

Chromium Trihalides CrX_3 (X = Cl, Br, I): Direct Deposition of Micro- and Nanosheets on Substrates by Chemical Vapor Transport

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The experimental observation of intrinsic ferromagnetism in single layered chromium trihalides CrX_3 (X = Cl, Br, I) has gained outstanding attention recently due to their possible implementation in spintronic devices. However, the reproducible preparation of highly crystalline chromium(III) halide nanolayers without stacking faults is still an experimental challenge. As chromium trihalides consist of adjacent layers with weak interlayer coupling, the preparation of ultrathin CrX₃ nanosheets directly on substrates via vapor transport proves as an advantageous synthesis technique. It is demonstrated that vapor growth of ultrathin highly crystalline CrX₃ micro- and nanosheets succeeds directly on yttrium stabilized zirconia substrates in a one-step process via chemical vapor transport (CVT) in temperature gradients of 100 K (600 °C \rightarrow 500 °C for CrCl₃ and 650 °C \rightarrow 550 °C for CrBr₃ or Crl₃) without a need for subsequent delamination. Due to simulation results, optimization of synthesis conditions is realized and phase pure CrX₃ nanosheets with thicknesses ≤25 nm are obtained via short term CVT. The nanosheets morphology, crystallinity, and phase purity are analyzed by several techniques, including microscopy, diffraction, and spectroscopy. Furthermore, a potential subsequent delamination technique is demonstrated to give fast access to CrX₃ monolayers using the example of CrCl₃.

1. Introduction

The contemporary semiconductor industry is heading for a considerable dilemma. On the one hand the digitization, e.g., in terms of e-mobility, industry 4.0 or big data analytics requires exponentially growing computational power of integrated circuits.^[1,2] On the other hand the physical limit of the minimum feature size of transistors of about 5 nm is reached soon.^[3] The predicted end of Moore's law^[3] between 2025 and 2032 requires

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the implementation of new materials, apart from silicon, to accomplish the ambitious technological aims.^[4-6] A promising approach to supersede Si electronic devices is the implementation of spintronic components, like in ultrathin CrX₃ layers (X = Cl, Br, or I), that use the electron spins as information memory instead of charge carriers.^[7-11] Electrically insulating chromium(III) halides CrX_3 (X = Cl, Br, I) exhibit strongly anisotropic magnetic properties, even in a single layer.^[12] By reason of the Cr3+ ions are in 3d3 electronic configuration with total spin 3/2 that form isotypic honeycomb nets, Huang et al. finally reported on the first experimental proof using CrI₃ (bulk $T_{\rm C} = 61$ K), which showed that the respective monolayer ($T_{\rm C} = 45$ K) and trilayer are ferromagnetic, while the bilayer couples antiferromagnetically.^[13,14] The CrX₃ anisotropy in atomically thin layers makes them intriguing candidates for sensing applications or future magnetoelectronics. Recently, Zhang et al. reported

on similar investigation of monolayer CrBr_3 .^[15] Moreover, the efficiency of CrCl_3 , used as catalyst material, could be enhanced due to nanoscaling and an enlarged surface-to-volume ratio, similar to a recently shown approach of TiCl_3 .^[16,17]

However, the preparation of highly crystalline CrX_3 nanolayers down to the monolayer limit is still an experimental challenge. The commonly employed state-of-the-art exfoliation technique proceeding from prior synthesized bulk CrX_3 platelets lacks due to absolute nonreproducibility. Ideally, in trigonal $CrBr_3$ each

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layer is shifted laterally by [2/3, 1/3] in fractional coordinates with respect to their neighboring layer, similar to a Bernal stacking, representing a Bil₃ structure type.^[18] In contrast, in ideal monoclinic CrCl₃ (AlCl₃ structure type) the reduction in symmetry originates from a further lateral shift of [1/3,0] and [2/3,0] of B- and C-monolayer units with respect to the ABC stacking.^[18,19] In fact, the individual stacking order of layers represents polytypic structures. However, by application of mechanical exfoliation several defects (mainly stacking faults) are easily introduced through the applied mechanical force because of very weak interlayer coupling of vander-Waals nature of CrX₃ compounds in laterally shifted ABC sequences.^[19-21] Furthermore, the exfoliated nanosheets often show irregular, not reproducible crystal shapes. In contrast to this, the direct growth of nanostructures by short term chemical vapor transport (CVT) shows many advantages. Initially CVT allows the straightforward deposition of specific CrX₃ nanolayers with high crystallinity and well-defined morphology on various substrates at very small timescales (only few minutes).^[10,17,22,23] Thus, an exfoliation step of as-prepared CrX₃ bulk flakes becomes completely redundant and stacking faults occur less through the as-grown approach. However, the main advantage of CVT in comparison with other growth techniques is that no additional carrier gas is needed and that all required gas species are formed out of the introduced starting materials (Cr and X). Further, the consumption (only a few milligrams) and thus the costs of necessary materials are very low. Herein we present to our knowledge the first results of CrX₃ nanosheets prepared via short term CVT directly on suitable yttrium stabilized zirconia (YSZ) substrates (see Figure 1). Further, it is shown how to individualize and isolate as-grown nanosheets on a substrate down to the monolayer limit by subsequent delamination techniques using the example of CrCl₃. Prior to the abovementioned synthesis approach, a rational evaluation of suitable synthesis conditions was aspired by application of thermodynamic simulations with respect to the occurring heterogeneous and homogeneous gas phase equilibria during vapor transports (applying the CalPhaD method by using TRAGMIN program package).^[24] Modeling furthermore enabled crystal growth optimization without resource consuming trial-and-error methods. The CrX₃ nanocrystals have finally been characterized and their properties were analyzed with various analytical methods proving morphology, composition, high crystallinity, and phase purity.



Figure 1. Scheme for the one-step synthesis and vapor transport of CrX₃ (X = Br, I) micro- and nanosheets directly on YSZ substrates shown by the example of CrBr₃. Prior to the CVT process for deposition of the respective nanolayers the introduction of chromium powder and bromine (Br₂ in small sealed capillaries) lead to the formation of CrBr₃ (solid) (Cr(s) + 1,5 Br₂(I) \rightarrow CrBr₃(s)) and gaseous CrBr_n (g) (n = 2, 3, 4) at T₂. By application of a temperature gradient (T₂ \rightarrow T₁) chemical vapor transport is achieved for deposition of CrBr₃ micro- and nanosheets on YSZ substrates directly. The reaction course is similar for the formation of CrI₃, while in contrast to this scheme CrCl₃ is utilized as presynthesized compound, that is not introduced by mixture of the elements.

2. Thermodynamic Description of CVT for Vapor Growth of CrX₃ Nanosheets

As previously described, the vapor transport of each chromium(III) halide CrX_3 is somehow nontrivial. That is why a rational synthesis strategy has been pursued by thermodynamic modeling^[24] of potential crystal growth pathways of chromium(III) halides thus significantly minimizing ineffective trial-and-error synthesis approaches. Withal the knowledge of the respective transport mechanism is most essential for choosing individual experimental conditions, which finally should allow a targeted growth of CrX_3 thin sheets directly on substrates without a need for subsequent delamination (see Sections 3.1–3.3).

In order to reflect real experimental conditions to the best fit (e.g., presence of traces of water within the ampoule), not only the halogen containing phases but also H- and O-containing species have been taken into account. Basically, the following heterogeneous (see Equations (1) and (2)) and homogeneous gas phase equilibria (see Equations (3) and (4)) occurring in all three halides CrX_3 (X = Cl, Br and I) due to thermal treatment of CrX_3 compounds can be identified

Heterogeneous equilibria (X = Cl, Br, or I)

$$\operatorname{Cr} X_3(s) \rightleftharpoons \operatorname{Cr} X_2(s) + 1/2X_2(g)$$
 (1)

$$\operatorname{Cr} X_3(s) \rightleftharpoons \operatorname{Cr} X_3(g)$$
 (2)

Homogeneous gas phase equilibria (X = Cl, Br, or I)

$$X_2(\mathbf{g}) \rightleftharpoons 2X(\mathbf{g})$$
 (3)

$$\operatorname{Cr} X_3(g) + 1/2X_2(g) \rightleftharpoons \operatorname{Cr} X_4(g)$$
 (4)

Due to these advantageous solid–gas equilibria, vapor transport reactions proved most suitable for crystal growth of thin layers on substrates. According to the modeling, vapor transport of CrX_3 sheets can fundamentally be realized either by sublimation, auto-transport (or self-transport), or by a regular CVT reaction, see Figure 2.

With this result in mind, the dominant transport mechanism strictly depends on i) the amount of inserted halide as compared to the reaction vessel volume and inner pressure (see Figure 2) and ii) the applied temperature (temperature dependency of partial pressures, see associated content, Figure S1, Supporting Information). Using the pure substance CrX_3 , vapor transport comes about through either sublimation or auto-transport (see Figure 2). With respect to the amount of inserted halide X = Cl, Br, or I, vapor transport acts as regular CVT in case of an excess of halide (either by adding pure X_2 or other halides) CrX_n (n > 3). However, even within a specified composition (Cr/X/O) the transport mechanism may change, due to the temperature dependency of partial pressures (see associated content, Figures S1 and S3, Supporting Information).

The simulation results of stoichiometric CrCl₃ indicate that the vapor growth is achieved by sublimation of CrCl₃(s) at relatively low temperatures ($\overline{T} \approx 550$ °C; see Equation (5) and associated content in Section S1.1, Supporting Information).





Figure 2. Ternary phase diagram of Cr/X/O with X = Cl, Br, or I; the composition of Cr-X-O determines whether the vapor growth is realized as sublimation, auto- or self-transport (both green area) without addition of a suitable transport agent or as chemical vapor transport reaction (CVT, red area) with an excess of halide, added either by the pure halogen X₂ (X = Cl, Br, I) or other halides.

The growth of thin CrI₃ sheet is likewise achieved due to sublimation of CrI₃(s) at slightly enhanced temperature ($\overline{T} \approx 600$ °C, see Equation (6) and associated content in Section S1.3, Supporting Information), albeit the thermal decomposition already runs to a large amount and thus substantial quantity of CrI₂ remains at the source. The decomposition ratio (Equation (1)) is way more balanced in case of CrBr₃. Hence, vapor transport works either as regular CVT (see Equation (7) and associated content in Section S1.2, Supporting Information) with a slight excess of bromine at mediate temperatures ($\overline{T} \approx 550$ °C) or as auto-transport ($\overline{T} \approx 700$ °C) with a stoichiometric approach (CrBr₃). With rising partial pressure of CrBr₃ at higher temperature ($\overline{T} > 700$ °C) even a sublimation becomes feasible.

Vapor transport by sublimation:

$$\operatorname{CrCl}_3(s) \rightleftharpoons \operatorname{CrCl}_3(g)$$
 (5)

$$\operatorname{CrI}_3(s) \rightleftharpoons \operatorname{CrI}_3(g)$$
 (6)

CVT reaction:

$$\operatorname{CrBr}_3(s) + 1/2\operatorname{Br}_2(g) \rightleftharpoons \operatorname{CrBr}_4(g)$$
 (7)

Definitely, for favorable formation of thin nanolayers on a substrate, the applied transport rates (deposited mass per time) should be low. In that sense, the simulations indicate relatively low deposition rates of less than 1 mg h⁻¹ at temperatures 873 K \rightarrow 773 K (600 °C \rightarrow 500 °C, CrCl₃), or 923 K \rightarrow 823 K (650 °C \rightarrow 550 °C, CrBr₃ and CrI₃) and thus prove to be suitable for short term vapor transport of CrX₃ nanolayers directly on substrates.

3. Crystal Growth by Vapor Transports of CrX_3 (X = Cl, Br, I)

 CrX_3 (X = Cl, Br, I) micro- and nanocrystals were grown by a pure vapor transport and deposited directly on YSZ substrates (yttria stabilized zirconia, $ZrO_2:Y_2O_3$) in an endothermic process in two-zone furnaces in sealed silica glass (quartz) ampoules. The specific experimental parameter and the characterization of as-grown CrX_3 micro- and nanosheets are presented separately for every chromium(III) halide subsequently.

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3.1. Chromium(III) Chloride (CrCl₃)

Based on the thermodynamic assessment of suitable conditions for crystal growth of CrCl₃ by vapor transport, a rational synthesis approach became possible (see Section 2 and associated content in Section S1.1, Supporting Information). For deposition of single layer or few layer sheets, temperatures below 600 °C and a deposition time not longer than 30 min proved to be successful. Finally, chromium(III) chloride microand nanosheets were prepared on YSZ substrates by means of CVT from $\vartheta_2 = 600 \ ^\circ C \rightarrow \vartheta_1 = 500 \ ^\circ C$ in two-zone furnaces for a few minutes (see Figure 3a). It has been observed that mainly by controlling furnace temperatures (ϑ_2 and ϑ_1) and growth durations (minutes to hours), the adjustment of the amount of deposited CrCl3 sheets on YSZ substrates became possible. By application of slightly lowered temperatures, e.g., $\vartheta_2 = 575 \ ^\circ C \rightarrow \vartheta_1 = 475 \ ^\circ C$ the amount of deposited structures was decreased heavily, preventing the condensation of thicker microsheets. Decreasing the temperatures even further lead to no crystal growth at all, since the transport relevant pressure of CrCl₃(g) is too low for efficient dissolution of the initial material at the source, and thus condensation of the respective thin sheets (see Figure 3a). It could be shown experimentally that an enlargement of both transport time and weighed portion of the starting material (CrCl₃) leads to a more defined growth of thicker sheets on the substrate. Applying finally optimized transport conditions, crystal growth of thin sheets with thicknesses ≤ 25 nm succeeded on YSZ substrates (see Figure 3d,e). However, we observed that ultrathin structures (≤25 nm) rarely occur. In addition, thicker structures up to the micrometer scale (microsheets) were deposited as well (see Figure 3b). Based on investigations by both optical microscopy and atomic force microscopy (AFM), a classification of CrCl₃ structures according to different layer thicknesses could be drawn (list in decreasing thickness, see Figure 3c): by means of optical microscopy CrCl₃ crystals with thicknesses $\geq 2 \ \mu m$ more likely are agglomerated with lateral dimensions of about 100 µm (see associated content, Figure S7, Supporting Information) and with black or white-lustrous appearances, depending on the angle of light incidence (pleochroism, see Figure 3b, yellow category). Isolated white-to-colorful sheets with black edges exhibit thicknesses from 100 nm-2 µm and lateral dimensions of 20-50 µm (see Figure 3b, white category). By decreasing the thickness of CrCl₃ sheets (<100 nm) thinner nanosheets appear dark blue to transparent. Thereby, thin sheets with black edges show thicknesses of 50-100 nm and lateral dimensions of about 20 µm (see Figure 3b, orange category). The

1901410 (3 of 11)







Figure 3. Crystal growth by vapor transports of CrCl3 on YSZ substrates: a) optical microscopy of CrCl3 micro- and nanocrystals at YSZ substrate, b) optical microscope image of YSZ substrate surface with CrCl₃ sheets with respective thicknesses in dotted boxes, c) distribution of thicknesses of CrCl₃ structures on a YSZ substrate after CVT (yellow), after one time of exfoliation (green) and after three times of exfoliation (purple), d) AFM measurement of a CrCl₃ nanosheet, e) corresponding microscope image of measurement of (d) the white arrow is indicating the measurement, f) AFM measurement of a CrCl₃ ultrathin sheet (red line) and monolayer (purple line) after three times of exfoliation, and g) corresponding microscope image of measurement of (f) the white line is indicating the monolayer AFM measurement.

thinnest observed nanosheets (≤50 nm) do not exhibit discernible edges and get more transparent the thinner they are, with lateral dimensions about 10 µm and weak dark-blue color (see Figure 3b, green category and associated content, Figure S4, Supporting Information). Monolayers could not be identified by pure optical microscopy. Up to now, no further thickness reduction succeeded by pure CVT, so that subsequent delamination of as-grown CrCl₃ micro- and nanosheets has been realized (see Figure 3c and associated content, Figure S7, Supporting Information). By subsequent exfoliation applying the Scotch tape method, the total amount of CrCl₃ structures could be reduced at all investigated thickness levels (microsheets $>2 \ \mu m$ down to nanosheets with thicknesses $<50 \ nm$). In fact, it proved difficult to detach individual layer stacks of microcrystals to gain access to thinner remnants of CrCl₃. However, in particular cases, thin residues of delaminated crystals could be investigated by AFM. Thus, the presence of ultrathin structures with thicknesses (<3 nm) could be confirmed (see red line in Figure 3f). Investigating the fragments in greater detail led to successful detection of individual, isolated monolayers of CrCl₃ on YSZ substrates (see purple line in Figure 3f,g), similar to those observed by McGuire et al.^[25]

CrCl₃ nanosheets deposited by pure CVT were investigated by scanning electron microscopy (SEM) and a tilted sample holder (tilt angle 30-45° depending on the investigated sheet) to locate ultrathin structures (see Figure 4d). Thereby, chromium(III) chloride sheets appear dark gray according to the secondary electron image contrast. SEM-energy dispersive X-ray (EDX) measurements confirmed CrCl₃ close the expected 1:3 stoichiometry (Cr:Cl, see Figure 4a). Note that the deviation from the expected composition could stem from the flat sheet structure, where a significant amount of the detected signal originates from the underlying YSZ substrate (Zr, Y, and O), which modifies EDX quantification. To investigate if the detected oxygen originates from the underlying substrate surface or the deposited nanosheets we applied X-ray photoelectron spectroscopy (XPS, see Figure 4b). By means of XPS of the nanosheets surface it is obvious that oxygen is only adsorbed at the crystal surface and is not incorporated into the lattice. Here we show survey spectra to demonstrate also the residual substrate influence to the measurements; the concentration calculations were done by high-resolution spectra (see associated content, Figure S9, Supporting Information). The amount of detected oxygen can be minimized down to 2 at% by sputtering with inert gas (argon). The sputtering process was necessary to exclude the influence of oxygen that was introduced by transfer of the respective samples and to eliminate several residue contaminations in the device chamber (e.g., carbon). With respect to the CrCl3 micro- and nanosheet samples the binding energy of chromium according to the Cr 2p_{3/2} orbital (577 eV) fit to those reported in the literature for CrCl₃ (see associated content, Figure S9, Supporting Information).^[26] Moreover, we investigated CrCl₃ nanosheets without the respective underlaying substrate by means of transmission electron microscope (TEM, Figure 4e). By scanning TEM (STEM)-EDX it has been proven that CrCl₃ nanosheets are not oxidized with quantification results close to 1:3 (Cr:Cl), according to CrCl₃ (see associated content, Figure S8, Supporting Information). Additionally,



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Figure 4. Characterization of CrCl₃ nanosheets on YSZ substrates: a) SEM-EDX spectrum of deposited CrCl₃ nanostructures. The elemental quantification proves a ratio of Cr:Cl close to the desired 1:3 (according to CrCl₃) with Cr-K: 31 at% and Cl-K: 69 at%. b) XPS spectra of CrCl₃ bulk flakes (black), CrCl₃ nanosheets deposited on YSZ substrates (blue), and the pure YSZ substrate (red). c) micro-RAMAN measurement of bulk CrCl₃ (black), CrCl₃ nanosheets (thicker layer, blue), CrCl₃ nanosheets (thinner layer, green), and of the pure YSZ substrate (red). d) SEM secondary electron pictures of CrCl₃ nanosheets deposited on YSZ with tilted sample holder, e) scanning TEM image of a CrCl₃ nanosheet, f) HR-TEM image of a CrCl₃ nanosheet, and g) SAED pattern of the respective CrCl₃ nanosheet both acquired in (001) orientation.

the atomic lattice planes could be revealed by high-resolution (HR)-TEM (Figure 4f). By means of selected area electron diffraction (SAED) it was shown that CrCl₃ nanosheets are highly crystalline with reflections fitting to the monoclinic space group C2/m (Figure 4g), in agreement with reported literature.^[25,27] Additionally, thicker flakes of CrCl₃, deposited under the exact same conditions, but longer CVT durations, were investigated by means of powder X-ray diffraction (PXRD). The recorded PXRD pattern (see associated content, Figure S5, Supporting Information) shows that the deposited structures are high crystalline and phase pure with reflections fitting to the abovementioned monoclinic space group (C2/m). For additional conformation of the sheets phase purity we performed SQUID magnetometry of CrCl₃ single crystals (see associated content, Figure S6, Supporting Information). In agreement with reported literature we observed that the spins of Cr³⁺ are aligned in-plain (perpendicularly to the *c*-axis).^[19] By utilizing small external magnetic fields (0,1 T) the antiferromagnetic ground state of $CrCl_3$ is preserved at $T_N = 13$ K. In contrast to this, the application of higher external fields (3 T) leads to an induced ferromagnetic state in CrCl3 which fits well to previously studied magnetic behavior of chromium(III) chloride (see associated content, Figure S6, Supporting Information).^[19] Furthermore, we investigated thin sheets of CrCl₃ by means of micro-RAMAN (Figure 4c) and compared a thicker and a thinner layer of CrCl₃ to the respective bulk material. Our measurements of bulk CrCl3 agree well with reported literature data.^[28-31] The RAMAN spectra of both the thicker and

thinner investigated CrCl3 layers are in good agreement with recent literature of a 27 nm layer (with respect to our thicker layer), and to a bi- or monolayer of CrCl₃ (with respect to our thin layer) investigated by Wang.^[29] While in the nano-CrCl₃ (thick layer) the four main peaks are decreased in intensity but still visible, the E_g lattice vibrations according to peaks at 115 and 345 cm⁻¹ are not visible at all. By measuring even thinner CrCl₃ nanostructures, the underlying substrate influences the obtained results heavily and only the most dominant peak at 298 cm⁻¹ (A_{1g} lattice vibration) is still identifiable. We observed a slight shift to lower phonon energies for thinner nanostructures of CrCl₃ of 2 cm⁻¹ at 298 cm⁻¹ (A_{1 σ}), respectively, of 8 cm⁻¹ at 246 cm⁻¹ (E_{o}), which could probably be caused by lattice strain as a result of a considerable lattice mismatch (\approx 10% with respect to the *a* lattice parameter) to the underlying substrate (see associated content, Figure S10, Supporting Information). Additionally, we observed a slight photosensitivity of CrCl₃ nanosheets due to an irreversible change in the appearance of thin layers (emergence of dark spots) by longer laser irradiation, similar to a phenomenon recently observed in CrI₃ nanosheets.^[32] As an indirect proof of a decreasing sample thickness in nanolayered CrCl₃, the intensity of the underlying substrate (YSZ) increases greatly, especially at about 625 cm⁻¹. In summary, the deposition of CrCl₃ micro- and nanosheets is feasible by pure chemical vapor transport down to layer thicknesses of ≤25 nm. Further, delamination gives rise to the location of few ultrathin structures down to the monolayer limit of prior as-grown micro- and nanolayers.





3.2. Chromium(III) Bromide (CrBr₃)

Similar to CrCl₃, the optimum vapor transport conditions have been deduced from thermodynamic modeling of CrBr₃ (see Section 2 and associated content in Section S1.2, Supporting Information). As a consequence, chromium(III) bromide microand nanosheets were successfully grown on YSZ substrates (see **Figure 5**a) in an endothermic chemical vapor transport process from mainly $\vartheta_2 = 650 \text{ °C} \rightarrow \vartheta_1 = 550 \text{ °C}$ in a two-zone furnace within a few minutes, proceeding from pure chromium powder and an excess of bromine (with respect to the aimed composition CrBr₃). Single crystalline sheets with thicknesses \leq 50 nm down to a minimum of ultrathin 1 nm were deposited on YSZ substrates (see Figure 5c–f). More than 20% of the deposited structures are nanosheets with thicknesses \leq 50 nm (see Figure 5d). However, the majority of deposited crystals exhibit layer thicknesses larger than 50 nm (CrBr₃ microsheets). It is observed that the mass of deposited CrBr₃ structures can be controlled by CVT, mainly by adjusting the applied temperatures (ϑ_2 and ϑ_1) and the transport time. By application of temperatures $\vartheta_2 = 650 \text{ °C} \rightarrow \vartheta_1 = 550 \text{ °C}$ and longer durations (24 h) the amount of deposited CrBr₃ (on YSZ substrates) is about 1.7 mg, mainly composed of microsheets. However, utilizing this temperature gradient and lower transport time (30 min), ultrathin chromium(III) bromide sheets with thicknesses of \leq 7 nm were obtained (Figure 5e). The amount of



Figure 5. Crystal growth by vapor transports of CrBr₃ on YSZ substrates: a) Optical microscope image of CrBr₃ deposited on a YSZ substrate. b) SEM image of deposited CrBr₃ micro- and nanosheets (the white area is indicating the enlarged image of (c)). c) Enlarged SEM image of CrBr₃ microand nanosheets, enlarged optical microscope image of CrBr₃ micro and nanosheets, and AFM measurement of a CrBr₃ nanosheet according to (f). d) Distribution of thicknesses of CrBr₃ crystals on a YSZ substrate. e,f) AFM measurements of CrBr₃ nanosheets, respectively, a CrBr₃ bilayer. g) EDX measurement of a CrBr₃ microsheet. the elemental quantification proves a ratio of Cr:Br close to the desired 1:3 (according to CrBr₃) with Cr-K: 21 at% and Br-L: 79 at%. h) XPS measurement of CrBr₃ bulk flakes (black), CrBr₃ nanosheets deposited on YSZ substrates (blue), and of the pure YSZ substrate (red). i) Micro-RAMAN measurement of bulk CrBr₃ (black), a CrBr₃ microsheet (red), and a CrBr₃ nanosheet (blue).

Adv. Mater. Interfaces 2019, 6, 1901410

1901410 (6 of 11)

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deposited material (CrBr₃) was subsequently minimized significantly ($m(CrBr_3) \approx 0.1 \text{ mg}$) by applying only slightly lowered temperatures ($\vartheta_2 = 600 \ ^\circ C \rightarrow \vartheta_1 = 500 \ ^\circ C$) and short reaction durations of 30 min (see associated content, Figure S11, Supporting Information), supporting an enhanced formation of few-layer sheets. In addition, a temperature gradient of 200 K $(\vartheta_2 = 750 \text{ °C} \rightarrow \vartheta_1 = 550 \text{ °C})$ was examined to generate ultrathin CrBr₃ nanosheets, within a period of 30 min, with thicknesses of around 1 nm, corresponding to a CrBr₃ bilayer (Figure 5f). As-grown CrBr₃ micro- and nanocrystals were investigated by means of optical microscopy (see Figure 5a, c and associated content, Figure S15, Supporting Information). Chromium(III) bromide microsheets (thickness >100 nm) initially seem to appear with a brown color according to Figure 5a due to residual bromine atmosphere. In fact, the crystals exhibit a green color in bright field mode: dark green for thicker and light green for thinner microsheets, similar to shiny green CrBr3 bulk flakes (see associated content, Figure S12a, Supporting Information). The appearance of thinner CrBr₃ nanosheets (thickness \leq 50 nm) changes to white-gray with structures becoming more transparent the thinner they are (see Figure 5c). Nano-CrBr₃ shows lateral dimensions of around 10–100 μ m, while thicker microsheets exhibit lateral dimensions larger than 100 µm, up to the sub millimeter range. Subsequently, CrBr3 micro- and nanosheets were investigated by SEM. Related to this, nanoflakes appear darker according to the secondary electron image contrast with smooth edges (see Figure 5b,c). Thin layers were investigated by means of EDX (see Figure 5g). The quantification results (Cr-K: 21%, Br-L: 79%) indicate a ratio close to the expected 1:3 (Cr:Br) for CrBr₃, whereby charging effects exacerbate an exact quantification. The crystallinity and phase purity of as-grown CrBr3 structures were confirmed by PXRD with CrBr₃ flakes deposited by longer transport times (24 h) at temperatures $\vartheta_2 = 650 \ ^\circ C \rightarrow \vartheta_1 = 550 \ ^\circ C$ (see associated content, Figure S12, Supporting Information). The measurement results indicate that deposited crystals are highly crystalline with trigonal space group $R\overline{3}$ in accordance with literature data.^[31,33–38] In addition, the magnetic properties of CrBr₃ sheets were investigated by means of SOUID (see associated content, Figure S13, Supporting Information). In good agreement with recent literature, our data confirm that the spins of chromium are aligned out-of-plane in CrBr3.^[35] Without or with a small applied external magnetic field (0.1 T) the magnetic ordering appears as A-type antiferromagnetic ($T_{\rm N} = 32$ K) with weak magnetocrystalline anisotropy. In contrast to this, the spins are fully polarized at higher magnetic fields (3 T) and a ferromagnetic state is induced. Deposited CrBr3 nanosheets were further analyzed by means of micro-RAMAN and the results were compared with those from bulk samples and a pristine YSZ substrate (see Figure 5i). The main spectroscopic features remain the same for bulk and micro- or nano-CrBr3 and agree very well with previously reported literature with respect to bulk CrBr₃.^[28,31] Note, that there is a significant decrease of intensity of the A1g peak at around 108 cm⁻¹ for micro- and nanosheets as compared to bulk samples. XPS data obtained from CrBr₃ flakes (see Figure 5h) suggest that the flake surfaces are clean with very low amounts of impurities (O and C). In contrast, XPS measurements according on CrBr3 nanosheets initially pointed toward oxidation of CrBr3, with an obvious decrease of the Br3d and Br3s



peaks, probable due to the presence of residual oxygen in the sample chamber. However, even by sputtering with argon, the detected oxygen was found not to be located only surficial and possibly incorporated into the surface crystal lattices, due to a binding energy of the Cr $2p_{3/2}$ orbital shifted to higher energies (580 eV), which is associated with the formation of Cr₂O₃ (see associated content, Figure S14, Supporting Information). This means that the sensitivity of CrBr₃ bulk flakes to oxygen is only moderate, but it increases rapidly by downscaling to microor even nanodimensions. Hence after a few minutes under ambient conditions first changes are observed, e.g., a reduction of the flake size increases the rate at which a color change (light to dark) is observed that starts from the edges (see associated content, Figure S15a,b, Supporting Information). A tentative explanation could be the reaction with ambient humidity and oxygen and resulting forming of intermediate chromium oxide bromides (see associated content in Equation (SE6), Supporting Information). Furthermore, the flake surface gets cluttered with island-like holes due to degradation down to the substrate surface (see associated content in Figure S15c,d, Supporting Information), probably induced by released HBr. Similar observations were recently reported by Richter, who instead suggested an incorporation of water in the CrBr₃ crystal lattice.^[39] However, analogous to deposited CrCl3 structures we could show, that the deposition of as-grown, high crystalline and phase pure CrBr₃ nanosheets, down to a bilayer, on YSZ substrates is possible due to a short term vapor transport technique.

3.3. Chromium(III) Iodide (Crl₃)

As with for CrCl₃ and CrBr₃, thermodynamic modeling led to rational prediction of applicable experimental conditions for crystal growth of CrI₃, too (see Section 2 and associated content in Section S1.3, Supporting Information). Chromium(III) iodide micro- and nanosheets were prepared on YSZ substrates by means of pure CVT in two zone furnaces $(\vartheta_2 = 650 \text{ °C} \rightarrow \vartheta_1 = 550 \text{ °C})$ within a few minutes of processing, starting from chromium metal and elemental iodine (see Figure 6a). These crystal growth conditions fully reflect the simulation results. Single crystalline sheets with thicknesses ≤50 nm could be obtained by pure vapor growth (see Figure 6b,e,f). In clear contrast to CrBr₃, and especially CrCl₃, chromium(III) iodide (CrI₃) tends to form large microsheets (thickness >200 nm) with a surface area up to 1,3 mm² by application of a temperature gradient of 200 K ($\vartheta_2 = 750 \ ^\circ C \rightarrow \vartheta_1 = 550 \ ^\circ C$, see Figure 6c). Nanosheets with thicknesses ≤50 nm and lateral dimensions of around 20 µm were observed by 30 min CVT time (see Figure 6b,e,f). However, the presence of thin nanosheets (<50 nm) was rather seldom and the majority (>75%) are thicker microsheets (>50 nm), despite short vapor transport durations of minutes (see Figure 6d). Thicker CrI₃ flakes appear as silver to blackish platelets, depending on the incidence of light, in accordance with literature^[19] (see associated content, Figure S16a, Supporting Information). In contrast to this, utilizing light microscopy led to the observation, that thinner sheets of CrI₃ appear as gray-silver sheets, while they get more transparent with decreasing thickness (see inlay of Figure 6f). By taking into account the Cr-K and I-L lines, SEM-EDX measurements

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Figure 6. Crystal growth by vapor transports of CrI₃ on YSZ substrates: a) Optical microscope image of CrI₃ deposited on YSZ substrates (only thicker microcrystals are visible). b) SEM picture of various CrI₃ nanosheets deposited on YSZ substrates. c) SEM picture of deposited CrI₃ microsheets with surface area of around 1.3 mm². d) Distribution of thicknesses of CrI₃ crystals on a YSZ substrate. e,f) AFM measurements to determine the thickness of two individual CrI₃ nanosheets resulting in thicknesses of 20 nm, respectively, 40 nm at the thinnest edge. g) EDX measurement of an CrI₃ nanosheets, with both Cr-K and I-L peaks originating from the CrI₃ sample and Zr-L, Y-L, and O-K peaks originating from the YSZ substrate. The elemental quantification proves a ratio of Cr:I close to the desired 1:3 (according to CrI₃) with Cr-K: 24 at% and I-L: 76 at%. h) XPS measurement of CrI₃ bulk flakes (black), CrI₃ nanosheets deposited on YSZ substrates (purple), and the pure YSZ substrate (red). i) Micro-RAMAN measurement of bulk CrI₃ (black), a CrI₃ microsheet (red), and a CrI₃ nanosheets (blue) on YSZ substrates.

of CrI₃ nanosheets prove a ratio of Cr:I close to the expected 1:3, according to CrI₃ (see Figure 6g). Yet, oxygen and small amounts of carbon are detected too, similar to the cases of CrCl₃ and CrBr₃ due to analogous sample preparations. Moreover, the high crystallinity and phase purity of as-grown CrI₃ structures were confirmed by PXRD with CrI₃ flakes deposited at longer transport times (24 h) at temperatures $\vartheta_2 = 750 \text{ °C} \rightarrow \vartheta_1 = 550 \text{ °C}$. We observed the trigonal space group $P3_112$, in agreement with earlier literature^[40] and recent studies (see associated content, Figure S16, Supporting Information).^[19] However, we did not obtain CrI₃ with monoclinic space group C2/m.^[13] In addition we investigated CrI₃ single crystals by SQUID magnetometry (see associated content, Figure S17, Supporting Information). Our observations agree very well with recent published literature^[19] and emphasize the strong magnetocrystalline anisotropy

in CrI₃. Similar to CrCl₃, XPS measurements confirmed that detected O and C are only adsorbed at the crystal surface, and neither bulk CrI₃ nor nanosheets are significantly oxidized under inert atmosphere (see Figure 6h). Moreover, both impurities are only surficial located and removable by sputtering with argon. It proved difficult, to compare our high-resolution measurements (see associated content, Figure S19, Supporting Information) with respect to individual Cr binding energies to previously obtained XPS CrI₃ measurements, as to our knowledge there are no data available. The extremely strong oxygen sensitivity at ambient conditions (even more than in CrBr₃), especially in nanosheets prohibits a comprehensive study of thin layer properties, e.g., by means of micro-RAMAN (see Figure 6i). Moreover, it has been shown recently that thin CrI₃ sheets are heavily photosensitive.^[32] To overcome this issue,



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an encapsulation of as-grown CrI3 nanosheets in a sandwich of other 2D materials would be advantageous, e.g., hexagonal boron nitride (h-BN) as reported recently in literature.^[32] Nevertheless, AFM of a CrI₃ nanosheet residue due to oxydation and moisture contamination by ambient conditions was performed (see associated content, Figure S18, Supporting Information). Although very thin (3 nm), the flake surfaces are probably oxidized to chromium(III) oxide. However, with particular attention to the exclusion of oxygen or oxygen-containing species, short term CVT is a suitable tool for the preparation of CrI₃ nanolayers directly on substrates. With our approach we show the first time ever that a condensation of chromium(III) halide nanolayers directly on substrates is feasible without the need for subsequent delamination by application of vapor transport proceeding from the pure elements (CrI₃, CrBr₃) or commercially available specimen (CrCl₃).

4. Conclusion

We prepared phase pure and highly crystalline CrX_3 (X = Cl, Br, I) micro- and nanosheets with thicknesses ≤25 nm on YSZ substrates by short term chemical vapor transport in temperature ranges of 650-500 °C. Commonly, the amount of deposited nanosheets (≤ 25 nm) is about 20%, while the remaining structures are microsheets with thicknesses ≥100 nm. Further, monolayers have been prepared by subsequently substrate exfoliation using the example of CrCl₃. Investigations of the chemical composition of as-grown CrX₃ thin sheets confirmed compositions close to the desired 1:3 (Cr:X) stoichiometry. The micro- and nanosheets are high crystalline revealed by powder- (CrX₃) and electron diffraction techniques (CrCl₃). It is further concluded that the detected impurities like oxygen are either only adsorbed at the crystal surface and not incorporated into the lattice (CrCl₃ and CrI₃) or led to surficial oxidation (CrBr₃). Moreover, with thin CrCl₃ sheets a significant shift of phonons to lower energies has been observed, indicating that there is strain present in deposited structures. To our knowledge for the first time, CrBr₃ micro- and nanosheets were analyzed by RAMAN and the position of the main spectroscopic peaks proved to be the same from bulk to nanosheets. However, a rapidly decreasing A_{1g} vibration at around 108 cm⁻¹ was observed in intensity of nanolayered CrBr3. Modeling the solid-vapor equilibria revealed that the description of the vapor transport for the chloride, bromide, and iodide is challenging and system specific. Related to these calculations, we concluded that the dominating transport mechanisms for CrCl₃ and CrI₃ is the sublimation of the solid trihalide, while vapor transport of CrBr₃ appears as a regular CVT. Thus a rational synthesis planning became possible. This approach allows for plain synthesis of highly crystalline and as-grown transition metal trihalide nanostructures directly on substrates. A considerable benefit, especially in comparison with other synthesis techniques, is that the preparation of thin CrX_3 sheets proceeds in a single step by application of a temperature gradient at very low timescales of only a few minutes. The main advantage is that a subsequent delamination of prior synthesized bulk flakes becomes redundant under optimized conditions. Applying this concept, the magnetic properties of CrX₃ micro- and nanosheets

on substrates will be compared to those of bulk structures. The short duration approach of CVT should be exploited to prepare even monolayers of other transition metal trihalides, since the strategy is not limited to CrX_3 structures only. Additionally, as-prepared heterostructures are chemically possible due to a subsequent CVT process in short durations.

5. Experimental Section

Crystal Growth and Thin Layer Delamination: Chromium (III) halides CrX_3 (X = Cl, Br, I) were prepared in glove box atmosphere (argon) and synthesized by CVT in two zone furnaces in sealed silica glass (quartz) ampoules of length of ≈12 cm and diameter of ≈1 cm. Chromium(III) chloride (CrCl₃) flakes and nanosheets were prepared from a few milligrams of commercial, anhydrous CrCl₃ (Alfa Aesar, 99.9% purity) without any purification in temperature gradients of 50-200 K for several days (bulk flakes) to minutes (nanosheets) without any transport agent. Both, chromium(III) bromide (CrBr₃) and chromium(III) iodide (CrI₃) flakes and nanosheets, were grown proceeding from the pure elements: chromium powder (≈100 mesh, Alfa Aesar, purity 99%), bromine (Acros Ogranics, 99.6% purity), and iodine (Merck, double resublimed for analysis) without any self-preceded purification step. CrBr3 and Crl₃ structures were prepared in temperature gradients of 50-200 K for several days (flakes) down to a few minutes (nanosheets) without any prior isothermal step for formation of Crl₃ or CrBr₃. To prevent a condensation of remaining gas phase onto prior deposited crystals while quenching with water (end of CVT process), samples were cooled down in air instead (source zone) with respect to Crl₃. The weighed portion of Br₂ was achieved by encapsulating an amount of around 10-40 mg of bromine in commercial glass capillaries (Fa. Hilgenberg, mark-tubes glass no. 14, length: 8 cm, diameter: 0.7 mm), with the help of liquid nitrogen, that were sealed with a lighter. To obtain a stoichiometric approach according to CrBr₃, the resulting amount of chromium powder was calculated and introduced. Note, that a slight excess of bromine (≈0.05 mmol) was applied in order to achieve a regular CVT, as predicted by thermodynamic modeling and according to previous reported literature.^[41] Similarly to CrBr₃, the weighed portion of iodine (I₂) was applied to obtain a slight excess of iodine (≈0.05 mmol) for CrI₃, in order to achieve a sublimation process, as predicted by thermodynamic modeling and similar to recently published literature.^[19] Moreover an YSZ substrate (yttria stabilized zirconia, ZrO2:Y2O3, CrysTec with surface area of 30 mm²) was introduced to deposit thin structures on before sealing the ampoule under vacuum. Note that in case of CrBr₃ experiments, the Br₂ glass capillary was broken after sealing due to a flame of pure hydrogen to prevent a burst of the ampoule while heating in the furnace.

Subsequently to the CVT process, the substrate with deposited thin layer crystals was treated beyond by exfoliation by the Scoth tape method. For this purpose, commercial Scotch tape was applied. The remain of crystals of few-layer-thickness was investigated after one and three exfoliation steps.

Thermodynamic Simulations: For the thermodynamic modeling of the chemical vapor transport process, the free available software TRAGMIN was utilized.^[24] Herein, the partial pressures and the solubility of all components in the gas phase, the transport rate of the deposited crystals, and the transport efficiencies of gaseous species (transport agent and transport efficient gas species) were calculated. To determine the abovementioned parameters, thermodynamic data of all possible condensated and gaseous compounds within the systems Cr/H/O/X were used.^[42] To calculate the state of heterogeneous decomposition and sublimation equilibria the free available software Thermodynamik was applied.^[43]

Characterization of Deposited Crystals: CrX_3 (X = Cl, Br, I) micro- and nanocrystals were investigated by means of light microscopy with the AXIO Imager.A1M (Zeiss, Germany). Therefore, the bright field or dark field image mode was used. Pictures were recorded with an integrated camera. Further, a LEICA M80 and an integrated camera were used with



Leica Application Software (v.4.8.0). SEM pictures were obtained using a Nova NanoSEM (FEI Company, USA) with a through the lens detector or an Everhart-Thornley detector. The chosen acceleration voltage varied between 2 and 15 keV with a spot size of 4.5. For the EDX analysis, a QUANTA 200/400 (AMETEX) was utilized with an acceleration voltage of 15 keV integrated into the SEM. For AFM measurements a Dimension Icon (BRUKER, USA) was used in tapping mode. The analysis of the data was performed with the program NanoScope Analysis v. 1.8. HR-TEM imaging and SAED measurements were performed using a double-corrected Titan³ 80-300 instrument (FEI Company, USA). The images were acquired at an acceleration voltage of 300 keV. For atomic resolution imaging, an aberration corrector was employed providing a resolution of up to 0.08 nm. Additional STEM measurements were established by means of a Tecnai F30 (FEI Company, USA) again at an acceleration voltage of 300 kV. For STEM-EDX measurements, an EDAMIII spectrometer (EDAX) was utilized. For HR- and STEM analysis as-grown CrCl₃ micro- and nanosheets on YSZ substrates were sonicated in 2 mL distilled water for 5 min in a conventional laboratory ultrasonication bath (BANDELIN company) without application of any cooling or heating steps. The suspension was dropped (five drops) on lacey-carbon copper grids, dried in ambient conditions and introduced into the device. Thicker CrX₃ crystals were characterized by means of PXRD. Herein, a STOE STADI-P (STOE Darmstadt) was used in transmission geometry with Mo- K_{α} radiation ($\lambda = 0.7093$ Å) from 5° to 60° 2 θ with a step width of 0.01. The phase identification was established with structure models of the Inorganic Crystal Structure Database (ICSD) and International Centre for Diffraction Data (ICDD) database. The samples were further characterized by means of XPS to rule out possible oxygen impact during preparation. The results were obtained with a PHI 5600 (Physical Electronics, USA). The excitation was carried out using monochromatic Al- K_{α} radiation (350 Watt). For the detection, a hemispherical analyzer was used. For surface cleaning, samples were sputtered with argon ions (3.5 keV, Ar purity: 99.999%) with a sputter rate of 3.5 nm min⁻¹. Despite considering possible changes by the ion impact such as preferential sputtering, this sputter cleaning was necessary because of surface oxidation during transport on air. Because the substrates were not completely covered by CrX₃ flakes, possible oxide content of the CrX₃ flakes was estimated by comparison with measurements of virgin sputter cleaned samples. Micro-RAMAN measurements were performed with a LabRAM HR Evolution (HORIBA) and a 458 nm laser with an acquisition time of 30 s. The magnetic measurements were performed utilizing an magnetic properties measurement system (MPMS) SQUID (Quantum Design) between 2 and 300 K and external magnetic field up to 3 T in field cooled and zero field cooled mode. For the measurements of several orientations (H perpendicular or parallel to c) individual crystal were utilized. The sheets were fixed between two stripes of adhesive tape and introduced into a plastic straw.

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

chemical vapor transport, $\mbox{Cr}X_3,$ crystal growth, nanosheets, transition metal halides

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Adv. Mater. Interfaces 2019, 6, 1901410 1901410 (10 of 11)

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