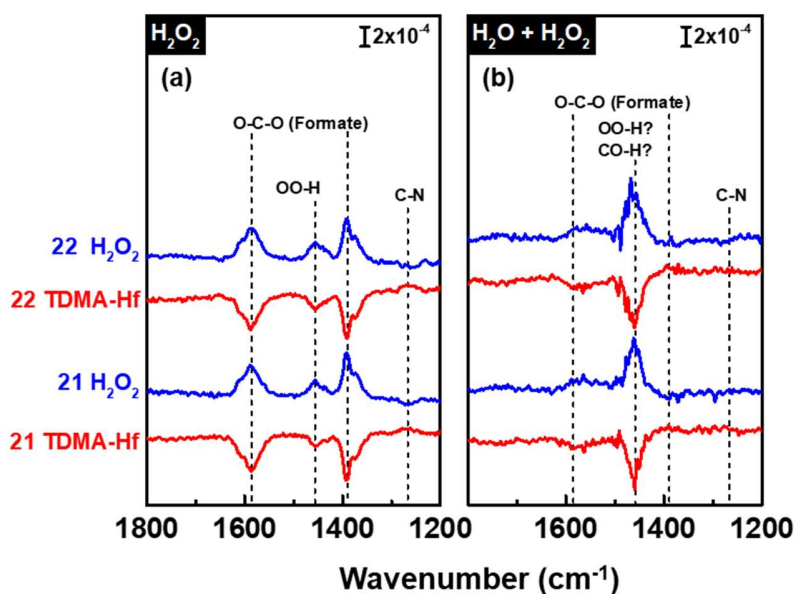


**Figure 1.** (a) Accumulation IR absorption spectra measured with *in-situ* RAIRS system while exposing H<sub>2</sub>O, O<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub> for 12 seconds in 3 second step on TiN substrate at 250 °C. (b) TiO<sub>x</sub> peak area changes from 600 to 1100 cm<sup>-1</sup> after getting exposed to oxidants with increasing exposure time demonstrating the increase of oxide interface on TiN.



**Figure 2.** Differential IR absorption spectra measured with *in-situ* RAIRS system for half-cycle study after 20 cycles of HfO<sub>2</sub> ALD at 250 °C. HfO<sub>2</sub> ALD was performed using two different types of oxidants which are (a) anhydrous H<sub>2</sub>O<sub>2</sub> and (b) a mixture of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> (H<sub>2</sub>O + H<sub>2</sub>O<sub>2</sub>). Anhydrous H<sub>2</sub>O<sub>2</sub> reacting with TDMA-Hf shows a formate and hydroperoxyl focused growth mechanism. On the other hand, Mixed H<sub>2</sub>O<sub>2</sub> reaction with TDMA-Hf generated methoxyl and hydroperoxyl reaction sites demonstrating a much milder reaction.