The Accurate Analysis of Phosphorus in PSG and BPSG Films

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Phosphorus doped oxides are important films in the processing of IC's, both as a planarization dielectric and as a passivation film. The behavior of these films is greatly affected by the concentration of dopants in the film. Consequently the accurate analysis of dopants it these films is of importance to process engineers.

The accurate analysis of dopants in these films is also of great importance to the analytical chemist. However, as equipment and materials for making these films change, these measurements, especially the measurement of phosphorus, become more complicated.

In the early years of producing phosphorus doped films, atmospheric CVD equipment produced only P_2O_5, in SiO_2 using SiH_4, PH_3, O_2 and N_2. However, it was shown in 1984 by Jerry Tong, et. al.[1], that LPCVD and PECVD doped films also contained P_2O_3. Balazs et. al. [2], in their paper in 1986 also found, besides P_2O_5 and P_2O_3, occluded PH_3 and a polymeric compound with a P-P-P chain.

Today more changes for producing PSG's and BPSG's have occured both in the equipment technology and the materials used for producing doped films.[3] Nitrous oxide, (N.0), tetraethoxysilane (TEOS), trimethyl phosphite (TMP) and tertiarybutylphosphene[4] are compounds that have been added to the list of materials that can be used.

Analytical evidence has recently been found that indicates that both the new equipment using PH_3/SiH_4, chemistry and the new materials being used are causing anamolies in analytical results which suggests the formation of previously unidentified phosphorus compounds in doped oxides. The evidence is presented in this paper.

Before presenting and discussing the data, however, it is important to discuss analytical techniques to some degree in order to understand some of the conclusions being drawn. The popular analytical techniques used today for measuring total weight percent phosphorus in doped oxides are Colorimetry, and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), X-ray Fluorescence Spectroscopy (XRF)[5] and Fourier Transformed Infra-Red (FTIR).[6,7,8] Other techniques such as Ion Chromatography (IC), X-ray diffraction (XRD), Secondary Ion Mass Spectrometry (SIMS)[9], Auger, and Rutherford Backscatter Spectroscopy (RBS) have also been utilized and reported.

Basically, these techniques fall into a wet chemical destructive category (colorimetry, ICP-AES, IC, ICP-MS) or into a dry vacuum technology category (XRF, FTIR, RBS). Both categories have advantages and disadvantages such as time of analysis, accuracy, destructiveness or availability.

It is important that the analyst and engineer understand what is being measured with these analytical tools and what weight percent phosphorus (wt % P) means from each of these tools. Therefore it is worthwhile to include a short discussion of the most widely used tools, since understanding them is key to understanding what the discrepancies between them mean when measuring P in PSG or BPSG.

Colorimetry utilizes the reaction between phosphate ion and molybdate ion to form a blue complex whose intensity is directly proportional to the quantity of phosphate ion present. It has been widely used and demonstrated to be very accurate and standardized against NIST standards and consequently is usually the technique used to standardize processes, equipment, and other analytical tools such as FTIR and XRF.

However, P_2O_3, forms phosphate ion in solution which does not react with molybdate to form a blue complex, and must be converted to the phosphate ion through the addition of a strong oxidizing agent before color development. Since the film is dissolved off of the water during the procedure, occluded phosphine or TMP, if they exist, may be lost to the atmosphere. Polymetric phosphorus (P-P-P) compounds or the other hand are auto redox compounds which do react to form a blue complex so they are therefore included in a colorimetric determination. Not all of the phosphorus atoms are oxidized to phosphate so some are not detected. Their presence however has never been found above the sub-ppm level in a thin film, and therefore has not been generally considered a significant issue.

ICP-AES, like colorimetry, requires that the film be dissolved off of the wafer. Therefore, like colorimetry, any occluded PH_3 is lost in this measurement and must be analyzed separately. ICP-AES detects any P atom found in solution no matter what molecule it comes from. However, it occasionally yields anomalous results which are believed to be caused by the quantity of P-O-F bonds formed on dissolution of the film in hydrofluoric acid. This species seems to have an effect on the ICP-AES nebulizer. ICP-MS acts like ICP-AES. Both of these tools, like colorimetry, can be standardized against NIST standards. Procedures using ICP are considerably faster than colorimetry.

XRF is a fast, dry procedure that can be used to measure phosphorus quickly and non-destructively. Using the X-ray energy emitted from excited P atoms, it can detect total phosphorus in the volume of sample being excited by the X-ray beam regardless of the compound. Therefore, it will detect not only the phosphorus oxides, but also any other phosphorus compound and occluded phosphine. It is imperative that the operator know the instrument. factors and do proper reduction of data. With proper care and standardization of this tool, which is essential, one can get accurate data.[10]

FTIR determines total weight percent phosphorus by focusing on the P = O bond stretching vibration energy band at 1300 - 1350 cm $^{-1}$ wave number. Therefore FTIR will measure only P_2O_3 or P_2O_5 in the oxide film. The wafers must be properly protected as moisture develops a bonding with P=O which causes it to lose its dipole moment and thus its response to IR. This results in a loss of energy or peak height which is interpreted as less wt % P than actually is in the film. B-O from BPSG oxides interfere with P = O measurement. Different mathematical techniques are used (i.e. K matrix[11] or overlapping peak expansion[12]) to obtain reliable measurement of P = O in a BPSG.

FTIR cannot be a primary standard and must be standardized using films of known concentration phosphorus. Generally four, but preferably six, wafers of different concentration and thickness, which have been protected from moisture are used to calibrate the tool.[13] It is imperative that spectral features remain constant. Varying types of CVD systems can cause shifts in the band shape, intensity, and position. These are caused by differences in stress, density, or molecular stoichiometry.

Balazs Analytical Laboratory measures thousands of PSG and BPSG for phosphorus annually. Feedback indicating that some of the calorimetric results did not agree with results measured by using other analytical methods led to a fairly extensive study of phosphorus doped films. Using both colorimetry, which should emulate FTIR, and ICP-AES, which should emulate X-ray (minus any occluded phosphine), 150 samples from twelve companies were analyzed in duplicate. Agreement of the percent phosphorus measured by these two different pieces of equipment is shown in Table 1. Percent differences were determined by using the absolute value from the following equation:

$$\left| \frac{\text{colorimetry avg. value - ICP avg. value}}{\text{colorimetry avg. value}} \right| \times 100$$

Table 1. Measurement total wt % P in doped oxides using two different analytical methods

% Difference	No. of Samples	% of Samples
< 1%	36	24%
< 3%	86	57%
> 3%	64	42%
> 5%	17	11%
> 7%	7	5%

Seven of the twelve companies had wafers that showed greater than 5% difference in phosphorus concentration. Following up on this information with the respective clients revealed the following:

1. Five of the 17 samples came from the same company and from a single piece of equipment.

2. Two of the companies were using the same kind of equipment.

3. One company was using TEOS instead of silane.

With 42% of the samples differing by more than 5%, a study was conducted to gain more information on these specific doped oxides. The program included collecting the following:

1. A comparison of the wet chemical analysis with X-ray or FTIR.

2. A study of occluded phosphine.

3. A study of the ratio of P_2O_3 and P_2O_5 on doped films as deposited and after annealing.

4. An ion chromatographic study to look for evidence of new peaks from samples that produced anomalous results or that were made using TEOS or TMP.

We were able to gather only one piece of data comparing the wet chemical results with X-ray or FTIR and that is shown in Table 2.

Table 2.				
Sample	X-ray %P	Colorimetry Total %P	P_2O_3	P_2O_5
1 AD	7.6	7.5	2.7	4.8
2 AD	5.0	4.9	1.5	3.4
3 AD	2.2	1.8	0.5	1.3
1 AN	8.0	5.9	1.1	4.8
2 AN	5.1	4.3	0.4	3.9
3 AN	2.3	1.7	<0.2	1.7
AD = as deposited, AN = annealed 800°C in N_2				

These results were really distressing because they revealed a new problem; namely how to describe a phosphorus compound containing P=O that can disappear during an annealing step. Since the colorimetry measures only P_2O_5 and P_2O_3 and it agreed with the phosphorus found by X-ray before anneal, what happened to it? Chemically, N_2 at 800°C cannot reduce P_2O_5 to a volatile compound. This suggests that perhaps it was driven into the substrate and thus was still detected by X-ray.

The study of occluded phosphine was done on 18 wafers from seven companies, two of which had wafers with greater than 7% differentiation in the colorimetry vs ICP-AES study. We could find phosphine at a concentration greater than our sensitively limit, which is 0.05%, in only one sample. This one wafer had a greater than 7% P in study shown in Table 1. The quantity of phosphine found was only 0.06%. From these data, occluded phosphine was eliminated as a reason for the differences found in wt %P.

A comparison of 18 wafers from four companies showing colorimeteric results as P_2O_3, P_2O_5, and total P and ICP-AES results of total P on both as deposited (AD) and annealed (AN) wafers is shown in Table 3. These results reveal some interesting information and raise more questions. For wafers that had high phosphorus concentrations, the total wt % P by ICP-AES was much higher than the wt % P found by colorimetry. This indicates the presence of a phosphorus compound that is not P_2O_3 or P_2O_5. Furthermore, P_2O_3 concentration went down significantly after annealing but P_2O_5 results do not show the same kind of increase. This suggests that P_2O_3 does not completely convert to P_2O_5 upon annealing nor does it oxidize in the P_2O_5 wet chemical sample preparation procedure. These results may be different for different annealing conditions but certainly indicate the presence of a different P bonding or compound.

Table 3.				
Samples	P_2O_3	P_2O_5	Total % P repeats	% P by ICP-AES
pyrox 1	0.24	2.86	3.10	3.22
2	0.24	2.48	2.69	2.77
PG 1	0.90	7.11	8.01	8.53
pyrox 1	0.38	3.53	3.91	3.78
2	0.43	3.67	4.10	4.06
PG 1	0.95	7.70	8.65	9.41
2	1.07	7.76	8.83	9.82
9% AD	1.4	7.2	8.6	10.1
AN	0.2	7.8	8.0	9.8
11% AD	2.4	8.7	11.1	13.4
AN	0.3	9.1	9.4	12.9
13% AD	3.0	9.7	12.7	15.9
AN	0.9	10.6	11.5	14.8
AD	1.3	4.7		N/A
AD	1.6	4.5		N/A
AN	0.2	5.2		N/A

Finally it was very interesting to note that the total P concentration by ICP-AES also went down after annealing, unlike the X-ray results that show that total %P stayed the same. It increases the suspicion that part of the phosphorus is lost by being driven into the substrate although this should not be possible at a temperature of only 800°C.

The last study was the ion chromatographic study which is shown in Table 4. This study is limited. It was stopped due to the discovery of an extensive number of peaks in several of the chromatograms. The identity of these peaks will require a much more intensive study.

Table 4.

| Co. Samples		Total P ICP-AES	Color	P_2O_3	P_2O_5	Total P as PO_4 by IC
A	AD	9.7	5.9	--	--	2.26
	AN	8.9	8.3	--	--	2.75
B	1	--	3.5	0.7	2.8	2.77
	2	--	3.5	<0.2	3.4	3.23
	3	--	5.8	0.9	4.9	4.48
	4	--	5.8	<0.2	5.7	5.55
C	AN	--	5.2	0.3	4.9	4.73
D	1		3.0	<0.2	3.0	3.04
	2		3.0	<0.2	3.0	2.92

The data from this study does reveal, however, that the quantity of PO_4^{-3} species is essentially the same whether measured by colorimetry or by IC. This information further suggests that phosphorus exists in different forms in doped oxides and also indicates that different procedures measure what they are supposed to measure.

In general we found from the IC work that those films that contained only P_2O_5 in the doped film (Company D) yielded spectra essentially the equivalent to Na_2HPO_4 in a 0.1% HF solution (see fig. 1). Company B revealed a peak at 4.36 which disappeared after annealing (see fig. 2).

Company A, however, revealed significant lower quantity of phosphorus as PO_4^{-3} than was expected. The spectra seen in figure 3 show the presence of essentially three equal peaks before annealing, only one of which can be PO_4^{-3}, and a significant change in the ratio of these three peaks after annealing. These results suggest not only that some chemical changes in phosphorus chemistry are occurring during the annealing processes, but also that this change does not result in the total formation of PO_4^{-3}.

Company A is the company whose samples have been showing anamolous behavior throughout the entire study and whose wafers were from a single machine. These wafers also are wafers whose XRF results show no difference in phosphorus concentration for as deposited wafers or annealed wafers.

It is of interest at this point to consider some characteristics of P_2O_3 chemistry. Knowing that P_2O_3 has a melting point at 28.8°C, vaporizes at 173°C, and thermally decomposes at 300°C one wonders how it is behaving in a doped oxide film while it is being annealed. For example, does it become more mobile in the film? If so, does it undergo known decomposition reactions which can produce other phosphorus oxides such as P_4O_7, P_4O_8, or P_4O_9 and do these affect analytical procedures? It is also known that the following P_2O_3 reactions can occur.

$$3H_3PO_3 + H_3PO_3 \rightarrow 3H_3PO_4 + PH_3 \uparrow$$

$$HF + H_3PO_4 \rightleftharpoons H_2PO_3F + H_2O$$
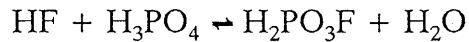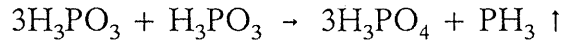
If they exist or occur, how do they affect analytical procedures and which ones do they affect? In the colorimetry procedure a deliberate step is included to prevent the formation of the H_2PO_3F. However, in other wet chemical procedures such as ICP-AES, this is not so.

This entire study raises several serious questions that require answers. These include:

1.   Which analytical procedure used to measure total wt % P gives the most useful answer? In other words, is the process engineer really interested in wt % P or wt % P=O?

2.   Does the ratio of P_2O_3 versus P_2O_5 make any significant difference to film performance such as the way it reflows or acts as a getterer?

3.   Do other compounds of phosphorus exist in today's doped oxide film that have not previously been identified, and if so, what are they and how do they affect performance?

4.   Should more than one analysis be done on doped oxide films in order to get not only a real understanding of what has been produced but an accurate wt % P?

5.   Does phosphorus get driven into the substrate when annealed at temperature >800°C or N_2 atmosphere and if not, how do we account for an apparent loss of phosphorus after annealing?

Conclusion:

Sufficient evidence has been found to demonstrate that BPSG films need to be accurately described for purposes of standardization and performance. New equipment, conditions and chemistries being used to produce BPSG has created a situation where analytical tools yield results that indicate that the measurement of total wt % P is dependent on the phosphorus species in the film. Consequently, these various analytical techniques frequently do not corroborate each other. More research is required to understand phosphorus chemistry in BPSG films.

References

1.   J. Tong, K. Schertenleib, Ronald A. Carpio, "Process and Film Characterization of PECVD Borophosphosilicate Films for VLSI Applications," <u>Solid State Technology, p.</u> 161, January 1984.

2.   J. Houskova, K. Ho, M. Balazs, "Characterization of Components in Plasma Phosphorus Doped Oxides," <u>American Chemical Society,</u> 1986.

3.   W. Kern, "Deposited Dielectrics for VLSI," <u>Semiconductor International,</u> p. 122, July 1985.

4.   G. Pignatel, J. Sisson, W. Weiner, "The APCVD Growth of PSG and BPSG Films Using Tertiarybutylphosphine as a Phorphorus Dopant, <u>Electrochem. Soc.,</u> Vol., 138, No. 6, June 1991.

5.   N. Parekh, C. Nieuwenhuizen, J. Borstrok and O. Elgersma, "Analysis of Thin Films in Silicon Integrated Circuit Technology by X-Ray Fluorescence Spectrometry," <u>J. Electrochem. Soc.,</u> Vol. 138, No. 5, May 1991.

6.   K. Hurley, "Process Conditions Affecting Boron and Phosphorus in Borophosphosilicate Glass Films as Measured by FTIR Spectroscopy," Watkins-Johnson Co., Scotts Valley, CA, In-house study.

7.   "FTIR Measurement of PSG and BPSG Films, Part I: IR principles and K-matrix Approach," <u>Nicolet Semiconductor Systems,</u> Technical Bulletin 1017.

8.   D. Haaland, "Quantitative Infrared Analysis of Borophosphosilicate Films Using Multivariate Statistical Methods, <u>Analytical Chemistry,</u> Vol. 60, No. 11, June 1, 1988.

9.   P. Chu, S. Grube, "Quantitative Determination of Boron and Phosphorus in Borophosphosilicate Glass by Secondary Ion Mass Spectrometry," <u>Analytical Chemistry,</u> Vol. 57, No. 6, May 1985.

10.   N. Parekh, C. Nieuwenhuizen, J. Borstrok and O. Elgersma, p. 1461.

11.   Nicolet, p. 4.

12.   D. Haaland.

13.   Nicolet, p.5.