

XPS AND TEM STUDIES OF STEAM-GROWN OXYNITRIDE

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Ultra-thin nitride is an attractive alternative to conventional gate dielectrics in MOSFETs at the 100nm node and beyond, due to stringent circuit-related requirements on gate leakage and boron penetration [1, 2]. Even though reasonably good electrical performance has been achieved in FETs using nitride or oxidized nitride as a gate dielectric [2], the nitride/Si interface and the behavior of the thin nitride in an oxidizing ambient have been a subject of intensive studies. In this work, we have investigated the chemical characteristics of oxidized nitrides using x-ray photoelectron spectroscopy (XPS), X-ray-excited Auger parameter and cross-sectional transmission electron microscopy (XTEM) analysis.

All nitride films in this experiment were CVD-deposited on bare Si [100] wafers using silane and ammonia gases. For the oxidation process, the first set of samples involved 500Å Si₃N₄ that was oxidized in a steam ambient at one of three temperatures: T=900, 950 or 1000°C. For each T value, the oxidation times were 11min, 5min and 2min, respectively, which would result in an identical oxide thickness (300±10 Å) on bare Si in all cases. The second set of samples involved 900°C-oxidized Si₃N₄ films with four different values of d_{nit}, the initial nitride thickness.

Fig. 1 shows the angle-resolved Si KLL Auger spectra of a 500Å nitride that was oxidized at 900°C for 11 min. The peak at a kinetic energy of 1607.6eV is attributed to the Si-O bond, and 1610.2eV to Si-N, both energies agreeing well with values found in the literature. The intensity originating from the Si substrate is negligible because the overlayer thickness is much greater than the KLL electron escape depth λ_{esc, KLL} at 45°. For comparison, the KLL spectrum of a pure (un-oxidized) nitride reveals a very weak 1607.6eV component, likely due to the native oxide at the nitride surface. The [Si-O]/([Si-O]+[Si-N]) ratio obtained from the 45° KLL spectra is plotted in Fig. 2 as a function of 1/T, where T is the oxidation temperature. Since these three different oxidation recipes share approximately the same D•t, it is seen that a ΔT of 50°C results in a change of oxide thickness of by about 10%. The presence of a thin oxynitride is further confirmed from an XTEM micrograph (inset of Fig. 1) of the 900°C-oxidized sample.

In the second set of experiments, we varied d_{nit} from 18 Å to 500Å for a fixed steam oxidation process--11 min. at 900°C. Fig. 3 displays the Si KLL spectra for these five samples measured at 45°. Unlike the 18Å, 40Å and 500Å samples, a third peak located at 1614.5eV, which is attributed to the Si-Si bond, is observed for d_{nit}=70Å and 100Å. This indicates that the total overlayer thickness on the d_{nit}=70 Å and 100Å samples is less than λ_{esc, KLL} at 45°. By comparing curve (b) of Fig. 3 with that of a 40 Å nitride prior to oxidization (not shown), we conclude that the contribution of native oxides between the Si substrate and the nitride was minimal. Therefore t⁺ spectra are analyzed assuming an oxide/nitride/stack, with the individual layer thickness as parameter that could be deduced from fitting the experimen

data. Fig.4 displays the relative intensity of each component in the Si KLL spectra. It is seen that as the initial nitride thickness increases, the [Si-O]/[Si-N] intensity ratio (and thus the oxide thickness) decreases. The disappearance of the [Si-N] component for the 18Å and 40 Å samples confirms findings from an XPS depth profiling using Ar⁺ ions. It is also consistent with XTEM images which show a single-layer contrast for these two samples. Based on these results, we hypothesize that for Si₃N₄/Si, the oxidizing species OH_x has to diffuse across both the already-formed oxide and the pre-existing nitride to the Si₃N₄/Si interface where the oxidation reaction occurs. In the meantime, OH_x+Si-N ↔ Si-O+NH_x [3], and the volatile nature of NH_x leads to the disappearance of nitrogen for the 18Å and 40Å samples.

Finally, Fig. 5 compares the KLL spectra for samples that were oxidized under steam or dry ambient. As expected, the [Si-O]/[Si-N] ratio increases with time in a steam ambient and the dry-oxidized sample exhibits the lowest intensity ratio.

In conclusion, we have studied the chemical composition of steam- and dry-grown oxynitrides using XPS and TEM. The depth profile of the films is obtained by varying the XPS measurement angle. The [Si-O]/[Si-N] KLL intensity ratio decreases as d_{nit} increases, and for d_{nit}=500 Å, the same ratio has a weak dependence on T.

References

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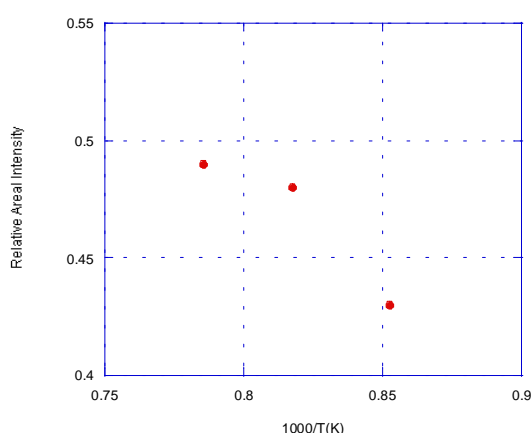
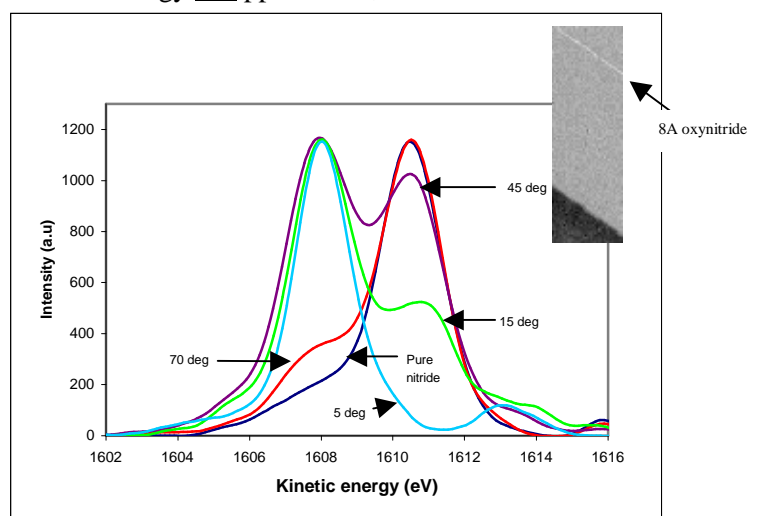


Fig. 2 The [Si-O]/([Si-O]+[Si-N]) ratio of Si KLL spectra as a function of inverse temperature, where T=900, 950 or 1000°C. No Si-Si peak originating from the substrate is observed. The take-off angle of the measurement is 45°.

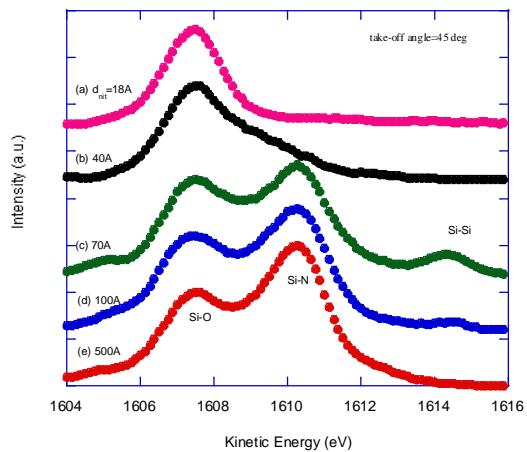


Fig. 3 Si KLL spectra (after a 900°C, 11 min wet oxidation) as a function of the initial nitride thickness d_{nit} . This oxidation process grows 300 Å of oxide on bare Si. The take-off angle of the measurement is 45°. The 1614.5 eV peak is attributed to the Si-Si originating from the Si substrate.

Fig. 1 Angle-resolved Si KLL spectra of steam-oxidized nitrides recorded at a take-off angle of 5°, 15°, 45°, and 70° with respect to the sample surface. The peak at a kinetic energy of 1607.6eV is attributed to the Si-O bond, and the 1610.2eV peak to Si-N. The initial nitride thickness d_{nit} is 500 Å. Spectrum of a non-oxidized 500 Å nitride recorded at 45° is shown for comparison. The inset shows a cross-sectional TEM image of an oxynitride/nitride/Si stack. The top nitride on the TEM sample is deposited for imaging contrast purposes.

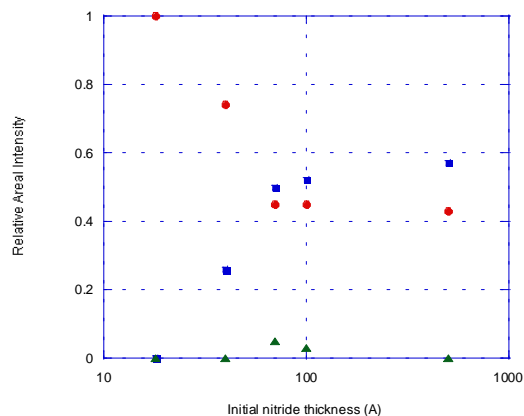


Fig. 4 The percentage intensity of 45° Si KLL spectra for five samples oxidized at 900°C for 11 min with d_{nit} = 18, 40, 70, 100 or 500 Å. The symbols represent Si-O (●), Si-N (■) and Si-Si (▲).

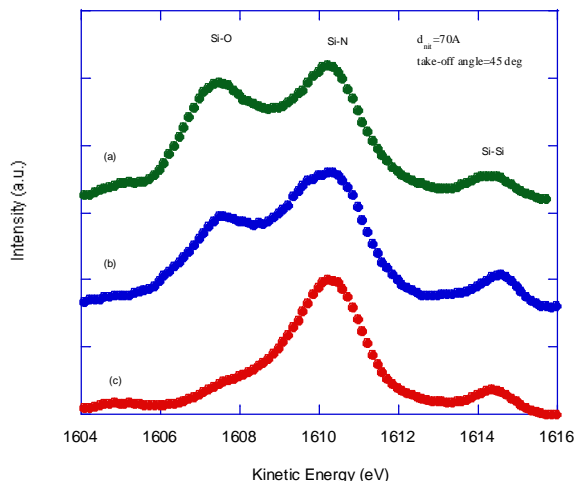


Fig. 5. Si KLL spectra for samples oxidized under three different oxidation conditions: (a) 900°C, 11 min, wet ambient, (b) 900°C, 4 min, wet ambient, and (c) 900°C, 45 min, dry ambient. The initial nitride thickness is 70 Å for all cases. The take-off angle of the measurement is 45°.