

Growth of Ta₂SnO₆ Films, a Candidate Wide-Band-Gap p-Type Oxide

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Cite This: *J. Phys. Chem. C* 2022, 126, 3764–3775

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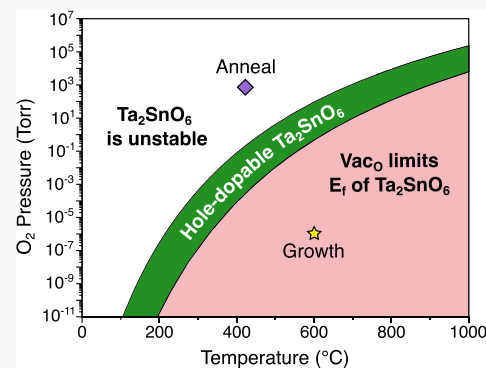
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ABSTRACT: In an effort to discover a high-mobility p-type oxide, recent computational studies have focused on Sn²⁺-based ternary oxides. Ta₂SnO₆ has been suggested as a potentially useful p-type material based on the prediction of simultaneously high hole mobility and a wide range of synthesis conditions over which it is the energetically favored phase. In this study, we synthesized this material epitaxially for the first time and evaluated its properties experimentally. We measured the band gap to be 2.4 eV and attempted to substitutionally dope titanium for tantalum (Ti_{Ta}) and potassium for tin (K_{Sn}) but found that both doped and undoped films were insulating. Amorphous Ta₂SnO₆ films were also grown via thermal atomic layer deposition (ALD) at 175 °C. Electrical characterization of the ALD-fabricated amorphous films found them to be insulating with an optical band gap of 2.24 eV. Density functional theory calculations indicate that, under MBE growth conditions, oxygen vacancies have a negative energy of formation in crystalline Ta₂SnO₆ when the Fermi energy lies near the valence band edge. These oxygen vacancies would lead to compensation of holes generated by Ti_{Ta} or K_{Sn} dopants, which is consistent with our observations. We conclude that the direct growth of epitaxial p-type Ta₂SnO₆ films using MBE-accessible growth conditions is thwarted by the spontaneous formation of oxygen vacancies. While our growth conditions do not yield p-type films, we calculate that there are conditions under which Ta₂SnO₆ is the thermodynamically stable phase and spontaneous formation of compensating defects does not occur, motivating further studies with different synthesis techniques.



INTRODUCTION

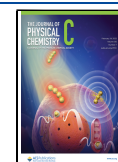
In the field of oxide electronics, few discoveries would be more disruptive than the demonstration of a scalable, wide-band-gap, and high-mobility p-type oxide.^{1–4} While there are demonstrations of n-channel oxide devices with high mobility using numerous materials,^{5–9} the complementary p-channel oxide devices lag behind for various reasons. First, p-type oxides with high hole mobility are rare because the top of the valence band is often dominated by oxygen 2p orbitals. These orbitals are relatively localized compared to orbitals of metal cations that make up the conduction band, meaning the effective mass of holes at the valence band edge tends to be much higher than that of electrons at the conduction band edge.¹⁰ Furthermore, oxygen vacancies are low-energy defects in many oxides, and these defects trap holes.¹¹ Oxygen vacancies also become increasingly favorable as more holes are introduced, which can result in their spontaneous formation before a useful carrier concentration is reached.^{1,12,13} These challenges, and others, have stymied the discovery of useful p-type oxides, hampering the development of transparent electronics^{2–4} and a low-power analogue of complementary metal oxide semiconductor (CMOS) technology at back-end-of-the-line temperatures for transistors.¹⁴

To engineer p-type oxides with high hole mobility, research has focused on suboxides such as SnO^{15–20} and Cu₂O^{11,21–24} in which filled cation orbitals contribute to the top of the valence band and acceptor cation vacancies are more energetically favorable.¹¹ Unlike valence bands composed of primarily oxygen 2p orbitals, these hybridized valence bands have delocalized hole states with lower effective masses. While this design principle has been understood for decades,¹⁰ attempts to fabricate practical devices from these binary oxides have yielded only modest success. For Cu₂O, hole mobilities up to ~100 cm²/(V·s)^{25,26} have been measured by the Hall effect, but the highest mobility of holes in transistors fabricated from Cu₂O thin films is only ~4 cm²/(V·s).²⁶ While SnO has a theoretical hole mobility of 60 cm²/(V·s) along the *c*-axis at room temperature,²⁰ such mobilities have yet to be realized in a transistor because the litharge crystal structure of SnO has

Received: December 14, 2021

Revised: January 25, 2022

Published: February 9, 2022



layers aligned perpendicular to the *c*-axis. These (001) layers have significantly lower surface energy than any other face,²⁷ meaning that growing an epitaxial SnO film with the *c*-axis in the plane of the film is difficult. In fact, all epitaxial SnO that has been reported is (001)-oriented,^{15,19} and in the (001) plane, the room-temperature mobility of a perfect crystal is predicted to be only 7.4 cm²/(V·s).²⁰ As a result, the highest reported field-effect hole mobility in a SnO-based transistor of 10.8 cm²/(V·s) was achieved using polycrystalline SnO.¹⁸ While this mobility may be acceptable for some applications, the low band gap of SnO (0.7 eV)¹⁵ excludes it from many others.

Due to these challenges and others, the search for device-relevant p-type materials has been broadened to ternary oxides, making the use of the same hybridized valence band design principle.^{1,10} Ternary oxides containing Sn²⁺ are candidates because the Sn 5s orbitals hybridize with the O 2p orbitals to form the valence band;^{28–31} however, many of these compounds are hard to synthesize because their phase stability windows are usually much smaller than those of Sn⁴⁺ oxides,³² and others (notably pyrochlores)^{29,30} have low mobility due to unfavorable orbital overlap geometry.²⁸ While only previously synthesized in the powder form,^{33,34} Ta₂SnO₆ is a compound containing Sn²⁺ with an unusually large region of phase stability, and the predicted room-temperature hole mobility is 32.5 cm²/(V·s) along the high-mobility direction, making it a strong candidate as a high-mobility p-type oxide.^{20,32} In addition to the thermodynamic stability and competitive hole mobility, a recent computational study has argued that dopability and the bonding environment in Ta₂SnO₆ make it the most promising candidate for the first p-type semiconductor with a mobility that is insensitive to disorder.³¹ If experimentally confirmed, amorphous films of Ta₂SnO₆ would be enticing as a p-type counterpart to the commercially successful n-type In–Ga–Zn–O (IGZO) system.³⁵ Such amorphous semiconductors are an extremely valuable engineering capability because they can be deposited on any substrate at low temperatures.

In addition to the attractive attributes of Ta₂SnO₆, there are some challenges to its synthesis. The thoreaulite crystal structure of Ta₂SnO₆ has low symmetry (space group: *Cc*), and its structure is different from any commercially available substrate. Further, Sn²⁺ is experimentally hard to stabilize, making epitaxial synthesis challenging. An isostructural compound that has been synthesized epitaxially by pulsed laser deposition is Nb₂SnO₆, but the authors of this work were unable to induce hole conductivity, citing the spontaneous formation of oxygen vacancies that trap holes.¹³ Nonetheless, p-type Nb₂SnO₆ has been synthesized by a solid-state reaction between SnO and Nb₂O₅ powders. A modest hole mobility of 0.38 cm²/(V·s) was achieved at room temperature.³⁶ Even though p-type Nb₂SnO₆ is thermodynamically unstable due to the spontaneous formation of oxygen vacancies,¹³ its synthesis was likely enabled by starting from an oxygen-rich heterogeneous mixture and kinetically suppressing oxygen loss. This hypothesis is supported by the observation that annealing at higher temperatures resulted in n-type films.³⁶

Here, we demonstrate the synthesis of epitaxial Ta₂SnO₆ films grown on TiO₂ (101) substrates by molecular-beam epitaxy (MBE), enabling the first experimental determination of the band gap (2.4 eV). Despite hole doping attempts, no conducting films were synthesized. The insulating nature of Ta₂SnO₆ is most likely explained by the formation of oxygen

vacancies, which have a negative energy of formation in p-doped films under growth conditions easily accessible by MBE. Oxygen vacancies trap would-be holes, preventing conduction. A thermal atomic layer deposition (ALD) process was also developed for growing amorphous Ta₂SnO₆ with a band gap of 2.24 eV. Unfortunately, Ta₂SnO₆ was found to be insulating in its amorphous phase as well. Even though we were unable to make use of the candidate p-type semiconducting oxide, epitaxial and ALD syntheses of Ta₂SnO₆ were reported for the first time, and our DFT calculations suggest that different synthesis strategies could be implemented to realize p-type Ta₂SnO₆ films without the spontaneous formation of compensating defects.

METHODS

Thin films of Ta₂SnO₆ were synthesized by MBE in a Veeco GEN10. A molecular beam of SnO was generated from an effusion cell containing SnO₂ powder, from which SnO is the most volatile species,³⁷ and tantalum was evaporated with an electron beam. Molecular oxygen was used as the oxidant by providing a background chamber pressure of 1 × 10^{−6} Torr O₂. Growth was investigated at substrate temperatures ranging from 500 to 630 °C by codepositing the cation-containing molecular beams at approximate fluxes of 7 × 10¹² Ta atoms/(cm²·s) and 1 × 10¹³ SnO molecules/(cm²·s) for a duration of 3600 s. When the substrate temperature was sufficiently hot, the excess SnO desorbed to form 15 nm thick stoichiometric Ta₂SnO₆ films. Having established the adsorption-controlled growth window for Ta₂SnO₆, we synthesized a 30 nm thick film to enable a more detailed structural analysis with X-ray diffraction (XRD). The substrate temperatures reported are measured by a thermocouple near but not in contact with the substrate. The TiO₂ (101) substrates were prepared according to the procedure described by Yamamoto et al.³⁸

Theoretical DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP)^{39,40} which uses projected augmented wave (PAW)^{41,42} pseudopotentials. The exchange–correlation potential energy was calculated at the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA-PBE) level. An energy cutoff of 520 eV was adopted for plane wave basis expansion throughout the calculations. The Brillouin zone was sampled by the γ -centered Monkhorst–Pack scheme with a *k*-point mesh density of 0.03/Å. Structures were optimized by the conjugate gradient (CG) method with the convergence criterion being the force on each atom less than 0.02 eV/Å. Electronic minimizations were achieved by the blocked Davidson scheme with the energy difference between two consecutive iterations no more than 10^{−5} eV.

The defect computations were carried out using a 1 × 2 × 2 supercell of the primitive cell under the DFT-PBE level. The formation energy of defect *X* in the charged state *q* $E^f[X^q]$ is calculated according to eq 1⁴³

$$E^f[X^q] = E_{\text{def}}[X^q] - E_{\text{bulk}} - \sum n_i \mu_i + q(E_F + E_{\text{VBE}}) + E_{\text{corr}}[X^q] \quad (1)$$

where $E_{\text{def}}[X^q]$ and E_{bulk} are the energies of the defective and perfect supercells, respectively. n_i and μ_i are the number and the chemical potential of *i*th defective atoms, respectively. The reference state for μ_i is unbonded atoms at a temperature of 0 K and a pressure of 1 atm. E_{VBE} is the valence band edge (VBE) of a pristine supercell and E_F is the Fermi level relative

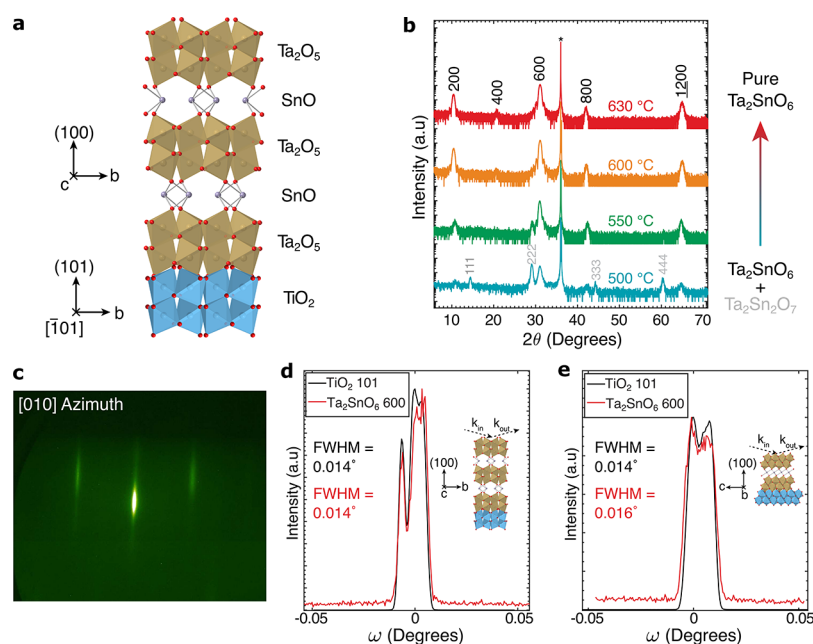


Figure 1. (a) Diagram of the untwinned thoreaulite crystal structure of Ta_2SnO_6 and its relation to the TiO_2 (101) substrate. TiO_6 and TaO_6 oxygen coordination polyhedra around Ti^{4+} and Ta^{5+} are colored blue and brown in the substrate and film, respectively. (b) XRD θ – 2θ scans of a series of samples grown at varying substrate temperatures, highlighting the adsorption-controlled growth of Ta_2SnO_6 . Peaks from Ta_2SnO_6 are labeled with black indices, and peaks from the SnO -rich impurity phase ($\text{Ta}_2\text{Sn}_2\text{O}_7$) are labeled in gray. The asterisk (*) indicates the 101 peak of the TiO_2 substrate. (c) Reflection high-energy electron diffraction (RHEED) pattern of a 15 nm thick Ta_2SnO_6 film collected along the [010] azimuth of Ta_2SnO_6 (d, e) Rocking curves of the TiO_2 101 peak and the Ta_2SnO_6 600 peak collected 90° apart in ϕ (indicated by inset diagrams) and normalized to the maximum value.

to E_{VBE} . The energy correction term, $E_{\text{corr}}[X^q]$, is to account for all spurious electrostatic interactions in the supercell. The energy correction term was calculated using the Freysoldt scheme.^{44,45} All defect computations were performed using VASP, followed by PyCDT⁴⁶ postprocessing for the defect formation energy calculation.

For the calculation of VBE energy position, a slab model consisting of the (100) plane terminated by the SnO layer was used (see Figure S1). Symmetric atomic configurations were adopted at both ends to eliminate a dipole moment across the slab. A 10 Å thick vacuum layer was inserted to decouple the image interaction between adjacent cells. The atomic core orbital energy level (O 1s) was used as the common reference level to align the VBE in the bulk phase and the vacuum level in the slab model.

ALD-derived films were deposited using a Savannah 200 reactor with a preinstalled quartz crystal microbalance (QCM) kit from Veeco Instruments, Inc. TiO_2 (101), Si (111), and glass substrates were prepared by sonicating in acetone for 30 min, followed by sonicating in isopropyl alcohol for an additional 30 min. Tris(ethylmethylamido)(*tert*-butylimido)-tantalum(V) (99.99%) was purchased from Sigma-Aldrich and N^2,N^3 -di-*tert*-butylbutane-2,3-diamidotin(II) was prepared using a previously reported synthesis.⁴⁷ Tantalum and tin precursors were pulsed from 50 cm^3 precursor cylinders heated to 115 and 75 $^\circ\text{C}$, respectively. DI water was used as the oxygen source and pulsed from a precursor cylinder at room temperature. The details of the ALD process and film growth characteristics can be found in the Supporting Information.

Spectroscopic ellipsometry measurements of amorphous and epitaxial Ta_2SnO_6 thin films were performed using a single rotating compensator multichannel ellipsometer (J.A. Woollam Co. M-2000).^{48,49} Standard ellipsometric spectra were

collected over a photon energy range of 0.74–5.89 eV (1675–210 nm) for the amorphous film, and generalized ellipsometric spectra were collected over a range of 1.00–5.89 eV (1550–210 nm) for the anisotropic epitaxial Ta_2SnO_6 film. Each measurement was performed at 50 and 70° angles of incidence. Details of the spectroscopic ellipsometry data analysis procedure for the films are available in the Supporting Information.

RESULTS AND DISCUSSION

A central challenge in trying to grow epitaxial Ta_2SnO_6 is picking a substrate for the low-symmetry thoreaulite crystal. The calculated mobility tensor at room temperature of

$$\text{Ta}_2\text{SnO}_6 \text{ is } \begin{pmatrix} 32.1 & 0 & 17.3 \\ 0 & 2.1 & 0 \\ 17.3 & 0 & 21.5 \end{pmatrix} \text{ cm}^2/(\text{V}\cdot\text{s}), \text{ where } x \text{ is parallel}$$

to [100], y is parallel to [010], and z is perpendicular to (001). Here x , y , and z are the orthonormal axes of the mobility tensor and the Miller indices given refer to the monoclinic crystallographic axes of Ta_2SnO_6 in what is called the second setting, where the [010] axis lies perpendicular to the c -glide plane of Ta_2SnO_6 . Note that this tensor is corrected from that reported previously.²⁰ The desired film orientation to provide the highest in-plane mobility is (010)-oriented Ta_2SnO_6 . Nonetheless, the observed cleavage of the thoreaulite mineral most easily along (100) planes (parallel to SnO and Ta_2O_5 layers)⁵⁰ suggests that synthesizing a (100)-oriented Ta_2SnO_6 thin film may be most practical due to the low surface energy. Even in this orientation, channels oriented along the c -axis could still demonstrate a very competitive room-temperature hole mobility. The ideal substrate for (100)-oriented Ta_2SnO_6 has a $4.87 \text{ \AA} \times 5.55 \text{ \AA}$ surface cell based on unit cell measurements of crystalline powder.^{33,34} Interestingly, the

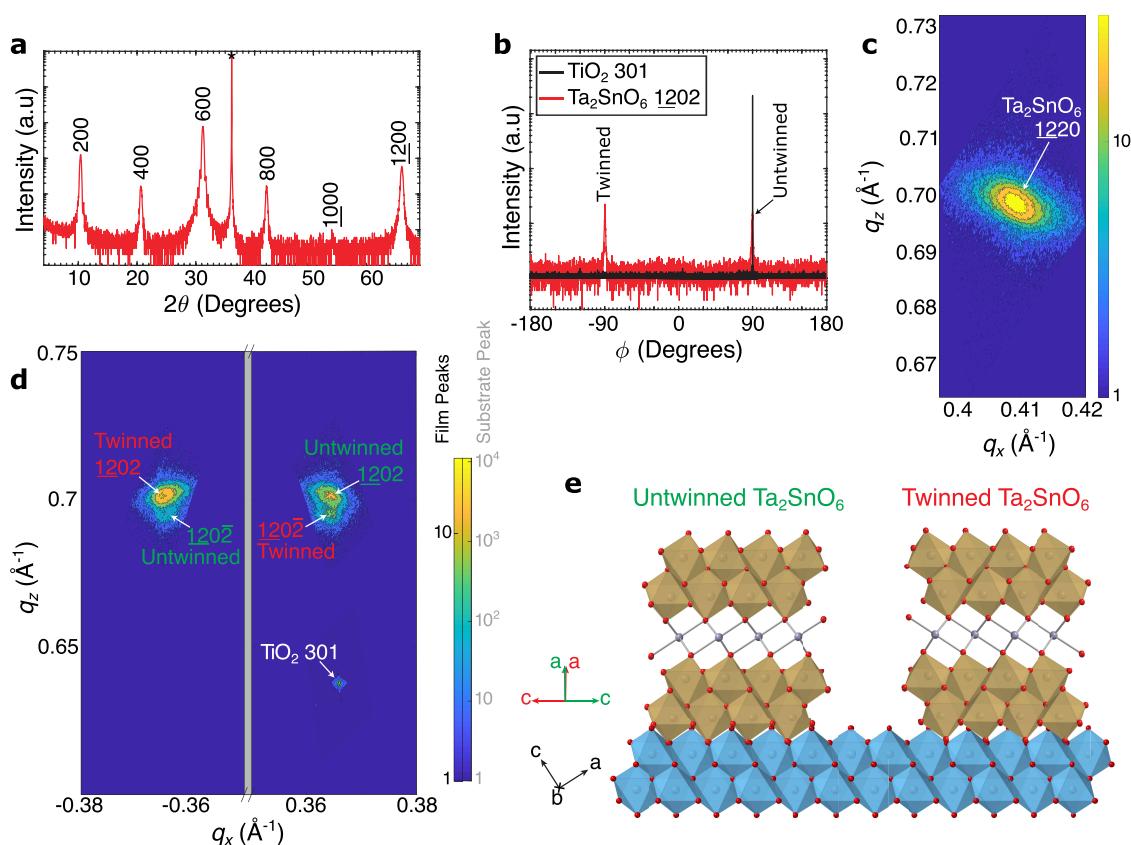


Figure 2. (a) XRD θ – 2θ scan of a 30 nm thick Ta_2SnO_6 film grown on TiO_2 (101). The asterisk (*) indicates the 101 peak of the TiO_2 substrate. (b) ϕ scan of the $\bar{1}202$ peak of Ta_2SnO_6 and the 301 peak of TiO_2 at $\chi = 62.58$ and 60.15° respectively, where $\chi = 90^\circ$ aligns the diffraction vector to be perpendicular to the plane of the substrate. (c) Reciprocal space map (RSM) of the $\bar{1}220$ peak of the Ta_2SnO_6 film. (d) RSMs of Ta_2SnO_6 showing the presence of two distinct twin domains (i.e., two sets of $\bar{1}202$ and $\bar{1}202$ peaks) and their position relative to the TiO_2 301 reciprocal lattice point. (e) Schematic of the epitaxial registry of Ta_2SnO_6 grown on TiO_2 (101) with the rutile Ta_2O_5 sublattice oriented identically to the rutile substrate (untwinned) and rotated 180° in the (100) plane (twinned).

Ta_2O_5 octahedra have the same structural motif as (101) planes of the rutile structure (Figure 1a).¹³ In fact, the (101) surface of rutile TiO_2 is a reasonable match yielding -5.8% strain along the b -axis of Ta_2SnO_6 and -1.6% strain along its c -axis. The epitaxial orientation relationship is Ta_2SnO_6 (100) $\parallel$ TiO_2 (101) and Ta_2SnO_6 [001] $\parallel$ TiO_2 [101] if the Ta_2O_5 rutile sublattice has the same orientation as the rutile substrate. We note, however, that a twinned film with Ta_2SnO_6 (100) $\parallel$ TiO_2 (101) and Ta_2SnO_6 [001] $\parallel$ TiO_2 $[\bar{1}01]$ would have the same substrate mismatch, but the Ta_2O_5 sublattice would have a different orientation from the rutile substrate (see Figure 2e). One drawback of TiO_2 (101) as a substrate is that, under our growth conditions, TiO_2 forms oxygen vacancies, making it conduct and undermine electrical measurements of the film. This problem can be mitigated by annealing the sample ex situ at 425°C and 1 atm O_2 to oxidize the TiO_2 substrate while largely preserving the crystallinity of the film. Further discussion of the in situ TiO_2 reduction, ex situ sample annealing, and attempted synthesis on other substrates is reported in the Supporting Information.

In addition, stabilizing the oxidation state of Sn^{2+} is a major concern, as its phase stability window is often limited. For example, SnO is only a stable phase below 270°C ; above that temperature, it disproportionates into tin and Sn_3O_4 (above 457°C Sn_3O_4 disproportionates into tin and SnO_2).⁵¹ We targeted Ta_2SnO_6 because it has a region of thermodynamic

stability, as calculated by density functional theory (DFT), that is exceptionally broad for Sn^{2+} phases.^{20,31,32}

Although Ta_2SnO_6 itself is quite stable, the reaction pathway from the incident molecular beams, which are traditionally elemental, to Ta_2SnO_6 must also be considered. Rather than using a molecular beam of elemental tin, we use a molecular beam of SnO . This has the advantage that the tin in the molecular beam is already in the desired oxidation state of Sn^{2+} , and we must only avoid oxidation or reduction. The molecular beam of SnO is produced by heating solid SnO_2 contained within an Al_2O_3 crucible. When solid SnO_2 is heated, the species with the highest vapor pressure is gaseous SnO . At typical MBE growth rates, the vapor pressure of SnO is about 3 orders of magnitude higher than those of any other species, meaning that the SnO molecular beam so formed is 99.9% SnO .^{37,52} While tin is supplied in its desired oxidation state, it is necessary to oxidize tantalum, which is incident as an elemental tantalum molecular beam. Molecular O_2 is used as an oxidant to achieve the desired oxidation of tantalum without further oxidizing Sn^{2+} . Our attempts to use O_3 as the oxidant resulted in further oxidation of Sn^{2+} , yielding rutile $\text{Sn}_{1-x}\text{Ta}_x\text{O}_2$. Nevertheless, we do not believe that molecular O_2 is sufficient to completely oxidize tantalum to Ta^{5+} —at least using the growth conditions employed here—but that the TiO_2 substrate supplies additional oxygen to the film as is well known for the case of SrTiO_3 substrates.^{53,54} The strongest evidence for this hypothesis is that attempting to grow

Ta₂SnO₆ using a bare rutile MgF₂ (101) substrate fails under the same conditions that are successful using a TiO₂ substrate despite only a <1% difference in the lattice parameter between the isostructural substrates. Attempts to grow Ta₂SnO₆ using a MgF₂ (101) substrate result in mixed-phase β -Sn and rutile Sn_{1-x}Ta_xO₂, containing Ta⁴⁺ rather than the intended Ta⁵⁺ of thoreaulite Ta₂SnO₆ observed using a TiO₂ (101) substrate (see the Supporting Information for more information).

The high volatility of SnO suggests that we might be able to utilize adsorption control to grow stoichiometric Ta₂SnO₆ by supplying excess SnO and adjusting the substrate temperature to evaporate SnO that does not incorporate into the crystal as has been accomplished in the growth of SnO.¹⁹ The achievement of adsorption-controlled growth of Ta₂SnO₆ is demonstrated by XRD θ - 2θ scans performed on a series of films of grown at different substrate temperatures (Figure 1b) with the same oxygen background pressure (1×10^{-6} Torr O₂) and a 1.4:1 flux ratio of SnO/Ta. Note that Ta₂SnO₆ has a Sn/Ta ratio of 0.5:1. Here, the SnO-rich impurity phase (the pyrochlore Ta₂Sn₂O₇) is present at low temperatures but eliminated by increasing the substrate temperature to volatilize excess SnO. At substrate temperatures of 600–630 °C, the excess SnO is desorbed to leave behind stoichiometric Ta₂SnO₆ with a film thickness of about 15 nm. At higher temperatures (>630 °C), SnO may be reduced to β -Sn or evaporated completely leaving Ta₂O₅, depending on the precise temperature, flux ratio, and oxidizing conditions.

Figure 1c shows a reflection high-energy electron diffraction (RHEED) image of a phase-pure Ta₂SnO₆ film, and Figure 1d,e shows rocking curves of the Ta₂SnO₆ 600 reflection along two orthogonal directions (i.e., 90° apart in ϕ). The two rocking curves are sensitive to different types of mosaicity, which is appropriate for the monoclinic crystal; they measure rotations of (100) planes about the *c*-axis (Figure 1d) and the *b*-axis (Figure 1e), which are not necessarily the same. Along both directions, the normalized rocking curve of the film is almost indistinguishable from that of the substrate, showing the low mosaicity of the epitaxial film.

Having established a growth window for Ta₂SnO₆ on TiO₂, we synthesize a 30 nm thick film to increase the intensity of diffraction peaks for more detailed structural characterization (see XRD in Figure 2). We measure the unit cell dimensions with reciprocal space maps (RSMs) in Figure 2c,d to compare them to bulk measurements:³³ $a = 17.18$ Å (0.4% greater than bulk), $b = 4.89$ Å (0.4% greater than bulk), $c = 5.49$ Å (1% less than bulk), and $\beta = 90.5^\circ$ (0.1° less than bulk). While the compliance tensor is unknown, these measurements are qualitatively consistent with a film uniaxially stressed along the [001] direction, i.e., no epitaxial stress is imparted by the substrate along the [010] direction (−5.8% mismatch) but the film is compressively strained along the [001] direction (−1.6% mismatch). We also find that our films are twinned, which is consistent with observations of (010) twin boundaries in thoreaulite minerals.⁵⁰ The orientation of the different twin domains with respect to the substrate is shown in Figure 2e. Twin domains are placed side by side in Figure 2e to clearly show the epitaxial relationship of the different domains, but the boundary between twin domains in Ta₂SnO₆ minerals is in the plane of the figure, (010). Because the crystal structure is nearly orthorhombic, the diffraction peaks of different twin domains are nearly coincident. Nonetheless, we are able to discern two different twin domains present in this 30 nm thick film by measuring a ϕ scan in which two $\bar{1}202$ peaks are

observable (Figure 2b) and by measuring RSMs near the $\bar{1}202$ reflections that show two sets of $\bar{1}202$ and $\bar{1}20\bar{2}$ peaks (one set per twin domain) in Figure 2d. Surprisingly, based on the intensity of diffraction peaks in Figure 2b,d, there appears to be a slight preference for the twinned orientation of Ta₂SnO₆ in which the rutile Ta₂O₅ sublattice is oriented differently from the rutile substrate versus the untwinned orientation where they have the same orientation. This is analogous to the A-type (same orientation) and B-type (180° in-plane rotation) twins seen in metal disilicides formed on Si(111)^{55,56} and in the epitaxial growth of bixbyites on Si(111).^{57–60} For these latter examples, it is also common for the dominant twin to be the one that is 180° rotated from following the motif of the underlying substrate, i.e., B-type.

While the diffraction data from RHEED during growth and XRD after growth suggest that phase-pure and epitaxial films were synthesized, scanning transmission electron microscopy (STEM) reveals that these films have various defects. Most obviously, the −5.8% strain along the *b*-axis leads to misfit dislocations; these dislocations are primarily confined to the first SnO layer (Figure 3a) because they have a low energy of formation within the partially van der Waals-bonded SnO network. We interpret that the low mosaicity of the film results from the preference of interfacial misfit dislocations rather than threading dislocations. In Figure 3a, we see both full

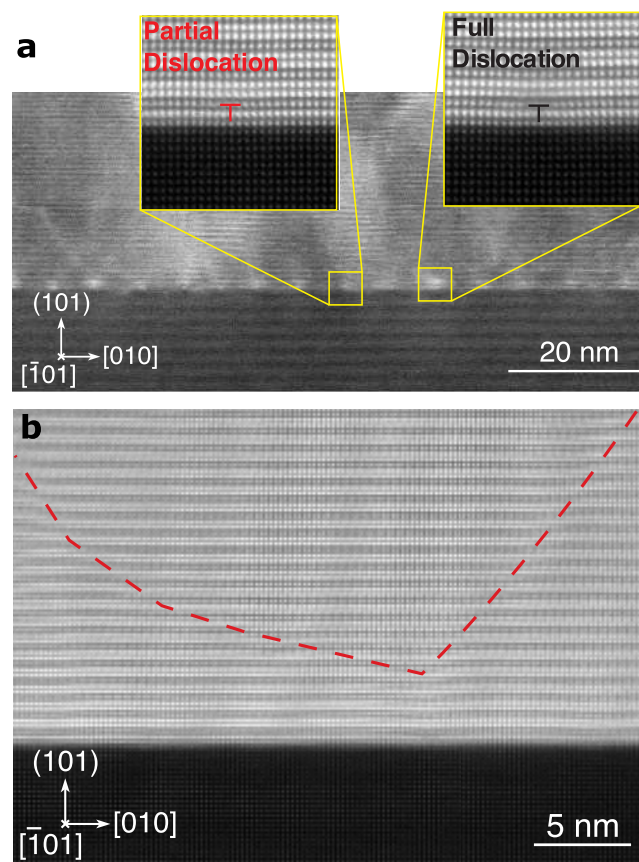


Figure 3. (a) Low-angle annular dark-field scanning transmission electron microscopy (LAADF-STEM) image showing an array of misfit dislocations with inset high-angle annular dark field (HAADF)-STEM images showing the atomic resolution of a partial and a full edge dislocation. (b) HAADF-STEM image with a dashed red line indicating the position of an out-of-phase boundary.

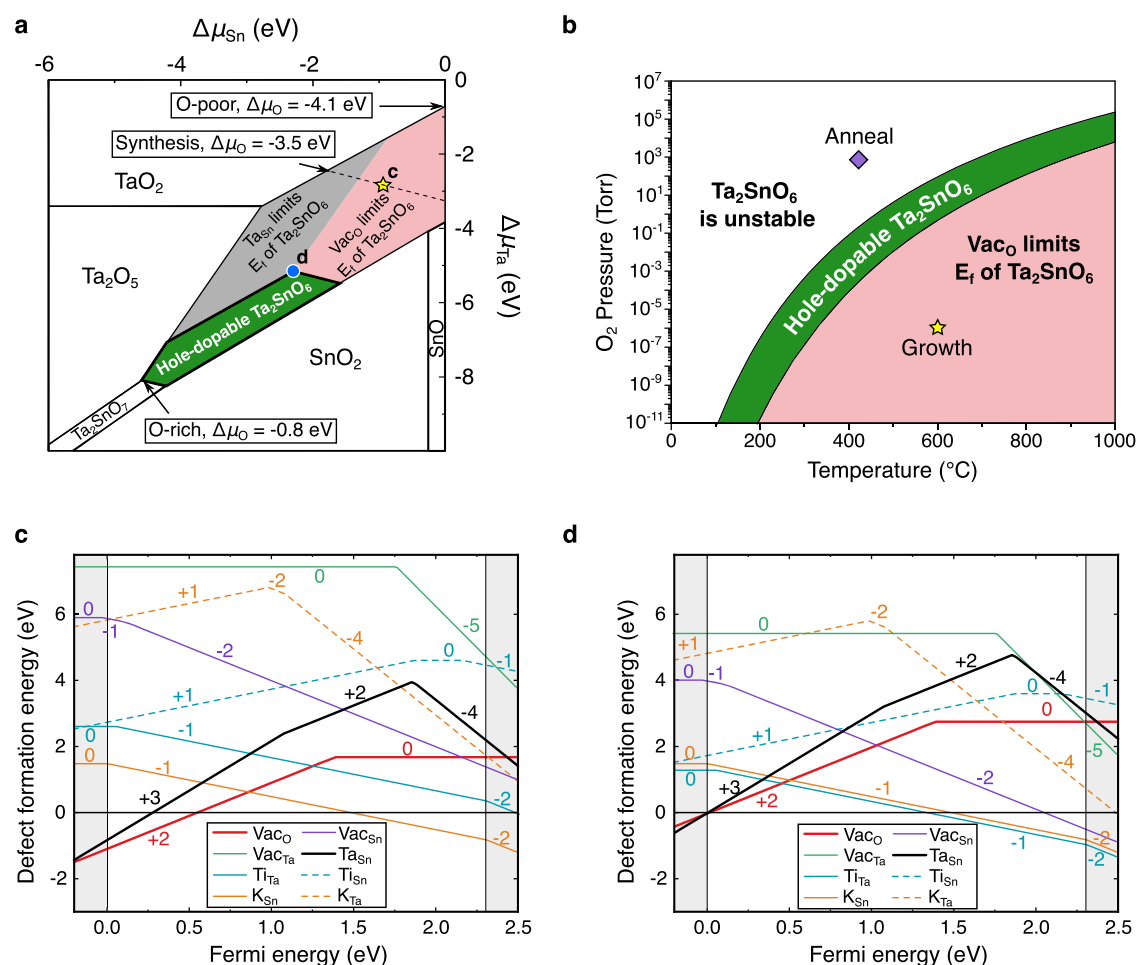


Figure 4. (a) Phase stability diagram of the Ta–Sn–O system. The region where the oxygen vacancy defect (Vac_O) determines the minimum Fermi energy is shaded pink, the region where Ta_Sn determines the minimum Fermi energy is shaded gray, and the region where the minimum Fermi energy is below the VBE is shaded green. The location in the phase space of the MBE growth conditions (600 $^\circ\text{C}$ and 1×10^{-6} Torr O_2) in phase space is indicated with a dotted line. The conditions used to construct c are indicated by a yellow star labeled “c”, and the conditions used to construct d are indicated by a blue circle labeled “d”. (b) Plot of the temperature and O_2 pressure conditions for which p-type Ta_2SnO_6 is calculated to be both stable and uncompensated by Vac_O (shown in green). Under the annealing conditions, indicated by a purple diamond, Ta_2SnO_6 is not the stable phase. Under the growth conditions, indicated by a yellow star, compensating Vac_O forms spontaneously. (c, d) First-principles-calculated defect formation energy versus Fermi energy in crystalline Ta_2SnO_6 . Chemical potentials used to compute defect energies are marked in a by a yellow star (c) and a blue circle (d). Numbers above plotted lines indicate the charge state of the defect. The zero of the Fermi energy is aligned to the VBE (~ 8 eV below the vacuum level), and valence and conduction bands are shaded gray.

dislocations with a Burgers vector of $[010]$ and partial dislocations with an apparent Burgers vector of $[0\ 1/2\ 0]$ in projection. The line vector of these partial dislocations, $[001]$, is in the (010) plane, which separates twin boundaries in thoreaulite minerals,⁵⁰ suggesting that these partial dislocations may be how the twinned domains that we observe with XRD nucleate. If this hypothesis is correct, the formation of twins would contribute to strain relaxation without forming full dislocations. Out-of-phase boundaries are also prevalent in the films (Figure 3b), and in this case, they appear to nucleate spontaneously rather than arising at step edges due to structural differences between the film and the substrate.^{61,62} More details on these out-of-phase boundaries, including a strategy for assessing their relative density film to film, are included in the Supporting Information.

The final, and most detrimental, defects we infer to be present in our films are oxygen vacancies. Attempts to hole dope our films by substituting Ti_Ta or K_Sn result in insulating films because would-be holes are trapped by oxygen vacancies.

Because the in situ oxidizing environment cannot be increased (i.e., using O_3 as an oxidant) without forming Sn^{4+} , the next best solution is to ex situ anneal in an oxidizing environment, but such attempts still yielded insulating films.

The formation of intrinsic hole-killing defects that impede p-type doping is an issue for many oxides. As the hole carrier concentration increases and the Fermi level shifts toward the valence band, compensating defects (e.g., oxygen vacancies) become more energetically favorable, preventing any further p-type doping. To better understand our failure to hole dope Ta_2SnO_6 , we have performed defect formation energy computations under conditions for which Ta_2SnO_6 is the stable phase. As shown in Figure 4a, in the majority of the phase stability region for Ta_2SnO_6 , we calculate that compensating defects form spontaneously when the Fermi energy lies at the valence band edge (VBE). Nonetheless, when we consider all chemical potentials that yield Ta_2SnO_6 , we find that there is a range of conditions (shown in green) for which Ta_2SnO_6 is stable and compensating defects do not form

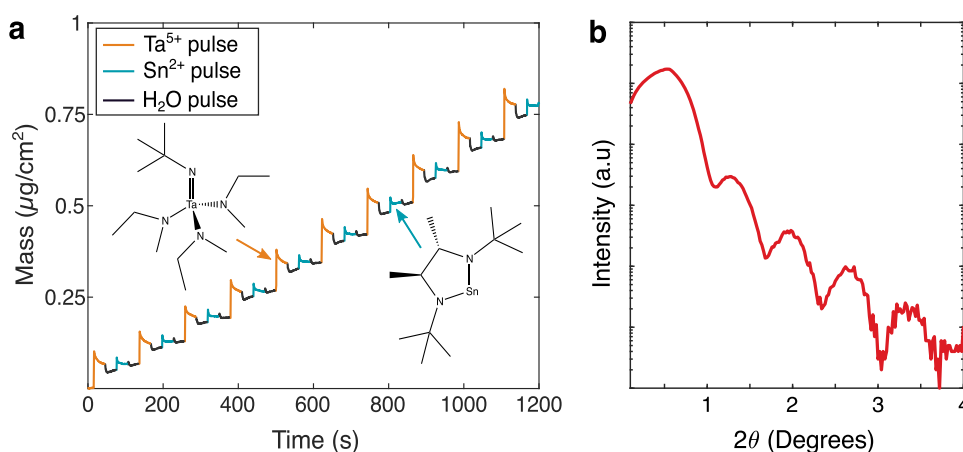


Figure 5. (a) QCM plot of 10 supercycles of Ta_2SnO_6 deposition by ALD consistent with self-limiting ALD growth with the target stoichiometry. (b) XRR measurement of Ta_2SnO_6 , revealing a highly conformal film that is 12.6 nm thick.

spontaneously. Our calculation that hole doping is achievable in Ta_2SnO_6 under oxygen-rich conditions is consistent with recent calculations by Zhang et al.³¹ Note that the portion of the phase diagram that corresponds to the oxygen chemical potential at growth conditions of 600 °C and 1×10^{-6} Torr O_2 (along the dotted line) has no overlap with the region for which p-type Ta_2SnO_6 is not spontaneously compensated. Here, the dotted line is calculated by eq 2

$$2\Delta\mu_{\text{Ta}} + \Delta\mu_{\text{Sn}} + 6\Delta\mu_{\text{O}} = E_f(\text{Ta}_2\text{SnO}_6) = -22.9 \text{ eV} \quad (2)$$

The reference state of $\Delta\mu_i$ is the bonded ground state (i.e., O_2 molecules for $\Delta\mu_{\text{O}}$ and metallic Ta and Sn for $\Delta\mu_{\text{Ta}}$ and $\Delta\mu_{\text{Sn}}$) at 0 K and 1 atm. To map out the experimental conditions that could yield p-type Ta_2SnO_6 , we construct a diagram of the O_2 pressure and temperatures highlighting the region in which Ta_2SnO_6 is both stable and hole-dopable (Figure 4b); similar diagrams have been used previously by Peng et al. to assist the experimental study of candidate p-type oxides.⁶³ Considering all conditions that could enable the synthesis of Ta_2SnO_6 without compensating oxygen vacancies, we find that there is no condition with both an MBE compatible pressure ($<10^{-5}$ Torr) and a high enough growth temperature to crystallize Ta_2SnO_6 (>550 °C). When growing oxides by MBE, this problem is often circumvented using ozone, a much more potent oxidant, but for Ta_2SnO_6 , we find that ozone increases μ_{O} too much, resulting in oxidation of Sn^{2+} to Sn^{4+} (see the Supporting Information). The computed defect formation energies using the approximate chemical potentials of our synthesis conditions indicated by the starred point on the dotted line are shown in Figure 4c. The defects considered include Ta, Sn, and O vacancies, the hole-compensating Ta_{Sn} antisite defect, and candidate extrinsic dopants Ti and K. Note that not all O^{2-} ions have the same bonding environment in this low-symmetry structure, so we show only Vac_{O} with the lowest energy of formation, i.e., those coordinated to two Sn^{2+} ions and one Ta^{5+} ion. Here, we see that K and Ti show preferential substitution on the target site (solid lines) over the unintended site (dashed lines) and a shallow charge transition level, supporting their efficacy as hole dopants. Unfortunately, we also see that under our growth conditions, oxygen vacancies are expected to form spontaneously if the Fermi energy is less than 0.5 eV above the VBE, making further reduction in Fermi energy thermodynamically unstable. In addition to parasitic

oxygen vacancies, we calculate that the compensating Ta_{Sn} antisite defect is also important to consider, as it limits hole doping in a substantial portion of the Ta_2SnO_6 phase stability region. The intersection of the three doping regimes within the Ta_2SnO_6 stability region is where both Ta_{Sn} and Vac_{O} have a formation energy of 0 at the VBE, as shown in Figure 4d.

There are at least two possible explanations why the ex situ annealing at 425 °C at 1 atm O_2 to fill oxygen vacancies does not result in p-type films. The first explanation is that these annealing conditions are far too oxidizing for Ta_2SnO_6 to be thermodynamically stable, as shown in Figure 4b. While we find that we can kinetically suppress nucleation of the thermodynamically stable phases under these conditions using temperatures lower than 425 °C, there is no guarantee that oxygen diffusion will be fast enough in Ta_2SnO_6 to fill the vacancies at these temperatures. Another possible explanation is that our synthesis conditions result in compensating Ta_{Sn} defects rather than oxygen vacancies, but based on our observation of the SnO-rich $\text{Ta}_2\text{Sn}_2\text{O}_7$ phase near our growth conditions, we suspect that the material is synthesized in the Vac_{O} -limited regime. Even if Ta_{Sn} defects do not exist in as-grown films, it is likely that they will appear during 425 °C annealing due to volatilization of SnO, which has been reported at as low as 360 °C.¹⁹ This is because SnO loss decreases $\Delta\mu_{\text{Sn}}$, promoting the formation of compensating Ta_{Sn} . With these challenges, we conclude that it is impractical to hole dope MBE-grown Ta_2SnO_6 films. Nonetheless, we hope that these defect calculations will enable compensating defects to be strategically mitigated using alternative synthesis techniques.

In the related Nb_2SnO_6 system, hole doping was unsuccessful by PLD due to spontaneous hole compensation,¹³ but p-type Nb_2SnO_6 was achieved by the solid-state reaction of powder precursors.³⁶ Here, we synthesize amorphous Ta_2SnO_6 films by thermal ALD in an effort to explore an alternative deposition process that is industrially practical; as noted by Zhang et al., the *s*-like valence band of Ta_2SnO_6 may enable high mobility even in amorphous films.³¹ ALD is a film growth technique that separates reaction cycles of vapor-phase precursors with a surface, purging the vapor precursor from the system between reactions. Metal and semi-metal precursors are typically metalorganic (MO) compounds that undergo a self-limiting reaction with a surface to enable conformal coverage with precise thickness control.⁶⁴ In this case, ALD

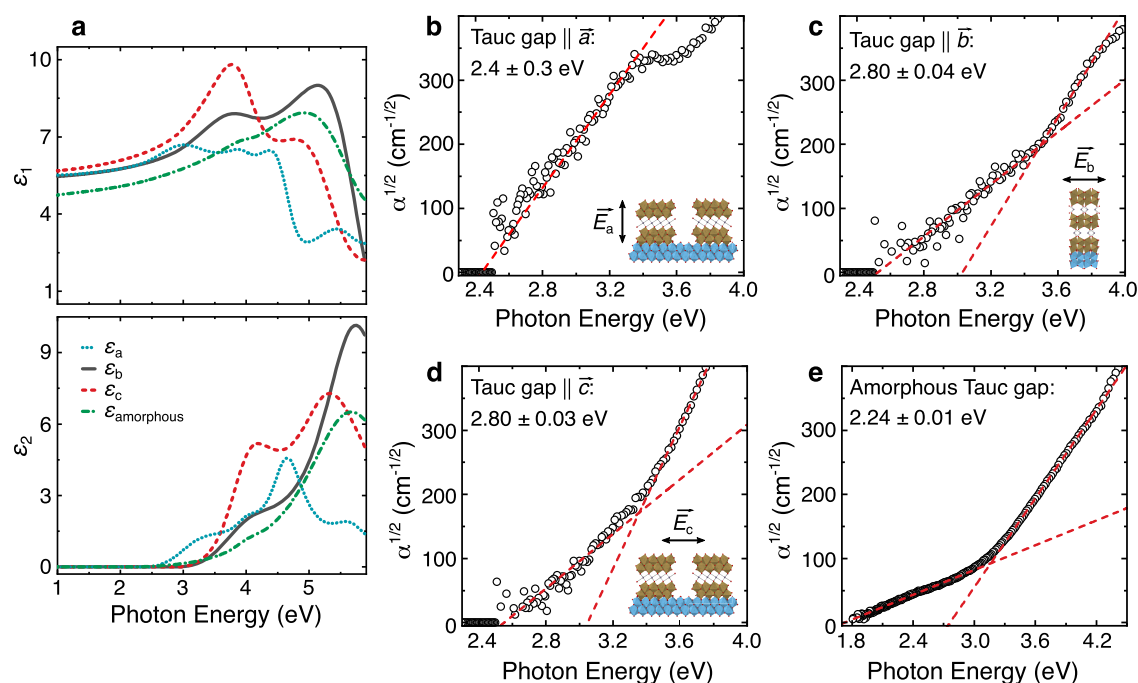


Figure 6. (a) Complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) spectra for each crystallographic direction of epitaxially grown Ta_2SnO_6 on TiO_2 (ϵ_a , ϵ_b , ϵ_c) and amorphous Ta_2SnO_6 on glass ($\epsilon_{\text{amorphous}}$). (b–e) Tauc plots of $\alpha^{1/2}$ as a function of photon energy for each crystallographic direction of epitaxial Ta_2SnO_6 and amorphous Ta_2SnO_6 . For spectra in which two distinct slopes are detectable due to phonon contributions (c–e), the Tauc gap is the average of the two extrapolations. Insets show the direction of electric field oscillation.

also benefits from delivering Ta^{5+} and Sn^{2+} precursors in their desired oxidation states at a low temperature compatible with back-end-of-line processing. Nonetheless, relatively few ALD processes deposit epitaxial films from MO precursors.⁶⁵ The Ta^{5+} and Sn^{2+} precursors used to grow Ta_2SnO_6 were tris-(ethylmethylamido)(*tert*-butylimido)tantalum(V) and *N*,*N*-di-*tert*-butylbutane-2,3-diamidotin(II) (referred to here as stannylene or the Sn^{2+} precursor), respectively. The Ta^{5+} precursor is commercially available, and the Sn^{2+} (stannylene) precursor was synthesized using previously reported methods.⁴⁷ The stannylene precursor was selected based on previous studies that show that tin does not oxidize to 4+ when allowed to react with H_2O , as long as stronger oxidants (e.g., H_2O_2) are not introduced.⁶⁶ Further discussion of the tin oxidation state can be found in the [Supporting Information](#).

ALD of Ta_2SnO_6 was attempted over temperatures ranging from 175 to 275 °C; however, films grown at 175 °C were determined to be of optimal composition. QCM analysis of the mass gain ratio of the $\text{Ta}^{5+}/\text{H}_2\text{O}$ and $\text{Sn}^{2+}/\text{H}_2\text{O}$ cycles revealed stoichiometric growth at 175 °C (Figure 5a), but low Sn incorporation into the films deposited at higher temperatures (200–275 °C). The low Sn incorporation at higher temperatures is consistent with previous reports of using the stannylene precursor by Gordon et al. who found a dramatic decrease in the growth rate of SnO_x formed using the stannylene precursor with H_2O_2 above 200 °C.⁶⁷ X-ray reflectivity (XRR) was used to characterize 250 supercycles of Ta_2SnO_6 grown at 175 °C on native oxide-coated Si(111). The analysis of XRR revealed that the thickness of the film was 12.6 nm, corresponding to a growth rate of 0.5 Å/supercycle (Figure 5b), and the clear fringes of the XRR spectrum indicate a smooth and homogeneous film. XRD analysis showed all films to be amorphous and attempts to anneal the films in a

600 °C inert atmospheric environment containing N_2 did not induce crystallinity.

The QCM mass gain plot in Figure 5a shows the mass gained over 10 supercycles of deposition. The shape of the QCM plot is consistent with self-limiting ALD growth as the MO precursors react with the $\text{*}-\text{OH}$ surface, resulting in a chemisorbed MO surface species. H_2O reacts with the surface MO ligands through protonation, replacing them with an $\text{*}-\text{OH}$ surface species. The mass loss after water dosing is due to the mass difference between the atomic weight of the $\text{*}-\text{OH}$ surface and the surface-bound ligands. Comparing the mass gained during one $\text{Ta}^{5+}/\text{H}_2\text{O}$ cycle and one $\text{Sn}^{2+}/\text{H}_2\text{O}$ cycle suggests that a 1:1 pulse ratio is appropriate for the stoichiometric growth of Ta_2SnO_6 . Despite successful deposition of Ta_2SnO_6 films, all films were found to be insulating when analyzed with four-point probe measurements in a van der Pauw geometry, making hole mobility measurements impossible.

Although electrical conductivity could not be induced into Ta_2SnO_6 , spectroscopic ellipsometry was used to deduce the band gaps. To measure the complex optical properties of the epitaxial Ta_2SnO_6 film from which the band gap is determined, we consider the anisotropic nature of both the monoclinic biaxial film²⁰ and the uniaxial (101)-oriented TiO_2 substrate. Although Ta_2SnO_6 is monoclinic, for simplicity, its structure is approximated as being orthorhombic. The primary reason for this approximation is that the comparable density of both twin domains increases the symmetry of the film, but even a single domain is nearly orthorhombic ($\beta = 90.5^\circ$). The crystallographic *b*- and *c*-axes of the Ta_2SnO_6 film are parallel to the surface plane, while the *a*-axis is perpendicular to the sample surface (using the orthorhombic approximation). Complex dielectric function spectra are obtained corresponding to electric field oscillations along each direction (ϵ_a , ϵ_b , ϵ_c), as

shown in Figure 6a. The amorphous film grown by ALD is isotropic, so a single set of complex dielectric function spectra ($\epsilon_{\text{amorphous}}$) describes the optical response (Figure 6a). Details of the analysis are provided in the Supporting Information.

The band gap energies of the epitaxial and amorphous films are determined using Tauc plots for indirect transitions,⁶⁸ as shown in Figure 6b–e, where α is the absorption coefficient ($\alpha = 4\pi k/\lambda$), k is the extinction coefficient obtained from $\epsilon = (n + ik)^2$, and λ is the photon wavelength. The band gap energy is determined by plotting $\alpha^{1/2}$ as a function of photon energy and using linear extrapolation of $\alpha^{1/2} = 0$ to identify the Tauc gap. This procedure is performed for the numerical inversion-determined spectra ϵ_a , ϵ_b , and ϵ_c with the lowest value indicative of the indirect band gap for the epitaxial film and using the ϵ obtained from numerical inversion of the amorphous film. The presence of two distinct slopes in $\alpha^{1/2}$ for ϵ_b , ϵ_c , and $\epsilon_{\text{amorphous}}$ indicates detectable contributions from phonons. In such a case, the average of the two extrapolations to $\alpha^{1/2} = 0$ is taken as the Tauc gap for the respective plot.⁶⁹ The Tauc gaps obtained optically for each direction are identified as 2.80 ± 0.04 eV for ϵ_b , 2.80 ± 0.03 eV for ϵ_c , and 2.24 ± 0.01 eV for $\epsilon_{\text{amorphous}}$. For the a -direction of the epitaxial film, a single intercept is identified at 2.4 ± 0.3 eV for ϵ_a . Here, relatively large uncertainty arises because the measurement configuration results in the least sensitivity to the out-of-plane optical response of the epitaxial film, ϵ_a .

The lowest intercept among the optical properties for the three crystallographic directions of 2.4 eV is considered the indirect gap for the epitaxial film, and an average intercept of 2.24 eV for the amorphous film is considered its indirect band gap. The measured band gap for the crystalline film is in reasonable agreement with the 2.3 eV band gap predicted by DFT using the generalized gradient approximation. Comparing the spectra in ϵ between epitaxial and amorphous Ta_2SnO_6 , transition strengths of critical point features in the amorphous film are dampened as would be expected when the long-range order of the crystal is interrupted. The lower band gap of the amorphous material is also expected because the disorder creates midgap states, widening the bands and decreasing the band gap.

CONCLUSIONS

We report the first epitaxial synthesis of Ta_2SnO_6 , enabled by leveraging its structural similarity to rutile¹³ and utilizing a SnO molecular beam generated by a SnO_2 source to stabilize Sn^{2+} .⁷⁰ Our films contained two twin domains with different epitaxial orientation relationships. For regions in which the Ta_2O_5 rutile sublattice was oriented identically to the TiO_2 substrate (untwinned), Ta_2SnO_6 (100) $\parallel$ TiO_2 (101) and Ta_2SnO_6 [001] $\parallel$ TiO_2 [10 $\bar{1}$]. For the twinned regions, Ta_2SnO_6 (100) $\parallel$ TiO_2 (101) and Ta_2SnO_6 [001] $\parallel$ TiO_2 [$\bar{1}01$]. The epitaxial synthesis of Ta_2SnO_6 enabled us to experimentally determine its band gap energy of 2.4 eV, but we were unable to induce hole conductivity in the films. We conclude with the assistance of DFT calculations that the spontaneous formation of compensating oxygen vacancies prohibits p-type conductivity in the films grown by molecular-beam epitaxy. Amorphous films of Ta_2SnO_6 were grown via thermal ALD for the first time. QCM growth analysis showed an ideal mass gain ratio for the $\text{Sn}^{2+}/\text{H}_2\text{O}$ and $\text{Ta}^{5+}/\text{H}_2\text{O}$ cycles at 175 °C. XRR analysis showed that a 12.6 nm thick film could be grown over 250 supercycles. The amorphous films have a band gap of 2.24 eV but were also determined to

be insulating. While we were ultimately unsuccessful in synthesizing p-type Ta_2SnO_6 films, we hope that our detailed study of Ta_2SnO_6 growth and compensating defect formation guides and encourages further study of this promising material.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.1c10382>.

First-principles calculated defect formation energy versus Fermi energy in crystalline Ta_2SnO_6 using (a) O-rich and (b) O-poor chemical potentials and (c) Atomic structure of the slab used to calculate the VBE of Ta_2SnO_6 with respect to vacuum. (Figure S1); (a) XRD θ – 2θ scans of several attempts to grow Ta_2SnO_6 on MgF_2 (101) using various experimental modifications and (b) comparison of the lattice match of candidate substrates for epitaxy of Ta_2SnO_6 (Figure S2); (a) two θ – 2θ scans of the same film collected 90° apart in ϕ , highlighting the difference in interaction with out-of-phase boundaries (Figure S3); (a) full QCM plot of the Ta_2SnO_6 film grown at 175 °C (Figure S4); fitted XPS spectra recorded for the (a–c) non-sputtered ALD-grown Ta_2SnO_6 thin film and (d–f) sputtered ALD-grown Ta_2SnO_6 thin film (Figure S5) (PDF)

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Notes

The authors declare no competing financial interest.

Additional data related to the films grown by MBE and their characterization by RHEED and XRD are available at <https://doi.org/10.34863/wqnq-vc64>.

ACKNOWLEDGMENTS

This work was primarily supported by ASCENT, one of the six centers in JUMP, a Semiconductor Research Corporation (SRC) program sponsored by DARPA. Materials synthesis was performed partly in a facility supported by the National Science Foundation [Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM)] under Cooperative Agreement No. DMR-2039380. Substrate preparation was performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Coordinated Infrastructure (NNCI), which is supported by the NSF (Grant No. NNCI-2025233). Spectroscopic ellipsometry analysis is based on research sponsored by the U.S. Air Force Research Laboratory under agreement numbers FA9453-19-C-1002 and FA9453-19-S-0002. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the U.S. Air Force Research Laboratory or the U.S. Government. This work made use of the UPS/XPS that is partially funded by the National Science Foundation #1849578.

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