1. Introduction

Since the exceptional physical properties of graphene have been discovered, atomically thin 2D materials have been intensively studied as a promising alternative to classical semiconductors in electronic and optoelectronic applications. Among them, the transition-metal dichalcogenides (TMDCs) have drawn significant research attention recently, in particular, because they feature an adjustable band gap. As a representative of this family, MoS 2 is the most extensively studied TMDC. Transistors based on this benchmark TDMC have shown a remarkably high on/off ratio due to its sizeable band gap. However, the high performance of MoS 2-based devices is limited by the material’s relatively low charge carrier mobility. Hafnium disulfide (HfS 2) is an emerging alternative, which is predicted to have a particularly high carrier mobility. However, a controllable growth of continuous HfS 2 films with selectivity for specific surfaces at a low temperature on a large scale has not been demonstrated yet. Herein, HfS 2 films are grown at 100 °C by atomic layer deposition (ALD) based on the precursors tetrakis(dimethylamido)hafnium and H 2S. In situ vibrational spectroscopy allows for the definition of the temperature range over which (Me 2N) 4Hf chemisorbs as one monolayer. In that range, sequential exposures of the solid surface with (Me 2N) 4Hf and H 2S result in self-limiting reactions that yield alternating surface termination with dimethylamide and thiol. Repeating the cycle grows smooth, continuous, stoichiometric films of thicknesses adjustable from angstroms to >100 nm, as demonstrated by spectroscopic ellipsometry, XRR, AFM, UV–vis and Raman spectroscopy, XPS, and TEM. The well-defined surface chemistry enables one to deposit HfS 2 selectively using, for example, patterns generated in molecular self-assembled monolayers. This novel ALD reaction combines several attractive features necessary for integrating HfS 2 into devices.
2. Results and Discussion

2.1. Fundamental Observations of the Precursor Surface Chemistry

Alkylamide-transition metal(IV) complexes are rapidly developing as a family of ALD precursors due to their high reactivity and volatility. In this paper, we choose tetrakis(dimethylamido)hafnium, (Me₂N)₄Hf, for the HfS₂ film growth. We start the study by investigating the adsorption behavior of (Me₂N)₄Hf under ultra-high vacuum (UHV) conditions on a model substrate, namely Co₃O₄(111), using infrared reflection absorption spectroscopy (IRAS). In the presence of water traces in the UHV environment, reactive OH groups are formed on the Co₃O₄(111) surface. However, the detection of such OH groups in IR is rather difficult, as those vibrations usually give rise to very broad and weak signals.

2.1.1. Multilayer Adsorption of (Me₂N)₄Hf at 150 K and Theoretical Calculation

At low coverages, the IR spectra recorded during the deposition of (Me₂N)₄Hf onto a Co₃O₄(111) sample maintained at 150 K (Figure S1, Supporting Information, compared with DFT-computed spectra of (Me₂N)₄Hf as summarized in Table S1, Supporting Information) exhibits features at 2848, 2814, 2760, 1461, 1249, 1155, and 954 cm⁻¹. The dimethylamine by-product generated upon the chemisorption of (Me₂N)₄Hf at the hydroxyl-terminated surface is difficult to detect however, because its characteristic bands are overlapping with those of the (Me₂N)₄Hf bands grow and additional absorption signals emerge at 3001, 2925, 1438, 1424, 1397, 1130, 1114, 1061, 1015, 975, 964, and 888 cm⁻¹. Comparison with theoretical results allows us to ascribe the new bands to a (Me₂N)₄Hf dimer due to the formation of a condensed multilayer.

2.1.2. Temperature-Programmed IRAS of (Me₂N)₄Hf at 150–450 K

When the (Me₂N)₄Hf multilayer is heated from 150 to 450 K (Figure 1), the intensity of all peaks decreases from 150 to 220 (±5) K (see Figure S2, Supporting Information). The system transforms from multilayer to monolayer at this temperature, which is characterized by sharper signals and shifts observable especially well below 1000 cm⁻¹. The low-temperature band at 954 cm⁻¹ with two shoulders at 975 and 964 cm⁻¹, respectively, not only decreases in intensity upon heating, it also shifts to 944 cm⁻¹, while the band at 964 cm⁻¹ picks up in intensity. These bands assigned to υ(HF-N) or υ(N-C) vibrations evidence a preferential orientation of the chemisorbed monolayer on the surface. Indeed, surface selection rules encode orientation information because only vibrations with a dynamic dipole moment perpendicular to the surface can be probed by IRAS.

2.1.3. Temperature-Programmed IRAS of Alternating Precursors’ Pulses at 300–650 K

In order to investigate the temperature-dependent behavior of the individual precursor reactions, we first prepared a thiol-terminated surface by exposing the Co₃O₄(111) substrate to 1 × 10⁻⁶ mbar of D₂S for 5 min. Subsequent exposure to
2.2. ALD Process Study

When the surface reactions studied in an UHV chamber are transferred to a commercial ALD reactor, the film growth rate measured by spectroscopic ellipsometry as a function of the \((\text{Me}_2\text{N})_4\text{Hf}\) pulse duration (Figure 3a) exhibits saturating behavior. This property confirms self-limiting surface chemistry, and therefore, ALD growth. In the undersaturated regime, that is \((\text{Me}_2\text{N})_4\text{Hf}\) pulses from 0.1 to 1.2 s, the film is highly inhomogeneous. In saturating conditions, the inhomogeneity measured over the size of the chamber (10 cm) is on the order of 10% for a thickness of around 6 nm. For \(\text{H}_2\text{S}\), saturation is observed from 0.1 s pulse duration, whereas 0.2 s pulse is taken as standard. The determination of the ALD temperature window is presented in Figure 3b. From 65 °C as the reaction chamber temperature (lower limit imposed by the evaporation temperature), the growth rate remains stable within experimental uncertainty at about 1 Å per cycle until 100 °C. At 120 °C and beyond, the deposition rate is significantly lower, consistent with the results gathered via the TP-IRAS analysis. In the standard conditions chosen, that is, 100 °C growth temperature, Figure 3c demonstrates a linear dependence of the film thickness on the number of ALD cycles performed with a growth determined (more accurately than in Figure 3b) to be 1.2 Å per cycle, and the inhomogeneity over the chamber decreases to less than 5%.

Figure 4 confirms the accuracy of this value. Taking a sample (Si/200 nm SiO\text{2}) with 50 ALD cycles, Figure 4a exhibits the spectroscopic ellipsometry data recorded before and immediately after deposition. The curve fits yield a thickness of 6.3 nm for the HfS\text{2} layer. Independently of it, an X-ray reflectometry measurement (Figure 4b) yields a thickness of 6.2 nm and a roughness of 0.5 nm.

2.3. Characterization of the ALD Film

The HfS\text{2} material is known to be unstable to aerobic oxidation and affords the highly stable hafnium dioxide at ambient conditions.\textsuperscript{[17]} Indeed, the prompt oxidation of the ALD film is observed in a transmission electron microscopy (TEM) experiment shown in Figure 5a. After 50 ALD cycles, the chamber is opened to air at room temperature for approximately a minute, reheated to 100 °C, and submitted to a further set of 100 cycles; a cross-section of the film exhibits a clear contrast at two-third of the depth. Further characteristics of the film include its outstanding smoothness demonstrated in Figure 5a, and its essentially amorphous character. The selected area electron diffraction (SAED) radial integrated intensity in Figure 5c reveals order on a very short length scale, which we would refrain from calling polycrystalline. This extraordinary low roughness of the ALD-grown HfS\text{2} is quantified by AFM (Figure 5, Supporting Information), with a root-mean-square value of 0.19 nm for an 18 nm thick film, close to the value of the substrate. The superb smoothness of the film observed by STEM and AFM agrees well with the roughness determined in XRR.

The chemical identity (elemental composition) of this film can only be determined after encapsulation with a protective layer. Although h-BN flakes,\textsuperscript{[17a]} polymer,\textsuperscript{[18]} and ALD...
oxide films, have been reported, we find that ZnS (by ALD) performs best, as a thin layer of it (7 nm) is sufficient to prevent the formation of oxide at room temperature for weeks. Energy-dispersive X-ray spectroscopic microanalysis performed of a ZnS-capped HfS$_2$ ALD coating (150 nm) on a porous alumina substrate (Figure 5d) yields an atomic composition of 27.5% S, 0.6% Zn, and 12.6% Hf. This yields an essentially perfect Hf/S stoichiometry of 1:2.1. We note that no other encapsulating layer that we have tested provides efficient protection from air. In our hands, all ALD processes using water, oxygen or ozone as the source of oxides end up forming substoichiometric HfS$_2$ (see Figure S5, Supporting Information), consistent with the partial conversion of HfS$_2$ into the corresponding oxide caused by the highly oxophilic character of hafnium(IV).

Further confirmation of the chemical composition, stoichiometry, and valence state of the ALD HfS$_2$ is provided by X-ray photoelectron spectroscopy (XPS) analysis: Figure 6 presents the ZnS-capped film (Figure S6, Supporting Information, shows the oxidized Al$_2$O$_3$-capped film for comparison). The survey spectra and the S 2p and Hf 4f region all concur to show exclusively ZnS at the surface of the pristine sample, whereas a short sputtering treatment exposes the underlying HfS$_2$. The S 2p doublet at 161.5 and 162.7 eV attributed to ZnS is now complemented by an additional contribution from HfS$_2$, at lower energies, 161.1 and 162.3 eV. Correspondingly, the Hf 4f region exhibits a beautiful doublet at 16.4 and 18.1 eV, matching reported HfS$_2$ data.

Raman spectroscopy is a versatile method to determine structural properties such as thickness, crystallographic structure, and...
presence of defects in thin layered materials.\textsuperscript{[21]} The Raman spectrum recorded of a HfS\textsubscript{2} coating (on a porous alumina substrate) upon excitation at 532 nm is presented in Figure 7a. The measurement has been taken immediately after growth. The main peak at 343.8 cm\textsuperscript{-1} corresponds to the $A_{1g}$ mode of HfS\textsubscript{2} and is due to out-of-plane vibration of S atoms. The weaker peak at 257 cm\textsuperscript{-1} is attributed to the $E_{g}$ mode and relates to S atom vibration in the basal plane; it is, in full agreement with the peaks obtained from the bulk HfS\textsubscript{2} material and the previous experimental reports.\textsuperscript{[8b,11a,22]} The small peak observed at 487 cm\textsuperscript{-1} is from the substrate. The fact that the observation of Raman modes corresponds to those known from crystalline HfS\textsubscript{2} indicates a high structural quality of HfS\textsubscript{2} domains within the film. This confirms the borderline (amorphous/polycrystalline) character observed by electron diffraction. Its optical properties corroborate a band gap of 2.5 eV, which is estimated from the UV–vis absorption spectrum, Figure 7b, and which is in line with literature data.\textsuperscript{[8b,d]}

2.4. Area-Selective ALD Growth

The well-defined surface chemistry characterized so far suggests that ALD growth should be selective on substrates or areas that carry suitable surface reactive groups. Here, patterned self-assembled monolayer (SAM) substrates are used, as the ALD selective growth is designed on thiol-terminated molecular monolayers, whereas areas carrying SAMs with perfluoroalkyl groups represent the inert areas (Figure S7, Supporting Information). Figure 8a shows the results of ALD growth of HfS\textsubscript{2} on the patterned SAM surface, with a stark contrast between the thiol-terminated and inert perfluorinated areas on the left and right sides of the sample, respectively. The EDX measurements in Figure 8b clarify that the Hf signal is detected from the thiol terminated sites but not on the inert perfluorinated areas after ALD growth. Furthermore, the SAM approach allows the experimentalist to tune the density of reactive groups in a mixed system. Figure 9 displays how the morphology of the HfS\textsubscript{2} layer obtained after 30 ALD cycles is affected by dilution of the active thiol sites in the inert perfluoroalkyl (see Figure S8, Supporting Information, for the rest of the AFM images). As quantified by atomic force microscopy (AFM), substrates carrying at least 50% thiols all yield a similar root-mean square roughness below 0.5 nm, whereas the diminishing density of nucleation sites gives rise to an increase in roughness to around 3.5 nm. In this case of individual nucleation sites essentially isolated from each other, the roughness corresponds perfectly to the
nominal film thickness measured on a Si wafer or expected based on the number of cycles. Ideally, the thiol-free substrate should give rise to no nucleation at all. Instead, the area investigated here of 2 µm × 2 µm exhibits approximately 380 nuclei (counted by an image processing software). Given the density of SAM of four molecules per square nanometer (see Figure S7, Supporting Information, for the molecules’ structures), these 380 nuclei are to be compared to the 1.6 × 10^7 molecular sites in this same 2 µm × 2 µm region. In other words, the nucleation probability on unreactive sites (or the defect rate) is 8 × 10^-7, or less than one part per million. This number remains essentially constant upon changes in substrate temperature or purge duration (Figure S9, Supporting Information). These observations speak for the level of control achievable by well-defined surface chemistry.

3. Conclusions

In summary, the present study provides the first low-temperature (≤100 °C), plasma-free ALD process for generating thin coatings of 2D semiconducting HfS₂. A very well behaved surface chemistry is consistently observed from UHV conditions to the low-vacuum conditions of applied ALD reactors. Overall, it is highly advantageous for an area-selective deposition. Temperature-programmed infrared reflection absorption spectroscopy evidences the transition from condensation to the formation of monolayer and finally the thermal decomposition of the (Me₂N)₄Hf precursor on an oxidic surface over a wide temperature range. The insight obtained in UHV is consistent with the temperature window established in a low-vacuum reactor, where the low-temperature growth of continuous, smooth HfS₂ films is successfully established with a precise thickness control from (Me₂N)₄Hf and H₂S as precursors. The film grows in a self-limiting manner at a rate of ca. 1.2 Å per cycle. The extremely air-sensitive HfS₂ is efficiently protected by an ALD deposited zinc sulfide layer of 7 nm thickness. Oxides, in particular Al₂O₃, are inadequate even if deposited directly after HfS₂ ALD without a vacuum break. Extensive material characterization by atomic force microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, UV–vis absorption spectroscopy, and transmission electron microscopy, yield a consistent picture of this borderline (amorphous/polycrystalline) characterized yet highly stoichiometric and pure material.

The choice of the highly reactive and volatile, homoleptic dialkylamido metal complex is instrumental in enabling film growth at low temperatures. In combination with the unique

Figure 6. X-ray photoelectron spectroscopy analysis obtained from ZnS encapsulated HfS₂ film. a) Survey spectra before and after sputtering etching. b) High resolution spectra of the Hf 4f and S 2p regions before sputtering etching. c) High resolution spectra of the Hf 4f and S 2p regions after sputtering etching.

Figure 7. a) Raman spectra of the HfS₂ coated anodic aluminum oxide (AAO) membrane (in gray), crystalline HfS₂ bulk material (in gray blue), and the bare AAO substrate (in brown). b) UV–vis absorption spectrum of HfS₂ deposited on quartz. The absorption spectra of the substrates and the capping material ZnS was also recorded.
versatility of the ALD technique, this allows the experimen-
talist to coat various substrates and even generate patterns
based on area-selective growth. The selectivity can be as high as
0.9999992. Overall, this low-temperature ALD HfS₂ chemistry
combines several advantages for its application in electronic
and optoelectronic devices.

4. Experimental Section

Chemicals: All chemicals are of analytical reagent grade and were
used as received without any further treatment. Tetrakis(dimethylamido)
hafnium and H₂S (3% in N₂) were ordered from Strem and Air Liquide,
respectively. Methanol (MeOH, ≥99%) and isopropanol (i-PrOH,
≥99.5%) were purchased from Carl ROTH, and phosphonic acids

Figure 8. a) The SEM micrograph of patterned SAM substrate with active sites (–SH terminated) on the left and inert sites (–F terminated) on the
right after 30 cycles HfS₂ ALD. b) EDX measurements obtained from the two different SAM surfaces after ALD deposition.

Figure 9. AFM images of SAM substrates with a) 0%, b) 50%, and c) 100% active sites after coating 30 ALD cycles of HfS₂. d) RMS roughness of SAM
surfaces after ALD coating as a function of the active site proportion.
were purchased from Sikemia. The standard SiO$_2$/Si wafer and quartz substrates were purchased from Silicon Materials, Inc., and Plan Optik AG, respectively. The specialized substrates anodic aluminium oxide (AAO) and Co$_3$O$_4$(111) thin films were fabricated according to literature procedures.[23]

**Characterization:** The thickness of the deposited HfS$_2$ layers was determined on Si (100) wafers with a spectroscopic ellipsometer Sentech SENpro equipped with a halogen lamp and a monochromator. Energy dispersive X-ray spectroscopy (EDX) was measured on a JEOl JSM 6400 PC equipped with a LaB$_6$ cathode and SDD X-ray detector. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a monochromatized Al K$_\alpha$ radiation (PHI Quantera II, Japan). Raman spectrum of the thin film was measured in ambient conditions on a WITec alpha-R Confocal Raman Microscope in backscattering with 532 nm excitation wavelength. Raman spectrum of HfS$_2$ bulk in backscattering geometry was recorded using a Horiba Jobin Yvon LabRAM Aramis Raman spectrometer. Neon lines were used to calibrate the spectrum. The optical absorption spectra were measured with an ultraviolet-visible spectrophotometer (Ocean Optics) equipped with a DH-2000-L light source, a HR40000 spectrometer, and an ISP-50-8-R integrating sphere. X-ray reflectometry measurements were performed at the Rigaku SmartLab Diffractometer with Cu K$_\alpha$ source ($\lambda$ = 1.54 Å) operating at 45 kV and 160 mA. Experimental data was background-corrected and a geometric footprint was applied due to the beam overspill effects at small incident angles. The data was fitted using the reflectivity fitting package of the software GenX.[24] Secondary electron microscope (SEM) images were acquired with an AURIGA featuring a GEMINI column from Zeiss. Atomic force microscope (AFM) imaging was carried out using a NanoMan VS (Bruker) with Bruker silicon probes (OTESPA, spring constant of 26 N m$^{-1}$), resonance frequency of 300 kHz), operated in a tapping mode. $1024 \times 1024$ pixels resolution was used for measured surface of $2 \times 2 \mu$m$^2$ and processed data were acquired with Gwyddion 2.42.

**IRAS Measurements:** The measurements were performed in an UHV setup with a base pressure of $1.5 \times 10^{-10}$ mbar which is described in detail elsewhere.[25] The (Me$_2$N)$_4$Hf was deposited onto the Co$_3$O$_4$(111) surface from a well-sealed glass crucible maintained at room temperature. The crucible was separated from the UHV chamber by a gate valve, and (Me$_2$N)$_4$Hf was pumped into the UHV chamber via a separate bypass crucible was separated from the UHV chamber by a gate valve, and pumping. To avoid possible deposition on the chamber walls, the precursor was exposed to 20 min of pumping.

**Temperature-Programmed IRAS Spectra during Alternating Exposures:** First, the as-prepared sample was exposed to D$_2$S for 5 min ($1.0 \times 10^{-4}$ mbar). Subsequently, the sample was exposed to 20 alternating cycles of (Me$_2$N)$_4$Hf/pumping and D$_2$S/pumping during sample heating, applying the following procedure for one cycle: Exposure of (Me$_2$N)$_4$Hf ($5.0 \times 10^{-7}$ mbar) for 3 min, then 2 min of pumping. Exposure of D$_2$S ($1.0 \times 10^{-4}$ mbar, Sigma-Aldrich, 97 atom% D) for 3 min, 2 min of pumping. For data analysis, again the procedure by Xu et al. was applied in this experiment.[26]

**DFT Calculations:** DFT calculations were performed using the TURBOMOLE suite v7.2.[27] The exchange correlation functional of Perdew, Burke and Ernzerhof[28] was used with the def2-TZVP basis set of Weigend and Ahlrichs.[29] Dispersion interactions were accounted for applying the D3 correction scheme of Grimme.[30] Calculations were accelerated through the RI-J approximation.[31] Vibrational frequencies were calculated within the harmonic approximation.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

2D materials, atomic layer deposition, dichalcogenides, hafnium disulfide, thin films

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