967, 7, 195.
20. Beeb (H.), Chapman (R. A.). *J. Phys. Chem. Solids*, 1967, 28, 2087.
21. Hass (W. E.), Schnöller (M. S.). *J. Electron. Materials*, 1976, 5, 57.
22. Chen (C. S.), Corelli (J. C.). *Phys. Rev. B*, 1972, 5, 1505.
23. Totterdell (D. H. J.), Newman (R. C.). *J. Phys. C*, 1975, 8, 589.
24. Goldstein (B.). Phys. Rev. Letters, 1966, 17, 428.
25. Neubrand (H.). *Phys. Stat. Sol.*, 1973, 17, 459.
26. Gross (C.), Gaetano (G.), Tucker (T. N.), Baker (J. A.). *J. Electro-chem. Soc.*, 1972, 119, 7.
27. Yatsurugi (Y.), Akiyama (N.), Endo (Y.), Nozaki (T.). J. *Electro-chem. Soc.*, 1973, 120, 975.
28. Pajot (B.). *Analusis*, 1977, 5, 293.
29. Ramsay (A.). *J. Amer. Chem. Soc.*, 1952, 74, 72.
30. Loewenstein (E. V.), Smith (D.), Morgan (R.). *Appl. Optics*, 1973, 12, 398.
31. Briggs (H. B.). *Phys. Rev.*, 1950, 77, 727.
32. Vidrine (D. W.). *Anal. Chem.*, 1980, 52, 92.
33. Glowinski (T. S.). *J. Phys. Chem. Solids*, 1977, 38, 963.
34. Baber (S. C.). *Thin Solid Films*, 1980, 72, 201.
35. Lerouellle (J.). *Appl. Spectrosc.*, 1982, 36, 153.
36. Rath (H. J.), Stallhofer (P.), Huber (D.), Schmitt (B. F.). J. *Electro-chem. Soc.*, 1984, 131 1920.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Africa	+43 1 333 5034 127
Australia	+61 2 8844 9500
Austria	+43 1 333 50340
Belgium	+32 2 482 30 30
Canada	+1 800 530 8447
China	+86 10 8419 3588
Denmark	+45 70 23 62 60
Europe-Other	+43 1 333 5034 127
France	+33 1 60 92 48 00
Germany	+49 6103 408 1014
India	+91 22 6742 9434
Italy	+39 02 950 591
Japan	+81 45 453 9100
Latin America	+1 608 276 5659
Middle East	+43 1 333 5034 127
Netherlands	+31 76 579 55 55
South Africa	+27 11 570 1840
Spain	+34 914 845 965
Sweden/Norway/Finland	+46 8 556 468 00
Switzerland	+41 61 48784 00
UK	+44 1442 233555
USA	+1 800 532 4752

www.thermo.com

Thermo Electron Scientific Instruments LLC, Madison, WI USA is ISO Certified.

AN50640_E 03/08M