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Advancements in the Characterization of “Hyper-Thin” Oxynitride Gate Dielectrics Through Exit Wave Reconstruction HRTEM and XPS

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Introduction

The physical thickness of silicon oxy-nitride gate dielectric materials currently in development have dimensions in the range of 15-20Å (~6-8 oxygen atoms), while approaching the dielectric constant equivalent oxide thickness (EOT) of 12Å silicon dioxide. These structures present serious challenges in meeting stringent requirements within the semiconductor industry for precise determination of thickness, interfacial roughness and chemical distribution. High-resolution transmission electron microscopy (HRTEM) has been considered by many end users of the data as a direct and accurate representation of the sample structure and the ultimate method to accurately measure film thickness. Strictly speaking, HRTEM images of periodic crystalline structures are interferograms. The image data is generated from the superposition of the multiple electrons beams scattered by the periodic atomic columns in the lattice interfering with the direct (“transmitted”) beam. Consequently, a HRTEM image may not reflect the actual structure of the sample depending upon the focus, astigmatism, the sample thickness, as well as other microscope parameters. Statistical analysis of HRTEM thickness measurements on 20Å oxynitride films indicated an uncertainty up to approximately 3.3Å¹ for the determination of the gate oxide thickness. Another study completed HRTEM image simulations of gate oxide structures and found that thickness measurements on a conventional HRTEM could not be determined with a precision better than 10% unless an aberration corrected (Cs=0) microscope was used². In the past it may have been possible to ignore the “relatively small” errors introduced in HRTEM measurements but as the critical dimensions have continued to shrink the magnitude of these errors represent a significant portion of the total measurement. The limitations in conventional HRTEM are *why* we sought a method that would minimize the error in the measurement. Our approach was to use the National Center for Electron Microscopy (NCEM) One Angstrom Microscope (OÅM),

together with focal series acquisition (FSA) and exit wave reconstruction (EWR) techniques to obtain <0.8Å interpretable resolution. HRTEM data on the same oxy-nitride materials from an aberration corrected (Cs=0) microscope were also collected as part of this work³, as were scanning TEM (STEM) measurements. The relative strengths and weaknesses of HRTEM versus scanning STEM for this particular gate oxide characterization are briefly discussed here and they are more fully elaborated upon elsewhere⁴.

The HRTEM characterization provides an absolute calibration and validation for a precise “near-line” metrology to determine gate oxide thickness and nitrogen dose using x-ray photoelectron spectroscopy (XPS).

Background

Materials characterization versus metrology.

There is an often overlooked but practical distinction between material characterization and metrology. Material characterization is the more general term that includes the broadest range of analytical tools and methods that may be applied to describe the physical properties of a material system. Metrology is a measurement method applied to a material system that inherently is associated with a pre-defined degree of precision, accuracy and speed. Typically the system is also designed to be simple to operate and features a certain level of automation to provide an unambiguous result to the non-expert end user. Likewise, the accuracy of the material characterization measurement can be confused with the relative importance of the precision of that measurement. While the best accuracy is always appreciated, it is generally the precision and sensitivity coupled with a well-behaved measurement response that defines the practical utility of a measurement, as that defines the ability to detect changes in the material system. In addition, the most accurate or versatile material characterization for a given material property measurement is rarely the most

practical or effective metrology method. Finally, even the most advanced material characterization method has accuracy and precision limitations. In the semiconductor industry metrology generally provides a handle for process control monitoring at various stages of the manufacturing process and thus sensitivity to changes with required precision is paramount.

The generic problem related to gate oxide measurements.

A six sigma manufacturing criteria leads to a gate oxide thickness tolerance of 5%. Assuming a precision-to-tolerance ratio of 0.1, it is necessary to measure a 2nm gate oxide thickness with a statistical precision of less than 0.02nm^5 . This is *why* we aspire to such high precision in a gate oxide thickness metrology.

During development of oxy-nitride gate dielectrics it has become apparent that nitrogen content, chemistry and distribution have significant impact on transistor properties, including EOT, leakage current, threshold voltage, channel mobility and reliability. Thus, transistor performance characteristics have become “gate-centric”. This is *why* we seek a precise metrology that is also sensitive to nitrogen parameters. Historically, the gate oxide metrology could be addressed with acceptable precision by optical methods. However, with the advent of nitrogen incorporation and evolution of other high-K dielectrics, including tertiary $\text{Hf}_x\text{Si}_y\text{O}_z$, optical methods have, to date, proved inadequate. However, recent discussion suggests that infrared spectroscopy may still be technically feasible, although the appropriate commercial instrument configuration does not exist⁶. The good news regarding “gate-centric” transistor performance is that if a precise metrology is developed that is sensitive to nitrogen, there is a possibility a “near-line” metrology measurement of the gate stack will correlate with final electrical performance. As will be demonstrated, XPS measurements have the suitable precision to determine both gate oxide thickness and nitrogen dose. In addition, these measurements have shown promise in correlating with final electrical test on the device, the only parameter that really matters in the end. A method to determine nitrogen distribution versus depth is also required for development and failure analysis purposes. In this capacity, the role of HRTEM and STEM

characterization is to provide calibration and validation of a gate oxide metrology.

Gate oxide thickness using the FSA and EWR method.

It is still a routine practice for HRTEM experts to apply HRTEM image simulations to determine the actual experimental conditions under which an image or image series was acquired, and thereby back out the actual sample structure. The FSA/EWR procedure can eliminate the need to perform image simulations and is rapidly becoming a reliable and accessible method for electron microscopists to obtain interpretable information up to the information limit of the microscope. The most accurate gate oxide thickness measurements by HRTEM to date were obtained using a specially modified CM300 with an information limit of 0.8\AA , named the NCEM OAM, in conjunction with the FSA/EWR process. The evolution of the NCEM OAM is described more fully elsewhere⁷. The FSA/EWR method consists of an experimental series of images acquired at fixed intervals of defocus which are then numerically processed using the Philips/Brite-Euram software for focal-series reconstruction by Coene and Thust⁸⁻¹⁰. Practical implementation of the FSA/ EWR method is described elsewhere¹¹.

To obtain the highest quality HRTEM images it is also critical that the samples are suitably thin

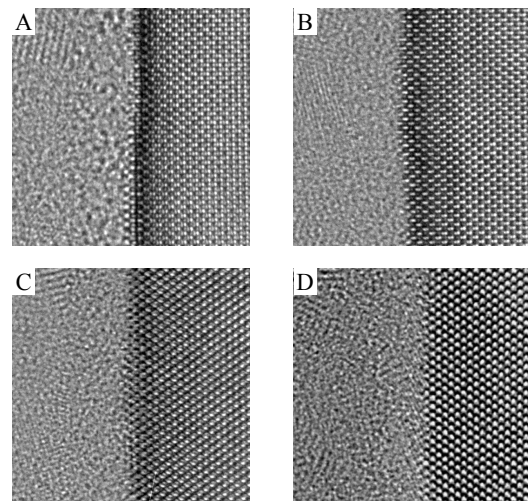


Figure 1. A) The sample is greater than 30nm thick. B) The sample is approximately 25nm. C) Sample is approximately 20nm. D) The sample is approximately 6nm and the "black band" is no longer observed.

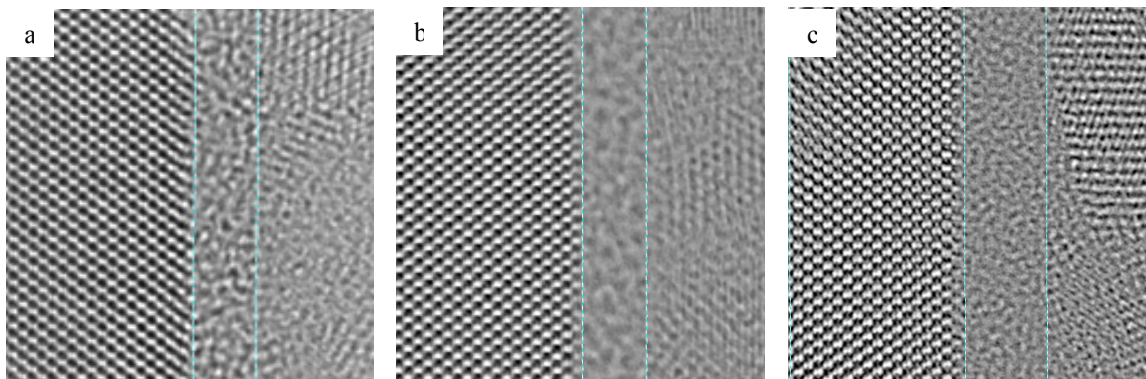


Figure 2. HRTEM images of gate dielectric materials recorded on two different microscopes. (a) A lattice image of starting oxide prior to nitridation obtained on a 200kV Cs=0 microscope. (b) A phase image of starting oxide on the same sample from the same Cs=0 microscope shown in (a). (c) A phase image of a gate dielectric following nitridation obtained on the OAM 300kV microscope. Panels (b) and (c) depict the phase of the electron exit wave reconstructed from a focal series of 20 images.

and have minimal surface roughness. Sample preparation can be achieved by a number of standard methods but the quality of the final surface is the most important result and when final ion milling is employed, is often dictated by the sputter conditions. Sample preparation is elaborated upon elsewhere¹². A series of images produced during this work is presented in Figure 1. It can be observed that samples with a thickness greater than approximately 60Å, as shown in panels A-C, indicate a “black band” along the gate oxide interface. This black band results when the local sample thickness is greater than the extinction distance. Many published TEM images of gate oxides contain this black band along the gate oxide interface but this artifact must be overcome to achieve the highest resolution HRTEM phase contrast image data. Note also the sample in panel D has a uniform texture without the “splotchy” dark areas that typically indicate holes and high surface roughness.

Figure 2 depicts three types of HRTEM images on gate dielectric materials. In panels (a) and (b) the images are from starting oxides prior to nitridation and are both obtained on an aberration corrected (Cs=0) 200keV electron microscope in Forschungszentrum Juelich (courtesy of C. Kisielowski at NCEM & M. Lentzen, K. Urban at Forschungszentrum Juelich). Panel (a) is a straight lattice image while Panels (b) and (c) represent the phase image of the electron exit wave following focal series reconstruction. The lattice image in panel (a) is unique as compared to a standard lattice image because it was obtained from aberration

corrected microscope (Cs=0). A standard lattice image pattern from a microscope with an objective lens that contains some nonzero amount of aberration (Cs≠0) will change rapidly with the focus setting of the microscope to produce misphased information, filter high spatial frequency information and produce delocalization of information along the interfaces. These artifacts all contribute to the errors discussed above when making gate oxide thickness measurements. The phase information

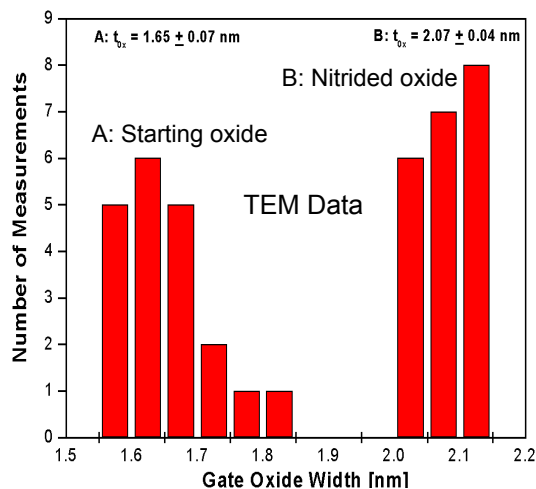


Figure 3. Summary of HRTEM gate oxide thickness measurements on both the starting oxide and following DPN. Five measurements were produced on each sample and then processed using four different image types: i) phase image following FSA/EWR on the 300keV NCEM OAM, ii) lattice image from Cs=0 Juelich microscope, iii) phase image following FSA/EWR on the Cs=0 Juelich microscope and iv) amplitude image following FSA/EWR on Cs=0 Juelich microscope.

has been recovered and delocalization has been removed through the FSA/EWR method in the reconstructed phase images in panels (b) and (c). Thus, all three images in Figure 2 represent nearly ideal HRTEM image data from which to attempt the most precise and accurate gate oxide thickness measurements. Figure 3 depicts the summary of the HRTEM results obtained from four different images types on both the starting oxide and after the Applied Materials decoupled plasma nitridation (DPN) process to produce the oxynitride gate dielectric. A total of 20 measurements were made on both the starting oxide and following DPN. The results indicate a starting oxide thickness of $1.65\text{nm} \pm 0.07\text{nm}$ and a gate dielectric thickness following DPN of $2.07\text{nm} \pm 0.04\text{nm}$. These results surpass the previous precision measurements on 20\AA oxynitride gate dielectric materials by $\approx 2.8\text{\AA}$.

Figure 4 is an enlarged view of the image in panel (c) of Figure 3. This image is useful to illustrate some challenges that remain even when working with the highest interpretable resolution HRTEM images. The inset shows a further

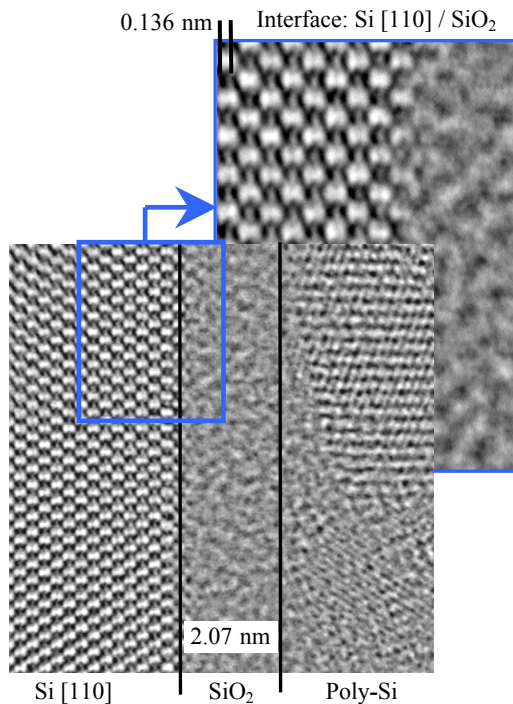


Figure 4. Enlarged view of the image shown in panel (c) of Figure 3. It is clear that the 1.36\AA dumbbells are resolved and the silicon substrate interface with the amorphous dielectric is well-defined. The interface along the poly-silicon interface is poorly defined due to random grain orientation and this complicates the HRTEM thickness determination.

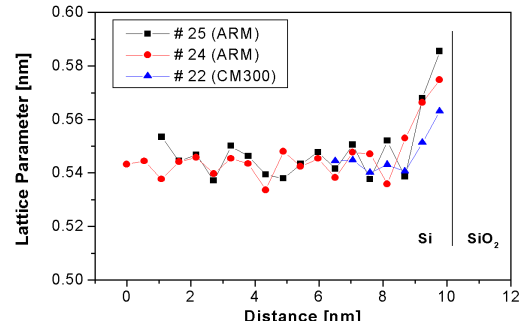


Figure 5. An example of strain displacement measurement. Shift in atomic positions approaching the substrate/oxide interface can be determined to picometer resolution following an exit wave reconstruction.

enlarged view of the silicon substrate interface with the amorphous gate dielectric. The silicon “dumbbells” are clearly resolved and are separated by 1.36\AA . Reconstructed images also exhibit excellent signal to noise due to improved microscope performance. It is also evident that the substrate interface is nearly atomically sharp and it is not very difficult to define the interface for measurement. However, the poly-silicon interface with the amorphous gate dielectric is more problematic. It should be mentioned that careful sample orientation along the zone axis is required for FSA/EWR method and this can often be a practical limitation in terms of the quality of the final result. So, while the substrate is well aligned along the zone axis, the pattern on the poly-silicon side is less defined due to the random grain orientation. Therefore, when defining the edge of the poly-silicon pattern it is necessary to locate the part of the polycrystalline pattern that extends furthest into the amorphous gate dielectric. Here one will have always to make assumptions about the visibility of pattern with respect to the location of the interface. This limitation accounts for some of the remaining subjectivity in the HRTEM measurement and may also explain the skew suggested in the distribution depicted in Figure 3. Due to the fundamentally different nature of image formation in STEM, the problem of defining the interface on the poly-silicon side of the dielectric is not an issue. The gate dielectric thickness can be determined reproducibly from the intensity traces across the annular dark field image, following the approach of Muller¹³. In addition, STEM thickness measurements can be completed on much thicker samples without degrading the precision ($<200\text{\AA}$). A detailed discussion of HRTEM and STEM measurements in gate oxide dielectric measurements is the

subject of reference 3. An approach to reduce the subjectivity of the HRTEM gate oxide thickness determination is to quantify the Fourier amplitude across the gate dielectric and define the pattern edge in frequency space. Validation of this approach is the subject of work in progress.

Another benefit of the phase reconstructed HRTEM images discussed here is that the atomic positions of the crystal lattice are resolved with picometer resolution. This allows precise and sensitive strain displacement measurements of the crystal lattice at interfaces. An example of the strain measured for three different gate oxide samples is provided in Figure 5.

XPS for SiON Gate Dielectric Films

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy[†] (XPS) is a surface analysis technique based on the photoelectric effect. The surface of the material or film to be analyzed is irradiated with soft x-rays, typically Al K α (1486.7 eV), and the kinetic energies of the photoelectrons ejected from the surface are measured. Due to the discrete energies of electrons in the atom, the energy of a given peak in the photoelectron spectrum indicates the presence of a given element in the sample surface region. A closer examination of the energies (typically displayed as electron binding energy) and the spectral line shapes gives further information on chemical bonding and the chemical environment of the atom of origin; this information can include chemical functionality and oxidation state.

Inelastic scattering of the photoelectrons before they escape the sample surface limits the information depth of the technique making it highly surface specific; this property of photoelectron transport is what makes XPS a valuable surface analysis tool that is widely used for materials and structural analysis. Photoelectrons have a probability of escaping the surface with initial energy intact that depends on the depth of the originating atom in the film. Photoelectrons created deeper than $\sim 40 - 50 \text{ \AA}$ in the sample surface are more likely to suffer energy loss and contribute to the spectral background, rather than spectral peaks.

SiON films in the current thickness ($< 40 \text{ \AA}$) and nitrogen content (5 – 15 atom %) range lend themselves very well to analysis by XPS since the entire film can be probed from a non-invasive surface measurement yielding information on film thickness, nitrogen content of the film, and, qualitatively, on nitrogen distribution versus depth below the surface. In addition, noble gas sputtering (ion milling) of the sample surface can be combined with XPS measurements to determine distribution of elements versus depth.

Application of XPS to the Characterization and Metrology of SiON

Film Thickness

XPS is a well-known technique for the measurement of film thickness and has been used previously to monitor (e.g.) thickness of lubricant films on hard disks. Linder & Mee published the method for the determination of film thickness¹⁴. This same method can be applied to the determination of any film overlayer on a substrate, providing acceptable spectra of the film and substrate and appropriate materials constants are available. An SiO₂ or SiON film on silicon provides an excellent opportunity for the exploitation of the film thickness method referenced above. Silicon XPS spectra measured on films that are less than approximately 40 \AA thick show peaks from both the Siⁿ⁺ species in the film and the elemental silicon in the wafer substrate. The ratio of these signals can be used to determine the thickness of the SiO₂ or SiON gate dielectric film.

Nitrogen Content

The nitrogen content of these films can be measured non-invasively by XPS because of the finite “escape depth” of photoelectrons from the surface and near surface region of the film. This means that nitrogen atoms can be detected in the film even though they may not be in the outermost surface layer. The distribution versus depth of nitrogen has an effect on the absolute nitrogen content measured at the surface; however, this effect can be measured and corrected if absolute measurements are required.

[†] Also known as Electron Spectroscopy for Chemical Analysis (ESCA).

XPS Studies Experimental Overview

A Physical Electronics, Inc. Quantera SXM Scanning X-ray Microprobe was used to determine film thickness, nitrogen content, and nitrogen distribution versus depth for a series of plasma nitrided SiON films. Film thickness and nitrogen content were determined quantitatively and non-invasively by XPS surface measurements. Depth distribution was determined quantitatively by XPS sputter depth profiling. Studies of XPS applicability were made to determine static and dynamic reproducibility, long-term reproducibility, and sensitivity to nitridation process conditions. Nitrogen content surface measurements were compared with the results of direct sputter depth profiling determinations of the nitrogen content for some of the wafers. The results of these studies follow.

XPS Results on SiON Films

Nitrogen Distribution versus Depth

The nitrogen distribution versus depth can be qualitatively estimated from angular measurements made from the sample surface or measured directly and more quantitatively by sputter depth profiling of the sample. Secondary Ion Mass Spectrometry (SIMS) is also used to measure nitrogen distribution versus depth in SiON films¹⁵.

Figure 6 illustrates an XPS sputter depth profile of silicon oxy-nitride, where the y-axis is atomic percent and the x-axis is a sputter-calibrated depth in angstroms. The profile has been mathematically processed to deconvolve the escape depth and has taken advantage of the nature of the sharp interface with the silicon substrate, as determined by the HRTEM data. From the deconvolved profile it is possible to observe that the Si⁴⁺ state is relatively constant while oxygen is exchanging with nitrogen in the film. The nitrogen, oxygen and Si⁴⁺ distribution as determined by XPS agreed well, qualitatively, with the electron energy loss spectroscopy (EELS) data from the same process conditions. The EELS data are not presented here, but are a part of an ongoing round robin study. The oxygen tail observed in figure 6 is believed to be a sputter artifact, as determined by applying short higher ion energy pulses, which quickly removed the oxygen. This is possibly due to re-deposition. However, the total integrated nitrogen dose determined by the profile is

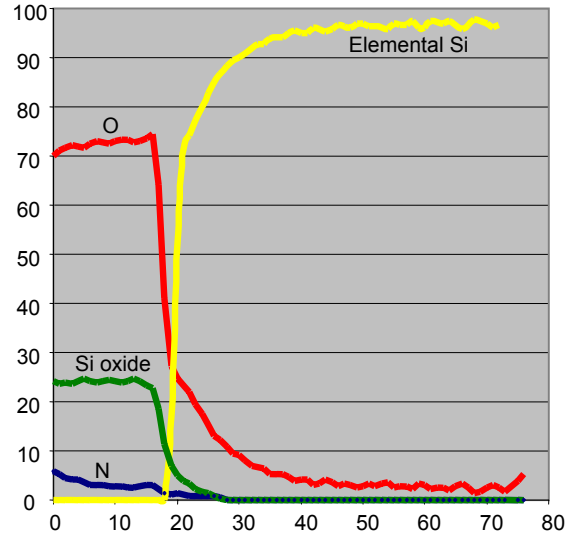


Figure 6. An XPS sputter depth profile following mathematical processing to deconvolve the escape depth function. The y-axis is atomic percent and the x-axis is a sputter calibrated depth in angstroms. Prior to removing the effect of the silicon substrate it is more difficult to quantify the distribution of elements in the gate oxide.

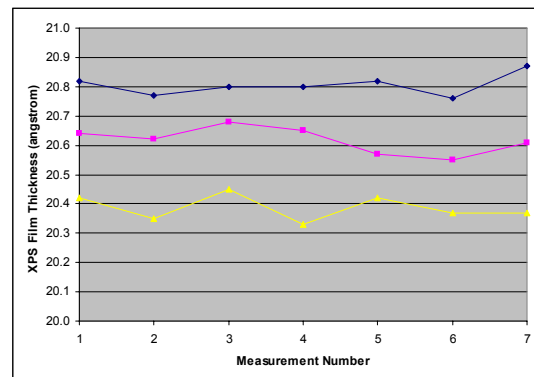


Figure 7. SiON film thickness dynamic reproducibility measurements at the wafer center (diamonds), R/2 (squares), and edge (triangles). The precision obtained was $\pm 0.04 \text{ \AA}$ or $\pm 0.2\%$ of film thickness, on average, at the 3 locations.

faithful and provides the calibration for surface measurements.

Short and Long Term Reproducibility

Dynamic Reproducibility of XPS Surface Film Thickness & Nitrogen Content

Fig. 7 shows the film thickness results of dynamic reproducibility measurements of a plasma nitrided SiON film; “dynamic” means that the wafer was moved sequentially between

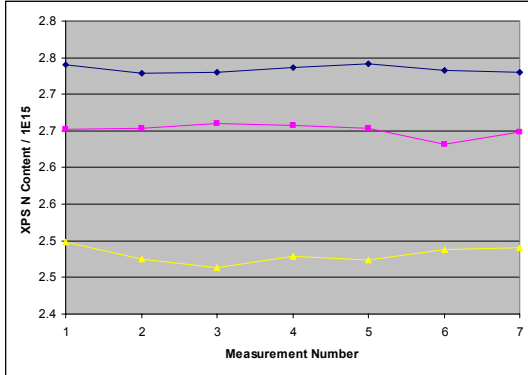


Figure 8. SiON nitrogen content dynamic reproducibility measurements at the wafer center (diamonds), R/2 (squares), and edge (triangles). The precision obtained was $\pm 0.009 \times 10^{15}$ atom/cm² or $\pm 0.35\%$ of nitrogen content, on average, at the 3 locations.

measurements and, therefore, that we are testing the reproducibility of both the optical and wafer manipulation systems of the tool. Seven repeat measurements were made at each wafer location and averages, and standard deviations (1σ) were calculated for film thickness at the center, R/2, and edge of the 200 mm wafer. Fig. 7 shows the individual measurements of film thickness and it can be seen that the average film thickness decreases somewhat from wafer center to the edge. The 1σ precision is $\pm 0.04 \text{ \AA}$ or $\pm 0.2\%$ of film thickness, on average for the 3 wafer locations.

Fig. 8 shows the results of nitrogen content measurements taken simultaneously with the thickness measurements at the same locations on the wafer. Similar precision of $\pm 0.009 \times 10^{15}$ atom/cm² or $\pm 0.35\%$ (average 1σ for 3 wafer locations) was achieved for the nitrogen content.

The precisions for film thickness and nitrogen content exceed currently understood metrology requirements.

Long Term Reproducibility of XPS Surface Film Thickness & Nitrogen Content

Fig. 9 shows the results of long term reproducibility measurements, expressed as percent variation in thickness, from a single SiON film. Measurements were repeated twice per day over a period of 12 days at the same locations (center, R/2, and edge) on the wafer. The wafer was removed from the tool after each measurement. Multiple measurements at each wafer location showed an average 1σ precision of $\pm 0.34\%$ of film thickness. Fig. 10 shows the corresponding variation in nitrogen content

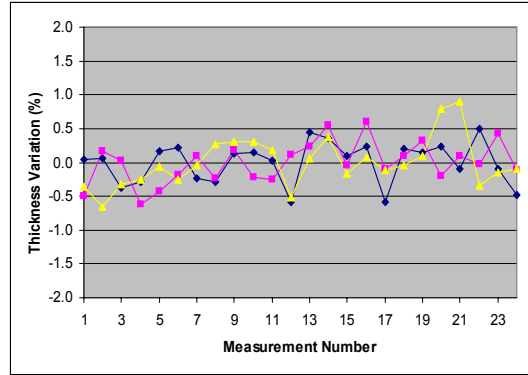


Figure 9. Long term variation in SiON film thickness measured twice per day at wafer center (diamonds), R/2 (squares), and edge (triangles). The wafer was removed from the tool after each measurement iteration. The precision obtained over the 12 day period was $\pm 0.34\%$.

measurements taken simultaneously with the thickness measurements at the same locations on the wafer. For nitrogen content $\pm 0.54\%$ (average, 1σ) was achieved for the three wafer locations.

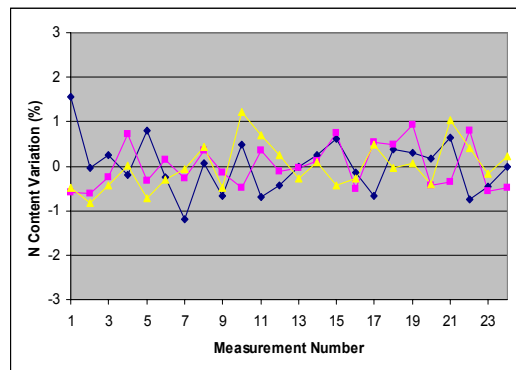


Figure 10. Long term variation in SiON nitrogen content measured twice per day at wafer center (diamonds), R/2 (squares), and edge (triangles). The wafer was removed from the tool after each measurement iteration. The precision obtained over the 12 day period was $\pm 0.54\%$.

Sensitivity to Processing Conditions

Since it could be argued that a tool exhibiting high precision may do so simply because of a lack of sensitivity, a series of SiON films was prepared using varying processing conditions. Both time and plasma nitrogen pressure were varied on the gate tool: time was varied over a range of 20 s and nitrogen pressure was varied over a range of 10 mTorr producing 9 films in all. The results of XPS measurements of

nitrogen content versus changes in process time and plasma pressure are given below.

Sensitivity of XPS Surface Film Thickness & nitrogen Content Measurements

Fig. 11 shows the dependence of nitrogen content, as measured by surface XPS, to changes in processing time. The 6σ error bars were calculated from repeat measurements on these wafers. If the XPS measurement uncertainty is translated into an uncertainty in process time, it is observed that a change of ± 1 s in processing (i.e., nitridation) time is detectable with certainty by the XPS surface measurement. Fig. 11 also shows that the linear correlation coefficient between nitrogen content and processing time

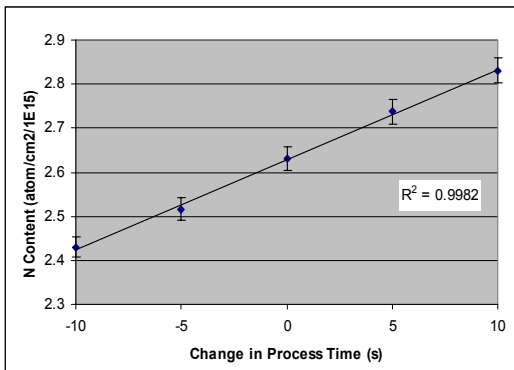


Figure 11. Surface XPS nitrogen content with change in processing time. The error bars represent 6 sigma uncertainty in the XPS measurement which translates into a process sensitivity of ± 1 s.

change is $R^2 = 0.998$, indicating excellent correlation.

Fig. 12 shows the non-linear dependence of nitrogen content, as measured by surface XPS, to changes in plasma pressure. Again, the 6σ error bars were calculated from repeat measurements on the wafers. Translating the XPS uncertainty into an uncertainty in plasma pressure, we can see that a change of ± 0.65 mTorr ($+0.67$ mTorr, -0.63 mTorr) in plasma nitrogen pressure is detectable with certainty by the XPS surface measurement. The correlation between XPS nitrogen content and plasma pressure change is $R^2 = 0.996$, again indicating excellent correlation between XPS and process conditions.

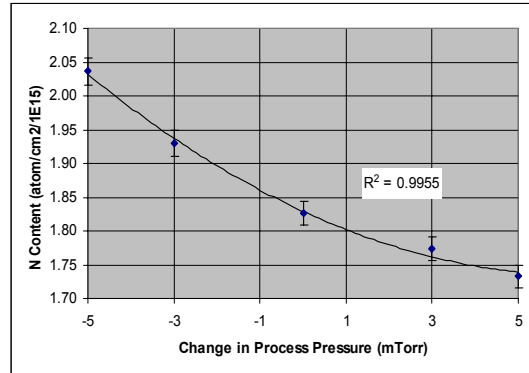


Figure 02. Surface XPS N content with change in processing pressure. The error bars represent 6 sigma uncertainty in the XPS measurement which translates into a process sensitivity of ± 0.65 mTorr.

Sensitivity of XPS Surface Measurements to nitrogen Distribution versus Depth

The nitrogen distribution can affect boron diffusion from the gate electrode and channel mobility. Even though it is now generally known that the plasma methods of nitridation produce a distribution that is largely invariant over a wide range of processing conditions it is necessary to detect a change in nitrogen distribution as well as changes in nitrogen content.

A photoelectron from an atom in a film has a finite probability of escaping the film surface that is a function of the distance of the atom below the surface and the escape depth of the photoelectron, which is dependent on the kinetic energy of the electron and the composition and structure of the film. This means that number of photoelectrons for (e.g.) nitrogen detected at the film surface is a function of the distribution versus depth of nitrogen in the film. A change in the distribution, even assuming no change in total nitrogen in the film, will be detected as a change in the XPS nitrogen content measured at the film surface. This effect can be both modeled and subsequently exploited in a metrology situation.

Fig. 13 shows some model distributions of nitrogen as a function of depth in a SiON film. The three distributions shown were chosen to center at a depth of 0 \AA (i.e., film surface), 10 \AA , and 20 \AA , which represents the SiON/Si wafer interface. The shape of each distribution is Gaussian and the widths were varied to approximate nitrogen distributions that might be obtained from plasma nitridation (diamonds),

thermal nitridation (squares), and a third -- and unknown -- process (triangles) giving a distribution that is the reflection of the diamond distribution about the central depth of the film; this third distribution is included for illustrative purposes.

The total nitrogen content of each of the three distributions was normalized to 1.0 in order to separate the effects of distribution from

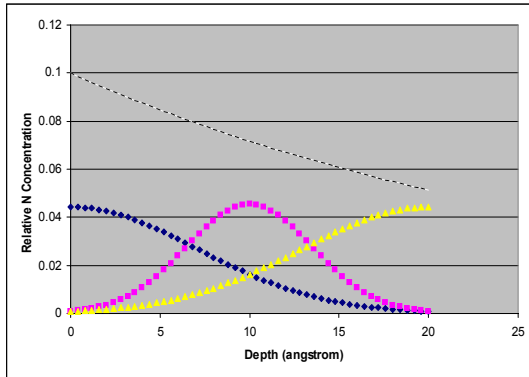


Figure 13. Model nitrogen distributions versus depth in the SiON film to estimate the effect of distribution on surface XPS nitrogen content measurements. The area under each of the 3 nitrogen distributions is 1.0. The dashed line estimates the escape probability for photoelectrons created at a given depth.

changes in nitrogen content. Fig. 13 also shows the probability of escape from the surface for photoelectrons calculated by an exponential model and scaled for purposes of display by a factor of 10; an escape depth of 30 Å was used for the escape probability calculation.

Fig. 14 shows the expected, relative, nitrogen content measured for each of the three distributions of Fig. 13 and two other similar distributions not shown in Fig. 13. The horizontal axis in Fig. 14 gives the depth centroid (the depth at which there is equal nitrogen above and below) of the nitrogen distribution in each case. The relationship between calculated nitrogen signal and centroid depth is nearly linear, and would be expected to be more nearly linear for greater nitrogen photoelectron escape depth, and indicates that the nitrogen content measured at the film surface would be expected to decrease at a rate of about $\Delta N = -2\% \text{ \AA}^{-1}$. Given the precision of XPS nitrogen content surface measurements above $\pm 0.35\%$ – the model suggests that a change in centroid depth of $< 1 \text{ \AA}$ would be detected by XPS. It has been shown, however, that the nitrogen distribution versus depth of (plasma)

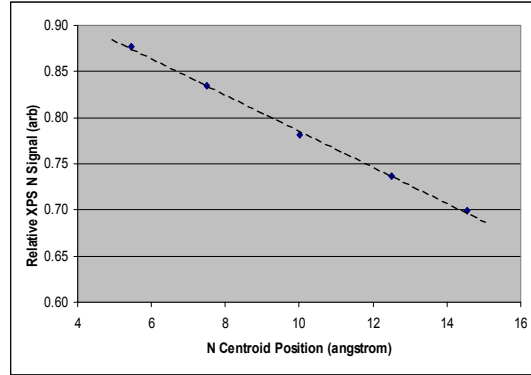


Figure 14. Expected change in XPS nitrogen signal available at the surface for the model distributions in Fig. 13 and two other intermediate distributions. The model indicates a signal loss of about 2% relative for every 1 Å shift of the nitrogen distribution centroid deeper into the film.

nitrided films is highly invariant to process conditions.

Correlation of XPS Surface & Depth Profile nitrogen Content Measurements

Fig. 16 shows the correlation of nitrogen content values measured by surface XPS plotted against the nitrogen content measured by sputter depth profiling the same films. This shows that, in the absence of a change in depth distribution, that the two methods for nitrogen content are linearly and very highly correlated. This property of the XPS measurements allows the nitrogen content to be determined quickly by a simple, non-invasive surface measurement.

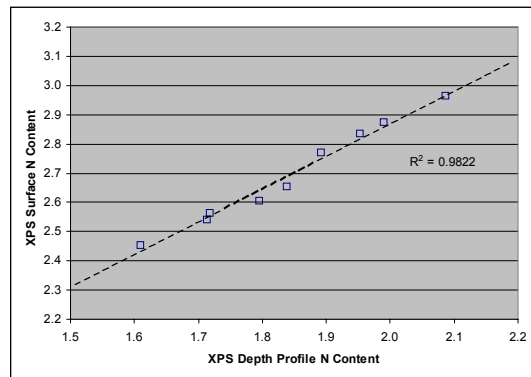


Figure 16. nitrogen content measured from surface XPS versus from sputter depth profiling. These are real data confirming the correlation between surface and invasive nitrogen content measurements.

Conclusions

Absolute gate oxide thickness measurements have been completed with a higher degree of accuracy and precision than previously demonstrated using focal series acquisition and exit wave reconstruction to achieve <0.08nm interpretable resolution. Similar results were achieved using a Cs=0 microscope. Both image types represent some of the most ideal HRTEM data currently accessible to characterize gate oxide thickness. The results indicate a precision between $\pm 0.04\text{nm}$ and $\pm 0.07\text{nm}$. The methods and instruments used to acquire the HRTEM image data presented here can be applied as an absolute calibration for XPS measurements, or another metrology, with the consideration that the X-sectional HRTEM samples include the additional interface between the poly-silicon layer and the gate oxide. It is still problematic to determine the edge of the poly-silicon and gate oxide interface by HRTEM. This represents a limitations in the accuracy and reproducibility of gate oxide thickness determined by the HRTEM technique.

XPS can be used for non-invasive measurement of SiON film thickness and nitrogen content with a precision for both measurements that exceeds current metrology requirements. In addition, XPS has the required sensitivity to process condition variations.

XPS surface measurements of nitrogen content are highly correlated to nitrogen content measurements made by sputter depth profiling.

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References

1. Scott, J.H.J., Windsor, E.S., Brady, D., Canterbury, J., Karamcheti, A., Chism, W., Diebold, A.C., "Gate Dielectric Thickness Metrology Using Transmission Electron Microscopy" in, Characterization and Metrology for ULSI Technology; 2000 International Conference, D.G. Seiler, et al., editors. Pgs 144-148 (2001).
2. Taylor, S., Mardinly, J., O'Keefe, M.A., Gronsky, R., "HRTEM Image Simulations for Gate Oxide Metrology" in Characterization and Metrology for ULSI Technology; 2000 International Conference, D.G. Seiler, et al., editors. Pgs 130-133 (2001).
3. M. Haider, H. Rose, S. Uhlemann, E. Schwan, B. Kabius, K. Urban, *Ultramicroscopy* 75 (1998) 53.
4. Diebold, A.C., Foran, B., Kisielowski, C., Muller, D., Pennycook, S., Principe, E., Stemmer, S., "Thin Dielectric Film Thickness Determination by Advanced Transmission Electron Microscopy", *Microscopy and Microanalysis*, (in press).
5. Diebold, A.C., Venables, D., Chabal, Y., Muller, D., Weldon, M., Garfunkel, E., *Materials Science in Semiconductor Processing*, 2, pgs. 103-147 (1999).
6. Recent discussion led by Will Chism during the International Sematech Analytical Laboratory Managers Council Meeting, Austin Texas, September 11-12, 2002.
7. O'Keefe, M.A., Herington, C.J.D., Wang, Y.C., Nelson, E.C., Turner, J.H., Kisielowski, C., Malm, J.-O., Mueller, R., Ringnald, J., Pan, M., Thust, A., "Sub-Angstrom High Resolution Transmission Electron Microscopy at 300 keV". *Ultramicroscopy*, 89, (2001) 4: 215-241.
8. Coene, W.M.J., Thust, A., Op de Beeck, M. Van Dyck, D., *Ultramicroscopy* 64 (1996) 109.
9. A. Thust, W.M. J. Coene, M. Op de Beeck, D. Van Dyck, *Ultramicroscopy* 64 (1996) 211.
10. A. Thust, M.H.F. Overwijk, W.M.J. Coene, M. Lentzen, *Ultramicroscopy* 64 (1996) 249.
11. Kisielowski, C., Hetherington, C.J.D., Wang, Y.C., Kilass, R., O'Deefe, M.A., Thust, A., "Imaging columns of the light elements carbon, nitrogen and oxygen with sub-Ångstrom resolution", *Ultramicroscopy*, 89, (2001)4:243-263.
12. Ibid.
13. Muller, D.A., "Gate Dielectric Metrology Using Advanced TEM Measurements" in, Characterization and Metrology for ULSI Technology 2000, Eds., D.G. Seiler, et al., AIP conference Proceedings 550, pgs 500-505.
14. R. E. Linder and P. B. Mee, IEEE Tran. MAG 18 (1972) 1073.

15. M. A. Douglas *et al*, J. Electrochemical Society, **147 (5)** 1893-1902 (2000).