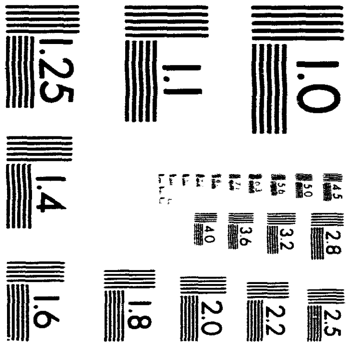
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Chemometric Analysis of Infrared Emission Spectra for Quantitative Analysis of BPSG Films on Silicon*

James E. Franke, Chuenyuan S. Chen, Songbaio Zhang, Thomas M. Niemczyk

Chemistry Department, University of New Mexico, Albuquerque, NM 87131

and

David M. Haaland

Sandia National Laboratories, Albuquerque, NM 87185

Abstract

Infrared emission spectra of 21 borophosphosilicate glass (BPSG) thin films on silicon wafers were collected with the samples held at constant temperature between 125-400°C using a heating stage designed for precise temperature control (±1°C). Partial least squares calibrations applied to the BPSG infrared emittance spectra allowed four BPSG thin-film properties to be simultaneously quantified with precisions of 0.1 wt% for boron and phosphorus, 35 Å for film thickness, and 1.2°C for temperature.

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Introduction

In the microelectronics industry, *in situ*, rapid, quantitative, and nondestructive quality control monitoring of dielectric thin films during CVD processing is desirable for reducing the error budget of the resulting device wafers. Infrared emission (IRE) spectroscopy combined with chemometric data analysis is one potential *in-situ* process monitor that fulfills the criteria outlined above (1,2). IRE and other infrared (IR) spectroscopic methods for the quantitative analysis of dielectric thin films have been recently reviewed (3). We report here on the use of the partial least squares (PLS) chemometric technique (4) to quantify boron, phosphorus, thickness, and temperature simultaneously from the IR emittance spectra of BPSG thin films on silicon wafer substrates.

Experimental

The BPSG calibration set used in this study was prepared at National Semiconductor (Santa Clara, CA) and consists of 21 BPSG films over 1000 Å thermal oxide on undoped 150 mm diameter silicon wafers. The calibration sample set spans 2.8-5.2 wt% B, 3.2-5.3 wt% P, and 0.76-0.92 μm film thickness. The B and P contents were determined by Balazs Laboratories (Sunnyvale, CA) using wet chemical analysis of a sister BPSG calibration set. Film thicknesses were measured with a Nanospec film-thickness analyzer.

An IRE apparatus was constructed for heating the BPSG samples up to 500°C in either a vacuum or a controlled, inert environment. The apparatus consists of a water-cooled aluminum box that has a KBr optical port at the top through which IRE radiation may be collected from samples heated on a thermocouple-controlled cable heater. The cable heater consists of a 5 cm diameter, 2.5 cm thick copper block that is internally wound with about 8 m of insulated nichrome wire that provides about 400 Watts of heating power. The thermal stability of the cable heater, i.e., temperature precision, was determined to be ± 1°C.

IRE spectra of the BPSG samples were collected with the described IRE apparatus separately over two temperature ranges, for a total of 126 spectra in each temperature range. The lower temperature range included spectra at 125, 145, 165, 185, and 225°C, while the higher temperature range included spectra at 300, 320, 340, 360, 380, and 400°C. Temperature was measured with a K-type thermocouple placed at the center of the area on the BPSG film surface from which IRE radiation was collected.

Single-beam IRE spectra of the BPSG samples at a given temperature were ratioed to "blackbody" reference spectra at the same temperature to yield IR emittance spectra that were used in the PLS calibrations. A graphite flat served as the "blackbody". All samples and the "blackbody" were heated in a nitrogen environment, and all IRE spectra were collected at 4 cm^{-1} resolution with signal-averaging of 128 scans using a HgCdTe detector operating at 77 K. PLS calibration models were calculated from the BPSG IR emittance spectra using the spectral data between 550 and 1600 cm^{-1}. The multivariate calibration models were built from spectra that were smoothed and transformed into first-derivative spectra to minimize spectral baseline variations prior to the PLS modelling step. To help ensure that all sample spectra were independent of each other during PLS modelling, the calibrations were done with cross-validation (CV) leaving out six samples at a time in order to remove a design point (i.e., the spectra from a given BPSG sample at each of the six temperatures were removed during each CV cycle). The PLSSNL software package (4) was used to perform all of the PLS calibration model calculations.

The experimental design of the 21-sample BPSG calibration set was chosen to eliminate any correlation between B, P, or film thickness but to maximize the filling of the calibration space formed by the ranges spanned by each component. The experimentally prepared BPSG samples were found to closely match the specified component values dictated by the experimental design, so any correlations among the B, P, and thickness components were minimized. In both the lower and higher temperature ranges, the order of data collection was randomized with respect to temperature to avoid any possible correlation with time-dependent drift in the spectral data sets.

Results and Discussion

Fig. 1 illustrates the IR emittance spectra of one BPSG thin film (Sample A) at both 125°C and 400°C and a second BPSG thin film (Sample B) at 400°C. Although Samples A and B differ in both dopant concentrations and film thicknesses, it is clear from Fig. 1 that there are few discernable differences between their IR emittance spectra at 400°C. If a univariate calibration approach was used on spectra having such small changes, it would not be possible to quantitatively determine BPSG film properties or temperature. This fact demonstrates the importance of using multivariate calibration techniques for deriving quantitative information from these BPSG IR emittance spectra.

Unlike the case of different samples at constant temperature, sharp differences exist among spectra at different temperatures, even for the same sample. In Fig. 1, for example, the silicon phonon band at 620 cm^{-1} in the 125°C IR emittance spectrum of Sample A is completely absent in the 400°C spectrum of the same sample. Furthermore, all of the spectral bands in the 400°C spectrum of Sample A in Fig. 1 appear more broadened and flattened than the bands in the 125°C spectrum of Sample A. The band maxima also shift in the two spectra, and spectral baselines completely change above 1450 cm^{-1} upon going from low to high temperature.

An understanding of the physical significance of these spectral changes requires one to consider the BPSG samples as parallel slabs of semitransparent materials (BPSG and thermal oxide layers) supported on a substrate material (Si wafer). Theory then predicts that the IR emittance spectra for this type of multilayer medium will be dominated by numerous optical parameters or effects (5-8) including the absorption coefficient and temperature of the materials, their surface reflectivities and thicknesses, the multiple internal reflections between layers, and the emissivity of the support material. For example, the disappearance of the silicon phonon band in Fig. 1 occurs because the emissivity of the Si wafer support approaches 1.0 (i.e., a blackbody emissivity) above 300°C. Thus, the Si substrate has become opaque to IR radiation in the high-temperature calibration region. In addition, the change in the Si support emissivity will affect the surface reflectivity at the sample/Si interface and the amount of IR radiation emitted from the Si wafer support, and both of these factors directly impact the appearance of the IR emittance spectra. Given that the change in just one of the optical parameters or effects due to temperature variations can complicate the entire spectral region shown in Fig. 1, it is again evident that a multivariate calibration technique such as PLS is needed to quantify BPSG thin-film properties from their IR emittance spectral data.

There are several difficulties to overcome in achieving a quantitative analysis of BPSG thin-film properties from their IR emittance spectra. Some of the difficulties, such as baseline variations, shifting of peak maxima, and dispersion in the refractive index of strongly absorbing bands, are similar to difficulties encountered by IR external reflection-absorption spectra that have been used successfully with PLS calibration to quantify phosphorus and thickness in phosphosilicate glass (PSG) thin films on silicon (9). Additional complications in the IR emittance spectra of BPSG thin films that must be correctly modeled by PLS include: 1) highly overlapped boron and phosphorus bands between 1250 and 1450 cm^{-1} and 2) emissivity changes in both the Si substrate (described above) and the dielectric film layers as a function of both the temperature and thickness.

Despite these difficulties, quantitative results can be achieved using PLS multivariate calibration. Fig. 2 and 3 illustrate the cross-validated PLS calibration results for boron and temperature based on the calibration set of 126 BPSG IR emittance spectra obtained between 300-400°C (21 BPSG samples each at six different temperatures). Boron is predicted with a cross-validated standard error of prediction [SEP(CV)] of 0.09 wt% B. Since 0.09 wt% B is not statistically different from the reported precision of the reference method for B (±0.1 wt%), the PLS model has achieved the highest possible precision for boron given the precision limitations of the reference methods.

Temperature is predicted with a SEP(CV) of 2.1°C over the 300-400°C range (see Fig. 3). However, the SEP(CV) for temperature might be expected to be about 1.4°C since the IR emittance data result from ratioing two single-beam spectra, each with an estimated temperature precision of ±1°C. The higher observed value of 2.1°C may be the result of experimental limitations such as: 1) difficulty in reproducing the contact of the samples with the cable heater (errors cause thermal gradients and inefficient heating), and 2) difficulty in reproducing the contact of the thermocouple with the BPSG sample surface (errors can cause inaccurate surface-temperature measurements).

The calibration results obtained using the IR emittance spectra of BPSG films are summarized in Table I for both the low and high temperature ranges. The table shows the SEP(CV) values obtained for B content, P content, sample temperature, and film-thickness predictions. The B, P, and thickness components are predicted with nearly identical precisions over the two temperature ranges. The precision of phosphorus prediction is about 0.1 wt% P for both temperature ranges, which is the same as the reported precision of the reference method for P determination. The thickness precisions are < 40 Å in the PLS model predictions, which is less than the estimated precision (±50 Å) of the Nanospec film-thickness analyzer. Temperature is predicted better in the lower temperature range, probably because the experimental limitations discussed above in measuring surface temperature are less prominent at the lower temperatures.

Conclusions

The small SEP(CV) values shown in Table I and in Figs. 2 and 3 demonstrate that B and P content, film thickness, and film temperature can be simultaneously determined from the IR emittance spectra of BPSG thin-film samples. These quantitative determinations have been achieved with precisions at least as good as the precisions estimated for the reference methods, and this has been accomplished over both a low (125-225°C) and high (300-400°C) temperature range. The demonstration of the quantitative analysis at 400°C is important since it is a temperature near which CVD-BPSG films are typically produced. The overall results confirm the potential of *in-situ* IRE spectroscopy coupled with PLS multivariate calibration for process monitoring of CVD-deposited BPSG thin films used in the microelectronics industry.

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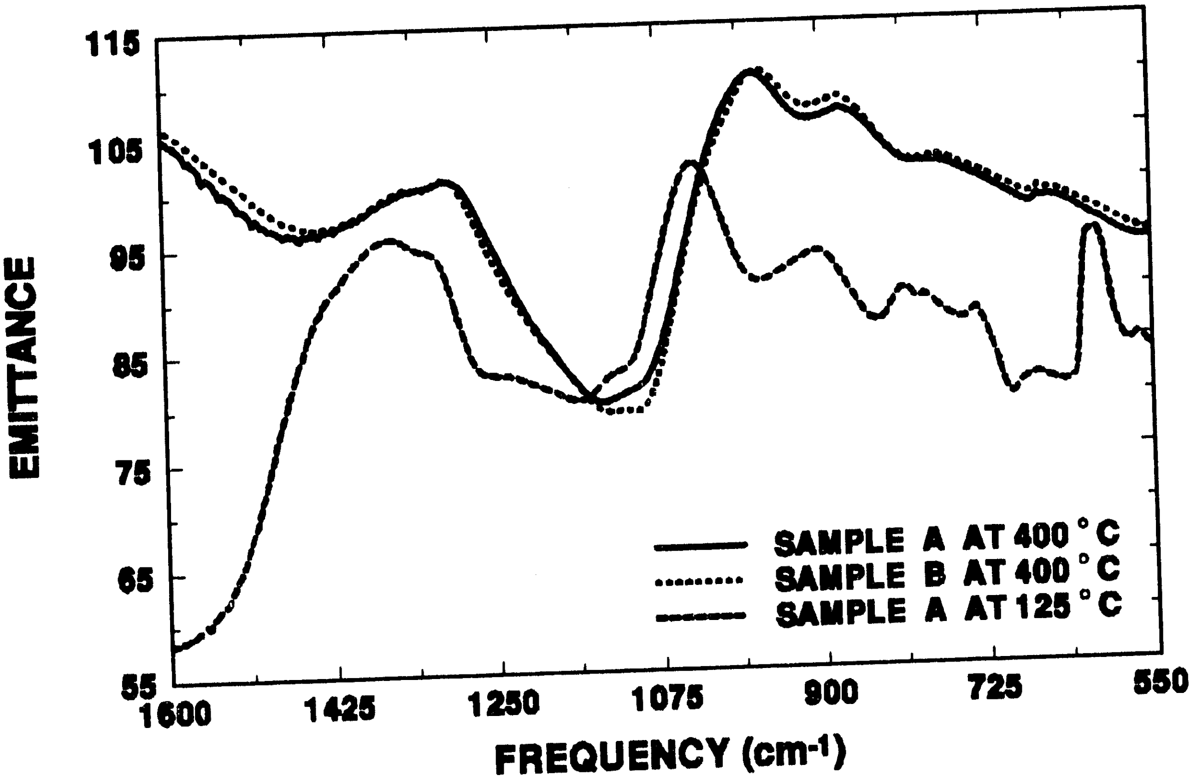
TABLE I. CV PLS Calibration Results Using 21 BPSG IR Emittance Spectra Collected over Two Temperature Ranges

COMPONENT	**SEP (CV)** (125 - 225°C)	**SEP (CV)** (300 - 400°C)
Boron (wt%)	0.10	0.09
Phosphorus (wt%)	0.11	0.08
Thickness (Å)	35	38
Temperature (°C)	1.2	2.1

Figure 1. IR emittance spectra of BPSG Sample A at 125 and 400°C and BPSG Sample B at 400°C.

Figure 2. Cross-validated PLS calibration results for boron using BPSG IR emittance spectra collected at 300-400°C. SEP(CV) is 0.09 wt% B.

Figure 3. Cross-validated PLS calibration results for temperature using BPSG IR emittance spectra collected at 300-400°C. SEP(CV) is 2.1°C.



115
105
95
85
75
65
55
EMITTANCE
1600
1425
1250
1075
900
725
550
FREQUENCY (cm-1)
SAMPLE A AT 400 °C
SAMPLE B AT 400 °C
SAMPLE A AT 125 °C

Figure 1

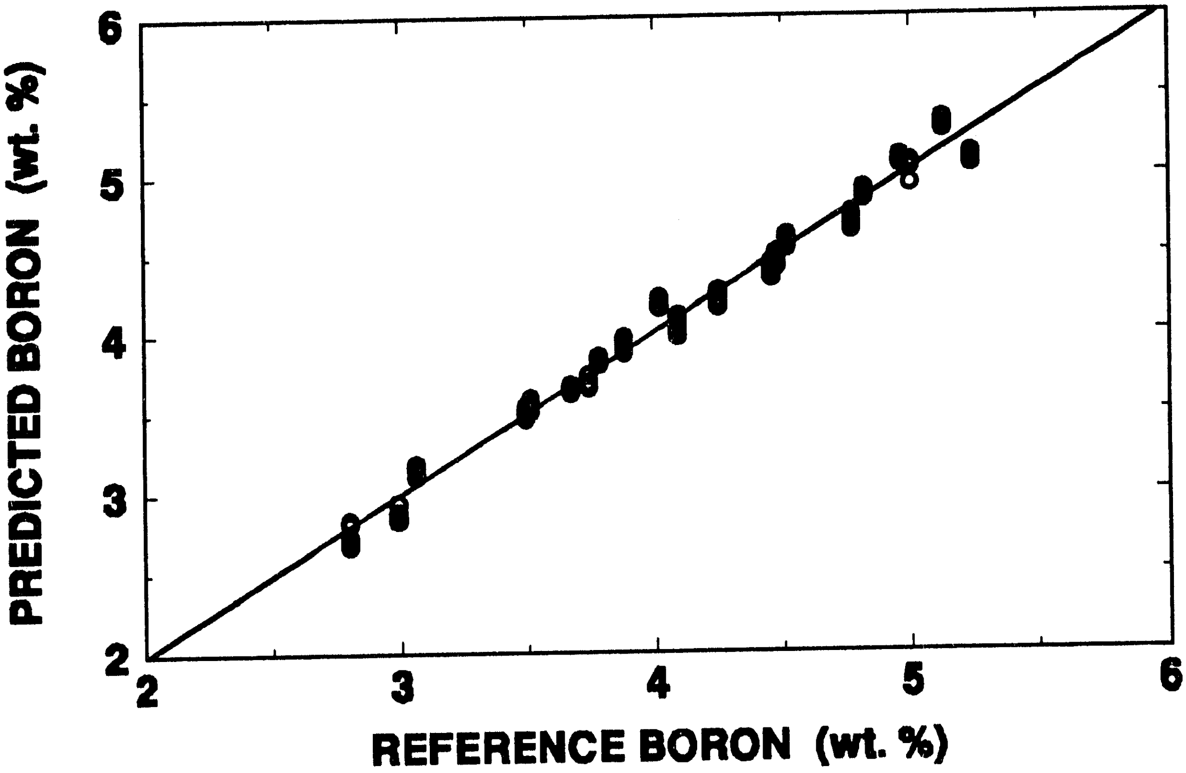


Figure 2

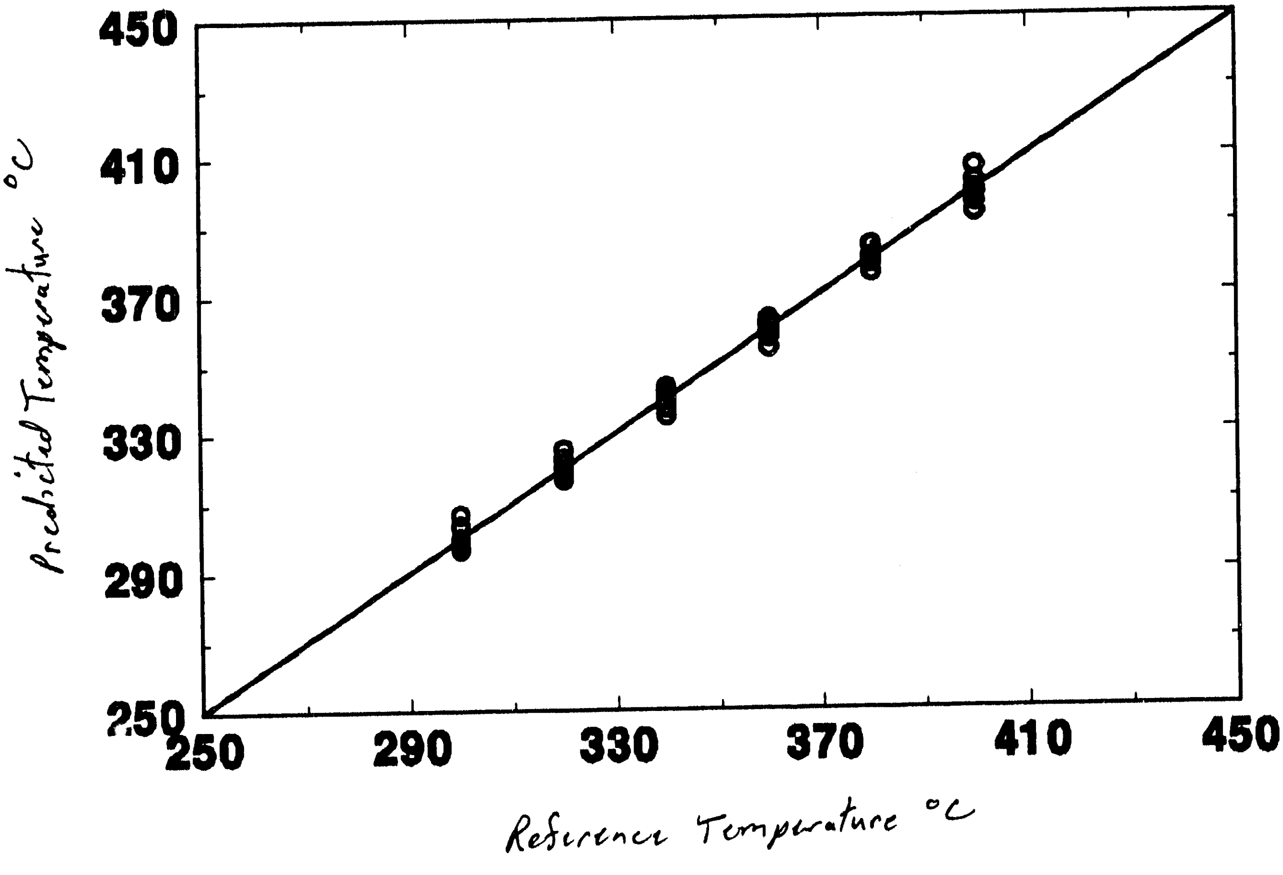

450
410
370
330
290
250
250
290
330
370
410
450
Predicted Temperature °C
Reference Temperature °C

Figure 3

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