Oxide Thickness Determination by XPS, AES, SIMS, RBS and TEM

J.R. Shallenberger, D.A. Cole, S.W. Novak and R.L. Moore, Evans East, 666 Plainsboro Road., #1236 Plainsboro, NJ 08536, USA
M.J. Edgell, S.P. Smith, C.J. Hitzman, J.F. Kirchhoff and E. Principe, Charles Evans & Associates, 301 Chesapeake Drive, Redwood City, CA 94063 USA
S. Biswas, Evans Europa, ETC Building, Brunel University, Uxbridge UB8 3PH, UK
R.J. Bleiler, Evans Texas, 425 Round Rock West Drive, Suite 100, Round Rock, TX 78681 USA
W. Nieveen, Surface Science Labs, 625-B Clyde Avenue, Mountain View, CA 94043 USA
K. Jones, University of Florida, 525 Engineering Bldg. #33 Gainesville, FL 32611

ABSTRACT- **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 ultra-thin oxide layers. A round-robin study was performed on a series of SiO_2 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 (XPS) and Auger electron spectroscopy (AES) offer precise measurements for ultra-thin (<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 polycrystalline silicon prior to performing a SIMS experiment can negate these effects. A comparison of SIMS on poly-encapsulated and as received films is made. Rutherford backscattering (RBS) 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.**

INTRODUCTION

The need for accurate and precise measurements of SiO_2 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: XPS, AES, SIMS, RBS, TEM, Nuclear Reaction Analysis (NRA), spectroscopic ellipsometry (SE) and capacitance-voltage (CV) measurements. In this study we will compare and contrast the first five of these techniques with the goal of determining the relative strengths and weaknesses of each.

EXPERIMENTAL

All oxides were present on Si (100) substrates. The samples were aged at least 6 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.

TEM measurements

TEM was performed on a Jeol 4000SX high resolution microscope using a 400 kV beam and 13 multi beam conditions on the Si (110) axis. The samples were thinned to ≈40 nm using standard polishing procedures. Images were acquired at 1,200,000X. TEM was performed on three samples with nominal thicknesses: 1, 4 and 10 nm.

XPS measurements

XPS experiments were performed in a Physical Electronics 5701 LSci and a Physical Electronics Quantum 2000. Both instruments were equipped with monochromatic Al kα x-ray sources and concentric hemispherical analyzers. All XPS measurements were made at a takeoff angle of 65°, with respect to the sample surface plane and an electron acceptance angle of ±7°. This takeoff angle was chosen to minimize photoelectron diffraction which can affect the intensity of electrons originating from the substrate at certain takeoff angles [1].

The SiO_2 thickness was determined using the following equation [1]:

$$t_{ox} = \lambda_{SiO2} \sin\theta \ln \{[(1/\beta)(I_{SiO2}^{exp} / I_{Si}^{exp})] + 1\} \quad (1)$$

where, λ_{SiO2} is the attenuation length of the Si 2p photoelectrons in SiO_2, θ is the angle between the sample surface plane and the electron analyzer, $\beta = I_{SiO2}^{\infty} / I_{Si}^{\infty}$ (the Si 2p intensity from infinitely thick SiO_2 and Si, respectively) and $I_{SiO2}^{exp} / I_{Si}^{exp}$ is the ratio of intensities from the unknown film. Unfortunately, there is considerable disagreement in the XPS literature in the two sample-dependent constants: λ_{SiO2} and β. Reported λ_{SiO2} values vary from 2.4-3.8 nm, while β varies from 0.6-1.01 [1-12]. It has been suggested that much of the discrepancy in the reported λ_{SiO2} values stems from the use of poorly calibrated ellipsometry 'standards' that tend to overestimate the thickness of ultra-thin SiO_2 films [3,13-16]. In theory, TEM yields an absolute measure of the oxide thickness because it makes no assumptions about

atom density and it has a built-in distance calibration in the Si-Si lattice constant. For this reason it was decided to use an attenuation length of 2.7 ±0.2 nm, averaged from four different TEM/XPS publications [2-5]. The determination of β was done by analyzing two different standard samples: a 5% HF etched Si (100) surface and a 85 nm thick thermal SiO_2 film. Both standards were lightly sputtered with 3 keV Ar^+ to remove adsorbed organic species and the native oxide and fluoride (on the HF etched Si sample). The β value measured in our experiments (after accounting for implanted argon and re-adsorbed gases) was 0.83.

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 µA electron beam 30° from the sample normal. 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 [17],

$$t_{ox} = 0.75\ \lambda_{SiO2} \ln \{[(1/\beta)\ (I_{SiO2}^{exp} / I_{Si}^{exp})] + 1\}. \quad (2)$$

The attenuation length, λ_{SiO2}, of Si KLL electrons was 3.2 nm, based on calculations done by Tanuma, Powell and Penn [6]. The 0.75 is a geometrical correction for the analyzer acceptance angle [18]. The β value measured by depth profiling a 100 nm SiO_2 film was 0.55. It was assumed that any contribution from Auger electrons generated by backscattered electrons would be minimal.

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^+ primary ion beam. A 600µm X 600µm crater was sputtered and CsO^+ and $CsSi^+$ 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 standard sample.

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^+ primary ion beam 60° from the sample normal. Negative ions ($^{16}O^-$ and $^{18}O^-$) were detected. Quantification of oxygen was done using an ion implanted standard. The magnetic sector instrument utilized a 14.5 keV 0.12 µA Cs^+ primary ion beam 24° from the normal. Quantification of $^{18}O^-$ 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 O at the *a*-Si/SiO_2/*c*-Si interface and assuming an oxygen atom density of 4.7E22 atoms/cc in SiO_2. It is anticipated that the encapsulation technique will only work for very thin films where the ion beam mixing depth is greater than the SiO_2 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 [19]. 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. Fig. 1 shows an oxygen depth profile from a typical sample highlighting the two different methods of measuring oxide thickness on an encapsulated sample.

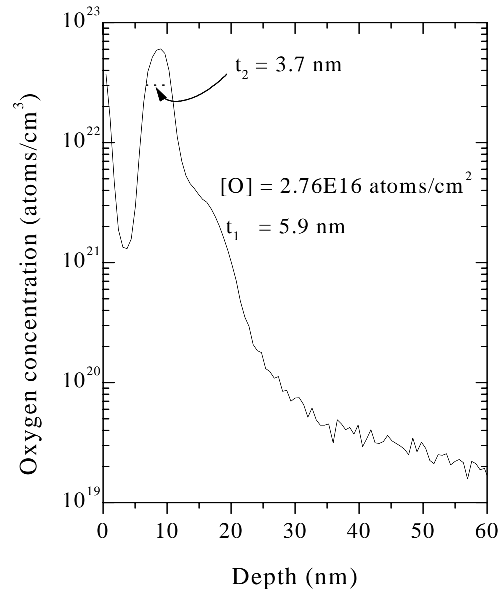

Fig. 1. SIMS oxygen depth profile from encapsulated sample D. Oxide thickness can be determined by quantifying the total amount of oxygen and assuming an oxygen atom density of 4.7E22 atoms/cm^3 for SiO_2 (t_1= 5.9 nm). However, better results were obtained when the oxide thickness was measured as the full-width-at-half-maximum of the O profile (t_2 = 3.7 nm). TEM found this sample to have a 3.7 nm oxide.

RBS measurements

The RBS experiments were performed on a National Electrostatics Corporation 3-SDH accelerator with a Charles Evans & Associates RBS end station. The

instrument used a 2.275 MeV He^{++} 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^2). This concentration was converted to oxide thickness by assuming an SiO_2 atom density of 7.0E22 atoms/cm^3.

RESULTS & DISCUSSION

The results are summarized in Table I. There was agreement to within 0.4 nm for the XPS measurements taken on two different instruments. However, the XPS determined thickness was lower than that measured by TEM for the two thicker oxides. One reason for the discrepancy may be the interface roughness which was 2.5 nm on sample F. The ability of XPS to measure precisely differences less than 0.1 nm for films <2 nm is highlighted in Fig.2. 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 yielded generally lower thickness values than TEM, XPS and RBS on films up to 10 nm, but 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 [20]. There is also reports of non-linear sputter rates in the first few tens of nanometers under certain bombardment conditions [21].

TABLE I

Summary of Oxide Thickness by Technique (in nm)

Technique	A	B	C	D	E	F	G	H
TEM	-	0.6	-	3.7	-	10.5	-	-
XPS 1	0.3	0.6	2.3	3.0	3.7	8.2	12.5	16.3
XPS 2	-	0.5	-	2.6	3.6	7.9	12.5	16.4
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)*	1.7	1.9	3.2	3.7	4.7	9.3	13.8	19.7
RBS	1.1	1.3	3.2	-	4.9	9.8	13.8	20.0

* Thickness measured as full-width-at-half-maximum of oxygen profile.

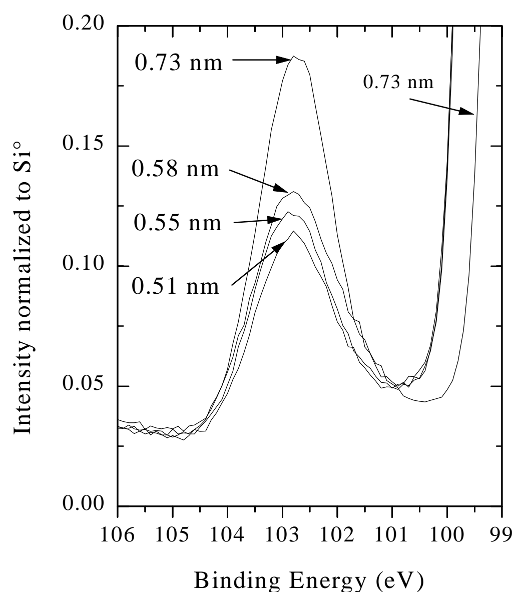

Fig. 2. XPS Si 2p spectra of four ultra-thin SiO_2 films showing the ability to measure extremely small (<0.1 nm) differences in thickness. The spectra have been normalized to the Si° peak. The offset in the binding energy of the Si° peak of the 0.73 nm film is the result of a difference in dopant type (As vs. B for the three thinner films).

Not surprisingly, encapsulation SIMS measurements showed a large divergence from the other techniques for films >1.5 nm. This divergence was worse on the films analyzed at lower primary ion beam energies where the SiO_2 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 ultra-thin 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_2 peak in the Si 2p spectrum, but roughly a monolayer of oxygen-containing organic species.

SUMMARY

In conclusion, TEM, XPS, AES, SIMS and RBS were all able to measure qualitative differences between SiO_2 films which varied from 0.3-20 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 most sensitive to differences on films < 3 nm thick, while RBS was able to monitor thickness over the

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 ±0.1 nm for films <3 nm	less precise for thicker films; calibration required	< 3 nm	≤ 20 nm
AES	inexpensive, readily available	not accurate, further calibration necessary	-	< 4 nm
SIMS	qualitative film thickness	further calibration required	-	≥ 20 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 ≤1 nm	≥ 1 nm	≥ 1 nm

widest range. Encapsulation SIMS proved less effective than the more traditional method of determining layer thickness. Table II summarizes the findings of the round robin study.

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