

## Science and Technology of MBE

### Room Ballroom A - Session ST-WeM1

#### Advancement in MBE Growth Approaches

Moderator: Dr. Darrell Schlom, Cornell University

8:00am **ST-WeM1-1 Thermal Laser Epitaxy - the Universal Epitaxy Tool(?)**, **Wolfgang Braun**, D. Kim, F. Hensling, T. Smart, L. Majer, B. Faeth, S. Smink, D. Dereh, Max Planck Institute for Solid State Research, Germany; H. Boschker, Epiray GmbH, Germany; J. Mannhart, Max Planck Institut for Solid State Research, Germany

Thermal laser epitaxy (TLE) uses quasi-CW lasers to heat the substrate and the sources in a deposition geometry similar to MBE. The high energy densities of the laser beams enable the evaporation or sublimation of any element in the periodic table in any combination and substrate temperatures exceeding the melting point of sapphire at 2040 °C. This leads to a dramatic expansion of the parameter space available to MBE-type growth modes such as, e.g., the adsorption-controlled growth of oxides.

In addition, TLE offers new opportunities in terms of the available gas pressures and environments during growth. A TLE growth chamber is conceptually simple, besides the laser entrance windows it basically contains only mechanical mounts for substrates and sources. This means that background gases at any pressure and with any reactivity are possible, as long as these parts do not get damaged, and the laser beam is not absorbed in the gas phase. This is the case for most reactive gases such as oxygen, ozone, plasma-excited nitrogen or ammonia.

As an example, we study the evaporation of Al in a molecular oxygen atmosphere. At high laser power densities, the flux of the source is independent of the oxygen pressure up to  $10^{-1}$  hPa. At lower power densities, the source flux depends on the oxygen pressure and the area of exposed metallic surface on the source. This is consistent with volatile suboxide molecules proportional to the oxygen flux being generated on the exposed surface. For the current maximum laser power, the source finally gets passivated by a stable oxide at pressures above  $10^{-1}$  hPa, and no longer produces a stable flux. The deposition rate on the substrate starts dropping at  $10^{-2}$  hPa for the given working distance of 80 mm, as the mean free path drops below this distance and the transport transitions from the ballistic to the diffusive regime. Irrespective of the reactive flux generation and deposition, the more than five orders of magnitude dynamical range of the deposition flux and high maximum growth rates are maintained.

This implies that TLE is able to cover the entire range of growth conditions traditionally employed in MBE, GS-MBE, MOMBE, MOCVD, CBE and CVD. TLE thereby enables the evaporation or sublimation of practically any combination of elements, together with reactive gas sources, at low and also very high growth rates. CVD growth modes, e.g. for thick buffer layers, may be combined with kinetically limited growth, e.g. for active layers at low temperatures, in a single growth to produce devices with very dissimilar layers and growth conditions in a single growth run.

Results of TLE with nitrogen and ammonia will be presented and discussed.

8:15am **ST-WeM1-2 Routes Towards Making BaZrSe<sub>3</sub> Thin Films in the Perovskite Structure by MBE**, **Ida Sadeghi**, K. Ye, J. Van Sambeek, R. Jaramillo, MIT

Chalcogenide (sulfide and selenide) perovskite semiconductors are anticipated to have favorable structural, optical and electronic characteristics for solar energy conversion. The most studied compound is BaZrS<sub>3</sub>, with a band gap of 1.9 eV. Alloying on the anion or cation sites has been explored to lower the band gap into a range suitable for single-junction solar cells. The pure selenide perovskite BaZrSe<sub>3</sub> is predicted to have band gap 0.5 eV lower than the sulfide.<sup>1</sup> However, BaZrSe<sub>3</sub> may form in different polymorphs, theory predicts that the needle-like (non-perovskite) phase with band gap below 1 eV is the most stable, and solid-state synthesis attempts have resulted in a semi-metallic hexagonal ordered defect phase.<sup>1,2,3,4</sup>

We previously reported the first epitaxial synthesis of chalcogenide perovskite thin films by gas-source MBE: BaZrS<sub>3</sub> film on LaAlO<sub>3</sub> substrate.<sup>5</sup> The films grow on a self-assembled interface layer that relieves the epitaxial strain. Here we demonstrate alloying BaZrS<sub>3</sub> with Se, including the first report of a pure selenide perovskite, and we confirm the tunability of the direct band gap of this alloy system.<sup>6</sup> We demonstrate two processing routes to make BaZrS<sub>(3-y)Se<sub>y</sub></sub> alloys in the perovskite structure. (i) We deposit BaZrS<sub>(3-y)Se<sub>y</sub></sub> on a BaZrS<sub>3</sub> template layer on LaAlO<sub>3</sub>. The template stabilizes

the perovskite structure for BaZrS<sub>(3-y)Se<sub>y</sub></sub>, which otherwise does not grow as a perovskite directly on LaAlO<sub>3</sub>. Scanning transmission electron microscopy analysis shows that there is anion intermixing between the sulfide template and the alloy during growth, such that the final film has nearly uniform composition. (ii) We deposit BaZrS<sub>3</sub> on LaAlO<sub>3</sub>, followed by post-growth selenization. The RHEED pattern during selenization remains unchanged, indicating that the crystal structure is static even as the sulfur and selenium anions exchange. Both processing routes can produce selenide perovskite films with band gap of 1.4 eV.

This work sets the stage for developing chalcogenide perovskites as a family of semiconductor alloys with properties that can be tuned with composition in high-quality epitaxial thin films, as has been long-established for other semiconductor materials. The band gap of high-selenium-content BaZrS<sub>(3-y)Se<sub>y</sub></sub> suggests applications in thin-film solar cells.

1. Sun, Y.-Y., et al. *Nano Lett.***15**, 581 (2015).
2. Tranchitella, L. J. et al. *J. Am. Chem. Soc.***120**, 7639 (1998).
3. Jess, A. et al. *Chem. Mater.***34**, 6894 (2022).
4. Aslanov, L.A. *Russ. J. Inorg. Chem.***9**, 1090 (1964).
5. Sadeghi, I. et al. *Adv. Funct. Mater.***31**, 2105563 (2021).
6. Sadeghi, I. et al. *arXiv:2211.10787*.

8:30am **ST-WeM1-3 Adsorption Controlled Homoepitaxial Growth of c-Plane Sapphire by Thermal Laser Epitaxy**, **Felix Hensling**, L. Majer, S. Smink, J. Mannhart, W. Braun, Max Planck Institute for Solid State Research, Germany

The interest in sapphire as an electronic material is due to its low cost, superior properties over silicon, high quality wafer availability, and the possible integration with silicon. Indeed, its rapidly growing market share suggests sapphire to be the substrate material of the future.[1] A cornerstone for further establishing sapphire in a wide range of (electronic) applications is the ability to grow high quality homoepitaxial sapphire films. Key applications that can benefit from this are, e.g. diodes and high-power electronics based on nitrides [1] and (ultra) wide band gap semiconductors, respectively [2,3]. However, epitaxial films of c-plane oriented sapphire, one of the most common cuts of sapphire, have so far been out of reach due to a preferred formation of the Al<sub>2</sub>O<sub>3</sub>-phase.[3]

I will present how thermal laser epitaxy (TLE) overcomes this issue thanks to the availability of a parameter space that far exceeds the reach of other deposition methods.[4] The substrate laser heating system allows to easily heat sapphire substrates even beyond their melting point. The high accessible temperatures enable a precise and smooth sapphire substrate preparation – the first step for successful homoepitaxy.[5] I further present how the crystal quality and surface smoothness of homoepitaxial sapphire increase with increasing substrate temperature in case the growth is performed in the adsorption-controlled mode. Even at the respective high temperatures growth rates far exceeding 1 μm/h can be realized. Films were investigated by scanning transmission electron microscopy, atomic force microscopy, and x-ray diffraction. At a growth temperature of 1600 °C, the films were found to be practically undistinguishable from the underlying substrate.

#### References

- [1] M.S. Akselrod, F.J. Bruni, “Modern trends in crystal growth and new applications of sapphire,” *J. Cryst. Growth*, 360, pp. 134-145, 2012.
- [2] H. Okumura, “Sn and Si doping of α-Al<sub>2</sub>O<sub>3</sub> (10-10) layers grown by plasma-assisted molecular beam epitaxy,” *JJAP*, 61, 125505, 2022.
- [3] R. Jinno *et al.*, “Crystal orientation dictated epitaxy of ultrawide-bandgap 5.4- to 8.6-eV α-(AlGa)<sub>2</sub>O<sub>3</sub> on m-plane sapphire”, *Sci. Adv.*, 7, eabd5891, 2021
- [4] W. Braun and J. Mannhart, “Film deposition by thermal laser evaporation,” *AIP Advances*, 9, 085310, 2019.
- [5] W. Braun *et al.*, “*In situ* thermal preparation of oxide surfaces”, *APL Mater.*, 8, 071112, 2020.

8:45am **ST-WeM1-4 Prediction of MBE-grown Oxide Film Composition Using Neural Networks and Big Data Analytics**, **Patrick Gemperline**, R. Paudel, S. Thapa, S. Provence, S. Battles, R. Markland, Auburn University; R. Vasudevan, Oak Ridge National Laboratory; R. Comes, Auburn University  
Reflected high energy electron diffraction (RHEED) is a highly common form of real time analysis used in growth systems such as molecular beam

# Wednesday Morning, September 20, 2023

epitaxy (MBE) and pulsed laser deposition (PLD). Traditional RHEED analysis focuses only on the intensity and shape of the diffraction pattern for a few still images taken during growth or on the intensity of a single diffraction peak in real time. While this information can be quite insightful, there is far more information that can be gleaned from RHEED, which is often qualitative and learned through many repeated trials by the film grower. In order to obtain greater insight from RHEED videos, component analysis (PCA) and k-means clustering were applied to the recordings of the RHEED taken during the MBE growth of epitaxial thin film perovskite oxides, including SrTiO<sub>3</sub>, LaFeO<sub>3</sub> and SrHfO<sub>3</sub>. To further enhance the utilization of RHEED, a generative adversarial neural network was trained to predict X-ray photoelectron spectroscopy data from RHEED images, thus allowing for real-time prediction of film stoichiometry. These methods yield more quantitative results from the RHEED with minimal time requirements and open the door for future development of real-time computer control of film growth for optimal growth conditions.

9:00am **ST-WeM1-5 Autonomous Synthesis in the MBE Using Real-Time Artificial Intelligence**, *Tiffany Kaspar, L. Wang, J. Christudasjustus, M. Sassi, B. Helfrecht, J. Pope, A. Harilal, S. Akers, S. Spurgeon*, Pacific Northwest National Laboratory

Materials are the key components of nearly all advanced technologies, including quantum information systems, microelectronics, catalysis, and energy conversion and storage. Modern synthesis methods enable the fabrication of an ever-expanding array of novel, non-equilibrium, and/or metastable materials and composites that may possess unique and desirable functionality. Thin film deposition by molecular beam epitaxy (MBE) can produce atomically precise (or nearly so) materials with a wide range of functional electronic, magnetic, ferroelectric/multiferroic, optical, and/or ion-conducting properties. The current state of the art in precision design of functional materials is to manually explore the "growth phase space" of the deposition technique to optimize the film properties of interest. Limitations of time and resources often result in incomplete exploration of the growth phase space and resulting properties. Faced with this lack of complete information, materials design and synthesis decisions are made based in part on intuition and luck, slowing both materials optimization and materials discovery. This current synthesis paradigm can be disrupted by employing artificial intelligence (AI)-accelerated analysis of in situ and ex situ data streams that will enable targeted synthesis of novel materials with desired structure, chemical stability, and functional properties. Here we present a preliminary implementation of such an AI-controlled MBE. We are integrating the control of key synthesis parameters (temperatures, gas flow rates, shutters) with AI-guided computer control. Guidance will be based on near-real-time analysis of reflection high energy electron diffraction (RHEED) patterns using sparse data analytics, with low-latency feedback to the control software. As an initial demonstration, we will control the morphology and phase purity of epitaxial anatase TiO<sub>2</sub> thin films.

9:15am **ST-WeM1-6 The Role of Optical Excitation on Misfit Dislocations in Epitaxial ZnS on GaP**, *Alexandra Fonseca Montenegro, M. Baan, A. Blackston, R. Myers, T. Grassman*, The Ohio State University

Light decreases dislocation mobility in bulk ZnS, as was recently shown through photo-indentation measurements. Here we investigate the impact of above band gap optical excitation on ZnS epilayers grown by molecular beam epitaxy (MBE) on (001) GaP. For example, optical excitation during MBE could potentially increase the critical thickness for misfit dislocation (MD) nucleation at the ZnS/GaP heterovalent interface. GaP (001) homoepitaxial buffer layers are prepared on GaP wafers, As-capped, and transferred to the chalcogenide system where ZnS is grown by compound source MBE at 150C on the As-desorbed GaP surface. Using electron channeling contrast imaging (ECCI), the MD ensembles are measured at various film thicknesses to determine the onset of MD formation. Although HRXRD shows negligible strain-relaxation in films up to 50nm, ECCI reveals that the MD nucleation processes begins at ZnS thicknesses of between 15 and 20nm, far lower than previously reported critical thicknesses. Additionally, high densities of dipole-like features appear at large densities, which appear to be dislocation loops nucleated at the surface. Image analysis is used to quantify the MD density, length, as well as the density of dipole features as a function of film thickness. We will discuss changes in the MD content with and without above band gap excitation. Additionally, post-growth strain biasing is used to increase the MD content taking advantage of the thermal mismatch via temperature cycling. Photoluminescence spectra are acquired revealing the emergence of a sub-band gap peak at 3.1 eV, which increases in intensity within ZnS epilayers upon repeated temperature cycles. We will discuss changes in the MD

content and PL spectra for samples thermally cycled with and without optical excitation.

## Author Index

**Bold page numbers indicate presenter**

— A —

Akers, S.: ST-WeM1-5, 2

— B —

Baan, M.: ST-WeM1-6, 2

Battles, S.: ST-WeM1-4, 1

Blackston, A.: ST-WeM1-6, 2

Boschker, H.: ST-WeM1-1, 1

Braun, W.: ST-WeM1-1, 1; ST-WeM1-3, 1

— C —

Christudasjustus, J.: ST-WeM1-5, 2

Comes, R.: ST-WeM1-4, 1

— D —

Dereh, D.: ST-WeM1-1, 1

— F —

Faeth, B.: ST-WeM1-1, 1

Fonseca Montenegro, A.: ST-WeM1-6, 2

— G —

Gemperline, P.: ST-WeM1-4, 1

Grassman, T.: ST-WeM1-6, 2

— H —

Harilal, A.: ST-WeM1-5, 2

Helfrecht, B.: ST-WeM1-5, 2

Hensling, F.: ST-WeM1-1, 1; ST-WeM1-3, 1

— J —

Jaramillo, R.: ST-WeM1-2, 1

— K —

Kaspar, T.: ST-WeM1-5, 2

Kim, D.: ST-WeM1-1, 1

— M —

Majer, L.: ST-WeM1-1, 1; ST-WeM1-3, 1

Mannhart, J.: ST-WeM1-1, 1; ST-WeM1-3, 1

Markland, R.: ST-WeM1-4, 1

Myers, R.: ST-WeM1-6, 2

— P —

Paudel, R.: ST-WeM1-4, 1

Pope, J.: ST-WeM1-5, 2

Provence, S.: ST-WeM1-4, 1

— S —

Sadeghi, I.: ST-WeM1-2, 1

Sassi, M.: ST-WeM1-5, 2

Smart, T.: ST-WeM1-1, 1

Smink, S.: ST-WeM1-1, 1; ST-WeM1-3, 1

Spurgeon, S.: ST-WeM1-5, 2

— T —

Thapa, S.: ST-WeM1-4, 1

— V —

Van Sambeek, J.: ST-WeM1-2, 1

Vasudevan, R.: ST-WeM1-4, 1

— W —

Wang, L.: ST-WeM1-5, 2

— Y —

Ye, K.: ST-WeM1-2, 1