Quantitative Determination of Dielectric Thin-Film Properties

Using Infrared Emission Spectroscopy*

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Abstract

We have completed an experimental study to investigate the use of infrared emission spectroscopy (IRES) for the quantitative analysis of borophosphosilicate glass (BPSG) thin films on silicon monitor wafers. Experimental parameters investigated included temperatures within the range used in the microelectronics industry to produce these films; hence the potential for using the IRES technique for real-time monitoring of the film deposition process has been evaluated. The film properties that were investigated included boron content, phosphorus content, film thickness, and film temperature. The studies were conducted over two temperature ranges, 125 to 225 °C and 300 to 400 °C. The later temperature range includes realistic processing temperatures for the chemical vapor deposition (CVD) of the BPSG films. Partial least squares (PLS) multivariate calibration methods were applied to spectral and film property calibration data. The cross-validated standard errors of prediction (CVSEP) from the PLS analysis of the IRES spectra of 21 calibration samples each measured at 6 temperatures in the 300 to 400 °C range were found to be 0.09 wt. % for B, 0.08 wt. % for P, 3.6 μm for film thickness, and 1.9 °C for temperature. By lowering the spectral resolution from 4 to 32 cm^{-1} and decreasing the number of spectral scans from 128 to 1, we were able to determine that all the film properties could be measured in less than one second to the precision required for the manufacture and quality control of integrated circuits. Thus, real-time *in-situ* monitoring of BPSG thin films formed by CVD deposition on Si monitor wafers is possible with the methods reported here.

Key Words: BPSG films, PLS, IR emission spectra

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Introduction

Doped silicon oxide thin films are widely used in the microelectronics industry as dielectrics between metallization layers, as passivation and planarization layers, and as traps (getters) for mobile alkali cations (1). The most commonly used doped silica is borophosphosilicate glass (BPSG). The presence of boron and phosphorous dopants in these films modifies the film properties. The most important desired property that is modified with these dopants is the flow temperature that is significantly lowered relative to that of pure silica films. BPSG films are generally deposited using chemical vapor deposition (CVD). The useful dopant content of the films ranges from 1–6 wt. % for B and 2–8 wt. % for P. Control of dopant concentrations is very important for films produced to have the targeted properties. The film thickness, usually between 0.5 and 1.0 μm, is also important for meeting the desired dielectric breakdown specifications.

Quality control during BPSG deposition is generally achieved by periodically depositing a film on a monitor wafer and measuring the B content, P content, and film thickness offline. Although a number of analytical methods can be used to perform these analyses, measurements based on infrared absorption (2–4) or infrared reflection (5–6) have been shown to be accurate, precise, rapid, and nondestructive. Further, the infrared measurements can be performed at-line so there is little danger of loosing a significant amount of product produced while waiting for analytical results to be returned from a laboratory. Although an at-line analysis using a single measurement tool is a significant improvement over remote, off-line analysis, the ideal situation is to use a sensor capable of monitoring the deposition process.

We have recently demonstrated that infrared emission spectroscopy (IRES) when coupled with chemometric data analysis is capable of making quantitative determination of the

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temperature and P content in phosphosilicate glass thin films deposited on silicon wafers (7–9). IRES offers the potential for passive *in-situ* monitoring of the CVD process, as no IR probe beam is needed. All that is required for *in-situ* monitoring is that there be optical access to the film being deposited, that data collection and processing be much faster than the deposition process, and that the sample temperature be different than that of the infrared detector. Infrared detectors are often cooled, and the substrate temperatures in CVD processes are often elevated. Thus, the later condition is not a limitation.

There are, however, two factors that might limit the application of IRES to *in-situ* monitoring of a BPSG deposition process. The addition of boron to the films adds complexity to the infrared data relative to the data collected from the PSG films discussed above. This additional complexity is analogous to the increased complexity observed in infrared reflection spectra collected from PSG films (10) and BPSG films (5). However, prior studies have shown that the infrared reflection data collected from BPSG films can be used to make accurate and precise determinations of the film properties as long as carefully designed experiments are carried out (5,6) during the calibration phase of the analysis. A more significant factor could be the large changes in the IRES data that result from changing film thickness that must be modeled if IRES is to successfully monitor a deposition process in real time. The IRES thin-film calibrations on thin films that have been previously published (7-8) involved phosphosilicate glass films that have not included any film thickness variation. Preliminary IRES results on BPSG films have been published in Ref. 9. The BPSG films discussed here include variations in thickness, B content, and P content. As will be shown below, IRES data can be modeled using multivariate calibration to produce accurate and precise calibrations for the film properties and

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film temperature. These data can be collected and analyzed rapidly; hence, IRES is a good candidate for a real-time *in-situ* film deposition monitor.

Experimental

A 21-sample calibration set of BPSG thin films was produced at National Semiconductor Corp. (Santa Clara, CA) following a three-factor orthogonal experimental design with a randomized run order. The calibration sample properties spanned the following ranges: 2.8–5.2 wt.% for boron, 3.2–5.3 wt.% for phosphorus, and 0.76–0.92 μm for film thickness. The BPSG films were deposited at 430 °C using a tetraethoxysilane plasma-enhanced CVD process on undoped 150-mm silicon monitor wafers, which had been previously coated with a 0.1 μm layer of thermal oxide. After deposition, each BPSG sample was annealed at 800 °C in steam for 10 min followed by 20 min at 900 °C in nitrogen. The film thickness of each sample was measured with a Nanospec film thickness analyzer. Each of the calibration wafers was then cleaved in half and one half was sent to Balazs Analytical Laboratories (Sunnyvale, CA) for quantitative determination of B and P content. A 32 × 32 mm square was cleaved from the other half for the infrared emission studies.

All the infrared emission spectral data were collected using a Nicolet Model 800 Fourier transform infrared (FTIR) spectrometer. The spectrometer's internal source, a glowbar, was turned off, and a germanium-coated KBr beam splitter and a liquid-nitrogen-cooled (77 K) mercury-cadmium-telluride (MCT) detector were used for all emission measurements.

An apparatus was constructed for heating the BPSG samples to precisely maintained temperatures up to 600 °C in either a vacuum or a controlled, inert environment. This apparatus consisted of two boxes. The outer box, which mated to the Nicolet 800 spectrometer, was used

to provide a nitrogen purged optical path for the infrared radiation. The interior aluminum box (100 × 100 × 70 mm) with water-cooled walls contained the sample mounted on top of a heater. The heater consisted of a 50 mm-diameter, 25 mm thick hollowed copper block that contained about 7.5 m of tightly wound insulated nichrome wire, which provided about 400 Watts of heating power. A K-type thermocouple used to measure the sample temperature was placed on the BPSG film surface from which infrared emission radiation was collected. At the top of the interior box directly above the sample was a KBr optical port through which the infrared emission beam passed to an elliptical mirror that directed the infrared emission radiation from the sample into the auxiliary port of the infrared spectrometer.

A proportional integral and derivative (PID) temperature controller, Model CN9111A from OMEGA Engineering, Inc., was used to achieve stable temperature operation. The combination of the high power heater and the PID controller produced stable temperatures on the surface of the wafer such that the digital readout varied by only ±1 °C. The interior box had an inlet port connected to a nitrogen source and an outlet port that could be connected to a vacuum pump or serve as a vent to the atmosphere. When operated at atmospheric pressure, the outlet port was connected to 4.5 m of tubing to assure that oxygen did not diffuse into the heated chamber during an experiment.

Infrared emission spectra of the 21 BPSG calibration samples were collected at six temperatures over two temperature ranges, for a total of 126 spectra in each temperature range. The lower temperature range included temperatures at 125, 145, 165, 185, 205, and 225 °C in order to demonstrate the ability to perform quantitative emission analysis at relatively low temperatures for passive monitoring. The higher temperature range included temperatures of 300, 320, 340, 360, 380, and 400 °C to demonstrate the potential for real-time monitoring of the

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deposition process. In the higher temperature range, experimental temperature errors become more important. The error sources include: 1) errors in reproducing the contact of the samples with the sample heater (resulting in thermal gradients or inefficient heating), 2) errors in reproducing the contact of the thermocouple with the BPSG sample surface (causing inaccurate surface temperature measurements), and 3) non-steady state heat losses from the sample surface (resulting in temperature fluctuations). In both the lower and higher temperature ranges, the order of data collection was randomized with respect to temperature to avoid any possible correlation of run order with temperature in the spectral data sets.

A graphite flat served as the "blackbody" reference. All samples and the blackbody were measured in a nitrogen environment, and all infrared emission spectra were collected from the center of the sample. Each single-beam spectrum was the result of signal averaging 128 4 cm^{-1} resolution scans. Single-beam spectra of the BPSG samples at a given temperature were ratioed to the blackbody reference spectrum at the same temperature to yield infrared emittance spectra, which were used for all data processing.

All spectral data were transferred from the Nicolet computer to a PC. Partial least squares (PLS) calibrations of the infrared emission spectral data obtained in both the lower and the higher temperature ranges were performed using the PC version of the multivariate calibration software package developed at Sandia National Laboratories (11). This multivariate software operates within the Array Basic programming language of GRAMS (Galactic Industries Corp., Salem, NH). All PLS calibration models were calculated using mean-centered data over the spectral region of 550 to 1600 cm^{-1}. Prior to the calibration step the spectral data were smoothed and then treated by taking the first derivative to minimize spectral baseline variations. In some cases, the spectra were also pathlength corrected by dividing the spectrum by the

relative thickness of the thin film. All calibrations were carried out using cross-validation (CV), leaving out either one spectrum, six spectra (a given BPSG sample at each of the six temperatures), or twenty-one spectra (all twenty-one samples at a given temperature) at a time.

Results and Discussion

Infrared absorption spectra of silica-based materials, including thin-film materials, have been widely studied and are well understood (4). IRES spectra are also relatively well understood, but many more factors affect the spectral data resulting in features that are more nonlinear with concentration compared to the corresponding features in absorption data (12–15). An example of the differences in the two types of spectral data can be seen in Figure 1 where an absorption spectrum of one of the BPSG samples is plotted with an infrared emission spectrum obtained from the same sample. An obvious difference in the spectra is a change in the strong silica feature near 1100 cm^{-1} in the absorbance spectrum to a derivative-like feature in the emission spectrum. This change in the emission spectrum is a result of a combination of absorption of radiation passing through the multiple layers and reflection losses at each interface. Reflection is a function of refractive index, and the refractive index of a material changes dramatically in the region of a strong absorption. The frequency-dependent refractive index of the film also accounts for the apparent frequency shift of weaker features, e.g. the B–O feature in the absorption spectrum at 1400 cm^{-1} shifts to 1355 cm^{-1} in the emission spectrum. The consequence is that any attempt to develop quantitative models to predict film properties from IRES data must take into account these complications and nonlinearities in the model.

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Figure 2 shows the infrared emittance spectra of one BPSG thin-film sample at the six temperatures in the lower temperature range. Various features in the thin-film spectra have been labeled. In particular, the strong B–O stretching band at 1355 cm^{-1}, the P=O stretching band at about 1320 cm^{-1}, and another band due to a Si–O–B bending centered at 900 cm^{-1} are the most obvious boron- and phosphorus-related features in the thin-film spectra. The intensities and positions of these features change with the temperature of the thin films. The P=O feature is strongly overlapped by the much broader B–O band in the BPSG emittance spectra, as can be readily seen in Figure 2. The Si–Si phonon band at 610 cm^{-1} indicates that infrared radiation emitted from the silicon substrate makes a significant contribution to the emittance spectra in the lower temperature range. Note, however, the intensity (relative to the baseline) of this band decreases as the temperature of the sample increases. The most dominant feature in the spectral data is in the region from 1000 to 1150 cm^{-1}, which is caused by the derivative nature of the strong Si–O band in these emittance spectra. When absorption spectral data of BPSG films are used to characterize the film properties, a strong correlation between the Si–O absorption band and film thickness is observed (2). One might expect the same correlation to exist in the emittance data, but a good correlation based on the height (depth) of this derivative feature was not found with these data. A consistent increase of baseline with the temperature in the region above 1450 cm^{-1} is observed, and almost all features in the spectra become less pronounced as the temperature increases. Less noticeable is the fact that the spectral features red shift with increasing temperature. For example, the B–O peak shifts from 1358 cm^{-1} at 125 °C to 1350 cm^{-1} at 225 °C.

The temperature dependence of the spectral intensities and feature positions at the six temperatures of the higher temperature range (300 to 400 °C) are illustrated in Figure 3. As can

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be seen, the baseline variations with temperature in the region above 1450 cm^{-1} are less dramatic than in the low temperature range, but the baseline still consistently shifts upward with temperature. However, other spectral feature changes that were readily apparent in the data collected over the lower temperature are not nearly as dramatic in the higher temperature spectra. For example, the B–O and P=O features near 1355cm^{-1} and 1320 cm^{-1} are not as pronounced in the high-temperature spectra. The most striking difference between the data in Figures 2 and 3 is the disappearance of the Si–Si phonon band near 610 cm^{-1}. As Si is heated to higher temperatures, the number of free electrons in the Si increases. At some point below 300 °C, the free electron concentration of the substrate becomes sufficiently high that the Si substrate becomes "mirror like," and the discreet spectral features of the Si phonon band disappear.

Figure 4 shows infrared emittance spectra collected at 400 °C of five BPSG samples with extremes in boron content, phosphorus content, and film thickness. It is clear from Figure 4 that there are discernible differences in spectral features and baselines due to changes in the thin-film properties. An examination of the spectra between 1250 and 1400 cm^{-1} shows that the B–O and P=O features change in relative intensity with changing B and P content, and the peaks shift in frequency. The high degree of complexity in these data makes it imperative that some sort of multivariate calibration algorithm be used if good quantitative models for the film properties are to be developed. The PLS algorithm was selected for this application based on the quantitative results that had been realized when applied to similar data (5–10). The calibration precisions achieved in these prior studies were shown to be generally limited by the precision of the reference data used in the calibration process.

Boron content of the films was measured using inductively coupled plasma atomic emission spectroscopy (ICP/AES), while phosphorus content was determined using colorimetry.

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The precision for both methods was estimated to be between 0.05 and 0.10 wt.%. The boron and phosphorus concentrations in BPSG films are known to vary slightly across a wafer. Since the reference values are obtained on one half of each wafer and the infrared data are collected from a small spot on the other half of the wafer, any variation in composition across the wafer will add to the apparent reference error. The film thicknesses were determined using a Nanospec film thickness analyzer with an estimated precision of ± 50 Å. Finally, the reference temperature precision will depend on the precision of the temperature measurements or on the precision of the temperature control, whichever is limiting. We estimate that the sample temperature in the apparatus used here is maintained to ±1 °C during a given spectral measurement. The PLS multivariate calibration of the infrared emission data is based on all these reference values. Therefore, the estimated precisions of property predictions from the PLS model are limited by the precisions of the corresponding reference methods.

There were a total of 126 infrared emittance spectra in each of the two (high and low temperature) calibration sets, i.e. 21 samples at 6 different temperatures. When carrying out a PLS calibration, a cross-validation process is performed. Cross-validation is introduced to determine the optimum number of PLS factors used by the model and to allow sensitive detection of outlier samples in the calibration data. When performing cross-validation, one or more samples are set aside, a calibration model is developed using the remaining samples, and the property values of the sample(s) set aside are predicted. The process is then repeated with a different sample or set of samples removed during the cross-validation procedure. This process is continued until all samples have been predicted as unknowns. The results of the cross-validation process is used to calculate the cross-validated standard errors of prediction (CVSEP):

$$CVSEP = \frac{\sqrt{\sum_{i=1}^{n}(x_i - \hat{x}_i)^2}}{n},$$

where x_i is the reference value for the ith sample, $\hat{x}_i$ is the predicted value for the ith sample, and n is the number of samples. Three types of cross-validation were used in modeling the IRES data: removal of one sample at a time (1OUT), removal of a sample at all six temperatures (6OUT), and removal of all data for a particular temperature (21OUT). The CVSEP's give an estimate of how well a calibration model would be expected to perform when predicting unknown samples.

When 1OUT cross-validation is employed, the model still includes information obtained from each sample removed since this sample is present in the model at the other five temperatures. Thus, there is a possibility that the CVSEP might be overly optimistic for the model's ability to predict a true unknown. 6OUT cross-validation removes all information for an individual sample from the modeling process. There are spectral data remaining in each cross-validated calibration for each temperature, but the samples included in each rotation of the cross-validation procedure are different. Thus, in this 6OUT cross validation, the CVSEP for temperature is likely representative of the model's ability to predict temperature in a true unknown sample. It is expected that the 6OUT and 21OUT CVSEP results are more representative of the true predictive ability of the PLS models since these CVSEP values should not have any likelihood of overfitting the data. In the case of the 21OUT cross validation, a large number of predictions of samples (21) are the result of extrapolating the models to either the low or high extremes in the temperatures. Since these PLS models are not expected to extrapolate well for these nonlinear data, the CVSEP for temperature is expected to actually be somewhat pessimistic relative to what could be obtained for true unknown samples. This effect of

increased errors for the extreme temperatures is clearly observed in Fig. 5 where the largest PLS model errors are found for the 300 and 400 °C data. Thus, the 6OUT CVSEP values for temperature are expected to be more representative of the true PLS model prediction ability for temperature.

Table 1 summarizes the best CVSEP results of the calibration for both the lower and higher temperature ranges with respect to the type of cross-validation that was performed. We tested the performance of calibrations with different combinations of spectral preprocessing methods such as linear spectral baseline correction, pathlength correction, Savitsky–Golay smoothing, and Savitsky–Golay derivatives of the spectral data. We found that the spectral preprocessing procedure that combined pathlength (i.e., film thickness) correction and Savitsky–Golay smoothing followed by taking the first derivative produced optimum calibration results for all properties except film thickness. The Savitsky–Golay smoothing reduces spectral noise and the harmful effects of trace water vapor or CO_2 in the purge gas, while the derivative treatment helps to minimize spectral baseline variations prior to the PLS modeling stage. The best results for film thickness were obtained by preprocessing the spectra with Savitsky–Golay smoothing followed by taking the first derivative. The pathlength correction scales the infrared emittance spectra to unit relative pathlength in order to minimize the multiplicative effect of film thickness in the emission spectra. However, the difference in the CVSEP's for thickness prediction achieved with and without pathlength scaling is small.

The cross-validated prediction results based on data from the higher temperature range for boron content, phosphorus content, film thickness, and temperature are illustrated in Figures 6–9. The data contained in Figures 6–9 were all obtained using 6OUT cross-validation. The R^2 values in the figure captions indicate the squared correlation coefficients between the reference

values and the PLS estimated values. The R^2 values are all equal to or better than 0.98. Similar PLS prediction plots obtained from the lower temperature range data have slightly better CVSEP and R^2 values. These results indicate PLS is capable of building a very good model relating the film properties and the complex infrared emission data.

Rapid measurements are generally required of any *in-situ* process-monitoring tool. When making infrared measurements using a Fourier transform spectrometer, two modifications can be readily made to increase the speed of the data collection: 1) reduce the amount of signal-averaging, and 2) decrease the distance traveled by the moving mirror. The first approach reduces the spectral signal-to-noise ratio, and the second decreases spectral resolution. The effect of decreasing spectral resolution is relatively easily tested by truncating the interferograms originally saved at 4 cm^{-1} resolution. The coadded interferograms were truncated and Fourier transformed to produce additional emittance spectra at 16 cm^{-1} and 32 cm^{-1} resolution. Table 2 shows the cross-validated calibration results (6OUT) for BPSG samples as a function of resolution. There are no statistical differences between the CVSEP values for either boron or phosphorus at 4 cm^{-1} and 32 cm^{-1}. The CVSEP values for both film thickness and temperature degrade slightly with decreasing spectral resolution.

The spectrometer stability and the method repeatability were determined by predicting film properties and sample temperature on 10 spectra repeatedly measured using identical conditions without reinserting the sample. Ten infrared emittance spectra from a single BPSG thin-film sample with signal averaging of 128 scans were obtained at 4 cm^{-1} resolution. Emittance spectra of the samples at resolutions of 16 cm^{-1} and 32 cm^{-1} were again obtained by truncating the corresponding interferograms prior to Fourier transformation. Table 3 lists the average standard deviations of the predicted film properties and sample temperature from the 10

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repeat spectra at different resolutions using PLS calibration models obtained from spectral data at the appropriate resolution with factor selection based upon 6OUT cross-validated calibrations. The values in the table are the average values of standard deviations determined at three different temperatures (i.e., 300, 360, and 400 °C). The standard deviations of the repeat determinations for all four properties are all considerably less than the corresponding CVSEPs, a fact that suggests the reference determinations (or film thickness variations) or model error limit these CVSEP results rather than spectral noise. Reference errors in temperature caused by temperature fluctuations of the wafer are a factor in the repeat measurements. Thus, the temperature precisions in Table 2 are probably dominated by these temperature fluctuations rather than by spectral noise.

The results in Tables 2 and 3 demonstrate that 4 cm^{-1} resolution data are not required to produce precise measurements. It takes approximately 64 seconds to collect 128 scans at 4 cm^{-1}. The loss in prediction precision when using 32 cm^{-1} data is not significant. 128 scans with 32 cm^{-1} resolution can be collected in approximately 20 seconds. Even if all the precisions in Table 3 were fully due to spectral noise, then the maximum inflation in precision for a single scan would be a factor of 11. For B and P, the precisions expected for a single scan are no worse than found in Table 1 for CVSEP calibration. Even for thickness and temperature, the prediction errors expected for a single scan at 32 cm^{-1} are less than 80 Å and 10 °C, respectively, which is adequate for process monitoring for this system. A single scan spectrum at 32 cm^{-1} can be obtained in a fraction of a second, which is clearly fast enough for real time measurement of the four thin film properties.

Conclusions

The small cross-validated CVSEP values shown in Table 1 and Figures 6–9 demonstrate that boron and phosphorus content, film thickness, and film temperature can be simultaneously determined from the infrared emittance spectra of BPSG thin film samples deposited on silicon wafers. The demonstration of quantitative analysis at a temperature of 400 °C is significant, because 400 °C is in the temperature range in which CVD-BPSG films are typically produced. The fact that the repeatability and low resolution results demonstrated such high precision suggests that infrared emittance spectral data could be obtained with considerably less signal averaging, hence much faster, with adequate precision. It should be possible, with less signal averaging and low-resolution operation, to collect spectral data in less than a second. This is a time scale that makes real-time *in-situ* monitoring of CVD film deposition using infrared emission compatible with feedback control of the CVD process. The expected prediction precisions either demonstrated or extrapolated in this paper are all adequate for process monitoring and control of the BPSG thin-film deposition process at normal processing temperatures.

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Table 1

Cross-validated PLS calibration results of 21 BPSG thin-film samples on silicon wafers.

COMPONENT	CVSEP (125–225 °C)			CVSEP (300–400 °C)		
	1OUT	6OUT	21OUT	1OUT	6OUT	21OUT
Boron (wt.%)	0.04	0.08	0.06	0.04	0.09	0.06
Phosphorus (wt.%)	0.04	0.10	0.04	0.05	0.08	0.06
Thickness (Å)	19	34	41	20	36	24
Temperature (°C)	0.8	0.8	1.5	1.5	1.9	3.4

Table 2

Cross-validated PLS Calibration Results (6OUT CVSEP values) of 21 BPSG Thin Film Samples at Different Resolutions (300-400 °C)

COMPONENT	RESOLUTION		
	4 cm^{-1}	16 cm^{-1}	32 cm^{-1}
Boron (wt.%)	0.09	0.09	0.09
Phosphorus (wt.%)	0.08	0.08	0.09
Thickness (Å)	36	36	70
Temperature (°C)	1.9	2.4	2.5

Table 3

The Average Standard Deviations in Property Measurements from Ten Repeat Spectral

Measurements at Temperatures of 300, 360, and 400 °C.

COMPONENT	RESOLUTION		
	4 cm^{-1}	16 cm^{-1}	32 cm^{-1}
Boron (wt.%)	0.003	0.003	0.006
Phosphorus (wt.%)	0.004	0.004	0.005
Thickness (Å)	5.5	7.2	7.2
Temperature (°C)	0.6	0.6	0.8

Figure Captions

Figure 1   Absorbance spectrum of BPSG film on an undoped Si monitor wafer (dashed line). Emittance spectrum of the same sample at 185 °C (solid line). B = 4.46 wt. %, P = 4.53%, and thickness = 0.8006 μm

Figure 2   Emittance spectra of the BPSG sample in Figure 1 at the six temperatures from 125 to 225 °C.

Figure 3   Emittance spectra of the BPSG sample in Figure 1 at the six temperatures from 300 to 400 °C.

Figure 4   Emittance spectra of five BPSG thin-film samples at 400 °C representing the range of spectral variation in the sample spectra. These five samples contain the high and low extremes of the B, P, and thickness in the sample set.

Figure 5   CVSEP temperature prediction results from PLS analysis of the emittance spectra of the 21 BPSG samples at the higher temperatures for each cross-validated rotation of 21 samples at a given temperature.

Figure 6   Cross-validated (6OUT) PLS predicted B content vs. reference B content from the thickness-corrected emittance spectra for the 21 BPSG samples over the 300 to 400 °C temperature range (R^2 = 0.99).

Figure 7   Cross-validated (6OUT) PLS predicted P content vs. reference P content from the thickness-corrected emittance spectra for the 21 BPSG samples over the 300 to 400 °C temperature range (R^2 = 0.98).

Figure 8   Cross-validated (6OUT) PLS predicted thickness vs. reference thickness from the

emittance spectra for the 21 BPSG samples over the 300 to 400 °C temperature range

($R^2 = 0.99$).

Figure 9   Cross-validated (6OUT) PLS predicted temperature vs. reference temperature from

the emittance spectra for the 21 BPSG samples over the 300 to 400 °C temperature
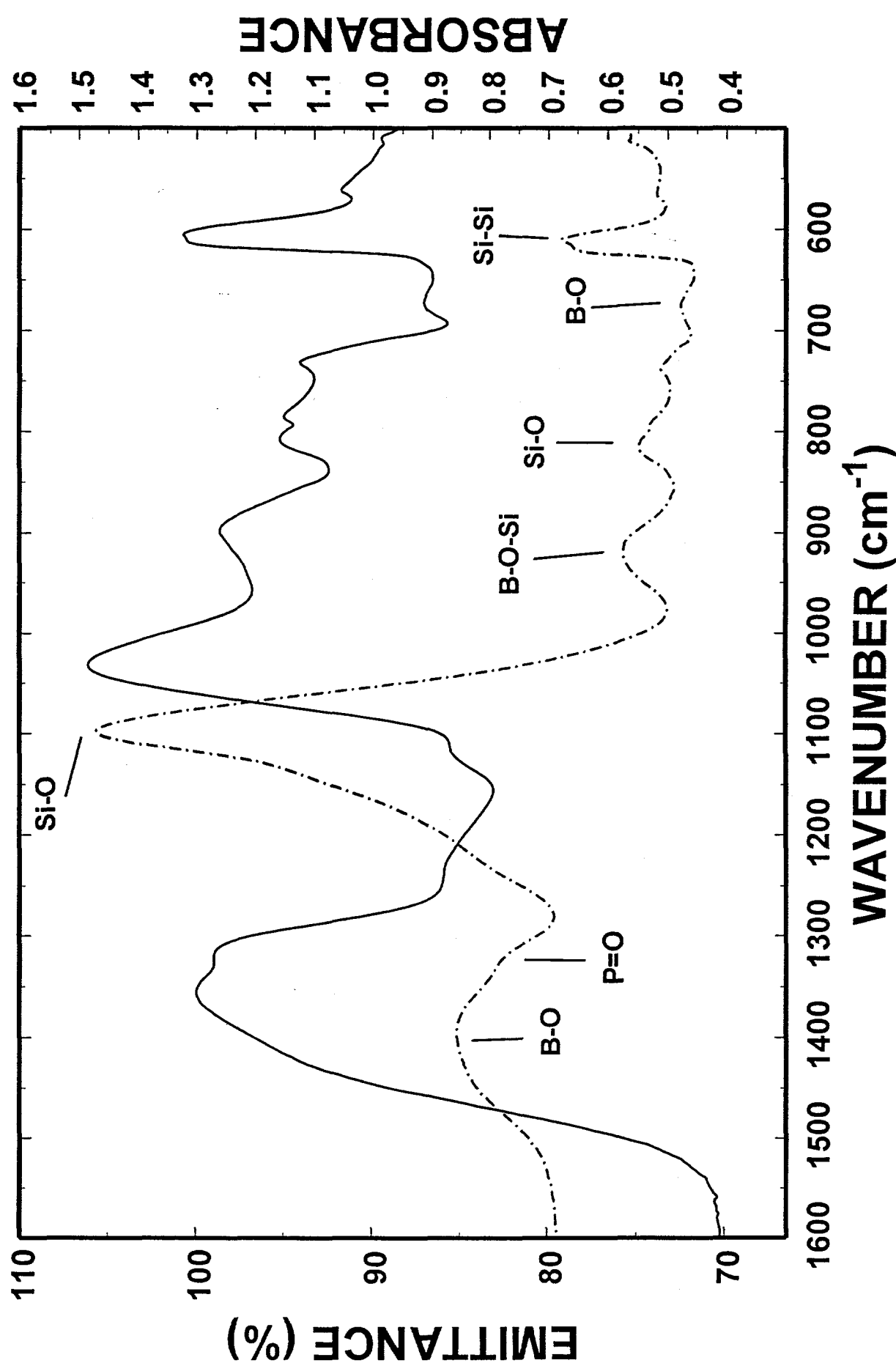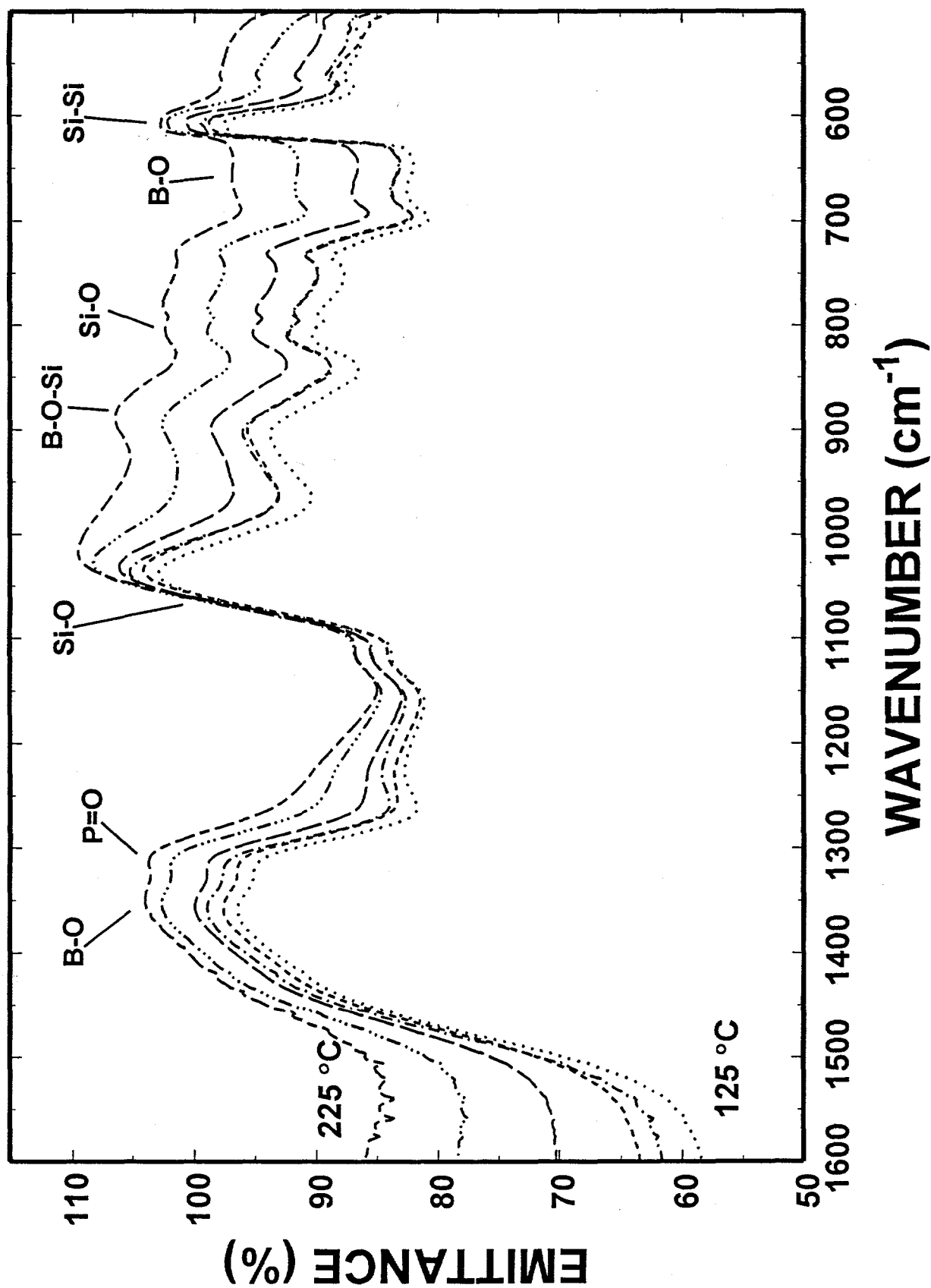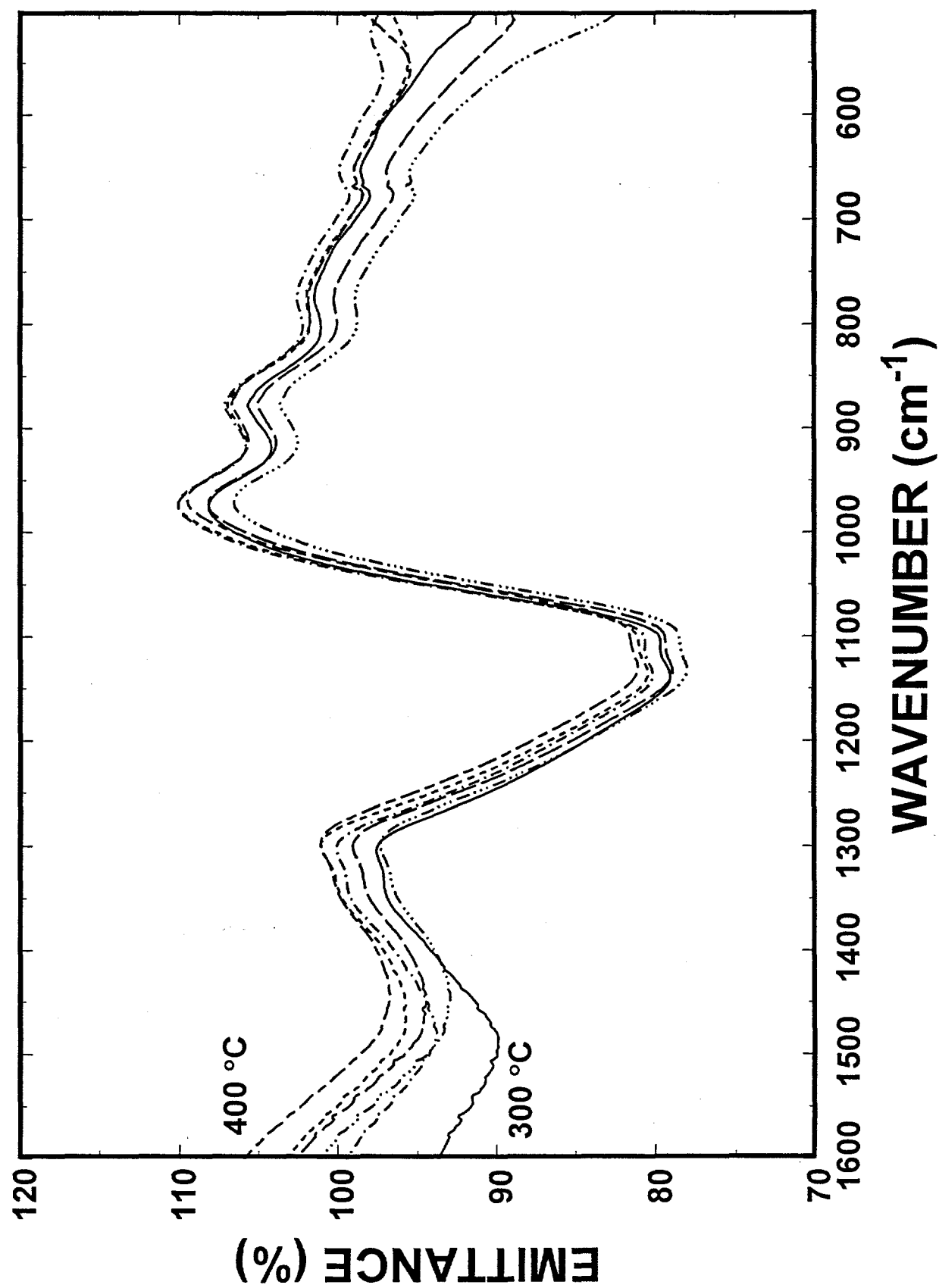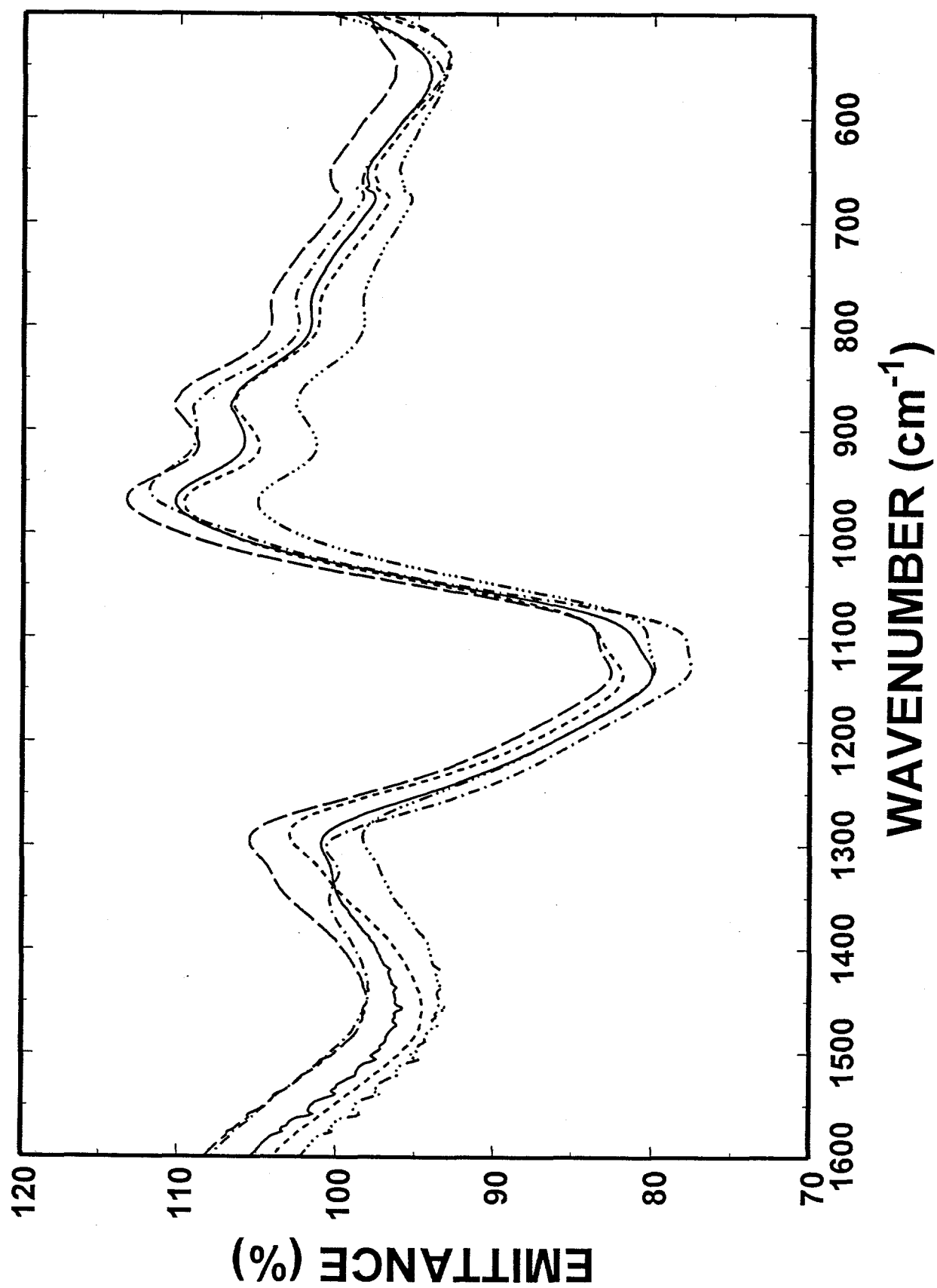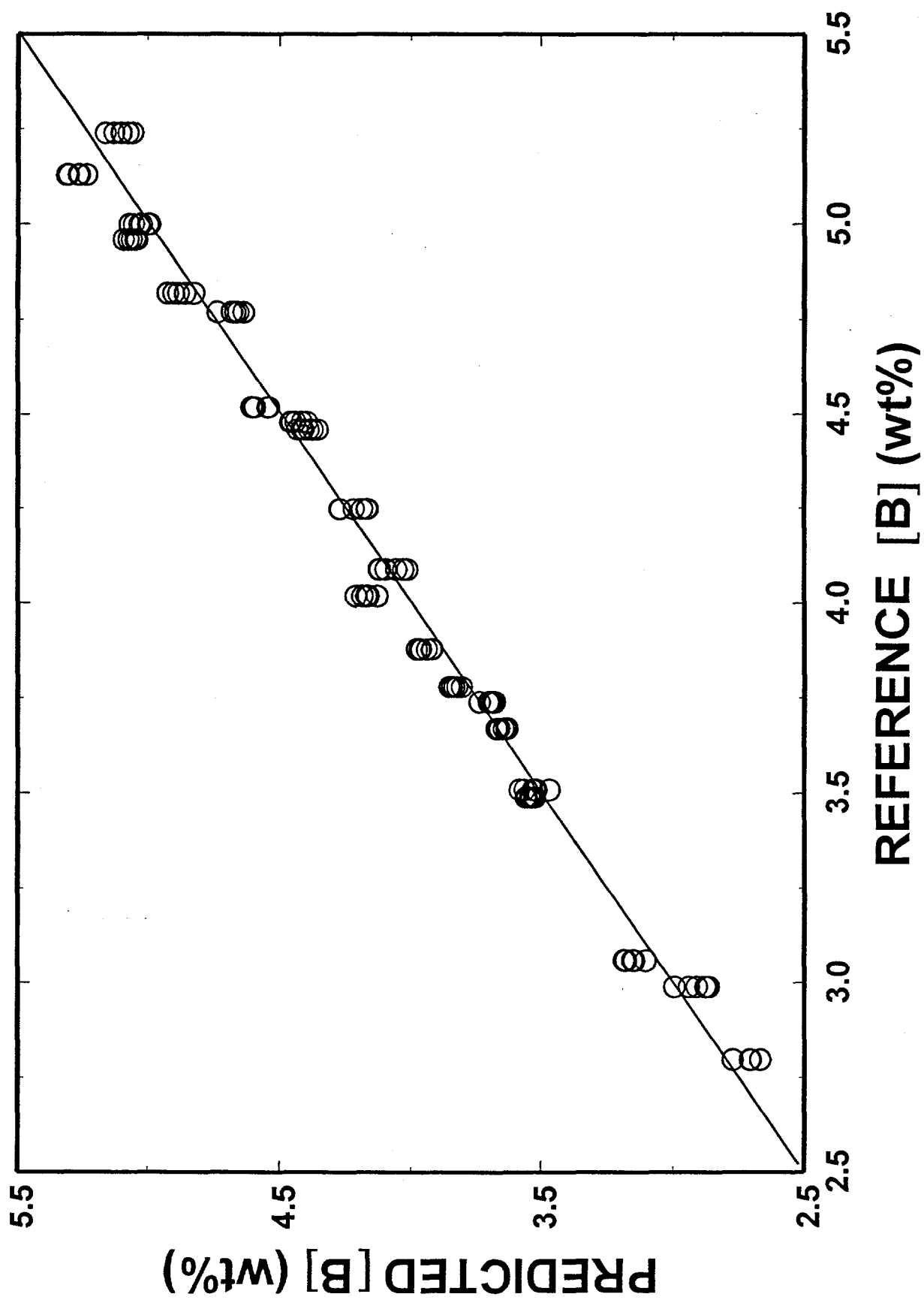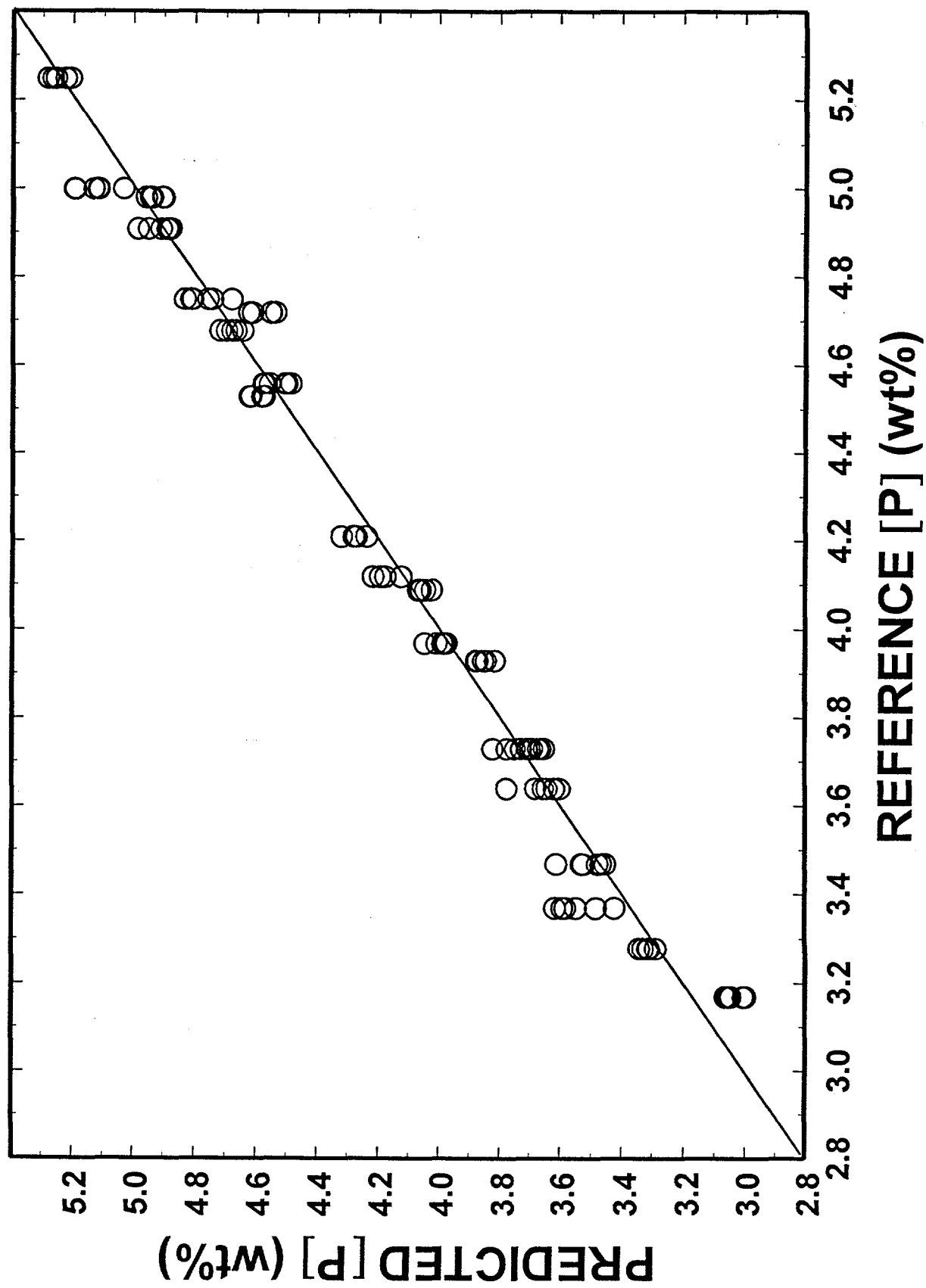
range ($R^2 = 0.9995$).

Figure 1

Figure 2

Figure 3

figure 4

Figure 5

figure 6

figure 7

REFERENCE [P] (wt%)

PREDICTED [P] (wt%)

Figure 8

REFERENCE TEMPERATURE (°C)

PREDICTED TEMPERATURE (°C)

Figure 9