Application Note: 31021

Characterization of High-k Dielectric Materials on Silicon Using Angle Resolved XPS

Key Words

- Surface Analysis
- Chemical State
- Distribution of Elements
- Film Thickness
- Uniformity

Introduction

The decreasing dimensions of transistors in integrated circuits require that the dielectric layer between the gate electrode and the channel becomes thinner. In order for the shrinkage to continue, silicon dioxide must be replaced as the dielectric material because, at the thickness required for the transistor design, the leakage current would become unacceptable. For this reason there has been a move towards materials having a high dielectric constant (high-k dielectrics). These materials are often based on hafnium.

The move away from silicon dioxide brings with it some new analytical requirements. In addition to the layer thickness, the following parameters become important:

- Thickness of any intermediate layer (silicon dioxide or metal silicate)
- The distribution of elements in the layer
- Quantity of the active material in the layer
- Chemical state of the elements in the intermediate layer
- The uniformity of these parameters across the wafer

The thickness of these dielectric layers is less than the sampling depth of XPS. It is therefore possible to analyze the whole of the dielectric layer at near normal electron emission angles without the need to remove any material.

XPS provides information about the chemistry of the layers and their interfaces while ARXPS provides additional information about layer thickness and the distribution of materials within the layer.

The basic principles of ARXPS and the way in which information can be obtained from ARXPS data are described in the application note 31014.

The purpose of this document is to illustrate the information available from XPS and ARXPS concerning high-k dielectric layers.

Relative Depth Plot

This simple method is useful for the examination of samples having more than one layer on the substrate. The method produces a chart on which the ordering of the elements with depth is clearly shown.

The plot is constructed for each species by taking the logarithm of the ratio of the peak area at near grazing emission angle to that at near normal emission. Figure 1 shows an example of a relative depth plot from a mixed layer of aluminum oxide and hafnium oxide on silicon dioxide on silicon. Carbon, a surface contaminant, can be seen nearest to the surface while the elemental silicon is deepest in the structure, as expected. The hafnium and aluminum occur at about the same position. Oxygen is present in two chemical states, as shown by the two O 1s binding energies in the XPS spectrum; the low binding energy associated with the hafnium and high binding energy associated with aluminum and silicon.

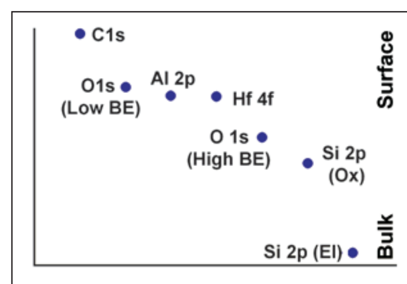

Figure 1: Relative depth plot from a mixed HfO_2, Al_2O_3 layer on SiO_2 on Si

The relative depth plot has the advantage of being independent of any model and does not require the knowledge of the physical constants for the material. It can show, for example, the change in position of a species due to some form of treatment, such as annealing. It is also used to determine the order of the layers prior to using the multi-layer thickness calculator.

Thickness

A multi-layer thickness calculator is a feature of the *Avantage* data system. This allows the simultaneous calculation of thickness for up to three thin layers on a substrate.

Figure 2 shows the results of using this technique to calculate the thickness of layers on a silicon substrate. The samples all had a layer of thermal oxide grown on them before growing aluminum oxide by atomic layer deposition (ALD). All samples had a layer of adventitious carbon. The plot shows that the Al_2O_3 layer thickness increases with increasing number of ALD cycles while the silicon dioxide layer remains at a constant thickness. The thickness of the adventitious carbon is greater when Al_2O_3 is present than it is on the silicon dioxide but is independent of the thickness of the Al_2O_3.

The shape of the Al_2O_3 line in Figure 2 has been confirmed by other techniques (e.g. TEM and ERD).

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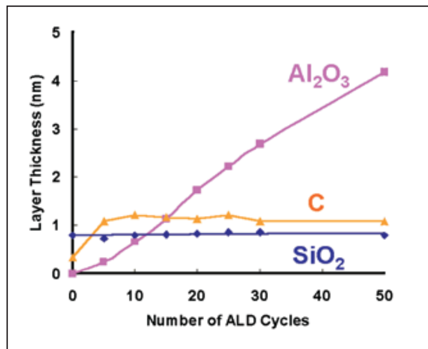

Figure 2: Thickness of carbon, aluminum oxide and silicon dioxide layers on a silicon substrate, as a function of the number of ALD cycles. Thickness was determined using the multi-layer thickness calculator in *Avantage*.

Uniformity

The uniformity of the high-k layer can be determined either by performing a line scan measurement or by mapping.

A thickness line scan across the whole diameter of the wafer is shown in Figure 3. The line scan shows clearly that the thickness decreases by about 0.7 nm.

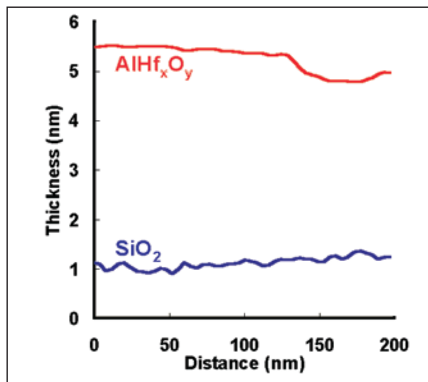

Figure 3: Thickness line scan across the diameter of the 200 mm wafer showing the variation of the thickness of the mixed Al_2O_3 and HfO_2 layer and the thickness of the SiO_2 interfacial layer.

Figure 4 shows Al 2p and Hf 4f maps from a 200 mm wafer on which a mixed Al_2O_3 and HfO_2 layer was grown. The conditions for the growth were deliberately chosen such that a non-uniform growth would occur.

The maps clearly reveal the non-uniformity of the growth.

Chemical State Maps

Oxygen associated with hafnium is in a different chemical state from oxygen associated with aluminum or silicon. Figure 5 shows a wafer map of oxygen in each of these two chemical states.

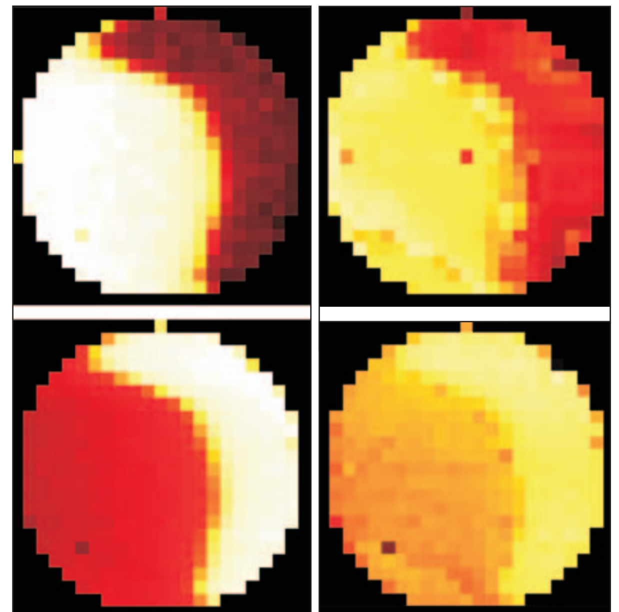

Figure 4: XPS maps of Al 2p (upper) and Hf 4f (lower) from a 200 mm wafer.

Figure 5: XPS maps of O 1s. The lower map is oxygen in a state with a low binding energy (usually associated with hafnium). The upper map is oxygen in a state with a high binding energy (usually associated with aluminum and silicon).

Interfacial Layer Chemistry

When high-k dielectrics are deposited on silicon, an interfacial layer will inevitably be present between the layer and the silicon substrate. The nature of this layer will have some influence upon the electrical properties of the layer.

The interfacial layers are usually composed of silicon in an oxidized form, an oxide or a silicate. Factors that might determine whether silicate is formed include:

- The method of preparation of the layer.
- The nature of the surface on which the high-k layer is deposited (i.e. how thick the silicon oxide layer is or if the oxide had been removed prior to the deposition of the layer).
- The deposition temperature.
- The treatment of the wafers following the deposition of the layer.

The binding energy of the Si 2p3/2 peak from silicon dioxide is 103.6 eV whereas the binding energy of the same peak in hafnium silicate is 102.7 eV.

Figure 6 shows the comparison between the Si 2p spectra from nominally 1 nm thick silicon dioxide, 1 nm SiO_2 with about 1 nm thick HfO_2 grown by MOCVD and 1 nm SiO_2 with 1 nm thick HfO_2 grown by ALD.

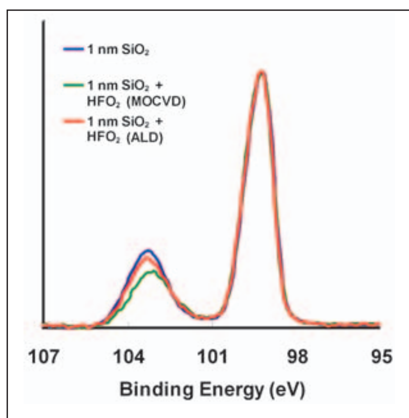

Figure 6: Comparison of Si 2p spectra from silicon dioxide (nominally 1.0 nm), with HfO_2 grown by ALD and MOCVD on the same material.

The spectra have had a Shirley background subtracted and are normalized to the elemental peak position. It is clear from these spectra that the oxidized silicon has remained as silicon dioxide with very little if any silicate formation because the binding energy remains at 103.6 eV and there is no evidence for a low binding energy shoulder on the peak. A similar conclusion can be drawn for HfO_2 grown on 0.5 nm (nominal thickness) silicon oxide (not shown).

However, the results are different when the HfO_2 is grown on thinner silicon dioxide layers. Figure 7 shows a comparison of Si 2p spectra from thin silicon dioxide (nominally 0.3 nm), thin oxide with HfO_2 grown by ALD and a hydrofluoric acid etched silicon surface with HfO_2 grown by ALD.

Hydrofluoric acid etching removes silicon dioxide from a silicon wafer. A wafer treated in this way will be referred to as an 'HF-last surface'. Again, the thin thermal silicon dioxide is clearly present as an oxide with no suggestion of a silicate. When HfO_2 is grown on nominally 0.3 nm SiO_2, there is a clear shift of the peak maximum and a broadening of the peak suggesting the presence of at least some silicate. On the HF-last surface, the peak is shifted even further to lower binding energies, suggesting the presence of hafnium silicate.

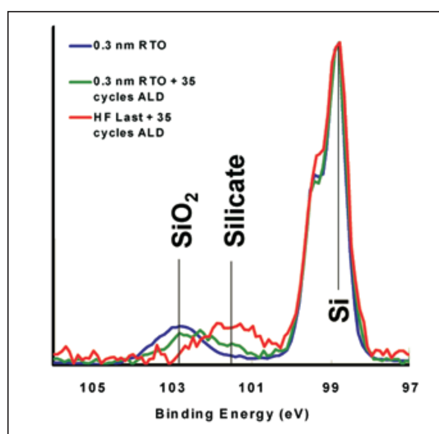

Figure 7: Comparison of Si 2p spectra from thin silicon dioxide (nominally 0.3 nm), with HfO_2 grown by ALD and an HF-last surface with HfO_2 grown by ALD.

Figure 8 shows the effect of growing a 4 nm HfO_2 layer by metal organic chemical vapor deposition (MOCVD) on a substrate at 300 °C during growth and the effect of annealing at 700 °C following growth. It appears from these spectra that there is silicate formation after the growth and that the amount of silicate increases after annealing. However, a significant proportion of the oxidized silicon remains as SiO_2.

Growth of similar layers at 485 °C followed by annealing at 700 °C shows similar effects.

If the HfO_2 layer is grown using ALD, rather than MOCVD, the chemistry is different, as illustrated in Figure 9.

In this case, there is very little silicate formation following the original growth. The amount of silicate increases following the annealing step but does not become as great as that when the layer is prepared using MOCVD, shown in Figure 8.

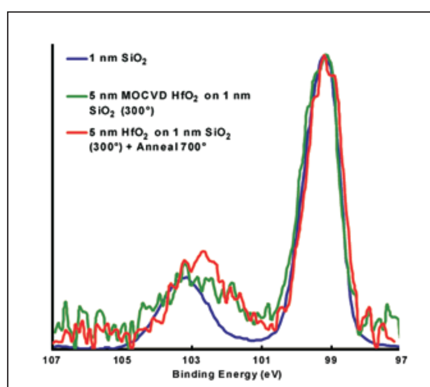

Figure 8: Comparison of Si 2p spectra from thin silicon dioxide (nominally 1.0 nm), with 4 nm HfO_2 grown by MOCVD on a substrate at 300 °C and following annealing at 700 °C.

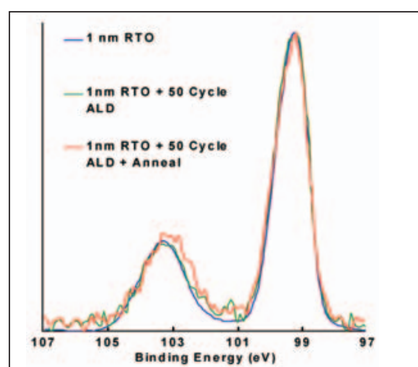

Figure 9: Comparison of Si 2p spectra from thin silicon dioxide (nominally 1.0 nm), with HfO_2 grown by ALD on a 1 nm RTO and following annealing at 700 °C.

Depth Profiles

Using methods that involve maximum entropy, it is possible to construct concentration depth profiles from ARXPS data. Such methods have been described in detail in the application note 31014.

Figure 10 shows an example of a depth profile through a mixed HfO_2/Al_2O_3 on SiO_2 on Si sample.

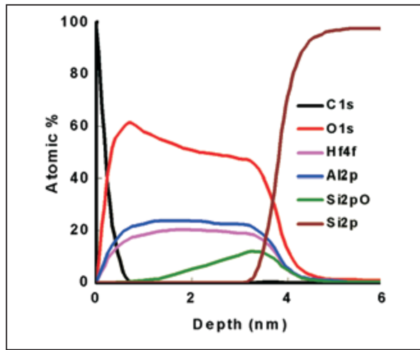

Figure 10: Profile through mixed Al_2O_3/HfO_2 on SiO_2 on SI

Figure 11 shows a reconstructed profile through HfO_2 on SiO_2 on Si.

This profile shows the existence of oxygen in two chemical states as well as carbon at the surface and the expected elements. The low binding energy O 1s peak is thought to be from the HfO_2 while the high binding energy O 1s peak is from both SiO_2 and the oxygen contained in adsorbed materials.

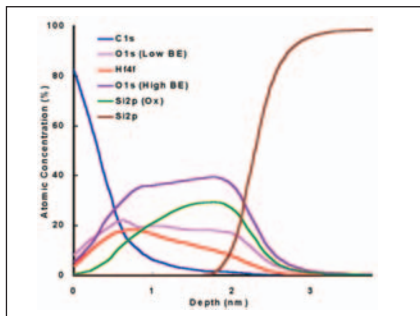

Figure 11: Example of a depth profile through a sample HfO_2 on SiO_2 on Si. The profile was constructed from ARXPS data.

Comparison with Sputtering

Alternative methods of analysis for these films involve sputter profiling with an ion beam. This approach may cause changes to the chemical states of the layer components.

Figure 12 shows the changes in the chemical state of Hf as a result of sputtering. The sample consisted of a 2.6 nm layer of HfO_2 on SiO_2 on Si. The HfO_2 layer was thin enough that metallic Hf would be visible in the spectrum if it were present at the start of the experiment. The first spectrum in the montage (labeled 'surface') was acquired before sputtering the sample, the next spectrum was acquired following removal of material by sputtering for a short time with 500 eV argon ions. Further sputtering took place following the acquisition of each spectrum until most of the Hf had been removed. The spectrum labeled 'interface' was the final spectrum acquired in this series. It is clear from this sequence of spectra that, as a result of sputtering, the hafnium oxide is being converted to hafnium metal.

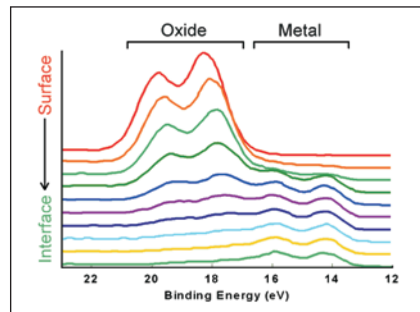

Figure 12: Montage of XPS spectra from Hf 4f region during a sputter profile experiment

Conclusions

Thermo Scientific Theta Probe and Theta 300 provide essential information for the next generation of gate dielectrics:

- Layer thickness
- Thickness of the intermediate layer
- Chemical states of the layer and the intermediate layer
- Uniformity of the layers
- Distribution of the material within the layer

ARXPS is non-destructive and avoids the use of sputtering with an ion beam. Sputtering has been shown to alter the composition of the layer and causes atomic mixing both of which can cause a misinterpretation of the data.

Acknowledgment

Some of the work reported here was performed with financial support of the European Union Growth Project "CUHKO"

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AN31021_E 05/08M

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