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Techniques for Analysis of Thin Films

Weight % Phosphorus (P) by colorimetry in PSG and BPSG Films
(T100, T101, T102)

The concentration of phosphorus in silicon oxide films is measured using classical wet chemical method. The absolute phosphorus concentration in oxide films is quantified accurately and precisely using NIST standards. This method enables the phosphorus species in the oxide film to be measured as total P (T100) and as P_2O_5 (T101) and P_2O_3 (P_4O_6) (T102). These absolute phosphorus results allow the parameters of a chemical vapor deposition equipment to be tracked accurately and reproducibly. Since the results are absolute and accurate, they can be used as standards to calibrate secondary analytical techniques such as X-ray instruments (EDS and WDS) and FTIR instruments.

In the method, a known weight of the doped oxide film is etched off the silicon wafer with hydrofluoric acid and diluted with ultrapure deionized water. A molybdate reagent and a reducing agent are added to the solution to react with the phosphorus to form a blue complex. The absorbency of this blue molybdate complex is measured at a selected wavelength on a UV/VIS spectrophotometer. The spectrophotometer is calibrated by a blank and three phosphorus standards which are prepared from a NIST certified phosphorus standard.

Total Wt % total P (T100) is a sum of the concentrations of P_2O_5 and P_2O_3 in the doped oxide film. In the colorimetry procedure, only P_2O_5 species and not P_2O_3 species reacts with the molybdate molecules to form the blue complex. In order to measure total amount of P, a strong oxidizing agent is initially added to the sample to convert all P_2O_3 into P_2O_5 active form.

However, in many instances, it is desirable to know the ratio of P_2O_5 and P_2O_3 species. It is believed that P_2O_5 is the most stable P species and that the reflow temperature of PSG and BPSG films is directly dependent on the P_2O_5 concentration in the film. The presence of a substantial amount of the unstable P_2O_3 species is undesirable since it is unstable and causes poor reproducibility of reflow temperature. In addition, P_2O_5 is believed to getter ionic, mobile impurities such as Na^+ much more efficiently than suboxides such as P_2O_3.

The concentrations of P_2O_5 and P_2O_3 can be obtained by differentiating the phosphorus dopant concentration as Wt % P and P_2O_5 (T101) and Wt % P as P_2O_3 (T102). In order to do this, the total amount of phosphorus is measured first following the procedure for Wt % P (T100). In another step, the concentration of P_2O_5 only is measured by not adding the oxidizing agent to the solution. The Wt % P as P_2O_3 (T102) is then determined by subtracting the Wt % P as P_2O_5 from the Wt % total P.

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The results for phosphorus concentrations are expressed as weight % and are reported to three significant numbers. The detection limit of the method is 0.20 Wt % P. The accuracy and precision (RSD) of the colorimetric procedure are ± 3.0% (three standard deviations). In terms of Wt % P, the accuracy and precision ranges are as follows:

Quality Control Criteria

0 - 1 wt %	±.05 wt %
1 - 3 wt %	±.075 wt %
3 - 5 wt %	±.10 wt %
5 - 7 wt %	± .125 wt %
>7 wt %	± .15 wt %

Each sample (or wafer) is analyzed by breaking two small pieces from the center of the wafer; the size of a piece is dependent on the thickness of the silicon oxide film. To obtain the best results, the thickness of the film should be between 2000 Å (0.2 µm) and 12,000 Å (1.2 µm).

Each wafer submitted for analysis is analyzed in duplicate. The average of the duplicate results is reported. The purpose of performing duplication of a wafer is to make sure the analytical method is working correctly every time on a batch to batch basis. Poor duplication of results also indicates that a client's wafer has poor homogeneity in the distribution of phosphorus in the film. However, the best evaluation of homogeneity of phosphorus concentration is by performing a wafer mapping test (T104).

Wafer Mapping - Weight % Total P at 5 areas on the wafer
(T104)

The purpose of this test is to determine the distribution of phosphorus dopant concentration in the thin film throughout the whole wafer. In this test, a small piece is selected from the center of the wafer, and four more other pieces are selected near the edge of the wafer as shown in Figure 1. These five pieces taken from the same wafer, are analyzed for Wt % total P following standard operating colorimetric procedure. Five values of Wt % total P are reported. The variation of these results shows how the phosphorus dopant concentrations distributed throughout the wafer.

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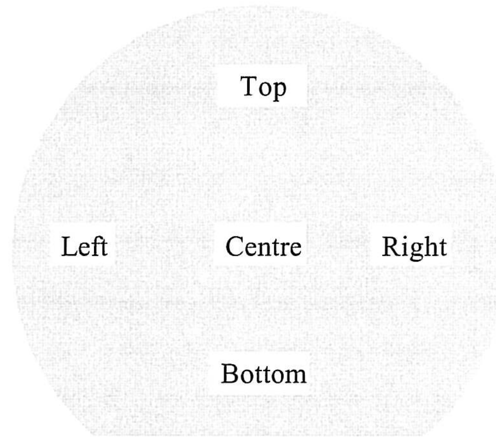

Figure 1. Wafer Mapping

Wt % Boron (B) and Wt % Phosphorus (P) by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) in PSG and BPSG Films
(T105, T106, T107, T151, T152, T153)

The total elemental concentration of B in silicon oxide films is measured by ICP-OES. In addition to colorimetry, total P concentration in a thin film can also be measured using ICP-OES. ICP-OES quantitatively and accurately measures the total amount of B and P in the oxide film regardless of their oxidation states or chemical forms provided that they are in solution. The B and P results obtained by ICP-OES are quantitated using NIST standards. These absolute B and P results allow the parameters of chemical vapor deposition equipment to be tracked accurately and reproducibly. Since the results are absolute and accurate, they can be used as standards to calibrate secondary analytical techniques such as X-ray instruments (EDS and WDS) and FTIR instruments.

In this method, a known weight of the doped oxide is etched off the silicon wafer with hydrofluoric acid and diluted with ultrapure deionized water to a known volume. The B and P concentrations in the solution are then determined by ICP-OES.

In the ICP-OES analysis, the solution is converted first into fine aerosol droplets via a nebulizer spray chamber system. The aerosol droplets are then introduced into a high temperature (6000K) argon plasma source. In the Argon plasma, the fine droplets are vaporized and elements in the sample such as B and P are atomized, ionized and excited. Electronically excited B and P atoms and ions emit photons during their transitions to the ground states. Emission photons at a selected wavelength are measured by a detector such as a photomultiplier tube as a signal. The concentration of B or P in the solution is

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directly proportional to the signal intensity obtained from the sample. Actual concentration is obtained by using NIST calibration standards.

The instrument used for the determination of B and P is a Thermo Jarrell Ash IRIS ICP-OES. B and P calibration standards are prepared from certified NIST standards. The results for B and P are reported to three significant numbers as Wt % B (T105, T106, T107) and as Wt % Total P (T151, 0.2 wt % B, and 0.2 wt % P, respectively). The accuracy and precision (RSD) of the ICP-OES method is about $\pm$ 3.0% (three S_x) for B and for P concentrations. In terms of Wt %, the ranges are as follows:

Quality Control Criteria

Range	Tolerance
0 - 1 wt %	$\pm$.05 wt %
1 - 3 wt %	$\pm$.075 wt %
3 - 5 wt %	$\pm$.10 wt %
5 - 7 wt %	$\pm$ .125 wt %
>7 wt %	$\pm$ .15 wt %

Each sample (or wafer) submitted for B and/or P analysis is analyzed by breaking two pieces from the center of the wafer. The size of the sample piece is dependent of the thickness of the silicon oxide film. To obtain the best results, the thickness of the film should be between 2000 Å (0.2 µm) and 12,000 Å (1 µm).

Each wafer submitted for analysis is analyzed in duplicate. The average of the duplicate results is reported. The purpose of performing duplication of a wafer is to make sure that the analytical method is working correctly every time on a batch to batch basis. Poor duplication of results also indicates that a client's wafer has poor homogeneity in the distribution of P in the film. However, the best evaluation of homogeneity of B and P concentrations in a thin film is by performing a wafer mapping test (T108 and T 154 respectively).

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Wafer Mapping - Wt % Total B and Wt % Total P at 5 areas on the wafer
(T108), (T154)

The purpose of this test is to determine the distribution of boron and phosphorus dopant concentration in the thin film throughout the whole wafer. In this test, a small piece is selected from the center of the wafer, and four more other pieces are selected near the edge of the wafer as shown in Figure 2. These five pieces taken from the same wafer, are analyzed for Wt % total B and/or Wt % P following standard operating ICP-OES procedure. Five values of Wt % total B and/or total P are reported. The variation of these results shows how the boron and phosphorus dopant concentrations are distributed throughout the wafer.

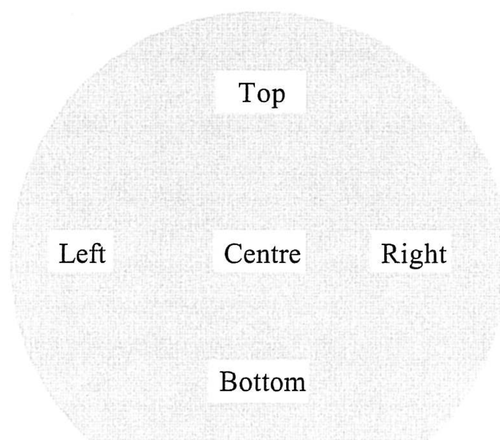

Figure 2. Wafer Mapping

Weight % Silicon by Colorimetry in Aluminum (Al) Film and Target
(T109)

The concentration of silicon in Al films and targets is measured using classical wet chemical method. The absolute silicon concentration is quantitated accurately and precisely using NIST standards. Since the results are absolute and accurate, they can be used as standards to calibrate secondary analytical techniques such as X-ray instruments (EDS and WDS).

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For the measurement silicon concentration in an Al thin film, the aluminum must be deposited on top of a silicon nitride film. The silicon nitride barrier layer should be at least 2000 Å (0.2 µm) thick and must be free from oxygen impurity. Silicon nitride layer which contains a significant concentration of oxygen is attacked by the etchant used in this procedure; this will result in a high result for silicon.

Aluminum target can be submitted for silicon analysis in the original target form, as small cutoff pellets or as shavings. The homogeneity of silicon concentration in the target can be revealed by sampling different areas of the A1/Si target.

In this method, a known weight of a Al film or target is dissolved by a etchant and diluted with ultrapure deionized water. The pH of the solution is adjusted and a molybdate and a reducing agent are added to the solution to form a blue complex with the silicon in a reaction similar to that for the determination of phosphorus in PSG and BPSG films. The absorbency of this blue molybdate complex is measured at a selected wavelength on a UV/VIS spectrophotometer. The spectrophotometer is calibrated by a blank and three silicon standards which are prepared from a NIST traceable silicon standard.

The result for silicon is expressed as weight % and is reported to three significant numbers or two decimal places. The detection limit of the Si colorimetric method is 0.10 wt %. Quality control criteria is $\pm$ .10 wt % for 1 wt % Si sample or maximum deviation of replicates of 0.2 wt %.

Each sample (or wafer) is analyzed by breaking a quarter section of the wafer. The size of this section is dependent on the thickness of the Al film. To obtain the best results, the thickness of the film should be between 3000 Å (0.3 µm) and 10,000 Å (1 µm).

Each sample is analyzed in duplicate. The average of the duplicate results is reported. The purpose of performing the analysis in duplicate is to make sure our analytical method is working correctly every time on a batch to batch basis. Poor duplication of results also indicates that a client's wafer has poor homogeneity in the distribution of silicon in the film.

Weight % in Copper by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) in Aluminum Film and Target
(T110)

The concentration of copper in Al film and target is measured using ICP-OES. The absolute copper concentration is quantitated accurately and precisely using NIST standards. Since the results are absolute and accurate, they can be used as standards to calibrate secondary analytical techniques such as X-ray instruments (EDS and WSD).

If an Al film is to be analyzed for copper concentration only the Al film can be deposited directly on a silicon wafer, on an oxide layer, or on a silicon nitride layer. However, if the

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same wafer is to be analyzed for Wt % Si (T109) as well, the Al film must be deposited on top of a silicon nitride film. The silicon nitride barrier layer should be at least 2000 Å (0.2 µm) thick and must be free from oxygen impurity. Silicon nitride layer which contains significant concentration of oxygen is attacked by the etchant used in the Wt % Si procedure; this will result in a high result for silicon.

Aluminum target can be submitted for copper analysis in the original target form, as small cutoff pellets or as shavings. The homogeneity of copper concentration in the target can be revealed by sampling different areas of the Al/Si target.

In this method, a known weight of a Al film or target is dissolved by an etchant and diluted with ultrapure deionized water to a known volume. The copper concentration of solution is analyzed by ICP-OES. The ICP-OES analysis, the solution is converted first into fine aerosol droplets via a nebulizer-spray chamber system. The aerosol droplets are then introduced into a high temperature (6000K) argon plasma source. In the Ar plasma, the fine droplets are vaporized and elements in the sample such as copper are atomized, ionized, and excited. Electronically excited copper atoms and ions emit photons during their transitions to the ground states. Emission photons at a selected wavelength are measured by a detector such as a photomultiplier tube as a signal. The concentration of copper in the solution is directly proportional to the signal intensity obtained from the sample. Standards are prepared from an NIST traceable copper standard.

The result for copper is expressed as weight % and is reported to three significant numbers or two decimal places. The detection limit of the copper in the Al film or target is 0.1 wt %.

Quality Control Criteria		Maximum Dev. of Replicates
0 - 1 wt %	±.05 wt %	0.1%
1 - 3 wt %	±.075 wt %	.15%

Each sample (or wafer) is analyzed using a quarter section of the wafer. The size of this section is dependent on the thickness of the Al film. To obtain the best results, the thickness of the film should be between 3000 Å (0.3 µm) and 10,000 Å (1 µm).

Each wafer is analyzed in duplicate. The average of the duplicate results is reported. The purpose of performing duplication of a wafer is to make sure our analytical method is working correctly every time on a batch to batch basis. Poor duplication of results also indicates that a client's wafer has poor homogeneity in the distribution of copper in the film.

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Weight % of bulk metal by ICP-OES in other type of thin films (T111, T112)

The concentration of bulk metals in other types of thin film such as titanium tungsten (TiW), nickel chrome (NiCr), and iron chrome (FeCr) films on silicon wafers can be quantitatively measured by ICP-OES. For example, the Wt % Ti and/or Wt % W can be measured in a TiW film, and Wt % Ni and Wt % Cr can be measured in a NiCr film. The concentrations of all metals analyzed by ICP-OES are calibrated using NIST standards. These Wt % are absolute results and are not normalized to 100% as in the case results provided by other technique such as RBS.

Since the etchant contains HF, for TiW films, the film must be deposited on a silicon nitride film or bare silicon. The silicon nitride film should be about 3000 Å and must be free of oxygen or hydrogen impurity. Results can be attained (but would not be absolute) for TiW on silicon oxide films by normalizing to 100%.

Using this method, a known weight of the thin film is etched off the substrate with a etchant and diluted with ultrapure deionized water to a known volume. The concentrations of the metal of interest in the solution are measured by ICP-OES. In the ICP-OES instrument, the solution is converted first into fine aerosol droplets via a nebulizer-spray chamber system. The aerosol droplets are then introduced into a high temperature (6000K) argon plasma source. In the Ar plasma, the fine droplets are vaporized and the elements are atomized, ionized and excited. The excited analyte atoms and ions emit photons during their transitions to the ground states. These photons at selected wave lengths are measured by a photomultiplier tube as a signal. Emission signal intensity at a selected wavelength is directly proportional to the concentration of that metal in the solution. The instrument used for the determination Wt % metal is a Thermo Jarrel Ash IRIS ICP-OES. Calibration standards are prepared from certified NIST standards.

The results for the thin film are expressed as weight % and are reported to three significant numbers. The method detection limits for most metal are in the ranges of 0.10 to 0.50 wt %. The accuracy and precision of the ICP-OES method is about $\pm$ 3.0 % (three S_x) for most metal concentrations. In terms of Wt % in the thin film, the ranges of a TiW film containing 8.00 Wt % Ti and 92.0 Wt % W are as follows:

Accuracy and Precision

Weight % Ti	Three S_x

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8.00	± 0.24 %
Weight % W	± 2.8 %

Each sample (or wafer) submitted for analysis is analyzed in duplicate by breaking two small sections from the center of the wafer. The actual size of the sample piece is dependent on the thickness of thin film. To obtain the best results, the thickness of the film should be between 5000 Å (0.5 µm) and 12,000 Å (1.2 µm). The average of the duplicate results is reported.