Angle Resolved X-Ray Photoelectron Spectroscopy Study of Ultrathin N₂O Oxides

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In this paper, the chemical structure and composition of ultrathin N₂O oxides have been investigated for the first time using angle resolved x-ray photoelectron spectroscopy (ARXPS) and compared to those of reoxidized NH₃-nitrided SiO₂. It is found that N₂O oxide shows evidence of N-O bonds in close proximity to the SiO₂/Si interface in addition to the typically observed N-Si bonds in reoxidized NH₃nitrided SiO₂. The difference between The Si(2p) and O(1s) binding energies in the N₂O oxide and reoxidized NH₃-nitrided SiO₂ with the take-off angle is negligible due to the interfacial nitrogen incorporation.

Boron-doped ~5 Ω cm (100) silicon wafers were used in this study. N₂O oxide was grown at 900°C in pure N₂O ambient. Reoxidized NH₃-nitrided SiO₂ (RONO) was prepared by NH₃-nitridation at 900°C for 5 min and reoxidation for 3 min at the same temperature. The thicknesses of both oxides measured by ellipsometry technique with fixed refractive index (1.462) were ~ 25 Å. An XPS system (base pressure= 4×10^{-11} Torr) with an Mg K_a (1253.6 eV) x-ray source and a variable take-off angle setup was used.

Fig. 1 (a) and (b) show sequential XPS spectra of N(1s) and Si(2p) at different take-off angles obtained from RONO and N₂O oxide, respectively. The N(1s) peaks in both RONO and N₂O oxide are found at 398.1 eV for every take-off angle, which is very close to that in LPCVD Si₃N₄ (397.8 eV). However, the N₂O oxide shows a second N peak at 399.8 eV at 90° take-off angle (deepest probing depth) in addition to the N peak observed at 398.1 eV. This second N peak at higher binding energy is speculated to be due to the stronger N-O bond at the interface. This result indicates that there exists a different kind of chemical bond, *i.e.*, N-O bond, in close proximity to the SiO₂/Si interface in N₂O oxides in addition to N-Si bonds observed in RONO. This N-O bond is even stronger than the Si-N bond, and is speculated to have even greater immunity to the electrical stress.

Fig. 2 plots the difference in binding energy of Si 2p from the N₂O oxide and Si substrate (BE_{Si,oxide}-BE_{Si,sub}) and that between Si(2p) and O(1s) (BE_{oxygen}-BE_{Si,oxide}) in the N₂O oxide as a function of the take-off angle. BE_{Si,oxide} near surface (10° take-off angle) is at 104.2 eV which is close to that of pure SiO₄ tetrahedral structure [1]. BE_{Si,oxide}-BE_{Si,sub} decreases by increasing the take-off angle, *i.e.*, closer to the SiO₂/Si interface. This can be due to the interfacial strain [1,2] as well as the existence of nitrogen [3]. However, the change in BE_{oxygen}-BE_{Si,oxide} with the take-off angle is within our XPS instrumentation error ($\leq \pm 0.1 \text{ eV}$), as seen in Fig. 2. Similar results are seen in RONO samples.

Relative nitrogen concentration, represented as [N]/([Si]+[O]) and [N]/([N]+[O]), in both N₂O oxide and RONO are obtained from the integrated areas of different peaks and plotted as a function of take-off angle in Fig. 3. Both oxides show higher nitrogen concentration at higher take-off angle, indicating a nitrogen pile-up near the SiO₂/Si interface. However, N₂O oxide shows lower nitrogen concentration than RONO, consistent with the results from AES and SIMS. Low reactivities of nitridation species (N₂O, NO and N₂) during N₂O-oxidation are believed to result in a small amount of nitrogen incorporated mostly at the SiO₂/Si interface, where there exist more reactive strained bonds than in the bulk oxide or at the oxide surface.

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Fig. 1 Three-dimensional plot of Si 2p and N 1s spectra vs. take-off angle for very thin reoxidized NH₃-nitrided SiO₂(top) and N₂O oxide (bottom).



oxide and Si substrate ($BE_{Si,oxide}$ - $BE_{Si,sub}$) and that between Si(2p) and O(1s) (BE_{oxygen} - $BE_{Si,oxide}$) in N₂O oxide as a function of take-off angle.

