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Supplementary information

Unidirectional Growth of Epitaxial Tantalum Disulfide Triangle Crystals Grown on Sapphire by Chemical Vapour Deposition with a Separate-Flow System

Takashi Yanase,[a,*] Miu Ebashi,[a] Kotaro Takamure,[b] Ise Wataru,[c] Hiroki Waizumi,[c] Akira Chikamatsu,[d] Yasushi Hirose,[e] Toshihiro Shimada[c]

[a.] Department of Chemistry, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan

[b.] Institute of Materials and Systems for Sustainability, Division of Materials Research, Nagoya University, Furocho, Chikusa-ku, Nagoya, Aichi 464-8601, Japan

[c.] Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8 Kita-ku, Sapporo, Hokkaido 060-8628, Japan

[d.] Department of Chemistry, Faculty of Science, Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan

[e.] Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minamiosawa Hachioji, Tokyo 192-0397, Japan

Corresponding author

* takashi.yanase@sci.toho-u.ac.jp

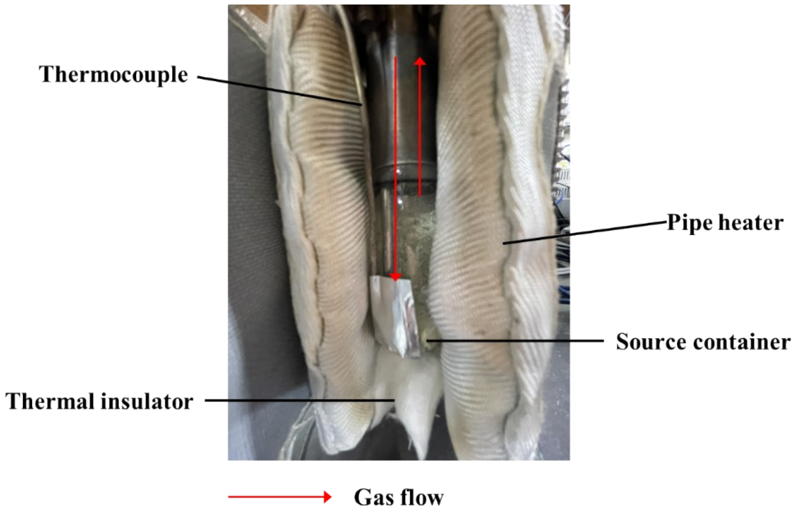


Fig. S1 The picture of the source container in the case of sulphur. The red arrows show the flow of carrier gas. The supplied power to the pipe heater was controlled by a PID controller for stable temperature.

DETAILED PROCEDURE OF CVD

After the inside of the quartz tube was evacuated at lower than 10 Pa using a rotary pump, the furnace was heated to 900–950 °C for 60 min. The time when the furnace was turned on was defined as $t = 0$ min. The time regions of $0 \leq t < 61$, $61 \leq t < 66$, and $t \geq 66$ were called the pre-step, growth step, and cooling step, respectively. When $t = 30$ min, the system was filled with 4% H_2 diluted by Ar. After the inside pressure reached 1 atm, the flow rates of the sulphur line and $TaCl_5$ line were set at 25 sccm and 10 sccm, respectively, to avoid air intrusion into the CVD system. When $t = 40$ min, the sulphur container was heated to 210 °C for 5 min. When $t = 45$ min, the flow of the $TaCl_5$ line was shut in order not to supply $TaCl_5$ vapour to the reaction zone at the pre-step. When $t = 50$ min, the $TaCl_5$ container was heated to 145–160 °C for 5 min. When $t = 60$ min, the flow rate of the sulphur line was raised to 500 sccm to fill the inside of the quartz tube with the sulphur vapour before moving to the growth step. When $t = 61$ min (growth step started), the $TaCl_5$ vapour was supplied to the reaction zone at the flow rate of 150 sccm, and the flow rate of the sulphur line was decreased to 350 sccm. The growth time was defined as the duration of the growth step. When $t = 66$ min (the cooling step started), the $TaCl_5$ heater and the furnace were turned off, and the flow of the $TaCl_5$ was stopped to avoid any undesired reaction. The furnace was naturally cooled to 300 °C while the sulphur flow was maintained in order for the $TaCl_5$ thin films not to be oxidized. When the furnace temperature reached 300 °C, the sulphur vapour supply was also shut off. The furnace was then forcedly cooled to room temperature by opening. Note that both lines downstream were heated at a temperature 20 °C higher than that of the corresponding source container to prevent clogging of the lines during the reaction.

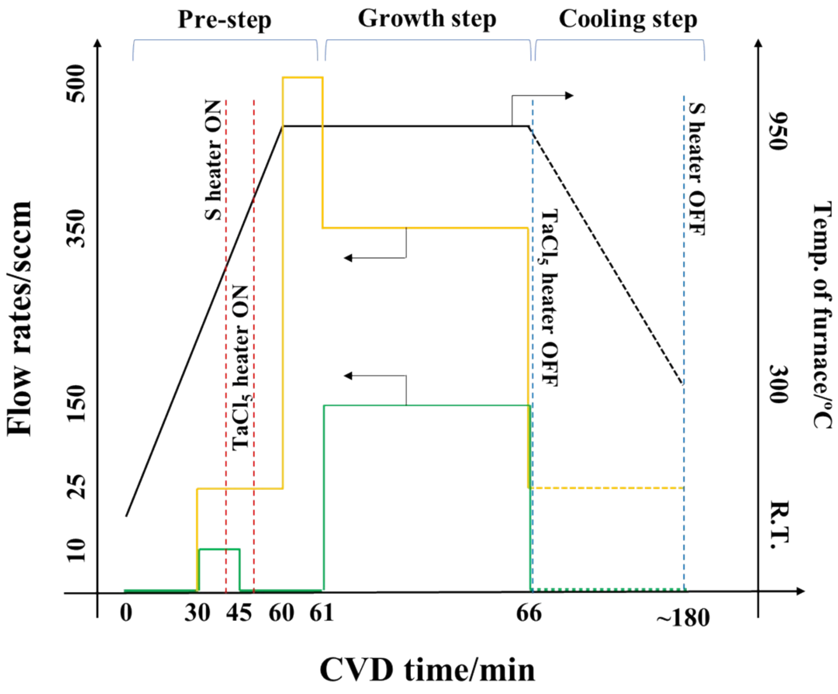


Fig. S2 The sequence of the temperature of the furnace and the flow rates of the sulphur and $TaCl_5$ lines, which was controlled by a computer program. The black, yellow, and green lines show the temperature of the furnace, the flow rates of the sulphur and $TaCl_5$ lines, respectively.

Sample number	Flow rate of S line	Flow rate of $TaCl_5$ line	Temp. of $TaCl_5$	Reaction temp.	Reaction time
(i)	350 sccm	150 sccm	145 °C	950 °C	5 min
(ii)	350 sccm	150 sccm	150 °C	950 °C	5 min
(iii)	350 sccm	150 sccm	160 °C	950 °C	5 min
(iv)	350 sccm	150 sccm	150 °C	925 °C	5 min
(v)	350 sccm	150 sccm	150 °C	900 °C	5 min

Table S1 Growth conditions for the synthesis of TaS_2 films. The temperature of sulphur was fixed at 210 °C in this study.

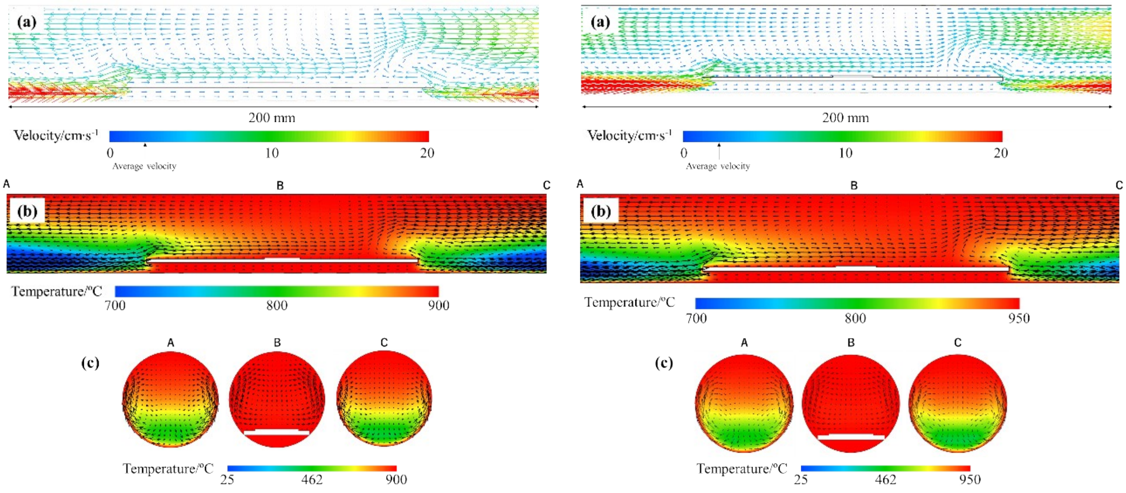


Fig. S3 Gas velocity (a) and temperature gradient (b, c) around a sapphire substrate simulated at 900 °C (left) and 950 °C (right) by CFD.

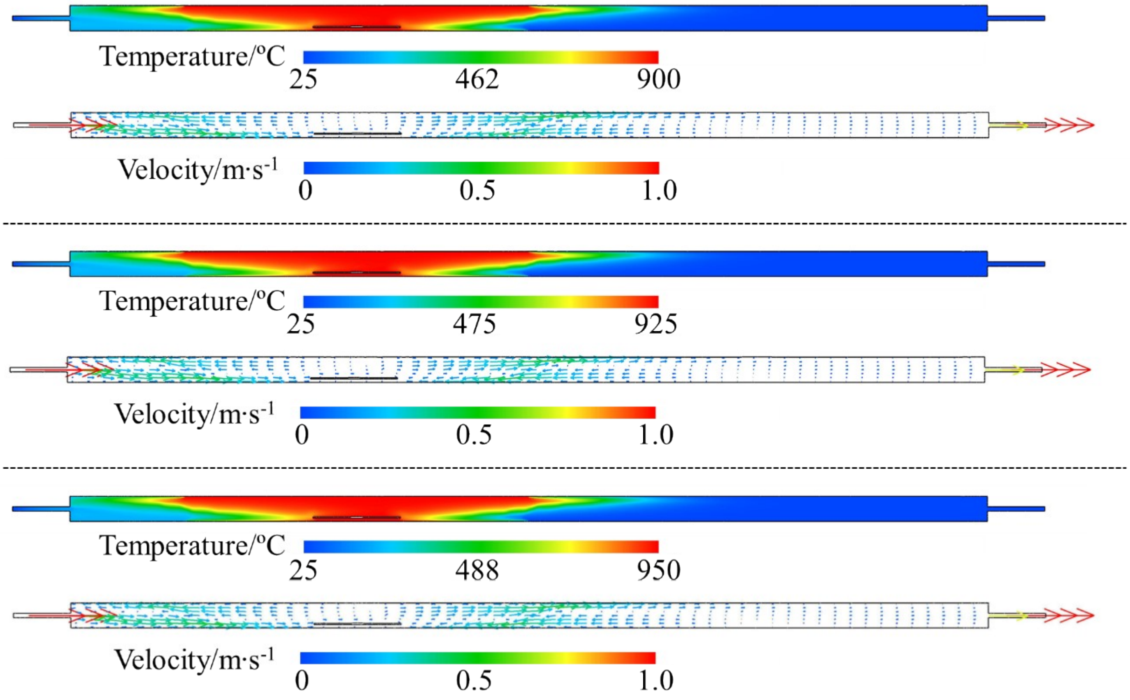


Fig. S4 Temperature gradient and gas velocity of the whole system simulated at 900 °C (top), 925 °C (middle), and 950 °C (bottom) by CFD.

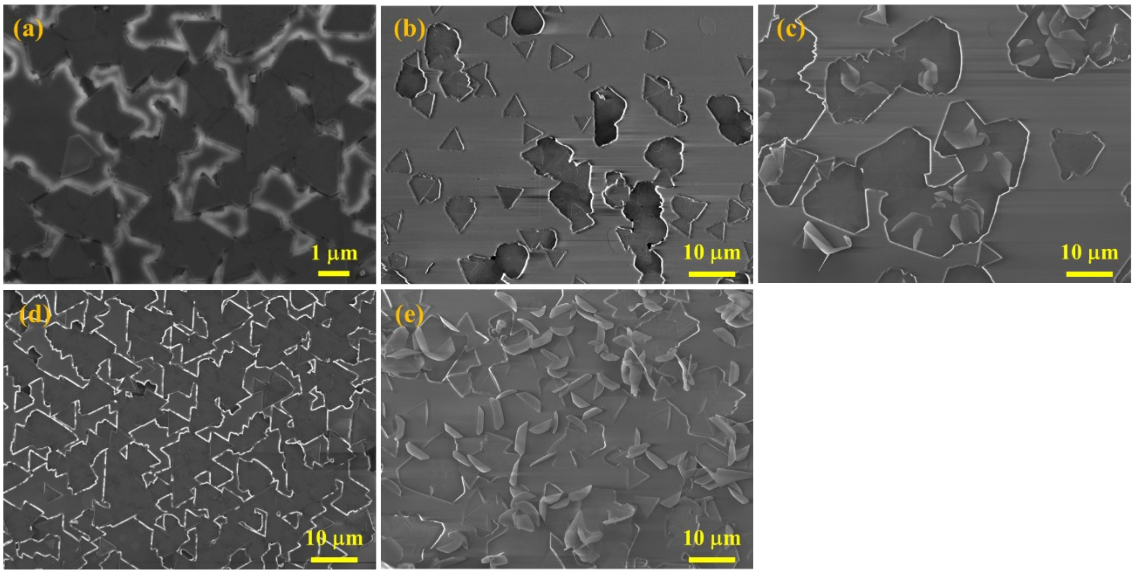


Fig. S5 SEM images of TaS_2 films. These images correspond to those of Figure 3a–e. The blurring at the sides of the triangle domains is due to the charge-up. (A sapphire is not electrically conductive.)

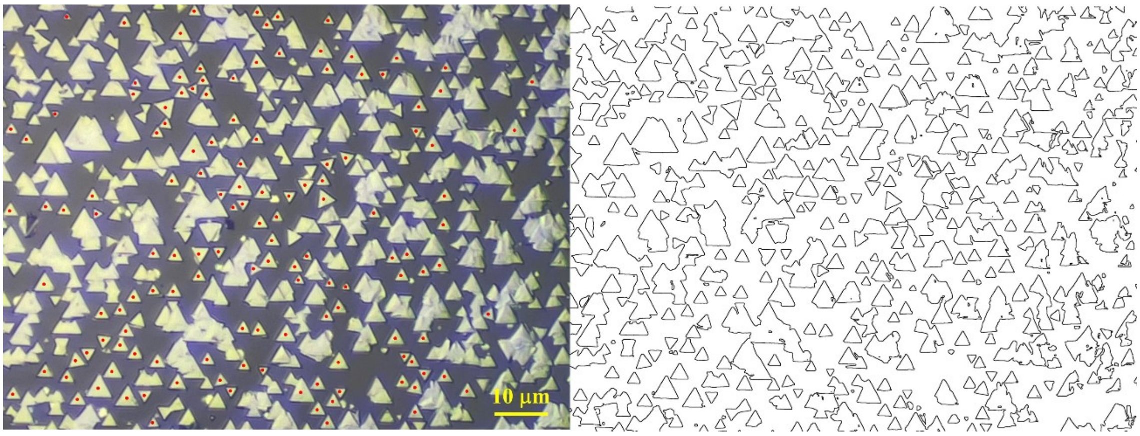


Fig. S6 (left) 136 selected triangular domains to make the orientation histogram in Figure 4(b) were marked with red circles. (right) Edges of the triangle domains were extracted using "Find Edges" function in imageJ (software). Theta (θ) illustrated in Fig. 4(b) was measured using a side within 0-60° of each triangle domain.

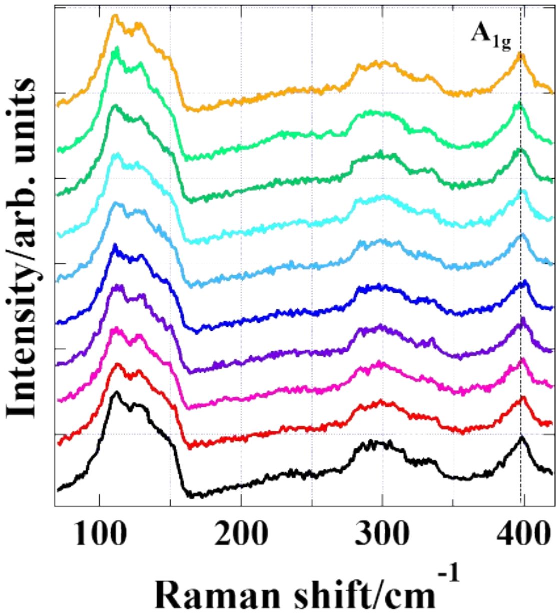


Fig. S7 The Raman spectra for the sample (iv) at ten different spots. A_{1g} peak centres are almost identical, showing the uniformity of the film.

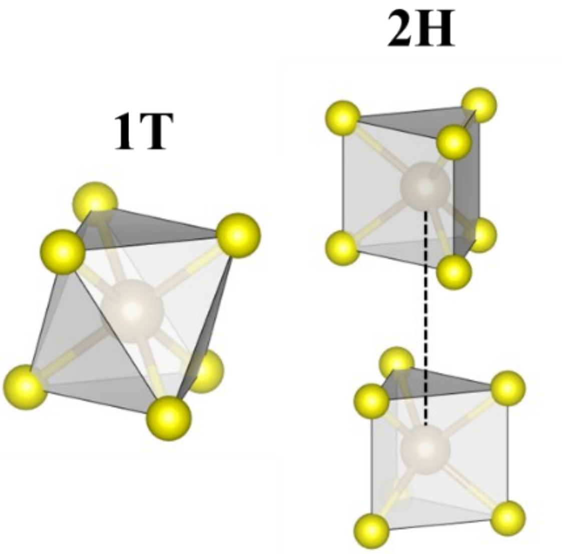


Fig. S8 The crystal structure of the 1T and 2H of TaS_2. Ta atoms of 1T and 2H phases consist of octahedral and trigonal prism coordination, respectively. Yellow and brown spheres represent S atoms and Ta atoms, respectively.

D_{3d}(-3m)	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$	linear functions /rotations	quadratic functions
A_{1g}	1	1	1	1	1	1	-	x^2+y^2, z^2
A_{2g}	1	1	-1	1	1	-1	R_z	-
E_g	2	-1	0	2	-1	0	(R_x, R_y)	(x^2-y^2, xy)(xy, yz)
A_{1u}	1	1	1	-1	-1	-1	-	-
A_{2u}	1	1	-1	-1	-1	1	z	-
E_u	2	-1	0	-2	1	0	(x, y)	-

D_{6h}(6/mmm)	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	linear functions /rotations	quadratic functions
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	-	x^2+y^2, z^2
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z	-
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	-	-
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1	-	-
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R_x, R_y)	(xy, yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0	-	(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-	-
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	-
B_{1u}	1	-1	1	-1	1	-1	1	1	-1	1	-1	1	-	-
B_{2u}	1	-1	1	-1	-1	1	1	1	-1	1	1	-1	-	-
E_{1u}	2	1	-1	-2	0	0	-1	-1	1	2	0	0	(x, y)	-
E_{2u}	2	-1	-1	2	0	0	1	1	1	-2	0	0	-	-

Table S2. Character tables for D_{3d} (upper one, 1T) and D_{6h} (lower one, 2H). Vibrational modes with a quadratic function are Raman active; otherwise not. Note that the crystal structure of the 1T phase at room temperature is distorted due to NCDW.

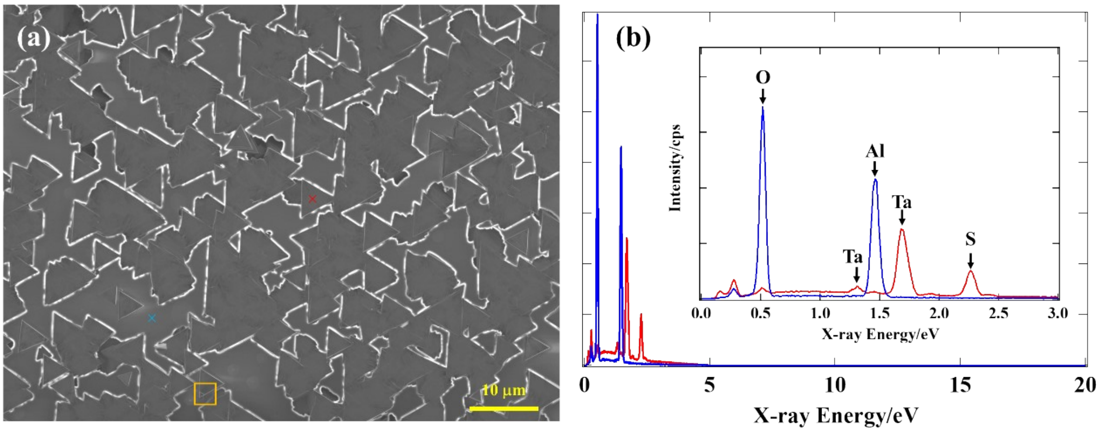


Fig. S9 (a) SEM image of sample (iv). (b) EDS analyses at the regions marked with red and blue crosses on SEM image. Ta and S were not detected in the region where triangular domains were absent. The orange rectangular region is expanded and shown in Fig. 8(a) of the main manuscript.

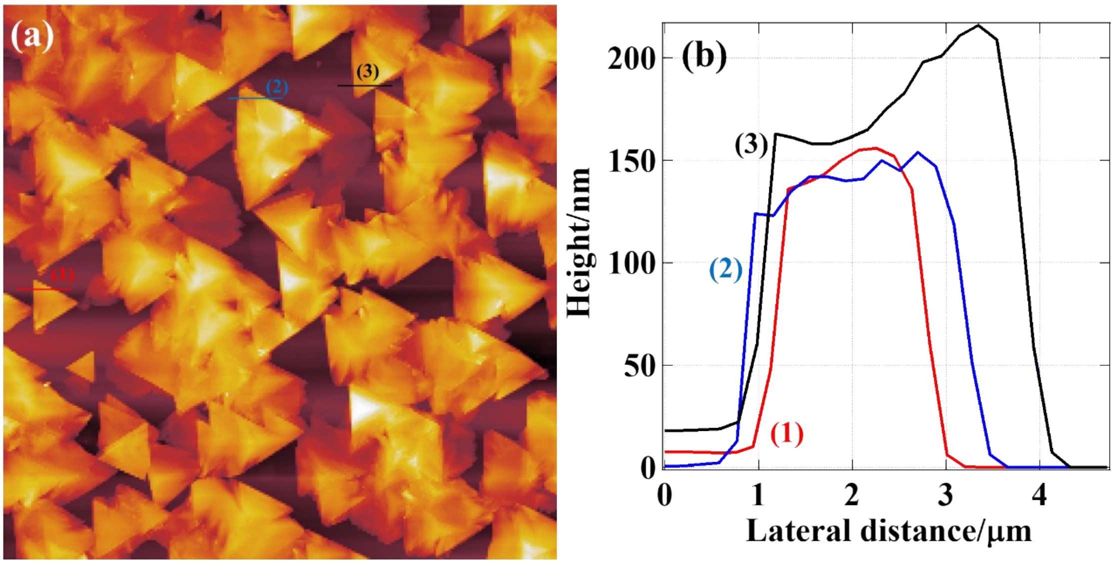


Fig. S10 (a) AFM image of sample (iv). (b) Hight profile of three selected lines (1)–(3) shown in (a). Average thickness of three is 154 nm.

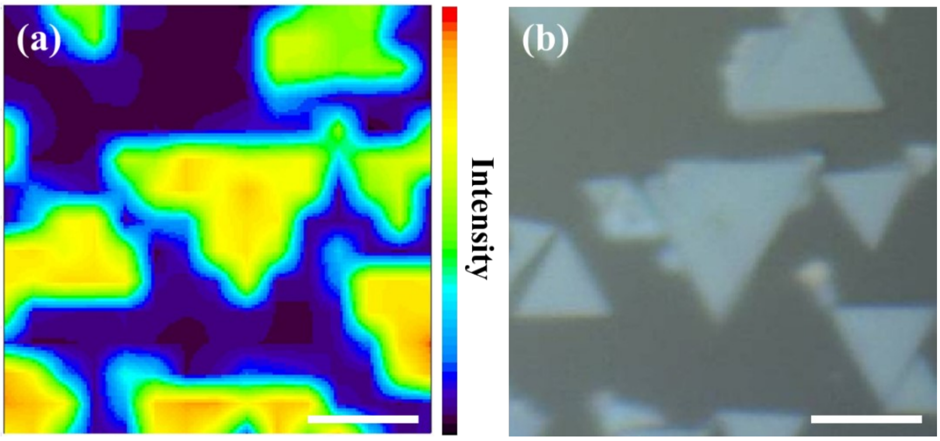


Fig. S11 (a) Raman mapping of the sample (iv). No TaS_2 signal was detected in the region without triangular domains. (b) The corresponding OM image of the Raman mapping. The scale bars represent 2.5 μm.

THERMODYNAMIC CALCULATIONS

Gibbs free energies of related reactions were calculated according to the following reactions and shown at the right side of the chemical formula.

Required Gibbs free energy of formation at 1200 K for each pure substance was tabled as below using reference S1.

Eq. 1 $TaCl_5(g) + 5/2H_2 + S_2 (g) \rightarrow TaS_2(s) + 5HCl(s)$ $\Delta_r G = -239.073$ kJ/mol

Eq. 2 $2TaCl_5(g) + 5H_2O(g) \rightarrow Ta_2O_5(s) + 10HCl(s)$ $\Delta_r G = -535.133$ kJ/mol

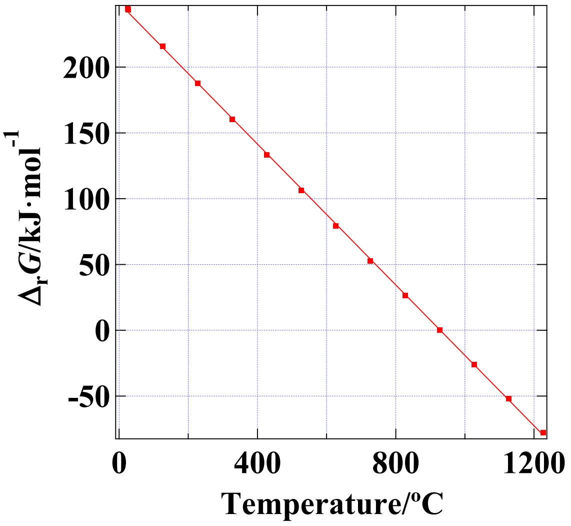
Eq. 3 $2TaCl_5(g) + 5/2O_2(s) \rightarrow Ta_2O_5(s) +5Cl_2(s)$ $D_r G = -577.257$ kJ/mol

	$\Delta_f G$ /kJ mol^{-1} at 1200 K
Tantalum pentachloride, $TaCl_5(g)$	-549.752
Tantalum disufide, $TaS_2(s)$	-278.700
Hydrogen chloride, HCl(g)	-102.025
Water, $H_2O(g)$	-181.572
Ditantalum pentaoxide, $Ta_2O_5(s)$	-1522.247

* $\Delta_f G$ of $TaS_2(s)$ at 1200 K was obtained by extrapolation due to the lack of data.

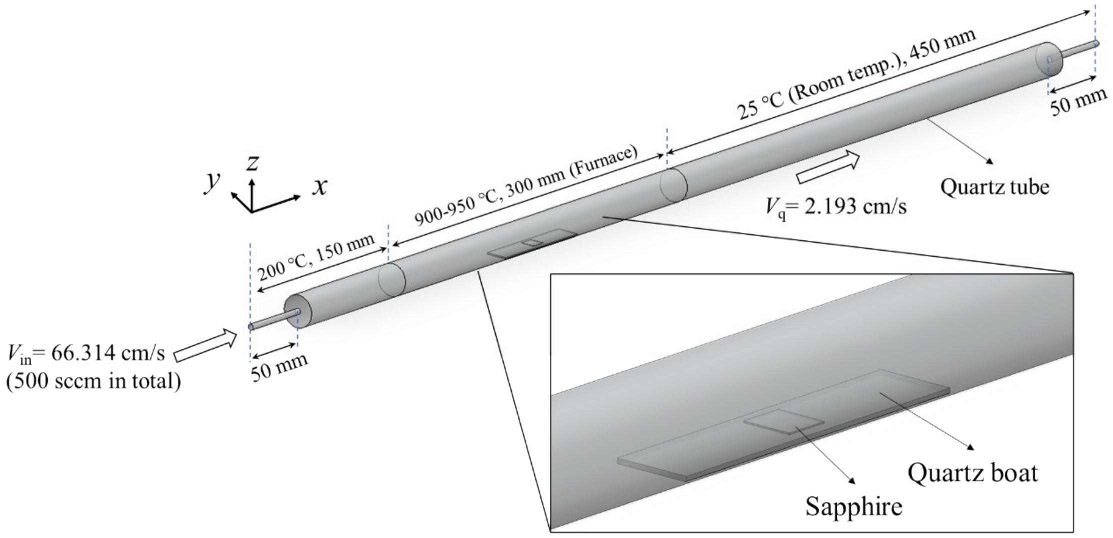
The temperature dependence of $\Delta_r G$ for the following reaction to form 1 mole of Ta_2O_5 was calculated as shown in the following figure. The data of the reference S1 was used for the calculation. The $\Delta_r G$ was fitted with a straight (solid) line. $\Delta_r G$ becomes negative at 928 °C that is close to the reaction temperature.

Eq. 4 $6TaCl_5(g) + 5Al_2O_3(s) \rightarrow 3Ta_2O_5(s) + 10AlCl_3(g)$



DETAILS OF CFD SIMULATIONS

In this study, a numerical simulation was performed using SCRYU/Tetra, a general-purpose three-dimensional thermo-fluid analysis system for unstructured grid systems, from Software Cradle. The governing equations are the normalized continuity and Navier–Stokes equations for incompressible flows and the heat transport equation. The fluid simulation was performed using a large eddy simulation, and the standard Smagorinsky model was used for the turbulence model. The gravitational acceleration was given as -9.8 m/s^2 in the z-axis direction. The number of grid points in the computational domain was approximately 35,620,000. The time step was set such that the Courant number (=$V_{\mathrm{in}}\Delta t/\Delta x$, where V_{in} is the inlet velocity, Δt is the time resolution, and Δx is the spatial resolution) for the inlet flow rate was less than 0.5. The velocity boundary condition for the inlet and outlet regions was the uniform velocity condition of V_{in} = 66.314 cm/s, corresponding to the average velocity at the quartz tube (V_{q}) of 2.193 cm/s (500 sccm in total). Besides, the pressure at the inlet and outlet was always static during simulations. In addition, a no-slip condition was applied to the surfaces of the CVD apparatus, sapphire, and quartz boat. The temperature boundary conditions inside the CVD apparatus were set at uniform temperatures of 200°C, 900°C, and 25°C in the ranges of 0–200mm, 200–500mm, and 500–950mm in the x direction from the inlet side, respectively. The detailed geometry, flow rate, and temperatures of the CVD apparatus for CFD simulations are shown below.



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(S1) Barin, I. I. Thermochemical Data of Pure Substances, Wiley-VCH, Weinheim **1995**. https://onlinelibrary.wiley.com/doi/book/10.1002/9783527619825.