Quantitative Determination of Boron and Phosphorus in Borophosphosilicate Glass by Secondary Ion Mass Spectrometry

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Secondary ion mass spectrometry (SIMS) using positive oxygen ion bombardment and positive secondary ion spectrometry was applied to the quantitative depth profile analysis of insulating borophosphosilicate glass (BPSG) films. The sample charging problem was alleviated by prior deposition of a thin gold layer onto the samples, use of an electron flood gun, and automatic sample voltage optimization. The SIMS results were compared to data acquired by wet chemical analysis and Rutherford backscattering (RBS), and excellent quantitative correspondence was obtained. The wet chemical analysis results were then used to calibrate the SIMS results quantitatively. In addition to the SIMS analytical procedures, the advantages of SIMS over conventional analytical techniques such as electron microprobe, wet chemical methods, and Auger electron spectroscopy are also discussed.

Phosphosilicate glasses (PSG) and borophosphosilicate glasses (BPSG) have found important applications in silicon semiconductor devices as the intermetal dielectric between aluminum metalization and polycrystalline or refractory metal silicide interconnects as well as a surface passivant and encapsulant layer (1, 2). There are several advantages of PSG and BPSG over undoped SiO$_2$ glasses. Phosphorus acts to provide trapping sites for alkali metals and thus minimizes impurity penetration into sensitive devices (3). Further, since microelectronic circuit manufacturing has recently adopted processing procedures operating below 1000 °C in order to minimize unintentional dopant diffusion, the reflow temperature of glasses can be reduced by increasing the P content (4–6). However, it is well-known that a substantial increase in the phosphorus content in particular next to the Al metallization can lead to corrosion of the aluminum runs, unstable film composition, and reliability problems (7–10). There is thus a practical upper limit of approximately 8–9 wt % of P in these films before these undesirable effects occur. It is also known that the addition of B to the glass serves to further lower the reflow temperature to a device-compatible range of significantly under 1000 °C. Unfortunately, B has no abilities at gettering ionic contaminants.

The boron and phosphorus concentration and in-depth distribution in BPSG are very important parameters for the glasses utilized in electronic device technology. For instance, an increase in the B concentration lowers the stress, while the film etch rate in HF solutions is determined by the ratio of the boron to phosphorus concentrations in the BPSG's (11). Although these glasses have significant advantages in device manufacturing, the high porosity and hygroscopicity of the BPSG films permit moisture to penetrate into the glass and react with the phosphorus to form phosphoric acid. Should this occur in close proximity with the underlying aluminum metalization, then corrosion of the aluminum runs by the phosphoric acid is highly probable. This is a significant cause of device failure in PSG or BPSG coated devices. Thus, the correct manufacturing process for deposition of these glasses not only must control the concentrations of the B and P but must also ensure that P is essentially depleted near the glass/metal interface, while B incorporation in this region provides the necessary suppression of the glass softening point.

To date, the most widely used analytical techniques for BPSG analysis have been electron microprobe analysis and wet chemical methods. These techniques are in general quite accurate, but do not provide information concerning the in-depth and lateral distribution of the B and P dopants. Moreover, the detection limit for B by electron microprobe analysis is not very good, usually about several atomic percent. Other analytical techniques less commonly used are Auger electron spectroscopy (AES), “He$^+$ Rutherford backscattering (RBS), and secondary ion mass spectrometry (SIMS). The principal drawbacks for AES analysis are that sample charging under electron bombardment and ion sputtering can sometimes be too severe to circumvent. Rutherford backscattering analyses provide accurate thickness measurement of the glass film and reasonably good dopant quantification but suffer from low phosphorus sensitivity because P is very close in mass to Si. The detection limit of P by RBS analysis is about 1%. The detection limit can be lowered if the BPSG films are thin (less than 5000 Å) and channeling techniques can be employed. The B sensitivity is very poor because of the dominant oxygen and silicon backscattering in the same energy range and the low B backscattering yield. Another drawback for electron microprobe and Rutherford backscattering analyses is that very little in-depth information is provided.

The SIMS technique is commonly used in the semiconductor field because of its high sensitivity and the capability to detect all the elements in the periodic table and to provide lateral and in-depth information. However, quantification of data obtained by SIMS is nontrivial because of the significant variation in secondary ion yields for different elements and for the same element in different materials (matrix effect). Bulk and ion implant standards are thus commonly used for quantification (12–14). Quantitative SIMS analysis of insulators is further hampered by sample charging under energetic ion bombardment. Negative oxygen ion bombardment is routinely used for insulators, especially in geological applications. However, the maximum attainable ion current and sputtering rate are about a factor of 50 less than that accomplishable by O$^+$ bombardment for the CAMECA IMS-3f, thus making O$^+$ sputtering inappropriate for routine depth profiling. In this paper, an analytical methodology to circumvent this sample charging problem using O$^+$ bombardment is described.
and the applications of secondary ion mass spectrometry (SIMS) to the quantitative analysis of BPSG are discussed. SIMS results for the analysis of BPSG are compared to results obtained from electron microprobe, wet chemical, and Rutherford backscattering (RBS) analyses. Excellent quantitative correlation among the various analytical techniques is observed.

EXPERIMENTAL SECTION

Sample Preparation. The phosphosilicate glass (PSG) and borophosphosilicate glass (BPSG) films were deposited with a commercial Watkins-Johnson WJ-985 atmospheric pressure chemical vapor deposition (APCVD) equipment with three deposition stages. This instrumental setup allows fabrication of up to three BPSG films with variable composition onto the same sample, requiring only one passage through the equipment (15, 16). The films were produced at 400°C with silane, phosphine, and diborane making up approximately half a percent of the injectors' flows and oxygen approximately 30%. The balance was nitrogen. Atmospheric CVD characteristics produced more fully oxidized films. Films produced at reduced pressures, especially plasma induced, contain substantial phosphorus, for example, as P₂O₅ and PH₃ as well as P₂O₅ (17).

Wet Chemical Analysis. BPSG films to be analyzed for B were deposited on 4 in. diameter Si(100) wafers with a Si₃N₄ surface layer 1500 Å thick and stripped by a NaOH solution. BPSG films were analyzed for P on 4 in. diameter Si(100) wafers and stripped by HF. The resulting solutions were analyzed by colorimetry employing a Sequoia-Turner spectrophotometer. Standards for P and B quantification were prepared from potassium dihydrogen phosphate and boric acid, respectively.

Electron Microprobe. The PSG samples were analyzed by using a CAMECA MBX electron microprobe relative to calibration standards of pure silicon and a phosphate mineral (apatite) with a known P content. The electron beam energy for X-ray excitation was 8 kV, and the k emission lines were analyzed. The total excitation depth was about 1 µm. These PSG films were specially made to be more than 2 µm thick in order to ensure that the excitation volume remained well within the PSG.

Rutherford Backscattering Spectrometry. Rutherford backscattering analysis was performed using a General Ionex Corp. Tandetron Model 4110A. A He⁺ beam of approximately 2 mm in diameter was accelerated to 2.275 MeV and impacted the sample at a highly normal incidence. The samples were mounted on a graphite disk with carbon paste. The backscattered particles were detected by surface barrier detectors placed at 170° and 110°. Each energy spectrum was taken after a total of 20 µC of backscattered particles had been integrated. The P concentrations in the films were calculated by comparing the number of He particles backscattered from P in the BPSG films to those from those backscattered from the Si atoms in the substrate. The ratio was then normalized by the inverse of the square of the respective atomic numbers to account for the variation in backscattering efficiency due to differences in the atomic nuclear backscattering cross section. The accuracy of this method is estimated to be about ±5%.

Secondary Ion Mass Spectrometry. To minimize sample charging under oxygen ion bombardment, the following steps were adopted: (1) a gold layer of about 1000 Å thick and stripped by a NaOH solution; (2) these gold-coated samples were mounted in a multiple sample holder made of tantalum and stainless steel, and conductive silver paint was used to ensure good electrical contact between the holder and the sample surface; and (3) an electron flood gun was utilized during the analysis to compensate for the residual sample charging.

A CAMECA IMS-3f ion microanalyser equipped with an oxygen duoplasmatron primary ion source was used. A primary oxygen beam composed of mainly O²⁻ was focused to about 50 µm in diameter and the ions were accelerated to 8 keV relative to the sample potential. The typical primary current was 1 nA, and the primary beam was rastered over an area of 500 by 500 µm². The secondary accelerating voltage was set at 4500 V and a Faraday cup was used as the detector. The IMS-3f was interfaced to an HP9825A microcomputer for instrument control, data acquisition, and data reduction. One BPSG sample was analyzed by using the PHI 6000 secondary ion profiler equipped with a quadrupole mass analyzer.

RESULTS AND DISCUSSION

The most serious problem encountered during SIMS analysis of insulators in general and BPSG in particular is sample charging which can significantly degrade the SIMS analysis. The steps described in the above paragraph minimized electrical charging, but charging was not totally eliminated. Moreover, the degree of sample charging was not constant throughout the depth profile analysis. Sample charging was observed to be more severe at the beginning of the analysis and became progressively less pronounced as the sputtering front approached the underlying conducting Si substrate. Since it was impractical to change the electron gun current during the course of the depth profile, the secondary ion accelerating voltage was scanned under computer control to establish the optimal secondary ion accelerating voltage for each analysis cycle. Since this automatic technique required a reference mass, the 30Si matrix ion was profiled simultaneously with B and P. In order to correct for any ion transmission variation due to changing sample charging states throughout the analysis, the B and P secondary ion intensities were normalized to the 30Si secondary ion current in each cycle, assuming that any variation in ion transmission would affect the matrix (Si) and the impurity (B and P) ion signals to the same extent. There is a molecular ion mass interference by 30Si/H at mass 31, the nominal atomic mass of P, and a mass resolving power of about 3500 is required for separating the 30P ion signal from the highest mass interference to provide a trace elemental detection limit. While this resolving power is routinely attainable on the CAMECA IMS-3f, the application of this high mass resolution technique is very difficult in the present analysis which requires a reasonably high sputtering rate using O²⁻ bombardment on insulating samples. As a consequence, the measurements were made under low mass resolution conditions. The practical detection limit for P by SIMS analysis with the hydride mass interference unresolved is about 0.08 atomic percent. This detection limit for P is quite acceptable for SIMS analysis, since the concentration of interest is generally above 1% for BPSG. The detection limit of B is determined by the Faraday cup detector dc offset. A lower B detection limit (parts per billion) can be achieved by reducing the mass spectrometer ion transmission and detecting the decreased B ion current on an electron multiplier with pulse counting electronics.

Figure 1 illustrates a SIMS depth profile for B, P, and Si in a test Si wafer sample which has a 1 µm thick BPSG passivation layer. Note that there is a buffer region which contains no detectable P between the BPSG and the underlying Si. This buffer layer is essential to the prevention of corrosion of the metalization in real electronic devices. Figure 1 also illustrates the extent of the actual secondary accelerating voltage adjustment (shown in the sample offset curve) required to obtain the maximum ion intensity for each analysis cycle. This curve thus reflects the variation in sample charging throughout the depth profile. It can be observed that sample charging is most severe in the near surface region and becomes progressively less pronounced during the course of the analysis. The detection limit of B and P is imposed by the Faraday cup dc offset and the hydride mass interference, respectively.

In order to evaluate the capability of SIMS to provide quantitative analyses, a set of PSG samples were analyzed by both electron probe microanalysis and SIMS, and the results obtained from the two techniques are compared to each other. A plot of the P concentrations (atomic percent) calculated from electron microprobe measurements vs. the 30P/30Si secondary ion intensity ratios obtained by SIMS is presented.
in Figure 2. Since the Si concentration varies with the P doping, the relationship is not linear. As a consequence of the variable matrix ion intensities for BPSG with different compositions, quantification schemes employing the use of ion implant standards are not very accurate because a constant matrix ion signal is usually assumed in the calculation. As shown in the same figure, good linearity is, however, observed if the SIMS ion intensity ratios of P to Si are plotted vs. the concentration ratios of P to Si acquired by the electron microprobe analysis. The use of $^{16}$O as the normalization reference is not appropriate, firstly, because under the present sputtering conditions, a significant fraction of the secondary oxygen ions are derived from the implanted primary oxygen ions, and, secondly, the secondary oxygen ion signal may depend on the vacuum. The poor linearity is demonstrated in the SIMS P/O ion intensity ratios vs. electron microprobe P/O concentration ratios plot shown in Figure 2.

The SIMS depth profile of one of the BPSG standards is exhibited in Figure 3. The in-depth distributions of B and P are observed to vary in these samples because these BPSG standards are a composite of three layers (individually adjustable). To confirm that the B and P variations in the BPSG film are real and not due to some instrumental artifacts, the sample was reanalyzed using a PHI 6000 secondary ion profiler. The results obtained are identical with those acquired on the CAMECA IMS-3F. In addition, as shown in Figure 4, the nonuniform in-depth distribution of P is clearly indicated in the RBS spectrum. Owing to these variations, the B, P, and Si ion intensity profiles must therefore be integrated over the total sputtered depth to obtain the total B and P concentrations in these BPSG films for comparison with the
Given appropriate cross-calibration, the same analytical invariants such as Na, K, and Cr in the glasses and the interfacial regions. Careful interpretation of the results is, however, necessary because of the high mobility of alkalis under anodic conditions. Careful interpretation of the results is, however, necessary because of the high mobility of alkalis under anodic conditions.

The B and P contents in the rest of the films were also measured by wet analysis/colorimetry and Rutherford backscattering spectrometry. The P concentrations were calculated from the RBS backscattered particle energy spectra by comparing the amount of He particles backscattered by P in the BPSG films to those backscattered by the Si atoms in the substrate, with the assumption that the densities of the BPSG films and bulk Si are the same. The linearity obtained from SIMS ion intensity ratios vs. wet chemistry concentration ratios and against RBS concentration ratios is again seen to be good (Figure 5).

On the basis of the results generated from the electron microprobe analysis, wet chemical analysis, and Rutherford backscattering analysis, relative sensitivity factors can be derived to convert the SIMS B/Si and P/Si ion intensity ratios into B and P concentrations. Once these relative sensitivity factors are established, the SIMS technique can then be applied to the in-depth concentration analysis of B and P in other PSG and BPSG samples. Figure 6 depicts the depth profile of the BPSG sample shown in Figure 3 replotted on concentration vs. depth scales using the appropriate relative sensitivity factors derived from wet chemistry data.

The advantages of SIMS in this type of analysis are 4-fold: (1) the depth profiling capability is intrinsic to the sputtering process and therefore provides a direct measure of the in-depth elemental distribution, (2) the fast sputtering rate achievable using O$_2$^+ provides routine analysis capability in a process environment, (3) with the aid of empirical standards, quantification using SIMS can be accurate to within ±15%, and (4) the high detection sensitivity of SIMS allows the detection of low concentrations of B and P as well as unintentional contaminants such as Na, K, and Cr in the glasses and the interfacial regions. Careful interpretation of the results is, however, necessary because of the high mobility of alkalis under an electric field.

In conclusion, the SIMS technique employing O$_2$^+ sputtering has been demonstrated to provide quantitative in-depth concentration profiles of B and P in PSG and BPSG films. Given appropriate cross-calibration, the same analytical methodology can be applied to other dielectric films such as CaF$_2$ or SrF$_2$ used for GaAs device passivation, ZnSe for HgCdTe device passivation, and other similar materials.

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