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INFRARED SENSOR FOR CVD DEPOSITION OF DIELECTRIC FILMS

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ABSTRACT

Infrared emission (IRE) spectra were obtained from two borophosphosilicate glass (BPSG) thin-film sample sets. The first set consisted of 21 films deposited on undoped silicon wafers, and the second set consisted of 9 films deposited on patterned and doped (product) wafers. The IRE data were empirically modeled using partial least-squares calibration to simultaneously quantify four BPSG thin-film properties. The standard errors of the determinations when modeling the 21 monitor wafers were <0.1 wt% for boron and phosphorus content, 36 Å for film thickness, and 1.9°C for temperature. The standard errors of the determinations based on the product wafers were 0.13 wt% each for B and P content, 120 Å for film thickness, and 5.9°C for temperature.

INTRODUCTION

In the microelectronics industry, *in-situ*, rapid, quantitative, and nondestructive quality control monitoring of dielectric thin films during CVD processing is desirable for maintaining the quality of the resulting device wafers. Infrared emission (IRE) spectroscopy combined with chemometric data analysis can produce a 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]. In the following discussion we show that IRE data, when combined with multivariate calibration, can be used to produce highly precise determinations of multiple thin-film properties. In addition, we demonstrate that the technique can be applied to the monitoring of product wafers and can produce the rapid analyses that are important for true *in-situ* monitoring.

EXPERIMENTAL

The large BPSG calibration set used in this study was prepared at National Semiconductor (Santa Clara, CA) and consists of 21 BPSG films over 0.1 μm 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, while total film thicknesses (BPSG plus thermal oxide) were measured with a Nanospec film-thickness analyzer.

An IRE apparatus was constructed for heating the BPSG samples to 500°C in either a vacuum or a controlled, inert environment. The apparatus consists of a water-cooled aluminum chamber 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 8 m of insulated nichrome wire to provide up to 400 Watts of heating power.

MASTER

IRE spectra of the BPSG samples were collected with the described IRE apparatus at 300, 320, 340, 360, 380, and 400°C for a total of 126 spectra for the 21 monitor wafer calibration set and 54 spectra for the 9 product wafer calibration set (also made by National Semiconductor). The reference temperature measurements were obtained using a K-type thermocouple placed at the center of the area on the BPSG film surface from where IRE radiation was collected.

Single-beam IRE spectra of the BPSG samples at a given temperature were ratioed to that of a blackbody reference spectrum at the same temperature to yield IR emittance spectra. These emittance spectra were calibrated using the partial least-squares (PLS) technique [4]. 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 operated 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 PLS models were empirically built using spectral data that were smoothed and transformed into first-derivative spectra to reduce high-frequency noise and to minimize spectral baseline variations. The calibrations were performed with cross validation (CV) leaving out six samples at a time (a given BPSG sample at each of the six temperatures). All standard errors of prediction (SEP) reported below are based on these CV calibrations. The PLSSNL software package [4] developed at Sandia National Laboratories 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 correlations among B content, P content, or film thickness components and to maximize the filling of the calibration space across the range spanned by each component. The component values of the BPSG samples were found to closely match the specified values of the experimental design. The 9 product wafer samples were a subset of the 21 point experimental design used to produce the monitor wafers. The order of data collection was randomized with respect to temperature to avoid any possible correlation of spectrometer drift with temperature in the spectral data sets.

RESULTS AND DISCUSSION

Figure 1 illustrates the IR emittance spectra obtained from two of the BPSG films deposited on monitor wafers. The samples, labeled A (2.80 wt% B, 4.91 wt% P, 0.9194 μm) and B (4.25 wt% B, 3.73 wt% P, 0.8048 μm), were selected to show the type and magnitude of the changes observed in IR emittance spectra of samples having large BPSG property differences and/or large temperature differences. The only consistent feature observed for all samples is an increase in IR emittance above ~1425 cm⁻¹ with increasing temperature. Otherwise, the spectra

Figure 1. IR emittance spectra of monitor wafers at two temperatures.

vary in a complicated manner as a function of changes in BPSG film properties and temperature, and in many cases the spectral variations are small. 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. Thus, it is important to use multivariate calibration techniques for deriving quantitative information from BPSG IR emittance spectra.

A qualitative 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 obtained from these multilayered media 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 emittance of the support material. For example, there is no evidence of the silicon phonon band at 620 cm^{-1} in Figure 1. At temperatures lower than 300°C , this band is readily observed [1,2]. At temperatures above 300°C , the mid-IR emittance of the Si wafer support approaches 1.0 (i.e., a true blackbody), which means that the Si substrate has become opaque to IR radiation. In addition, the change in the Si support emittance 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 one or more 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 presented by IR external reflection-absorption spectra. Reflection IR spectra have previously been used with PLS calibration to successfully quantify phosphorus and film 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) emittance changes in both the Si substrate (described above) and the dielectric film layers as a function of temperature, film thickness, and composition.

Despite these difficulties, quantitative results can be achieved using PLS multivariate calibration. Calibration plots based on the IRE data obtained from the 21 monitor wafers for boron content, phosphorus content, film thickness, and temperature demonstrate high prediction precision. Table I summarizes these PLS calibration results. The SEPs in column 2 for B and P contents and film thickness are statistically equivalent (two-tailed F-test, 10% significance level)

Table I. SEP Results (4 cm^{-1} data) for IRE PLS Calibrations of Different Sample Sets.

BPSG Component	21 Monitor Wafers	9 Product Wafers	9 Monitor Wafers
Boron (wt%)	0.09	0.13	0.06
Phosphorus (wt%)	0.08	0.13	0.11
Film Thickness ($\text{\AA}$)	36	120	89
Temperature ($^{\circ}\text{C}$)	1.9	5.9	4.2

to the reported precisions of the reference methods (≤ 0.1 wt% B or P, ± 30 Å film thickness). Thus, for the 21 monitor wafer samples the PLS calibrations of BPSG properties are limited by the precisions of the reference methods. Table I further shows that temperature is predicted with a SEP of 1.9°C using the 21 monitor wafer samples over the $300\text{--}400^{\circ}\text{C}$ range, which is not statistically equivalent (two-tailed F-test, 10% level) to the estimated temperature precision of the IRE apparatus ($\pm 1^{\circ}\text{C}$). The statistically inequivalent SEP of 1.9°C may be caused by experimental limitations: (1) in ratioing two single-beam IRE spectra each having $\pm 1^{\circ}\text{C}$ error, (2) in the ability to reproduce the contact of the samples with the cable heater (errors cause thermal gradients or inefficient heating), and (3) in the ability to reproduce the contact of the thermocouple with the BPSG sample surface (errors cause inaccurate surface temperature measurements).

The IR emittance spectra at 400°C obtained from the 9 BPSG product wafer samples are shown in Figure 2. These spectra are similar to the spectra of the BPSG monitor wafer samples at 400°C shown in Figure 1. The similarity between the product and monitor BPSG IRE spectra

Figure 2. IR emittance spectra of the nine product wafers at 400°C .

suggests that the patterned structure below the BPSG films does not significantly alter the IRE spectral data. Calibration plots for phosphorus content and film thickness for the 9 product wafer samples are shown in Figures 3 and 4 respectively. Note that the multiple points plotted at each value of phosphorus content or film thickness are the result of performing the experiment at six different temperatures. The PLS results are summarized in column 3 of Table I. These results

Figure 3. PLS-predicted P content versus reference P content for the 9 product wafers. Each cluster of points represents six PLS predictions of the same sample at 6 different temperatures.

Figure 4. PLS-predicted versus reference film thickness for the 9 product wafers. Each cluster of points represents six PLS predictions of the same sample at 6 different temperatures.

are not quite as good as those obtained from the set of 21 monitor wafers. We believe the degradation in the boron, phosphorus and film thickness results is due to having only 9 of the 21 design points in the product wafer calibration set. When only nine of the design points are included in a PLS calibration, the effects due to changes in the component parameters may not be adequately modeled. Some evidence for this is shown in the results obtained by performing a PLS calibration using the 9 sister wafers from the monitor wafer set that correspond to the 9 product wafer samples. The results for the calibration using only 9 of the 21 monitor samples are included in column 4 of Table I. As can be seen, boron and phosphorus prediction errors correspond fairly well with the results obtained from the monitor wafers, while film thickness and temperature prediction errors are degraded relative to the calibration using the complete data set.

Studies designed to determine the reproducibility of the determinations as well as the IRE method's sensitivity to decreased resolution were also carried out. The reproducibility results were obtained by repeating the determination of a single sample and calculating the standard deviation of the component determinations. The results are summarized in Table II. The results for B and P content and thickness suggest that the data collected have very high signal-to-noise ratio, and that the predictions would not suffer if far less signal averaging were employed. The standard deviation of the repeat temperature determinations is quite good, but not relatively as good as the three BPSG properties repeat determinations. This latter result is most likely due to instability of the temperature control over the time period required to perform the 10 repeat determinations.

Also included in Table II are the PLS calibration results of the IRE spectral data at 32 cm^{-1} resolution for the 21 monitor wafers. The SEPs for B and P determinations at 32 cm^{-1} resolution are statistically equivalent (two-tailed F-test, 10% level) to those obtained at 4 cm^{-1} resolution

Table II. BPSG IRE Reproducibility and Resolution Studies

BPSG Component	Std. Dev. (400°C), 10 Repeats	SEP (32 cm^{-1}), 300-400°C
Boron (wt%)	0.005	0.10
Phosphorus (wt%)	0.002	0.11
Film Thickness (Å)	4.3	70
Temperature (°C)	0.55	2.54

(column 2 of Table I). The film thickness determination degrades by a factor of 2 at the lower resolution, and the temperature determination degrades by about 25%. The degradation of the temperature and thickness determinations with lower resolution may be due to the fact that the information used by the PLS model to predict these parameters is somewhat based on band shifts.

CONCLUSIONS

The small SEP values shown in Tables I and II and in Figs. 3 and 4 show 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 can be made with precisions equivalent to or slightly worse than the precisions of the reference methods. Furthermore, these results have been achieved in a temperature range near that typical for CVD-BPSG thin-film deposition. The results obtained using product wafers confirm the potential of IRE as an *in-situ* monitor of BPSG thin-film deposition. The fact that the repeatability results demonstrated such high precision suggests that IRE spectral data could be obtained much faster with adequate precision. Thus, it would be possible to use the IRE results in a feedback control loop to insure that the film being produced was within the target specifications. The results obtained at low (32 cm^{-1}) resolution suggest that the required instrumentation can be small and rugged, attributes that are consistent with the requirements of process monitoring instrumentation.

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