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Ultrafast growth of high-quality monolayer WSe₂ on Au

*Yang Gao, Yi-Lun Hong, Li-Chang Yin, Zhangting Wu, Zhiqing Yang, Mao-Lin Chen, Zhibo Liu, Teng Ma, Dong-Ming Sun, Zhenhua Ni, Xiu-Liang Ma, Hui-Ming Cheng, and Wencai Ren**

Dr. Y. Gao^[†], Y. -L. Hong^[†], Dr. L. -C. Yin, Dr. Z. Q. Yang, M. -L. Chen, Z. B. Liu, Dr. T. Ma, Prof. D. -M. Sun, Prof. X. -L. Ma, Prof. H. -M. Cheng, Prof. W. C. Ren

Shenyang National Laboratory for Materials Science

Institute of Metal Research

Chinese Academy of Sciences

72 Wenhua Road, Shenyang 110016, P. R. China

E-mail: woren@imr.ac.cn

[†] These authors contributed equally to this work.

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Y. -L. Hong, M. -L. Chen

School of Materials Science and Engineering
University of Science and Technology of China
72 Wenhua Road, Shenyang 110016, P. R. China

Z. T. Wu, Prof. Z. H. Ni

Department of Physics
Southeast University
Nanjing 211189, P. R. China

Prof. H. -M. Cheng

Tsinghua-Berkeley Shenzhen Institute
Shenzhen 518055, P. R. China

We report the ultrafast growth of high-quality uniform monolayer WSe₂ with a growth rate of ~26 $\mu\text{m s}^{-1}$ by chemical vapour deposition on reusable Au substrate, which is ~2 – 3 orders magnitude faster than those of most 2D transition metal dichalcogenides grown on non-metal substrates. Such ultrafast growth allows for the fabrication of millimetre-size single-crystal WSe₂ domains in ~30 s and large-area continuous films in ~60 s. Importantly, the ultrafast grown WSe₂ shows excellent crystal quality and extraordinary electrical performance comparable to those of the mechanically exfoliated samples, with a high mobility of up to ~143 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and ON/OFF ratio up to 9×10^6 at room temperature. Density functional theory calculations reveal that the ultrafast growth of WSe₂ is due to the small energy barriers

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and exothermic characteristic for the diffusion and attachment of W and Se on the edges of WSe₂ on Au substrate.

Keywords: ultrafast growth, high quality, monolayer, WSe₂, chemical vapor deposition

Atomically thin two-dimensional (2D) layered materials, such as graphene, *h*-BN, transition metal dichalcogenides (TMDCs) and phosphorene, have been attracting increasing interests because of their unique properties and a wide range of promising applications.^[1-3] Compared with other methods such as micromechanical cleavage and liquid exfoliation, chemical vapour deposition (CVD) shows a great potential to grow large-area monolayer 2D materials, which are highly desired for electronic and optoelectronic applications.^[4-6] Crystal nucleation is known to be a quantum probability event, so the number of nuclei formed during the whole growth process should be proportional to the growth time.^[7] In addition, CVD is an energy-consuming process in terms of high reaction temperature, typically ~1,000 °C for graphene growth for instance.^[8] Therefore, ultrafast growth is not only beneficial for the

fabrication of large-area single crystals of 2D materials but also can greatly reduce the production cost by shortening growth time.

Very recently, several strategies have been developed to realize ultrafast growth of graphene on metal substrates by CVD.^[7, 9, 10] Increasing the feedstock concentration is a direct way to speed up the growth rate but usually leads to the formation of multi-layer graphene.^[10] Alternatively, lowering the energy barrier of the decomposition of carbon feedstock by optimizing the catalytic ability of the metal substrate is more promising. For instance, Xie *et al.* achieved a growth rate of $3.9 \mu\text{m s}^{-1}$ by using a $\text{Cu}_{85}\text{Ni}_{14}$ alloy with superior catalytic activity as growth substrate, and fabricated 1.5-inch single-crystal graphene domains in 2.5 h.^[9] Very recently, Xu *et al.* realized the ultrafast growth of graphene with an incredible growth rate of $60 \mu\text{m s}^{-1}$ by continuous introduction of oxygen to a Cu substrate, which allows the fabrication of single-crystal graphene domains with a lateral size of 0.3 mm in just 5 s.^[7] However, the ultrafast grown graphene shows an unsatisfactory quality.^[7]

Different from the catalytic growth of graphene on metal substrates, for TMDC growth, inert non-metal substrates such as SiO_2/Si and sapphire are usually used based on the van der Waals epitaxial mechanism.^[11-22] The poor catalytic activity of these substrates leads to a number of problems such as low growth rate, unsatisfactory quality and poor controllability on

the number of layers (Table S1 and S2). Although the growth rate can be increased by increasing the feedstock concentration or using a gas-phase promoter, typically it is still less than $0.5 \mu\text{m s}^{-1}$, which is significantly lower than that of ultrafast grown graphene.^[7, 9] In addition, the TMDCs obtained usually show carrier mobility smaller than $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and non-uniform thickness. Recently, Au has been used to grow monolayer to few-layer MoS_2 and uniform monolayer WS_2 , but the growth rate is also very low (less than $0.7 \mu\text{m s}^{-1}$) along with low carrier mobility.^[23-26]

Here we report the ultrafast catalytic growth of monolayer WSe_2 , a promising semiconducting TMDC for electronics and optoelectronics with very high theoretical mobility, with a growth rate of $\sim 26 \mu\text{m s}^{-1}$, by ambient-pressure CVD using Au foils as reusable substrate. This growth rate is $\sim 2 - 3$ orders of magnitude faster than those reported for most 2D TMDCs,^[11-22] even comparable to the reported highest rate of CVD-grown graphene,^[7] allowing the fabrication of millimetre-scale monolayer single-crystal WSe_2 domains in just 30 s. Importantly, the WSe_2 keeps strictly monolayer and very high quality during ultrafast growth process, showing a high mobility of up to $\sim 143 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and ON/OFF ratio up to 9×10^6 at room temperature, comparable to those of the mechanically exfoliated samples. Density functional theory (DFT) calculations reveal that such intriguing growth behaviour of WSe_2 is

due to the small energy barriers and exothermic characteristic for the diffusion and attachment of W and Se on the edges of WSe₂ on the Au substrate.

As described in Methods, **Figure 1** and Figure S1, monolayer WSe₂ was grown on highly annealed polycrystalline Au foils at 950 °C by ambient-pressure CVD using WO₃ powder and Se pellets as precursors. For detailed structure characterization and property measurements, after growth, the WSe₂ samples were transferred from Au foils onto arbitrary substrates such as SiO₂/Si and transmission electron microscopy (TEM) grid, by non-destructive electrochemical bubbling method (Methods and Figure S2), without sacrificing the Au substrate. This allows the repeated use of Au foils for WSe₂ growth (Figure S3). Figure 1a-d shows the structural evolution of WSe₂ domains on Au with a time interval of 10 s. It can be seen that all the domains show a regular triangular shape, which is a characteristic of single crystals of WSe₂. Similar to the growth of graphene and other 2D materials on metals,^[7, 23, 24, 26-31] the single-crystal WSe₂ domains can grow across the grain boundaries of Au substrates. We used a similar method to that proposed by Xu *et al.*^[7] to quantitatively analyse the growth rate of WSe₂ on Au. The time $t = 0$ s is defined as the moment when the triangle WSe₂ domains are big enough to be visualized easily by optical microscopy (~20 μm), and it is no more than 65 s later than the start of the reaction (Table S3). At time t , we stop WSe₂ growth

immediately by rapidly moving precursors and the Au substrate to low temperature. It is surprising to see that millimetre-sized triangular WSe₂ domains are formed within 30 s. To determine the growth rate of WSe₂, a large number of domains were measured for each time t , which show quite uniform size (Figure 1e and Table S4). As shown in Figure 1e, the average sizes of the WSe₂ domains show a linear relationship with time t , giving an average growth rate of $\sim 26 \mu\text{m s}^{-1}$. It is worth noting that this growth rate is $\sim 2 - 3$ orders of magnitude higher than those of monolayer TMDCs previously reported^[11-24, 26] (Figure 1f and Table S1), and comparable to the highest rate reported for the CVD-grown graphene^[7].

Importantly, WSe₂ keeps monolayer without adlayers formed during ultrafast growth on Au (Figure 1a-e and Figure S4), which is the second important feature of our method. As shown in Figure 1a-e and Figure S4a-c, the WSe₂ domains obtained with different time t have the same and uniform optical contrast. We used atomic force microscopy (AFM), high-resolution transmission electron microscopy (HRTEM), Raman and photoluminescence (PL) spectroscopy to further study the structure of the millimetre-sized WSe₂ domains that were grown with a rate of $\sim 26 \mu\text{m s}^{-1}$ and transferred onto SiO₂/Si substrates or TEM grids.^[24, 27] AFM measurements show that the WSe₂ has a uniform thickness of $\sim 0.75 \text{ nm}$ and average surface roughness of $\sim 0.3 \text{ nm}$ (Figure 2b and Figure S4d-f). Similar to the CVD-grown

graphene on metals such as Cu, Ni and Pt,^[8, 27, 32] our WSe₂ shows many wrinkles, which are formed due to the different thermal coefficient between WSe₂ and Au. The HRTEM image of the folded WSe₂ edge shows a single dark line (Figure 2c). The typical Raman spectrum shows a single E'_{2g} peak at ~250 cm⁻¹ and A'_{1g} peak at ~261 cm⁻¹, and is absence of B'_{2g} peak at ~304 - 307 cm⁻¹ (Figure 2d). The PL spectrum shows a single sharp peak at ~752 nm with a full-width at half-maximum of ~29 nm (Figure 2e), a characteristic of direct band gap semiconductors. Moreover, the Raman spectra taken from 20 random positions show the same feature in terms of peak position and intensity (Figure 2f). All these results indicate that the ultrafast grown WSe₂ domains on Au are uniform monolayers.^[17, 21, 22]

Figure 3a,b, respectively, shows an optical image (transmitting mode) and the corresponding selected area electron diffraction (SAED) pattern of an 800 μm WSe₂ domain transferred on a TEM grid. The SAED pattern shows two different families of spots, *i.e.* $\mathbf{k}_a = \{(\bar{1}100), (10\bar{1}0), (0\bar{1}10)\}$ and $\mathbf{k}_b = -\mathbf{k}_a$, which are transformed from the six $\{\bar{1}100\}$ diffraction spots in the six-fold bulk WSe₂ lattice due to symmetry breaking in monolayer (Figure S5). Moreover, the $\mathbf{k}_a$ spots are ~5 % brighter than $\mathbf{k}_b$ spots (Figure S6). These results indicate our WSe₂ has a hexagonal structure with three-fold symmetry, similar to other monolayer TMDCs such as MoS₂^[13] and WS₂^[24]. Figure 3c shows superimposed 20 SAED

patterns that were collected randomly in the triangular domain in Figure 3a. The perfect coincidence of these patterns confirms that the millimetre-sized triangular domain is a single crystal. More importantly, extensive atomic-resolution high-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM) observations show that our ultrafast grown monolayer WSe₂ single crystals have very high crystalline quality without defects and vacancies even over a large area (Figure 3d,e). Further analyses indicate that all the triangular monolayer WSe₂ domains have zigzag edges terminated with W or Se atoms (Figure 3f and Figure S7). The very high quality of WSe₂ is the third important feature of our growth method, and enables excellent electrical performance even in the case of the presence of wrinkles, the imperfect ohmic contact between WSe₂ and electrodes, and relatively large trap density between WSe₂ and SiO₂/Si substrate, as shown below.

To evaluate the electronic quality of our ultrafast grown monolayer WSe₂, we fabricated back-gate field effect transistors (BG-FETs) with electrochemical bubbling transferred WSe₂ domains on SiO₂/Si substrates (**Figure 4a**). All output and transfer characteristics were measured under ambient conditions at room temperature. The slight nonlinear output characteristic indicates an imperfect ohmic contact between the Au electrodes and WSe₂ samples (Figure 4b), and the transfer characteristic suggests that our WSe₂ is a typical p-type

doped semiconductor (Figure 4c). It can be seen that the off-current almost remains stable as the level of 10^{-11} A when changing V_{ds} (Figure 4c and Figure S8), which demonstrates that the source-drain current in our WSe₂ FETs can be shut down completely. The field-effect carrier mobility extracted from Figure 4c under V_{ds} of -1 V is $139 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and the corresponding ON/OFF current ratio is 9.2×10^6 . It is worth noting that this carrier mobility is higher than those of monolayer WSe₂ directly grown on SiO₂/Si substrates reported so far ($\sim 1 - 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[18-22] and comparable to those of mechanically exfoliated samples ($\sim 140 - 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)^[33-35] measured under similar conditions, and represents the highest value of the CVD-grown monolayer TMDCs (Figure 4d and Table S2). Extensive transport measurements show that our samples are very uniform and have carrier mobilities ranging from $\sim 100 - 150 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and ON/OFF current ratios ranging from $2 \times 10^6 - 9 \times 10^6$ (Table S5). Moreover, there is no domain size dependence in carrier mobilities (Table S5). These results further confirm the uniform high quality of our ultrafast grown monolayer WSe₂, implying their potential applications in electronics and optoelectronics. However, due to the inevitable contaminations at the interface between WSe₂ and SiO₂/Si substrate generated during the transfer process, the interface trap density ($3.58 \times 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$) extracted based on our device (see Methods) is a bit larger than those reported previously based on CVD grown WSe₂ on SiO₂/Si substrate.^[36, 37] There are more works need to do in the future,

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including reducing the polymer residues and interfacial contaminations generated during transfer, improving the contact between WSe₂ and electrodes, and optimizing the FET structure, to further improve the performance of WSe₂ devices.

In our experiments, we found that the feeding rate of precursors and the growth temperature play key roles in the ultrafast growth of WSe₂ (**Figure 5a,b** and **Figure S9**). The WO₃ was placed at a high temperature zone close to the Au substrate, which ensures sufficient W feeding. The Se pellet was placed at a low temperature zone and its feeding rate was controlled by the heating temperature (**Table S6, 7**). As shown in **Figure 5a**, the growth rate increases dramatically with increasing the feeding rate of Se (FR_{Se}) but no longer increases after a certain value. The maximum growth rate obtained at 800 °C is $\sim 8.3 \mu\text{m s}^{-1}$. The growth rate can be further increased by increasing growth temperature (T_1), and the influence of the growth temperature shows a similar trend with the influence of FR_{Se} (**Figure 5b**). It increases significantly before 900 °C and then the increase rate slows down and becomes almost saturate at 950 °C. Therefore, the ultrahigh growth rate of $\sim 26 \mu\text{m s}^{-1}$ was achieved at a high growth temperature (950 °C) with a high FR_{Se} (55 sccm). The linear relationship between the growth rate and time t in all cases suggests that the feeding of Se and W precursors is sufficient. We also tried to grow monolayer WSe₂ on SiO₂/Si substrate

using the conditions that were used for the Au substrate. However, even under the conditions (800 °C, $FR_{Se} \sim 1.4$ sccm) corresponding to a very low growth rate of $\sim 0.26 \mu\text{m s}^{-1}$ on Au, only small particles and thick triangular flakes of WSe_2 were obtained (Figure S10a-c), indicating the overfeeding of precursors. Moreover, with increasing the growth temperature and FR_{Se} , no big change of growth rate was observed except for thickening (Figure S10d-f). The above results indicate that, in the case of sufficient feeding of Se and W sources, Se and W prefer to attach onto the edges of monolayer WSe_2 on Au substrate rather than onto its surface as on the commonly used SiO_2/Si substrates.

In order to further understand the role of Au in the ultrafast growth of monolayer WSe_2 , we carried out DFT calculations to simulate the WSe_2 growth on Au (Figure 5c-f). The electron backscatter diffraction (EBSD) measurements show that the crystalline orientation of the Au surface used in our experiments is (111) dominated (Figure S11). Therefore, we used Au(111) as the substrate in our DFT calculations. Considering the low sublimation temperature (melting point, ~ 220 °C) of elemental Se and the observed rapid growth of WSe_2 on Au substrates, it is reasonable to take very small Se and W clusters (for example, dimer), or Se and W atoms as the most possible Se and W sources, respectively, during the ultrafast

growth of WSe_2 . Here, we first studied the adsorption and diffusion behaviour of Se_2 and W_2 dimer on $\text{Au}(111)$ surface.

Calculation results show that the chemisorption of the Se_2 dimer on $\text{Au}(111)$ surface is a highly exothermic process with a large chemisorption energy of ~ 2.39 eV. Due to the elongated Se-Se bond length ($2.44 \text{ \AA}$), the Se_2 dimer then spontaneously dissociates into two isolated Se atoms without any obvious barrier (Figure S12). The highest barrier for the diffusion of Se atoms on $\text{Au}(111)$ surface was calculated to be 0.36 eV, and therefore Se prefers to take an atomic rather than a dimer form (Figure S12). In contrast, W energetically prefers to take a dimer form on $\text{Au}(111)$ surface, with a total energy about 3.11 eV lower than that of two isolated W atoms. As shown above, the ultrafast grown WSe_2 domains are zigzag edged (Figure 3f and Figure S7). Therefore, we simply considered the attachment of a Se atom to the zigzag edge of a triangular WSe_2 cluster with one Se vacancy firstly, then the attachment of a W_2 dimer to the zigzag edge of a triangular WSe_2 cluster, as the growth process of WSe_2 on $\text{Au}(111)$ surface. As shown in Figure 5c, e, the diffusion of a Se atom and its attachment to the zigzag edge of a WSe_2 cluster on $\text{Au}(111)$ surface is an exothermic reaction with an energy decrease of 0.88 eV and two small energy barriers (0.27 and 0.32 eV). Similarly, the attachment of a W_2 dimer at the zigzag edge of a WSe_2 cluster is also an

exothermic reaction (Figure 5d, f), with a large energy decrease of 3.12 eV and two moderate energy barriers (0.55 and 0.54 eV). The above results suggest that the diffusion and attachment of W_2 and Se are not the rate-limiting process for WSe_2 growth on Au, and therefore ultrafast growth of monolayer WSe_2 can be achieved by quick supply of W and Se sources in the case of high feeding rates of Se and W precursors and high growth temperature (Figure 5a, b). When the growth front of WSe_2 meets the grain boundary of Au substrate, the exothermic characteristic for the attachment of W and Se onto the edges of WSe_2 can work as a strong driving force for the continuous growth of WSe_2 film to step across the grain boundary of Au substrate (Figure 1a-d).

The ultrafast growth of high-quality uniform monolayer WSe_2 on reusable Au substrates and its non-destructive transfer pave a way for various applications, especially in next-generation electronics and optoelectronics. First, the ultrafast growth enables the fabrication of continuous monolayer WSe_2 films within $t \sim 60$ s (Figure S13), which greatly reduce the production cost. In contrast, no continuous monolayer WSe_2 films have been reported on SiO_2/Si substrates. More importantly, similar to the monolayer WS_2 grown on Au,^[24] the good flexibility and chemically inert of Au foils allow that this film can be transferred onto flexible substrates such as PET and PEN by using the roll-to-roll bubbling method for

flexible device applications. Second, the ultrafast growth effectively reduces the probability of nucleation event because of the greatly reduced growth time (Figure S14), which is beneficial for the fabrication of large-area single-crystal monolayer WSe₂ domains. In contrast, the nucleation density is much larger and the size of the single-crystal WSe₂ obtained is much smaller in the case of lower growth rate (Figure S14). We believe that inch-sized high-quality single-crystal monolayer WSe₂ could be fabricated within minutes with the development of nucleation-control strategies as the case of graphene.

In summary, we have demonstrated the ultrafast growth of high-quality uniform monolayer WSe₂ by CVD using Au as a reusable substrate. We synthesized millimetre-size single-crystal WSe₂ domains in just ~30 s with a growth rate of ~26 $\mu\text{m s}^{-1}$, which is ~2 - 3 orders of magnitude faster than those reported for most 2D TMDCs. DFT calculations reveal that the ultrafast growth of WSe₂ is due to the small energy barriers and exothermic characteristic for the diffusion and attachment of W and Se on the edges of WSe₂ on the Au substrate. Moreover, the ultrafast grown materials show excellent crystal quality and extraordinary electrical properties comparable to those of exfoliated samples. These findings provide important information for the large-scale production of large-area single crystals and continuous films of high-quality monolayer WSe₂ at a low cost, and pave the way for their

applications in next-generation electronics and optoelectronics.

Experimental Section

Ultrafast CVD growth of monolayer WSe₂ on Au foils: We grew monolayer WSe₂ on Au foil by ambient-pressure CVD. As shown in Figure S1, a piece of polycrystalline Au foil (99.95 wt %, 100 μm thick, $2 \times 1 \text{ cm}^2$ size, Alfa Aesar) was finely polished and annealed at 1,040 $^{\circ}\text{C}$ for over 10 h to reduce its surface roughness before the first use, and then placed in a small quartz boat (Boat 1) together with 100 mg WO₃ powder (99.998 wt %, Alfa Aesar) upstream, loaded at the reaction zone (Zone 1) of a horizontal CVD furnace equipped with 1-inch-diameter quartz tube. Another small quartz boat (Boat 2) containing 1,000 mg Se pellets (99.99 wt %, Sigma Aldrich) was placed upstream at the low temperature zone of the furnace (Zone 2), where the temperature (T_2) was controlled by the temperature of Zone 1 (T_1) and the distance between Se and Au substrate ($D_{\text{Se-Au}} = 15 - 18 \text{ cm}$; Table S6). The Au substrate was first heated to 800 - 950 $^{\circ}\text{C}$ in ultrahigh-purity Ar atmosphere (100 sccm), and then annealed for 2 min to remove organics absorbed on its surface. Although Se and WO₃ have been evaporated in this case, no WSe₂ was formed at all (Figure S15). Then we introduced a small flow rate of H₂ (0.5 - 1 sccm) to initiate WSe₂ growth (Figure S15), since H₂

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can reduce WO_3 to provide a sufficient amount of WO_{3-x} , which is widely believed to be the active precursor for the growth of WSe_2 .^[11] After CVD growth for a certain time (30 s for millimetre-size single-crystal WSe_2 growth at 950 °C), we rapidly stopped the growth by quickly moving the two boats to low-temperature zone. The flow rates of the mixed gas flow remained constant during the growth and cooling processes (H_2 , 0.5 - 1 sccm; Ar, 100 sccm). Note that there is nearly no change in the growth rate when varying the flow rate of H_2 (Figure S16), which further confirms sufficient W feeding.

Characterization: The morphology and size of the WSe_2 domains were characterized using an optical microscope (Nikon Eclipse LV100D), and their thickness were measured using an AFM (Bruker's Dimension Icon AFM System). EBSD measurements were performed with a scanning electron microscope (SEM, Nova NanoSEM 430, operating at 20 kV and 6 nA). BF-TEM imaging and SAED measurements were performed on a TEM operating at 120 kV (FEI Tecnai T12); HRTEM imaging was performed on a field-emission TEM (FEI Tecnai F20) operating at 200 kV; HAADF-STEM imaging was performed on an aberration-corrected and monochromated TEM (Nion UltraSTEM 100) operating at 60 kV. Raman and PL spectra were collected with a confocal Raman spectrometer (Jobin Yvon LabRAM HR800) using a 532 nm

laser as the excitation source. The laser spot was $\sim 1 \mu\text{m}$ and the laser power on the sample surface was kept below $30 \mu\text{W}$ to avoid any heating effects.

Device fabrication, electrical property measurements and related calculations: To investigate the electrical properties of the monolayer WSe_2 , BG-FETs were fabricated with an electron-beam-free transfer method on Si substrates with 285 nm SiO_2 dielectric to minimum the damage introduced during the fabrication process.^[35] First, we used the electrochemical bubbling method to transfer monolayer WSe_2 from Au onto SiO_2/Si wafers.^[24, 27] Then, the 100-nm -thick Au source and drain electrodes were fabricated onto the monolayer WSe_2 by using a micromanipulator. After that, the BG-FET devices were annealed in vacuum at 130°C for 2 h . The electrical properties of these devices were measured using a semiconductor analyser (Keithley 2612) under ambient conditions at room temperature.

The trap density was calculated by the following formula^[38] :

$$SS = \left(1 + \frac{C_s + C_{it}}{C_{ox}} \right) \frac{kT}{q} \ln 10$$

where SS is the subthreshold swing of 2.9 V/dec obtained from the transfer characteristics in Figure 4c, C_s is the capacitance in the WSe_2 conducting channel, $C_{it} = qD_{it}$ is the capacitance owing to interface trap density D_{it} and $C_{ox} = \epsilon_{ox}/t_{ox}$ is the oxide capacitance, here, q , ϵ_{ox} and t_{ox}

is 1.6×10^{-19} C, 3.452×10^{-11} F/m and 285 nm, respectively. The semiconductor capacitance is negligible in the deep-subthreshold region.

DFT calculations: The first-principles calculations were performed by using the Vienna *Ab-initio* Simulation Package^[39] with the projector augmented wave method^[40]. The Perdew-Burke-Ernzerhof functional^[41] for the exchange-correlation term was used for all calculations. The projector augmented wave method was used at a plane-wave cutoff of 400 eV to describe the electron-ion interaction.

In this work, the Au(111) surface was modelled by periodically repeated slab consisting of five Au atom layers for dissociated adsorption of Se₂ dimer, and surface diffusion of Se atom and W₂ dimer. In order to simulate the growth of WSe₂ on Au surface, a Au(111) surface with three Au atom layers was constructed, on which a triangle WSe₂ cluster (W₁₀Se₂₄H₆) with three Se-terminated zigzag edges was placed and each vertex W atom was saturated by two H atoms. The thickness of vacuum layer was set to be 15 Å in both cases. Only the Gamma point was used due to large supercell of the Au(111) surface and the Au atoms in the bottom layer were fixed for all calculations, whereas the rest of the atoms were allowed to fully relax during geometry optimization with the convergence criteria of 1×10^{-6} eV in total free energy.

In order to achieve the minimum energy paths for Se₂ dissociation, diffusion of Se atom and W₂ dimer, and attachments of Se atom and W₂ dimer at the edges of a triangle WSe₂ cluster on Au(111) surface, we employed the climbing image nudged elastic band method,^[42] and the convergence tolerance of force on each atom for searching minimum energy path was set to be 0.05 eV Å⁻¹.

Supporting Information

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

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Figure 1. a-d) Typical optical images of single-crystal monolayer WSe₂ domains grown on a Au foil at time $t = 0$ s (a), 10 s (b), 20 s (c), and 30 s (d). e) Edge length of single-crystal monolayer WSe₂ domains as a function of time t with a linear fit, giving an average growth rate of $\sim 26 \mu\text{m s}^{-1}$. The error bars represent the edge length variations of the monolayer WSe₂ domains obtained at the same t (Table S4). f) Comparison of the growth rates of our monolayer WSe₂ on Au and those monolayer TMDCs reported in the literature.^[11-24,26]

Figure

2. a) Optical image of a 430 μm WSe₂ triangle domain transferred on a SiO₂/Si substrate. b) AFM image of the WSe₂ domain in a, showing a thickness of 0.729 nm. c) BF-TEM image of a folded edge of a WSe₂ domain transferred on a TEM grid. d,e) Typical Raman (d) and PL (e) spectrum taken from the sample in (a). f) Raman spectra randomly taken from 20 positions in the domain shown in (a).

Figure

3. a) Optical image of an 800 μm single-crystal WSe_2 domain transferred on a TEM grid (orange colour area). b) Typical SAED pattern of the sample in (a). c) Superimposed image of 20 coloured SAED patterns randomly collected from 20 different areas across the WSe_2 sample in (a). d,e) Low-magnification (d) and high-magnification (e) HAADF-STEM images of the inner area of the WSe_2 domain in (a). f) BF-TEM image of an unfolded edge from the

WSe₂ domain in (a). The inset is the corresponding HAADF-STEM image. The bright spots in (d-f) correspond to W atoms, and the dim spots correspond to the two stacked Se atoms.

Figure 4. a) Schematic of the monolayer WSe₂-based BG-FET. b,c) Room-temperature output (b) and transfer (c) characteristics of a monolayer WSe₂ BG-FET on a SiO₂/Si substrate (inset in c). The current-voltage curves with different gate voltages from 0 to -100 V in steps of 10 V and the nonlinear curve indicates a Schottky barrier between the electrodes and WSe₂. The carrier mobility and the

corresponding current ON/OFF ratio extracted from (c) are $139 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 9.2×10^6 , respectively.

d) Comparison of the carrier mobilities of our ultrafast grown monolayer WSe_2 and the monolayer TMDCs reported in the literatures measured with similar device structure at room temperature (Table S2). The error bar shows the variation of the mobilities of our monolayer WSe_2 (Table S5).

Figure

5. a) Influence of the feeding rate of Se (FR_{Se}) on the growth rate of WSe₂ at 800 °C. The growth rate is $\sim 0.26 \mu\text{m s}^{-1}$ for $FR_{Se} = 1.4 \text{ sccm}$, $\sim 2.3 \mu\text{m s}^{-1}$ for $FR_{Se} = 7.5 \text{ sccm}$, $\sim 7.6 \mu\text{m s}^{-1}$ for $FR_{Se} = 42.4 \text{ sccm}$, and $\sim 8.3 \mu\text{m s}^{-1}$ for $FR_{Se} = 65 \text{ sccm}$. b) Influence of the growth

temperature (T_1) on the growth rate of WSe_2 . The growth rate is $\sim 8.3 \mu\text{m s}^{-1}$ for $T_1 = 800^\circ\text{C}$ and $FR_{\text{Se}} = 65 \text{ sccm}$, $\sim 11 \mu\text{m s}^{-1}$ for $T_1 = 850^\circ\text{C}$ and $FR_{\text{Se}} = 58.2 \text{ sccm}$, $\sim 23 \mu\text{m s}^{-1}$ for $T_1 = 900^\circ\text{C}$ and $FR_{\text{Se}} = 88.2 \text{ sccm}$, and $\sim 26 \mu\text{m s}^{-1}$ for $T_1 = 950^\circ\text{C}$ and $FR_{\text{Se}} = 55 \text{ sccm}$. c,d) Calculated minimum energy path for the attachment of a Se atom to the zigzag edge of a WSe_2 cluster with one Se vacancy on Au(111) surface (c) and for the attachment of a W_2 dimer to the zigzag edge of a WSe_2 cluster on Au(111) surface (d). e,f) The schematic structures corresponding to the different states in (c) and (d), respectively. IS, initial state; TS1, transition state 1; LS, local state, TS2, transition state 2; FS, final state. The Au atoms in the 1st, 2nd, and 3rd top layers are represented by yellow, light blue, and green balls, respectively. The H, Se, and W atoms are represented by white, red, and grey balls, respectively.

Ultrafast growth of high-quality uniform monolayer WSe_2 is achieved by chemical vapour deposition using Au as a reusable substrate. The growth rate is $\sim 2 - 3$ orders of magnitude faster than those reported due to the small energy barriers and exothermic characteristic, and the materials show excellent crystal quality and extraordinary electrical properties comparable to those of exfoliated samples.

ultrafast growth, high quality, monolayer, WSe₂, chemical vapor deposition

Y. Gao, Y. -L. Hong, L. -C. Yin, Z. T. Wu, Z. Q. Yang, M. -L. Chen, Z. B. Liu, T. Ma, D. -M.

Sun, Z. H. Ni, X. -L. Ma, H. -M. Cheng, and W. C. Ren*

Ultrafast growth of high-quality monolayer WSe₂ on Au

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Author/s:

Gao, Y;Hong, Y-L;Yin, L-C;Wu, Z;Yang, Z;Chen, M-L;Liu, Z;Ma, T;Sun, D-M;Ni, Z;Ma, X-L;Cheng, H-M;Ren, W

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