

Iron-Intercalated Zirconium Diselenide Thin Films from the Low-Pressure Chemical Vapor Deposition of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2]_2$

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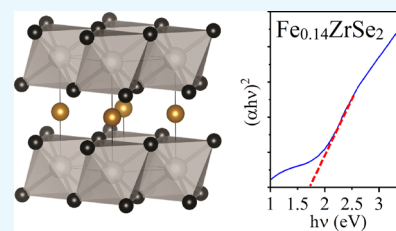


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ABSTRACT: Transition metal chalcogenide thin films of the type Fe_xZrSe_2 have applications in electronic devices, but their use is limited by current synthetic techniques. Here, we demonstrate the synthesis and characterization of Fe-intercalated ZrSe_2 thin films on quartz substrates using the low-pressure chemical vapor deposition of the single-source precursor $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2]_2$. Powder X-ray diffraction of the film scraping and subsequent Rietveld refinement of the data showed the successful synthesis of the $\text{Fe}_{0.14}\text{ZrSe}_2$ phase, along with secondary phases of FeSe and ZrO_2 . Upon intercalation, a small optical band gap enhancement ($E_{\text{g}(\text{direct})}^{\text{opt}} = 1.72$ eV) is detected in comparison with that of the host material.



INTRODUCTION

Transition metal dichalcogenide (TMD) layered materials have attracted a great deal of interest due to their unique physical properties beyond those of graphene as they are generally non-toxic and abundant, have energy band gaps well-suited for solar energy conversion and high absorption coefficients in the visible range.¹ TMDs of group 4, 5, and 6 metals are diamagnetic semiconductors with band gap values in the range of 0.2–2.0 eV.^{2,3} They have received special interest due to their mechanical and electrical anisotropy^{2,4} and charge density wave transitions, related to their structures being composed of layers of TX_2 (T = transition metal; X = chalcogen) stack along the *c* axis via van der Waals forces.^{2,5} Zirconium diselenide (ZrSe_2) in particular has attracted considerable attention in the fields of physics, chemistry, and materials due to their unique structural, optical,^{6,7} and electronic properties. While the use of ZrSe_2 in secondary lithium batteries confronts electrochemical challenges,^{8,9} it shows many potential applications as working materials in photovoltaic solar cells^{10,11} given that its band gap falls in the visible region of the electromagnetic spectrum ($E_{\text{g}(\text{indirect})}^{\text{opt}} = 1.20$ eV; $E_{\text{g}(\text{direct})}^{\text{opt}} = 1.61$ eV).^{6,12} Group 4 (d^0) TMD such as ZrSe_2 stabilize 1T structures under normal conditions, with a CdI_2 (HCP packing) structure and $P\bar{3}m1$ symmetry.¹³ This structure type allows the intercalation of small molecules or atoms (electron donors) between TX_2 layers,⁵ which transfer electrons from the intercalate to the transition metal unoccupied d band.⁴ The intercalation of electron-donating atoms in TMD layered materials can be used to modulate the intrinsic physical properties of the host material⁴ that result into band gap changes,¹⁴ phase transition processes,^{15,16} and development of magnetic and superconducting behaviors.^{2,4,5} In the case of ZrSe_2 different alkali,¹⁷ transition^{15,16,18,19} and

post-transition²⁰ metals have been intercalated to modulate electronic states and dramatically change the opto-electronic and magnetic properties of the host material. In some cases, a relatively low intercalation produces a significant change while virtually retaining the host structure.¹³

ZrSe_2 is one of the few metal chalcogenide hosts able to accommodate Fe both into tetrahedral and octahedral sites between layers,¹⁵ with the Fe relative site distribution dependent on the total amount of Fe and the thermal treatment of the material.¹⁶ At intercalation levels $x = 0$ –0.16, a semiconducting Fe_xZrSe_2 phase exists with a trigonal structure $P\bar{3}m1$ derived from that of ZrSe_2 , intermediate between 1T- CdI_2 and NiAs types, and at the critical iron concentration of $x = 0.41$, the material becomes metallic.¹³ Hybridization of the 3d bands of Zr and Fe, along with the overlap of their d_{z^2} electron shells along the *c* axis leads to a covalent interaction between ZrSe_2 layers, ultimately affecting the unit cell lattice constants.^{19,21} As the intercalation of transition metals in TMD 1T polymorphs donates free carriers to their empty conduction band, increasing their conductivity,^{4,22} they can be selectively used to fine-tune the electric, magnetic, optical, and structural properties of the host materials in a controllable way to fit application requirements.⁵

ZrSe_2 and Fe_xZrSe_2 materials have traditionally been synthesized from high-purity elements^{8,13,15,16,23} (long multi-step processes at high temperatures) or chemical vapor

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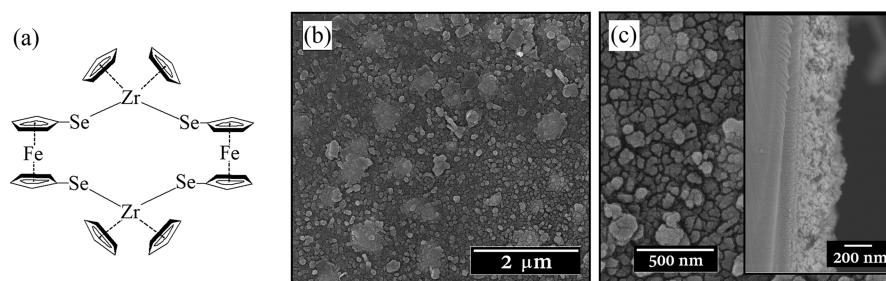


Figure 1. (a) Schematic representation of precursor $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2]_2$ used in LPCVD to grow Fe_xZrSe_2 thin films. (b, c) SEM images of the thin film at $\times 10\text{k}$ and $\times 40\text{k}$ magnification, respectively. The inset shows the cross-sectional image to reveal a film thickness of *ca.* 300 nm.

transport reactions,^{2,6,8,17,24} mainly as single crystals and, in few cases, in nanoparticle form.^{25,26} The synthesis of ZrSe_2 thin films has been mainly reported *via* electrodeposition methods,^{11,27–29} although the synthesis using MBE³⁰ and CVD³¹ has been reported as an alternative for the requirement of conductive substrates, which can be problematic for device applications. The absence of studies of Fe_xZrSe_2 in thin film form is likely due to the lack of precursors for these ternary systems using established deposition methods. Low-pressure chemical vapor deposition (LPCVD) of organometallic precursors appears to be a suitable alternative due to its versatility toward the use of alternative air/moisture-sensitive precursors. This method allows growth of high-quality thin films from volatile, temperature-sensitive reagents and has been used extensively in the past decade for the synthesis of thin films of functional materials, many of them metal selenides.^{32–34} In the present paper, we investigate the ability of single-source precursor $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2]_2$ (**1**) to successfully generate thin films of Fe-intercalated ZrSe_2 (i.e., Fe_xZrSe_2) using a convenient single-step deposition process *via* LPCVD and record the optical band gap shift resultant from the intercalation.

RESULTS AND DISCUSSION

Following our previous work on Fe_xTiSe_2 thin films *via* LPCVD from the single-source precursor $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2]_2$,³⁴ Fe_xZrSe_2 thin film synthesis from $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2]_2$ (**1**) (Figure 1a) was investigated.

The highly reflective and black Fe_xZrSe_2 films grown using LPCVD under a dynamic pressure of 10^{-1} Torr at 1000°C were air/moisture-sensitive but highly robust with complete coverage of the quartz substrate. Scanning electron microscopy (SEM) analysis of the films showed that the surface morphology consisted of irregular quasi-spherical grains uniformly distributed over the entire surface of the substrate (Figure 1b,c), in a similar way as previously reported for ZrSe_2 thin films.²⁸ The film is fairly densely packed both laterally and vertically, and the cross-sectional SEM imaging of the film showed a thickness of ~ 300 nm (Figure 1c, inset).

Glancing-angle X-ray diffraction (XRD) analysis of the Fe_xZrSe_2 films was not possible due to fluorescence of iron in the presence of the $\text{Cu K}\alpha_1$ radiation. Therefore, the films were scraped off to give powders that were then analyzed *via* powder XRD (PXRD) using a $\text{MoK}\alpha_1$ source in order to obtain patterns with reduced fluorescence effects. Rietveld refinement, carried out on the data to determine the crystallographic properties of the films (Figure 2), showed that layered ZrSe_2 with intercalated Fe had indeed been formed.

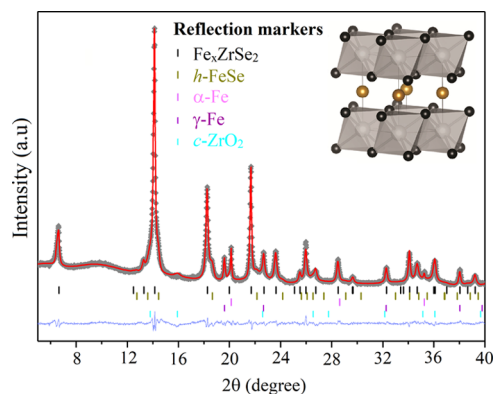


Figure 2. Rietveld refined powder diffraction data (crosses), fit (red line), difference curve (shifted blue line), and reflection markers for all phases (ticks).^{13,35–38} Structural analysis was performed using the GSAS package,³⁹ and reference patterns from ICSD were used. Embedded in the right corner is an image of the Fe_xZrSe_2 structure drawn from structurally refined PXRD data using VESTA,⁴⁰ showing Zr and Se atoms (gray and black spheres) making up edge-linked layers of ZrSe_2 octahedra in the *ab* plane, separated by Fe atoms (gold spheres) randomly occupying the octahedral vacancies within the van der Waals gap with a refined occupancy of $\sim 14\%$.

However, small additional crystalline secondary phases of α - and γ -Fe, hexagonal FeSe, and ZrO_2 were also observed. The secondary phase formation is likely due to a combination of post-deposition oxidation (semi-amorphous nature of ZrO_2) during post-deposition film handling and due to possible Fe saturation in between the layers (e.g., FeSe and α - and γ -Fe) (Figure 2). The parent compound ZrSe_2 is known to crystallize in the CdI_2 structure type with $P\bar{3}m1$ symmetry, identical to that of TiSe_2 , as shown from the Rietveld analysis. The structure exists as sheets of Zr atoms, octahedrally coordinated by Se atoms, with each Se bonded to three Zr atoms. The two-dimensional ZrSe_2 sheets are AA stacked and weakly bound, with the space between sheets commonly referred to as the van der Waals gap. Structural modifications to the parent ZrSe_2 lattice upon the intercalation of variable amounts of Fe within the van der Waals gap have previously shown a change of symmetry due to intercalant site ordering at $x \geq 0.41$ (in Fe_xZrSe_2), along with the onset of metallicity.¹³ In addition to the impurity phases, the two-dimensionality of the material (stacked layers) leads to the expected preferred orientation effects that were modeled within the refinement (see Supporting Information, Table S1 and Figure S1 for further refinement details). The Fe_xZrSe_2 material shows no sign of superstructure and was best modeled using the parent $P\bar{3}m1$ space group, indicating no site ordering of intercalated Fe

atoms and a value of the intercalation of $x < 0.41$.¹³ Changes in lattice parameters are often used as an indication of intercalation in transition metal dichalcogenides. The interlayer distance is expectedly found to increase upon the intercalation of transition metals, resulting in an increase of the c lattice parameter (e.g., Fe_xZrSe_2 ¹³ or Cu_xZrSe_2 ¹⁹).

Our observed interlayer lattice parameter, $c = 6.1336(3)$ Å, lies between the values reported for $x = 0.18$ ($c = 6.138(2)$ Å) and $x = 0.465$ ($c/2 = 6.011(1)$ Å).¹³ Care must be taken when interpreting this effect, however, due to the possibility of non-stoichiometric Zr:Se ratios. Non-stoichiometry of Zr:Se has been seen to significantly influence both the lattice parameter and electron transport properties.⁴¹ Our observed c lattice parameter is larger than the reported value for near-stoichiometric $\text{ZrSe}_{1.937}$ ($c = 6.1297(9)$ Å) while being only slightly smaller than Se-deficient $\text{ZrSe}_{1.851}$ ($c = 6.1510(9)$ Å), complicating interpretation as evidence of intercalation.⁴¹ While the refinement of structural details has been attempted, reported errors on the values obtained may vary due to the data quality and the modeling of preferred orientation and additional phases. The refinements were improved upon the introduction of Fe within the van der Waals gap modeled in an identical manner to that previously seen in Fe_xZrSe_2 , placing Fe directly between the layers on the 1b Wyckoff site (0, 0, and 1/2) and refined to a value of $x = 13.5(5)\%$, suggesting $\text{Fe}_{0.14}\text{ZrSe}_2$ (Table 1).

Table 1. Selected Parameters from Rietveld Refinements of Powder X-ray Diffraction Data

target composition	Fe_xZrSe_2
space group	$\bar{P}3m1$
lattice parameters (Å)	$a = 3.77239(6)$; $c = 6.1336(3)$
Fe fractional occupancy, x	0.135(5)
Fe_xZrSe_2 phase fraction (wt %)	61.9(10)
impurity phase fractions: h-FeSe, α -Fe, γ -Fe, c-ZrO ₂ (wt %)	9.11(12), 3.55(6), 5.18(9), 20.25(19)
goodness of fit, wR_p (%), R_p (%), χ^2	1.04, 0.77, 4.167

The structural properties of the thin films were further investigated using Raman spectroscopy (Figure 3). The Raman measurements were carried out after only minimal exposure to air (*ca.* 5 s) and after 5 min of exposure in an effort to study

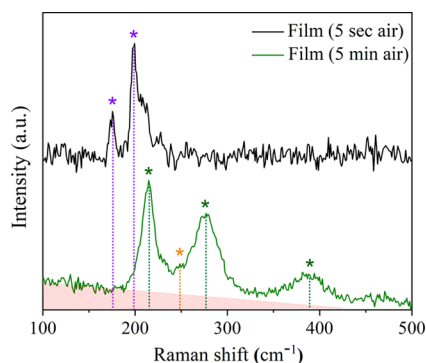


Figure 3. Raman spectra of the LPCVD grown Fe_xZrSe_2 films after minimal (*ca.* 5 s) and 5 min exposure to air. Bands corresponding to the contribution of Fe_xZrSe_2 (purple), iron oxide (α - Fe_2O_3 , green), selenium (Se, orange), and amorphous zirconia (ZrO_2 , red) are detected in the spectra.

any changes due to film oxidation. The Fe_xZrSe_2 films showed a minor scattering band at 173 cm^{-1} and a major scattering band at 197 cm^{-1} , which were respectively consistent with the E_g and A_{1g} bands for ZrSe_2 -like materials with $\bar{P}3m1$ symmetry.^{30,42} No sign of the characteristic Raman bands for amorphous or crystalline ZrO_2 ⁴³ or Fe_2O_3 ^{44,45} were detected from the 633 nm laser excitation.

After exposure of the samples to air for 5 min, characteristic bands of α - Fe_2O_3 were detected^{44,45} together with a small contribution from amorphous selenium^{46,47} (since the symmetric Se–Se stretching mode shows a very intensive Raman band, this spectrum indicates that the Se content is not very large). The uneven background in these spectra suggests the existence of amorphous ZrO_2 (red), which was also detected from XRD;⁴³ however, no FeSe_x phases could be observed.^{48,49}

X-ray photoelectron spectroscopy (XPS) was used to study the surface composition of the Fe_xZrSe_2 films. Zr, Se, Fe, and O were detected in the high-resolution XPS scans. The Zr 3d spectrum (Figure 4a) was fitted with a major doublet with the

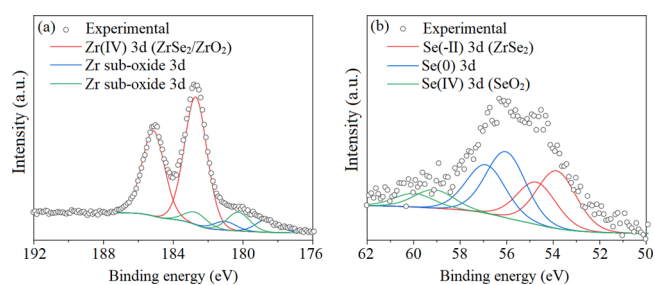


Figure 4. XPS data for a LPCVD grown Fe_xZrSe_2 film showing the (a) Zr 3d and (b) Se 3d transitions.

Zr $3d_{5/2}$ transition centered at 182.7 eV corresponding to Zr(IV) bound to Se or O and therefore providing evidence for the presence of ZrSe_2 and/or ZrO_2 .^{30,50} It has been previously reported that the intercalation of ZrSe_2 (Zr $3d_{3/2} = 183.05$ eV) with a transition metal provokes a small shift of the Zr 3d environment to a lower energy (Zr $3d_{3/2} = 182.6$ eV),¹⁹ overlapping with the Zr environment from ZrO_2 (Zr $3d_{3/2} = 182.3$ eV).⁵² A further two minor sub-oxide environments were also found with the Zr $3d_{5/2}$ transitions at 178.6 and 180.3 eV.⁵⁰ The Se 3d spectrum (Figure 4b) was broad and best fitted with three sets of doublets with a $3d_{5/2}$ - $3d_{3/2}$ separation of 0.86 eV. Se $3d_{5/2}$ peaks of almost equal intensity were found at 53.8 and 56.0 eV corresponding to Se^{2-} bound to Zr and metallic Se (Se^0), respectively, therefore providing evidence for the ZrSe_2 -based phase also seen from the XRD data as well as elemental selenium, a secondary product ZrSe_2 oxidation.^{30,51} The third environment with the Se $3d_{5/2}$ peak at 59.5 eV matches with Se(IV) in the form of SeO_2 , a possible native oxide product.⁵¹ Fe was only detected with a low signal-to-noise ratio, and therefore the spectrum was not deconvoluted to determine oxidation states (see Supporting Information, Figure S3).

Compositional analysis of the surface of the film suggests a high excess of Se and O on the surface of the films relative to Zr (and Fe), suggesting surface segregation of the Se and native oxide formation, respectively. Depth profiling studies on a layer of ~ 100 nm into the Fe_xZrSe_2 films revealed the total Fe-to-Zr ratio to be 0.12. It should be noted that the elemental composition calculations of O and Se were not carried out due

to the error associated with preferential sputtering of these lighter elements relative to Zr and Fe during the etching process.

The optical absorption spectrum of the Fe_xZrSe_2 thin film was calculated from sample transmittance and is shown in Figure 5 (black line). The direct optical band gap of the thin

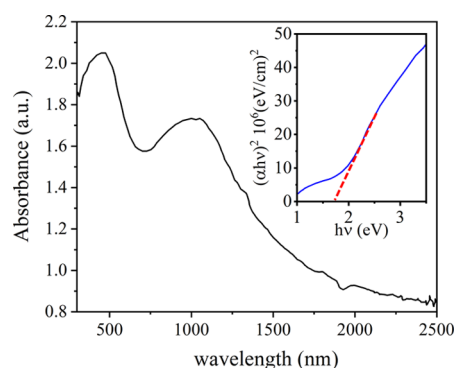


Figure 5. Absorbance (black line) of the thin film after minimal exposure to atmospheric conditions showing a Fe_xZrSe_2 absorption band centered at ~ 1000 nm and a second absorption band centered at ~ 450 nm due to the formation of $\alpha\text{-Fe}_2\text{O}_3$ ⁵² upon exposure of the thin film to air prior to/during measurement. Graphical representation of band gap calculation using a Tauc plot is depicted in the inset.

film was determined plotting $(\alpha h\nu)^2$ against the photon energy ($h\nu$) (blue line) and extrapolating the linear part of the plot (broken red line). The obtained optical band gap value (1.72 eV) shows a small band gap increase (~ 0.2 eV) with respect to previously published values for ZrSe_2 .^{12,27,28}

CONCLUSIONS

In conclusion, the formation of the Fe_xZrSe_2 ($x = 0.14$) thin films *via* LPCVD from $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2]_2$ was verified using PXRD, XPS, and Raman spectroscopy. The morphology of the thin films was evaluated using SEM and shown to consist of densely packed domes. Rietveld refinement analysis of PXRD data of the powder from film scrapping indicates the formation of a major phase of Fe_xZrSe_2 ($x = 0.14$) and small impurity phases of Fe and FeSe presumably due to excess Fe plus post-deposition oxidation product ZrO_2 . Raman bands show the expected A_{1g} and E_g modes for Fe_xZrSe_2 ($x = 0.14$) (CdI_2 structure type, $P\bar{3}m1$). No bands for oxidation products were detected in freshly deposited films, whereas bands due to oxidation/decomposition products were found in films exposed to air for longer times. A small shift in the direct optical band gap was detected for $\text{Fe}_{0.14}\text{ZrSe}_2$ thin films with respect to the host material ZrSe_2 . The extreme sensitivity of the Fe_xZrSe_2 materials requires a carefully designed and sealed setup for its synthesis, and therefore a single precursor offers better chances of homogeneity in the samples. Although utilization of the related precursor $[(\text{tBuSe})_2\text{Se}]$ ³¹ could possibly be used for the synthesis of Fe_xZrSe_2 films in combination with an iron precursor, its higher toxicity and volatility makes its use far less desirable. Additionally, the selection of an oxygen-free iron source is not straightforward, as risk of carbon contamination can increase exponentially due to the increase of burned hydrocarbonated ligands and the use of alternative carbon-free sources (e.g., FeCl_3) could involve addition of undesired halogen doping. Although the proposed single-source precursor does not lead to a pure Fe_xZrSe_2

system using the described synthetic conditions, this study represents a proof of concept that the system can be synthesized from organometallic sources; the continuous development of organometallic sources with a variable ratio of Fe is extremely important for the future viability of these mixed metal selenides in industrial processes.

EXPERIMENTAL SECTION

Precursors were synthesized according to literature procedures.⁵³ N,N,N',N' -Tetramethylethylenediamine “TMEDA” (Aldrich) was distilled over sodium and stored over 3 Å molecular sieves (20% m/v) for 24 h. Ferrocene (Merck, 99%) was freeze-dried for 12 h prior to use. Selenium (shot, Aldrich), $n\text{-BuLi}$ (2.5 M in hexane, Aldrich), and bis-(cyclopentadienyl)zirconium(IV) dichloride (Aldrich) were used as purchased. Dry tetrahydrofuran (99.9% in Argon, Sigma) and dry toluene were stored over a sodium mirror for 24 h prior to use, and pre-dried dichloromethane was dried over 3 Å molecular sieves (20% m/v) for 48 h prior to use. All preparations were undertaken using Schlenk techniques, and all glassware was dried for 12 h at 150 °C prior to use. The synthesis and purification of the precursor was performed under argon, which was passed over a drying column. After isolation, the polycrystalline powder precursor was stored in a glovebox under an argon atmosphere. Synthesis and purification of the precursor were confirmed by NMR and elemental analysis.⁵³ $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Se})_2\text{Zr}(\eta^5\text{-C}_5\text{H}_5)_2]_2$ (1): A bright red polycrystalline powder was isolated (1.25 g, 74%). ¹H NMR (600 MHz) δ /ppm (C_6D_6): 5.67 (s, 10H, Cp); 4.35 (m, 8H, Fc); ¹³C{¹H} NMR (600 MHz) δ /ppm (C_6D_6): 110.08 (m, Fc); 113.14 (m, Cp); ⁷⁷Se NMR (400 MHz) δ /ppm (tetrahydrofuran): 558.0; elemental analysis ($\text{C}_{40}\text{H}_{36}\text{Se}_4\text{Fe}_2\text{Zr}_2$): Calc. C, 42.64; H, 3.22. Found: C, 42.58; H, 3.35.

LPCVD experiments were carried out in a quartz tube under dynamic vacuum (10^{-1} Torr) embedded inside a furnace to allow uniform heating, which was controlled using Pt–Rh thermocouples. The polycrystalline powder precursor (*ca.* 0.20 g) was spread evenly in a glazed aluminosilicate ceramic boat ($0.9 \times 1.4 \times 10.3$ cm, VWR cat. no. 459-0224) and heated up at 20 °C/min to 1000 °C and kept at that temperature for 1 h with the goal of achieving its sublimation over quartz slides (2.5 cm \times 1.0 cm \times 2 mm, Multi-Lab), which prior to use were cleaned using acetone (99%), isopropanol (99%), and distilled water and dried at 180 °C overnight. The method was followed by a gradual cooling process involving an initial cooling step of 13 °/min until reaching 355 °C followed by a second cooling step of 2 °C/min until reaching room temperature (switched off). The tube under vacuum was then transported inside a glovebox, where the films on both the quartz substrate and glazed aluminosilicate ceramic boat were stored for characterization. PXRD data were collected on a STOE diffractometer using monochromated $\text{MoK}_{\alpha 1}$ radiation (0.70903 Å, 50 kV, 30 mA) and four scans per measurement over the 2θ range of 10–40°, with a step size of 0.5° and a count time of 10 s per step. Polycrystalline powders were ground in a metal mortar within the glovebox, loaded into sealed 3 mm borosilicate capillaries, and analyzed using a STOE Stadi P diffractometer ($\text{MoK}_{\alpha 1}$ radiation, 0.70903 Å, 50 kV, 30 mA), in which less fluorescence was detected. Rietveld refinements were performed using GSAS and EXPGUI.³⁹ Raman spectroscopy of both powders and films was carried out using a Renishaw 1000 spectrometer equipped with a 633 nm laser. The Raman

system was calibrated using a silicon reference. X-ray photoelectron spectroscopy (XPS) of powders and films was performed using a Thermo K alpha spectrometer with monochromated AlK_{α} radiation (8.3418 Å), a dual beam charge compensation system, and a constant pass energy of 50 eV. Survey scans were collected in the range of 0–1200 eV. High-resolution peaks were used for the principal peaks of Zr (3d), Fe (2p), Se (3d), and C (1s). XPS data was analyzed using CasaXPS software, and the peaks were calibrated to adventitious carbon at 284.8 eV. Scanning electron microscopy (SEM) studies of film surfaces were carried out for thin film samples using JEOL 6301 (10 kV) and JEOL JSM-6700F field emission instruments after sputtering of the samples with a thin layer of gold to reduce charging. UV/Vis/near-IR transmission and reflection spectra were recorded in the range of 300–2500 nm using a Perkin-Elmer Fourier Transform Lambda 950 UV/Vis/NIR spectrometer. The transmission spectra background was taken against an air background, and a Labsphere reflectance standard was used as a reference material.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c00413>.

A table with the refined parameters for Fe_xZrSe_2 powder data, a high-quality image of the Rietveld refined powder data with the derived Fe_xZrSe_2 structure, and XPS survey and Fe surface scans of the thin film samples (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

TMDs, transition metal dichalcogenides; ITMDs, intercalated transition metal dichalcogenides; LPCVD, low-pressure chemical vapor deposition

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