Analysis of waveguide silica glasses using Raman microscopy

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Received 20 August 2007
Available online 29 February 2008

Abstract

A spectroscopic method to determine dopant concentrations in silicas used in silica on silicon planar waveguides has been developed. Raman spectroscopic measurements in the range 740 cm\textsuperscript{-1}–1370 cm\textsuperscript{-1} of cross-sections of the glass layers identified correlations between simple, rapidly calculated, spectral features related separately to each of the three dopants, boron, phosphorous and germanium, and the wt\% analyses results for these dopants from inductively coupled plasma mass spectrometry (ICP-MS) measurements on fragments from the respective wafers. The calibration wafers comprised a set of monitor wafers with dopant concentrations spanning the ranges used in devices. The Raman-based analyses were able to determine boron and phosphorous wt\% s in boro-phosphosilicate cladding glasses with accuracies of \(\approx 0.1\) wt\% and germanium wt\% s in core glasses with an accuracy of at least \(\approx 0.3\) wt\% (small batch size). The method, which performed successfully in blind tests, provides a spatially resolving and rapid alternative to ICP-MS analyses of monitor wafers. Exploratory face-on measurements were performed on device wafers. Spectra of the cladding, core and underlayer were obtained from AWG samples. The effects of the confocal volume’s finite size and refractive index differences were observed. Exploratory measurements using UV Raman excitation showed potential advantages for cladding glass analyses.

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PACS: 61.43.Fs; 63.50.+x; 78.30.-j; 78.30.Ly

Keywords: Raman scattering; Rayleigh scattering; Planar waveguides; Chemical vapor deposition; Glasses; Optical microscopy; Raman spectroscopy; Oxide glasses; Silica

1. Introduction

The telecommunications industry has stimulated the development of a remarkable range of optical and optoelectronic component technologies to meet the demand for higher bandwidth optical communication systems. Amongst these component technologies are silica on silicon planar waveguide structures.

The performance of low-loss microscopic planar waveguide devices such as arrayed waveguide gratings (AWG) is strongly dependent on the properties of the constituent materials, in particular, of the doped silicas that define the structures. It is essential, for example, to control the index of refraction, tensile stress and the viscosity/re-flow properties of the core and cladding glasses during manufacture to consistently achieve high device yields and performance. All of these properties are intrinsically related to the microscopic and nanoscale composition of the core and cladding glasses used.

Planar waveguide cladding silicas are typically doped with phosphorous to produce phosphosilicate glass (PSG) or doped with both boron and phosphorous to produce boro-phosphosilicate glass (BPSG). Typical waveguide core glasses are doped with germanium. Detailed accounts of the function of doped silica glasses in waveguides have been published \cite{1,2}. As the compositions of the core and cladding glasses are critical to the performance of waveguide devices it is important to have available analytical
techniques which can serve as part of a manufacturing quality control system or as a diagnostic tool in device development, etc. The most desirable performance features of a suitable analytical technique would be:

(i) is capable of separately determining the boron and phosphorous concentrations in cladding glass and the germanium concentration in core glass each with both an accuracy and a precision of \( \sim 0.1 \text{ wt\%} \) or better, i.e., with an accuracy and precision at least as good as currently used methods (see below);
(ii) is intrinsically non-destructive making possible, for example, measurement at different stages of device manufacture;
(iii) is capable of creating 3D maps of glass composition and sampling as much as possible of the entire volume of deposited glassy material;
(iv) has a spatial resolution commensurate with the dimensions of the structural features of waveguide devices, i.e., to have 1 \( \mu \text{m} \) or better resolution in all three co-ordinates;
(v) has an intrinsic measurement cycle time that is compatible with the times of individual steps in the manufacturing process;
(vi) requires little or no sample preparation and is able to operate at ambient temperature and pressures.

Overall, this list of desirable characteristics is a formidable one. The importance of achieving quantitative knowledge of the glass composition and thereby control of the manufacturing process, has resulted in a number of analytical techniques being applied to this problem. The techniques used include the following:

(a) X-ray techniques; energy dispersive X-ray fluorescence (EDX-RF) \([1,3,4]\) and wavelength dispersive X-ray fluorescence (WDX-RF) \([1,3–5]\);
(b) inductively coupled plasma-atomic emission spectrometry (ICP-AES) \([6,8]\) and inductively coupled plasma-mass spectrometry (ICP-MS) \([7,9]\);
(c) secondary ion mass spectrometry (SIMS) \([1,10,11]\);
(d) colorimetry \([1,5]\);
(e) nuclear reaction analysis (NRA) \([12,13]\);
(f) ion chromatography (IC) \([5]\);
(g) IR and Raman vibrational spectroscopies.

(N.B. the references are meant only to provide access to relevant literature).

Table 1 provides a broad overview of major features of each of these techniques. Of course, each is capable of meeting the basic analysis requirements, i.e., criterion (i) above, albeit with widely varying accuracies. The remaining criteria do discriminate, however, the techniques quite markedly. In particular the need for non-destructive measurements under ambient conditions reduces the list essentially to those that are based on either IR or Raman vibrational spectroscopy.

Fourier transform infra-red spectroscopy (FTIR) \([14–17]\), infra-red external reflection absorption spectroscopy (IRRAS) \([18]\) and infra-red emission spectroscopy (IRES) \([19]\) have all been used to analyze for boron and phosphorous content in BPSG. These infra-red spectoscopic techniques give valuable structural information in addition to compositional analysis but, unfortunately the wavelengths involved limit their ability to target and analyze particular regions of planar waveguide structures. In addition, FT-IR analysis is limited to material that lies within \( \approx 2 \mu \text{m} \) of the waveguide’s top surface and is not compatible with, for example, the non-destructive analysis of core glass regions which are typically between 10 \( \mu \text{m} \) and 20 \( \mu \text{m} \) below the waveguide’s surface.

Raman spectroscopy has been used extensively to investigate silica glasses \([20–29]\). The excitation wavelengths available in modern Raman instrumentation, which range

<table>
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<tr>
<th>Technique</th>
<th>Criterion</th>
<th>Relative cost</th>
<th>Refs.</th>
</tr>
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<td>x</td>
<td>x</td>
<td>V</td>
</tr>
<tr>
<td>WDX-RF</td>
<td>x</td>
<td>x</td>
<td>V</td>
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<tr>
<td>ICP-AES</td>
<td>x</td>
<td>x</td>
<td>x</td>
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<tr>
<td>ICP-MS</td>
<td>x</td>
<td>x</td>
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<tr>
<td>Ion chromatography</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>SIMS</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Colorimetry</td>
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</tr>
<tr>
<td>IR-ES</td>
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<td>x</td>
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<tr>
<td>IRRAS</td>
<td>x</td>
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</tr>
<tr>
<td>Raman</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Raman microscopy</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The criteria used to categorize the techniques are discussed in the text. Relative costs are approximations only.
from the UV through to the near-IR, are significantly shorter than the wavelengths of vibrational features characteristic of glasses and they provide intrinsically better spatial resolution than IR techniques. The shorter wavelengths used in Raman also coincide with regions of transparency in many glassy materials making buried structures accessible to measurement. Raman microscopy, first developed in the 1970s [30,31], combines these measurement advantages with the potentially confocal performance and automated volume mapping capabilities of a research microscope; it has the potential to meet each one of the six measurement criteria identified above.

In this paper, we report the use of Raman microscopy to perform highly spatially resolving, non-destructive spectroscopic measurements to determine the wt% dopant concentrations in silica glasses used in silica on silicon planar waveguide structures. Specifically, we have demonstrated a technique that is able to determine the wt% of boron and phosphorous concentrations in BPSG cladding glasses and the germanium concentration in germanium-doped silica core glasses used in waveguide devices to an accuracy of \( \approx 0.1 \) wt%. A preliminary account of our work on these systems has been given previously [32]. During the course of this work a study of the phosphorous content of PSG thin films using confocal Raman microscopy was reported [33].

2. Experimental

2.1. Samples

The samples used to develop the Raman-based analysis method comprised thin films of doped silica glasses with thicknesses ranging from 2.9 \( \mu \)m to 6 \( \mu \)m deposited on silicon monitor wafers by plasma-enhanced chemical vapor deposition. Such coated wafers are used routinely to monitor the refractive index and composition of glasses being laid down simultaneously on adjacent planar waveguide device wafers. The samples all originated from the Optoelectronics Division of Nortel Networks in Harlow, UK. In total 35 BPSG samples were used in the study of cladding glasses and five germanium-doped silica glass samples were used in a more limited study of core glasses. The dopant concentrations in these samples were in the following wt% ranges: boron 3.0–7.0; phosphorous 1.8–3.0; and germanium 8.0–12.0. Independently obtained ICP-MS measurements of glass composition for the same set of wafers were used to evaluate a number of different possible procedures to interpret the Raman data. The studies of BPSG were complemented with studies of a number of binary borosilicate (BSG) and phosphosilicate (PSG) glass samples.

To explore briefly the application of the new Raman-based analysis method in the face-on analysis of device wafers, i.e., the highly spatially resolving, non-destructive analysis of structures in complete device wafers, two AWG devices with similar layer thicknesses but different dopant wt% were obtained.

2.2. Instrument

The Renishaw Series 1000 Raman Microscope [34] used in this work comprises a Raman spectrometer interfaced with an upright Leica research optical microscope, model DMLM. The strong Rayleigh component in the backscattered signals is efficiently rejected at the entrance to the spectrometer using a holographic notch filter; the Raman signal transmitted by the notch filter is dispersed by a 2400 lines mm\(^{-1}\) holographic grating and on to a thermodiectedly cooled charge coupled device (CCD) detector giving an overall spectral resolution per pixel of 1.1 \( \text{cm}^{-1}\) when using 514.5 nm excitation, as used here. The instrument acquires spectra in either confocal or non-confocal modes, a choice controlled by adjusting a pre-grating slit (horizontal orientation) and a post grating ‘virtual’ slit on the CCD pixel array (vertical orientation). The horizontal slit is operated by a micrometer screw and is set to either 50 \( \mu \)m (normal) or 15 \( \mu \)m (confocal). The vertical ‘virtual’ slit is set at either 20 pixels (normal) or 4 pixels (confocal) wide. The confocal nature of the Raman microscope design has been described previously [35]. The instrument was used in confocal mode for the measurements reported in this paper.

Either one of two metallurgical microscope objectives (\( \times 50 \) (NA = 0.75); \( \times 100 \) (NA = 0.95)) were used in this work to both focus the excitation laser light onto the sample and to collect the backscattered Raman-Rayleigh signals. The power of the 514.5 nm laser excitation at the sample was maintained at \( \sim 5 \) mW.

Wafer fragments obtained by cleaving were mounted in the microscope on an automated \( x-y-z \)-translation stage in either ‘face-on’ (wafer’s surface plane normal to the microscope’s optical axis) or ‘edge-on’ (wafer’s surface plane parallel to the microscope’s optical axis) orientations.

Measurements with a 0.025 \( \mu \)m resolution, non-contact, fiber optic displacement sensor showed that there is a temperature dependence of the objective-sample separation distance of 0.8 \( \mu \)m/\( ^{\circ} \text{C} \); as a consequence the temperature of the microscope’s environment was monitored and maintained constant to better than \( \pm 0.5 \) \( ^{\circ} \text{C} \) both before and during measurements.

The measured Raman shifts were routinely calibrated using both the 546.08 nm Hg (I) emission from a low-pressure Hg–Ar discharge, which is equivalent to a Stokes Raman shift of 1122.6 cm\(^{-1}\) when using 514.5 nm excitation, and the intense, sharp first order Raman scattering signal from a polycrystalline silicon wafer at 520.6 cm\(^{-1}\). The silicon wafers used for calibration were mounted face-on and rotated to an angle where the signal at 520.6 cm\(^{-1}\) is a maximum to avoid possible effects due to the polarization of the excitation laser source.

As discussed below, it is a necessary part of the analysis procedure developed in this study to subtract contributions to the Raman signals of glassy layers that originate from proximate silicon substrate. In this case, in contrast to the case of Raman shift calibration, the wafer fragment is rotated about the optical axis until the silicon component
in the spectrum of the glassy layer is minimized. The separate measurements of the glassy layer and the adjacent substrate, described below, are then performed with the wafer in this orientation.

The vertical, i.e., z-direction, resolution of the objectives with respect to an air–dielectric interface was determined using a polycrystalline silicon wafer orientated normally, i.e., face-on, to the direction of the incident laser light. Raman spectra centered at 520.6 cm\(^{-1}\) (measured as the integral of the Raman intensity in the range 510 cm\(^{-1}\) to 530 cm\(^{-1}\)) were taken in static mode for a series of objective-sample separation distances where the air–silicon interface of the sample was moved through the focal plane of the objective. The intensities of the silicon peak at 520.6 cm\(^{-1}\) were then plotted against the separation distance for both objectives (Fig. 1a). The FWHM of the resulting normalized intensity distributions were 3.5 \(\mu m\) \((\times 50)\) and 1.6 \(\mu m\) \((\times 100)\).

The transverse, i.e., x–y plane, resolution of the objectives with respect to an air–dielectric interface were determined using a polycrystalline silicon wafer orientated edge-on to the direction of the incident laser light. The intensity of the silicon peak at 520.6 cm\(^{-1}\) as a function of the distance between the optical axes of \(\times 50\) and \(\times 100\) objectives and the surface of a silicon wafer (edge-on), with the respective focal planes being in the plane of the exposed edge of the wafer, are shown in Fig. 1b. The resolutions in this plane were estimated to be 1.1 \(\mu m\) \((\times 50)\) and 0.7 \(\mu m\) \((\times 100)\). The intensities were obtained under identical measurement conditions, except for the lens being changed, and the results demonstrate the advantage in respect of signal accumulation times of using the \(\times 50\) objective in measurements the highest spatial resolution is unnecessary. In both these measurements of spatial resolution the wafer was rotated about the optical axis to the angle where the silicon signal was maximized.

A few measurements were performed on BPSG samples using a Renishaw UV Raman Microscope equipped with 244 nm and 325 nm excitation sources; the motivation being to explore opportunities to reduce signal recovery times.

### 2.3. Processing the Raman spectra of doped silica glass phases

The basis of the analysis procedure for BPSG layers developed in this work is a set of Raman spectra of doped silica glass films with different compositions.

In the first stage of the analysis it is important to remove from the unprocessed spectra any contributions which originate from sources other than the BPSG. Two sources of such spectral ‘contamination’ were identified: the first is instrument related; the second is due to scattering from silicon substrate material present within the diffuse boundaries of the confocal analysis volume.

It is an implicit assumption in the correction procedures that were developed that the various contributions to the measured Raman spectrum are additive. In general, such an assumption is a reasonable one in Raman spectroscopy. Reasons why it may not hold in the present studies related to the propagation of excitation and scattered light within the thin films, especially when using the ‘edge-on’ configuration (see below).

### 2.3.1. Instrument related corrections to measured Raman spectra

Contributions to the measured Raman spectra from the instrument itself were found to originate both from the CCD detector and from Raman and Rayleigh scattering within the microscope and spectrometer. The contributions from the CCD were determined by closing the pre-grating slit and recording ‘spectra’ for a series of times that spanned overall the measurements times used to obtain sample spectra. The combined contributions of the CCD and scattering within the instrument were then determined by recording ‘spectra’ with the pre-grating slit open at its normal value of 15 \(\mu m\) and the laser light exiting the \(\times 50\) objective (i.e., the objective used in edge-on measurements)
captured in a beam dump for periods of time which again spanned the measurement times used for samples. In both cases the measurements were made with the instrument in static mode and centered at 1064 cm\(^{-1}\), just as done in measurements of the spectra of the doped silica glasses (see below).

The results revealed contributions from the CCD that were not uniform with pixel number, and instrument contributions that were generally independent of pixel number but for a weak broad feature centered near 800 cm\(^{-1}\). However, the intensities of the contributions from both sources were found to increase linearly with exposure time, with no residual contribution at short times, making it straightforward to apply corrections to each of the measured spectra by subtracting a background spectrum scaled to the respective measurement time. The necessary subtractions were performed using an algorithm\(^{[36,37]}\) in the GRAMS32 data processing software\(^{[38]}\) which complements the Renishaw WiRE v1.3 instrument control software\(^{[34]}\). The spectral distributions and magnitudes of these systematic background contributions were checked routinely throughout the measurements reported below.

### 2.3.2. Sample based corrections to measured Raman spectra

An important issue when performing Raman analysis of silica films on silicon monitor wafers, and on actual device structures, is the intense Raman scattering from the silicon substrate itself. The thickness of the silica films being analyzed is typically only a few \(\mu m\) which is comparable with the axial dimension of the confocal volume of the Raman microscope (3.5 \(\mu m\) using a \(\times 50\) objective as measured at an air–silicon interface – see above). In general, therefore, there are contributions from silicon in each of the measured Raman spectra, only the relative amount of the silicon contribution changes. The prominent silicon Raman bands that appear in the region likely to be of interest in analysis of the doped silica glasses are the first order peak at 520.6 cm\(^{-1}\) and the relatively much weaker second order peak at 980 cm\(^{-1}\).

Two measurement configurations are of interest in Raman-based BPSG analyses: the first is ‘edge-on’ measurement of glass layers exposed by cleaving the monitor wafers; the second is ‘face-on’ measurement of wafer fragments or whole wafers.

The advantage of edge-on measurements is that the Raman scattering contribution from the silicon substrate is minimal, although still requiring careful removal in the signal processing. For each of the edge-on measurements performed in this study a reference spectrum of silicon was taken from the exposed edge of the silicon wafer immediately adjacent to the glass layer being measured. The only adjustment necessary between the two measurements being a small, few \(\mu m\), translation of the sample in the horizontal plane through the center of the confocal volume. The silicon spectra were used then in the processing of the respective silica glass spectra. This configuration is the most obvious one to use in measurements to identify the spectral features that can be used as a basis for quantitative analyses.

The major potential advantage of face-on measurements is that it makes unnecessary the sectioning of wafers whether they are monitor wafers or device wafers. If they are device wafers then the high transverse resolution of Raman microscopy offers the potential of investigating individual, few \(\mu m\) sized, waveguide channels and other structures. To realize this potential there are two issues requiring quantitative analysis: firstly, the refractive effects of the glass layers on the position of the focal plane inside the glass layers (a different issue from that of axial resolution at an air–silicon surface discussed above); and secondly, the much larger relative contribution of the silicon substrate to the measured signal in comparison to edge-on measurements due to the axial extent of the confocal volume (N.B. a major reduction in the substrate’s contribution to spectra in this configuration is achieved by rotating the sample about the optical axis until its relative contribution is minimized. In the case of monitor wafers the necessary silicon background spectrum (see below) is taken at the same sample rotation angle from the glass–silicon interface immediately below the glass layer being measured: in the case of device wafers the background spectrum is taken from the glass–silicon interface in an adjacent region where core silica layers are absent).

Edge-on measurements of doped silica glass films on monitor wafers are used in the present work to identify a spectroscopic basis for the separate determination of the wt% compositions of boron, phosphorous and germanium. Although not suitable for analyzing device wafers, such edge-on measurements constitute an analysis method that nevertheless is competitive in terms of feedback time and accuracy (see below) with the present analysis method of choice for monitor wafers, namely ICP-MS. The identification of spectral features suitable as a basis for the analysis of doped silica glass compositions underpins subsequent work to establish Raman-based, face-on analysis of device wafers. A few exploratory face-on measurements on AWG devices are reported at the end of the paper.

### 2.4. Choice of Raman spectral region for the analyzes

Previous Raman studies of BSG, PSG and germanium-doped silica glass system have identified characteristic structural and species related spectral features over a wide range of Raman spectral shifts. The glass composition analysis method described below is based on measurements of Raman spectra in the region from 740 cm\(^{-1}\) to 1370 cm\(^{-1}\) for the following reasons:

(i) it contains strong, and relatively isolated, spectral features that are separately characteristic of the respective boron, phosphorous and germanium contents\(^{[22]}\);

(ii) it enables the instrument to be used in its efficient ‘static’, i.e., non-scanning, data collection mode;
(iii) it does not include the main silicon peak at 520.6 cm\(^{-1}\) but does include the second order silicon peak at 980 cm\(^{-1}\) enabling accurate subtractions of the silicon background to be made.

2.5. Typical measurement procedure

A typical procedure to recover the Raman spectrum of a doped silica glass layer on a wafer fragment in edge-on configuration and using the \(\times 50\) objective is as follows:

(a) the Raman spectrum from the silicon substrate immediately adjacent to the targeted glass region is collected in static mode for 22 repeats of 20 s accumulations after rotation of the sample about the optical axis to a point where the silicon signal is a minimum (total time: 7 min 20 s);
(b) the Raman spectrum of the targeted glass region is collected in static mode for 14 repeats of 200 s accumulations with the sample in the same angular position as determined in (a) (total time: 46 min 40 s);
(c) the instrument background contributions are removed from the spectra obtained in (a) and (b) using reference spectra obtained separately after adjustment for the respective total measurement times;
(d) the two corrected spectra obtained in (c) are subtracted from each other to recover the desired spectrum of the silica glass materials.

The procedure is illustrated in Fig. 2 for the case of a sample comprising a 2.9 \(\mu\)m thick BPSG layer on a silicon substrate; the figure shows the separate sample, background and substrate Raman spectra and the recovered Raman spectrum of the doped silica glass layer. The glass layer thickness is just less than 3.5 \(\mu\)m FWHM of the axial resolution of \(\times 50\) objective and a face-on spectrum from this same sample would be expected to contain a relatively much larger contribution from the silicon substrate than seen in Fig. 2.

The Raman spectra shown in Fig. 2, and in following figures, which comprise 575 data points each, are smoothed using a 3-point adjacent average for the purpose of display only. Unsmoothed spectral data are used in all spectral analysis procedures.

2.6. Independent measurements of glass composition

Fragments from each of the wafers examined in this study were sent for analysis using ICP-MS. The method used involves the dissolution of the glassy material from the surface of the wafer.

3. Results

3.1. Boron and phosphorous-doped silica glasses

The Raman spectra of films of vitreous silica, PSG and BSG on silicon substrates obtained using the procedure outlined in Section 2.5 are shown in Fig. 3.

The Raman spectra of vitreous silica [22,24,25] and the binary silica glasses GeSG, BSG and PSG [22–24,27,39–41] have been reported previously in the literature. The assignments of the spectral features that appear in the spectral region from 740 cm\(^{-1}\) to 1370 cm\(^{-1}\) for: (a) vitreous silica; (b) a high silica phosphosilicate glass; and (c) a high silica borosilicate glass. The spectra are normalized with respect to the Raman band at approximately 800 cm\(^{-1}\).
**Table 2**

Assignments of the Raman bands observed in boron, phosphorous and germanium-doped silica glasses

<table>
<thead>
<tr>
<th>Raman Shift / cm(^{-1})</th>
<th>Assignment</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silica</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>799</td>
<td>(v_1) symmetric Si–O–Si stretch</td>
<td>[24,25]</td>
</tr>
<tr>
<td>903</td>
<td>2(v_4) Si–O–Si bend</td>
<td>[22]</td>
</tr>
<tr>
<td>961</td>
<td>(v_1) (TO) Si–O–Si stretch</td>
<td>[24,25]</td>
</tr>
<tr>
<td>1197</td>
<td>(v_3) (LO) Si–O–Si stretch</td>
<td>[24,25]</td>
</tr>
<tr>
<td><strong>Phosphosilicate glass</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>799</td>
<td>(v_1) P–O–P bend</td>
<td>[22,28]</td>
</tr>
<tr>
<td>1025</td>
<td>(v_2) P–O–P stretch</td>
<td>[21,28]</td>
</tr>
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<td>1068</td>
<td>(v_1) (TO) Si–O–Si stretch</td>
<td>[24,25]</td>
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<tr>
<td>1137</td>
<td>P–O–Si stretch</td>
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</tr>
<tr>
<td>1200</td>
<td>(v_1) (LO) Si–O–Si stretch</td>
<td>[24,25]</td>
</tr>
<tr>
<td>1235</td>
<td>(v_3) P=O O stretch</td>
<td>[22,28]</td>
</tr>
<tr>
<td><strong>Borosilicate glass</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>806</td>
<td>(v_1) symmetric Si–O–Si stretch</td>
<td>[24,25]</td>
</tr>
<tr>
<td>935</td>
<td>B–O–Si stretch</td>
<td>[22,43]</td>
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</tr>
<tr>
<td>1360</td>
<td>B–O–B stretch</td>
<td>[41]</td>
</tr>
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<td><strong>Boro-phosphosilicate glass</strong></td>
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<tr>
<td>800–806</td>
<td>(v_1) P–O–P bend</td>
<td>[22,28]</td>
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</tbody>
</table>

The incorporation of only small concentrations of dopants, i.e., amounts in the range from 3 to 7 wt%, into the random network of SiO\(_2\) tetrahedra gives rise to several distinct new Raman bands. In high silica PSG a sharp peak at 1325 cm\(^{-1}\) is observed that is attributed to a P–O bond stretching vibration [22,28]. The position of this band varies with the concentration of phosphorous present and in the limit of a pure phosphate glass system it appears at 1390 cm\(^{-1}\) [36,37]. Other related bands are present in the measurement region; bands at 1025 cm\(^{-1}\) and 1200 cm\(^{-1}\) have been assigned to P–O–P stretching vibrations [21,28] and a peak at 1137 cm\(^{-1}\) is assigned to a P–O–Si stretching vibration [22,28]. The phosphorous content in high silica PSG has been shown to be proportional to the intensity of this 1137 cm\(^{-1}\) peak relative to that of the Si–O–Si stretching vibration at 800 cm\(^{-1}\) [22].

In high silica BSG there are three new Raman bands associated with the presence of boron. Bands at 935 cm\(^{-1}\) and 1150 cm\(^{-1}\) correspond to B–O–Si stretching vibrations and a peak at 806 cm\(^{-1}\) has contributions from the symmetric Si–O–Si bond stretching vibration and the B–O–B symmetric breathing mode of a boroxyl ring structure [24–26,39,41,42]. An additional boron related feature at 1360 cm\(^{-1}\) appears at the edge of the measurement region and has been assigned to a B–O–B bond stretching vibration [22,41].

The Raman spectrum of a BPSG sample, typical of the set of wafers studied, is shown in Fig. 2(d). The Raman bands identified in silica and the BSG and PSG samples, and shown in Fig. 3, are present in the Raman spectra of the BPSG sample in Fig. 2(d). Each of the BPSG samples prepared in this work were found to possess five distinct Raman bands as follows: (i) 806 cm\(^{-1}\) (from Si–O–Si, P–O–P and B–O–B); (ii) 932 cm\(^{-1}\) (from B–O–Si); (iii) 1072 cm\(^{-1}\) (from Si–O–Si, P–O–P and B–O–P); (iv) 1145 cm\(^{-1}\) (from P–O–Si, BO–Si, Si–O–Si and B–O–P); and (v) 1315 cm\(^{-1}\) (from P=O and B–O–B).

The position of the band at or near 1315 cm\(^{-1}\), and its intensity relative to that of the 806 cm\(^{-1}\) band, are each sensitive to boron content. The band appears at higher Raman shifts, i.e., 1320 cm\(^{-1}\), for BPSGs with relatively low boron content, and at lower Raman shifts, i.e., 1313 cm\(^{-1}\), for BPSGs with relatively high boron content. In general, the relative intensity of the 1313 cm\(^{-1}\) band observed in BPSGs with high boron content is low whereas the relative intensity of the band at 1320 cm\(^{-1}\) in low boron BPSGs is high. The relative contribution of a weaker overlapping Raman band at 1360 cm\(^{-1}\) due to a B–O–B stretching vibration governs the degree of asymmetry apparent in the ‘1315 cm\(^{-1}\)’ P=O Raman band.

For samples where the total boron and phosphorous dopant concentrations are low then, as expected, the BPSG Raman spectra in the measurement region show more clearly features that are related to the Raman spectrum of pure vitreous silica (Fig. 3a). The two most important of these are bands in the range 802–806 cm\(^{-1}\) and a band which appears as a shoulder in the Raman shift region between 1140 cm\(^{-1}\) and 1155 cm\(^{-1}\) and which corresponds with the increased relative contribution from the Si–O–Si band at 1200 cm\(^{-1}\).

### 3.2. Germanium-doped silica glass

The Raman spectrum of a high silica, germanium-doped, silica glass is shown together with that of vitreous silica in Fig. 4. The noticeable difference near 750 cm\(^{-1}\) corresponds to the effects of a Raman band at 675 cm\(^{-1}\) outside the measurement region which relates to a Ge–O–Si
3.3. Analysis of Raman spectra

Separate analysis procedures were developed in this study to determine each of the phosphorus, boron and germanium contents of the doped silica glasses. The collected results given in this section show correlations between the wt% compositions obtained from the analyses of the Raman spectra and ICP-MS measurements of the respective wt% obtained from samples taken from the same wafers. The error analyses associated with each of the separate correlations for boron, phosphorous and germanium take into account the following:

(i) repeatability of measurements made at the same measurement position on the wafer's surface (a set of seven repeat measurements at a fixed position in the center of a BPSG layer in a particular wafer found an average wt% for phosphorus of 2.32 with a standard deviation of 0.14 wt%, and an average wt% for boron of 6.05 wt% with a standard deviation 0.06 wt%);
(ii) variation of the glass composition across the surface of a wafer (each of the results are an average of three measurements taken from three fragments (one measurement each) from different positions in the central part of the respective wafer. The standard deviations were found to be fully compatible with the repeatability measurements in (i));
(iii) local, i.e., few µm scale, inhomogeneity in the glass composition (not found from measurements to be an important factor in this study);
(iv) size of the sample sets (details given below);
(v) uncertainty in the ICP analyses which provide the reference phosphorus, boron, and germanium wt% data (a single value of 0.1 wt% was assumed for this in the data analyses given below); and
(vi) drift in the laser power at the sample during signal accumulation and from sample to sample (the laser power was measured prior to each measurement and the results scaled accordingly; laser power during single accumulations was found not to be significant).

3.3.1. Phosphorous analysis in BPSG

The procedure developed to determine the phosphorous content of BPSG samples was identified after, firstly, performing a best-fit curve-fitting in the region from 863 cm$^{-1}$ to 939 cm$^{-1}$ for each of the Raman spectra taken from a batch of sample wafers with reference to a single spectrum selected from within the set of spectra being processed. This best-fit curve-fitting procedure does not correspond simply to a normalization of the spectra to the peak value of the 933 cm$^{-1}$ Raman band, a B–O–Si stretching vibration [22,43], as it considers the entire area under the band and any slight changes in its shape. The only distinction of the spectrum selected from the others in the set to act as a reference spectrum is that it has a good signal-to-noise ratio in the region of curve fitting. An example set of results obtained for three samples using this procedure is shown in Fig. 5. The changes in the intensity of the band at 1145 cm$^{-1}$, a band known to arise from the P–O–Si stretching vibration [22,28], that are revealed by this procedure (Fig. 5) are found to correlate very well with the wt% of phosphorous in the films, i.e., the higher this band the higher the phosphorous content and vice versa. The presentation of the Raman spectra in this way effectively suppresses the contributions from the boron and silicon related species and highlights a band that is closely related to the phosphorous content.

The correlation between this measure of phosphorous content derived from Raman measurements, i.e., the area under the curve-fitted Raman spectra between 1051 cm$^{-1}$ and 1200 cm$^{-1}$, with the separately measured ICP-MS phosphorous analyses of samples taken from the respective wafers, is shown in Fig. 6. The linear regression fit shown in the figure, i.e., $P \text{ (wt\%)} = -2.06 + 5.33 \text{ (area)}$, includes data from a sample set comprising 31 wafers, although data for only 9 wafers are shown to preserve commercial confidentiality. A simple average of the difference between the ICP-MS values and those predicted by the regression is 0.06 wt%.

3.3.2. Boron analysis in BPSG

The Raman band at 806 cm$^{-1}$ has contributions from all three of the glass components, i.e., from the symmetric Si–
O–Si stretching vibration, the P–O–P bending vibration and the symmetric B–O–B breathing mode of the boroxyl ring \((v_1)\). The boron contribution, however, is the dominant contribution and realization of this led to a method for the quantitative analysis of the boron concentration in BPSG. Fig. 7 shows the Raman spectra of three BPSG samples normalized to the intensity of the band at 806 cm\(^{-1}\). The decreasing width of the normalized band correlates with increasing boron content of the samples.

The second order polynomial regression shown in the figure, i.e., \(B\text{ (wt%)} = 1.75 + 25.90 \left(\text{area}\right) - 25.15 \left(\text{area}\right)^2\), is for data from a sample set comprising 37 wafers although data for only 18 wafers are shown to preserve aspects of commercial confidentiality. A simple average of the difference between the ICP-MS values and those predicted by the regression is 0.16%.

3.3.3. Germanium analysis in germanium-doped silica glasses

The method developed to determine the germanium content in core silicas glasses was identified after, firstly, normalizing the Raman spectra of germanium-doped silica glasses to the intensity of silica bands at 1060 cm\(^{-1}\) and 1200 cm\(^{-1}\) (Fig. 9). These bands are associated, respectively, with the TO and LO modes of the Si–O–Si asymmetric stretching vibration \((v_3)\). In effect, by processing the
spectra in this way the contributions from the silica glass species are suppressed and those related to germanium are highlighted. It is apparent in the example spectra shown in Fig. 9 that increasing germanium content is closely related to the intensity of the band that develops at 1120 cm$^{-1}$ between the two silica bands at 1060 cm$^{-1}$ and 1200 cm$^{-1}$.

Fig. 10 shows the correlation between the area of the normalized spectra in the range from 1060 cm$^{-1}$ to 1200 cm$^{-1}$ and the separately measured ICP-MS germanium compositions determined from separate fragments of the respective samples, for a number of germanium-doped silica glass samples.

The linear regression shown in the figure, i.e., $(\text{Ge (wt\%)} = -22.08 + 34.06 \times \text{area})$, is for data from a sample set comprising only five wafers. A simple average of the difference between ICP-MS values and those predicted by the regression is 0.37 wt%. This value is significantly larger than those found for the phosphorous and boron analyses but the germanium concentrations in the sample wafers spanned a much larger range and the batch size was much smaller.

### 3.3.4. Blind tests

A blind test of the methods developed above was conducted using 10 BPSG monitor wafers in which the phosphorous wt% ranged between 1.49 and 2.67 and the boron wt% ranged between 3.37 and 6.20. The measurement conditions were identical to those used in the studies to develop the phosphorous and boron calibration curves described earlier.

The average difference between the wt% amounts of phosphorous determined using the Raman method developed in Section 3.3.1 (spectra were taken at three different positions on each wafer) and that determined by ICP-MS analysis was $-0.059$, with a sample standard deviation of 0.061.

The average difference between the wt% amounts of boron determined using the Raman method developed in Section 3.3.2 and that determined by ICP-MS analysis was 0.197, with a sample standard deviation of 0.129. The relatively large systematic error in this case implies a difference in the background subtraction procedures applied in the case of the monitor wafers used to develop the calibration curve and applied to the wafer samples submitted to blind test. The functional shape of the best-fit correlation curve between the Raman and ICP-MS analyses is very closely similar to that found in the calibration study.

In general the results of the blind test are regarded as supportive of the proposed Raman-based analysis method.

### 3.3.5. Face-on measurements

As mentioned in Section 2.3.2, performing measurements using a face-on configuration, in contrast to the edge-on measurements used so far, is expected to introduce two major problems. Firstly, the lower spatial resolution of the microscope in confocal mode along its optical axis compared to that in lateral directions, as demonstrated in Fig. 1a and b, is likely to result in significantly larger relative contributions from the silicon substrate to the Raman spectra of the glass layers. The effect is greater than can be compensated for using the polarization suppression of the silicon bands mentioned earlier. Secondly, depth profiling measurements in Raman microscopy are subject to large distortions because the optical design of the objectives used are unable to accommodate step changes in the refractive index within the focal range. Modelling of the effect predicts that the apparent position of a buried coating-substrate interface rises towards the air-coating interface, i.e., makes it appear that the coating is thinner than it actually is [44]. The effect is moderated significantly by the use of oil-immersion objectives in place of the metallurgical objectives used in this study [45].
Fig. 11 is a schematic diagram of the surface structure of an AWG device obtained for Raman investigation. A 35 μm thick glass coating on a silicon substrate comprises a 15 μm BPSG cladding layer, a 5 μm germanium-doped core glass layer, and a 15 μm under-cladding layer of thermal silica. The layer thicknesses were determined by measurements on a section through the AWG region of the device.

The depth profiling problem is illustrated in Fig. 12 which shows the intensity of the Raman band of silicon at 520.6 cm$^{-1}$ as a function of the distance between the objective lens and the air–glass interface measured in a face-on configuration using ×50 (dashed line) and ×100 (full line) objectives.

![Fig. 11. A schematic diagram of the three glass layers in the investigated AWG device. The right hand scale shows the actual layer thicknesses as measured from the edge of a fragment taken from the AWG. The left hand scale shows the apparent depth of the layers as found from the apparent position of the glass–silicon interface (see text and Fig. 12).](image)

The instrument corrections were applied as in the edge-on studies and the silicon reference spectrum was taken at an apparent depth of 20 μm (see Fig. 12).

On the basis that the spectrum at the air–glass interface comprised mainly the spectrum of the cladding layer this spectrum was subtracted from the spectra obtained from progressively greater depths. The difference spectrum revealed was associated with the second layer and continuation of the process revealed finally a spectrum of the underlayer. The procedure is successful only because of the assumption that there are only three layers, and the silicon background, contributing potentially to each of the measured spectra. The recovered spectra are shown in Fig. 13 and should be compared with equivalent spectra in Figs. 2 and 4.

Finally, the behavior with depth of the Raman-based BPSG analysis method was investigated by processing the spectra obtained as a function of depth in the AWG device.

![Fig. 12. Intensity of the Raman band of silicon at 520.6 cm$^{-1}$ (see text) as a function of the distance between the objective lens and the air–glass interface measured in a face-on configuration using ×50 (dashed line) and ×100 (full line) objectives.](image)

![Fig. 13. Raman spectra of the three consecutive silica layers, i.e., BPSG, germanium-doped silica and thermal silica, in an Arrayed Waveguide Grating (AWG) obtained by deconvolution of spectra obtained in a face-on configuration as a function of depth below the air–glass interface.](image)
as well as exploiting the excitation wavelength sources where there is a possibility of due to the local heating of the sample, or to use lower excitation wavelengths, which may introduce problems and the most obvious means of achieving these is to increase the laser power, which may introduce problems. However, shorter times would be an advantage just acceptable for an off-line monitor wafer analysis method. Nevertheless, the procedure for boron analysis given in Section 3.3.2. The results obtained for two different AWG devices with the same layer thicknesses but with different boron wt% are shown in Fig. 14. The results show that the boron wt% analyses are relatively stable down to apparent depths of 6 μm but as the core layer is approached the boron wt% slowly declines. However, it does not fall to zero either in the apparent region of the core layer or beyond it in the apparent region of the under-cladding layer. Similar behavior with depth was found for the phosphorous wt%.

Clearly, these results indicate that depth profile analyses of AWGs in a face-on configuration are not viable using metallurgical microscope objectives. The findings of a recent comparative study of the performance of different designs of microscope objectives in depth profile studies suggest that such measurements could become viable if an oil immersion objective were to be used [46].

3.3.6. UV Raman excitation

The long signal accumulation times involved in obtaining the edge-on spectra in Sections 3.1 and 3.2 would be just acceptable for an off-line monitor wafer analysis method. However, shorter times would be an advantage and the most obvious means of achieving these is to increase the laser power, which may introduce problems due to the local heating of the sample, or to use lower excitation wavelengths sources where there is a possibility of pre-resonance or resonance-Raman signal enhancement as well as exploiting the ρ scattering factor.

A comparative experiment was performed on a Renishaw Raman microscope equipped with 244 nm and 325 nm excitation sources in addition to a 514 nm source similar to that used in this work. A 244 nm spectrum of BPSG was found to be almost identical to a 514 nm spectrum in the dopant analysis region identified in this study and, importantly, a spectrum with similar signal-to-noise ratio as a 514 nm spectrum was obtained in a 27× shorter time! Unfortunately, accurate lasers were not available to make a more direct comparison, however, that identical spectra from the same sample could be obtained so much more efficiently identifies another promising route for extending the present studies.

Unfortunately, the potential advantage of using UV excitation for Raman-based dopant analyses does not extend to the problem of germanium wt% analysis as each of the germanium-doped samples were found to fluorescent very strongly using both 244 nm and 325 nm excitations.

4. Conclusions

The paper has identified a Raman Microscopy analysis method to determine with good accuracy and precision the dopant concentrations in doped silica glasses used in silica-on-silicon waveguide structures. Separate procedures have been developed to determine the boron and phosphorous wt% compositions in BPSG, and the germanium wt% composition in germanium-doped silica glass.

The method is competitive in accuracy with the current method of monitor wafer analysis, ICP-MS, and, unlike this wet technique, is compatible with clean room environments. The measurement cycle time is already acceptable but methods to reduce it significantly have been identified.

There is potential to increase further the accuracy of the spectral analysis procedures by performing a more extensive mapping of the dopant concentration ranges and improving the algorithms. The present method is already at a level of accuracy where it is able to detect variations in composition across the surface of a wafer (not reported in this paper).

There is potential also for the method to become a three-dimensional spatially resolving, non-destructive, analysis method for device wafers. The issues involved in realizing the necessary face-on measurement configuration are discussed.

Acknowledgments

REN is grateful to the EPSRC and Nortel Networks for a research fellowship. The authors are grateful to Professor David Batchelder, Leeds University, for providing access to the UV Raman Microscope.

References
