Electrical depth profiling in thin SiON layers

A. Rozenblat, Y. Rosenwaks, L. Segev, and H. Cohen

Materials Science and Engineering, Tel-Aviv University, Ramat-Aviv 69978, Israel
School of Electrical Engineering, Tel-Aviv University, Ramat-Aviv 69978, Israel
Materials and Interfaces, The Weizmann Institute of Science, Rehovot 76100, Israel
Chemical Research Support, The Weizmann Institute, Rehovot 76100, Israel

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The internal structure of SiON films is extracted electrically, demonstrating an efficient, noncontact, nondestructive means for depth compositional analysis in gate oxides. The electrical data, obtained using x-ray photoelectron spectroscopy (XPS) based controlled surface charging (CSC), are compared with independent time of flight secondary ion mass spectroscopy and angle resolved XPS data. Inhomogeneous composition with significant nitrogen enrichment at the top of the oxide layer is observed. Capabilities of the CSC method in treating heterostructures of poor chemical contrast are discussed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3073050]

Characterization methods that can determine compositional profiles across nanometer thick layered structures are of utmost importance to ultrathin gate oxide based devices, in particular, and to the current microelectronic science and industry in general. Such an example is the process dependent nitrogen distribution in silicon oxynitride (SiON) films, where nitrogen atoms are intentionally added to the SiO2 network to obtain improved diffusion barrier properties and enhanced immunity from hot carrier damage.

As depth profiling probes, secondary ion mass spectroscopy (SIMS) and Ar milling in core electron spectroscopy are commonly used. However, these destructive tools frequently induce major profile distortions. High depth profiling accuracy was demonstrated with nondestructive angle resolved x-ray photoelectron spectroscopy (ARXPS) of thin structures up to ~10 nm thick. ARXPS requires relatively long measurements and careful interpretation of a nonunique solution associated with an ill-defined inverse problem. Its analysis is largely improved by considering the role of elastic scattering events, and considerable progress can be achieved by evaluating also the background and satellite line intensities.

An alternative approach, which does not rely on the analysis of line intensities, has been proposed for nondestructive profiling: controlled surface charging (CSC). CSC extracts spatial information from the energy axis of the spectrum while creating potential gradients across the studied volume. Extension of CSC to consistent chemically resolved electrical measurements (CREM) has been recently demonstrated. CREM and CSC are both noncontact methods, proposing unique capabilities, down to atomic scale resolution of the electrostatic potential. In the present work, we exploit the CSC capabilities for characterizing the internal structure of SiON layers, where the chemical contrast across the layer is rather poor. Line shape analysis is applied for continuous intermixing distribution functions, and comparison with alternative techniques is presented.

Oxynitride films were prepared on p-type (1015 cm−3 boron) Si (100), growing first thermal SiO2 layers on precleaned substrates, and subsequently applying rapid thermal nitridation under pure NH3 atmosphere at 1050 °C. Different N concentrations were obtained via temperature control in a range of ±10 °C. The data presented below correspond to SiON layers, 36 Å thick. Ellipsometry was used as a reference for thickness evaluation.

XPS and CSC measurements were performed on a Kratos AXIS-HS instrument using a monochromatic Al (Kα) source. The angular width of our XPS detection system is normally about ±15°. Complementary measurements were performed in an electrostatic mode with angular acceptance of about ±2° only. Samples were connected to the sample holder by a double-sided carbon tape after scratching mechanically the back side of the sample. CSC input signals were applied with (1) an electron flood gun (eFG), controlled via filament current and two bias voltages and (2) a Keithley 487 electrometer for biasing the back contact of the sample. Additional details can be found elsewhere. ToF-SIMS was conducted with a Physical Electronics TRIFT II instrument using a dual beam-phased mode, with a 15 KeV Ga+ ion beam at the analysis phase and a 250–500 eV Cs+ ion beam at the sputtering phase. Implant standards in SiO2 and Si were used in the quantification of the nitrogen profiles. For the interface region, a relative sensitivity factor was applied as a function of the Si intensity signal (see Ref. 23).

The spectra in Fig. 1(a) correspond to three different sample bias (Vb) values under fixed eFG conditions (2.5 V, 1.85 A). Clear line shifts of the substrate (Si\textsuperscript{wafer}) peak are observed, whereas the oxidized Si (Si\textsuperscript{ox}) peak shifts are considerably smaller. The actual potential values developing across the measured structure are extracted from these line shifts (ΔE), corrected for the trivial shifts under V\textsubscript{fb} changes, i.e., \(V = ΔE/ΔV_{fb}\), where \(V\) is the electron charge, and zero potential is arbitrarily determined at the first measurement, i.e., at the step of minimal current. Absolute potential values are not required in the present application.

A complete set of element specific I-V characteristics is summarized in Fig. 1(b). The experiment is conducted by first increasing V\textsubscript{fb} in steps of 0.4V and then lowering it back by the same increments. All the curves exhibit minor hysteresis in potentials and a more pronounced current hysteresis, originating in capacitive effects, which have a minor impact on the present analysis (to be discussed in a future work). The carbon (a top marker of the structure) and the substrate (a bottom marker, Si\textsuperscript{wafer}) present the two extremes

\(2^a\)Author to whom correspondence should be addressed. Electronic mail: hagai.cohen@weizmann.ac.il.
in potential variations, as expected from their vertical positions. Interestingly, differences evolve also between N and both O and Siox, suggesting an inhomogeneous composition with N enrichment at the top of the layer.

As an independent technique, we provide the ToF-SIMS. Elemental concentration profiles are shown in Fig. 2 (top). Both O and N are probed via Si-containing fragments of comparable yields, SiO3 and SiN, subsequently divided by the Si signal to get the net elemental curves. These net curves are subject to a marked artifact change in the Si sensitivity factor across the interface but the resultant error restricted to a relatively deep region hardly affects the analysis below.

The ToF-SIMS and CSC profiles are compared in Fig. 2. Both methods clearly show N-surface enrichment. O-surface enrichment is further resolved by ToF-SIMS and by complementary XPS data, not shown, attributed to surface contamination (e.g., OH groups). Accordingly, a small difference between O and SiOx is observed in the CSC data (Fig. 2, bottom), and also in line shape modifications described below. Finally, a relatively small N enrichment is resolved at the inner interface (around 280 s in the ToF-SIMS profile, not observed by CSC), which is driven chemically by the large number of interface dangling bonds.8,9

The results of a second independent technique, ARXPS, applied in situ, are shown in Fig. 3, top curve. The angle dependent N/SiOx intensity ratios,26 probed in the electrostatic mode, manifest a minimum at $\theta=75^\circ$. Such nonmonotonic angle dependence may pose questions on the above indicated N surface enrichment. However, using the ToF-SIMS N and Si profiles, and applying a standard attenuation correction for their XPS signal, it is straightforwardly shown that the expected ARXPS should indeed consist of a minimum around $75^\circ$ (see Fig. 3 intermediate curve). Energy dependence of the electron attenuation length is accounted for, using 25.3 and 20.7 Å for Si and N, respectively. Previous simulations8–10 suggested a similar minimum when a second N-enriched region was introduced at the interface with the substrate. Here, however, the inner N-enriched layer contributes <2% of the N signal, with no significant effect on the XPS data. The bottom curve in Fig. 3 is calculated with the top part only of the oxide layer, down to the depth of 210 s sputtering, thus excluding the inner interface and yet it retains the unusual angular dependence. Thus, this specific example demonstrates a general difficulty in obtaining conclusive interpretation of ARXPS in nontrivial structures.

Compared to ToF-SIMS and ARXPS, CSC proposes several important advantages. It is nondestructive, relatively quick and easy for operation, and can, in principle, achieve excellent depth resolution in dielectric systems consisting of

![FIG. 1. (Color online) (a) Selected Si 2p spectra under $V_g$ changes by steps of 0.4 V. Differences in peak shifts reflect potential gradients created across the structure. (b) The corresponding I-V characteristics under stepwise variations in $V_g$ ($-0.4$ V, 0 V, +0.4 V, 0 V, -0.4 V) and fixed eFG parameters. The initial (first measurement) line positions are chosen arbitrarily as zero potential points.](image1)

![FIG. 2. (Color online) Comparison of the ToF-SIMS (top) and the CSC-derived (bottom) depth profiles. Note that the ToF-SIMS sputtering hardly resolves the surface O enrichment from the underlying N enrichment.](image2)

![FIG. 3. (Color online) Comparison of N/SiOx ARXPS data with calculated ratios based on ToF-SIMS profiles: experimental (red triangles), calculated, full layer (blue diamonds), and calculated partial layer (pink squares).](image3)
sufficient chemical contrast, down to the atomic scale. The accuracy in line-shift determination is typically around 20–50 meV, frequently even <10 meV, which corresponds here to depth resolution on the order of 1–2 Å. On the other hand, as indeed observed in the O and Si\textsuperscript{ox} signals, potential gradients across layers of finite thicknesses impose line shape distortions which can, in general, be quite large. In the present case, the experimental error for O and Si\textsuperscript{ox} increases to ~100 meV. Still, the two N-enriched layers should be resolved easily (~500 meV split for ~25 Å spatial separation), with a clear advantage over ARXPS, provided that the inner N concentration is higher. It was, in fact, hardly observable by the ToF-SIMS as well. Notably, the C and N lines did not show observable line shape distortions, indicating small thickness of the corresponding layers; and in particular, less than 1 nm for the top N-enriched slab.

A challenge yet to be answered is regarding the CSC capabilities in extracting fine details of continuous distribution functions along with poor chemical contrast. The Si\textsuperscript{ox} and O profiles represent intermixed, nonidentical distributions, while their data points in Fig. 2 correspond to peak shifts, namely, to weighted average values. Obviously, peak shifts do not reveal such fine details; the slab thickness information is expressed in line broadening, and fine distribution details affect the detailed line shape.

To quantitatively inspect these effects, we assume the development of an approximately constant internal electric field, such that the z-axis is linearly projected on the potential scale. This assumption is justified here since the dielectric constant of SiON (here, ~4% N) is very close to that of SiO\textsubscript{2}. Using the SIMS-derived profile (Fig. 2), we calculate a depth dependent (attenuated) signal and convolute this function with the initial line shape. Figure 4(a) presents two experimental O lines: initial (I) and electrically distorted (D). Computed convolution of the former with the attenuated profile function is also shown, yielding close agreement with the experimental (distorted) spectrum. A similar agreement is obtained for the Si\textsuperscript{ox} distortion. Slight deviations are observed in both cases, partially due to the above mentioned inaccuracies in the Si SIMS profile, and also due to the fact that the constant field assumption cannot be extended to the surface contamination region.

Obviously, when the CSC sensitivity is limited, electron attenuation considerations become very useful. Combining line intensity quantification and line shift and shape analysis is particularly powerful since these are two orthogonal spectral effects (intensity versus energy) of any depth profile, which can be used complementarily to improve reliability and versatility of the method. This approach should be preferably applied to the inverse problem of profile reconstruction in systems of poor chemical contrast.

In summary, CSC depth profiling of thin SiON layers revealed marked inhomogeneity in the internal nitrogen distribution, confirmed by complementary techniques, ARXPS and ToF-SIMS. The CSC method proposes fast, nondestructive identification of the major compositional features in modern microelectronic devices, and further, provides fine details of the elemental distribution functions.

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References

24. Note that the potential at zero current conditions is not uniquely defined in capacitive systems.
26. Due to the OH surface contamination, the angular dependence of the O signal slightly differs from that of Si\textsuperscript{ox}.

FIG. 4. (Color online) O 1s line shape analysis: the initial spectrum (I) in solid black line, distorted spectrum (D) in dashed blue line, and computed convolution of (I) with the corresponding ToF-SIMS-based concentration profile in solid red (D). Arbitrary zero is chosen for the energy scale.