UNCLA
SECURITY CLAS

AD-A197 791

~~DTIC FILE COPY~~

④

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704 0188

1a REPORT SECURITY CLASSIFICATION
Unclassified

1b RESTRICTIVE MARKINGS

2a SECURITY CLASSIFICATION AUTHORITY

3 DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release; distribution unlimited

2b DECLASSIFICATION/DOWNGRADING SCHEDULE

4 PERFORMING ORGANIZATION REPORT NUMBER(S)
Technical Report No. 4

5 MONITORING ORGANIZATION REPORT NUMBER(S)

DTIC
ELECTE
AUG 1 1 1988
S D
E

6a NAME OF PERFORMING ORGANIZATION
Naval Research Laboratory

6b OFFICE SYMBOL (If applicable)

7a NAME OF MONITORING ORGANIZATION
Office of Naval Research

6c ADDRESS (City, State, and ZIP Code)
4555 Overlook Ave., SW
Washington, DC 20375-5000

7b ADDRESS (City, State, and ZIP Code)
Chemistry Program
800 N. Quincy St.
Arlington, VA 22217-5000

8a NAME OF FUNDING/SPONSORING ORGANIZATION
Office of Naval Research

8b OFFICE SYMBOL (If applicable)

9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
N00014-87-WX-24204

8c ADDRESS (City, State, and ZIP Code)
800 N. Quincy Street
Arlington, VA 22217-5000

10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
Unclassified Technical Report 4. In Situ Infrared Reflection Absorption Spectroscopic Characterization of Plasma Enchanced Chemical Vapor Deposited SiO_2 Films.

12 PERSONAL AUTHOR(S)
K.B. Koller, W.A. Schmidt, and J.E. Butler

13a TYPE OF REPORT
Technical

13b TIME COVERED
FROM Oct.86 TO Sept 87

14 DATE OF REPORT (Year, Month, Day)
88/8/1

15 PAGE COUNT
30

16 SUPPLEMENTARY NOTATION

17 COSATI CODES

FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The sensitivity and selectivity of double modulation Fourier Transform Infrared Reflection Absorption Spectroscopy for absorbing species on a reflecting surface has been employed for the in situ analysis of low temperature Plasma Enhanced Chemical Vapor Deposition formed SiO_2 films deposited on HgCdTe, Silicon, and Aluminum substrates. An oblique angle of incidence of ca. 55° was chosen to yield maximum sensitivity for the longitudinal optical phonon mode of SiO_2 on Si. The peak frequency and shape of the LO mode absorption band varied with the quality of the SiO_2 films thus providing a means of in situ assessment of reaction conditions at any stage of film growth. This diagnostic technique can be readily applied to the in situ analysis of dielectric thin films formed under a variety of reaction conditions.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a NAME OF RESPONSIBLE INDIVIDUAL
J.E. Butler

22b TELEPHONE (Include Area Code)
(202) 767-1115

22c OFFICE SYMBOL
6174

DD Form 1473, JUN 86 Previous editions are obsolete SECURITY CLASSIFICATION OF THIS PAGE

S/N 0102-LF-014-6603

OFFICE OF NAVAL RESEARCH

Contract N00014-87-WX-24204

R&T Code 413e009

Technical Report No. 4

In Situ Infrared Reflection Absorption Spectroscopic Characterization of Plasma Enhanced Chemical Vapor Deposited SiO_2 Films

by

K. B. Koller, W. A. Schmidt and J. E. Butler

Prepared for Publication

in the

Journal of Applied Physics

Naval Research Laboratory
Washington, D.C. 20375-5000

August 1, 1988

Reproduction in whole or in part is permitted for any purpose of the United States Government

*This document has been approved for public release and sale; its distribution is unlimited

* This statement should also appear in Item 10 of the Document Control Data-DD Form 1473. Copies of the form available from cognizant contract administrator.

In Situ Infrared Reflection Absorption Spectroscopic Characterization of Plasma Enhanced Chemical Vapor Deposited SiO_2 Films.

Kent B. Koller[1], William A. Schmidt, and James E. Butler[2]
Naval Research Laboratory
Washington, DC 20375-5000

---

[1] National Research Council/Naval Research Laboratory Research Associate

[2] Corresponding Author: Chemistry Division, Gas/Surface Dynamics Section, Code 6174.

ABSTRACT

The sensitivity and selectivity of double modulation Fourier Transform Infrared Reflection Absorption Spectroscopy for absorbing species on a reflecting surface has been employed for the *in situ* analysis of low temperature Plasma Enhanced Chemical Vapor Deposition formed SiO_2 films deposited on HgCdTe, Silicon, and Aluminum substrates. An oblique angle of incidence of ca. 55° was chosen to yield maximum sensitivity for the longitudinal optical phonon mode of SiO_2 on Si. The peak frequency and shape of the LO mode absorption band varied with the quality of the SiO_2 films thus providing a means of *in situ* assessment of reaction conditions at any stage of film growth. This diagnostic technique can be readily applied to the *in situ* analysis of dielectric thin films formed under a variety of reaction conditions.

INTRODUCTION

Dielectric thin films of SiO_2, formed at low substrate temperatures by Plasma Enhanced Chemical Vapor Deposition (PECVD) have been used to fabricate microelectronic devices of temperature sensitive materials. Of particular interest to the authors is the compound semiconductor HgCdTe (MCT). The optimization of the process of deposition to yield high quality dielectric layers and dielectric/semiconductor interfaces has required the proper choice of many variables (e.g., choice of reactants, flow rates, pressure, carrier gas dilution, substrate temperature, reactor configuration)(1). This is a tedious and expensive procedure which could be greatly expedited by the availability of *in-situ* analytical diagnostics. SiO_2 thin films have been characterized by many techniques, e.g., capacitance and impedance measurements, ellipsometry, etch rate, Auger, XPS, photoelectron, Rutherford back scattering, and infrared vibrational spectroscopies. With the exception of ellipsometry (2), none of these techniques have been applied to an *in-situ* analysis of thin films. In this paper we present an IR spectroscopic method for evaluating PECVD SiO_2 thin films *in-situ*, thus enabling on-line reaction parameter adjustment.

IR transmission spectroscopy has been used successfully as a nondestructive technique for analysis of SiO_2 thin films (3-9). Normal incident IR spectra of SiO_2 show absorption bands at 1080 cm^{-1}, 800 cm^{-1}, and 455 cm^{-1}, corresponding to Si-O stretching, bending, and rocking vibrations respectively (10). Impurities such as Si-OH (3660), Si-H (2250), N-H (3400), and H-OH (1630) are also observable. The reststrahlen band (1080 cm^{-1}) is the most prominent feature of the SiO_2 spectrum and arises from the interaction of the IR photons with the transverse optical (TO) mode phonons. The position and shape of this band are sensitive to SiO_x stoichiometry, density, and nitrogen impurities (3-9). *In-situ* analysis of SiO_2 thin films by transmission spectroscopy on various substrates has not been attempted due, in part to, the severe restrictions placed upon the reaction chamber configuration. Berreman first reported (11) that the longitudinal optic (LO) modes of thin films of cubic crystals strongly absorb p polarized light at non-normal angles of incidence. The LO mode of oxide layers on technical Si wafers has been observed using oblique angle external reflection IR spectroscopy (12,13). The intensity of the LO band is dependent on the angle of incidence of the p polarized light and is observable in either non-normal angle of incidence transmission spectroscopy or external reflection spectroscopy when the thin films are on a metallic or dielectric substrate. The frequency of longitudinal optical phonons, ω_l, is related to that of transverse optical phonons, ω_t, by the Lyddane-Sachs-Teller relation (14):

$$\omega_l^2/\omega_t^2 = \epsilon_\infty/\epsilon_0 \qquad (1)$$

where ϵ_∞ is the dielectric constant at the high frequency limit (where the ions cannot follow the oscillation of the electric field and polarization is due entirely to electron motion) and ϵ_0 is the dielectric constant at the low frequency limit. The LO peaks occur at maxima of $\mathrm{Im}(-1/\epsilon)$ ($\epsilon = \epsilon_1 + i\epsilon_2$ is the dielectric constant) and the TO peaks occur at maxima of ϵ_2. The differences in both the peak frequency and intensity of the LO mode from that of the TO mode are due to the sensitivity of the longitudinal components of infrared-active vibrations to long-range electric forces within the film in addition to the short-range interatomic forces that affect both modes (15).

Sensitivity is the limiting factor in the spectroscopic detection of thin films. Fourier Transform Infrared Reflection Absorption Spectroscopy (FT-IRRAS) employing a high frequency polarization modulator was chosen for this study. This double modulation technique (16,17) provides superior performance characteristics, such as the spectral coverage attainable with adequate signal to noise in a short time, the reduction in detector noise at the characteristic frequencies of the normal (dc) rapid scan interferogram and the high frequency modulated interferograms, and the cancellation of the polarization insensitive absorptions. The developmental groundwork of several groups (16-21) was used to establish the experimental configurations used in this work. A photoelastic modulator is used to rapidly modulate the phase delay, Φ, between the s and p polarized components of the light at a frequency ω. The total intensity reaching the detector as a function of time and wavenumber, $\bar{\nu}$, is:

$$I(\bar{\nu},t) = C\,[\,1+\rho^2 + (1-\rho^2)\cos\Phi - 2\rho\sin\Delta\sin\Phi\,] \tag{2}$$

where

$$\Phi = A(\lambda)\sin\omega t\ , \tag{3}$$

$\rho = \tan\psi = r_p/r_s$, and $\Delta = \delta_p-\delta_s$ in terms of the Fresnel coefficients $r_p\exp(i\delta_p)$ and $r_s\exp(i\delta_s)$. After expansion of the sin/cos terms using Bessel functions, one obtains:

$$I(\bar{\nu},t) = C\,\{[1+\rho^2 + (1-\rho^2)J_0(A)] - 4\rho J_1(A)\sin\Delta\sin\omega t + 2(1-\rho^2)J_2(A)\cos 2\omega t\} \tag{4}$$

and then, ratioing the 2ω term to the "dc" gives

$$I_{2\omega}/I_{dc} = 2(1-\rho^2)J_2(A)/[1+\rho^2 + (1-\rho^2)J_0(A)] \tag{5}$$

which reduces to

$$I_{2\omega}/I_{dc} = J_2(A)(I_S - I_P)/(I_S + I_P) \tag{6}$$

when $J_0(A=137.8°) = 0$, and using $\rho^2 = I_P/I_S$. Since the amplitude $A(\lambda)$ of the phase delay is wavelength dependant, the above analysis is rigorously correct only at the wavelength corresponding to A=137.8°(19), at which optimal sensitivity is obtained. The dependance of $I_{2\omega}/I_{dc}$ on the Bessel functions (eqn. 5) in our FTIR experiments is corrected for by computing a spectral change, δS, between a modified surface and the original surface:

$$\delta S = \left.\frac{(I_{2\omega}/I_{dc})_{null}}{(I_{2\omega}/I_{dc})_{calib}}\right|_{modified} - \left.\frac{(I_{2\omega}/I_{dc})_{null}}{(I_{2\omega}/I_{dc})_{calib}}\right|_{original} \tag{7}$$

where the $I_{2\omega}/I_{dc}$ obtained at the null position of the polarizers is ratioed to that obtained when both polarizers are parallel to either the s or p orientation of the surface.

The absorption by a thin film of p polarized light at an oblique angle of incidence has the potential, under optimum conditions, of being 25 times more sensitive than normal angle of incidence transmission through an unsupported thin film (20). Figure 1 shows the variation of the reststrahlen TO peak intensity modeled from reported dielectric constants (21), and that of the corresponding LO mode peak, with angle of incidence for a thin film of SiO_2 on Si. It is noteworthy that the TO mode would be completely suppressed in the case of a metallic substrate, due to the negligible electric field at the interface parallel to a metallic surface.

EXPERIMENTAL

The PECVD reaction chamber used is a modification of one previously described (1) and is shown schematically in Figure 2. The modification consisted of fitting the quartz reaction chamber with two KBr windows on the sides of the reactor tube, oriented so that the optical path was normal to the axis of the reactor tube and the angle between the incoming and reflected beams was 112 degrees at the sample. This modification is shown in more detail in Figure 3. The plasma was usually confined to within the rf coil and optimum growth was obtained in the geometry shown (1). The distance from the windows to the sample was 12 cm. The clear aperture of the windows was 2.54 cm and was the limiting aperture of the light focused on the sample. Thus the angle of incidence on the sample was variable between 50 and 60 degrees. Both Si and $Hg_{1-x}Cd_xTe$ (MCT)(x=.3) single crystal substrates were used for deposition of the dielectrics. The Si crystals were (100) oriented, n-type, 50mm dia. polished wafers. The MCT crystals were 15mm dia., unoriented, n type ($N_d < 5x10^{15}cm^{-3}$), wafers that had been polished and etched in Br/methanol solutions.

Silane (0.5% in argon) and nitrous oxide were used as reactants. The optimal reaction conditions were flow rates of 50 and 25 sccm for N_2O and SiH_4/Ar, respectively, at a pressure of 400 mtorr in the reactor. All layers were deposited on samples at 70° C and employed a rf power of 25 watts at 13.5 MHz. Extensive work had been performed previously to determine the conditions to give the best quality films (1). Film thicknesses were measured by ellipsometric measurements at 632.8nm.

The spectra were obtained with a FTIR spectrometer (Mattson Instruments, Sirius 100) at 4 cm^{-1} resolution. The IR light was polarized by passing through an etched metallic gird on ZnSe (Science Services Inc.) and modulated at 28KHz using a photoelastic modulator (PEM)(Hinds International). The IR signals, sensed by a liquid nitrogen cooled photoconductive MCT detector, consisted of interferograms at the various harmonics of the PEM carrier frequency. The normal (dc) interferogram was isolated by two low pass filters (Ithaco 4302 Dual 24dB/Octave) in series, while the interferogram carried on the second harmonic of the PEM frequency was demodulated by a lock-in amplifier (Brookdeal, model 9503) using the smallest possible time constant (0.1 milliseconds) in order to pass the necessary side band information. Additional analog filters (Ithaco 4302 Dual 24dB/Octave Filter) isolated the frequencies of interest in the 2ω interferogram. The relationship between Fourier frequency, f, wavenumber, $\bar{\nu}$, and mirror velocity, V_S, is $f = 2V\bar{\nu}$, which was used to calculate the filter settings. Typically, the mirror velocity was 1.27 cm/s, and the wavenumber region of interest was 4000 to 700 cm^{-1}. 100 scans and 500 scans were averaged for the dc and 2ω interferograms respectively. The RF power was turned off and film growth stopped during measurements because of inadequate electrical shielding of the detector. The specific filter settings are given in figure 3.

A calibration spectrum was obtained from a reference aluminum mirror or from a bare substrate prior to CVD deposition by orienting both polarizers parallel to p (or s). The null interferogram was obtained when the second polarizer, A (see figure 3), was left in the p polarized position and the first, P, was adjusted to minimize the peak amplitude of the 2ω interferogram, i.e., setting "I_p equal to I_S". The normal FFT algorithm uses the position of the largest positive peak in the interferogram as the zero path retardation peak from which it calculates the phase information necessary to correctly transform the interferogram into spectral intensities. Since the I_s - I_p peaks can be either positive or negative and the point of zero path retardation represents the sum of all intensities, it is not necessarily the most intense peak in the interferogram. Thus it was necessary to use the phase information from the 2ω calibration interferogram to process the nulled signal 2ω interferogram.

RESULTS

Figure 4 shows the spectra for SiO_2 deposited by PECVD sequentially on an MCT substrate and an Al substrate. The intensity of the spectral change in the LO peak of SiO_2 increased with the thickness of the film in a slightly nonlinear fashion as shown in Figure 5. No increase in LO mode peak intensity was observed for films over 2500 Å thick. However, the TO mode peak increased steadily with film thickness. On Si and MCT substrates, the LO peaks are negative and represent a loss in reflectivity whereas the TO peaks are positive and are caused by an increase in reflectivity. The TO peaks of SiO_2 were observed on Si and MCT substrates but were completely suppressed on an Al substrate. The peak frequency of the LO mode band varied with reaction conditions and was always less than that observed for thermal oxide grown on Si. IR spectra of three, equal thickness, SiO_2 films prepared in different ways, are shown in Figure 6. Two samples (Figure 6b and 6c) represent the observed extremes, due to reaction conditions (1), in PECVD growth quality while the third is a thermally grown oxide (Figure 6a) which indicates the optimum IR spectrum of an SiO_2 film.

The results obtained for PECVD films deposited on Si, MCT, and Al substrates using similar reaction conditions were the same, with the exception of the suppression of the TO mode peak on Al. The peak frequency of the LO mode shifted to higher wavenumber by ca. 10 cm^{-1} as the film thickness was increased from ca. 50 Å to ca. 500 Å after which the peak frequency became independent of film thickness. SiO_2 films less than 50 Å thick exhibited absorption bands that were too broad for accurate determination of peak frequencies.

A shift in the optical properties of a PECVD sample was observed when annealed overnight in air at 450° C. The optical properties as determined by ellipsometry changed from an index of refraction and thickness of 1.420 and 2110 Å, respectively, to 1.425 and 1782 Å. The LO mode peak frequency moved from 1234 cm^{-1} to 1246 cm^{-1}.

The LO mode peak frequency and optical constants of several SiO_2 films, prepared by different methods, were determined and are presented in Table I. The frequency of the LO mode peak increases with the temperature of the preparation method. Films grown in two reaction chambers were evaluated. The films grown in the reaction chamber fitted with the IR windows were not as good (lower optical constants and LO mode peak frequencies) as those grown in the chamber without IR windows. Also, differences in film quality were noted when the wafers were placed on a pad of filter paper versus when the wafers were placed directly on the graphite support block.

Silicon wafers that were polished on both sides were placed on an aluminum mirror to evaluate the effect of increased reflectance from the mirror. It was observed that the sensitivity for the LO mode peak was not improved by the presence of the mirror as compared to samples that were polished on one side and rough on the back surface even though the intensity of the reflected light was significantly increased. As shown in Figure 7, an interstitial oxygen peak at 1106 cm^{-1} (25) was observed when this Si wafer (both sides polished) was placed on the aluminum mirror. This peak is not observed for samples with rough backs since the light that passes through the wafer is diffusely reflected and does not reach the detector. The presence of the native SiO_2 layer (ca. 15 to 20 Å thick) is observable when the spectrum from this Si wafer on Al is subtracted by that from the bare Al wafer as shown in Figure 7. The signal from the ber by ca. 10 cm^{-1} as the film thickness was increased from ca. 50 Å to ca. 500 Å after which the peak frequency became independent of film thickness. SiO_2 films less than 50 Å thick exhibited absorption bands that were too broad for accurate determination of peak frequencies.

A shift in the optical properties of a PECVD sample was observed when annealed overnight in air at 450° C. The optical properties as determined by ellipsometry changed from an index of refraction and thickness of 1.420 and 2110 Å, respectively, to 1.425 and 1782 Å. The LO mode peak frequency moved from 1234 cm^{-1} to 1246 cm^{-1}.

The LO mode peak frequency and optical constants of several SiO_2 films, prepared by different methods, were determined and are presented in Table I. The frequency of the LO mode peak increases with the temperature of the preparation method. Films grown in two reaction chambers were evaluated. The films grown in the reaction chamber fitted with the IR windows were not as good (lower optical constants and LO mode peak frequencies) as those grown in the chamber without IR windows. Also, differences in film quality were noted when the wafers were placed on a pad of filter paper versus when the wafers were placed directly on the graphite support block.

Silicon wafers that were polished on both sides were placed on an aluminum mirror to evaluate the effect of increased reflectance from the mirror. It was observed that the sensitivity for the LO mode peak was not improved by the presence of the mirror as compared to samples that were polished on one side and rough on the back surface even though the intensity of the reflected light was significantly increased. As shown in Figure 7, an interstitial oxygen peak at 1106 cm^{-1} (25) was observed when this Si wafer (both sides polished) was placed on the aluminum mirror. This peak is not observed for samples with rough backs since the light that passes through the wafer is diffusely reflected and does not reach the detector. The presence of the native SiO_2 layer (ca. 15 to 20 Å thick) is observable when the spectrum from this Si wafer on Al is subtracted by that from the bare Al wafer as shown in Figure 7. The signal from the values of δS versus angle of incidence over the reststrahlen band region (700 to 1500 cm^{-1}). As can be seen from Figure 9b, the best sensitivity can be obtained on either side of Brewsters' angle, 72°. In this work the light is focused on the sample, giving a range of incidence angles (~10°), hence the incidence angle of ~56° was selected. The model calculations used Fresnel equations (11) with no approximations and optical constants for SiO_2 and Si (21). Only calculating the change in the p polarized component, while valid for metallic substrates, should be avoided for dielectric substrates because the p polarized reflectivity is zero at Brewsters' angle.

The model calculations show that the optimum angle of incidence varies with film thickness (Figure 10). The calculation of the film thickness dependence of δS shows that there is an optimum thickness for a maximum δS intensity, known as the Berreman thickness (12). For 55° and 60° the Berreman thicknesses are 1720 Å and 1110 Å respectively. However, this effect was not observed in the present work (Figure 5) where the IR beam was focussed on the sample, and the angle of incidence is between 50 and 60 degrees. This range of angles includes the optimum angle of reflection for a maximum in δS for films up to 2000 Å thick, and thus prevented the experimental observation of the Berreman thickness effect. There is good agreement for the thickness dependence of δS intensity at the LO band and the δS intensity versus thickness calculated at the optimum angle for each thickness (Figure 10c).

The LO mode peak frequency for the low temperature PECVD grown films was observed to be always less than that for thermal SiO_2. It was previously observed that thermal SiO_2 has the same transmission IR spectrum as bulk vitreous SiO_2 (3), and that the TO mode peak of PECVD SiO_2 shifts to higher frequency, and the optical constants and density of the film approach that of thermal oxide, when the films are heat treated (5). The improvement in film quality is attributed to structural changes in the SiO_2 lattice brought about by thermal annealing. This is in agreement with our observation that the LO mode peak frequency is also shifted to the blue following heat treatment of the PECVD grown films. The characteristics of the LO mode band (frequency, intensity, and shape) are affected by many factors (stoichiometry, density, voids, and impurities) and are a sensitive indicator of film quality. While the LO mode absorption peak can not differentiate between these factors, their presence is indicated by comparison to the appearance of the absorption peak for the pure material. Impurities might also be detected by peaks in other regions of the IR spectrum. Work by one of us has shown that SiO_2 layers deposited at low temperatures contains voids, as well as Si-H and OH bonds that are detrimental to the quality of the layer and the electronic properties of the passivated dielectric/semiconductor interface (1). These defects form at the expense of the Si-O bond and large numbers of such defects are accompanied by a decrease in the x value of SiO_x. The x value has been directly related to the position of the 1080 cm^{-1} peak in these low temperature films since the stress related changes in the vibrational mode can be ignored in low temperature layers.

As mentioned previously, the LO peak position and the optical constants indicated that the films grown in the modified reaction chamber were not of the same quality as those grown in the original chamber. The LO mode peak frequencies of the films grown on samples in the original reaction chamber were measured by putting the samples in the IR diagnostic reaction chamber and purging with nitrogen. These LO peak frequencies were consistently shifted to the blue of the LO frequencies of films grown in the modified reaction chamber. The obvious differences between the two reaction chambers were the presence of the IR windows and the placement of the substrate relative to the RF induced plasma (ca. 3 cm closer in the diagnostic chamber). Previous work (1) has indicated that the placement of the substrate relative to the plasma is critical. Unfortunately, the positioning of the IR windows did not allow for the same sample verses plasma configuration as in the original reaction chamber used to develop the low temperature PECVD technique. Other problems with this modified reaction chamber were clearly indicated by the coating of the quartz tube with an unidentified white powder which does not occur in the original reaction chamber. Clearly, some further engineering work is needed to permit in-situ measurements without compromising the design of the PECVD reactor.

CONCLUSION

This paper has demonstrated the utility of PEM modulated FTIR spectroscopy as an *in-situ* analysis technique for PECVD SiO_2 films. The *in-situ* analysis capability allows for significant savings in time through on-line reaction parameter adjustment and optimization, routine monitoring of material quality, and benefits by the elimination of misleading results due to contamination and damage caused by the handling of samples when moved from the reaction chamber to an analysis site. The use of the PEM provides an improvement in signal to noise ratio and selectivity for processes occurring at the surface or interface of interest. Model calculations of the IRRAS experiment were shown to be beneficial in selecting the appropriate angle of incidence for optimum sensitivity at the interface of interest. Sensitivity sufficient to detect the reststrahlen band of the native oxide of silicon was demonstrated. Other dielectric films such as B_2O_3-, P_2O_5-, As_2O_3-SiO_2, Si_3N_4, and SiN_xO_y (3) have LO modes in the IR range and could be characterized using this technique.

ACKNOWLEDGEMENTS

This work was supported in part by a grant from the Office of Naval Research. We are grateful to Drs. V.M. Bermudez, E.D. Palik, P.J. McMarr, A.G. Revesz and R.E. Stahlbush for enlightening and stimulating discussions, and to D. Waltz and S.L. Fetheroff for technical assistance.

REFERENCES

1. J. R. Waterman and W. A. Schmidt, Proceedings IRIS Detector Specialty Group Meeting (1986).
2. E. Gould and E. A. Irene, J. Electrochem. Soc. 134, 1535 (1988).
3. J. Wong, J. Electron. Mater. 5, 113 (1976).
4. P. G. Pai, S. S. Chao, Y. Takagi and G. Lucovsky, J. Vac. Sci. Technol. A 4, 689 (1986).
5. P. Pan, L. A. Nesbit, R. W. Douse and R. T. Gleason, J. Electrochem. Soc. 132, 2012 (1985).
6. A. L. Shabalov and M. S. Feldman, Thin Solid Films 151, 317 (1987).
7. G. Lucovsky, M. J. Manitini, J. K. Srivastava and E. A. Irene, J. Vac. Sci. Technol. B 5, 530 (1987).
8. G. Lucovsky and D. V. Tsu, J. Vac. Sci, Technol. A 5, 2231 (1987).
9. L. I. Popova, E. D. Atanassova, D. I. Kolev and B. M. Nikolova, J. Non-Cryst. Solids 85, 382 (1986).
10. R. J. Bell, N. F. Bird and P. Dean, J. Phys. C 1, 299 (1968).
11. D. W. Berreman, Phys. Rev. 130, 2193 (1963).
12. B. Harbecke, B. Heinz, and P. Grosse, Appl. Phys. A 38, 263 (1985).
13. P. Grosse, B. Harbecke, B. Heinz, R. Meyer, and M. Offenberg, Appl. Phys. A 39, 257 (1986).
14. R. H. Lyddane, R. G. Sachs and E. Teller, Phys. Rev. 59, 673 (1941).
15. J. F. Scott and S. P. S. Porto, Phys. Rev. 161, 903 (1967).
16. W. G. Golden, D. S. Dunn, and J. Overend, J. Catal. 71, 395 (1981).
17. L. A. Nafie and D. W. Vidrine, in *Fourier Transform Infrared Spectroscopy*, Vol. 3, edited by J. R. Ferraro and L. J. Basile, (Academic Press, Inc., Orlando, 1982) p. 83.

18. S. N. Jasperson and S. E. Schnatterly, Rev. Sci. Instr. 40, 761 (1969).

19. A. E. Dowrey and C. Marcott, Appl. Spectro. 36, 414 (1982).

20. V. M. Bermudez and V. H. Ritz, Appl. Opt. 17, 542 (1978).

21. S. N. Jasperson, D. K. Burge, R. C. O'Handley, Surf. Sci. 37, 548 (1973).

22. R. G. Greenler, J. Chem. Phys. 44, 310 (1966).

23. D. F. Edwards, and H. R. Philipp in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic Press, Inc., Orlando, 1985) pp. 547 and 749.

24. L. A. Nafie and M. Diem, Appl. Spectrosc. 33, 130 (1979).

25. K. Krishnan and R. B. Mundhe, SPIE, Spectroscopic Characterization Techniques for Semiconductor Technology 452, 71 (1983).

26. J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. 24, 417 (1971).

Table I

Peak Frequency of the LO Absorption Band of SiO_2

Type	Peak frequency
Thermal oxide	1257 to 1260 cm^{-1} (a)
PECVD 70°C	1205 to 1234 cm^{-1} (b)
PECVD 400°C	1242 cm^{-1}
PECVD	
deposited at 70°C	1240 cm^{-1}
annealed at 400°C	1244 cm^{-1}

(a) range for 8 samples

(b) range for SiO_2 deposited on Si, HgCdTe, and Al

LIST OF FIGURES

1. Modeled IRRAS spectra (δS, as defined later in the text) of a 1000 Å film of SiO_2 on Si for angles of incidence of 55°, 45°, 35°, 25°, and 15°. The LO and TO modes of the stretching vibrational mode are shown at 1260 cm^{-1} and 1080 cm^{-1} respectively, as well as the LO mode of the bending mode at 800 cm^{-1}.

2. Schematic of the PECVD reaction chamber used for deposition of SiO_2 films with *insitu* monitoring by FT-IRRAS.

3. Diagram of the insitu optical diagnostics of the PECVD reaction system. A full discussion is given in the text.

4. (a) IRRAS spectra (δS, as defined by Eqn. 7) of PECVD SiO_2 on MCT was recorded after reaction times of 1, 3, 5, 10, 15, 20, 30, and 43 minutes. The thickness after deposition was 1795 Å, giving an average growth rate of 42 Å/min. The refractive index of the final film was 1.438. Spectra of PECVD SiO_2 grown on Si under the same conditions are identical to the spectra shown here (see Figure 5).

   (b) IRRAS spectra of PECVD SiO_2 on Al was recorded after reaction times intervals of 2, 7, 12, and 22 minutes. The final thickness was 676 Å, giving an average growth rate of 31 Å/min. Note the change in the ordinate scale which shows that δS is smaller, for an equivalent film thickness, for Al substrates than for Si substrates due to the higher reflectivity of the bare Al surface. Also notice that the TO absorption band (at 1080 cm^{-1}) is completely suppressed on metallic substrates.

5. Intensity of the spectral change, δS, at the LO absorption band peak vs. film thickness of SiO_2 on Si. The spectra from which the data were obtained are shown in the insert.

6. (a) IRRAS spectrum of thermally grown SiO_2 on Si, thickness = 1161 Å, n = 1.47, using a calibration spectrum from a different bare Si wafer.

(b) typical spectrum of "good" PECVD SiO_2 on Si, grown at 70° C, d = 1079 Å, n = 1.422.

(c) typical spectrum of "poor" PECVD SiO_2 on Si, grown at 70° C, d = 1127 Å, n = 1.33.

7. An IRRAS spectrum (δS) for a bare Si wafer, polished on both sides, placed on an Al mirror and using the Al mirror reflectivity as the initial conditions (Eqn. 7). Absorption bands are due to interstitial oxygen (1106 cm^{-1}) and native oxide at the gas/oxide interface (1224 cm^{-1}).

8. (a) A transmission spectrum from the ratio of the dc interferograms from a SiO_2 film covered Al substrate to that from the bare Al. The LO and TO bands are at 1217 cm^{-1} and 1055 cm^{-1} respectively. This spectrum represents all deposition induced absorptions in the optical path.

(b) A transmission spectrum from the ratio of the ac interferograms that were obtained at the same time as the above dc interferograms. The LO absorption band is at 1218 cm^{-1}. This spectrum represents only polarization dependent absorptions from material deposited on surfaces at non-normal angles of incidence to the IR beam.

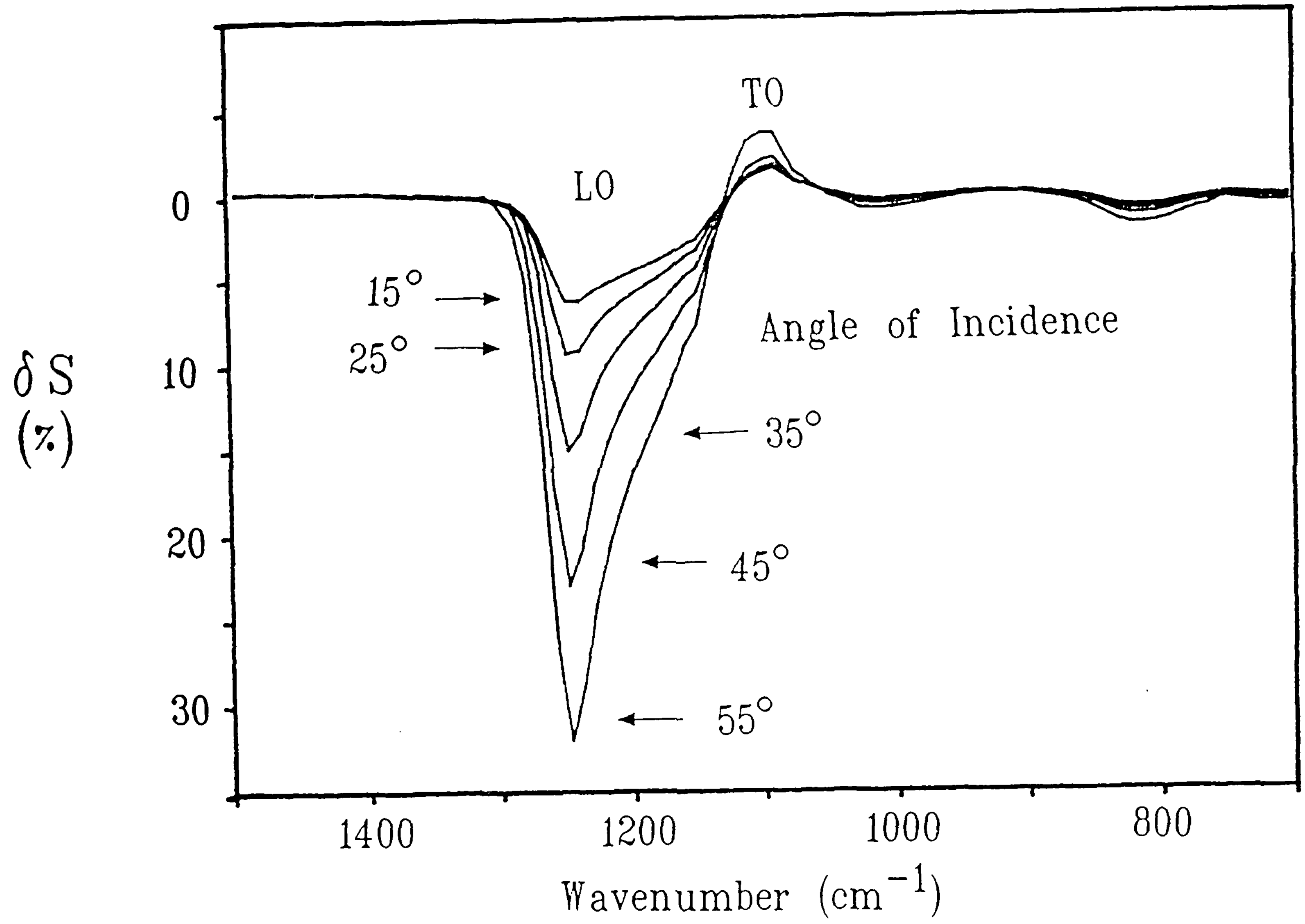
9. (a) The IRRAS spectrum (δS) calculated for 100Å of SiO_2 on Si in the reststrahlen band region versus angle of incidence (intervals of 2°) using the wavelength dependant optical constants for SiO_2 and Si. In this calculation the background non-absorbing surface was modeled by setting the imaginary part of the refractive index, k, of SiO_2 to zero.

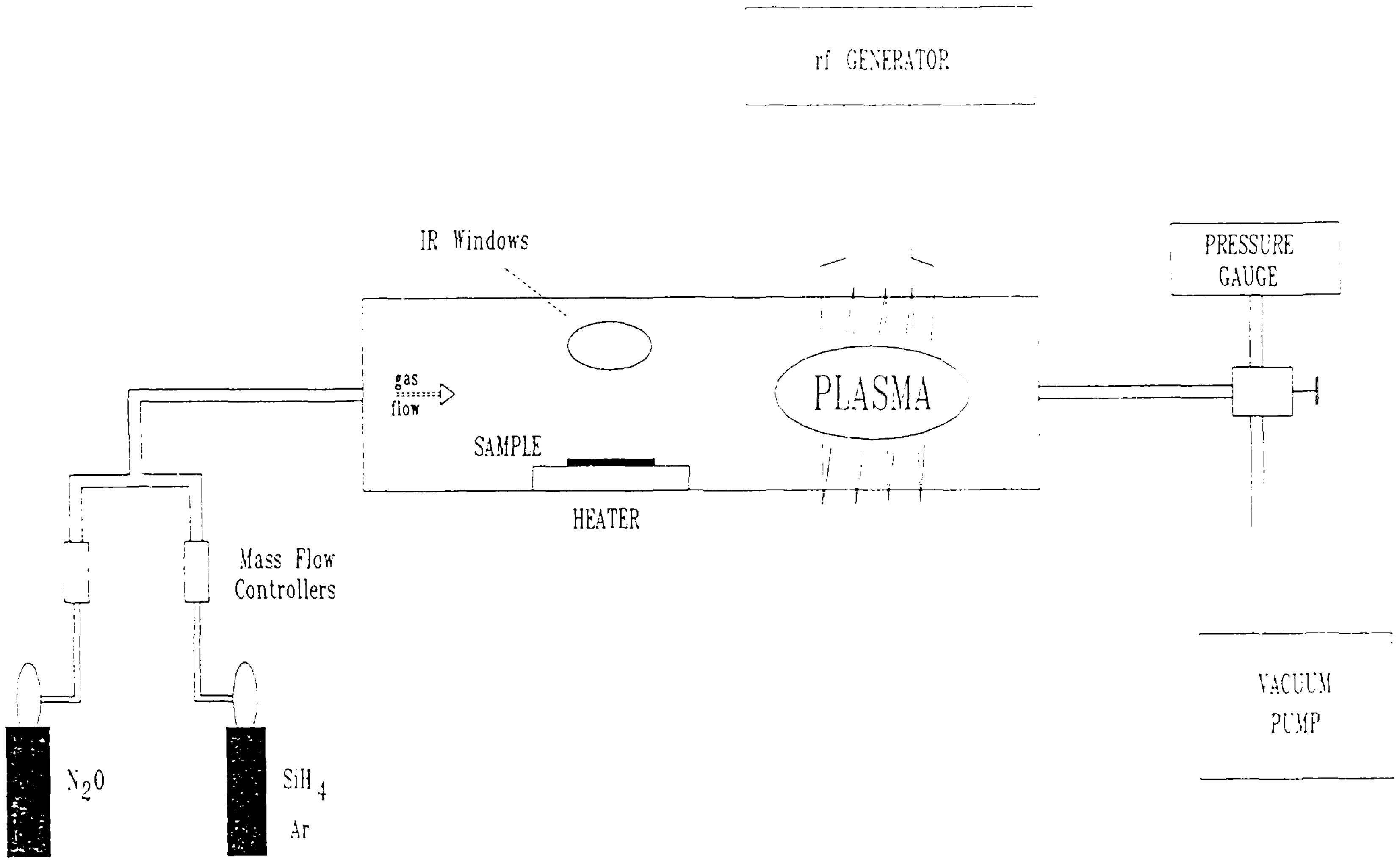
(b) δS from figure 9(a) at 1260 cm^{-1} versus angle of incidence. Brewsters angle, 72°, is noted on the figure.

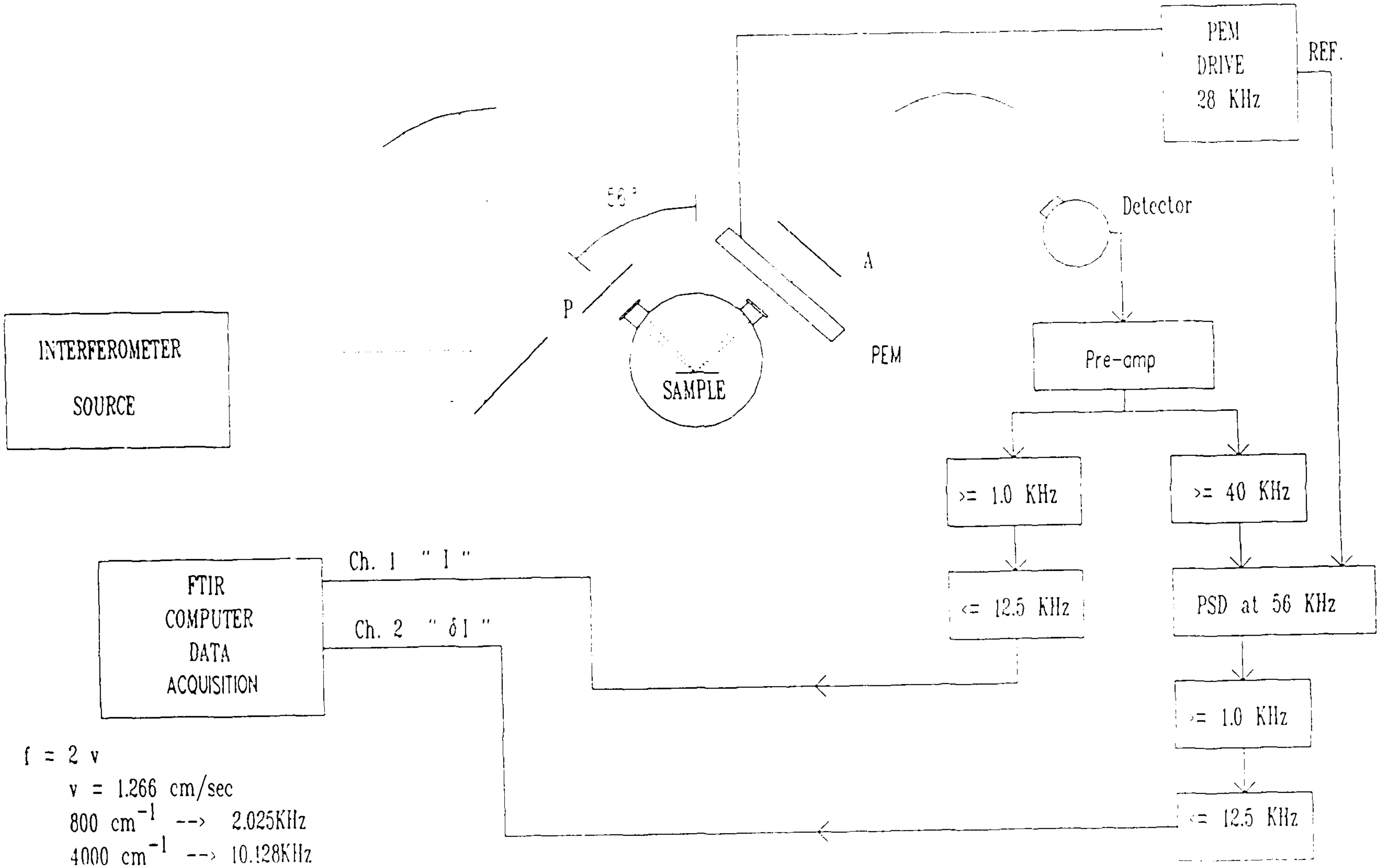
10. (a) δS calculated for SiO_2 on Si versus wavenumber and increments of 100Å in thickness, d. The angle of incidence was 60°.

(b) The angle corresponding to the maximum in δS (i.e. the optimum angle for IRRAS sensitivity) below the Brewsters angle for a given thickness, d, of SiO_2 on Si versus the thickness of the SiO_2 film.

(c) δS versus the thickness of the SiO_2 film, d, for the optimum angle of incidence at each thickness, and for the fixed angles of incidence, 60° and 55°.


δS
(%)
0
10
20
30
1400
1200
1000
800
Wavenumber (cm^{-1})
LO
TO
15°
25°
35°
45°
55°
Angle of Incidence


rf GENERATOR
IR Windows
PRESSURE GAUGE
gas flow
PLASMA
SAMPLE
HEATER
Mass Flow Controllers
VACUUM PUMP
N_2O
SiH_4
Ar

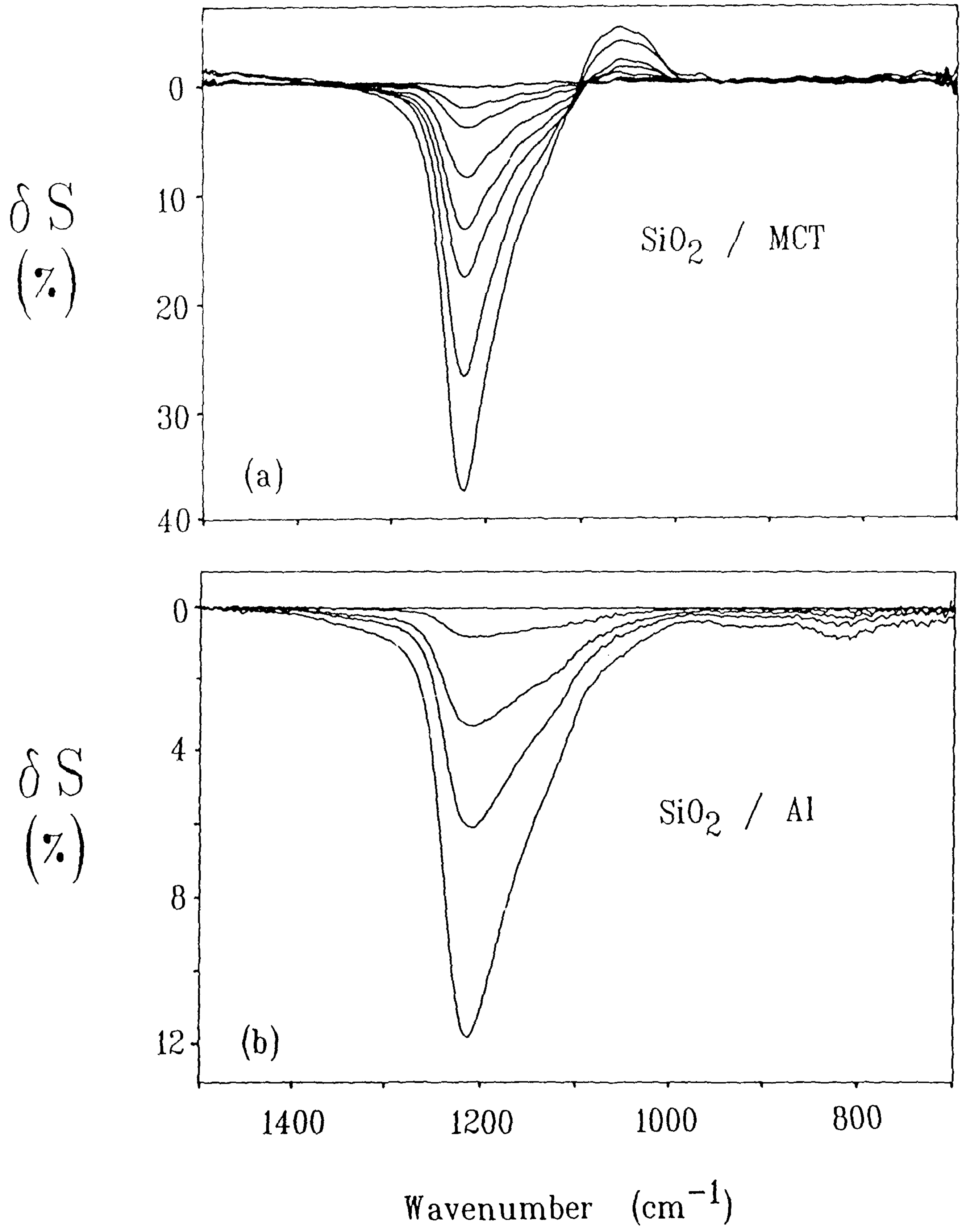


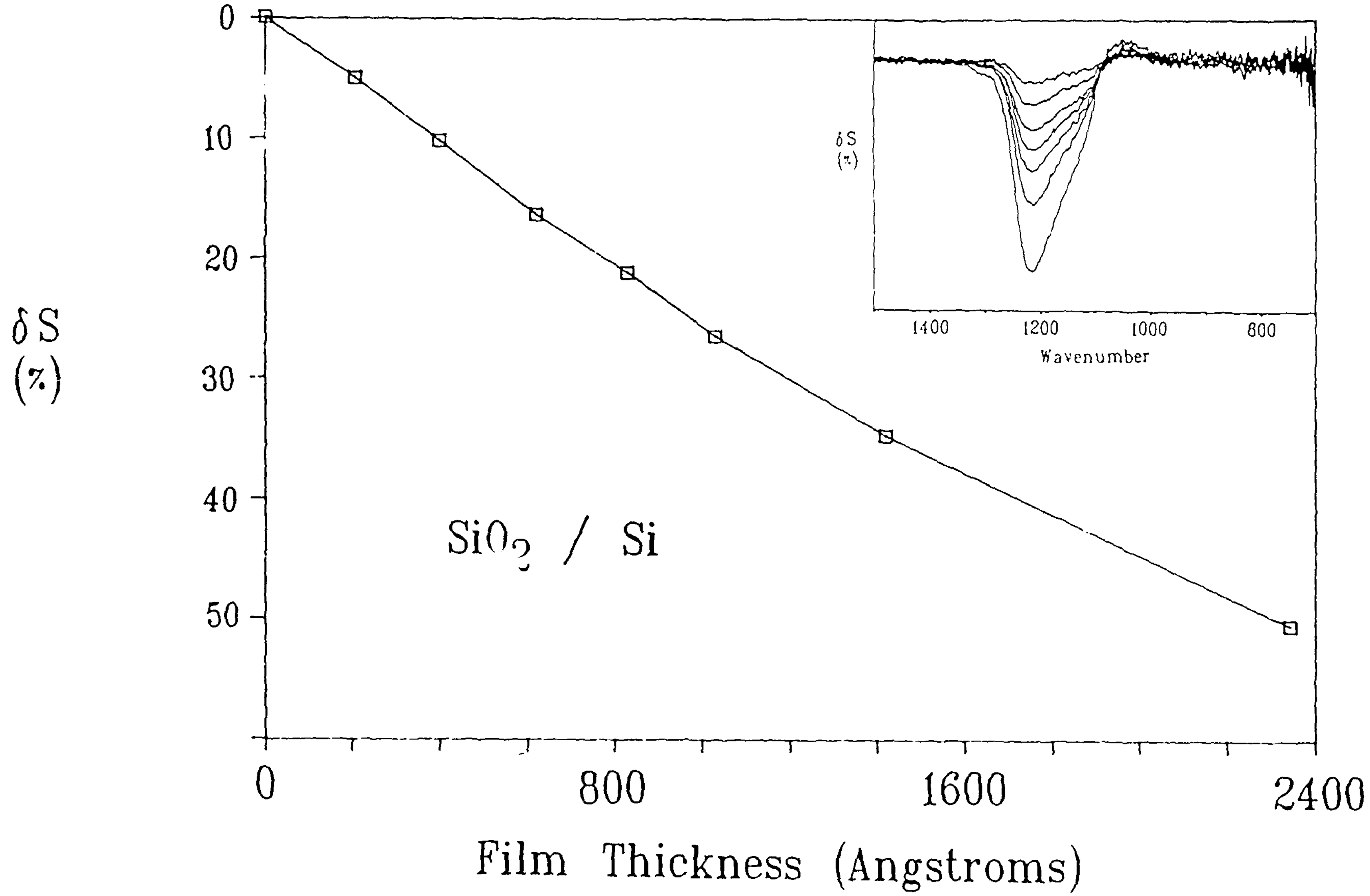
$f = 2v$

$v = 1.266$ cm/sec

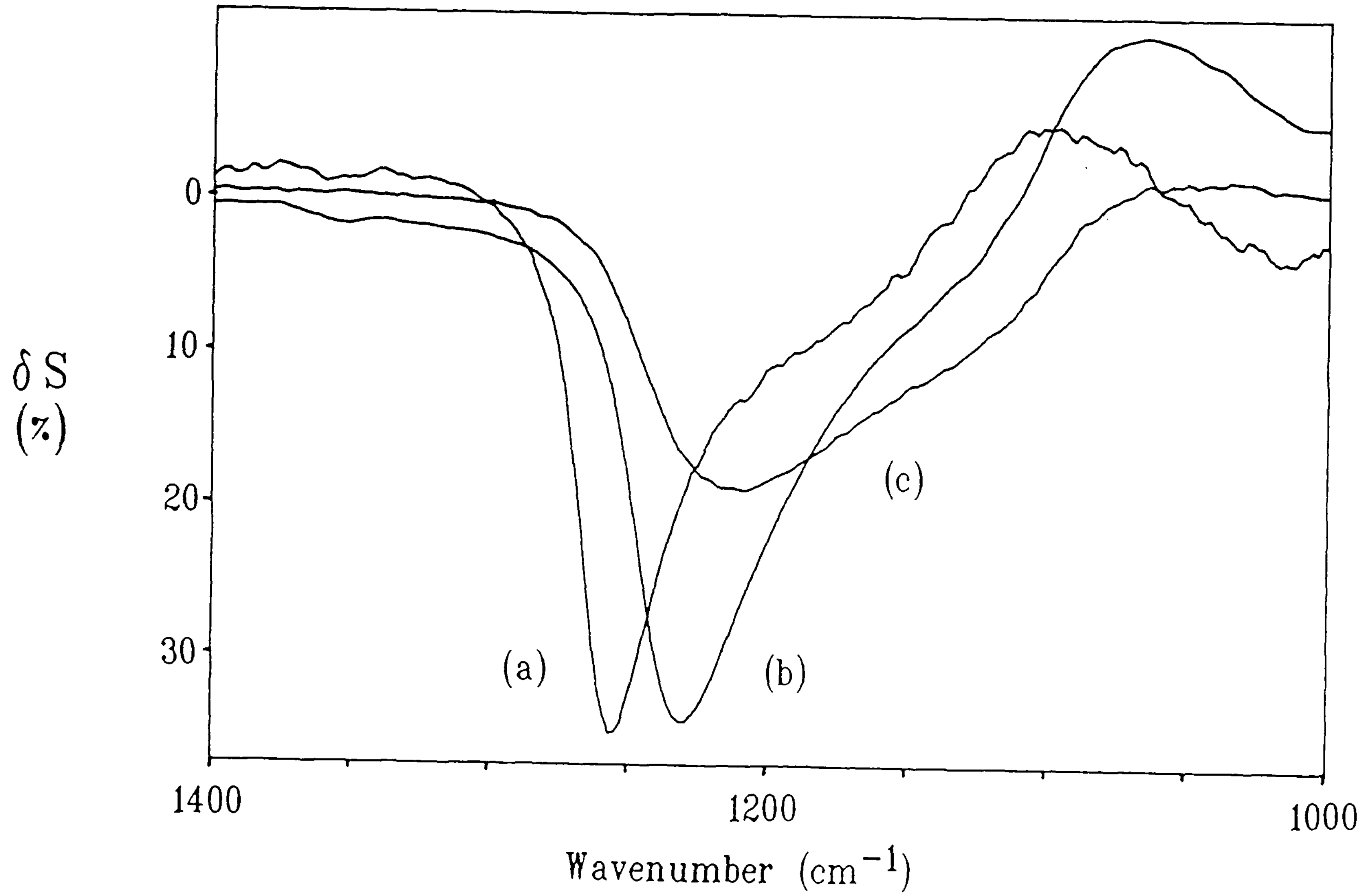
800 cm^{-1} --> 2.025KHz

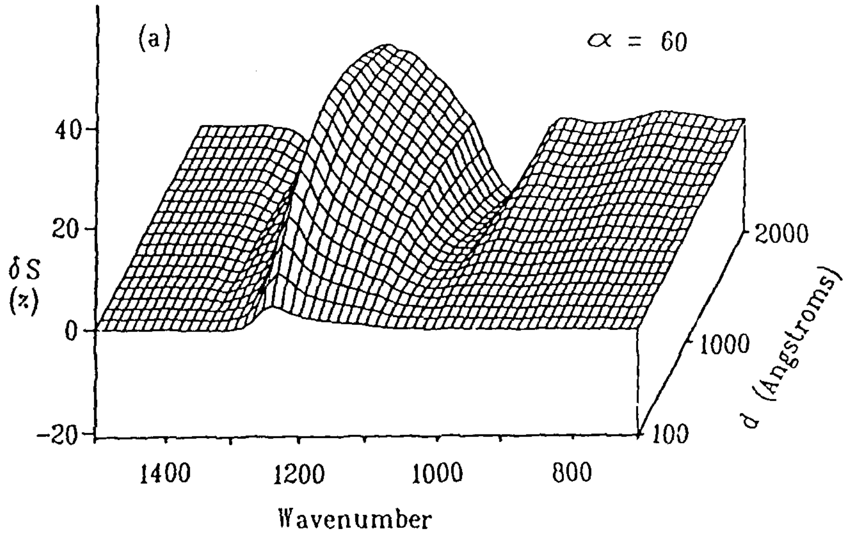
4000 cm^{-1} --> 10.128KHz

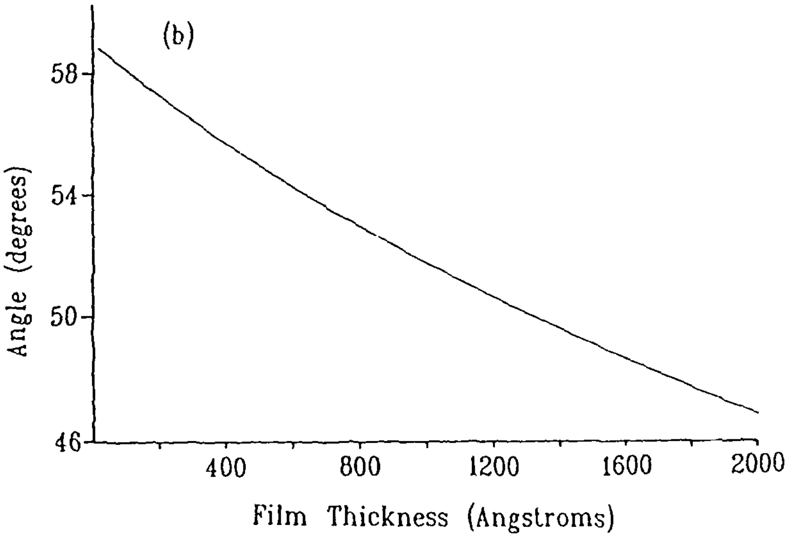

δS (%)
0
10
20
30
40
SiO$_2$ / MCT
(a)
δS (%)
0
4
8
12
SiO$_2$ / Al
(b)
1400
1200
1000
800
Wavenumber (cm^{-1})

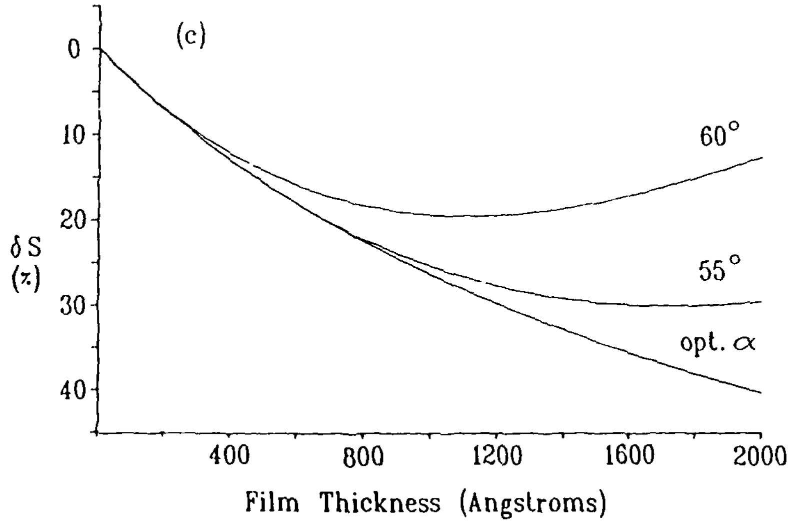


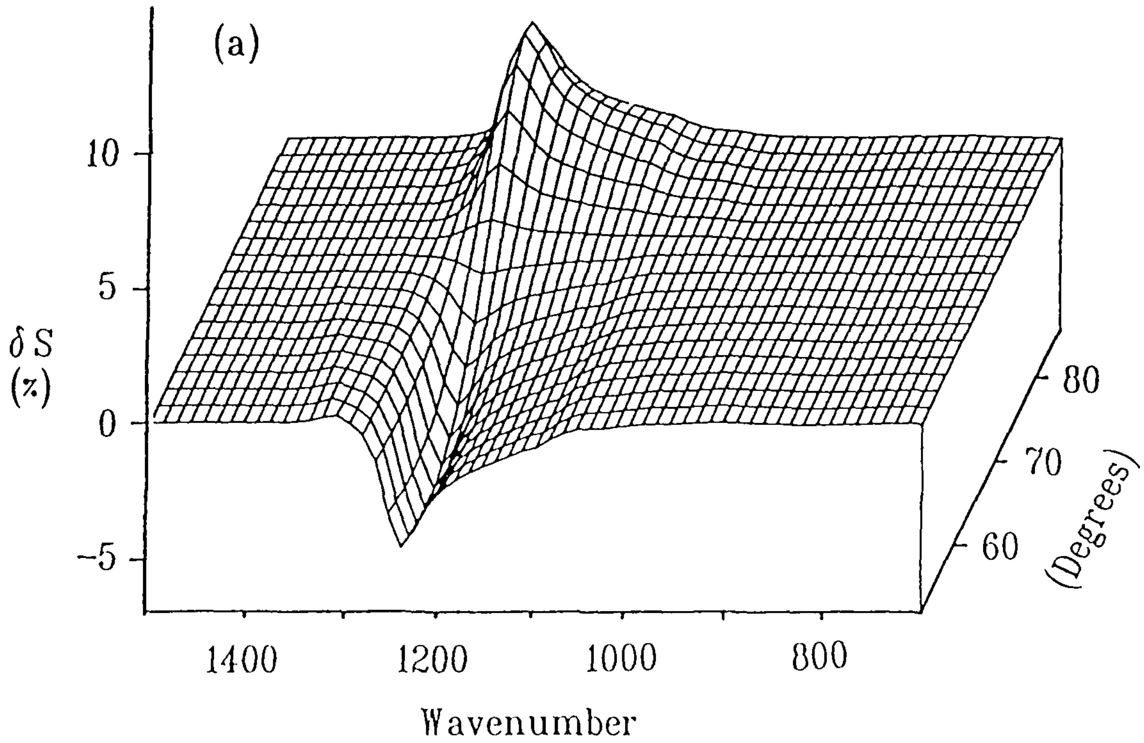
δS
(%)
0
10
20
30
40
50
0
800
1600
2400
Film Thickness (Angstroms)
SiO2 / Si
δS
(%)
1400
1200
1000
800
Wavenumber

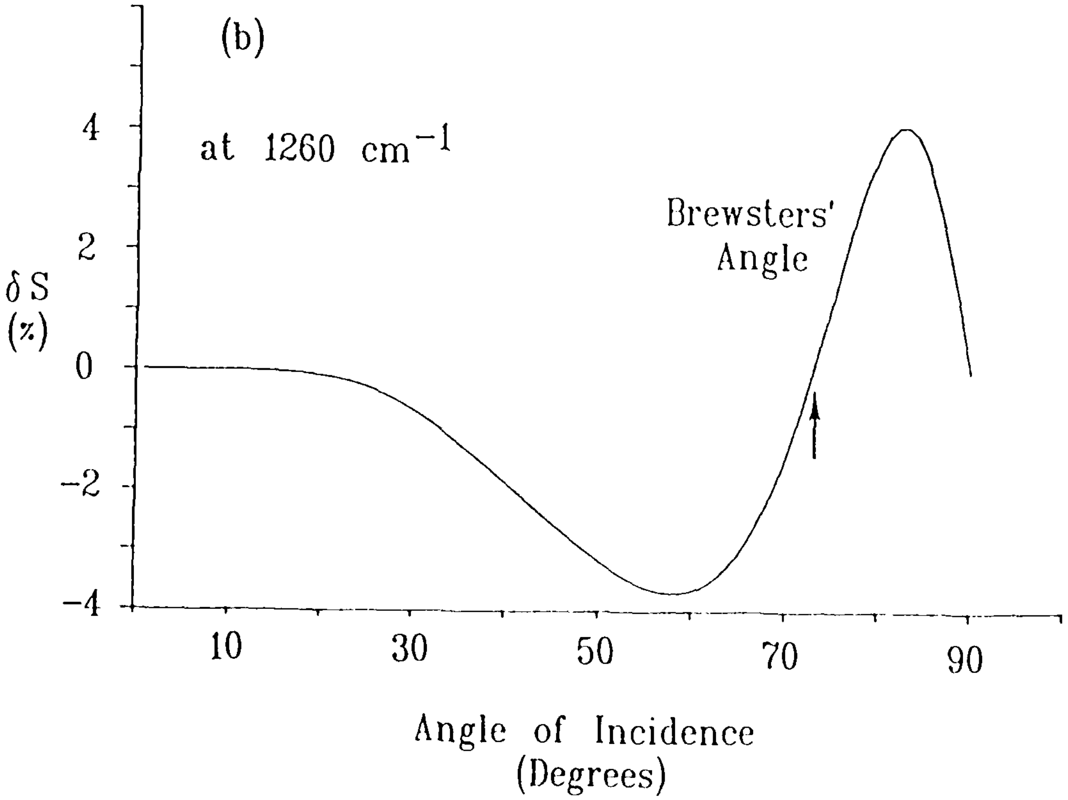

δS
(%)
0
10
20
30
(a)
(b)
(c)
1400
1200
1000
Wavenumber (cm⁻¹)

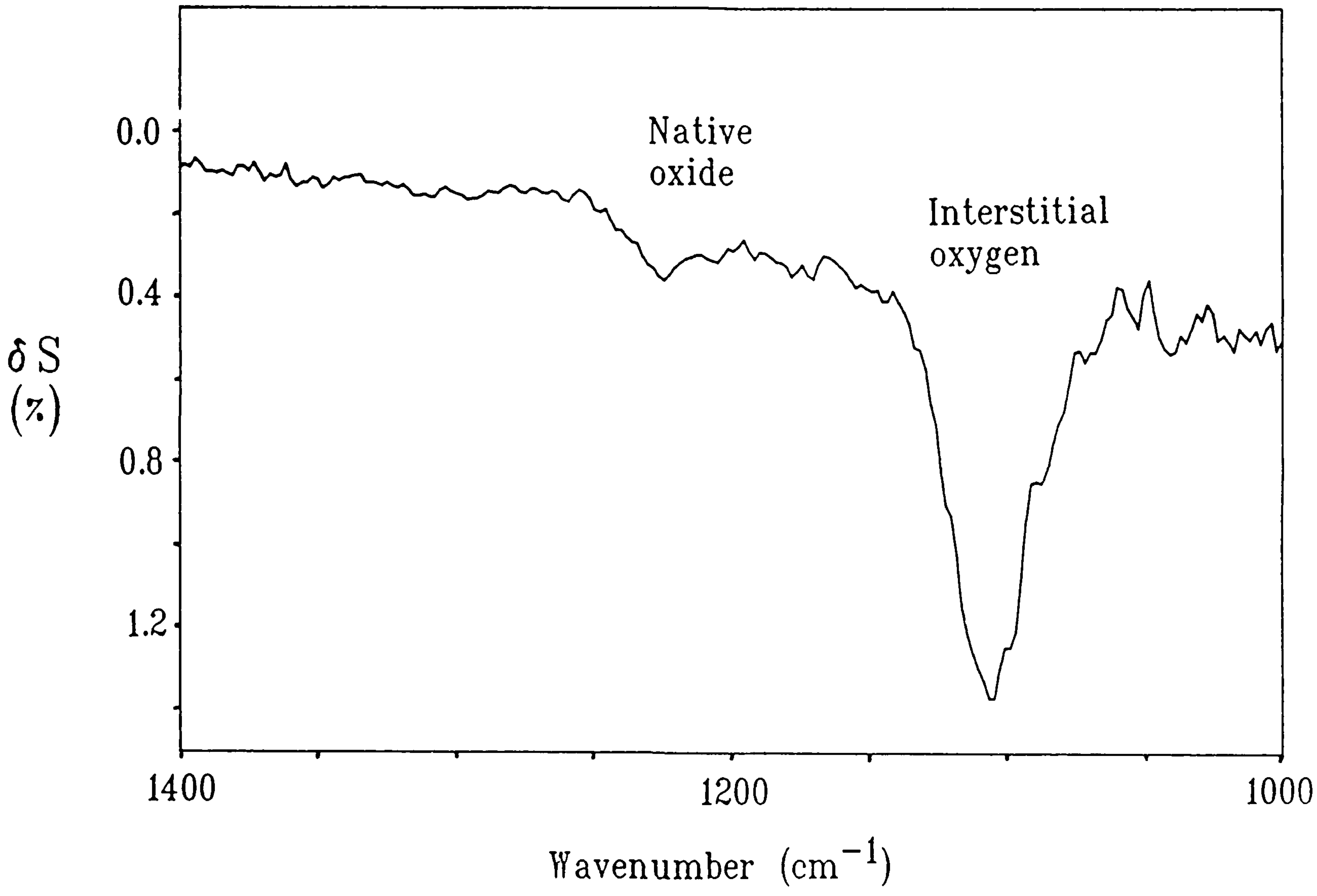

(a)
α = 60
40
20
0
−20
δS
(%)
1400
1200
1000
800
Wavenumber
2000
1000
100
d (Angstroms)

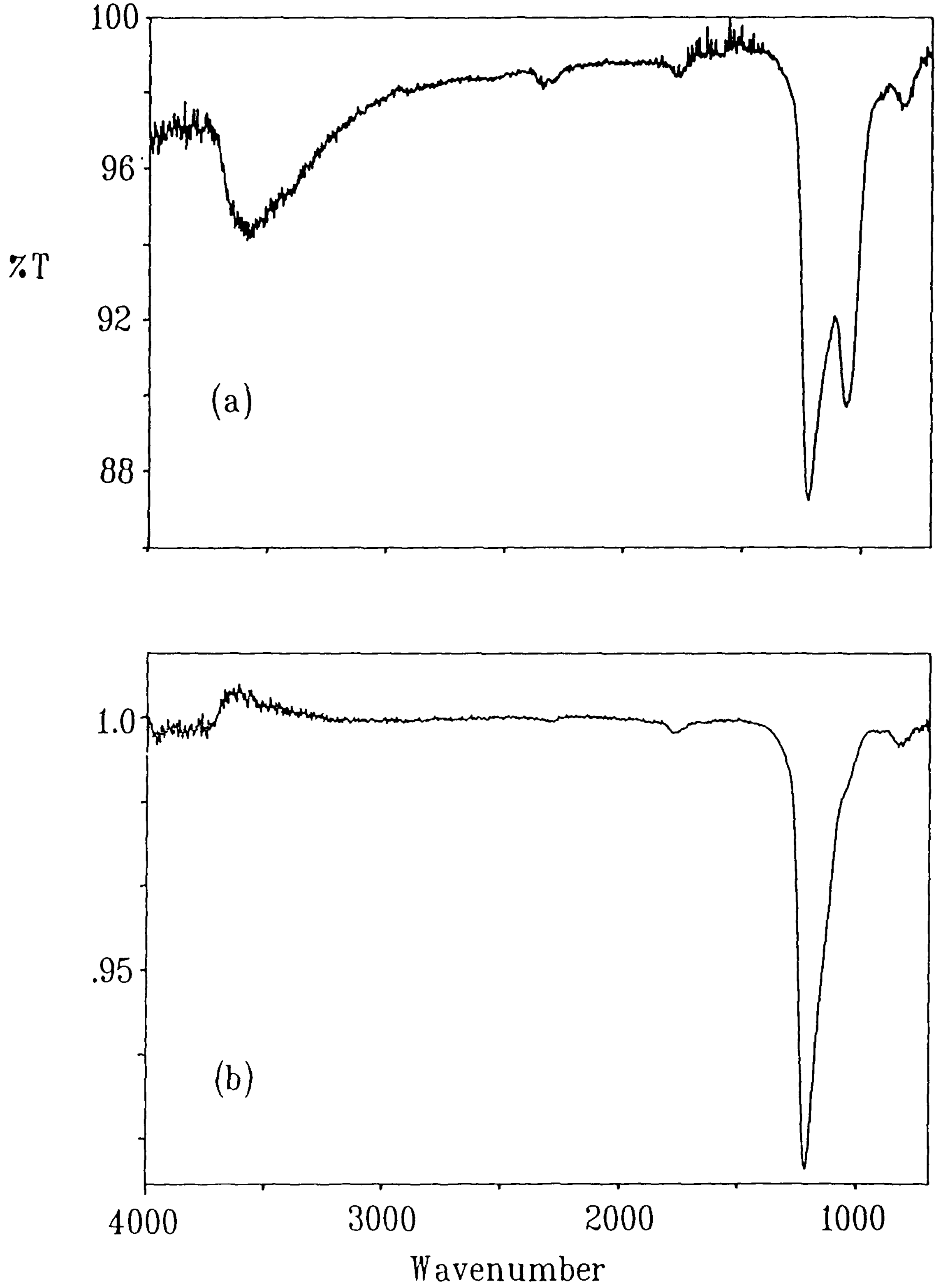

(b)
58
54
50
46
Angle (degrees)
400
800
1200
1600
2000
Film Thickness (Angstroms)


(c)
0
10
20
30
40
δS
(%)
60°
55°
opt. α
400
800
1200
1600
2000
Film Thickness (Angstroms)


(a)
10
5
0
−5
δ S
(%)
1400
1200
1000
800
Wavenumber
80
70
60
(Degrees)


(b)
at 1260 cm⁻¹
4
2
0
−2
−4
δ S
(%)
Brewsters' Angle
10
30
50
70
90
Angle of Incidence
(Degrees)


Native
oxide
Interstitial
oxygen
δS
(%)
0.0
0.4
0.8
1.2
1400
1200
1000
Wavenumber (cm^{-1})


100
96
%T
92
(a)
88
1.0
.95
(b)
4000
3000
2000
1000
Wavenumber