Characterization of Silicon Oxide and Oxynitride Layers

Introduction

Thermo Scientific Theta Probe and Theta 300 have been used to characterize ultra-thin layers of silicon dioxide and silicon oxynitride on silicon using Parallel Angle Resolved XPS (PARXPS). Comparison with ellipsometry shows that the accuracy of the technique is excellent and high precision was demonstrated with a dynamic stability test. PARXPS also provides reproducible, non-destructive depth profiles of the chemical states within the layer.

This document will illustrate how PARXPS measurements of silicon oxynitride samples provides:

• Film thickness and uniformity

• Chemical state information

• Nitrogen distribution in each of its chemical states

• Nitrogen dose

The accuracy and precision of the data will also be illustrated.

Accuracy

A set of silicon oxide on silicon samples was analyzed. The thickness of the oxide had previously been measured using ellipsometry. The results, Figure 1, show excellent linearity with a unity gradient to within ~ 1%. The offset is caused by surface contamination which could not be distinguished from the oxide layer using ellipsometry. SIMS analysis shows that there is a layer of contamination approximately 0.8 nm thick, in good agreement with the PARXPS data.

Precision

Two silicon oxynitride wafers were used for a dynamic repeatability test of Theta 300. Thickness and nitrogen dose measurements were made at three sites on each wafer. The measurements were repeated ten times and the wafers were removed from Theta 300 between measurements.

The mean, standard deviation and relative standard deviation (RSD) figures are shown for thickness and nitrogen dose.
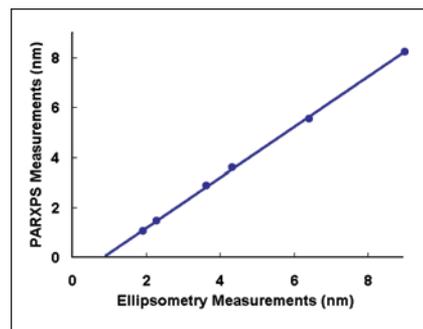

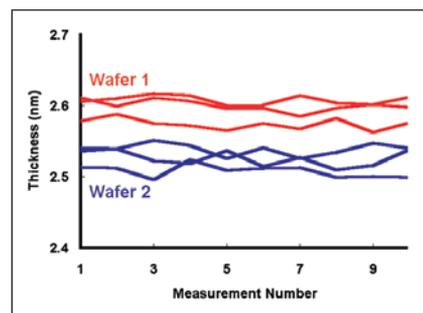Figure 1: Comparison of PARXPS and ellipsometry

Figure 2: Dynamic repeatability tests showing the thickness of the oxynitride layer at three points on each of two wafers
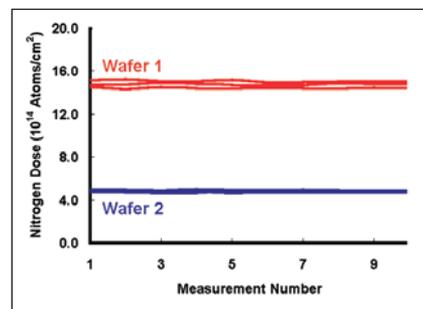

Figure 3: Dynamic repeatability tests showing the nitrogen dose in the oxynitride layer at three points on each of two wafers

Oxynitride Thickness

		SITE 1	SITE 2	SITE 3
Wafer 1				
	Mean (nm)	2.15	2.53	2.54
	SD (nm)	0.0087	0.0118	0.0082
	RSD	0.35%	0.47%	0.32%
Wafer 2				
	Mean (nm)	2.57	2.61	2.60
	SD (nm)	0.0080	0.0069	0.0088
	RSD	0.31%	0.26%	0.34%

Table 1: Reproducibility of thickness measurements from dynamic repeatability test

Nitrogen Dose

		SITE 1	SITE 2	SITE 3
Wafer 1				
	Mean (10^{14} atoms cm^{-2})	4.89	4.77	4.74
	SD (10^{14} atoms cm^{-2})	0.049	0.065	0.062
	RSD	1.00%	1.37%	1.31%
Wafer 2				
	Mean (10^{14} atoms cm^{-2})	15.10	14.80	14.43
	SD (10^{14} atoms cm^{-2})	0.091	0.097	0.066
	RSD	0.61%	0.66%	0.46%

Table 2: Reproducibility of nitrogen dose measurements from dynamic repeatability test

Wafer Map [1]

A wafer map was acquired from half a 200 mm wafer. At each of the 522 mapping points the oxide thickness was calculated from the PARXPS data and a thickness map constructed, Figure 4. A summary of the data is shown in Table 3.

The same wafer was also mapped using ellipsometry. Line scans were extracted from both the PARXPS and the ellipsometry maps. These are compared in Figure 5 and show close agreement.
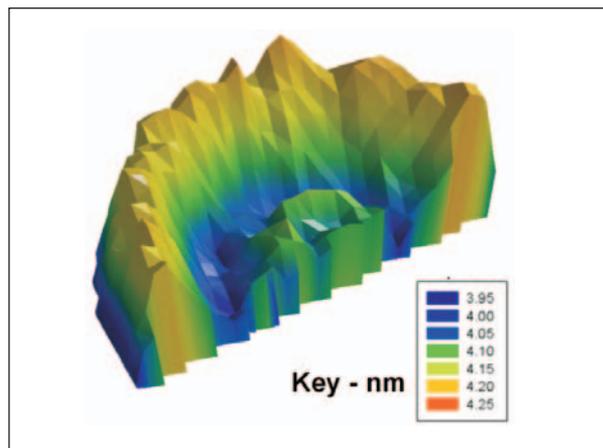

Figure 4: 3D representation of oxide thickness on 200 mm wafer from ARXPS data

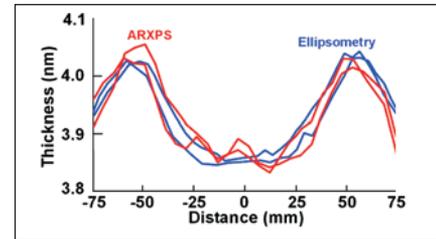| Number of mapping points	522
Acquisition time per point	30 s
Mean oxide thickness	3.93 nm
Standard deviation	0.02 nm
Relative standard deviation	0.5%

Table 3: Summary of the data in the wafer map

Figure 5: Comparison of the thickness measured using PARXPS with that measured using ellipsometry

Qualitative Analysis

Chemical States

Figure 6 shows the N 1s spectra from a silicon oxynitride layer taken at a bulk sensitive and a surface sensitive angle. These spectra show the presence of at least two chemical environments for nitrogen, (N_a and N_b) as illustrated in Figure 7.

PARXPS measurements from a silicon oxynitride layer on silicon show marked changes in the nitrogen chemistry with angle, Figure 6. While N_a is a major peak throughout the angular range, N_b is diminished at the more grazing emission angles, suggesting that N_b is located below the surface near the oxynitride/silicon interface.
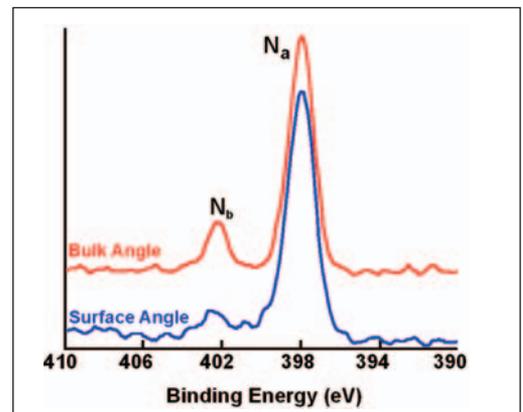

Figure 6: N 1s spectra from an oxynitride layer from bulk and surface sensitive angles
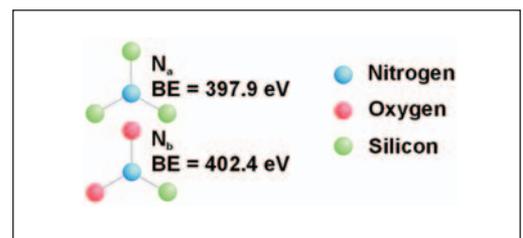

Figure 7: N 1s binding energies for the chemical environments present in oxynitride layers

Relative Depth Plot

A relative depth plot shows the ordering of the chemical species in the layer. It is obtained by measuring the peak areas from a small range of surface sensitive angles, dividing this by the intensity in a small range of bulk sensitive angles and taking the natural logarithm. This process is repeated for each species present in the spectrum and the results plotted on a chart. An example is shown in Figure 8.

This figure clearly shows the expected carbon layer at the surface, the nitrogen species at different depths within the layer and the elemental silicon (substrate) deepest within the layer.

The relative depth plot does not provide quantitative depth information, but provides an accurate indication of the ordering of layers. This method is independent of any model and so provides a very useful check when the quantitative depth information is calculated.
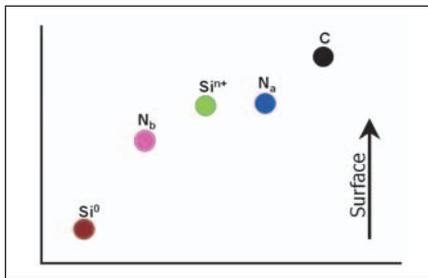

Figure 8: Relative depth plot from a silicon oxynitride layer

Depth Distribution

Using the method of maximum entropy it is possible to construct a non-destructive concentration depth profile from PARXPS data. Figure 9 shows such a profile
In this profile, it can be seen that the major nitrogen species persists through the oxynitride layer whereas the minor species (N_b) is only present near the silicon interface.

The depth profile in Figure 9 is consistent with the relative depth plot, shown in Figure 8 but provides additional essential information. Table 4 shows a summary of the thickness and dose information derived from Figure 9.
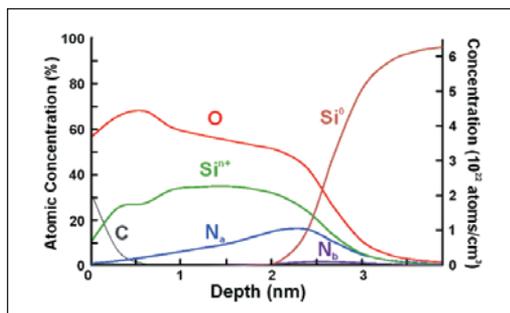

Figure 9: Concentration depth profile through a silicon oxynitride layer constructed using the Maximum Entropy method. Note that concentration axes do not apply to Si° and C profiles.

Film thickness	2.6 nm
Dose N_a	1.8×10^{15} atoms cm^{-2}
Dose N_c	1.6×10^{14} atoms cm^{-2}

Table 4: Quantitative information extracted from the depth profile in Figure 9

Comparison with Sputtering

Oxynitride layers can be analyzed by sputter profiling, using low energy ion beams. Figure 10 shows an example in which argon ions with an energy of 500 eV were used.

The sputter profile results show that N_b disappears during the early stages of the profile. This gives the impression that N_b is located close to the surface. From the PARXPS data, this interpretation is clearly incorrect. The correct interpretation of the sputter profile is that, under the influence of the ion beam, N_b is being converted into N_a. This conversion does not happen during PARXPS analysis.

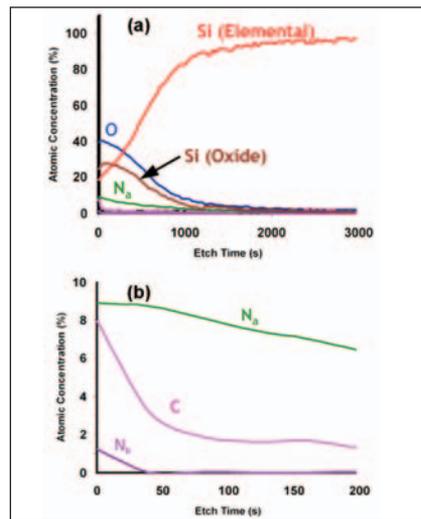Similar results were obtained using an ion energy of 250 eV.

Figure 10: Sputter profile through the same oxynitride layer as that shown in Figure 9. The ion energy used for this profile is 500 eV. (a) is the full profile and (b) is an enlargement of the early part of the profile.

Reproducibility of Profiles

In order to test the reproducibility of the data and the Maximum Entropy method for profile generation, data from an oxynitride layer were acquired three times from the same point on a wafer. The results are shown in Figure 11. In this sample nitrogen was only present in one chemical state.
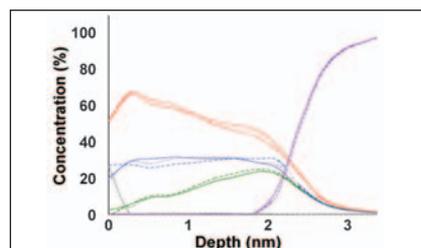

Figure 11: Comparison of three depth profiles generated from the same point on a wafer using the Maximum Entropy method. The data show excellent reproducibility.

Dose and Thickness Measurement

Both thickness and dose can be measured at various points on a wafer to produce either a profile or a map. Using Theta 300 these can be produced from complete wafers. Figure 12 shows a 49-point oxynitride thickness map from a 300 mm wafer. The mean thickness of this layer is 1.733 nm with a total thickness range of 0.054 nm and a standard deviation of 0.79%
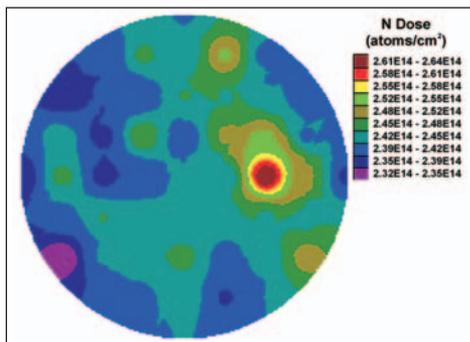

Figure 12: A 49-point oxynitride thickness map from the whole of a 300 mm wafer

A nitrogen dose map can be constructed from the same data set and is shown in Figure 13. Nitrogen dose is calculated after first correcting for its depth distribution. In this case the mean dose is 2.43×10^{14} atoms/cm^2 with a total variation of dose over the whole wafer of 0.32×10^{14} atoms/cm^2 and a standard deviation of 2.15%
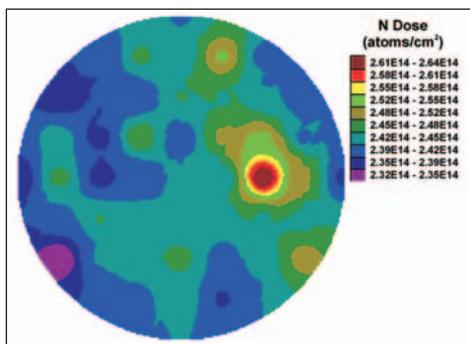

Figure 13: A 49-point nitrogen dose map from a 300 mm wafer

Conclusions

When compared with ellipsometry, for the measurement of film thickness, both the accuracy and precision of PARXPS are found to be excellent. Unlike ellipsometry, PARXPS can distinguish the chemical states of nitrogen present in the layer and provide their distribution with depth.

Ellipsometry will not take account of the thin layer of contamination which will inevitably be present at the surface of a wafer. There is a danger that measured layer thickness will include the layer of contamination. Using PARXPS the contamination layer is not included in the measurement of oxide or oxynitride thickness.

As dielectric layers become thinner, the contamination layer becomes a significant proportion of the layer thickness. It is now essential that the dielectric layer be distinguished from the contaminant layer.

Chemical state maps and thickness maps of a wafer can be constructed from the same data set.

An oxidized form of nitrogen has been found by PARXPS to be present at the interface with the silicon. When this layer is analyzed using sputter depth profiling the oxidized form of nitrogen is removed during the initial stages of profile acquisition. This could lead to the false conclusion that the oxidized nitrogen is at the surface of the layer not at the interface between the oxynitride and the silicon. This is because the range of the argon ions used for sputtering is similar to the layer thickness. It is possible, therefore, for the ion beam to interact with the interface region of the layer from the start of the profiling. In this case the result of the interaction is to reduce the oxidized nitrogen to the lower binding energy.

Reference

1. M.P. Seah and R.G. White Surface and Interface Analysis, 2002, 33, 960

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