

Non-destructive analysis of ultrathin dielectric films

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Using angle-resolved x-ray photoelectron spectroscopy (ARXPS) it is possible to determine thickness, composition and depth distribution information for ultrathin samples in the region of ~ 5 – 10 nm. With ARXPS determining both quantitative elemental information and chemical state information, it provides chemical state profiles from surface and buried layers non-destructively.

This paper illustrates how ARXPS data can provide measurements of overlayer thickness and interface layer thickness for high- k dielectric layers on silicon. Elemental and chemical state depth distribution information is also provided in the form of reconstructed concentration profiles. Further examples are provided where ARXPS has been used to study the influence of surface pretreatment of the silicon substrate prior to deposition of hafnium oxide. It will be shown that the pretreatment determines whether a silicon oxide or silicate is formed. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: XPS; ARXPS; thickness; overlayer; silicon; hafnium oxide

INTRODUCTION

As the size of transistors in integrated circuits becomes smaller, the dielectric layer between the gate electrode and the channel must become thinner. Traditionally, silicon dioxide has been used as the gate dielectric but this will have to change in order to allow the continued shrinkage of the devices. The reason why a change is necessary is that leakage currents in very thin layers of silicon dioxide will become too great and the devices will be unable to function correctly.

Already, silicon oxynitride is beginning to replace silicon dioxide as a gate dielectric. This is because its dielectric constant is greater than that for silicon dioxide, allowing a thicker layer of the oxynitride to be used and leakage currents to be maintained at a low level. It will soon become necessary to move away from dielectrics based on silicon to those having an even higher dielectric constant. Currently, HfO_2 , Al_2O_3 and mixtures of these materials are under investigation for this application. The time-scales for these changes are described in the International Technology Roadmap for Semiconductors.¹

The move away from silicon dioxide brings with it some new analytical requirements. Not only will the layer thickness need to be measured but also that of any intermediate layer. The distribution of the elements in the layer will become important, as will the quantity of active materials within the layer (e.g. the dose of nitrogen present in an oxynitride). If there is an intermediate layer between

the dielectric and the silicon wafer then the chemical state of its component elements will be important in controlling the electrical properties.

The total thickness of these layers is of the order of a few nanometres, which means that a combination of XPS and angle-resolved x-ray photoelectron spectroscopy (ARXPS) is highly suited to making the above measurements because the layer thickness is now less than the sampling depth of the technique. It is now possible to analyse the whole of the dielectric layer at near-normal electron emission angles without the need to remove any material.

Single-angle XPS provides information about the chemistry of the layers and their interfaces and ARXPS provides additional information about layer thickness and the distribution of materials within the layer. Such measurements are the subject of this paper.

EXPERIMENTAL

The ARXPS data were collected using a parallel angle-resolving x-ray photoelectron spectrometer (VG Theta Probe) fitted with monochromated, microfocused Al $K\alpha$ sources and hemispherical electron energy analysers. The lens system and two-dimensional electron detector fitted to this system allow data to be collected simultaneously in 96 channels over a 60° range of photoelectron emission angles (23 – 83° with respect to the surface normal). 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 analysis point without tilting. The photoelectron emission angles quoted in this work are measured with respect to the surface normal.

The high- k dielectric materials used in this work were grown either by metal organic chemical vapour deposition (MOCVD) or by atomic layer deposition (ALD). They were

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RESULTS AND DISCUSSION

Thickness measurements

It is well known that ARXPS can be used to measure the thickness of thin films. Such measurements recently have been the subject of a comprehensive series of papers.^{2–4} Briefly, the method used involves manipulation of the Beer–Lambert equation. For thin oxide on its own metal (e.g. SiO₂ on Si) the equation can be simplified to

$$d/[\lambda \cos(\theta)] = \ln[1 + R/R_0] \quad (1)$$

where d is the thickness of the layer, λ is the attenuation length of the detected electron in the oxide layer, θ is the emission angle of the electron, R is the ratio of the signal intensities from the oxide and metal, respectively, and R_0 is the ratio of signal intensities from thick layers of the materials. Detailed discussions on the values of λ are given elsewhere.^{3,6} A standard database is available from the National Institute of Standards and Technology, Gaithersburg, MD USA. This provides values of λ for a wide range of instrument geometries, a detailed description of the methods used and a list of references concerning the determination of attenuation lengths.⁷

The gradient of a graph of $\ln[1 + R/R_0]$ vs. $1/\cos(\theta)$ provides the quantity d/λ from which the layer thickness can be calculated easily if λ is known. The simplification that allows Eqn. (1) to be used is based upon using the same XPS transition (e.g. Si 2p) for both the metal and its oxide. Because of the small energy difference between such peaks, the attenuation length is very similar in each case. For more complex structures (e.g. layers of HfO₂ on Si) the simplification cannot be used. The equation that results under these circumstances cannot be linearized and so a method of least-squares fitting must be used.

The situation becomes even more complicated with multilayer structures (e.g. layers of adventitious carbon on HfO₂ on SiO₂ on Si). The following methodology has been developed to deal with these materials. Again, from manipulation of the Beer–Lambert equation the ratio of the XPS peak intensity from layer i to that of the substrate will be

$$\frac{I_i}{I_s} = R_{0,i} \left[1 - \exp \left(\frac{-d_i}{\lambda_{ii} \cos \theta} \right) \right] \times \exp \left[\frac{1}{\cos \theta} \left(\sum_{j=1}^{j=i} \frac{d_j}{\lambda_{sj}} - \sum_{j=1}^{j=i-1} \frac{d_j}{\lambda_{ij}} \right) \right] \quad (2)$$

and the ratio of peaks between adjacent layers, i and $i + 1$, will be

$$\frac{I_i}{I_{i+1}} = \frac{R_{0,i}}{R_{0,i+1}} \frac{\left(1 - \exp \frac{-d_i}{\lambda_{ii} \cos \theta} \right)}{\left(1 - \exp \frac{-d_{i+1}}{\lambda_{i+1,i+1} \cos \theta} \right)} \times \exp \left[\frac{1}{\cos \theta} \left(\sum_{j=1}^{j=i} \frac{d_j}{\lambda_{i+1,j}} - \sum_{j=1}^{j=i-1} \frac{d_j}{\lambda_{ij}} \right) \right] \quad (3)$$

In these equations, the term λ_{ij} is the attenuation length of an electron emitted from layer i in layer j . Using least-squares fitting to the experimental data, the thickness of each layer, d_i , can be calculated. Values for the attenuation length may be either determined experimentally or calculated using, for example, the Tanuma, Powell and Penn equation.⁵ This method of simultaneous calculation of the thickness of all of the layers takes into account the attenuation of electrons from (or passing through) a given layer by the material in the layers above. It does not assume that the attenuation of electrons of different energies is the same.

Figure 1 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 HfO₂ by ALD. All samples had a layer of adventitious carbon. The plot shows that the HfO₂ layer thickness increases with increasing number of ALD cycles but the SiO₂ layer remains at a constant thickness. The thickness of the adventitious carbon is greater when HfO₂ is present than it is on SiO₂ but is independent of the thickness of the HfO₂.

Angular asymmetry factor

In conventional ARXPS, spectra are obtained as a function of the tilt angle of the sample. This means that the angle between the incoming x-rays and the emitted photoelectrons remains constant. As a consequence of this, it is not necessary to take into account the angular asymmetry factor in the calculations. When using parallel collection of the angular information, as for the data presented here, the angle between the x-ray beam and the collected photoelectrons is a function of the collection angle. This means that the angular asymmetry should be taken into account. The equation given by Reilman *et al.*⁸ has been used but, because it applies to photoemission from gas-phase, molecules it was modified for solid-state emission using the factor given by Jablonski.⁹

Concentration–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 elsewhere^{10,11} and the description will not be repeated here.

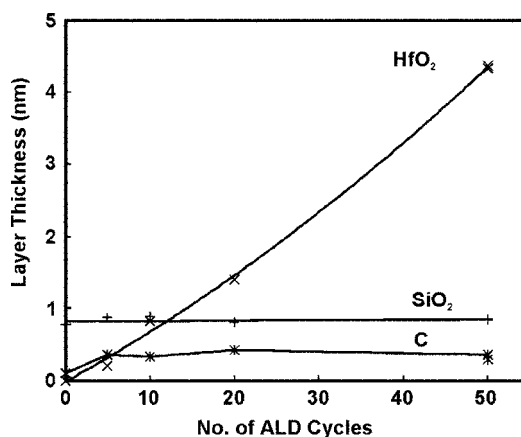


Figure 1. Thickness of carbon, HfO₂ and SiO₂ layers on silicon. The HfO₂ layers were grown on the thermal silicon dioxide.

Figure 2 shows an example of a depth profile through on $\text{HfO}_2/\text{SiO}_2/\text{Si}$ sample. 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 and the high-binding-energy O 1s peak is from both SiO_2 and the oxygen contained in adsorbed materials. This is illustrated in Fig. 3, which compares the O 1s spectra from a 1 nm layer of SiO_2 on Si, 1 nm of HfO_2 on 1 nm SiO_2 on Si and a thick (nominally 100 nm) layer of HfO_2 on Si. The low-binding-energy peak is missing from the spectrum from SiO_2 and the high-binding-energy shoulder on the thick HfO_2 layer is a surface species, confirmed using the ARXPS data. The binding energies of the peaks shown in Fig. 3 and their assignments are consistent with those reported in the NIST X-ray Photoelectron Spectroscopy Database.¹²

Repeatability of depth profiles constructed using the maximum entropy method has been reported elsewhere.¹³ Accurate depth profiles cannot be produced using methods

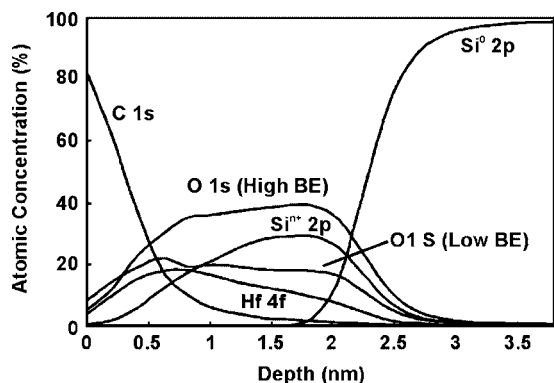


Figure 2. Example of a depth profile through a sample of HfO_2 on SiO_2 on Si. The profile was constructed from ARXPS data.

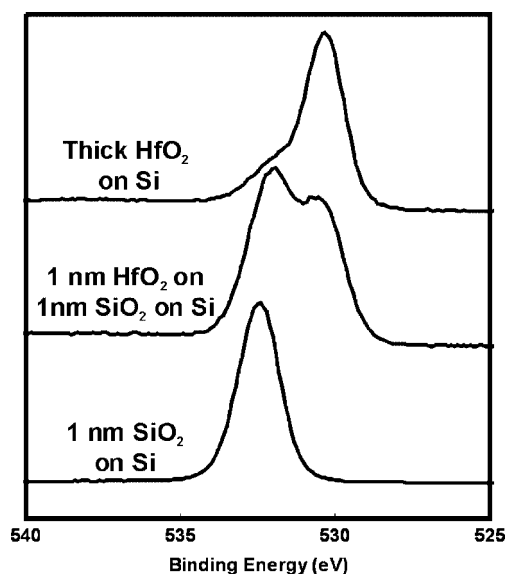


Figure 3. The O 1s spectra from a 1 nm layer of SiO_2 on Si, 1 nm of HfO_2 on 1 nm SiO_2 on Si and a thick (nominally 100 nm) layer of HfO_2 on Si.

based upon sputtering because of the presence of sputter-induced artefacts, in this case reduction of HfO_2 to Hf metal and atomic mixing.

Figure 4 shows Hf 4f spectra acquired during a sputter depth profile; the reduction of the oxide to the metal is clearly visible in this profile. The sputter profile was obtained using argon ions at an energy of 500 eV while rotating the sample to optimize depth resolution. It should be noted that the HfO_2 layer is sufficiently thin that any metallic Hf present in the original layer would be visible in all of the spectra.

The appearance of the sputter profile and the profile generated from ARXPS differ significantly (see Fig. 5). The formation of metallic Hf can be seen clearly in this profile. In addition, metallic Hf can be seen to persist into the substrate. Such phenomena are not observed in the ARXPS, non-destructive depth profile. The sputter profile can, in principle, be improved by calculating the effect of the sampling depth upon the depth resolution. This would improve the depth resolution but it would not correct for the chemical changes induced by the sputtering process.

Dose measurements

It is important to be able to measure the dose of nitrogen in silicon oxynitride layers because this affects its electrical properties. If the distribution of nitrogen is not uniform, however, the dose of nitrogen cannot be measured directly from the N 1s/O 1s peak intensity ratio in the XPS spectrum. If the nitrogen is mainly near the surface of the layer then the ratio will overestimate the quantity of nitrogen, whereas if the distribution is centred near the oxynitride/silicon interface then the quantity will be underestimated.

Figure 6 shows examples of two oxynitride profiles constructed from ARXPS data using the maximum entropy technique. The first of these shows that the nitrogen concentration is greatest near the oxynitride/silicon interface whereas the second profile shows a higher concentration near the surface. If the N/O ratio had been used to calculate the nitrogen dose for either of these materials, then an incorrect result would have been reported. The dose is more accurately determined by integrating under the nitrogen curve on the depth profile.

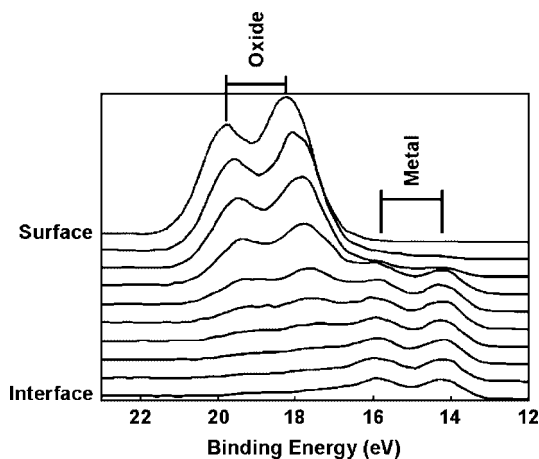


Figure 4. Montage of XPS spectra from the Hf 4f region during a sputter profile experiment.

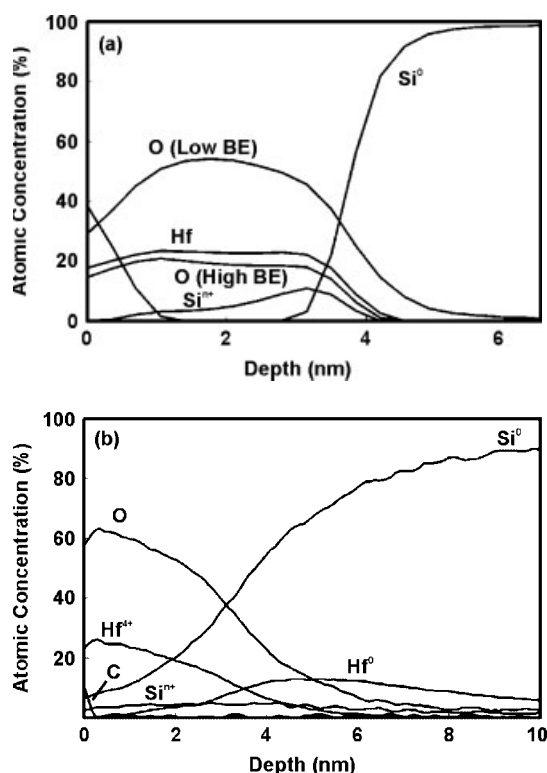


Figure 5. Comparison of depth profiles from ARXPS data (a) and from sputtering (b).

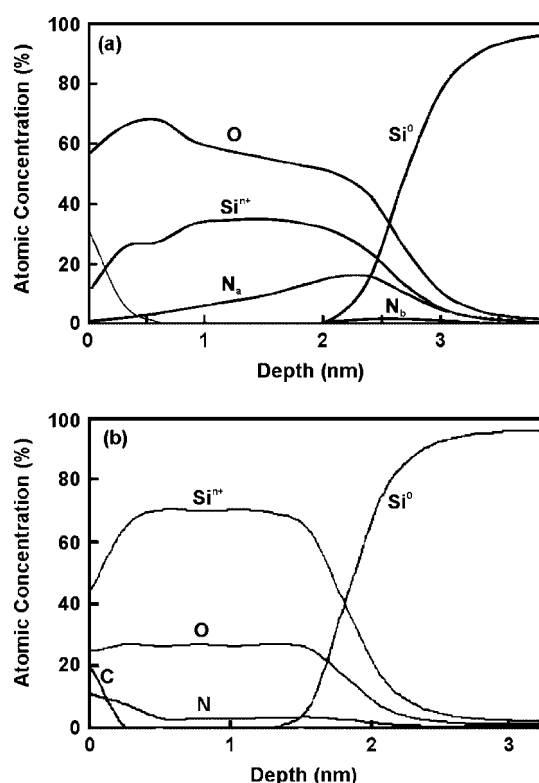


Figure 6. Profiles showing differing oxynitride distributions.

A simple method that can be used to check the nature of the distribution is to measure the N 1s/O 1s peak intensity ratio as a function of emission angle in the ARXPS spectra from the materials. If the ratio increases as the emission

angle increases, then the nitrogen distribution peaks near the surface. Conversely, if the ratio decreases, then the distribution peaks near the interface. This behaviour can be seen clearly in Fig. 7 even for the sample whose profile is shown in Fig. 6(b), where the near surface peak is small.

Interfacial chemistry

When high-*k* dielectrics are deposited on silicon an interfacial layer inevitably will 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. The presence of silicon suboxides at the SiO₂/Si interface has been observed and reported³ and calculations of the binding energies of the Si 2p electrons^{14,15} show good agreement with the experimentally determined values.

In this work we have found that, in addition to these suboxides, silicon can be present in the form of a silicate. Factors that might determine whether silicate is formed include:

- (1) The method of preparation of the layer.
- (2) 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).
- (3) The deposition temperature.
- (4) The treatment of the wafers following deposition of the layer.

The binding energy of the Si 2p_{3/2} peak from silicon dioxide is 103.6 eV¹² whereas the binding energy of the same peak in hafnium silicate is 102.7 eV.¹⁶

Figure 8 shows the comparison between the Si 2p spectra from nominally 1 nm thick silicon dioxide, 1 nm SiO₂ with ~1 nm thick HfO₂ grown by MOCVD and 1 nm SiO₂ with 1 nm thick HfO₂ grown by ALD. 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 SiO₂ with very little, if any, silicate formation because the binding energy remains

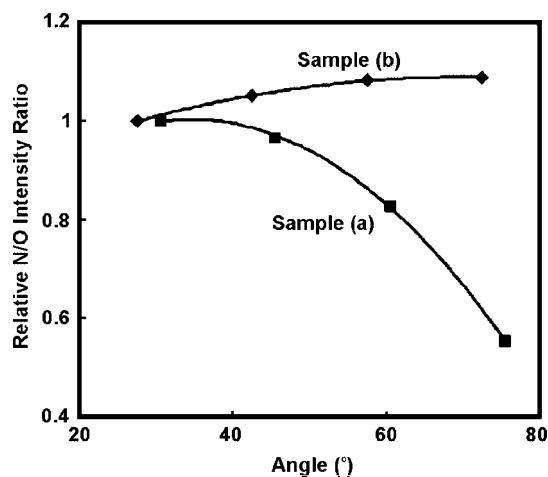


Figure 7. The N 1s/O 1s ratio as a function of emission angle from samples whose profiles are shown in Fig. 6.

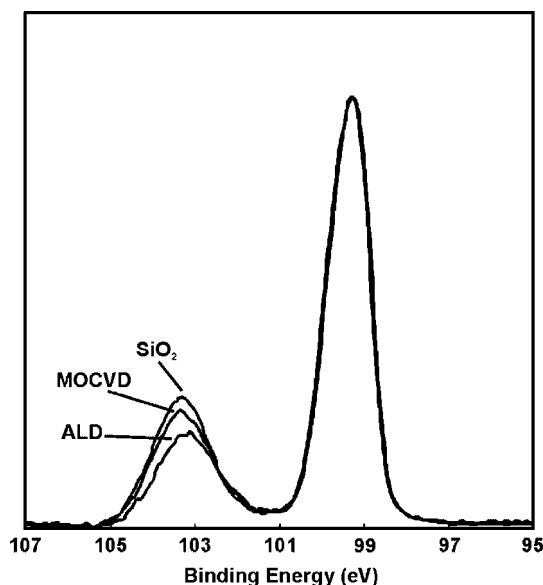


Figure 8. Comparison of Si 2p spectra from SiO₂ (nominally 1.0 nm), with HfO₂ grown by ALD and MOCVD on the same material.

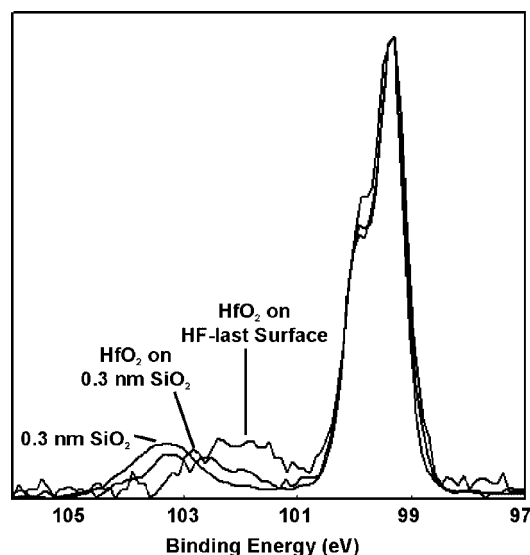


Figure 9. Comparison of Si 2p spectra from thin SiO₂ (nominally 0.3 nm), from thin SiO₂ with HfO₂ grown by ALD and from an HF-last surface with HfO₂ grown by ALD.

at 103.6 eV and there is no evidence of a low-binding-energy shoulder on the peak. A similar conclusion can be drawn for HfO₂ grown on 0.5 nm (nominal thickness) silicon oxide (not shown).

However, the results are different when HfO₂ is grown on thinner SiO₂ layers. Figure 9 shows a comparison of Si 2p spectra from thin SiO₂ (nominally 0.3 nm), thin oxide with HfO₂ grown by ALD and a hydrofluoric acid-etched silicon surface with HfO₂ grown by ALD. Hydrofluoric acid etching removes SiO₂ from a silicon wafer. A wafer treated in this way will be referred to as an 'HF-last surface'. Again, the thin thermal SiO₂ is clearly present as an oxide with no suggestion of a silicate. When HfO₂ is grown on nominally 0.3 nm SiO₂ 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 silicon in an oxidation state lower than +4 or the formation of hafnium silicide. A binding energy of ~102 eV is consistent with that reported by Punchaipetch *et al.*¹⁶ for hafnium silicide.

Figure 10 shows the effect of growing a 4 nm HfO₂ layer by 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 SiO₂. Growth of similar layers at 485 °C followed by annealing at 700 °C shows similar effects.

If the HfO₂ layer is grown using ALD, rather than MOCVD, the chemistry is different, as illustrated in Fig. 11. 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 Fig. 10).

CONCLUSIONS

Both XPS and ARXPS have been shown to be capable of making many of the measurements required for the characterization of transistor gate dielectrics. Measurement of the thickness of the layers can be achieved rapidly by fitting the experimental data to equations derived from the Beer–Lambert law. With a suitable mathematical formalism, the thickness of each layer in a multilayer stack can be measured simultaneously. This method takes account of the differing attenuation lengths for electrons emitted from different atoms or in different materials to provide more accurate results.

Depth profiles can be constructed from ARXPS data. These are important as an end in themselves or as a means for determining the dose of the constituent materials (e.g. nitrogen in an oxynitride). The chemical state of each of the

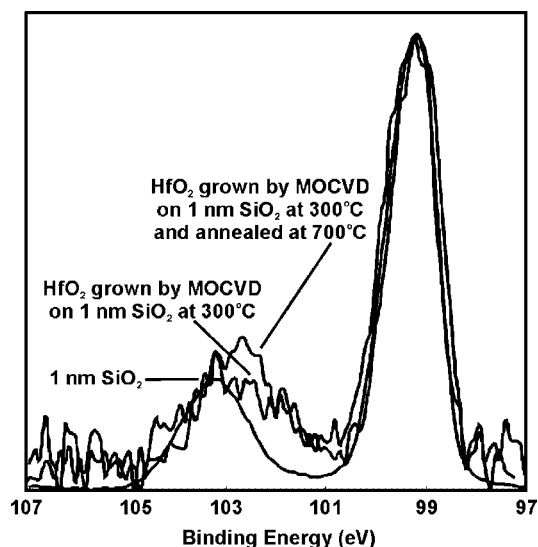


Figure 10. Comparison of Si 2p spectra from thin SiO₂ (nominally 1.0 nm) and from thin SiO₂ with 4 nm HfO₂ grown by MOCVD at 300 °C and following annealing at 700 °C.

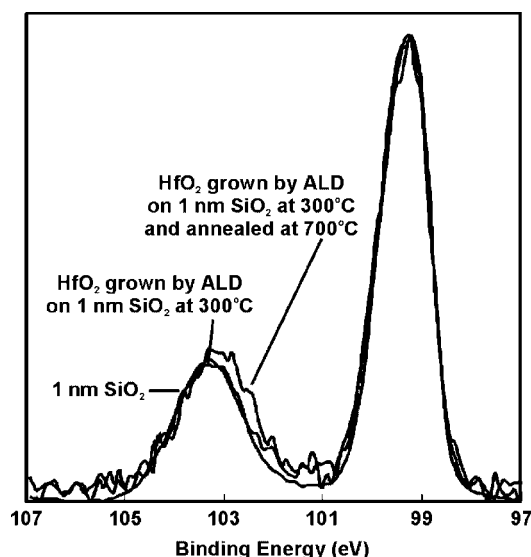


Figure 11. Comparison of Si 2p spectra from thin SiO₂ (nominally 1.0 nm) and from thin SiO₂ with HfO₂ grown by ALD at 300 °C and following annealing at 700 °C.

constituent elements can be determined and related to the method of preparation or post-preparation treatment.

Now that the layer thickness in these materials closely matches the escape depth of the photoelectrons produced during XPS, the technique is expected to become much more widespread as a metrology tool in the semiconductor industry.

Acknowledgement

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