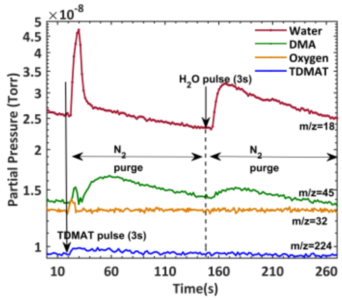

Figure 1. Transient sampling of gas phase species by residual gas analysis during the TDMAT and H_2O ALD pulses. Excess precursors and reaction by-products are purged with constant flow of N_2 gas for 120 s. Subsequent purges result in a rapid decrease of their respective RGA signal to noise levels.

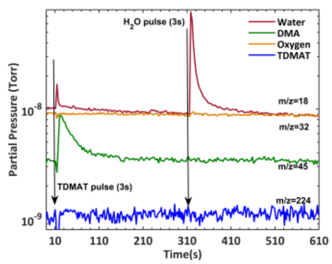

Figure 2. Transient sampling of gas phase species by residual gas analysis during the TDMAT and H_2O ALD pulses, while excess precursors and reaction by-products are purged with constant flow of N_2 gas for 300 s. In this case, DMA by-product is purged until it was undetectable prior to the H_2O pulse. Increasing the purging time to 300s gives a dramatic decrease in the growth per ALD cycle (GPC) as well as a slight increase in the film density from 3.6 to 4.5 g/cm^3. X-ray reflectivity fitting was used to calculate the thickness and the density of ALD TiO_2 films from a 2Theta-Omega scan using a Fourier transform method.

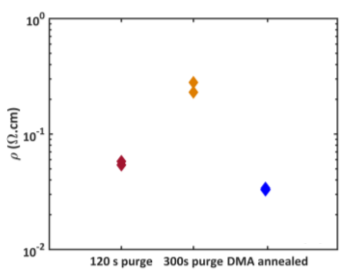

Figure 3. The obtained average resistivity of deposited TiO_2 films with different ALD conditions, which shows a decrease in the resistivity after annealing of the TiO_2 films in DMA for 30 min [1, 2].

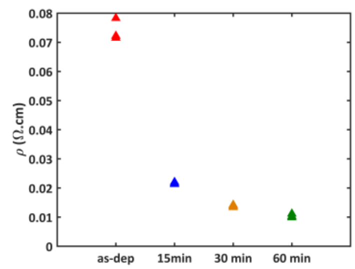

Figure **4.** Transient changes in TiO_2 resistivity as a function of DMA annealing Time. As shown, the presence of DMA during the ALD TiO_2 can transiently decrease the resistivity of the deposited films. For sufficiently large oxygen vacancy concentrations, nanoscale TiO_{2-x} can exhibit band gap narrowing and a high density of donor-type oxygen vacancies near the TiO_2 conduction band edge, enhancing its electronic conductivity [3, 4].

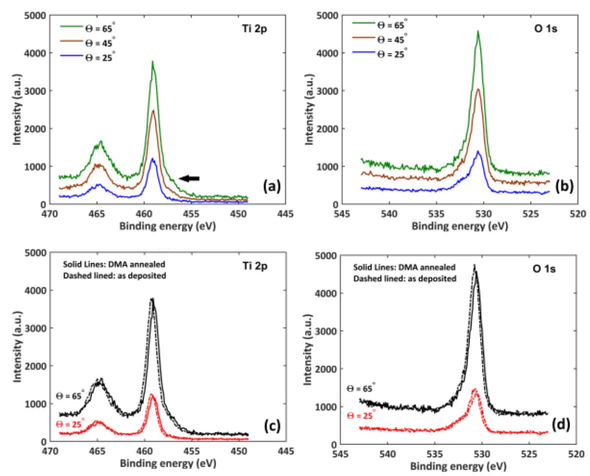

Figure 5. Angle-resolved XPS spectra for (a) Ti2p (b) O1s for the TiO_2 sample annealed in DMA. Comparison of XPS data for DMA annealed (30 min) and as deposited TiO_2 samples. The angle between the incident X-ray beam and the electron energy analyser was maintained at ~ 45°. Surface sensitivity was increased by tilting the sample with respect to the analyser over θ values of 25°, 45° and 65°. The angel, θ is defined relative to the film surface normal. Comparison of XPS data between the bulk or surface sensitive spectra for DMA annealed TiO_2 shows a shoulder at lower binding energy in more surface sensitive Ti2p spectra collected at θ=65° which could corresponds to Ti^{+3} states [5].

The research described here may facilitate the control of electronic conduction in ALD-grown TiO_2 thin films, which are widely used as electron-selective contacts, and can help in materials selection and design rules for optimal reliability in TiO_2 applications including optical coatings, high-k dielectrics, and TiO_2-based memory devices.

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1. Slagle, I.R., J.F. Dudich, and D. Gutman, *Direct identification of reactive routes in the reaction of oxygen atoms with dimethylamine.* Chemical Physics Letters, 1979. **61**(3): p. 620-624.
2. Slagle, I.R., J.F. Dudich, and D. Gutman, *Identification of reactive routes in the reactions of oxygen atoms with methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, and triethylamine.* The Journal of Physical Chemistry, 1979. **83**(24): p. 3065-3070.
3. Widjaja, Y. and C.B. Musgrave, *Quantum chemical study of the mechanism of aluminum oxide atomic layer deposition.* Applied Physics Letters, 2002. **80**(18): p. 3304-3306.
4. Naldoni, A., et al., *Effect of Nature and Location of Defects on Bandgap Narrowing in Black TiO2 Nanoparticles.* Journal of the American Chemical Society, 2012. **134**(18): p. 7600-7603.
5. Pan, J.M., et al., *Interaction of water, oxygen, and hydrogen with TiO2(110) surfaces having different defect densities.* Journal of Vacuum Science & Technology A, 1992. **10**(4): p. 2470-2476.