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**Characterization of Components in
Plasma Phosphorus Doped Oxides**

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Three compounds of phosphorus have been verified in plasma deposited phosphosilicate glass and borophosphosilicate glass films. They are phosphorus pentoxide, phosphorus trioxide, and phosphine. Evidence is given for the presence of a fourth phosphorus-containing compound. Data are given from analysis by colorimetry, ion chromatography, and P-31 NMR on standards, plasma, plasma enhanced, and atmospheric CVD films. Some information on LTO/LPO deposited films is included.

In past years, the analysis of doped dielectric MOS films has always led to the conclusion that the dopant materials existed in their fully oxidized state. Thus, phosphorus existed as phosphorus pentoxide and as such could easily be quantitatively measured in aqueous solutions as the phosphate ion. Although many suspected the presence of phosphorus trioxide, there was no evidence of its existence.

In the spring of 1983, however, during a routine analysis of a set of PSG silicate films, a distinct foul odor was detected coming off the wafers during etching. The suspicion that this odor was phosphine led to a renewed study of all glass films. Because the set of wafers that yielded the foul smelling gas was plasma deposited doped glass, our first study was on plasma and plasma enhanced CVD PSG films.

Our immediate concern about the presence of phosphine in doped oxide films was safety in handling these materials. The permissible exposure limit (PEL) set by OSHA is 0.3 ppm, and the concentration immediately dangerous to life and health (IDLH) is 200 ppm. All precautions must be taken when etching plasma PSG or BPSG wafers. A basket of twenty 3 inch wafers, 5000 angstroms thick, containing 5 wt. % phosphorus could release as much as 2500 ppm of phosphine or 5 times the IDLH.

To identify the foul smelling gas, we built a closed system in which the film was dissolved. The liberated gas was driven to a reaction chamber and oxidized. If the gas were phosphine, it would be converted to phosphate ion and as such could be analyzed. This test was positive for every plasma and plasma enhanced phosphorus doped oxide that was analyzed. Deductively it was concluded that the

Table I. Phosphorus Oxides and Acids

Basic Oxide Forms	Combination Oxide Forms	Acid Forms*	
P_4O_6 $(PO_2)_n$	P_4O_6 P_4O_7 P_4O_8	H_3PO_2	hypo
		HPO_2	meta -
		$H_4P_2O_5$	pyro -
		H_3PO_3	ortho
P_4O_{10}	P_4O_9 P_4O_{10}	$H_4P_2O_6$	hypo
		HPO_3	meta -
		$H_4P_2O_7$	pyro -
		H_3PO_4	ortho

phosphorus acid

phosphoric acids

*These acids form various ionic species depending on the pH of the solution.

agent. The results showed that acids containing a -P-P-P straight cycle chain gave color development similar to those we found in plasma time studies (Figure 4). These acids, plus $H_4P_2O_5$, gave a blue green color in a molybdate solution when no reducing agent was added. Tests on plasma PSG samples gave a positive blue green color when no reducing agent was added to a molybdate solution.

With the anion detection system on our ion chromatograph (IC) and sodium carbonate solutions in various pH ranges as an eluent, an effort was made to distinguish the oxo phosphorus acids that existed in a hydrofluoric acid solution of PSG films. The phosphate and phosphite ions were readily detected and quantitated when compared with known standards of these ions, as shown in Figure 5 (a)-(i). The standard solution gave a single peak for the phosphite and the phosphate ions, with retention times (RT) of 3.05 and 18.07, respectively. The chromatographic spectra of the samples contained as many as seven peaks. Those that were identified are hydrofluoric acid peaks (RT = 1.43, 2.16) and the known phosphite and phosphate peaks, Figure 5 (a)-(c).

Two peaks were found in the plasma films that were not identified and later proved to be important. They were those with RT of 4.38 and 6.38, see Figure 5 (e). Atmospheric CVD samples, Figure 5 (d), do not have a peak at 4.38 and the peak at 6.38 is much smaller. Also, the ratio of phosphite to phosphate ion is noticeably higher on plasma wafers.

The disadvantage of chromatographic systems is that compounds can remain on the columns or move down the column so slowly that they are missed. For example, under the conditions for phosphate and phosphite ions, no peaks were found for pyrophosphate or hypophosphite ions. Other oxophosphorus acids, including those mentioned in Ohashi and Yoza's paper, were not available for this study. Other chromatographic conditions may reveal these and other phosphorus compounds in a PSG film.

Because only two compounds were found by ion chromatography, whereas the wet chemical data indicated the presence of three compounds, the total quantity of phosphorus found by colorimetry using

No attempt has been made to date to quantitate the suspected fourth compound.

Table III. Weight Percent Phosphorus in Plasma Doped Oxides

No.	Total	P ₂ O ₅	P ₂ O ₃	PH ₃
A-1	9.5	6.2 (65.3)*	2.9 (30.5)	0.4 (4.2)
A-2	5.6	4.0 (71.4)	1.1 (19.6)	0.5 (9.0)
A-3	5.2	3.9 (75.0)	0.9 (17.3)	0.4 (7.7)
A-4	5.0	4.1 (82.0)	0.4 (8.0)	0.5 (10.0)
A-5	5.4	3.9 (72.2)	1.0 (18.5)	0.5 (9.3)
B-1	4.1	3.3 (80.5)	0.6 (14.6)	0.2 (4.9)
B-2	4.1	3.4 (82.9)	0.5 (12.2)	0.2 (4.9)
C-1	5.0	3.8 (76.0)	1.1 (22.0)	<0.1 (2.0)
C-2	2.3	1.9 (82.6)	0.4 (17.4)	<0.05 (<1.0)
C-3	7.5	6.2 (82.7)	1.3 (17.3)	<0.05 (<1.0)

*Numbers in parentheses are relative percents of weight percent phosphorus.

Many LTO/LPO samples have also been studied. The results indicate that they have characteristics similar to plasma PSG. However, the quantity of the partially or unoxidized species is smaller. Like plasma PSG, the LTO/LPO also contain phosphorus pentoxide, trioxide, and phosphine. The 4.38 IC peak was not found in most of these films; however, when it was found, it appeared as a very slight trace.

One interesting result on one set of "atmospheric CVD" PSG films is worth mentioning. This set gave higher colorimetric results on oxidation indicating the presence of suboxides of phosphorus. Not having seen suboxides of phosphorus in atmospheric CVD films, we questioned the process used to make these films. The oxides were grown in an atmospheric system using a silane/oxygen ratio of 1/17 and various amounts of 5% phosphine in argon. The system, however, had been connected to a vacuum system and the temperature used was 410°C. In other words, the system had been converted to an LTO/LPO system and gave results accordingly.

In conclusion, it has been shown that plasma, plasma enhanced, and LTO/LPO PSG and BPSG films contain phosphorus pentoxide, phosphorus trioxide, and phosphine. Although not discussed, we have found that BPSG films act the same as PSG films in this regard. There is strong evidence by both colorimetry and ion chromatography that a fourth compound exists. The fourth phosphorus compound that is indicated by colorimetry may or may not be the same as that causing the 4.38 peak in ion chromatography. The data to date on the presence and identification of this compound are ambiguous and need further study.

The known compound in PSG films can be quantitatively measured colorimetrically. The ion chromatographic data based on the measurement of phosphate and phosphite ion do not give accurate results for total weight percent of phosphorus. The difference between the IC results and colorimetric results is believed to be due to unidentified or missing peaks in the IC that contain phosphorus. Until these compounds are identified, the most reliable method for measuring the

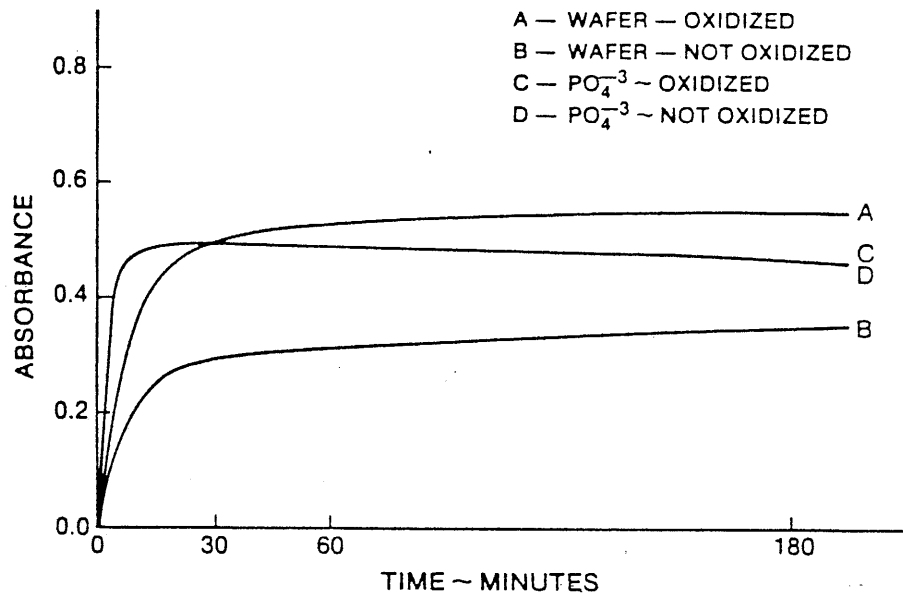


Fig 1 - Color Development Vs. Time

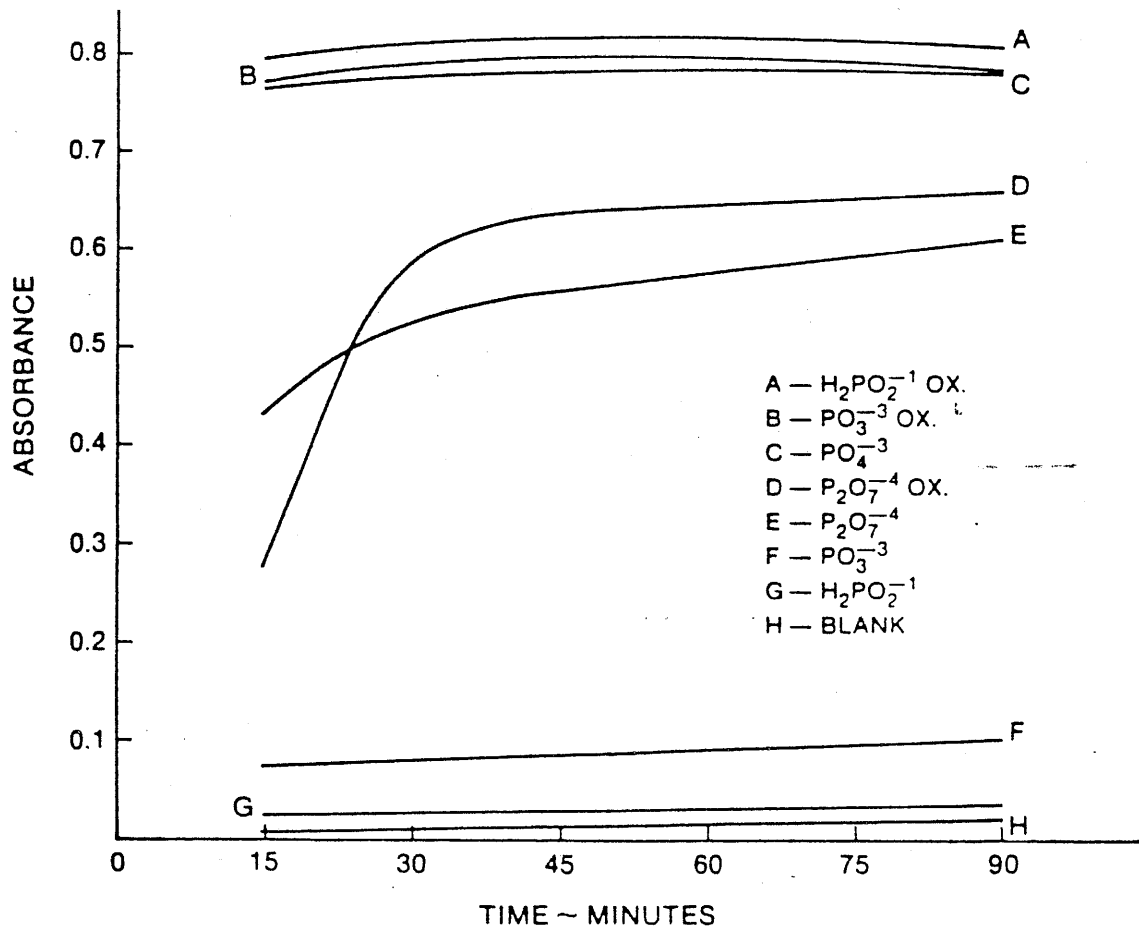


Fig 2 - Time Study on Oxoacids of Phosphorus Molybdate Blue Reaction

Fig 4 - Phosphorus compounds that give positive Mo ion tests without a reducing agent.

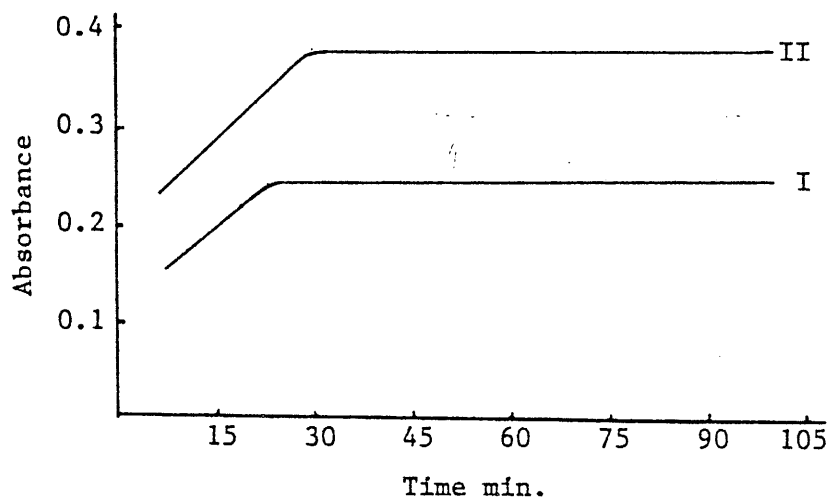
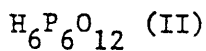
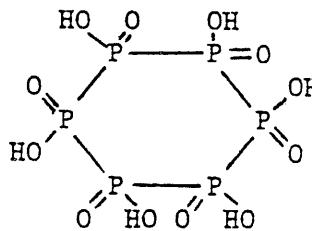
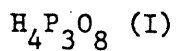
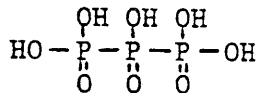
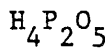
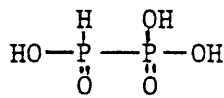


Fig 5 Ion Chromatography Study - cont.

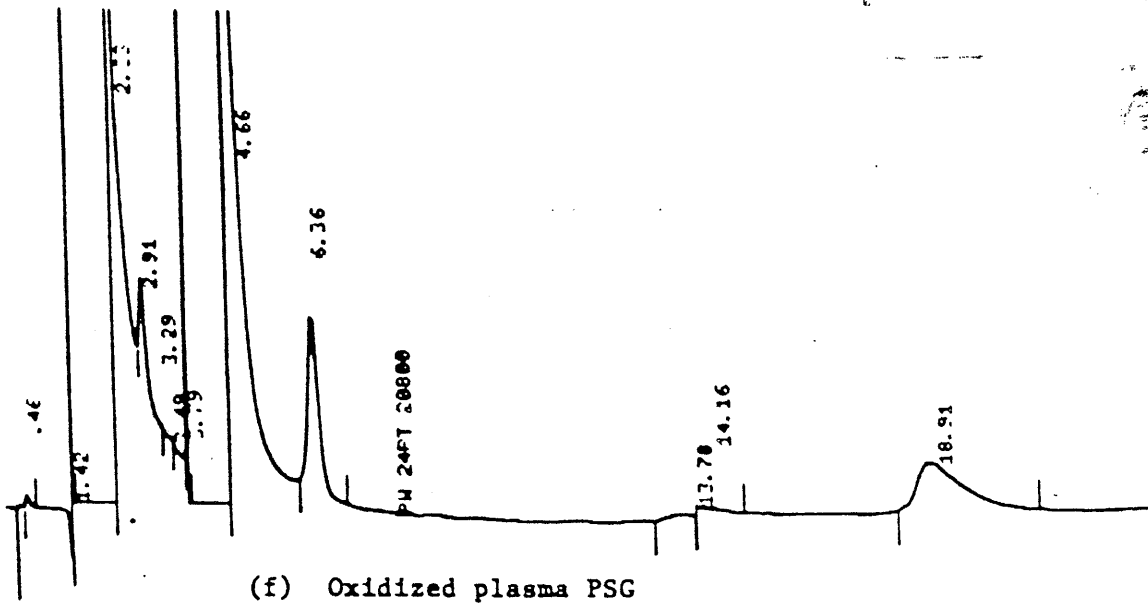
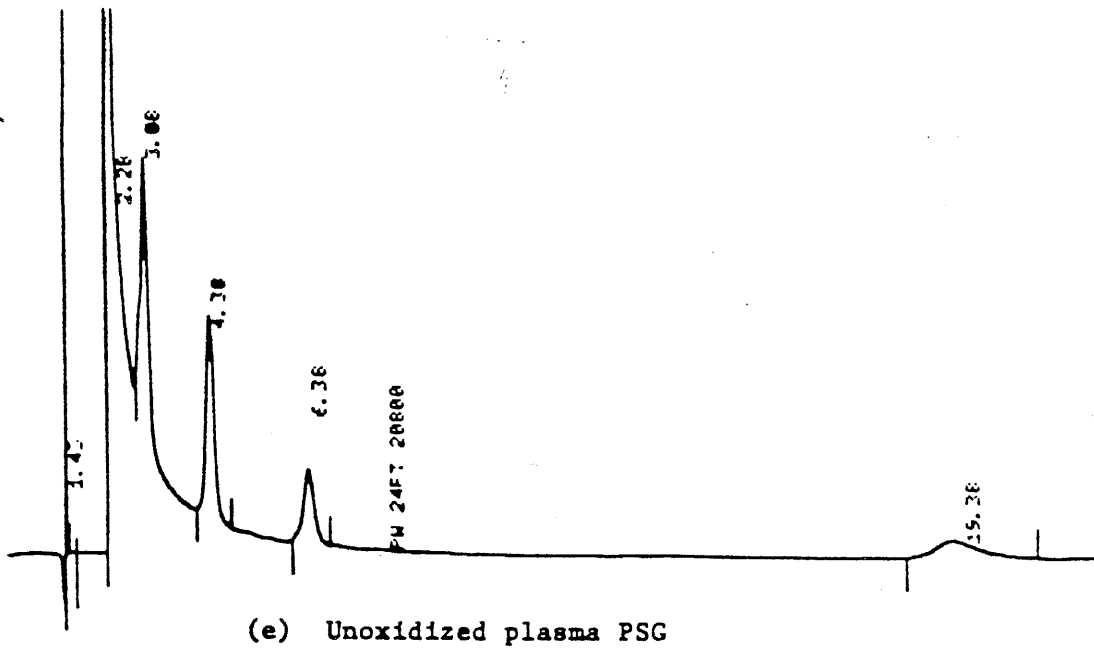
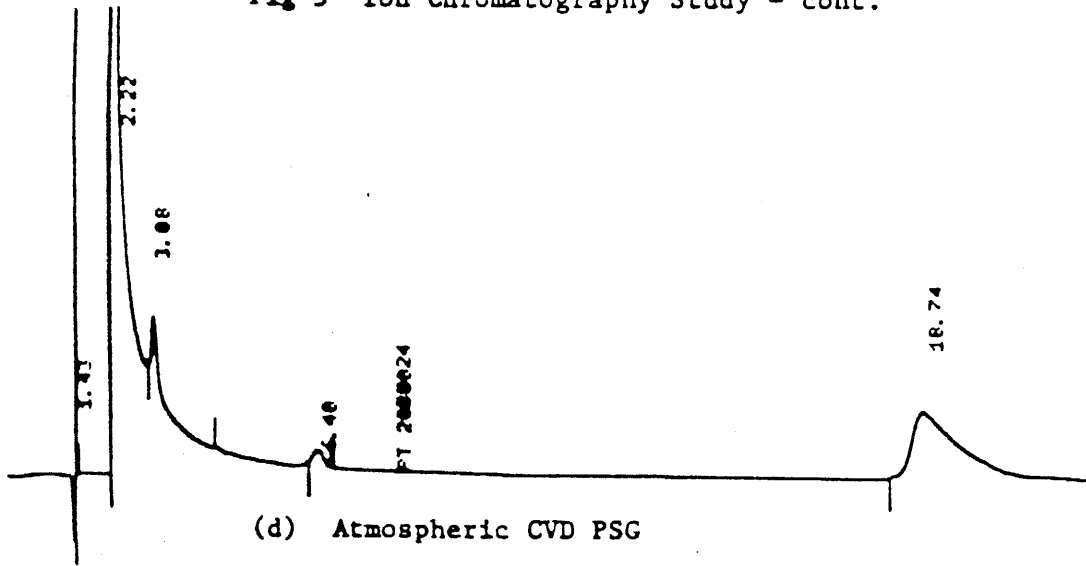


Fig 6 - P-31 NMR of plasma PSG film.

N1915.. 001 RMK
BALAB'S SAMPLE

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TWO-LEVEL DECOUPLING
P2* 4.00 USEC
D3= 10.00 MSEC
D5= 2.00 SEC
NA = 2000
SIZE = 32768
AT = 475.14 MSEC
OPD ON = 1
ABC ON
BUTTERWORTH FILTER ON
DB ATT = 3
ADC = 12 BITS
AI = 6
SW = +/- 17241.3
DM = 29
RC = 10 USEC
DE = 29 USEC
TL HIGH POWER ON
OF = 11388.31
9F = 121.479633
EM = 3.00
PA = 51.6
PB = 6.8
SCALE = 50.00 HZ/CM
TWO-LEVEL OF .1115 PPM/CM

4.325

