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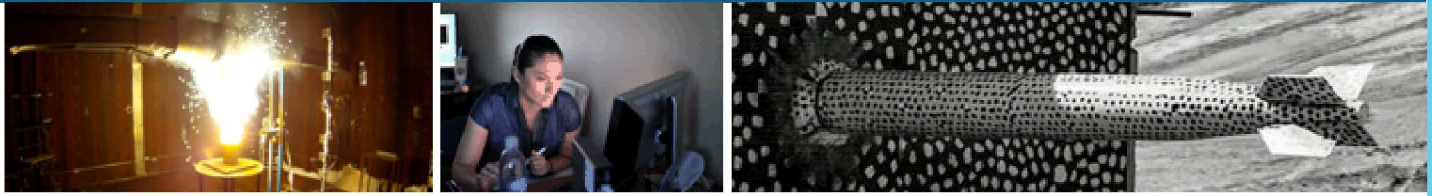
Infrared absorption oscillator strength factors in SiN_x thin films



PRESENTED BY

Sara DiGregorio

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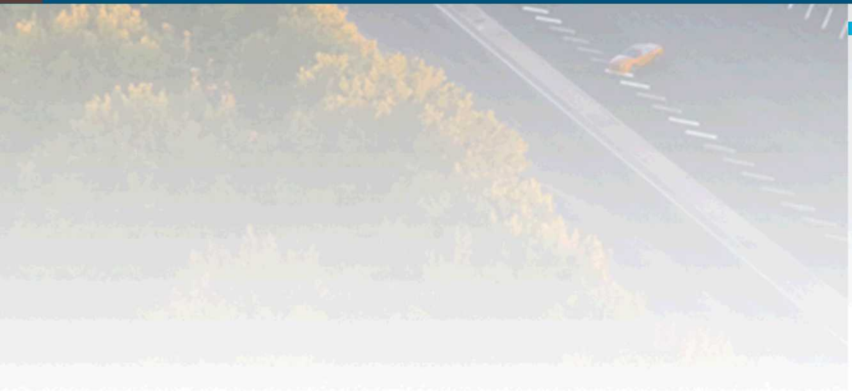
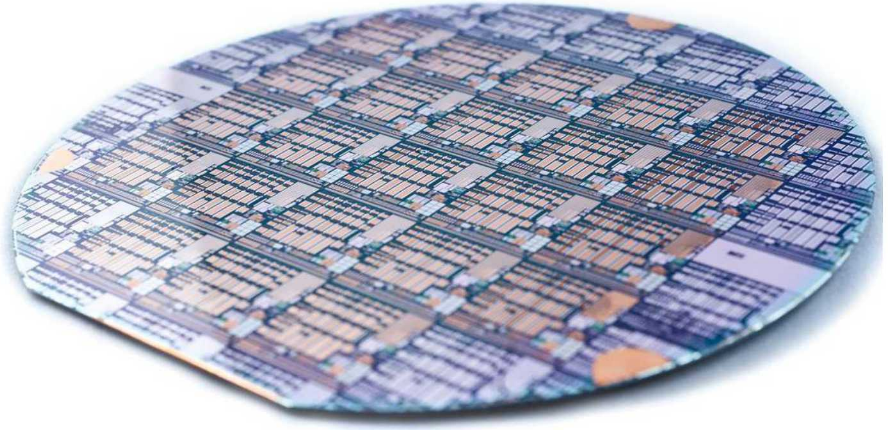
Background



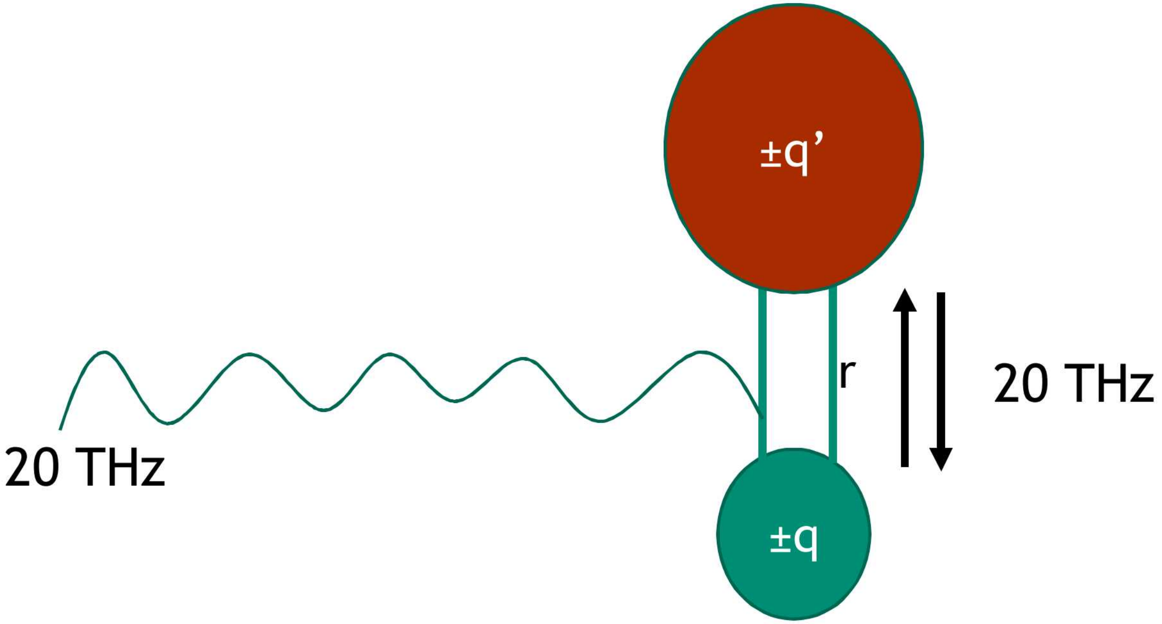
Silicon nitride, SiN_x, is used in microelectronics fabrication



- Chemically and thermally stable
- Useful dielectric properties
- Many deposition techniques available
- Many properties have been published
- The oscillator strength factor (K) of the SiN_x asymmetric stretch mode is the subject of this study
- We used IR absorption to characterize the K value for each film

Absorption occurs when an oscillating dipole interacts with light of the same frequency

- Bonds vibrate at natural resonating frequencies
- Bond dipole = q*r
- If the incoming light wave oscillates at the same frequency as the molecular dipole, absorption occurs



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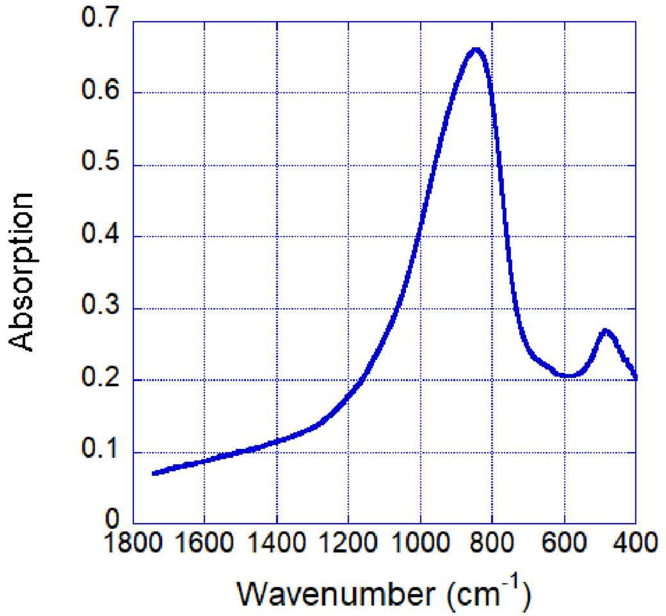
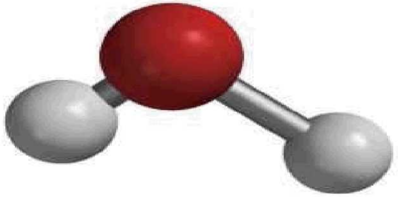
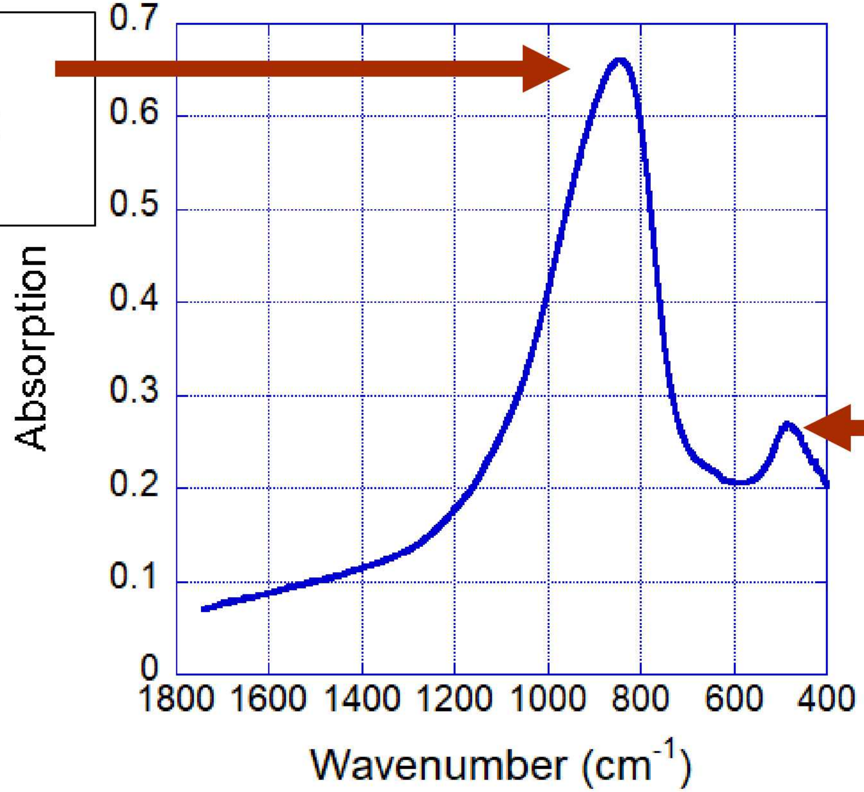


The oscillator strength factor, K is characterized by Si-N infrared active asymmetric stretch mode

- The two IR active Si-N modes are symmetric stretching centered about 480 cm^{-1} and asymmetric stretching centered about 830-875 cm^{-1}

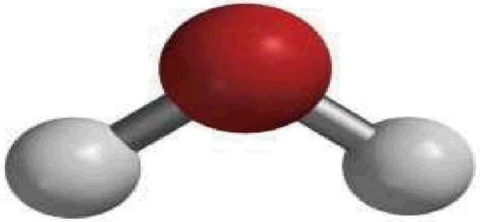




Si-N asymmetric stretching

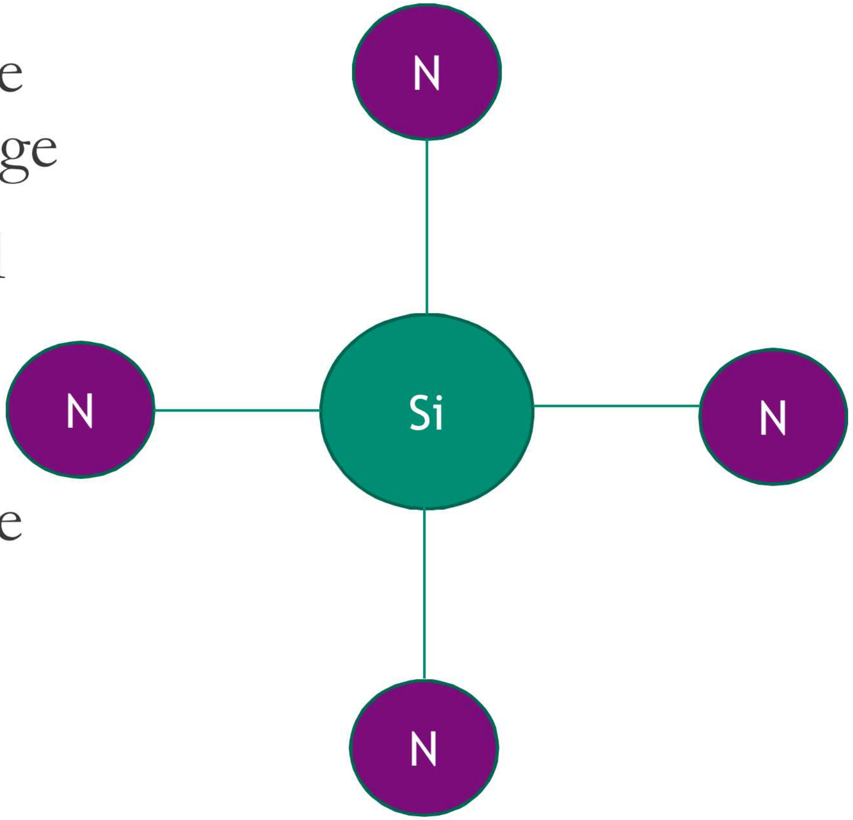
Si-N symmetric stretching

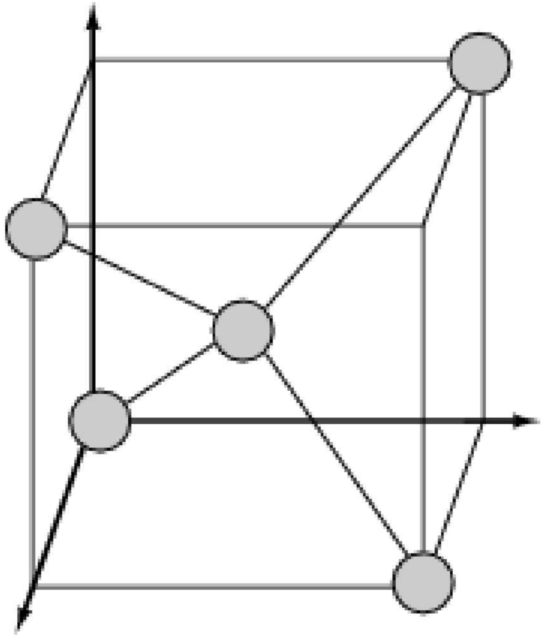
Absorption spectra of a stoichiometric SiN_x film of 142.7 nm



The Si-N asymmetrical stretch mode is sensitive to changes in Si content

- An increase in Si content causes the SiNx tetrahedron structure to change
- Compositionally induced structural changes alter the IR properties
- We wanted to see how the IR properties changed with altering the local bonding structure by varying film composition and thickness

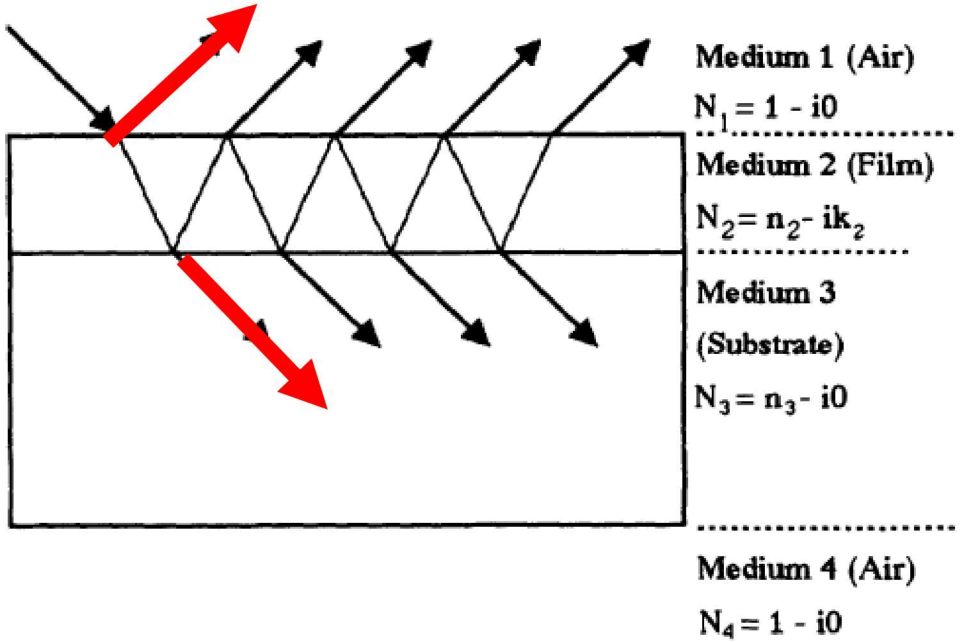




Stoichiometric Si_3N_4 structural tetrahedron

Multiple reflections must be accounted for in thin film spectroscopy

- IR measurements are used to characterize the compositionally induced changes to the Si-N asymmetric stretch mode
- Multiple reflections occur at the film substrate interface and within the substrate



Multiply reflected beams off the film substrate interface

$$T = \frac{(1-R_{12})(1-R_{23})(1-R_{34})e^{-\alpha d}}{(1-R_{23}R_{34})-(R_{12}R_{23}+R_{12}R_{34}-2R_{12}R_{23}R_{34})e^{-2\alpha d}} .$$

Full expression for transmittance with multiply reflected beams

Maley, N. (1992). Physical Review B, 46(4) 2078-2085

Absorption coefficient must be defined in terms of transmission and reflection to account for multiple reflections

- The absorption coefficient is solve from IR transmission where reflections at the film substrate interface are negligible and reflections within the substrate are incoherent

$$T(\omega) = \frac{(1-R(\omega))^2 e^{-\alpha(\omega)d}}{1-R(\omega)^2 e^{-2\alpha(\omega)d}}$$

- Thus, $\alpha(\omega)$ is then given by

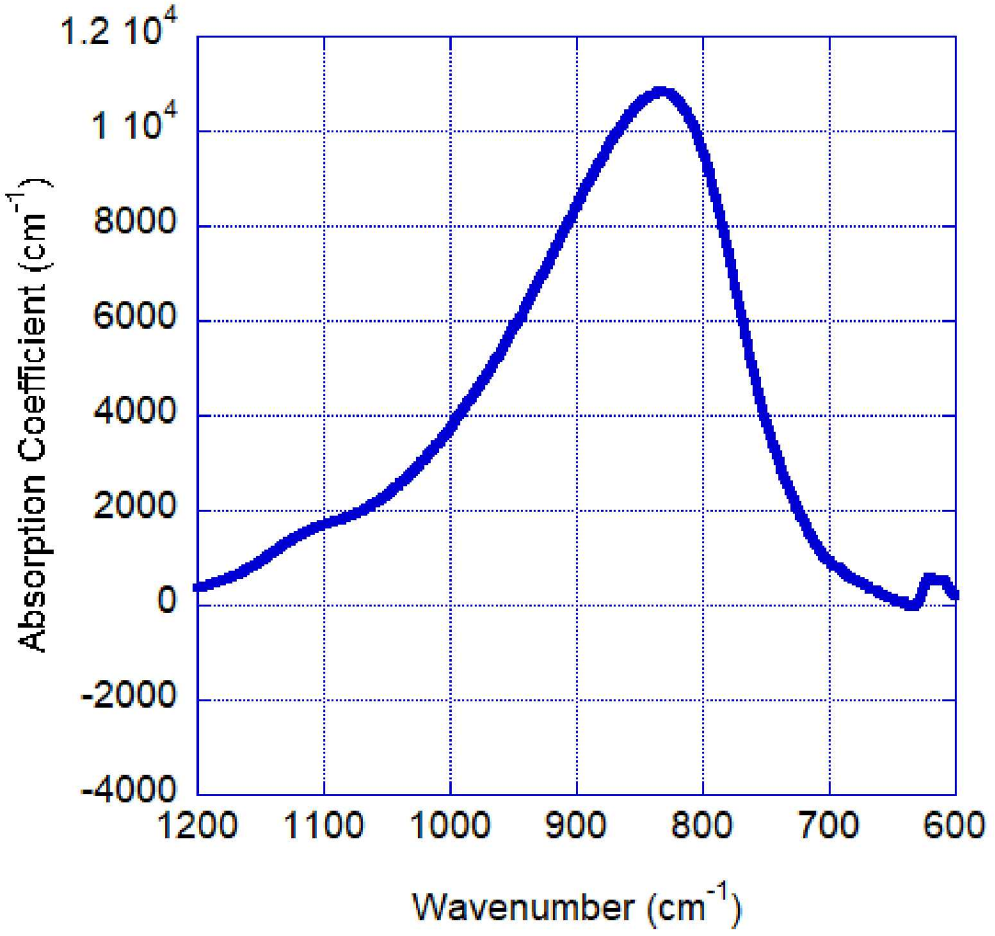
$$\alpha(\omega) = \frac{-1}{d}\ln(\frac{A(\omega)^2}{T(\omega)}[(1+(\frac{T(\omega)}{A(\omega)^2 R(\omega)})^2)^{1/2}-1])$$

- where

$$A(\omega)^2 = \frac{(1-R(\omega))^2}{2R(\omega)^2}$$

Brodky, M.H., Cardona, M. & Cuomo, J.J. (1977). Physcal Review B, 16(8), 3556-3571. Stavola, M. & Fowler, W.B. (2018). Journal of Applied Physics, 123.

Each film has a characteristic absorption coefficient



Absorption coefficient for a Si_3N_4 film 238.2 nm thick

- Each film has a characteristic absorption coefficient that takes into account multiple reflections
- The integrated absorption coefficient is what is used to solve for K

The oscillator strength factor (K) is a parameter that relates bond density to the integrated absorption coefficient

$$[N] = \frac{c^2 n \omega_t \mu}{\pi q^2} \int \frac{\alpha(\omega)}{\omega} d\omega$$

- [N]=nitrogen bond concentration
- n=refractive index
- ω_t=peak frequency of the Si-N asymmetric stretch mode
- μ=reduced mass
- q=effective oscillating charge
- α(ω)=absorption coefficient

$$K \equiv \frac{c^2 n \omega_t \mu}{\pi q^2}$$

$$\boxed{K = \frac{[N]}{\int \frac{\alpha(\omega)}{\omega} d\omega}}$$

Oscillator strength factor (K)

Motivation for characterizing K was to find a universal parameter that could be used to solve for [N] for any SiN$_x$ film

$$\boxed{K = \frac{[N]}{\int \frac{\alpha(\omega)}{\omega} d\omega}}$$

- [N] could be found from film thickness and IR measurements alone if K was constant for every film composition

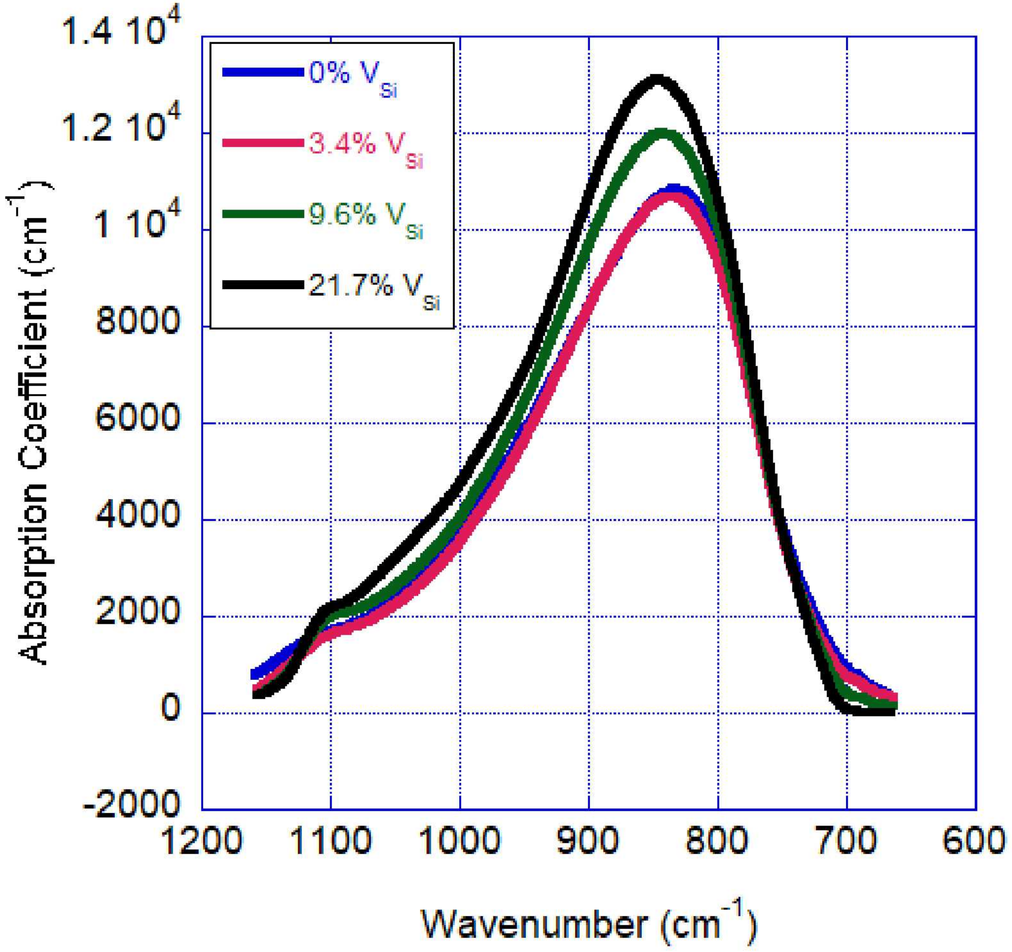
Experimental

SiN_x LPCVD films were prepared in a vertical thermal reactor for films of varying composition and thickness

- Low pressure chemical vapor deposition (LPCVD)
- Dichlorosilane and ammonia
- $3SiH_2Cl_2+NH_3 \rightarrow Si_3N_4+3HCl+6H_2$
- Composition ranged from 0-25% volume fraction silicon (V_{Si})
- Thickness ranged from 136-558 nm
- [N] was calculated for each film from density and ellipsometry measurements
- T and R were collected for each film
- Absorption coefficient was calculated for each film

Results

Increasing V_{Si} leads to less tensile film strain



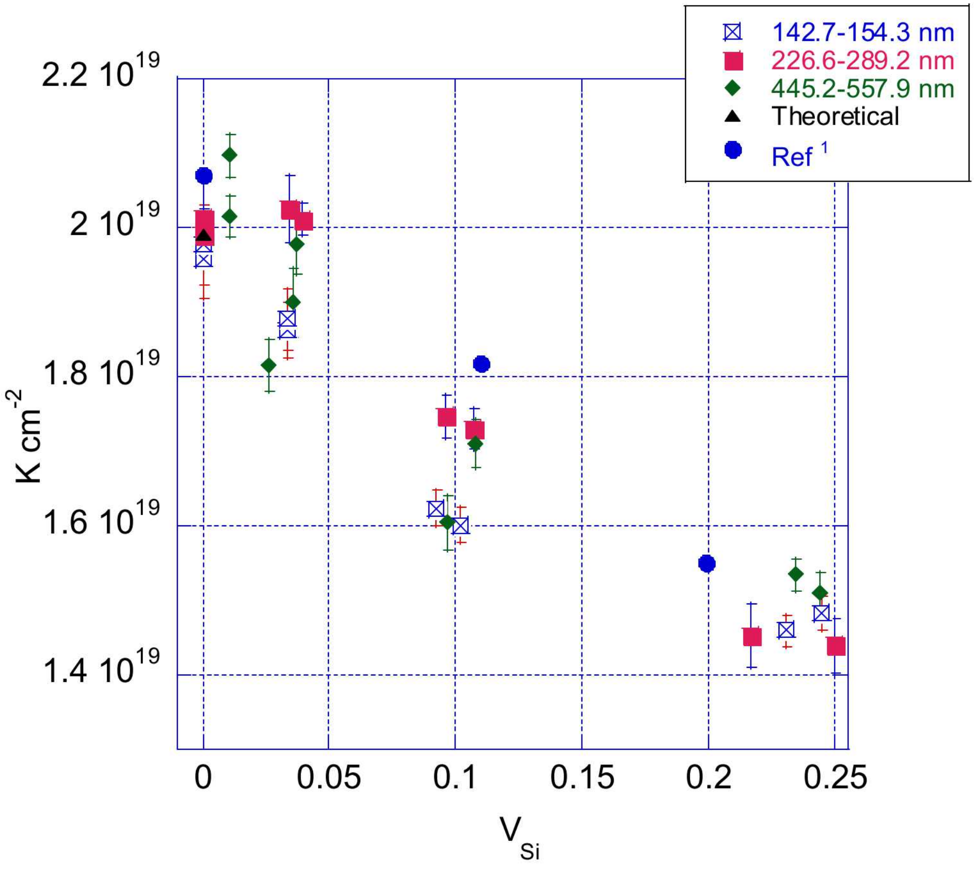
Absorption coefficient for SiNx films in the 226-289 nm thickness range and varying compositions

- Peak shifts to higher frequencies with increasing V_{Si}
- ε is the intrinsic bond strain
- $\nu 1$ is the wavenumber associated with a reference condition (848 cm^{-1})
- $\nu 2$ is film peak wavenumber

$$\varepsilon = \frac{\nu 1 - \nu 2}{\nu 1}$$

Central force model

An increase of V_{Si} leads to a decrease in oscillator strength factor

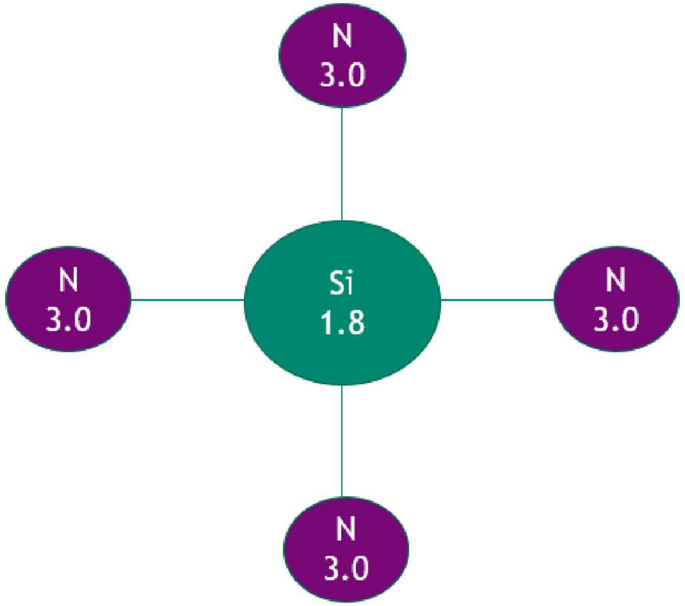


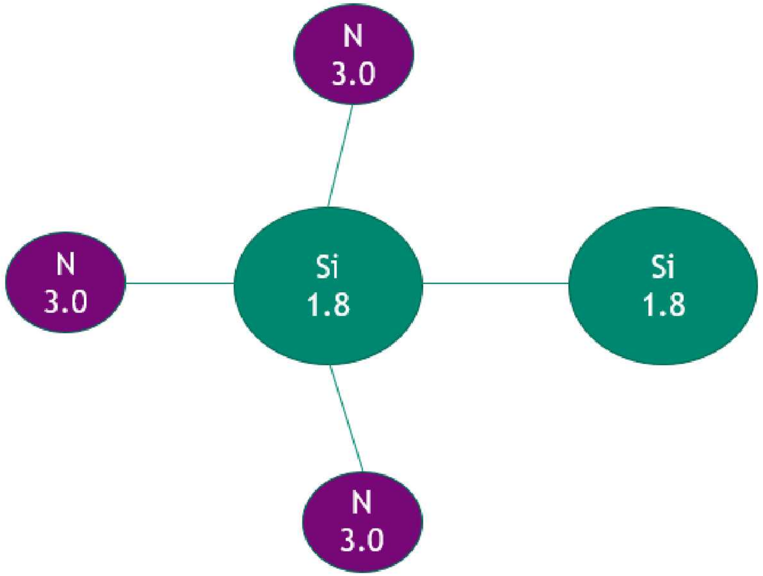
Oscillator strength factors for films of varying composition and thickness

- We found that K is NOT a constant parameter across varying compositions
- This means that it cannot be used to solve for [N] for any SiNx film
- Verified statistically significant by linear regression significance testing
- Note that the values for K are thickness corrected values

K decreases as increasing V_{Si} induces charge transfer

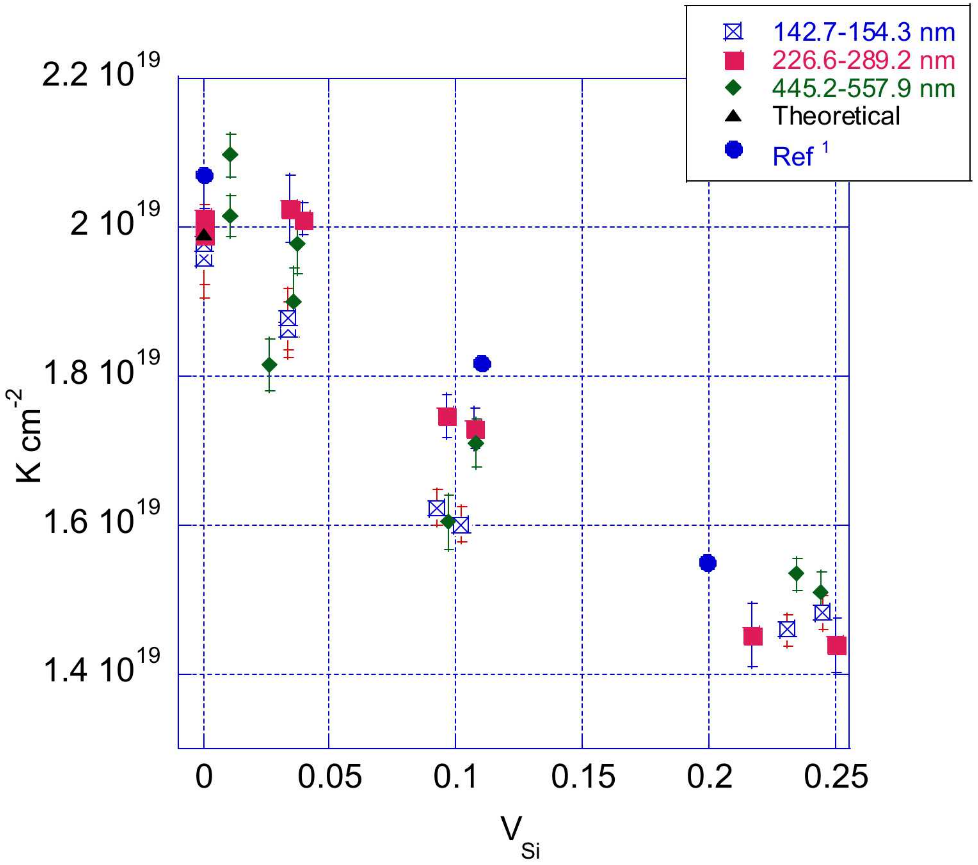
- The substitution of electronegative N atoms for a less e^- negative Si atom will modify the charge of other bonds to that atom
- The modified charge distribution induces structural changes to the basal tetrahedron
- Structural changes affect the bond strain which alters the effective dipole moment and modifies the IR absorption





Trends observed with LPCVD films are similar to PECVD films

- Plasma enhanced chemical vapor deposition (PECVD)
- A value of 2.07×10^{19} cm^{-2} is reported for a ~700 nm thick stoichiometric SiNx film deposited by PECVD
- This agrees with our results for films deposited by LPCVD
- Suggests that impurities introduced by PECVD do not effect the Si-N charge transfer
- K values appear to be independent of deposition method

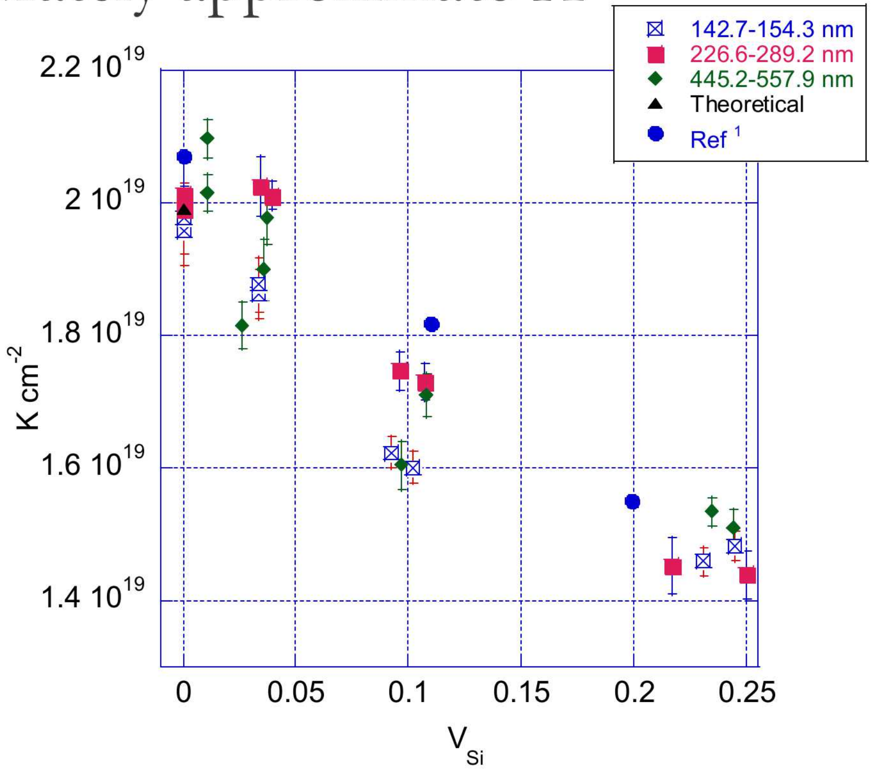


Theoretical K value was found by assuming q=1.4e

- A theoretical K value was found to be 1.99×10^{19} cm^{-2} for a stoichiometric film
- q typically ranges from .3e-3e
- q was found to be 1.4 times greater than 1e to accurately approximate K
- This value for q is within the expected range

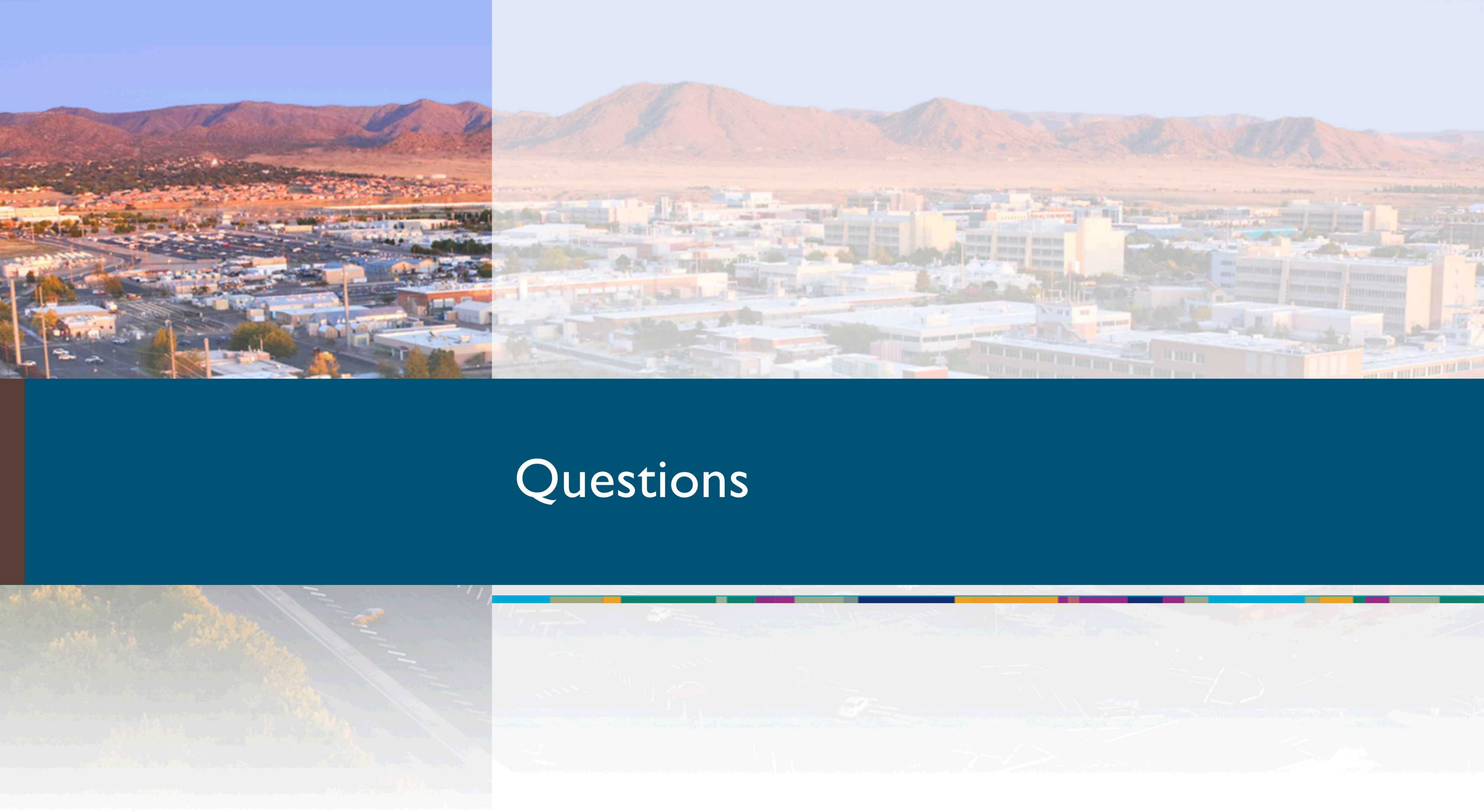
$$K \equiv \frac{c^2 n \omega_t \mu}{\pi q^2}$$

$n=2.4$
$\omega_t=840$ cm^{-1}
$\mu=1.56 \times 10^{19}$ kg
$q=6.72 \times 10^{-10}$ esu



Summary

- K values for films of varying composition and thickness were measured
- K decreases with increasing V_{Si}
- Believed to be due to a charge transfer which affects the film strain
- Differences in strain alter the effective dipole moment which changes the IR properties
- Si-rich SiN_x films have a higher absorption probability
- K is a parameter which is ostensibly independent of deposition method



Questions