

# The redox chemistry of oxide molecular beam epitaxy

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The materials class of crystalline oxides provides a plethora of functional (dielectric, semiconducting, superconducting, ferroelectric, or ferromagnetic) properties. For harnessing this potential, molecular beam epitaxy (MBE) has proven an established method that realizes high quality oxide thin films. In its mostly used variety, the corresponding cation is evaporated from an effusion cell in vacuum onto the heated substrate where it gets oxidized by molecular oxygen, ozone, or an oxygen plasma.

This contribution will review the peculiar redox chemistry of oxide MBE, related to the existence of suboxides with significantly higher vapor pressure than their cation elements, not only taking place at the growth surface but also in effusion cells. I will discuss the implications of this chemistry on growth rate, film composition, and flux emanating from the effusion cells with the example of the plasma-assisted MBE growth of the semiconducting oxides Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, GeO<sub>2</sub>, SnO<sub>2</sub> and its suboxide SnO. Three major reactions describe the suboxide-related chemistry:

- (1.) The reaction of the metal with its oxide towards the suboxide, which can be utilized to etch oxide films in-situ [1,6], but also provides efficient suboxide sources [2].
- (2.) The reaction of the cation element with oxygen, resulting in unintentional suboxide fluxes from elemental sources, leading to unexpectedly high cation incorporation in the grown films [3]. On the substrate, the same reaction provides the *p*-type oxide SnO [4] as well as an efficient way of removing a cation layer in-situ. Generally, the suboxide formation on the growth front is the first step during oxide growth, its desorption limits the growth rate.
- (3.) The reaction of the suboxide with activated oxygen in the source leads to source passivation [9]. On the growth front, it is the second step that completes oxide growth. A kinetic growth model that involves both these steps, describes the observed, peculiar growth rate dependence on metal-to-oxygen flux ratio and substrate temperature for SnO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> [5], and GeO<sub>2</sub> [6]. A simpler, single- and zero-step growth kinetics can be realized when the suboxide instead of an elemental cation flux is provided to the growth front, as demonstrated for SnO<sub>2</sub> [2], Ga<sub>2</sub>O<sub>3</sub> [7], and SnO [8] films grown by suboxide MBE (S-MBE).

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