

# Controlling The Oxidation State Of Manganese During Plasma Enhanced Atomic Layer Deposition Using The Mn(thd)<sub>3</sub> Precursor

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Manganese oxide is an interesting material as battery electrode and in catalysis [1]. In atomic layer deposition (ALD) literature, two thermal ALD processes have been reported so far: Mn(II)O grown with the Mn(II)(EtCp)<sub>2</sub> precursor and H<sub>2</sub>O [2] and Mn(IV)O<sub>2</sub> with the Mn(III)(thd)<sub>3</sub> (thd = 2,2,6,6-tetramethylheptan-3,5-dione) and O<sub>3</sub> [3]. Here, we report on plasma enhanced ALD (PE-ALD), combining the Mn(thd)<sub>3</sub> precursor with plasmas of NH<sub>3</sub>, H<sub>2</sub>, H<sub>2</sub>O, and compare with the thermal ALD process using O<sub>3</sub>. Depositions were performed in a high-vacuum reactor (10<sup>-7</sup> mbar), using *in-situ* ellipsometry, *in-situ* mass spectrometry and *in-situ* optical emission spectroscopy to monitor growth rate, reaction products and plasma species respectively.

The ALD temperature window was found to be 140°C-250°C above which precursor decomposition occurs, while below 140°C precursor condensation leads to CVD-like behavior. This shows that the precursor properties alone control the window, which is therefore identical for all studied processes. As expected for ALD, saturation and linearity were confirmed for all processes. The growth rate per cycle was ~0.02 nm for all processes, limited by precursor ligands blocking surface sites and surface site density of the growing film. Conformality in 60:1 aspect ratio pillar structures was confirmed for the PE-NH<sub>3</sub> process, using SEM based EDX line scans.

In Mn(thd)<sub>3</sub> manganese is in the +III oxidation state. XRD and XPS characterization (fig. 1) of the as deposited layers demonstrated that the use of ozone or different plasma species enables controlling the oxidation state of the Mn in the as deposited layers from +II to +IV. XRD showed that the films were crystalline as deposited and XPS peak separation in accordance with literature [4] on selected samples confirmed the oxidation state suggested by XRD and XPS concentration analysis. Reductive plasma (NH<sub>3</sub>) lowered the oxidation state all the way down to the +II state (MnO) while the most oxidative gas (O<sub>3</sub>) yielded the +IV state (MnO<sub>2</sub>). The other plasmas yielded the in-between phase Mn<sub>3</sub>O<sub>4</sub> and a mixed phase. This demonstrates an effective method for the deposition of a range of manganese oxides MnO<sub>x</sub> (1 < x < 2) with a single precursor.

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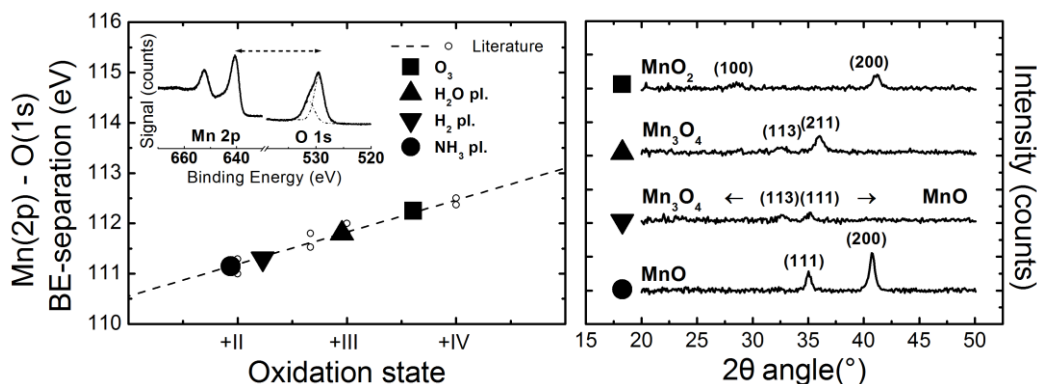


Figure 1: XPS analysis of the Mn 2p<sub>3/2</sub> – O 1s splitting (left), with fit to literature data [4] and XRD analysis of the crystal phase (right) of the as-deposited films, showing oxidation state control by choice of (plasma) gas combined with the Mn(thd)<sub>3</sub> precursor.