Non-Destructive Characterization and Metrology for Ultra-Thin High-k Dielectric Layers.

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Abstract. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) has been used to characterize non-destructively silicon oxynitride and high-k film samples. The ARXPS data have been processed to provide accurate and precise measurements of thickness of surface and interface layers. Concentration depth profiles have been reconstructed from the ARXPS data to provide elemental and chemical state distribution information. For silicon oxynitride samples, nitrogen doses have been calculated from the concentration profiles, thereby accounting for the distribution of the nitrogen within the oxynitride layer. A comparison of ARXPS with modeled single-angle XPS experiments illustrate the potential errors in calculation of both thickness and dose using the latter technique. Sputter depth profiles are also shown to contain potentially misleading information when compared to reconstructed ARXPS depth profiles.

INTRODUCTION

The continuing requirement for smaller equivalent oxide thickness (EOT) for gate dielectrics will lead to the introduction of new materials with higher dielectric constants than silicon dioxide (high-k dielectrics). Already, silicon oxynitride is being used but work is being done on future generations of high-k materials. Aluminum oxide, hafnium oxide and mixed aluminum/hafnium oxides are currently being evaluated as candidate materials for this application. There is a clear requirement to understand these systems in greater detail. Measurements of dose, stoichiometric distribution and chemical state are particularly important, together with detection of contaminants and impurities. Furthermore, these measurements may be needed over the whole of a wafer to establish uniformity.

Complete characterization of high-k gate dielectric materials requires a number of complementary analytical techniques [1]. The density of ultra-thin high-k films, for example, can be measured using X-ray reflectometry (XRR) whereas contaminants present in extremely low concentrations can be identified using secondary ion mass spectrometry (SIMS). It has been demonstrated previously, however, that angle-resolved X-ray photoelectron spectroscopy (ARXPS) can be used to measure a number of physical and chemical characteristics of these materials within a single experiment [2,3,4].

X-ray photoelectron spectroscopy (XPS) can provide quantitative information, not only about elements present but also their chemical state. The information depth of the technique varies with the sample. For materials commonly encountered in semiconductor device fabrication, information from the top 10 nm of the sample is available. This information depth varies with photoelectron emission angle. In angle-resolved XPS, electrons are collected over a range of angles to access this depth-related information. In traditional ARXPS measurements, samples are tilted to obtain angle-specific data. If the angular information is collected in parallel, however, it is not necessary to tilt the specimen during the measurement process. This allows ARXPS data to be collected easily from multiple points on a complete wafer. Since no material is removed in the generation of the concentration profile, the method is non-destructive. All of the angle-resolved XPS data reported here were collected in parallel, without tilting the sample.

ARXPS studies of silicon oxynitrides have been reported by Chang et al. [2]. In that work it was shown...
that ARXPS could be used to measure the thickness of ultra-thin SiO\textsubscript{x}N\textsubscript{y} films and that the dose and distribution of nitrogen within these films could be determined non-destructively from the same data. A number of oxynitride films, prepared under different conditions, were analysed, demonstrating that ARXPS was able to distinguish the dose and distribution for nitrogen in different chemical states in each case.

The potential of using ARXPS to study high-\textit{k} films grown by atomic layer deposition (ALD) was demonstrated by Renault and co-workers [3], who studied the growth of Al\textsubscript{2}O\textsubscript{3} on Si and on SiO\textsubscript{2}/Si. In that work it was shown that ARXPS could be used to characterize the samples in terms of chemical defects (due to Al-OH groups) and interfacial growth upon annealing.

Although the work of Chang et al. [2] and Renault et al. [3] clearly show the potential of ARXPS as a technique for characterizing high-\textit{k} materials, the complexity traditionally involved with collecting and interpreting angle-resolved data has prevented it from becoming more widely used. Recent advances in spectrometer design, however, allow angle-resolved data to be collected as easily as standard XPS spectra. In this work, a parallel angle resolving X-ray photoelectron spectrometer was used to acquire ARXPS data rapidly from a number of silicon oxynitride and high-\textit{k} film samples. The aim of this work was to characterize non-destructively each sample according to film thickness and elemental and chemical state composition and distribution.

**EXPERIMENTAL**

ARXPS data were collected using one of two parallel angle-resolving X-ray photoelectron spectrometers (Theta Probe and Theta 300, Thermo VG Scientific) fitted with monochromated, microfocused Al K\text{\alpha} sources (h\nu = 1486.6 eV) and hemispherical electron energy analyzers. The lens system and 2D electron detector fitted to these systems allows data to be collected simultaneously in 96 channels over a 60° range of photoelectron emission angles. The data in the 96 angle channels were integrated into 16 angle channels, each with an angular acceptance of 3.75°, and so 16 angle-resolved XPS spectra were acquired simultaneously at each point on the samples. (The photoelectron emission angles quoted in this work are defined with respect to the surface normal.)

**THICKNESS MEASUREMENTS USING ARXPS**

The thickness of a silicon dioxide layer on a silicon wafer is readily determined with ARXPS. Recently it was reported by Seah and White [5] that ARXPS can be used to map SiO\textsubscript{2} thickness across a wafer with good precision (relative standard deviation of approximately 0.5%). The method of taking ARXPS data and deriving the oxide thickness is fully described in that work and will not be discussed here.

The accuracy of the parallel ARXPS technique has been established by comparison with ellipsometry [5]. Furthermore, XPS can distinguish between the oxide layer and the carbonaceous overlayer, which is always present at the surface of the oxide, whereas the measurement from ellipsometry is unable to account for a carbonaceous layer.

The application of ARXPS thickness measurements to multi-layer systems was demonstrated by using the technique to study the effect of process variations during the atomic layer deposition (ALD) of hafnium oxide films on thermally grown SiO\textsubscript{2}. The hafnium oxide layers were deposited by alternating pulses of HfCl\textsubscript{4} and H\textsubscript{2}O. ARXPS was used to measure the thickness of the hafnium oxide layer and the interfacial SiO\textsubscript{2} layer as a function of the number of ALD cycles (see FIGURE 1).

![FIGURE 1. Thickness of HfO\textsubscript{2} and SiO\textsubscript{2} layers on Si as a function of the number of ALD cycles.](image-url)
FIGURE 2. Repeatability of thickness measurements from two oxynitride samples. In this case the mean thickness was 1.82 nm with a standard deviation of 0.012 nm (RSD = 0.66%).

This illustrated level of precision demonstrates the suitability of ARXPS for mapping the thickness of oxide layers over the surface of wafers, where only a small degree of thickness non-uniformity is expected. Such a measurement was made on a 200 mm wafer segment using a Theta 300 spectrometer [5]. In that work, a comparison was made with ellipsometry, and good agreement was found between the two techniques. A wafer thickness map taken from the same sample is shown in Figure 3. The full range of the thickness variation on this wafer was only 0.2 nm.

ARXPS DEPTH PROFILE CONSTRUCTION

Concentration depth profiles may be constructed from ARXPS data using the Maximum Entropy method described by Smith and Livesey [6]. In this manner, the profile in FIGURE 4 was constructed for a layer of silicon dioxide on silicon.

FIGURE 3. Thickness map of 200 mm wafer segment generated from ARXPS data.

FIGURE 4. ARXPS Concentration profile of a 2.1 nm layer of SiO₂ on Si, constructed using the Maximum Entropy method.

This profile is of the expected form, having a layer of adventitious carbon at the surface, a distinct layer of silicon dioxide and a silicon substrate.

A similar approach was adopted for a silicon oxynitride layer on silicon. FIGURE 5 shows that the nitrogen concentration through the layer is not uniform but increases towards the interface.

FIGURE 5. ARXPS concentration profile of a silicon oxynitride layer.

From this profile it is possible to calculate the total nitrogen dose of \(3.2 \times 10^{15}\) atoms.cm\(^{-2}\) in the 2.6 nm thick layer. This value was obtained by integrating under the nitrogen and oxygen profiles.

The X-ray photoelectron spectrum shown in FIGURE 6 shows that multiple chemical states of nitrogen may be present in a silicon oxynitride sample. The weaker components to higher binding energy (N\(_b\), N\(_c\)) indicate the presence of nitrogen in higher oxidation states than in the main component N\(_a\).
Nitrogen in different chemical environments can be shown to have different concentration profiles, as illustrated in FIGURE 7.

In this case, the \( N_C \) form of nitrogen is clearly located at the oxynitride/silicon interface. However, when the layer is subjected to the more traditional sputter profiling, a quite different result is obtained.

An analysis of the sputter profile would conclude that \( N_C \) lies close to the surface, since this component disappears rapidly on etching. However, the reconstructed ARXPS profile shows that \( N_C \) is an interfacial species. A qualitative appraisal of the raw ARXPS data confirms that \( N_C \), whose signal is strongest in the bulk-sensitive angles, is a deep-lying species. The misleading conclusions drawn from the sputter profile arise from the probable modification of the sample during etching.

The ARXPS concentration profile methodology is also applicable to more complex overlayer structures.

FIGURE 8 shows a concentration profile generated from ARXPS data from a mixed hafnium-aluminum oxide overlayer sample.

![FIGURE 8](image)

The construction of depth concentration profiles will be essential for samples where the chemistry of the materials and their interface properties are considerably more complex than that of SiO\textsubscript{2} on Si. In addition to the elemental concentrations, important chemical state information is also available. In FIGURE 8, for example, oxygen can be profiled in two distinct chemical states, those states being derived from fitting the O 1s spectrum, as shown in FIGURE 9. The data also indicate that the oxidized silicon is in the form of silicate.

![FIGURE 9](image)

FIGURE 9. The O 1s spectrum from the mixed hafnium – aluminum oxide layer on SiO\textsubscript{2} on Si whose profile is shown in FIGURE 8.

**UNIFORMITY MEASUREMENTS**

In addition to measuring the thickness of layers and distribution of materials through layers, ARXPS can
be used to measure the uniformity of the layers. The data shown in FIGURE 3 gives some indication of this.

FIGURE 10 shows a line scan performed on a portion of a wafer. It shows both the oxynitride thickness and the nitrogen dose in the layer as a function of the position on the wafer.

If required, of course, a full depth profile can be constructed at each point on the line scan. An example of such a profile is shown in FIGURE 11.

If the measurement is made using the geometry shown in FIGURE 12, then there will be errors in the thickness determination. These errors take the form of an underestimate of oxide thickness and will depend upon the thickness of the layer and the material being measured. The size of the errors is shown in FIGURE 13. The reason for these errors is that some photoelectrons from the silicon will be elastically scattered in the overlayer increasing the intensity of the silicon peak and causing the method for thickness measurement to fail. The effect will be greater for thicker samples and at larger emission angles. If a large angular range is used to collect the data then the elastically scattered electrons will be collected and contribute to the calculation of thickness. The influence of elastic scattering upon the measurement of oxide thickness has been discussed in detail elsewhere [7].

These errors can be avoided if ARXPS data are used. This is achieved by restricting the angular range used in the calculation of thickness to those angles where scattering does not cause significant inaccuracies. The appropriate angular range depends upon the thickness of the material. For example, if the layer thickness of SiO$_2$ on Si is in the region of 1 nm then angles up to about 75° can be used but, if the thickness is in the region of 8 nm, elastic scattering
becomes significant at angles above about 50°. The data shown in FIGURE 13 is one example derived from a specific geometry (illustrated in FIGURE 12). The extent of the errors will depend upon both the polar angle of the analyzer and the angular range that it accepts.

Single-angle measurements may also lead to inaccurate evaluation of N dosage within oxynitride samples. For example, very large errors can result if it is incorrectly assumed that the nitrogen distribution is uniform in a sample, when actually the nitrogen is either situated in a layer near the surface or near the interface with the silicon. The errors in dose measurement will be dependent upon the photoelectron emission angle and the thickness of the layer. The calculated errors are shown in for this type of situation in FIGURE 14. If, however, ARXPS is used then the nitrogen distribution can be measured. The dose can then be calculated with much greater accuracy using information about the distribution.

![FIGURE 14.](image)

FIGURE 14. The errors associated with nitrogen dose measurements from single angle XPS measurements if the nitrogen distribution is assumed to be uniform in an oxynitride layer.

**CONCLUSIONS**

Angle-resolved XPS is a powerful technique for the measurement of layer thickness up to about 10 nm (depending upon the material). It can do this with a high degree of accuracy and precision. Buried layers are also accessible to the technique and their thickness can be measured.

Concentration depth profiles can be constructed from the ARXPS data. These enable the elemental and chemical state distributions of elements within the samples to be determined with greater confidence than would be obtained using sputter profiling. These profiles allow the total quantity of each chemical state component in each layer to be measured. It is also possible to measure the total dose of nitrogen in an oxynitride layer from these profiles.

All of these parameters can be measured as a function of position on the wafer in the form of a map or line scan.

Using Parallel ARXPS, this type of measurement can be made easily and rapidly, thus avoiding the errors and uncertainties that can be introduced by measurements made at a single angle.

**REFERENCES**


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