

In-Situ and Operando Measurements for the Characterization of Next-Generation Sensor Materials

Rudi Tschammer¹, Dominic Guttmann¹, Carlos Morales¹, Carlo Tiebe²,
Karsten Henkel¹, Jan Ingo Flege¹

¹ BTU Cottbus-Senftenberg, Konrad-Zuse-Straße 1, 03046 Cottbus, Germany

² Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, 12205 Berlin, Germany
tscharud@b-tu.de

Summary:

In this contribution, we highlight the use of *in-situ* X-ray photoelectron spectroscopy and *operando* spectroscopic ellipsometry for the characterization of ultra-thin (<20nm) atomic layer deposited layers for the use in next-generation miniaturized sensor devices. By targeting tin oxide layers, we show how we can use these techniques to gain insights into material composition, thickness, and optical properties, thus paving the way for unraveling the correlations between material properties and sensing performance.

Keywords: In-situ characterization, X-ray photoelectron spectroscopy, Ellipsometry, Tin oxide, Atomic Layer Deposition

Background and Motivation

Transitioning to an energy system based entirely on renewable energies requires significant use of energy carriers such as hydrogen (H₂) and its derivatives. While considerable effort is devoted to improving the generation, storage, and utilization of H₂, new developments for secondary components, such as gas sensors, will be necessary to ensure a swift and secure transition. Today's sensors rely on expensive materials such as noble metals for conductometric hydrogen sensors [1], expert personnel, careful maintenance, and high investment costs, making them unsuitable for large-scale deployment and necessitating the development of cheap, mass-producible gas sensors capable of operation near room temperature (RT) and without noble metals.

Among the available deposition methods, atomic layer deposition (ALD) has emerged as an attractive option for conformally depositing ultra-thin films with atomic-scale thickness control on the wafer scale [2]. In addition, ALD results in amorphous and defect-rich deposits, leading to material properties deviating from their crystalline and well-ordered counterparts. Interestingly, this has enabled us to demonstrate the sensing behavior of ALD-CeO_x towards H₂ in O₂ (~1 mbar) by near-ambient pressure X-ray photoelectron spectroscopy (XPS) [3].

Due to the low electrical conductivity of pure CeO₂, we aim to combine ALD-CeO₂ with other metal oxides, such as tin oxide (SnO₂), to lower

the resistivity and improve electrical conductivity and gas sensing performance by exploiting interfacial interactions.

In this context, the sequential nature of the ALD process offers high flexibility for combining different materials during the growth process, either as heterostructures or mixed oxides, by using appropriate super-cycles [4]. However, this requires *in-situ* and *operando* material investigation techniques such as XPS and spectroscopic ellipsometry (SE) to control oxide composition and thickness during growth and monitor potential contaminants due to reaction residues. Combined with the amorphous nature of the thin films, this bottom-up approach allows for fine-tuning the deposit properties towards optimal gas-sensing performance, following a standard procedure to determine sensor characteristics for H₂/air or H₂/nitrogen.

Description of the New Method or System

From *in-situ* XPS and *operando* SE measurements of the SnO₂ film growth using TDMASn + O₃ at 160 °C in our ALD cluster described elsewhere [5], we have analyzed the detailed evolution of material composition, thickness, and growth rate depending on the number of ALD cycles. In addition, gas-sensing measurements based on ALD-SnO₂ show a correlation between sensor response and material properties. In the future, the successful preparation of simple SnO₂/CeO₂ heterostructures will be demonstrated as a first step toward more complex material compositions and the impact on mate-

rial properties such as Ce cation oxidation state will be determined.

Results

Operando spectroscopic ellipsometry enables rapid ALD recipe optimization for TDMASn and O_3 . The growth per cycle (GPC) has been determined to 0.6 Å to 0.7 Å between 0 and 750 cycles (0 nm to ~50 nm, respectively), in line with expectations based on the literature. No significant nucleation delay or change in the GPC for ultra-thin layers has been observed, showing ideal linear film growth on Si (see Fig. 1 as an example).

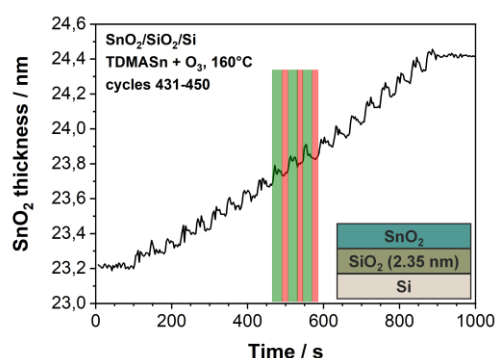


Fig. 1. The thickness evolution of SnO_2 was determined by operando SE during the ALD process. Green and red bars indicate the precursor and oxidant doses, respectively. A Drude-Lorentz model has been used to describe the SnO_2 layer, the optical model is shown in the lower right.

In-situ Sn 3d XPS measurements during different stages of the deposition process indicate the absence of Sn metal in the ALD deposit. Early results from Auger parameter measurements hint at the presence of pure Sn^{4+} , with notable changes in the Auger parameter during the initial stages of growth. Together with information derived from the Si 2s core level associated with the native SiO_2 of the substrate, this is tentatively assigned to a change in the chemical environment, e.g., when transitioning from the SnO_2/SiO_2 interface to the SnO_2 film. This interfacial region could be especially relevant for ultra-thin SnO_2 films used in heterostructures or mixed oxides.

The amount of carbon and nitrogen residues from the TDMASn precursor in the film has been investigated by monitoring the C 1s and N 1s core level intensity evolutions with ALD cycles, respectively. Both show a noticeable intensity decrease compared to Sn 3d with increasing cycle number (cf., Fig. 2), indicating a difference in precursor reaction mechanism during the transition from hetero- to homoepi-

taxial growth [6], again relevant for use in future heterostructures.

Investigations of the sensing behavior of ALD- SnO_2 grown on sensor substrates with integrated electrodes are ongoing and will shed light on the influence of material properties on sensor response. In addition, surface decoration with small amounts of CeO_x nanoparticles and ultrathin layers will be investigated to evaluate the impact of the heterostructure approach on operation temperature and sensor response.

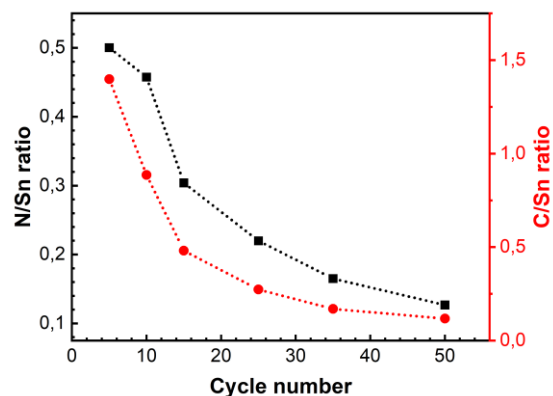


Fig. 2. Ratio of nitrogen and carbon to tin depending on ALD cycle number.

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