

High Vacuum Chemical Vapor Deposition: High Growth Rate ALD-Like Film Synthesis and Epitaxial CVD for Integrated Photonics

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Introduction & Motivation

Investigation of surface kinetics of ALD systems poses a major challenge, due to the complexity of the process and limited control over relevant process variables. Such studies typically require a range of time-consuming experiments, which becomes hardly accessible at a large number of process variables. High-vacuum chemical vapor deposition (HV-CVD) offers a significant improvement in effectiveness of such studies. Owing to the high-vacuum (HV) conditions, the gas-phase reactions can be neglected and the chemical reactions occur strictly on the substrate surface. When the substrate temperature is set within the ALD window, the film growth is governed by ALD kinetics, as we have shown for the TiO_2 growth from common ALD precursors TTIP and H_2O [1]. The precursor flux can be tailored across the substrate in a combinatorial fashion, thus allowing to examine a large range of process parameters in a single synthesis. At higher substrate temperatures, the growth occurs in a CVD mode in which highly crystalline epitaxial films can be obtained, owing to the HV [2]. The combinatorial approach facilitates an efficient search for optimal growth conditions. We have recently utilized HV-CVD to grow BaTiO_3 (BTO) from $\text{Ba}(\text{iPr}_3\text{Cp})_2$, TTIP and O_2 for applications in integrated photonics.

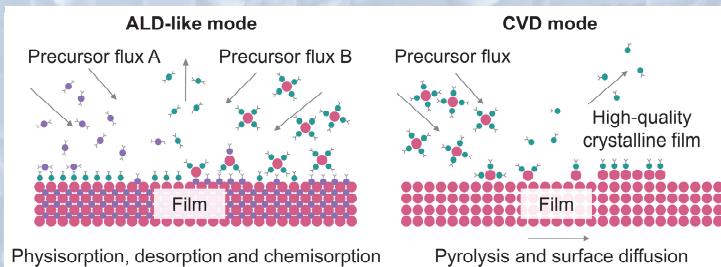


Figure 1: HV-CVD in ALD-like mode and in CVD mode, depending on the substrate temperature. ALD-like growth at simultaneous precursor injection is facilitated by negligible gas-phase interactions in high vacuum.

Combinatorial effusion in HV-CVD

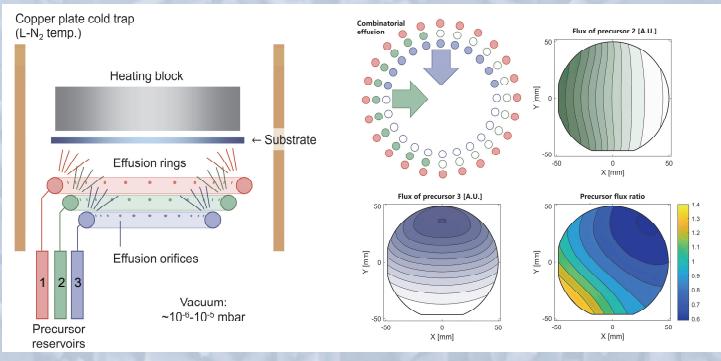


Figure 2: HV-CVD setup schematic and precursor flux simulation in a combinatorial mode

The precursor compounds are delivered by effusion rings. The precursor trajectories are ballistic, allowing for an accurate simulation of the precursor fluxes. When selected effusion orifices are open, a range of precursor fluxes is explored in a single synthesis, which is referred to as *combinatorial mode*.

XRD analysis of BaTiO_3 grown by HV-CVD

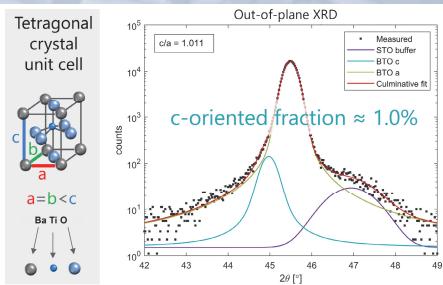


Figure 5: Crystal unit cell of tetragonal BTO and out-of-plane XRD of BTO film grown in STO-b-Si.

Out-of-plane and in-plane (not shown) XRD analysis indicated that 99% of the film is oriented with the tetragonal axis in-plane, which is important for the application in planar photonic systems, while the tetragonal axis is the axis of ferroelectric polarization of BTO. The RMS film roughness measured by AFM is of the order of only a few angstroms, which is promising for subsequent fabrication steps of integrated photonic devices.

Surface kinetics of TiO_2 growth

| | Physisorption and desorption | Pyrolysis | Hydrolysis | Steady state |
|--------------------------------------|--|--|---|--------------|
| $\frac{dI_{\text{TTIP}}}{dt}$ | $+J_{\text{TTIP}} s_{\text{TTIP}} \left(1 - \frac{I_{\text{TTIP}}}{I_{\text{TTIP}}^{\text{ad}}} \right) - k_{\text{TTIP}}^{\text{des}} I_{\text{TTIP}}$ | $-k_{\text{pyrolysis}}^{(1)} I_{\text{TTIP}} - k_{\text{pyrolysis}}^{(2)} (I_{\text{TTIP}})^2$ | $-k_{\text{hydrolysis}} I_{\text{TTIP}} I_{\text{H}_2\text{O}}$ | $= 0$ |
| $\frac{dI_{\text{H}_2\text{O}}}{dt}$ | $+J_{\text{H}_2\text{O}} s_{\text{H}_2\text{O}} \left(1 - \frac{I_{\text{H}_2\text{O}}}{I_{\text{H}_2\text{O}}^{\text{ad}}} \right) - k_{\text{H}_2\text{O}}^{\text{des}} I_{\text{H}_2\text{O}}$ | | $-k_{\text{hydrolysis}} I_{\text{TTIP}} I_{\text{H}_2\text{O}}$ | $= 0$ |

Equation 1: Rate equations for TiO_2 growth kinetics from TTIP and H_2O [1]. I – adsorbate surface concentration, I^{ad} – max. surface concentration, J – vapor flux, s – adsorption probability, k – kinetic rate coefficients, temperature-dependent via Arrhenius law. As the steady state is assumed, the temporal derivatives reduce to zero.

The combinatorial deposition was used to examine the TiO_2 growth using ALD precursors TTIP and H_2O . The rate coefficients k were evaluated

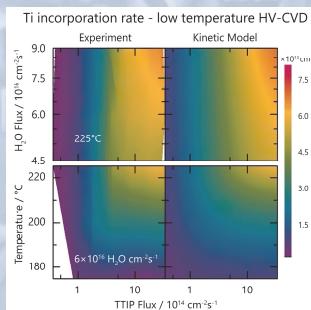


Figure 3: Ti incorporation rate – experimental results vs. fitted kinetic model [1]

| | Frequency factor [s^{-1}] | Reaction enthalpy [kJ mol^{-1}] |
|-----------------------|--------------------------------------|--|
| Decomposition | $4.7 \times 10^{10} \text{ cm}^2$ | 86 |
| | $1.3 \times 10^8 \text{ cm}^2$ | 185 |
| Desorption | 2.0×10^{10} | 114 |
| | 5.0×10^3 | 81 |
| Sticking coefficients | 0.30 | |
| | 0.91 | |

Epitaxial growth of BaTiO_3 films

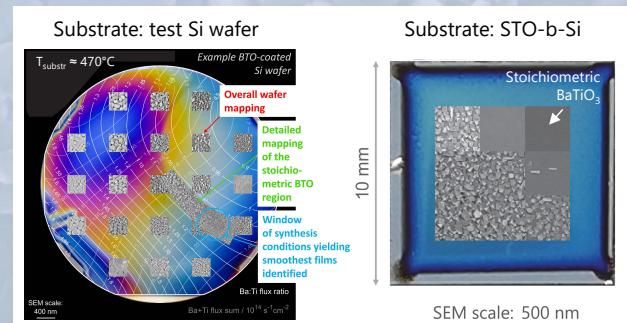


Figure 4: BTO film synthesis results on test Si wafer and SrTiO_3 -buffered Si

Combinatorial syntheses on test Si wafers coupled with flux simulations allowed pinpointing the growth conditions for the stoichiometric BTO films. The optimized conditions were transferred to Si substrates buffered with 4 nm SrTiO_3 (STO-b-Si). The STO provides an advantageous interface for epitaxial growth of BTO, owing to their closely matching crystal lattice constants. High-quality films were identified by SEM. The film stoichiometry and negligible contamination (<1 at.% of C and H) was confirmed with Rutherford Backscattering and Elastic Recoil Detection (RBS/ERDA), an accurate and precise elemental characterization technique.

Conclusions

HV-CVD is a versatile technique, which can be used to evaluate kinetic parameters of ALD systems, as well as to grow thin films at high growth rates, as shown for the case of TiO_2 synthesis. At higher temperatures, highly crystalline epitaxial films can be achieved, as presented for the case of BTO.

References

- [1] Reinke, M. et al. Surface Kinetics of Titanium Isopropoxide in High Vacuum Chemical Vapor Deposition. *J. Phys. Chem. C* **119**, 27965 (2015). doi:10.1021/acs.jpcc.5b07177
- [2] Borzi, A. et al. Microstructure analysis of epitaxial BaTiO_3 thin films on SrTiO_3 -buffered Si: Strain and dislocation density quantification using HRXRD methods. *Materialia* **14**, 100953 (2020). doi:10.1016/j.mtla.2020.100953

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