Making BaZrS₃ Chalcogenide Perovskite Thin Films by Molecular Beam Epitaxy

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The making of BaZrS₃ thin films by molecular beam epitaxy (MBE) is demonstrated. BaZrS₃ forms in the orthorhombic distorted-perovskite structure with corner-sharing ZrS₆ octahedra. The single-step MBE process results in films smooth on the atomic scale, with near-perfect BaZrS₃ stoichiometry and an atomically sharp interface with the LaAlO₃ substrate. The films grow epitaxially via two competing growth modes: buffered epitaxy, with a self-assembled interface layer that relieves the epitaxial strain, and direct epitaxy, with rotated-cube-on-cube growth that accommodates the large lattice constant mismatch between the oxide and the sulfide perovskites. This work sets the stage for developing chalcogenide perovskites as a family of semiconductor alloys with properties that can be tuned with strain and composition in high-quality epitaxial thin films, as has been long-established for other systems including Si-Ge, III-Vs, and II-VIs. The methods demonstrated here also represent a revival of gas-source chalcogenide MBE.

1. Introduction

Sulfides and selenides in the perovskite and related crystal structures—chalcogenide perovskites, for brevity—may be the next family of high-performing semiconductors.[1] Chalcogenide perovskites share key physical properties with oxide perovskites, including record-high dielectric polarizability, while also featuring bandgap ($E_g$) in the visible and near-infrared (VIS-NIR).[1–4] Chalcogenide perovskites are also distinguished by their good thermal and chemical stability, and nontoxic and abundant elemental components.[5,6] Chalcogenide perovskites have been demonstrated to have slow nonradiative excited-state charge recombination, direct bandgap (in most cases), and strong above-band-gap optical absorption.[7–9] Theoretical predictions, preliminary experiments, and chemical intuition suggest that chemical alloying may produce materials with continuously tunable direct bandgap spanning from $E_g = 0.5$ to 2.3 eV.[4,8,10,11] These and other, related results suggest that the chalcogenide perovskite semiconductor alloy system may be useful for optoelectronic and energy-conversion technologies, particularly for solid-state lighting and solar energy conversion.

Most experimental studies to-date on chalcogenide perovskites have focused on bulk materials (e.g., powders) and microscopic single crystals.[11,12] Thin-film synthesis is the next, outstanding challenge. High-quality thin films are needed to enable fundamental studies of excited-state charge transport and applied studies of device performance. Thin-film synthesis may also be essential for studies of chemical doping and alloying. The good thermal stability of chalcogenide perovskites comes hand-in-hand with high material processing temperature. The formation of compounds including low-vapor pressure refractory metals and high-vapor pressure chalcogens poses a particular challenge, common to chalcogenide perovskites and many layered and two-dimensional materials. Zr and Hf are sluggish to form crystalline compounds, requiring very high temperature for synthesis, but at very high temperatures S- and Se-containing precursors are extremely volatile, leading to chalcogen loss from the growing material, and highly-corrosive conditions for the experimental equipment. Published report of chalcogenide perovskite thin-film synthesis have appeared recently.[6,8,13–15] All reports to-date are of two-step processes that separate the processes of sulfide formation (all are sulfides to-date) and film synthesis, and all have resulted in small-grained and randomly-oriented thin films. High-quality, epitaxial, single-crystal film synthesis remains an essential goal to enable the potential of chalcogenide perovskites, as the history of other semiconductor and complex oxide materials systems teaches us.[16] Epitaxial film growth may also be able to stabilize high-selenium-content alloys in the perovskite structure, since pure selenides form instead in nonperovskite, needle-like structures.[4,17]

Here we demonstrate the making of BaZrS₃ thin films by molecular beam epitaxy (MBE). BaZrS₃ forms in the orthorhombic distorted-perovskite structure with corner-sharing ZrS₆ octahedra (space group Pnma, no. 62), has a direct bandgap energy ($E_g$) in the range $E_g = 1.8 – 1.9$ eV, and is the most-studied chalcogenide perovskite.[9,18] The single-step MBE process results in films smooth on the atomic scale, evidenced by reflection high-energy electron diffraction (RHEED) measurements during growth and by atomic-force microscopy (AFM). The films are mirror-smooth and are brightly colored even at 20 nm thick, indicating strong optical interaction. Epitaxial growth on LaAlO₃ is confirmed by X-ray diffraction (XRD) and scanning transmission electron
microscopy (STEM). Films grow via two, competing epitaxial growth modes: (M1) buffered epitaxy, with a self-assembled interface layer that relieves the epitaxial strain, and (M2) direct epitaxy, with rotated-cube-on-cube growth that accommodates the large lattice constant mismatch between the oxide and the sulfide.

2. Results

We deposit films on (001)$_{PC}$-oriented LaAlO$_3$ single-crystal substrates (MTI Corp.). LaAlO$_3$ transforms from a rhombohedral (space group $R3c$) to a cubic crystal structure at elevated temperature (approximately at 500 °C).[19] In this work, Miller indices marked with substrate “PC” (as above) indicate pseudocubic indexing; otherwise, we index LaAlO$_3$ in its rhombohedral structure, with room-temperature lattice constants $a = b = 5.370$ Å, $c = 13.138$ Å. For a material $ABX_3$ with corner-sharing $BX_6$ octahedra, the pseudocubic lattice constant $a_{PC}$ is an average $B$-$X$-$B$ distance; for LaAlO$_3$, $a_{PC} = 3.8114$ Å. Orthorhombic BaZrS$_3$ has lattice constants $a = 7056$ Å, $b = 9.962$ Å, $c = 6.996$ Å, and $a_{PC} = 4.975$ Å.[20] The growth modes M1 and M2 are competing mechanisms to accommodate this large lattice constant mismatch.

We prepare the substrates by outgassing in the MBE chamber at 900 °C in a flow of H$_2$S gas. We deposit films from elemental Ba and Zr, and H$_2$S gas. The chamber pressure during film growth varies between 5 x 10$^{-5}$ to 9 x 10$^{-5}$ torr and is controlled by the H$_2$S gas flow. For the results shown here, the H$_2$S flow rate ($Q_{H2S}$) during outgassing and film growth is between 0.6 and 0.8 sccm. The Ba and Zr rates are 0.021 and 0.0075 Å s$^{-1}$ (1:1 stoichiometry), measured at the substrate position by a quartz crystal monitor (QCM). The substrate temperature during growth is held at 900°C (measured at the thermocouple), and the film growth rate is 0.04 Å s$^{-1}$, confirmed by X-ray reflectivity (XRR). The H$_2$S gas flow is maintained during cooldown after growth. More details on the deposition methods are presented below (see the Experimental Section).

Reflection high-energy electron diffraction (RHEED) data acquired during growth show evidence of atomically smooth, crystalline, epitaxial films. In Figure 1a, we present the RHEED pattern measured on the outgassed substrate along the [100]$_{PC}$ azimuth at 900 °C. Before the start of film growth. The indices and light gray lines mark reflections measured along the substrate [100]$_{PC}$ azimuth. b,c) RHEED data measured during film growth with the sample oriented along the [100]$_{PC}$ and [110]$_{PC}$ substrate azimuths, respectively. The RHEED data in (a)–(c) are scaled and centered similarly, so that the spacing of the different reflections can be compared directly. The substrate (light gray) and film (orange) reflections are labeled using pseudocubic indexing. d) XRR result showing Kiessig fringes indicating a smooth surface. e) Photograph of a typical sample; film is 23.52 ± 0.21 nm thick and is uniform across the 1 cm$^2$ substrate. f) Photograph of a sample reflecting the image of a small flower, demonstrating that the film surface is mirror-smooth. g) AFM data showing a smooth surface interrupted by depressions corresponding to areas of M2 growth mode; the image root-mean-square roughness is 3.46 ± 0.82 Å.

Figure 1. Growth of smooth and epitaxial BaZrS$_3$ thin films on LaAlO$_3$ by MBE. a) RHEED data measured on a LaAlO$_3$ substrate at 900 °C before the start of film growth. The indices and light gray lines mark reflections measured along the substrate [100]$_{PC}$ azimuth. b,c) RHEED data measured during film growth with the sample oriented along the [100]$_{PC}$ and [110]$_{PC}$ substrate azimuths, respectively. The RHEED data in (a)–(c) are scaled and centered similarly, so that the spacing of the different reflections can be compared directly. The substrate (light gray) and film (orange) reflections are labeled using pseudocubic indexing. d) XRR result showing Kiessig fringes indicating a smooth surface. e) Photograph of a typical sample; film is 23.52 ± 0.21 nm thick and is uniform across the 1 cm$^2$ substrate. f) Photograph of a sample reflecting the image of a small flower, demonstrating that the film surface is mirror-smooth. g) AFM data showing a smooth surface interrupted by depressions corresponding to areas of M2 growth mode; the image root-mean-square roughness is 3.46 ± 0.82 Å.
In Figure 2, we present the results of optical property measurements. We compare the absorption coefficient measured by spectrophotometry and spectroscopic ellipsometry to that reported by Nishigaki et al. based on spectroscopic ellipsometry measurements on BaZrS$_3$ ceramic samples, and to reference data for other direct-bandgap semiconductors.[9,20] Our BaZrS$_3$ films have a strong and steep absorption onset corresponding to a bandgap of $\approx 1.9$ eV, in near exact agreement with Nishigaki et al.

In Figure 3, we present x-ray diffraction (XRD) data. The out-of-plane scan (Figure 3a) shows the BaZrS$_3$ (H0H) family appearing with the LaAlO$_3$ (00L)$_{PC}$ family of reflections. The rocking curve of the (202) film peak has a full-width of 0.409°. Two competing epitaxial growth modes contribute to this rocking curve width, as discussed below. In Figure 3b, we present azimuthal ($\phi$) scans that identify the in-plane epitaxial relationship between film and substrate. The film (200), (121), and (002) peaks align with the substrate (110) peaks, corresponding to alignment of the pseudocubic edges of the film and substrate crystal structures (M1). We also observe a secondary, weaker set of film (200), (121) and (002) reflections that are offset by 45° from the primary reflections and that correspond to rotated-cube-on-cube growth (M2).

We use the XRD data to analyze the film strain state. We measure the lattice parameter using coupled $\theta/2\theta$ scans of the film peaks (202), (200), (121), and (002), focus on the dominant set of reflections found in the phi scan, and model the film as a material with tetragonal symmetry (with lattice constants $a = c$) to simplify the analysis. We find $a = c = 7.0624 \pm 0.0055$ Å and $b = 9.9923 \pm 0.0117$ Å, which agree well with reference room-temperature lattice constants (above). We conclude that the dominant growth mode (M1) with aligned pseudocubic edges results in a fully-relaxed film.

To better understand the film structure and epitaxial growth modes, we turn to scanning transmission electron microscopy (STEM). From the high angle annular dark-field (HAADF) STEM overview, Figure 4a, we see that the film thickness is largely uniform, $23 \pm 0.5$ nm. Distributed along the film are notched locations, $\approx 20$–$40$ nm wide, where the film thickness decreases to 17$\pm 1.2$ nm, marked with red arrows in Figure 4a. At the atomic scale, HAADF STEM data confirms that the sulfide BaZrS$_3$ thin film grows epitaxially on the oxide LaAlO$_3$ substrate (Figure 4b,c). The predominate epitaxial relationship is (100)$_{BZS}$ || (001)$_{LAO-PC}$ and [010]$_{BZS}$ || [010]$_{LAO-PC}$, meaning that the pseudocubic edges of the substrate and film are parallel (growth mode M1) (Figure 4b). At the interface, the structure differs from the bulk of the thin film. The atomic
number-sensitive HAADF intensity is significantly decreased across two atomic planes, likely due to compositional differences and/or static displacements along the column.[24,25] Further, the interface is incommensurate with the substrate, with the coincident site lattice (CSL) alignment roughly every five substrate planes and four film planes. The La atom column intensity drops at the CSL positions, suggesting vacancies or off-stoichiometry. The film appears to be completely relaxed with no measurable epitaxial strain within and past the “buffer” layer.

At the notched locations marked in Figure 4a, there are substrate step edges, and the epitaxial relationship changes to (010)_{BZS} || (001)_{LAO-PC} and [11\bar{T}]_{BZS} || [010]_{LAO-PC} (Figure 4c). This is the rotated-cube-on-cube relationship (growth mode M2). These regions represent ≈20% of the observed area and produce the weak 45°-offset reflections seen in the XRD ϕ-scan (Figure 3b). In these regions, there is a significant amount of plane bending that accommodates the step edge and the surrounding M1-oriented regions (Figure 4d). This inclination may be due to nucleation and growth on substrate step edges, contributing to the width of the out-of-plane reflection rocking curves (Figure 3a). At the interface, the HAADF contrast is significantly lower than the film, with film and substrate appearing to be directly bonded due to local atom column distortions at the interface, visible in the Fourier-filtered image (Figure 4e). An extra plane in the film, or misfit dislocation, is present roughly every 14 planes in the substrate. Comparing the interplanar distances at this orientation, $d_{BZS} = 3.5213$ Å and $d_{LAO} = 3.8114$ Å, we conclude that the misfit dislocations accommodate a majority of the lattice constant mismatch, lowering the film strain from 8% to 1%. Away from the interface, there is no visible strain gradient, with projected interatomic spacings in agreement with the bulk crystal structure. In these regions of growth mode M2, the film thickness is reduced, indicating a slower growth rate than for growth mode M1. This is likely due to the higher strain energy associated with the directly-bonded interface, resulting in thermodynamically less-favored growth compared to the relaxed “buffered” growth seen in the M1 structure, where evidence for direct bonding is absent.

From energy dispersive X-ray spectroscopy (EDS) in STEM, we find that the composition of the “bulk” of the film is nearly stoichiometric BaZrS$_3$: (in at%) Ba: 19.25 ± 2.69, Zr: 20.60 ± 3.20, S: 60.15 ± 5.39. Atomic-resolution EDS maps show the perovskite structure of the BaZrS$_3$ films (Figure 5a). To determine chemical interdiffusion, we use electron energy loss spectroscopy (EELS) due to its greater sensitivity to oxygen detection, relative to EDS. The EELS maps reveal that there is negligible interdiffusion across the interface, with coincidence of film and substrate species limited to a 2–3 nm wide region (Figure 5b). Importantly, we see from the line profiles (Figure 5c) that the oxygen signal follows the same trend as the La and Al signals, and that all are undetectable within the “bulk” of the film, away from the narrow interface region. Similarly, the integrated Ba, Zr, and S signals become undetectable in the substrate. We observe an increase in oxygen signal at the film top surface. The topmost 5 nm of the film appears to be nonstoichiometric BaZrS$_3$, likely a result of exposure to oxygen or sample preparation (Figure 5b,c). We hypothesize that this nonstoichiometry results from sulfur loss from the near-surface region during sample handling and TEM preparation, combined with the thermodynamic driving force for Zr metal oxidation. In previous work, we studied the mechanism by which Zr-based transition metal dichalcogenides readily form an oxide several-nm thick in ambient conditions; the surface oxidation observed here in BaZrS$_3$ may proceed by a similar mechanism.[26]

We find planar defects throughout the film, corresponding to boundaries between rotation variants, as well as antiphase boundaries. In Figure 6a, we highlight a boundary between 90° variants of the M1 growth mode. We find that the b direction remains in-plane for all M1 domains. However, given the four-fold symmetry of the substrate, the in-plane orientations [10\bar{T}]_{BZS} || [010]_{LAO-PC}, [010]_{BZS} || [010]_{LAO-PC}, and [010]_{BZS} || [010]_{LAO-PC} are equally favorable, creating planar boundaries where these domains meet. These boundaries introduce local changes in the ZrS$_6$ octahedra tilt and distortion patterns that
are likely correlated with the band-edge electronic structure and semiconducting properties (e.g., bandgap). At substrate step edges we find antiphase boundaries in the film, as shown in Figure 6b. The normalized intensities of atom columns near the planar defect emphasize differences in Z-contrast and highlight the antiphase boundary. This is consistent with the hypothesis that M2 growth nucleates at substrate steps.

The combined XRD and STEM data allow us to describe the two epitaxial growth modes, in context with the challenges present in epitaxial chalcogenide perovskite thin film growth. Chalcogenide perovskites including BaZrS$_3$ have much larger unit cells than their oxide counterparts. This poses a challenge to identify appropriate substrates for cube-on-cube epitaxy. In Figure 7a we compare a$_{PC}$ of select chalcogenide perovskites to those of some commonly-available substrate materials. We present the sulfide perovskites SrHfS$_3$, SrZrS$_3$, BaHfS$_3$, and BaZrS$_3$; we also present the selenide BaZrSe$_3$, which potentially could be stabilized in the perovskite structure through epitaxy.$^{[4,17]}$ Chalcogenide perovskites feature a$_{PC} \gtrsim 5$ Å, whereas typical perovskite oxides feature a$_{PC} = 3.7$–4.1 Å. This large lattice constant mismatch can be accommodated by a 45° rotation between film and substrate, referred to as rotated-cube-on-cube growth (or “root-2 epi”). We label this as direct epitaxy, growth mode M2. For BaZrS$_3$ (a$_{PC} = 4.975$ Å) on LaAlO$_3$ (a$_{PC} = 3.8114$ Å), this results in a tensile strain of 8%. STEM data shows that a majority of this strain is relieved by the presence of misfit dislocations, with residual strain visible in the rotated direct bonds at the interface (Figure 4). We also observe that this material grows more slowly than the rest of the film, resulting in a notched film surface. Meanwhile, the majority of the film grows in a relaxed state on a self-assembled interface (“buffer”) layer that fully relieves the epitaxial strain. The pseudocubic edges of film and substrate align, but there is no direct bonding between the perovskite structure of film and substrate. We label this as buffered epitaxy, growth mode M1. M1 growth is faster than M2, and presumably dominates everywhere except for where M2 domains have nucleated at step edges and grown to a critical size. The balance between M1 and M2 changes with the H$_2$S flow rate. Evidence for M2 growth disappears from the XRD data when $Q_{H2S}$ changes from 0.6 to
0.8 sccm. We suggest two mechanics by which the M1 mode, already the faster of the two, would further outcompete M2 due to an increase in H₂S supply rate. H₂S is effective at surface passivation, both in its molecular form and after dissociation; for instance, H₂S is frequently studied for surface passivation of semiconductors including Si and III-Vs. [27,28] Since we observe that M2 nucleates at substrate steps, its nucleation site density would be reduced by surface passivation. Surface passivation also enhances adatom mobility across step-free areas of the substrate, leading to faster lateral growth of M1-type crystallites. Therefore, surface passivation by H₂S may affect nucleation and growth rates to favor M1 over M2. We also note that the self-assembled buffer layer that enables M1 has characteristics of a van der Waals gap (see for instance Figure 4b): surface passivation by H₂S may enable fully stain-relieved film growth akin to van der Waals epitaxy.[29]

3. Conclusion

This work sets the stage for developing chalcogenide perovskites as a family of semiconductor alloys with properties that can be tuned with strain and composition in high-quality epitaxial thin films, as has been long-established for other
systems including Si-Ge, III-Vs, and II-VIs. This work also relates to the established field of complex oxide epitaxial growth and materials physics. Our work suggests that extended defects and the tilt and distortions of corner-sharing octahedra may be controlled through epitaxy, as they are in complex oxides. In the oxides, these structural parameters couple to properties such as dielectric response, magnetism, and insulator-metal transitions, via strong correlations between atomic and electronic structure. Chalcogenide perovskites exhibit similar correlations, with the notable difference that, as semiconductors with bandgap in the VIS-NIR spectral region, we expect to control properties useful for optoelectronics such as bandgap, luminescence yield, and charge transport mobility. Our work sets the stage for studying the impact of extended defects on transport and excited-state properties using spatially resolved probes of excited states such as STEM-cathodoluminescence and two-photon time-resolved photoluminescence. These and other such studies will guide efforts to control optoelectronic properties through strain, substrate engineering, doping, and alloying, and for device demonstrations and applications. The methods demonstrated here also represent a revival of gas-source chalcogenide MBE, with potential for impact on research on chalcogenide perovskites and other sulfur- and selenium-containing compounds.

4. Experimental Section

Films were grown in a chamber custom-modified for gas-source chalcogenide MBE (Mantis Deposition M500). The substrate was heated radiatively from a SiC filament and was rotated at 2 rpm. Ba metal was supplied from an effusion cell (Mantis Comcell 16–500), and Zr metal from an electron-beam (e-beam) evaporator (Telemark model 578). Ferrite clamps were used on power cables running between the control rack and the MBE chamber to reduce the impact of e-beam arcing events on other components; left unaddressed, e-beam arcs could cause other components including effusion cells and the substrate heater to shut down. Sulfur was supplied in the form of H2S gas. The gas was supplied from a condensed, liquified source of 99.9% purity (Matheson Research Grade), and run through a purifier (Matheson Purifilter) before entering the MBE chamber. The gas was injected in close proximity to the substrate using custom-made gas lines and nozzles (SS310 construction), so that the pressure experienced at the substrate was higher than the chamber pressure reading. It was estimated from Monte-Carlo gas flow simulations (using MolFlow+, results not shown) that the H2S pressure at the substrate during growth was 50% higher than the chamber pressure.

RHEED data were measured using a 20 keV electron gun (Staib) and a digital acquisition system (k-Space Associates, kSA 400). The strong magnetic field from the permanent magnets in the electron-beam evaporator interfered with RHEED measurements. The magnetic field strength reached as high as ~10 Oe along the RHEED electron beam path; such a strong field distorted the RHEED pattern, and could even cause the beam to miss the imaging screen entirely. This problem was addressed partially by installing custom magnetic shielding along much of incident and reflected beam paths, so that the RHEED beam path was unshielded for only several inches, as it encountered the substrate. Even so, the RHEED beam could not be centered on the screen, and the pattern at times appeared tilted. This did not affect the analysis presented here.

Optical properties were measured using spectrophotometry and spectroscopic ellipsometry. Reflection and absorption spectra were measured for both the film-on-substrate samples and bare LaAlO3 substrates, using a Perkin Elmer 1050 UV/VIS/NIR spectrophotometer.

An integrating sphere was used because the substrates were one-side polished, with a rough back surface. The authors accounted for internal reflections using methodology described by Look and Leach, with additional corrections to account for the Fresnel coefficients at the internal film-substrate interface, and for absorption in the substrate.[30] Spectroscopic ellipsometry measurements were performed using a Semilab SE2000. Data were measured for both film-on-substrate samples and a bare LaAlO3 substrate. The substrate was single-side polished and therefore its optical properties could be determined by direct inversion of the spectroscopic ellipsometry data. This substrate model was then used in the analysis of the film-on-substrate data, to better infer film optical properties.

XRR measurements were performed using a Rigaku Smartlab in parallel-beam mode, with a Cu target, and a tube power of 9 kW (45 kV, 200 mA). XRD was performed using a Bruker D8 High-Resolution X-ray diffractometer with a Ge (022) four-bounce monochromator in parallel-beam mode, with a Cu target, and a tube power of 1.6 kW (40 kV, 40 mA).

Samples for STEM measurements were prepared by nonaqueous wedge polishing, followed by single-sector ion milling (Fischione 1051) using ion-beam energies of 2, 1, and 0.5 kV.[31,32] STEM data were acquired on a probe-aberration-corrected Thermo Fisher Scientific Themis Z S/STEM operated at 200 kV using a convergence angle of 17.9 mrad. HAADF images were acquired using a collection angle of 63–200 mrad, and drift-corrected using the Revolving STEM (RevSTEM) method.[33,34] EDS was performed at low magnification using Super X detectors at a beam current of 500 pA and quantified using the Thermo Fisher Scientific Velox software. Atomic-resolution EDS maps were filtered using a radial Wiener filter with a high frequency cutoff of 0.08 px−1. EELS was performed using a Gatan Continuum spectrometer with an energy dispersion of 1.5 eV ch−1, and a sample thickness of ~60 nm.[35] The resulting spectra were extracted using the HyperSpy python package and denoised using principle component analysis (PCA), retaining only the first four components, which accounted for 96.8% of the variance.[36]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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