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Silicon Nitride Formation From A Silane-Nitrogen ECR Plasma

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Good quality, low temperature silicon nitride and oxynitride films were deposited downstream from an electron cyclotron resonance (ECR) plasma source using SiH_4 and N_2 gas mixtures. The Si/N ratio and H content in the deposited films were determined using Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD). The H concentration was minimum for films with compositions closest to that of stoichiometric Si_3N_4. The optimum conditions for producing a stoichiometric Si_3N_4 were: a SiH_4/N_2 flow ratio between 0.1 and 0.2, and an electrically isolated sample far from the ECR source. Infrared absorption spectra showed that as the film composition changed from N rich to Si rich the dominant bonds associated with H changed from N-H to Si-H. The addition of O_2 to the background gas formed an oxynitride with a low H content similar to the stoichiometric Si_3N_4.

I. Introduction

Thin films of high quality silicon nitride are important as dielectric materials in semiconducting electronic and optoelectronic devices. Desirable dielectric characteristics for SiN_x films include: a high dielectric constant, low current leakage, high breakdown voltage, control of fixed charge and charge trapping, and low dielectric/semiconductor interface-state density. These characteristics are dependent upon the Si/N ratio and hydrogen content in deposited films [1]. Further, Kapoor and Turi [2] have shown that the addition of oxygen to an SiN_x film can improve the electrical performance of nonvolatile memory silicon-oxide-nitride-silicon (SNOS) devices.

Conventional nitride deposition techniques include chemical vapor deposition (CVD) and plasma-enhanced CVD (PECVD). The CVD technique has the disadvantage that it is a high temperature technique (≥600°C) which is not compatible with all device structures on a wafer or compatible with compound semiconductors. PECVD techniques, using RF or DC plasma deposition, reduce the deposition temperature (≈300°C) but often incorporate too much hydrogen (≈20% H) into the dielectric and other materials; and these plasma techniques can cause ion-beam damage due to the high energy ions (hundreds to thousands of eV). In contrast, SiN_x films have been deposited at room temperature to 150°C from electron cyclotron resonance (ECR) plasmas [3-7] in which the ion energy is only 20-30 eV. The ECR technique uses microwaves at 2.45 GHz to excite the plasma and the resonance condition is established by applying an 875 Gauss magnetic field in the region of the plasma. The ECR condition helps to obtain a high ion-density plasma at lower pressures than for the other plasma techniques.

Past work [3, 6] has mainly estimated the hydrogen content in ECR plasma deposited SiN_x from the Si-H and N-H stretch-mode peaks in infrared (IR) absorption spectra, and Manabe et el. [6] estimated the H content to be between 2 and 10% H depending on pressure. However, an accurate measurement of the H content in an ECR deposited film has not been made. This paper will use Rutherford backscattering spectrometry (RBS) to examine the stoichiometry and elastic recoil detection (ERD) to examine the H content of ECR plasma deposited SiN_x films made from SiH_4 and N_2. Changes in the stoichiometry and H content will be correlated to changes in the types of bonds observed in IR absorption spectra. Also, the effects of a small addition of O_2 to the ECR process will be discussed.

II. Experiment

Two different deposition systems were employed in these experiments in order to test the dependence of the deposition rate on gas flow rates and operating pressure. Both apparatae consisted of a Microscience 906 ECR source attached to a reaction chamber such that the plasma stream was extracted into the reaction chamber by a divergent magnetic field. The ECR chamber has an inner diameter of approximately 14 cm and a length of 16.5 cm. Microwave power at a frequency of 2.45 GHz was transmitted to the ECR plasma chamber through a quartz window. The forward power was adjustable from 0 to 1000 Watts and the reflected power was minimized by a three-stub tuner which acted as a matching network, adjacent to the vacuum window. Both forward and reflected microwave power were monitored using a directional coupler. A mirror magnetic field configuration was produced by two separate coils surrounding the ECR chamber, with one coil centered about the end of the ECR chamber (at the quartz vacuum window) and the other coil separated from the first by approximately 8 cm. For these experiments, the magnetic field was maximum at the vacuum window and decreased along the chamber axis with the ECR condition established at the midpoint of the ECR chamber.

The first system (pumped by a 1500 l/s turbomolecular pump) had an ultimate base pressure of $2x10^{-9}$ Torr and an operating pressure of $2x10^{-4}$ Torr. This apparatus introduced a SiH_4/N_2 gas mixture (SiH_4/N_2 ratio = 0.2) into the ECR chamber near the quartz window at a combined flow rate of 20 sccm. The substrates (n-type Si wafers) were positioned at three different downstream locations relative to the end of the ECR chamber: 10 cm, 17 cm and 22 cm. Most of the samples were left electrically isolated relative to ground (the chamber walls); however, one sample was biased negatively by 160 Volts relative to ground. The sample temperature was monitored by a thermocouple bonded to an adjacent Si wafer on the sample holder. The temperature was held approximately constant during the deposition except for the biased sample which was heated by the plasma from 100°C to 480°C during the deposition. The samples deposited at these lower pressures were deposited at microwave powers from 100-250 Watts.

The second system had higher flow rates and an order of magnitude higher operating pressure. The second system (pumped by a 880 l/s turbomolecular pump) had a base pressure of $2x10^{-6}$ Torr and an operating pressure of $1\text{-}1.5x10^{-3}$ Torr. In this latter system the sample position was fixed at ≈20 cm downstream from the ECR chamber and SiH_4 (in N_2 or Ar carrier gas) was introduced at 3 cm upstream from the sample. Either Ar or N_2 gas (the opposite of the carrier gas) was introduced near the quartz window in the ECR chamber to form the plasma. The SiH_4 flow rate for these higher pressure depositions was varied from 9 sccm to 23 sccm, and correspondingly the SiH_4/N_2 ratio varied from 0.1 to 3. The samples for this system were deposited nominally at room temperature and at microwave powers from 240-300 Watts. For several samples, in order to determine the effects of a small addition of oxygen on the deposited nitride, O_2 was introduced into the background residual gas just before the process was begun. The results from these two deposition systems will be given in the following section in two parts: first from the low flow-rate depositions, and second from the higher flow-rate depositions.

III. Results and Discussion

The relative composition of Si and N was determined using RBS [8] with 3.5 MeV He^+ at a scattering angle of 164°. For this energy, the Si scattering cross section obeys the Rutherford formula but the N scattering cross section is twice that given by the Rutherford formula for the entire thickness of these films (up to 600 nm). The N cross section was determined by calibration from a stoichiometric Si_3N_4 film deposited by the CVD technique at 850°C. The H content was determined using ERD [9] with 24 MeV Si^{+5} at a scattering angle of 30°. IR absorption spectra were collected with 4 cm^{-1} resolution at room temperature on a 60SX Nicolet FTIR spectrometer. The following absorption peaks were monitored: Si-N stretching mode at 870 cm^{-1}, N-H bending mode at 1190 cm^{-1}, Si-H stretching mode at 2160 cm^{-1}, and the N-H stretching mode at 3360 cm^{-1}.

Figure 1 shows results from the RBS analysis of two samples deposited at the low SiH_4 flow rate in comparison to the CVD standard sample. The surface energies for N, O and Si scattering peaks are indicated with arrows. The spectrum with the dashed line is very nearly the same as that for the Si_3N_4 standard. This ECR sample was deposited at 17 cm downstream at a temperature of 425°C, and is representative of the unbiased samples deposited at ≥ 17 cm downstream for temperatures from 100°C to 425°C. Analysis showed this sample had a composition of $Si_{2.8}N_4$ and was 290 nm thick. The accuracy of the Si/N ratio determination was ≈7% as a result of the large Si background under the N signal. No oxygen was detectable in any of the samples deposited in this system.

The spectrum with the solid line in Fig. 1 is from the sample deposited at 22 cm downstream and biased to -160 V. Biasing of the sample caused the plasma density to increase and caused a visible sheath region (0.5-1 cm) to appear, which was not visible under normal electrical isolation. Initially, the sample was at 100°C but the plasma heated the substrate to 480°C. This sample deviated from a stoichiometric nitride composition more than similarly deposited electrically isolated samples, as evident in the Si signal in Fig. 1. The biased sample (≈310 nm thick) varied in composition from $Si_{2.4}N_4$ near the substrate to $Si_{2.6}N_4$ near the surface.

The hydrogen concentration profiles in Fig. 2 were determined from the ERD spectra from the same samples as given in Fig. 1. The H peak in the ERD spectra is superimposed onto the N peak which must be subtracted to yield the H profile; and as a result of this background peak, counts appear at negative depths (-400 to -1000 A) which should be disregarded. The H content for both the standard (filled circles) and the ECR $Si_{2.8}N_4$ sample (dashed line) are constant in depth and the ECR sample has a low H concentration nearly equal to the 5.8% H concentration obtained for a high temperature CVD deposited sample. The lowest H content obtained was 6.7% H for the $Si_{2.8}N_4$ sample (although an Si_3N_4 sample deposited at 22 cm downstream had only 7% H), and the highest H content was 16% H near the substrate for the biased sample. The H profile for this latter sample (average composition $Si_{2.5}N_4$) is shown as the solid line in Fig. 2, and the H concentration was approximately constant in depth at a value of 14% H except near the substrate. This deviation from uniformity may be due to either residual H from a H plasma precleaning step or from initial plasma fluctuations when establishing the plasma under biased conditions.

IR absorption spectra (Fig. 3) for the biased $Si_{2.5}N_4$ and the unbiased $Si_{2.8}N_4$ samples show approximately the same intensity in the Si-N stretching mode peak. This equal intensity indicates an equal number of Si-N bonds are present in the two samples which have nearly the same thickness and similar N concentrations. In contrast, the intensities of the Si-H and N-H stretching mode peaks for the $Si_{2.5}N_4$ sample are greater than for the $Si_{2.8}N_4$ sample, corresponding to the difference in H content. Although the absolute intensity of these peaks differs between the samples, the relative intensities in the Si-H and N-H peaks is the same for each sample indicating that the increase in H content does not change the predominant type of bonds formed with H. The N-H peak is the dominant peak associated with hydrogen for these ECR deposited nitrides, similar to the behavior for CVD deposited nitrides, whereas rf-plasma deposited nitrides often show a much stronger Si-H peak [1].

A summary of the deposition conditions and the resultant film properties for the nitrides deposited at the low flow rate is given in Table I. All of these samples have H contents and SiN_x compositions as good as or better than typical rf-plasma deposited nitrides. The first sample in Table I had a stoichiometric composition of Si_3N_4 with only 7% H and was therefore evaluated for its electrical properties. Capacitance-voltage (C-V) measurements at 1 MHz from this sample showed a flat-band voltage of $\leq$-0.5 V due to fixed charge. This value is almost as low as that obtained from high temperature CVD nitrides and is lower than that from rf-plasma deposited nitrides. Also, the shape of the C-V curve is consistent with a moderate interface trap density ~10^{11} cm^2/eV.

The other samples in Table I are all slightly N rich, and a general trend shows that the conditions corresponding to low deposition rates yielded samples with low H concentrations and SiN_x compositions closer to stoichiometric Si_3N_4. The deposition rate did not depend strongly on substrate temperature or microwave power. The deposition rate increased by only 19% when the microwave power was increased from 100 W to 250 W. However, deposition rate and the composition are strongly dependent upon the sample position and electrical biasing of the substrate. A -160 V bias increased the deposition rate by a factor of three and moving the sample from a position of 22 cm from the ECR source to a position of 10 cm caused the deposition rate to increase by more than a factor of four. In addition to the loss of stoichiometry and increased H content with increased deposition rate, the uniformity of the film thickness across a 2 inch wafer was markedly decreased. Therefore, the conditions which produce the best quality nitride film (an electrically isolated sample far from the source region) also yield the lowest deposition rates.

An order of magnitude increase in the operating pressure did not increase the deposition rate or significantly alter the film composition as seen by comparing the first sample listed in Table II to the last sample listed in Table I. (The samples listed in Table I were all deposited at a downstream position of ≈20 cm and at a pressure of $1\text{-}1.5 \times 10^{-3}$ Torr.) In fact, the SiN_x composition and H content agree surprisingly well in comparing similar samples from two different deposition apparatae. The deposition rate and the Si content in the films increased as the SiH_4 flow rate increased (Si arrival rate). These films showed a transition from being slightly N rich to being Si rich as the SiH_4 flow rate and SiH_4/N_2 ratio were increased. The SiH_4/N_2 ratio which apparently yields the composition closest to Si_3N_4 is between 0.1 and 0.3, as was used for the films listed in Table I. The films listed in Table II are also similar to those in Table I in that samples which are farther from the stoichiometric Si_3N_4 composition showed a larger H content.

The addition of oxygen to the background gas resulted in the deposition of an oxynitride film as shown by the last three samples listed in table II. The addition of O_2 to the process also suppressed the incorporation of H into the films. This behavior is similar to what has been observed [10] for 380 kHz rf-plasma deposition of oxynitrides from a SiH_4-NH_3-(N_2O)-N_2 gas mixture in which the NH_3/N_2O ratio is varied in order to vary the oxygen content and H content of the deposited films. The Si-N stretching-mode IR absorption peak also broadened and shifted (not shown) to a higher frequency with the incorporation of oxygen in the $Si_{3.4}N_4O_{1.4}$ ECR deposited film. This shift is characteristic of an Si-O-N network found in an oxynitride.

The Si-H stretching mode and N-H stretching mode IR absorption peaks for the four samples listed in Table II are shown in Fig. 4. As the samples varied from N rich to Si rich the intensity of the N-H bonds decreased and the intensity of the Si-H bonds increased. Also the position of the Si-H stretching mode peak shifted to lower frequencies toward the position [6] for hydrogenated amorphous Si (2060 cm^{-1}), whereas the position of the N-H stretching mode peak remained constant. This decreased frequency is consistent with an increase in the Si-H bond length.

V. Conclusions

A stoichiometric Si_3N_4 film with low H content (7% H), similar to high temperature CVD nitrides, can be deposited downstream from an ECR SiH_4/N_2 plasma at 110°C. Rutherford backscattering spectrometry and elastic recoil detection were used to determine the optimum conditions for depositing a stoichiometric Si_3N_4 film. The lowest H content was found for an Si/N ratio of 3/4 (±7%), and the optimum SiH_4/N_2 flow ratio was between 0.1 and 0.3. However, the conditions which are optimal for minimizing the incorporation of H into the nitride (an electrically isolated substrate 22 cm from the ECR source) also yield the lowest deposition rates. This Si_3N_4 film exhibited an IR absorption spectrum more like that of a CVD nitride than an rf-plasma deposited nitride, i.e., the dominant bonds associated with H were N-H bonds rather than Si-H bonds. Also, this film exhibited better electrical quality (smaller flat-band voltage) than obtained for typical rf-plasma deposited nitrides. Finally, the addition of O_2 to the background gas caused the formation of an oxynitride which was also deposited at a low temperature and with a low H content (7% H).

TABLE I

Composition	Thickness (nm)	Temperature (°C)	Power (W)	Downstream Pos. (cm)	Dep. Rate (nm/min)
Si_3N_4, 7%H	100	110	100	22	3.3
$Si_{2.9}N_4$, 11%H	200	125	250	17	5.7
$Si_{2.8}N_4$, 6.7%H	290	425	100	17	4.8
$Si_{2.8}N_4$-$Si_{2.4}N_4$ 9-16%H	600	150-250	150	10	14.3
$Si_{2.6}N_4$-$Si_{2.4}N_4$ 14-16%H, -160 V Bias	310	100-480	100	22	10.7

TABLE II

Composition	Thickness (nm)	SiH_4 Flow (sccm)	SiH_4/N_2 Ratio	Power (W)	Dep. Rate (nm/min)
$Si_{2.7}N_4$, 13%H -390 V Bias	100	9	0.1	240	6.7
$Si_{3.4}N_4O_{1.4}$, 7%H	125	14	0.3	300	12.5
$Si_4N_4O_{0.4}$, 14%H	210	20	0.3	250	21
$Si_8N_4O_{0.4}$, 25%H	170	23	3.0	250	17

Figure Captions

Fig. 1. RBS spectra, using 3.5 MeV He^+ ions, taken from samples tilted at 45° relative to the incident ion beam. The scattering angle was 164°. At this energy, the N scattering cross-section is twice as large as the N Rutherford cross-section.

Fig. 2. The H concentration profiles determined from ERD spectra for the same samples as given in Fig. 1. Based on a density of 9×10^{22} atoms/cm^3, the H concentrations are: 5.8% H for Si_3N_4, 6.7% H for $Si_{2.8}N_4$, and 14%H (16% H at 300 nm) for $Si_{2.5}N_4$.

Fig. 3. IR absorption spectra for two samples with different H concentrations but the same ratio for intensities of the N-H/Si-H stretching-mode peaks. N-H bonds are the dominant bonds formed with hydrogen, similar to a CVD deposited nitride.

Fig. 4. IR absorption spectra for nitride and oxynitride samples as a function of increasing Si concentration. The Si-H stretching mode peak becomes dominant as the samples vary from N rich to Si rich.

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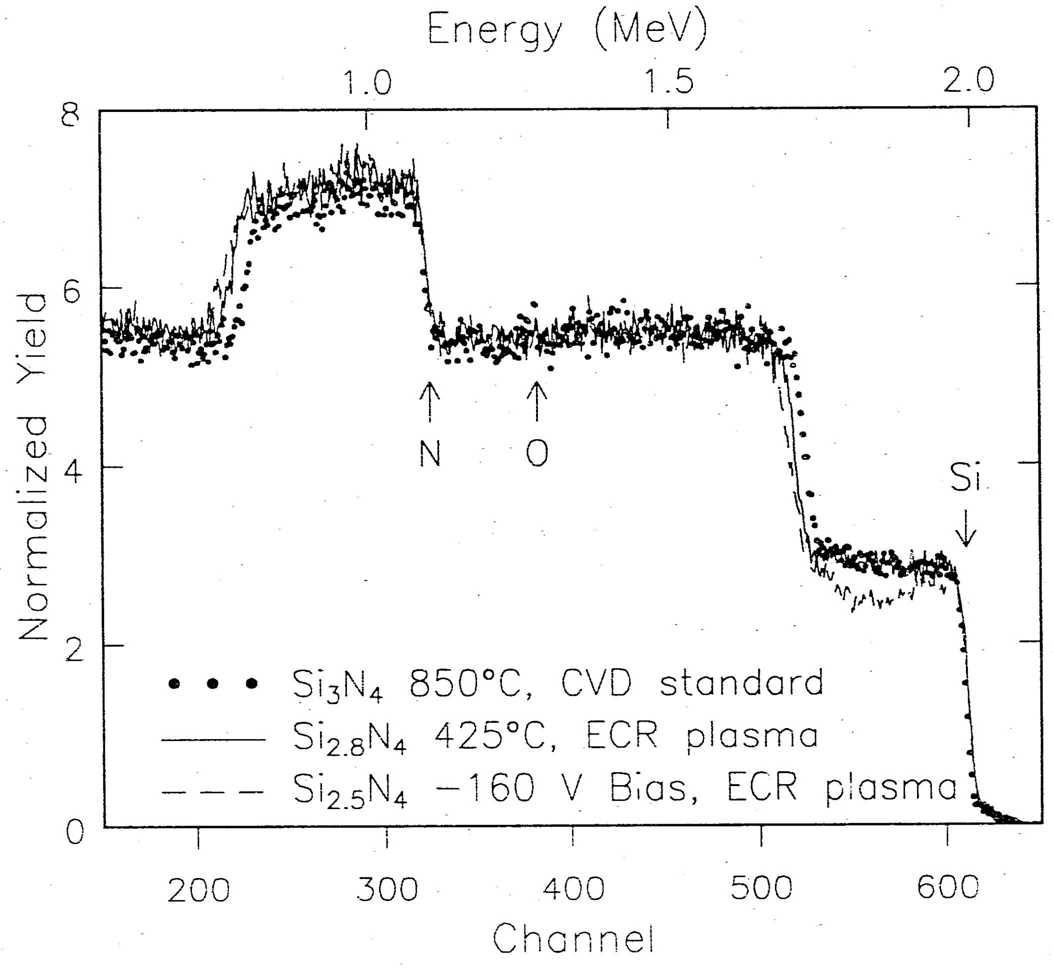
Energy (MeV)
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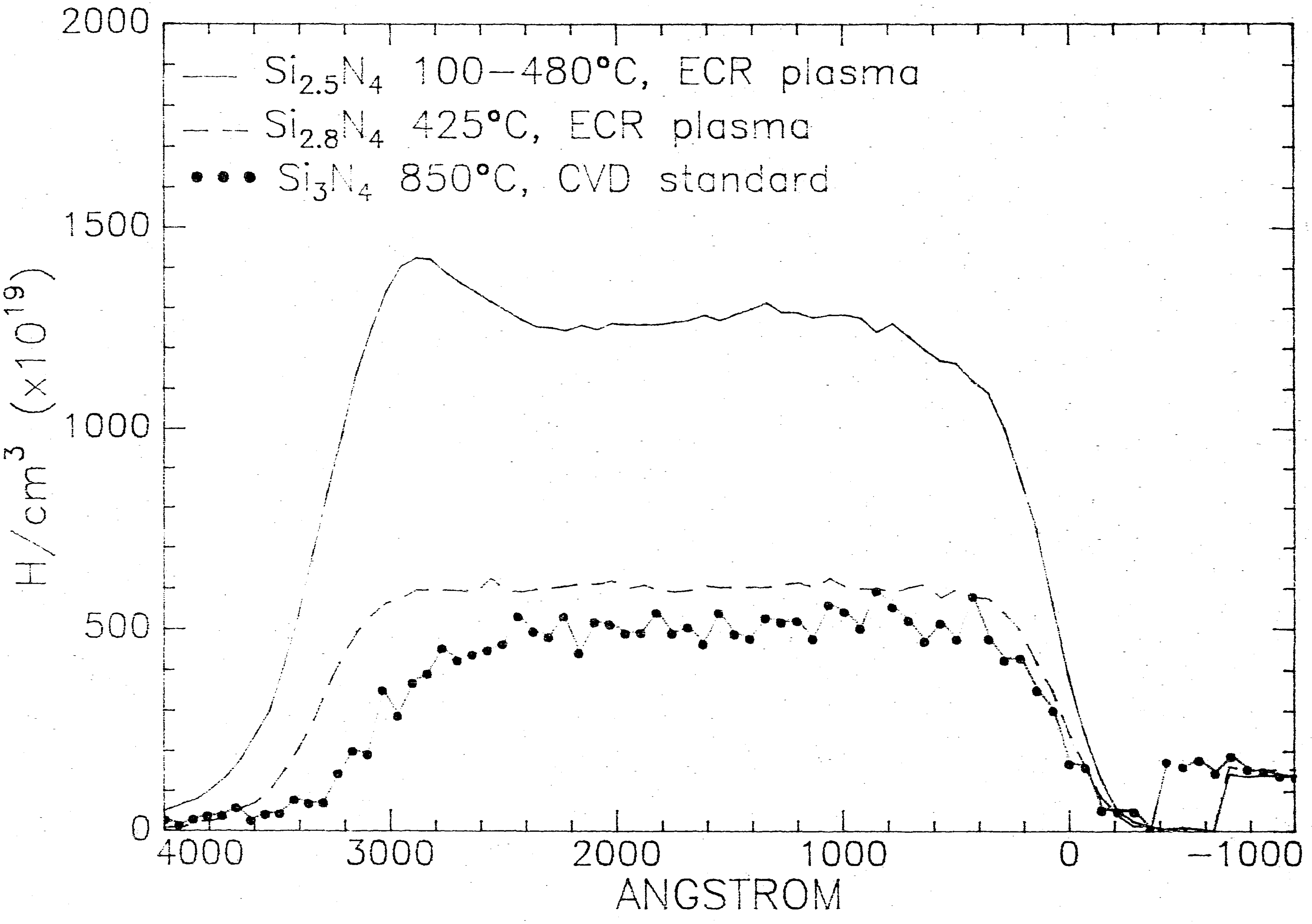
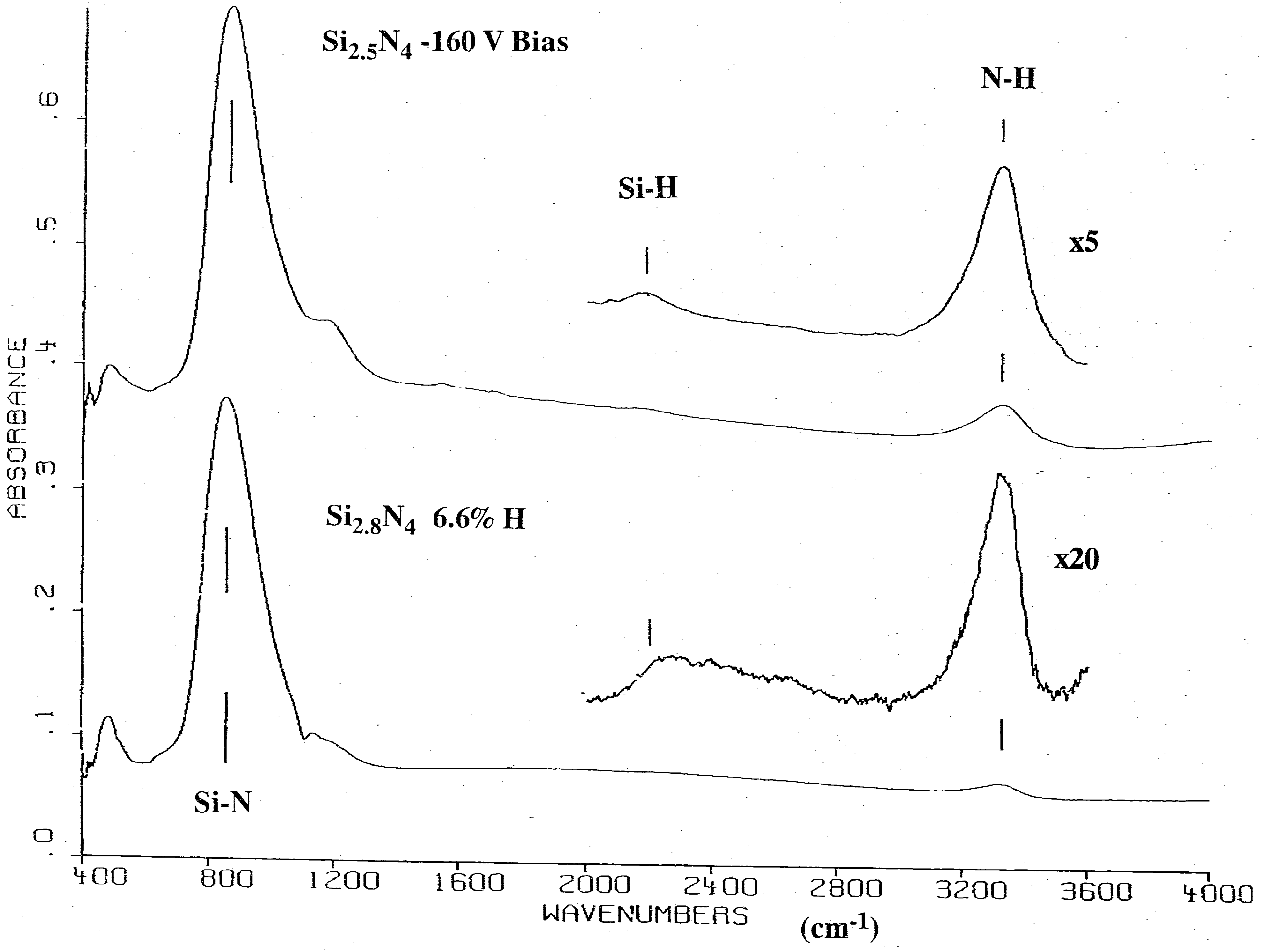
1.5
2.0
8
6
4
2
0
Normalized Yield
N
O
Si
Si_3N_4 850°C, CVD standard
$Si_{2.8}N_4$ 425°C, ECR plasma
$Si_{2.5}N_4$ −160 V Bias, ECR plasma
200
300
400
500
600
Channel



— $Si_{2.5}N_4$ 100−480°C, ECR plasma
– – $Si_{2.8}N_4$ 425°C, ECR plasma
● ● ● Si_3N_4 850°C, CVD standard
2000
1500
1000
500
0
H/cm^3 ($\times 10^{19}$)
4000
3000
2000
1000
0
−1000
ANGSTROM



$Si_{2.5}N_4$ -160 V Bias
N-H
Si-H
x5
$Si_{2.8}N_4$ 6.6% H
x20
Si-N
ABSORBANCE
0.
.1
.2
.3
.4
.5
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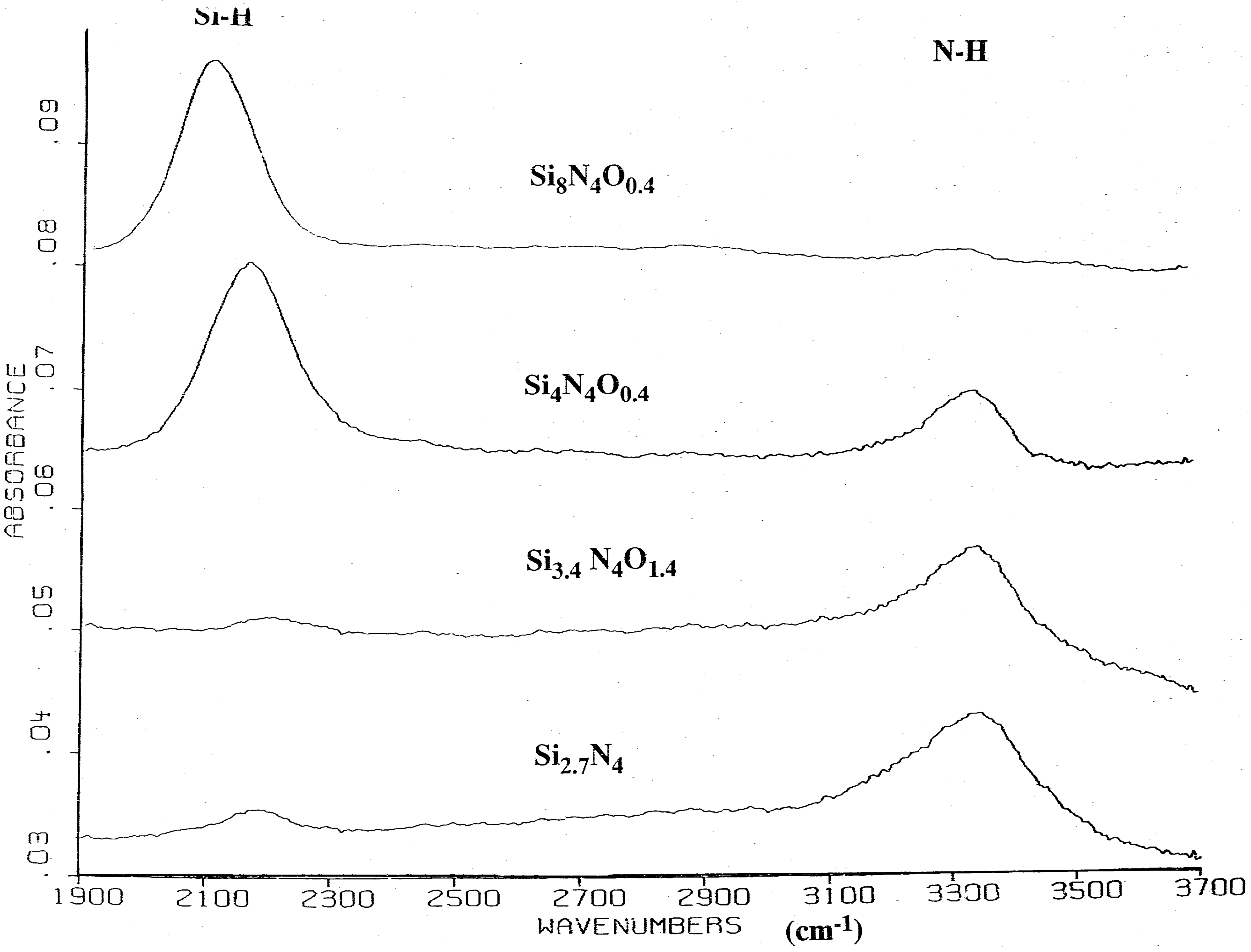
400
800
1200
1600
2000
2400
2800
3200
3600
4000
WAVENUMBERS
(cm^{-1})


Si-H
N-H
$Si_8N_4O_{0.4}$
$Si_4N_4O_{0.4}$
$Si_{3.4}N_4O_{1.4}$
$Si_{2.7}N_4$
ABSORBANCE
.09
.08
.07
.06
.05
.04
.03
1900
2100
2300
2500
2700
2900
3100
3300
3500
3700
WAVENUMBERS
(cm^{-1})

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