

# SiO<sub>2</sub> thickness determination by x-ray photoelectron spectroscopy, Auger electron spectroscopy, secondary ion mass spectrometry, Rutherford backscattering, transmission electron microscopy, and ellipsometry

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As the  $R_p$  of ion implants steadily decreases an ever-increasing percentage of the implant species lies in the oxide layer and is, therefore, not electrically active. For this reason, it is important to have analytical techniques capable of accurately measuring the thickness of ultrathin oxide layers. A round-robin study was performed on a series of SiO<sub>2</sub> films ranging from 0.3 to 20 nm in order to evaluate the advantages and disadvantages of five commonly used analytical techniques. High-resolution cross-section transmission electron microscopy (TEM) offers the only true measurement of oxide thickness because no density assumptions are made. In this study, TEM is used as the standard for all the other techniques. X-ray photoelectron spectroscopy and Auger electron spectroscopy offer precise measurements for ultrathin (<3 nm) films, but are limited for thicker films (>15 nm) due to the exponential decay functions that describe the sampling depth in both techniques. Secondary ion mass spectrometry (SIMS) has historically been used for characterizing relatively thick films (>10 nm) but not for thinner films because of atomic mixing effects. Encapsulating oxides with amorphous silicon prior to performing a SIMS experiment can negate these effects. A comparison of SIMS on encapsulated and as received films is made. Rutherford backscattering is an excellent technique for determining oxide thickness over a wide thickness range by channeling the Si signal from the crystalline substrate and analyzing oxygen from the amorphous oxide. Ellipsometry, being both rapid and low cost, is one of the most widely used techniques capable of accurate measurements on thick films (>10 nm). © 2000 American Vacuum Society. [S0734-211X(00)08401-8]

## I. INTRODUCTION

The need for accurate and precise measurements of SiO<sub>2</sub> thickness is becoming ever more crucial due, in part, to decreases in the projected range,  $R_p$ , of low energy ion implants. There are a number of analytical techniques capable of measuring oxide thickness on films <10 nm thick. These techniques include: x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), Rutherford backscattering (RBS),

transmission electron microscopy (TEM), spectroscopic ellipsometry (SE), nuclear reaction analysis (NRA), and capacitance-voltage ( $C-V$ ) measurements. In this study, we will compare and contrast the first six of these techniques with the goal of determining the relative strengths and weaknesses of each.

## II. EXPERIMENT

All oxides were present on Si(100) substrates. The samples were aged at least six months to ensure a static oxide thickness for all techniques. The samples were selected to cover a wide thickness range and, as such, originated from a variety of sources.

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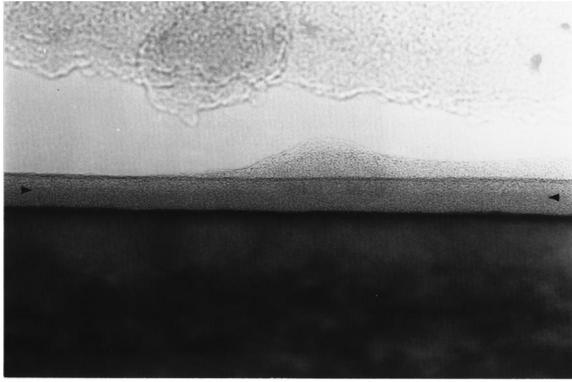


FIG. 1. Cross-sectional TEM image of sample D showing a 3.7 nm oxide.

### A. TEM measurements

TEM was performed on a JEOL 4000 FX high-resolution microscope using a 400 kV beam. The samples were thinned to  $\approx 40$  nm using standard polishing procedures. The glue applied to aid polishing was resolved from the surface oxides by way of the differences in densities and short range order. Under these conditions, the point to point resolution at Scherzer defocus is 0.185 nm. The magnification was calibrated from the fringe spacing of the {111} planes of the silicon lattice. TEM images were acquired at 1 200 000 $\times$  on three samples with nominal thicknesses: 1, 4, and 10 nm. Figure 1 shows a typical TEM image. The error in these measurements arises primarily from roughness of the interface and variations associated with defocusing. The typical error for these high-resolution images is  $\pm 0.20$  nm.

### B. XPS measurements

XPS experiments were performed in a Physical Electronics 5700 LSci and a Physical Electronics Quantum 2000. Both instruments were equipped with monochromatic Al  $k\alpha$  x-ray sources and concentric hemispherical analyzers. All XPS measurements were made at a takeoff angle of  $65^\circ$  from the sample plane and an electron acceptance angle of  $\pm 7^\circ$ . This takeoff angle was chosen to minimize photoelectron diffraction that can affect the intensity of electrons originating from the substrate at certain takeoff angles.<sup>1</sup>

The SiO<sub>2</sub> thickness was determined using the following equation:<sup>1</sup>

$$t_{\text{ox}} = \lambda_{\text{SiO}_2} \sin \theta \ln \left[ \left( \frac{I_{\text{Si}}^\infty}{I_{\text{SiO}_2}^\infty} \frac{I_{\text{SiO}_2}^{\text{exp}}}{I_{\text{Si}}^{\text{exp}}} \right) + 1 \right], \quad (1)$$

where  $\lambda_{\text{SiO}_2}$  is the attenuation length of the Si  $2p$  photoelectrons in SiO<sub>2</sub>,  $\theta$  is the angle between the sample surface plane and the electron analyzer,  $I_{\text{Si}}^\infty/I_{\text{SiO}_2}^\infty$  is the ratio of Si  $2p$  intensities from “infinitely” thick Si<sup>0</sup> and SiO<sub>2</sub>, respectively.  $I_{\text{SiO}_2}^{\text{exp}}/I_{\text{Si}}^{\text{exp}}$  is the ratio of intensities from the unknown film. Unfortunately, there is considerable disagreement in the XPS literature in the two sample-dependent constants:  $\lambda_{\text{SiO}_2}$  and  $I_{\text{Si}}^\infty/I_{\text{SiO}_2}^\infty$ . Reported  $\lambda_{\text{SiO}_2}$  values vary from 2.4 to 3.8 nm,

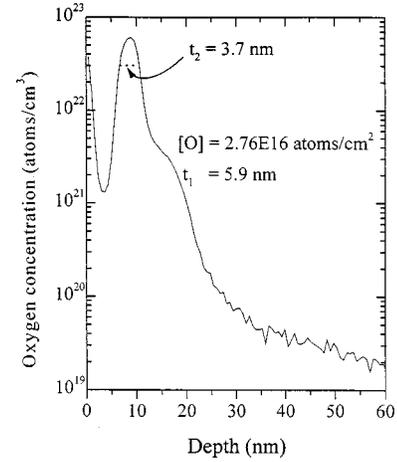


FIG. 2. SIMS oxygen depth profile from encapsulated sample D. Oxide thickness can be determined by quantifying the total amount of oxygen and assuming an oxygen atom density of  $4.7\text{E}22$  atoms/cm<sup>3</sup> for SiO<sub>2</sub> ( $t_1 = 5.9$  nm). However, better results were obtained when the oxide thickness was measured as the full width at half maximum of the O profile ( $t_2 = 3.7$  nm). TEM found this sample to have an 3.7 nm oxide.

while  $I_{\text{Si}}^\infty/I_{\text{SiO}_2}^\infty$  varies from 0.99 to 1.92.<sup>1–13</sup> The attenuation length,  $\lambda_{\text{SiO}_2}$ , was determined from several of the samples in this study that were analyzed by TEM. The determination of  $I_{\text{Si}}^\infty/I_{\text{SiO}_2}^\infty$  was done by analyzing two different standard samples: a 5% HF etched Si(100) surface and a 85 nm thick thermal SiO<sub>2</sub> film. Both standards were lightly sputtered with 3 keV Ar<sup>+</sup> to remove adsorbed organic species and, in the case of the HF etched Si sample, to remove the native oxide. The  $I_{\text{Si}}^\infty/I_{\text{SiO}_2}^\infty$  value measured in our experiments (after accounting for implanted argon and readsorbed gases) was 1.20.

### C. AES measurements

AES was performed in a Perkin–Elmer 660 spectrometer equipped with a cylindrical mirror analyzer. The Si KLL spectra were acquired using a 10 keV, 1.0  $\mu\text{A}$  electron beam  $60^\circ$  from the sample plane. The sample was rotated at 1 rpm to minimize channeling of the incident beam and diffraction effects of the Auger electrons. The electron analyzer was operated at 0.3% energy resolution. The equation used to determine oxide thickness by AES is very similar to the XPS equation given above<sup>14</sup>

$$t_{\text{ox}} = 0.75 \lambda_{\text{SiO}_2} \sin \theta \ln \left[ \left( \frac{I_{\text{Si}}^\infty}{I_{\text{SiO}_2}^\infty} \frac{I_{\text{SiO}_2}^{\text{exp}}}{I_{\text{Si}}^{\text{exp}}} \right) + 1 \right]. \quad (2)$$

The attenuation length,  $\lambda_{\text{SiO}_2}$ , of Si KLL electrons was 3.2 nm, based on calculations done by Tanuma, Powell, and Penn.<sup>6</sup> The 0.75 is a geometrical correction for the analyzer acceptance angle.<sup>15</sup> The  $I_{\text{Si}}^\infty/I_{\text{SiO}_2}^\infty$  value measured by depth profiling a 100 nm SiO<sub>2</sub> film was 1.8. It was assumed that any contribution from Auger electrons generated by back-scattered electrons was minimal.

TABLE I. Summary of oxide thickness by technique (in nm).

Technique/sample	A	B	C	D	E	F	G	H
TEM	...	0.6	...	3.7	...	10.5	...	...
XPS 1	0.4	0.7	2.9	3.6	4.7	10.3	16.0	20.5
XPS 2	...	0.6	...	3.3	4.5	9.9	15.7	20.7
AES	...	0.2	1.7	1.5	4.0	...	...	...
SIMS (quad)	0.3	0.5	1.6	2.1	3.5	9.3	15.0	21.0
ncap-SIMS (mag)	...	1.0	3.8	3.4	6.9	17.3	24.0	30.6
ncap-SIMS (quad)	1.3	1.5	6.2	5.9	11.6	21.0	25.7	36.9
ncap-SIMS (quad) <sup>a</sup>	1.7	1.9	3.2	3.7	4.7	9.3	13.8	19.7
RBS	1.1	1.3	3.2	3.6	4.9	9.8	13.8	20.0
Ellipsometry	...	2.8	3.9	...	7.3	10.5	15.3	...

<sup>a</sup>Thickness measured as full width at half maximum of oxygen profile.

#### D. SIMS measurements

SIMS was done on both as-received samples and samples encapsulated with 10–20 nm of *a*-Si deposited at 560 °C. The as-received samples were analyzed with a Physical Electronics 6650 quadrupole-based SIMS instrument using 100 nA, 1 keV Cs<sup>+</sup> primary ion beam. A 600 μm × 600 μm crater was sputtered and CsO<sup>+</sup> and CsSi<sup>+</sup> cluster ions detected from the center 25% of the crater. The oxide thickness was determined by measuring the time to the 50% drop in the O intensity and applying the sputter rate determined from a thermal oxide standard.

The encapsulated samples were analyzed on two different instruments: a Physical Electronics 6600 quadrupole-based spectrometer and a Cameca IMS-3f magnetic sector-based instrument. The quadrupole instrument used a 5 keV, 100 nA Cs<sup>+</sup> primary ion beam 60° from the sample normal. Negative ions (<sup>16</sup>O<sup>-</sup> and <sup>18</sup>O<sup>-</sup>) were detected. Quantification of oxygen was done using an ion implanted standard. The magnetic sector instrument utilized a 14.5 keV, 120 nA Cs<sup>+</sup> primary ion beam 24° from the normal. Quantification of <sup>18</sup>O<sup>-</sup> was done using an ion implanted standard sample. The sputter rates in both experiments were determined by measuring the crater depth with a stylus profilometer (Tencor Instruments Alpha-step 200). No corrections were made for sputter rate differences between the oxide and silicon.

Oxide thickness on the encapsulated samples was determined indirectly, by quantifying the total oxygen at the *a*-Si/SiO<sub>2</sub>/*c*-Si interface and assuming an oxygen atom density of 4.7E22 atom/cc in SiO<sub>2</sub>. It was anticipated that the encapsulation technique would work best for thin films (<5 nm) where the ion beam mixing depth is greater than the SiO<sub>2</sub> layer thickness. Yamazaki and Takahashi found very poor agreement between XPS and encapsulation SIMS over the 0.3–1.0 nm range measured in their study.<sup>16</sup> The oxide thickness on one set of profiles was also determined by measuring the full width at half maximum (FWHM) of the oxygen profile at the interface. Figure 2 shows an oxygen depth profile from a typical sample highlighting the two different methods of measuring oxide thickness on an encapsulated sample.

#### E. RBS measurements

The RBS experiments were performed on a National Electrostatics Corporation 3-SDH accelerator with a Charles Evans and Associates RBS end station. The instrument used a 2.275 MeV He<sup>++</sup> beam with a 2.5 mm diameter spot. Spectra were acquired at backscattering angles of 160° and 101° with samples mounted in an optimally ion channeled orientation. RBS measured the total oxygen concentration (in atoms/cm<sup>2</sup>). This concentration was converted to oxide thickness by assuming a SiO<sub>2</sub> atom density of 7.0E22 atoms/cm<sup>3</sup>.

#### F. Ellipsometry measurements

Ellipsometry was performed using an Instruments S. A. Uvisel Phase Modulated Ellipsometer. The samples were aligned to maximize signal throughput. The optical parameters, Ψ and Δ, were collected as a function of wavelength. All measurements were performed with an incident angle of 70°. To determine the film thickness of each sample, the

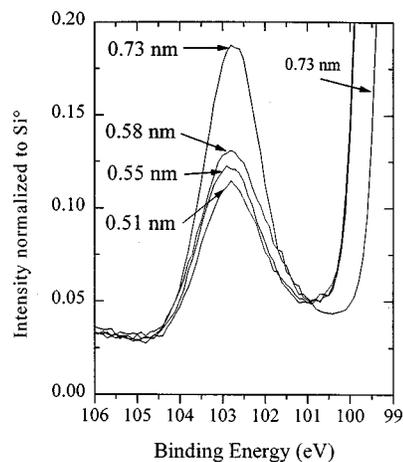


FIG. 3. XPS Si 2p spectra of four ultrathin SiO<sub>2</sub> films showing the ability to measure extremely small (<0.1 nm) differences in thickness. The spectra have been normalized to the Si<sup>0</sup> peak. The offset in the binding energy of the Si<sup>0</sup> peak of the 0.73 nm film is the result of a difference in dopant type (As vs B for the three thinner films).

TABLE II. Summary of findings.

Technique	Advantages	Disadvantages	Optimum range	Useful range
TEM	accurate without standards	expensive; very small area analyzed	>1 nm	>1 nm
XPS	precise to $\pm 0.1$ nm for films <3 nm	less precise for thicker films; accurate over wide range	<10 nm	$\leq 20$ nm
AES	inexpensive, readily available	not accurate, further calibration necessary	...	<4 nm
SIMS	qualitative film thickness	further calibration required	$\geq 20$ nm	$\geq 10$ nm
encap-SIMS	qualitative over wide range	not accurate for films >1.5 nm; expensive	...	<1.5 nm
RBS	accurate without Standards	not precise for films $\leq 1$ nm	$\geq 1$ nm	$\geq 1$ nm
Ellipsometry	inexpensive, fast	not accurate for films <2 nm	>10 nm	>2 nm

Bruggemen effective medium approximation model<sup>17</sup> was used to fit each spectrum to reference data of SiO<sub>2</sub> on polycrystalline silicon<sup>18</sup> with film thickness being the only variable parameter.

### III. RESULTS AND DISCUSSION

The results are summarized in Table I. In general, we take the TEM measurements as the true measure of oxide thickness. The error in the TEM measurements is  $\pm 0.2$  nm and arises primarily from roughness of the interface and variations associated with defocusing. There was agreement to within 0.3 nm for the XPS measurements taken on two different instruments. XPS also agreed well with the TEM measurements taken on three samples. The ability of XPS to precisely measure differences less than 0.1 nm for films <2 nm is highlighted in Fig. 3. The upper limit for qualitative thickness measurements by XPS proved to be in the range of 15–20 nm, where the contribution from the substrate is much less than 1% of the total silicon signal.

AES signal from the substrate was only observed on films up to 5.0 nm thick. The values on the films <4 nm thick were considerably lower than the TEM, RBS, and XPS values.

SIMS measurements on the as-received samples have estimated errors of 5% yet yielded generally lower thickness values than TEM, XPS, and RBS on films up to 10 nm, and higher values for films >10 nm. The reason is unclear although ion beam induced atomic mixing will lead to a decrease in O intensity prior to the analytical crater reaching the substrate.<sup>19</sup> There are also reports of nonlinear sputter rates in the first few tens of nanometers under certain bombardment conditions.<sup>20</sup>

Not surprisingly, encapsulation SIMS measurements showed a large divergence from the other techniques for films >5 nm. This divergence was worse on the films analyzed at lower primary ion beam energies where the SiO<sub>2</sub> film was not mixed as effectively with the neighboring Si

layers. Better agreement was realized when the oxide thickness was measured directly from the oxygen profiles.

RBS showed excellent agreement with TEM. On ultrathin films there was, however, a background level of oxygen (observed even a freshly HF-etched Si wafer). This oxygen may, in fact, be due to organic species on the wafers. XPS analysis on a similar film found no SiO<sub>2</sub> peak in the Si 2*p* spectrum, but roughly a monolayer of oxygen-containing organic species. Ellipsometry also overestimated thin films (<10 nm) possibly for the same reason.

### IV. SUMMARY

In conclusion, TEM, XPS, AES, SIMS, RBS, and ellipsometry were all able to measure qualitative differences between SiO<sub>2</sub> films that varied from 0.3 to 20 nm. No single technique was able to accurately and precisely measure thickness across the entire range. TEM offers the only true measure of oxide thickness, but analysis on films <1 nm is difficult. XPS was useful for a wide range of thickness, but most sensitive to differences on films <3 nm thick. AES is limited to films <4 nm and still requires further calibration. RBS was able to monitor thickness over the widest range. Encapsulation SIMS proved less effective than the more traditional SIMS method of determining layer thickness. Spectroscopic ellipsometry was able to accurately measure films >10 nm. Table II summarizes the findings of the round-robin study.

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