

Strategies to Produce Boron-Containing ALD Thin Films Using Trimethyl Borate Precursor: From Thermal to Plasma to Combined-Plasma Approach

Arpan Dhara,¹ Andreas Werbrouck,¹ Jin Li,¹ Jolien Dendooven,¹ Christophe Detavernier^{1,†}

¹Department of Solid State Sciences, COCOON research group, Ghent University, Belgium

† christophe.detavernier@ugent.be

Recent research takes interest in boron-comprising thin layers that are useful in many applications such as dopant for semiconductors, neutron detection and absorption layer in nuclear reactors, ceramic reinforcements, and lithium ion batteries. The most fundamental boron-containing layer, B₂O₃, is highly hygroscopic, and therefore ternary oxides (like Al_xB_yO_z) or B-doped oxide (like ZnO:B) are more commonly prepared, using a so-called ALD supercycle approach. Generally, the boron concentration in these films is unequivocally poor (~1-10%) when the metal oxide to boron oxide cycle ratio is 1:1. Stoichiometric films are obtained only from a particular (pyrazolyl) type of precursor, however the high vaporization temperature (~200°C) hampers their practical use. Therefore, there is a need of finding a suitable precursor and convenient process to produce boron-containing thin films.

In this work, we demonstrate different strategies (figure 1) to produce aluminium borate thin films by ALD using trimethyl borate (TMB) as the boron source. Films obtained from *thermal* processes (**TMA-H₂O-TMB** or **TMA-H₂O-TMB-H₂O**) show a moderate growth per cycle (GPC, 0.85 & 1.5 Å respectively), and contain considerable carbon impurities. Also, a constant increase in growth rate is observed with temperature which suggests a low reactivity of the TMB molecule. The reactivity can be improved by using oxygen plasma (**TMA-O₂*-TMB-O₂***) instead of H₂O as O source. The GPC certainly improves a bit (~1.8 Å) along with a reduction in carbon contamination. However, the boron concentration in the films remains very low for the investigated processes (~5-10%).

To improve the growth rate and boron concentration further, we introduce a novel approach where a combination of H₂O and TMB is used in plasma form (**TMA-[TMB+H₂O]***). It is proposed that the TMB molecules *polymerize in-situ* in the plasma, as reported before for trimethyl phosphate plasma.¹ However, using TMB alone in plasma form does not yield self-limiting ALD growth, as polymerized species continuously accumulate on the substrate. Interestingly, by adding H₂O to the TMB plasma, saturated growth of aluminium borate films is achieved with a high GPC of ~3.5 Å/cycle. Moreover, the films contain a considerably larger amount of boron (15-20%). We hypothesize that H₂O in the TMB plasma helps to hydrolyse surface groups, which in turn aids in preventing continuous polymerization. We also performed *time resolved transient in-situ mass spectroscopy* (figure 2) and *in-vacuo XPS* studies to reveal the mechanism of all three different approaches explained above.

1. Dobbelaere, T., Roy, A. K., Vereecken, P. & Detavernier, C. Atomic layer deposition of aluminum phosphate based on the plasma polymerization of trimethyl phosphate. *Chem. Mater.* **26**, 6863–6871 (2014).

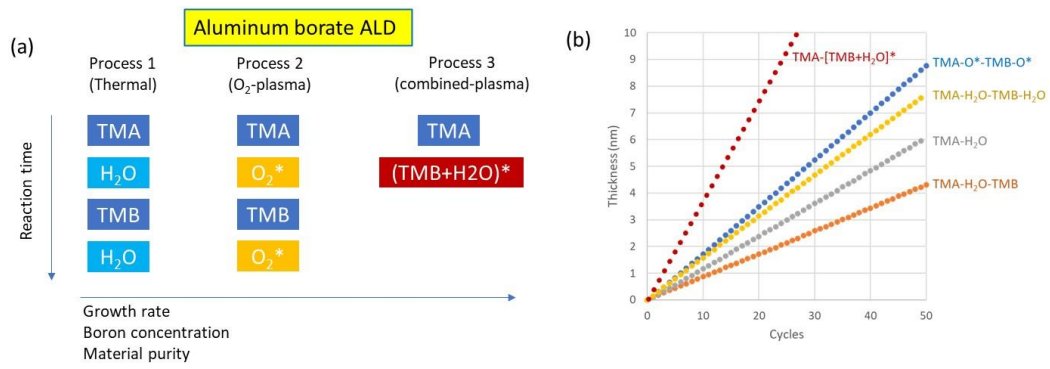


Figure 1(a) Schematic and (b) growth profile of different processes to obtain aluminum borate films by ALD

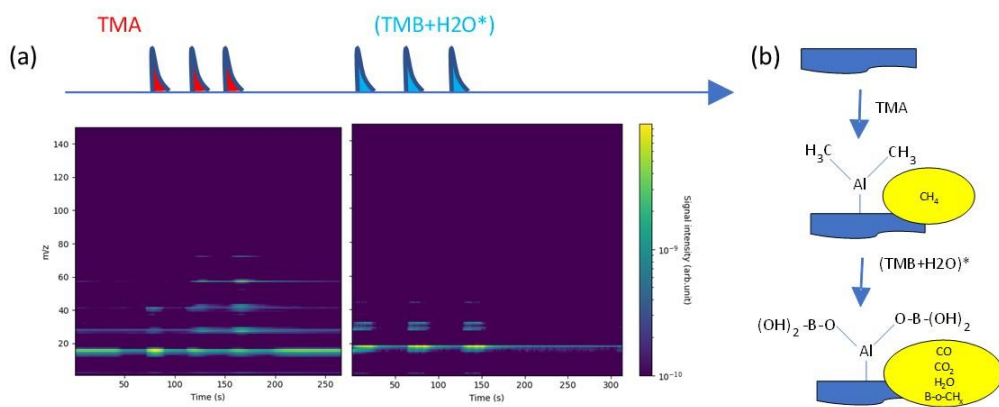


Figure 2 (a) Time resolved in-situ mass spectra and (b) a possible mechanism of TMA-[TMB+H₂O]* process