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High-Resolution Depth Profiling of Ultrathin Silicon Oxide/Nitride/Oxide Layers

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ABSTRACT

We demonstrate that in situ ellipsometry in conjunction with reactive ion etching is capable of providing high-resolution (≤0.3 nm) compositional depth profiles of thin (∼5 nm) silicon oxide/nitride/oxide (ONO) structures, which are superior to those which can be obtained by other methods. A low pressure (75 mTorr), low power (50 W) CF$_4$ plasma was employed to etch slowly the ONO multilayer structure with Si$_3$N$_4$/SiO$_2$ etch rate ratio of ~4. The instantaneous etch rate as a function of depth was measured by automated ellipsometry, providing a measure of the composition.

Oxide-nitride-oxide (ONO) multilayer structures have lower defect density than thin oxide films and also provide a barrier against boron diffusion. They are the dielectric of choice for storage capacitors in dense dynamic-random-access memory (DRAM) chips. Compositional depth profiles of thin (∼5 nm) ONO structures on silicon are important in ONO process development, but are beyond the capabilities of Auger and secondary ion mass spectrometry profiling. A quantitative study of these structures requires the determination of the location of the oxide/nitride interface with a precision of about 0.1 nm. The techniques available for this purpose can be divided into two groups: (i) “sputter profiling” methods and (ii) nonsputtering techniques. For sputter profiling techniques the sample surface is continuously sputtered with energetic ions while a preselected element is detected as a function of erosion time. Secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES) are examples of this approach. The depth resolution of these methods is ~2.5 nm. Widely used nonsputter profiling methods are transmission electron microscopy (TEM) and spectroscopic ellipsometry. Both techniques require sufficient contrast between the physical properties of the individual films (electrical for TEM and optical for ellipsometry), which is only marginally present for ONO layers.

In this article, we describe a method for obtaining high-resolution compositional depth profiles of ultrathin ONO multilayer structures using in situ ellipsometry in conjunction with reactive ion etching (RIE). The use of RIE to remove material slowly from a surface instead of the more conventional physical sputtering offers two major advantages: initial transient phenomena inherent with sputtering are avoided, and intralayer mixing due to the high energy ion bombardment is diminished. Furthermore, the chemical nature of the process makes it possible to optimize the etch rate ratio (ERR) of Si$_3$N$_4$ over SiO$_2$. If the Si$_3$N$_4$/SiO$_2$ ERR is sufficiently high, the etch rate may be used as a measure of the local film composition.

Single or multilayer structures of oxide and nitride on HF cleaned silicon substrates were grown on Si (100) wafers using thermal oxidation for the initial SiO$_2$ layer followed by chemical vapor deposition (CVD) of the Si$_3$N$_4$ and/or additional SiO$_2$ layers. The thicknesses of these structures ranged from 3 to 20 nm. The reactive ion etching/ellipsometry profiling (RIE/EP) experiments were performed in a conventional parallel-electrode dry etching system. It consists of a 0.5 m diam chamber, with a 0.3 m diam quartz covered water cooled electrode made of aluminum. An RF power of 50 W at 13.56 MHz, corresponding to an electrode power density of 0.01 W/cm$^2$, was supplied to the electrode. The samples were placed in the center of the electrode and maintained at a temperature of 25°C. Etching was carried out with a total gas flow of 100 sccm of CF$_4$, at a pressure of 75 mTorr. The etch rates of the samples were determined in situ using ellipsometry. The ellipsometer is an automated, rotating compensator type in the polarizer-sample-compensator-analyzer (PSCA) configuration, operating at the He-Ne laser wavelength of 632.8 nm. This ellipsometer has an accuracy of about 0.01 degree in $\Psi$ and $\Delta$. An angle of incidence of ~74° was used in this work, which provides higher surface sensitivity than 70°, which is conventionally used. A measurement of $\Psi$ and $\Delta$ was performed once per second.

An example of a $\Psi$-$\Delta$ plot of an ONO/Si sample is given in Fig. 1. Successive pairs of $\Psi$-$\Delta$ data were taken after 1 s

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troscopy (AES) combined with Ar ion sputter profiling was taken to be 3.88 ± 0.019, 1.48, and 1.98 for Si, SiO₂, and that the interface is sharp for RIE/EP depth profile but smeared out for AES measurements.

Also performed to estimate the elemental composition and to the system. The refractive indexes (at 632.8 nm) were the now known thickness and refractive index is "added" to the thickness is calculated, and the infinitesimal layer with the etch rate depth profile from the Δh contour is started. The elemental concentrations of Si, SiO₂, and Si₃N₄ (and their ratios) and the sputtering rate of these materials is determined with a depth resolution of ~0.3 nm, and (iii) the interface region of oxide and nitride appears as sharp as ~0.5 nm, corresponding to ~1-2 monolayers of SiO₂ or Si₃N₄, and (ii) the differences of etch rates between oxide and nitride films provide a sharp interface region which is less than ~0.3 nm, corresponding to ~1-2 monolayers of SiO₂ or Si₃N₄, and (iii) the interface region of oxide and nitride appears as sharp as the interface between the oxide and the silicon substrate. The elemental concentrations of Si, SiO₂, and Si₃N₄ (and their ratios) and the sputtering rate of these materials (~5 Å/min) are used for the AES compositional depth profiles. The AES results are shown in Fig. 3a and 4a, indicate that (i) the thickness of each ultrathin oxide and nitride film can be clearly determined with a depth resolution of ~0.3 nm, (ii) the differences of etch rates between oxide and nitride films provide a sharp interface region which is less than ~0.3 nm, corresponding to ~1-2 monolayers of SiO₂ or Si₃N₄, and (iii) the interface region of oxide and nitride appears as sharp as the interface between the oxide and the silicon substrate.

The AES results agree qualitatively very well with the RIE/EP results. According to the AES measurements, the total thicknesses of the two-layer and three-layer structures are ~60 and ~90 Å, respectively, both slightly greater than the RIE/EP results. A possible reason is that the RIE-induced surface modifications were minimized.

The results obtained with a thin SiO₂ or Si₃N₄ layer on a Si substrate are superimposed in Fig. 2. The etch rates were found to be ~0.5 and ~2 Å/s for the oxide and nitride film, respectively. These rates provide good depth resolution (0.5-2 Å) as well as sufficient etch selectivity (Si₃N₄/SiO₂ ERR ~4). In the following we also exploit the fact that for the RIE conditions used here the etch rates of SiO₂ films deposited by different methods (thermal oxidation, CVD, or PECVD) differ by less than a factor of 2, even when doped with up to 7% of phosphorus or 5% of boron. These results along with the etch rate obtained with a thickness (~500 nm) Si₃N₄ sample under the same RIE conditions are also shown in Fig. 2.

Figures 3 and 4 present the depth profiles of two different samples, one with two layers (ONO/Si) and one with three layers (ONO/Si) that were obtained with RIE/EP and AES, respectively. The depth profiles obtained with RIE/EP, shown in Fig. 3a and 4a, indicate that (i) the thickness of each ultrathin oxide and nitride film can be clearly determined with a depth resolution of ~0.3 nm, (ii) the differences of etch rates between oxide and nitride films provide a sharp interface region which is less than ~0.3 nm, corresponding to ~1-2 monolayers of SiO₂ or Si₃N₄, and (iii) the interface region of oxide and nitride appears as sharp as the interface between the oxide and the silicon substrate. The elemental concentrations of Si, SiO₂, and Si₃N₄ (and their ratios) and the sputtering rate of these materials (~5 Å/min) are used for the AES compositional depth profiles. The AES results are shown in Fig. 3b and 4b. The AES results agree qualitatively very well with the RIE/EP results. According to the AES measurements, the total thicknesses of the two-layer and three-layer structures are ~60 and ~90 Å, respectively, both slightly greater than the RIE/EP results. A possible reason is that the RIE-induced surface modifications were minimized.

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Fig. 3. The depth profiles (etch rate vs. depth) of ON/Si two layer structures obtained from (a) RIE/EP and (b) AES measurements. It is clear that the interface is sharp for RIE/EP depth profile but smeared out for AES measurements.
also examined using high resolution Rutherford backscattering (RBS) and ion channeling techniques. The layer thicknesses estimated from the total oxygen, nitrogen, and the silicon area densities in the top multilayer and their ratios obtained by RBS and channeling were also in agreement with the RIE/EP results.

A basic assumption of the new technique is that the interfaces of the multilayer samples are abrupt. If the thin film processing produces roughness at the interface between SiO\textsubscript{2} and Si substrate, e.g., reoxidation at high temperature, then the interpretation of the ellipsometry data will be difficult and the depth profiles will not be accurate. For instance, an ONO sample reoxidized at 950°C for 20 min in dry O\textsubscript{2} was examined using the RIE/EP technique. The \( \Psi - \Delta \) data indicated in this case that (i) the final thermal oxidation treatment increased only the thickness of the inner oxide layer and (ii) the interface between the inner oxide and the Si substrate became rough as a result of the oxidation (possibly due to oxygen nonuniformly diffusing through the very thin nitride film). Although the technique is unable to provide an accurate profile in this case, it is capable of detecting the presence of interface roughness and identifying situations which cannot be analyzed correctly.

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Fig. 4. The depth profiles (etch rate vs. depth) of ONO/Si sandwich-like structures obtained from (a) RIE/EP and (b) AES measurements.

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