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Advanced Approach in Engineering the Interface of Metal/High-k Oxide Stacks for Next-Generation DRAM Applications

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The reliability and electrical performance of metal–insulator–metal (MIM) capacitors in dynamic random-access memory (DRAM) devices are strongly influenced by the interfaces between their electrodes and the high-k dielectric thin film. In memory technologies, interface formation is particularly critical, as it contributes to increased leakage current and higher equivalent oxide thickness (EOT). This issue becomes even more pronounced in scaled devices, where surface properties exert a greater influence on device operation. A key example is the oxidation of TiN electrodes during the atomic layer deposition (ALD) of metal oxides. This occurs when the oxidant diffuses through the chemisorbed precursor layer, reaching the substrate and forming an interfacial layer. Since dielectric layers are typically only a few nanometers thick, the additional interfacial layer can degrade the effective dielectric thickness and reduce capacitance.

To address industry challenges, RASIRC, in collaboration with UT Dallas, has been investigating the effects of various oxidants on metal electrode and interface formation in metal/high-k oxide stacks. These studies utilize a unique *in-situ* infrared spectroscopy system, Reflection Absorption Infrared Spectroscopy (RAIRS), to monitor real-time surface changes during the atomic layer deposition (ALD) process. Using a reflectance geometry, this system enables direct observation of metal oxide growth mechanisms on metal substrates, specifically TiN, closely replicating MIM structure fabrication. Herein, the study reports the implication of oxidant choices on metal surface oxidation. Some of these findings were presented at the ALD/ALE 2023 Conference.

The oxidation effects were first investigated. In this study, TiN substrates were subsequently exposed to water (H₂O), ozone (O₃), anhydrous BRUTE[®] Peroxide (BP), and hydrogen peroxide mix (H₂O:H₂O₂ = 4:1) generated via RASIRC Peroxidizer[®] (PXD) at 250°C. The formation of different oxide species was monitored in the 650–1200 cm⁻¹ region of the FTIR spectra (Figure 1). The IR spectra revealed significant changes in the TiN surface, with distinct features corresponding to Ti–O species, such as Ti–O–Ti (~1000 cm⁻¹),¹ Ti–O–O (~900 cm⁻¹),² TiN–O (~850 cm⁻¹),³ and Ti–O (~800 cm⁻¹).¹ These positive peaks emerge after just 3 s of O₃, BP, and PXD pulses. In contrast, H₂O showed no observable changes in the IR spectrum, indicating its limited reactivity. Oxide formation with BP and PXD reached saturation within 6 s and 9 s, respectively, whereas the oxide peak area for O₃ continued beyond 9 s pulse. The saturation of oxide species formed on TiN surface upon H₂O₂ exposures (BP and PXD) suggests that the reaction is more closely associated with surface hydroxylation or hydroperoxylation

rather than extensive surface oxidation. Once the TiN surface is fully saturated with hydroxyl or hydroperoxyl groups, no further reactions occur. This finding suggests that H₂O₂ could be beneficial in limiting interfacial layer formation during oxide ALD processes. Moreover, it is observed that the amount of surface species formed with PXD was slightly higher than with BP. This difference can potentially be attributed to the greater stability of the H₂O₂ mix compared to anhydrous H₂O₂, resulting in a lower decomposition rate in the delivery line and allowing more molecules to reach the metal substrate.⁴

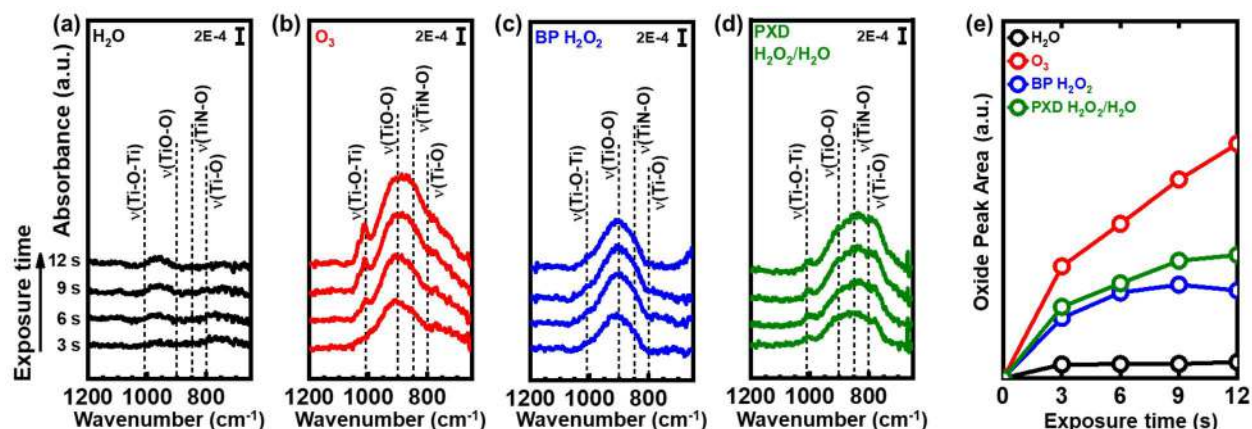


Figure 1. The FTIR spectra, between 650–1200 cm⁻¹ region, of TiN surface after various pulses of (a) H₂O, (b) O₃, H₂O₂ delivered from (c) BP, and H₂O₂ generated from (d) PXD at 250°C. (e) The integrated area of oxide-related peaks emerging after different oxidant pulses, as extracted from the obtained IR spectra.

The recent findings, along with previous results, further underscore the potential of H₂O₂ as a novel oxidant for oxide ALD processes in next-generation microelectronic devices. Additional information and optimization opportunities are available upon request.

About RASIRC

RASIRC innovations convert low vapor-pressure liquid chemistries into safe and reliable gas flow for most processes. RASIRC technology delivers hydrazine gas and hydrogen peroxide gas in controlled, repeatable concentrations. RASIRC products include BRUTE® Peroxide, BRUTE Hydrazine, Peroxider® and RainMaker® Humidification System. These products incorporate proprietary and patented technology that enables them to deliver gas to process with precision. BRUTE Peroxide generates ultra-dry hydrogen peroxide gas and can be used with or without a carrier gas. The Peroxidizer is the first commercial vaporizer capable of delivering concentrations greater than 5% H₂O₂ gas by volume from 30% H₂O₂ liquid source.

Reference

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