AXIC APPLICATION REPORT

Analysis of Phosphorus in PSG and BPSG with the Axic-100 XRF System

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CONTROL OF PHOSPHORUS CONCENTRATIONS in all types of chemical vapor deposited (CVD) silicate films is critical. The amounts of phosphorus, and boron in the case of BPSG, influence film etch rates and reflow temperature. Also, excess phosphorus in the presence of moisture can lead to the formation of corrosive phosphoric acid and device failure. Of primary importance as device geometries shrink, is precise measurement of dopant concentrations to better than ±0.1 Wt. % (2σ) in both borophosphosilicate (BPSG) and phosphosilicate (PSG) glasses in order to control reflow temperature accurately. This kind of measurement precision is not easily attained and demands close attention to all key factors affecting instrument stability as well as counting statistics.

X-ray fluorescence spectrometry (XRF) is particularly well suited for analyzing all types of silicate glass films, for several reasons:

- Measurement is fast and nondestructive and can be performed in the fabrication area by unskilled personnel;
- Both film thickness and composition can be determined simultaneously;
- Total average elemental concentrations of phosphorus (P) can be determined, regardless of film thickness, composition, and phosphorus speciation (oxide and other forms of phosphorus present);
- High precision measurement is possible.

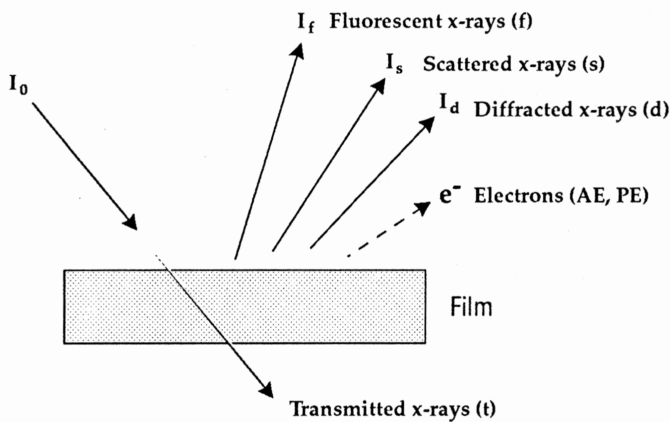
Two types of XRF systems have been employed to measure thin films: *energy dispersive* (EDS) and *wavelength dispersive* (WDS). Each has its advantages and weaknesses, depending on film type and composition. The EDS system is able to analyze many elements simultaneously, but detector resolution is inferior by a factor of 10 to 20 (depending on whether the detector is a silicon diode or proportional counter) than that of a WDS system. Detector resolution is only critical when the characteristic lines of two or more elements overlap severely; e.g., silicon and phosphorus, silicon and aluminum, tungsten and silicon, tantalum and silicon, platinum and silicon, and others. Also, provided there is ample excitation flux, a WDS system can handle higher x-ray count rates than an EDS system; hence, it often will provide better measurement precision. However, without multiple detectors and crystals a WDS system can only analyze one element at a time. And the close-coupled geometry of an EDS system, combined with a high power x-ray source, allows use of secondary targets and monochromatic excitation, which result in lower background and improved excitation efficiency. Which type of XRF system is optimal for measurement of a given film system will depend on the elements present and on the measurement precision required.

The physics of XRF glass films analysis

Measurement of phosphorus concentrations in glass films involves three key logarithmically related variables: composition of the film and substrate, film thickness and film density. While counting and relating the number of characteristic phosphorus x-rays emanating from the sample film to the average total weight percent P present is simple in principle, the actual determination is not trivial. This is particularly true if the other two variables are unknown, which frequently is the case. Let us examine the physics of the x-ray fluorescence spectrometry measurement process in more detail (see Figure 1, following page).

To measure the composition of a silicate glass film, regardless of whether an EDS or WDS system is used, a beam of incident x-rays from a source (often a rhodium target x-ray tube) is aimed at the sample. The incident beam, primarily composed of Rh L-lines at 2.7 keV and Bremsstrahlung radiation, passes through the glass film and penetrates several microns into the substrate, fluorescing the elements present—Si, O, and P, and B in the case of BPSG. The characteristic x-rays coming from each excited element have different energies and related escape depths from within the film. The lighter the element, the shallower the escape depth.

Glass films can be very complex matrices, even though they are elementally simple; chemistry and density can vary widely. The most difficult variable to deal with is film density, since it is dependent not only on composition but film structure as well. While film density might be measured by weighing the substrate before and after deposition and measuring the average film thickness with an ellipsometer, there is no way of measuring the film density directly by XRF unless the film thickness is known in advance. This is possible, for XRF fundamentally measures mass per unit area; thus, knowing a film's thickness, its density can be calculated. Therefore, when making accurate phosphorus concentration determinations in glass by XRF, it is necessary to use calibration standards having the same density as the unknowns (e.g., APCVD standards for APCVD films, but not APCVD standards for LPCVD or PECVD films) or to measure the film thickness prior to making the XRF film measurement, then enter the independently determined thickness value in the XRF algorithm to make the density correction.



Absorption of x-rays and electrons from the substrate

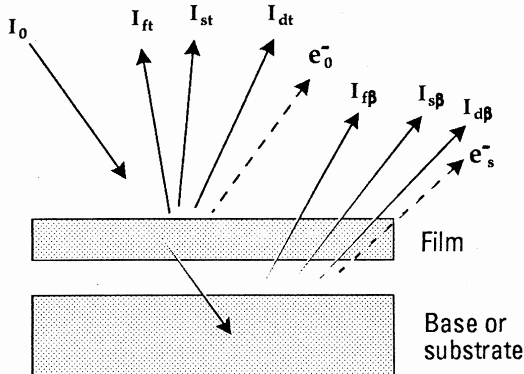
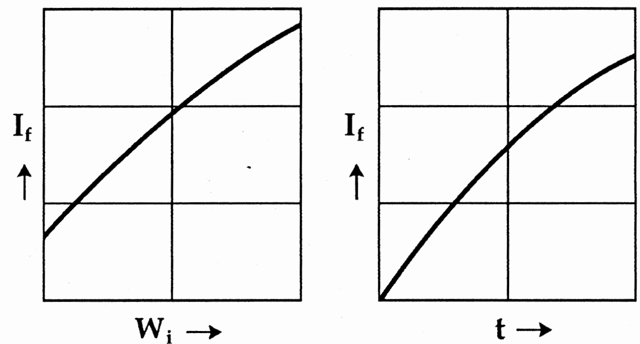


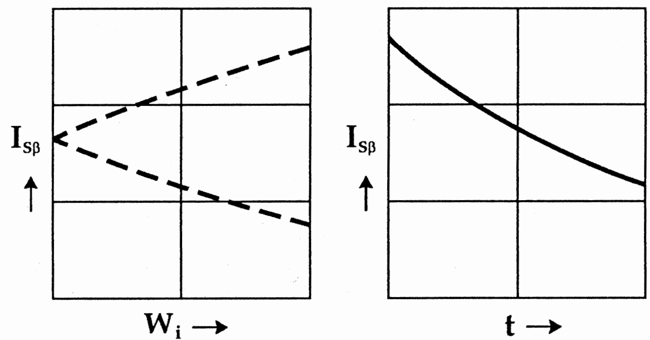
Fig. 2. Matrix effects affecting the intensity of characteristic x-rays.



a. Emission line intensity from the film. *The intensity of characteristic phosphorus x-rays increases logarithmically with increasing phosphorus concentration (W_i) and film thickness (t).*

$$I = \frac{Q_t P_t I_o}{\mu \rho}\left[1 - \exp(-\mu\rho t)\right]$$

Where:
μ = *Mass absorption coefficient*
ρ = *Film density*



b. Absorption of the substrate signal in the film. *The intensity of characteristic silicon x-rays coming from the substrate, however, decrease with an increase in film thickness, but may increase or decrease in proportion to the component ratio of the elements in the film.*

$$I = A\exp\left[-(\mu \csc \phi_1 + \mu \csc \psi_2)\rho t\right]$$

Where:
ϕ_1 = *Incident beam angle*
ψ_2 = *Take-off angle of Si line*

Fig. 1 (left). Interaction of x-rays with matter. *When a beam of x-rays is allowed to impinge upon a film and/or substrate, several events occur simultaneously. Some incident x-rays are scattered, some are diffracted if the film or substrate are single crystal material, and fluorescent characteristic x-rays for each element, as well as Auger (AE) and photoelectrons (PE), are generated. It is the characteristic x-rays which are of interest, for they allow simultaneous analysis of film thickness and composition.*

Phosphorus measurement procedures with the AXIC-100

The AXIC-100, a combined wavelength dispersive (WDS) and energy dispersive (EDS) XRF system, is ideally suited for measuring total phosphorus concentrations in a fabrication environment. Small in size (2 feet square and 20 inches high), this dedicated tabletop system can be easily operated by production personnel. It is able to make rapid, nondestructive, and precise determinations of film thickness and composition on silicon wafers from 2 to 8 inches (500 to 2000 mm) in diameter. All types of phosphorus doped glass films (PSG, BPSG, and polysilicon) can be analyzed over a broad range of film thicknesses and phosphorus concentrations:

- Typical range of film thicknesses: 300 to 30,000Å
- Typical phosphorus concentration range: 0.1 to 10+ Wt%

Overall measurement precision—a function of the film thickness, composition and density, overall instrument mechanical and electrical stability, and the analysis time—is typically ±0.1 Wt% (2σ) after a few minutes of data collection. The thinner the film and/or the lower the phosphorus concentration, the longer the analysis time or the higher the x-ray tube current must be in order to provide good counting statistics and measurement precision.

System calibration

Before the instrument can be calibrated, it is necessary to generate a matrix of standard films (all from the same CVD process) covering the range of film thicknesses and phosphorus concentrations to be monitored. This matrix should include several samples for each matrix point, because it will be necessary to destroy some of the samples in the analysis process. All matrix samples should first be analyzed nondestructively by XRF and ellipsometry. Then selected samples should be analyzed by two independent methods for phosphorus concentration—wet chemistry and microprobe—and the results cross-correlated. Films must be at least 5,000 Å thick in order for accurate microprobe measurement to be made.

AXIC has complete sets of carefully characterized PSG and BPSG calibration standards for different CVD processes; hence, it may be more convenient for the customer to send samples to AXIC for characterization as secondary standards. Film thickness readings, preferably film thickness maps by an ellipsometer or film thickness analyzer (FTA), should be provided with each sample.

Instrument calibration is achieved by plotting a regression curve, using a proprietary AXIC algorithm, from data acquired from a matrix of standard films. When running standards, long acquisition times are used in order to improve measurement precision. Once a calibration curve has been established for a set of well-characterized standards covering a broad range of film thickness and composition, the curve is programmed into an EPROM. The system is calibrated at AXIC prior to shipment using the customer's own standards. The table below lists a typical matrix of APCVD PSG standard films.

T_{given} (kÅ)	T_{Axic} (kÅ)	$\%P_{given}$ (Wt%)	$\%P_{Axic}$ (Wt%)
3.38	3.41	2.1	2.0
10.03	10.14	2.0	1.9
3.51	3.43	3.9	3.8
10.11	10.31	3.9	3.9
3.37	3.20	6.3	6.4
9.81	10.07	6.0	5.9
3.36	3.44	8.2	8.2
6.49	6.60	8.2	8.2
9.73	9.70	8.1	8.2

After delivery to the customer, it is possible to analyze any type of phosphorus doped glass film, regardless of any differences in density or film type. If the density of the unknown film is different from that of the standards, a correction to the P concentration value must be made by independently measuring the film thickness at the same spot at which the XRF measurement was made. The difference in the AXIC and ellipsometer or FTA thickness values, measured at the same location, is primarily due to differences in the densities of the standards and the measured film.

Corrections for differences in film density

To make a correction for the difference in density between an unknown film and calibration standards, it is simply a matter of dividing the XRF thickness value by

	HD Film	LD Film
T_{Axic}	10.49 kÅ	8.72 kÅ
$T_{ellipsometer}$	10.14 kÅ	9.78 kÅ
$\%P_{Axic}$	3.9 Wt%	5.5 Wt%
$\%P_{density\ corrected}$	4.0 Wt%	4.9 Wt%
Calculations:	(10.49/10.14)(3.9) = 4.0 (8.72)/9.78)(5.5) = 4.9	

the ellipsometer or FTA value and multiplying the result by the XRF phosphorus concentration determination. For example, the density corrected phosphorus values are calculated for a high density (HD) annealed film and a low density (LD) PECVD film above.

When using the AXIC-100 XRF system with the optional RS-232 interface and personal computer package, the density correction can be made automatically by simply entering the film thickness into the program before analyzing the film.

Variations in density between APCVD, LPCVD, and PECVD films—and even within one CVD process run under different deposition conditions—can be considerable. Hence, it is important to check film thickness independently to verify measurement accuracy. If variations in film density are of concern, the safe procedure is to enter an independent film thickness into the AXIC software program before analyzing the sample.

System analysis procedure

All glass film measurements are normalized to the signal from a blank silicon wafer permanently mounted at the rear of the AXIC-100 sample drawer. This is accomplished by periodically (two or three times a day) running a short calibration procedure—collecting a reference signal from the blank silicon wafer for several minutes, before analyzing a standard or unknowns. The silicon reference value is used to calculate the film thickness. After the silicon reference has been run, the overall system calibration can be checked by analyzing a phosphorus standard wafer. Once calibrated, unknown samples may be run by simply placing them one at a time in the sample drawer and closing it. Analysis is automatic. After acquiring data for a few minutes, the film's thickness and phosphorus concentration are displayed.

If no samples have been run for a period of over 30 minutes, the system automatically goes into the silicon calibration mode to correct for any drift which may have occurred. The silicon calibration routine may be run at any time, if necessary, through keyboard selection. Finally, if it is necessary to correct for variations in film density when analyzing an unknown, it is simply a matter of entering the film thickness (only possible if the optional RS-232 interface/computer based model is being used) before closing the sample drawer.

Summary

To summarize, the advantages of the AXIC-100 XRF system for analysis of phosphorus in silicate glasses in the fabrication environment include the following:

- The system is a tabletop unit with a small footprint;
- No vacuum system is required; the sample chamber is helium flushed;
- Precise phosphorus measurements are possible in just a few minutes;
- The system is easy to calibrate and to use;
- Corrections for film density variations can be made.

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