Patterning two-dimensional materials into specific spatial arrangements and geometries is essential for both fundamental studies of materials and practical applications in electronics. However, the currently available patterning methods generally require etching steps that rely on complicated and expensive procedures. We report here a facile patterning method for atomically thin MoSe$_2$ films using stripping with an SU-8 negative resist layer exposed to electron beam lithography. Additional steps of chemical and physical etching were not necessary in this SU-8 patterning method. The SU-8 patterning was used to define a ribbon channel from a field effect transistor of MoSe$_2$ film, which was grown by chemical vapor deposition. The narrowing of the conduction channel area with SU-8 patterning was crucial in suppressing the leakage current within the device, thereby allowing a more accurate interpretation of the electrical characterization results from the sample. An electrical transport study, enabled by the SU-8 patterning, showed a variable range hopping behavior at high temperatures.

1. Introduction

Layered two-dimensional (2D) materials such as graphene and the transition metal dichalcogenides (TMDs, e.g. MoS$_2$, WS$_2$ and WSe$_2$) have attracted significant interest as a result of their interesting electronic and optical properties.$^{1-3}$ To make use of these unique material properties in practical applications, we need to be able to produce these materials in a scalable manner. Chemical vapor deposition (CVD)$^4$-$^7$ and liquid exfoliation$^8$ have been reported to produce layered TMD films with promisingly large areas and at high production rates. The next crucial step in the manufacture of these 2D materials into devices and systems for various electrical studies and applications is the patterning of the films into specific spatial arrangements and geometries. However, the absence of dangling bonds on the surface of 2D TMDs results in a variable range hopping behavior at high temperatures.

Several experimental procedures have been used to pattern TMDs and most of these have been demonstrated using MoS$_2$. At present, the patterning of TMDs is usually carried out via lithography and a dry etching process with reactive gases (e.g. SF$_6$ and XeF$_4$). However, reactive ion etching requires multi-step procedures (including both lithography and the etching process itself) and involve highly specialized equipment. Plasma etching that spatters the 2D materials using ion bombardment has also been reported, but sample removal may not be thorough using this technique because the process does not produce volatile by-products and is prone to redeposition. A thinning method using a laser beam has also been introduced, but this method may not be scalable because direct laser writing is required. Other thinning methods, such as thermal annealing, are ineffective for patterning that is targeted to a confined area. Top-down patterning has also been reported; this incorporates stamping approaches and, although an ordered pattern can be achieved, the sample may have a large variability in layer thickness, unlike CVD synthesis which can produce very thin layers in a controlled manner.

We report here a patterning method on a layered 2D film using SU-8 negative resist as a stripping layer. The 2D film is first spin-coated with SU-8 and then the region of SU-8 exposed by electron beam lithography (EBL) can be used to strip the film beneath it. The patterning method with SU-8 requires neither chemical nor physical etching steps. The SU-8 patterning is therefore simpler than the currently available patterning methods for 2D materials, incurring potential economic advantages in industrial-scale fabrication. Our approach
also minimizes the possibility of affecting the pre-existing structure or device on the sample compared with other ion etching methods.

As a case study, we have demonstrated SU-8 patterning on an MoSe$_2$ film grown by CVD. The patterning is effective for the atomically thin samples that we produce, which can be primarily controlled to thicknesses of 1–6 layers. We have also fabricated devices from a patterned CVD MoSe$_2$ ribbon channel as a field-effect transistor (FET) to study the electrical transport properties of MoSe$_2$ produced by CVD. Although MoS$_2$ and MoSe$_2$ are both layered TMD crystals, the much lower natural abundance of MoSe$_2$ causes the studies on MoSe$_2$ to be less common than those on MoS$_2$. With the recent emergence of CVD synthesis for the production of atomically thin MoSe$_2$ over large areas, it is now important to investigate the electrical transport properties of MoSe$_2$. SU-8 patterning enables the fabrication of well-defined channels in the MoSe$_2$ film that minimize the leakage current, thus allowing the electrical characterization results to be accurately interpreted.

2. Experimental

2.1 Sample preparation

Large area atomically thin MoSe$_2$ films (~1 cm$^2$) were synthesized on highly p-doped Si substrates with 100 nm thick SiO$_2$ (University Wafers, Prime grade) using CVD. The fabrication and patterning of the MoSe$_2$ devices were carried out using EBL (a JEOL JSM-7001F instrument equipped with a Deben beam blanker and Nanometer Pattern Generation System) at an acceleration voltage of 30 kV. The contact was 50 nm of Ni in all the devices. Negative epoxy-based SU-8 2002 (MicroChem) was used in all the SU-8 patterning. SU-8 was spin-coated on the sample at 4000 rev min$^{-1}$ for 40 s and then soft-baked on a hot-plate at 65 °C for 1 min, followed by another 1 min at 95 °C. After the EBL exposure the sample was immersed in SU-8 developer (MicroChem) for 1 min, baked post-exposure at 95 °C for 1 min, immersed in Remover PG (MicroChem) at ~65 °C for 10–30 min to remove the SU-8 pattern and then blow-dried with an N$_2$ flow.

2.2 Characterization

The samples were characterized by scanning electron microscopy (SEM; JEOL JSM-7001F) and tapping mode atomic force microscopy (AFM; Veeco Dimension V). SEM was performed with a 5 kV acceleration voltage in the top view by detecting the secondary electron emission from the sample. Raman spectra were obtained on a triple-grating micro-Raman spectrometer (Horiba-JY T64000). All the samples were excited with a 532 nm laser. The signal was collected through a 100× objective, dispersed with a 1800 g mm$^{-1}$ grating, and detected using a charge-coupled device cooled by liquid N$_2$. Raman mapping was performed with a Renishaw InVia Raman system using 532 nm laser excitation. The device measurements were made on a probe station (Lakeshore) connected to a current pre-amplifier and controlled by a Semiconductor Device Analyzer (Keithley). The electrical measurements were made at several temperatures between 350 and 83 K, with pressure $<$10$^{-5}$ mbar.

3. Results and discussion

3.1 Patterning of atomically thin MoSe$_2$ film with SU-8

Fig. 1 illustrates schematically the process of patterning with SU-8. Briefly, after the synthesis of the large area and atomically thin MoSe$_2$ film with CVD on an SiO$_2$/Si substrate, the SU-8 solution was spin-coated and soft-baked on top of the sample. As SU-8 is a negative resist, EBL was used to expose the area of the SU-8 layer in a defined shape and size that remained on the sample after the resist development step. The developed SU-8 structure carries the MoSe$_2$ layer along beneath it on removal of the SU-8 layer with the Remover PG solvent. Thus the MoSe$_2$ film is removed in an area, the shape of which corresponds to the SU-8 area exposed during the EBL process.

Fig. 2a and 2b show the fabrication process for an array of hexagons opening from the MoSe$_2$ film grown by CVD as seen using optical microscopy. The color contrast between the MoSe$_2$ film and the exposed SiO$_2$ substrate is not immediately distinguishable since the film thickness is only within a few nanometers. Fig. 2c shows the same sample area under SEM, where the difference in the yield of the secondary electron emission signal from the MoSe$_2$ film and SiO$_2$ substrate is sufficient to produce an image with a visible difference in contrast. The MoSe$_2$ under the SU-8 regions not exposed by EBL is not noticeably changed by the patterning (Fig. S2†).

To corroborate the success of the SU-8 patterning, we compared the Raman spectra collected from the area from which MoSe$_2$ was removed with that from the layer where MoSe$_2$ remained (Fig. 2d). Raman spectroscopy is a reliable tool to characterize the presence of atomically thin TMDs as phonon frequencies are not only sensitive to the materials being studied, but are also rich in information with which to probe interlayer coupling and layer thickness. The micro-Raman setup also allows signal collection from only the local area where the MoSe$_2$ film has been removed. The Raman signatures of MoSe$_2$ were identified from the remaining layer, in which the signal from the out-of-plane A$_{1g}$ mode was particu-
larly intense. These Raman modes were not seen in the spectrum of the area from which MoSe₂ had been removed. The mapping of the Raman intensity of the A₁g mode (241 cm⁻¹; Fig. 2e) shows that the MoSe₂ layer was removed by the SU-8 patterning method (AFM; Fig. 2f) at the boundary of the removed area on a similarly patterned sample, which verifies that the patterning can result in the clean removal of 2D materials with a relatively sharp edge. Interestingly, we did not observe redeposition issues with SU-8 patterning, unlike with the etching methods that rely on purely physical means (Fig. S3†).

We attribute the mechanism behind the removal of MoSe₂ by SU-8 patterning to the adhesion between the exposed SU-8 and the MoSe₂ film. As long as the adhesion between the MoSe₂ film and SU-8 is sufficiently stronger than the adhesion between the MoSe₂ film and the SiO₂ substrate, the MoSe₂ will be removed when the SU-8 is dissolved. In addition, the adhesion of the films to the SiO₂ layer is generally difficult; to achieve good adhesion, an intermediate layer that can be oxidized (e.g., Cr, Ti) is needed to block the transport of oxygen from within the SiO₂ to the interface. As MoSe₂ does not oxidize rapidly in air, the adhesion between MoSe₂ and SiO₂ is relatively weak and therefore the SU-8 layer can be used to peel the MoSe₂ film off from the SiO₂.²³

Similar to most other negative resists, exposure to EBL and post-exposure baking cause the SU-8 polymer to be highly cross-linked and more rigid. The rigidity of the exposed SU-8 structure helps to improve the conformal contact with the area of MoSe₂ below the SU-8, ensuring that the MoSe₂ layer is uniformly stripped from the substrate as a single unit – as opposed to being dissolved in smaller patches – for the complete removal of the MoSe₂ along with the SU-8 stripping. Given the inertness of the (0001) plane of MoSe₂, we do not assume that there are any unique chemical bonds between SU-8 and MoSe₂ that allow the patterning. Consistent with our assumption, we observed that the patterning approach is not unique to SU-8; we found that patterning can be achieved using a metal sacrificial layer which strips the MoSe₂ film when the metal is etched (Fig. S1†). SU-8 patterning can also be used to remove MoS₂ flakes produced on SiO₂ by the exfoliation method (Fig. S4†). It is conceivable that similar methods could be developed using other lithography resist polymers. However, the inability of other EBL resists, such as polymethyl methacrylate (PMMA), to be used as the stripping layer for patterning was attributed to the poorer adhesion between PMMA and MoSe₂.

With respect to the adhesion mechanism of the removal, we believe that the SU-8 patterning method will be especially useful for layered material samples with small grains. When the grain size of MoSe₂ is smaller than the feature size of the SU-8 pattern, the presence of the grains will help to ensure that the film will break following the shape of the SU-8. Thus we believe that the SU-8 patterning method will have important applications in layered material films produced from processes such as liquid phase exfoliation⁸ and certain CVD synthesis approaches.⁶¹⁷

3.2 Device applications
An immediate application of the SU-8 patterning is to define a conduction channel for electrical characterization. We patterned
oxide, may form due to imperfections in the production of the substrate, the high temperature during sample synthesis (as also observed for the MoS$_2$ FET grown by CVD) or during the device fabrication and processing steps. The creation of oxide defects is particularly problematic as it generally creates reliability issues, such as a short circuit of the back gate with source/drain electrodes. Before patterning, the MoSe$_2$ film may have an electrical connection with these defects, which results in appreciable gate leakage. The current leakage issue is exacerbated as a result of the large area (~1 cm$^2$) of the as-grown film, which causes a connection between the device and existing oxide defects somewhere on the substrate. By reducing the area of the active conduction channel by SU-8 patterning it is possible to avoid electrical connection between the MoSe$_2$ layer and such oxide defects, thus eliminating the gate leakage current.

Consistent with our hypothesis that SU-8 patterning may break the electrical connection between a device and any oxide defects, we showed that SU-8 patterning can also be used to electrically isolate the device. By performing SU-8 patterning on the conduction channel (Fig. 3e), the channel can be cut to produce an open circuit. Before the channel cut, the drain current flows in response to the application of a bias voltage (Fig. 3f). However, the drain current becomes insensitive to the bias voltage after the channel cut, decreasing to about the pA level, which corresponds to the noise level of the measurement (Fig. 3f, inset). This result confirms that the removal of MoSe$_2$ from the channel was complete.

3.3 Electrical transport measurements

The SU-8 patterning method enables a more in-depth characterization of the transport properties of the MoSe$_2$ grown by CVD. Temperature-dependent electrical characterizations were performed on the sample (Fig. 4a). The MoSe$_2$ channel had a high resistance of tens of MΩ at room temperature, multiple orders of magnitude higher than that of the contact resistance between MoSe$_2$ and Ni, which reaches only hundreds of kΩ at a 35 V gate overdrive. The drain current was also strongly dependent on temperature, showing an insulating behavior where the conductance decreased with decreasing temperature. The current level at temperatures <80 K was beyond our measurable noise level. This suggests that the MoSe$_2$ grown by CVD is highly disordered and that electron localization and thermally activated hopping conduction may play important roles in the electronic transport within the MoSe$_2$ grown by CVD. We also noted that the temperature-dependent conductance data show non-linearity when graphed in an Arrhenius plot (Fig. 4b). The non-linearity of the graph indicates that the simple thermally activated model of transport, where $\sigma \propto \exp(-E_g/\k_B T)$, does not explain the temperature dependence of our sample. Thus we attempt here to explain the transport behavior in terms of the variable range hopping (VRH) mechanism.

VRH transport has been observed in both monolayer and few-layered 2D materials, including MoS$_2$. Likewise, VRH has also been reported in bulk MoSe$_2$. However, the transport behavior in ultra-thin MoSe$_2$ remains elusive. Previous
experimental data on few-layered MoSe₂ exfoliated from powders seemed to indicate phonon-limited transport, where the device mobility decreases with increasing temperature. In both exfoliated MoS₂ and bulk MoSe₂, the VRH behavior only started at temperatures <200 K. In contrast, our MoSe₂ deposited by CVD devices show VRH at high temperatures (350 K), similar to that seen in previous work on reduced graphene oxide.

In VRH, the electrons occupy localized states which have a distribution of energy and positions in real space. Hopping occurs due to the mutual overlap of the eigen-functions of neighbouring states. The conductance of electrons is proportional to the probability per unit time of hopping occurring, which is given by

$$P(r) \propto \exp[-2r/\xi - \Delta E(r)/k_BT],$$

where $r$ is the hopping distance, $\xi$ is the localization length and $\Delta E$ is the activation energy. For Mott-VRH in 2D materials it is assumed that the density of states $N(E)$ is constant near the Fermi level. The most likely hopping maximizes $P(r)$ by circumcribing $dP/dr = 0$. This results in the VRH conductivity, which can be written as

$$\sigma(T) = \sigma_0 \exp\left(-T_0/T\right)^{1/3},$$

where $T_0$ is a fitting parameter. We note that there have been different accounts of the temperature dependence of the exponential prefactor, $\sigma_0$, in 2D Mott-VRH. Ghatak et al. reported that $\sigma_0 \propto T^{0.8}$, as determined in a theoretical study. Other previous experimental and theoretical works have reported a value of $\sigma_0$ that is independent of temperature, whereas other workers have reported different types of temperature dependence. For our experiments, we note that the temperature dependence of $\sigma_0$ would not dramatically affect our conclusion and hence we assume in the following discussion that $\sigma_0$ is constant.

We extracted the temperature-dependent conductance of the sample at the quasi-Ohmic regime near $V_{ds} = 0$ V. Fig. 4c shows that the data can be fitted adequately with the Mott-VRH model from eqn (1), giving a coefficient of determination ($R^2 > 0.995$) for all values of $V_g$. The inset shows the $T_0$ fitting parameter with respect to the carrier concentration, $n = C_g(V_g - V_{th})$, where $C_g = 3.45 \times 10^{-4}$ F m⁻² is the gate capacitance and $V_{th}$ is the threshold voltage. In support of our conclusion about hopping transport, we find that the mobility of the sample increases with temperature (Fig. 4d). This observation is in contrast with the band-like diffusion transport observed in MoS₂ and MoSe₂ flakes from exfoliation. Moreover, the mobility also follows an $\exp[-T_0^*/T]^{1/3}$ trend, in agreement with a Mott-VRH in 2D samples.

In MoS₂, Qiu et al. attributed the carrier localization responsible for VRH to the sulfur vacancies, which are also the electron donors for the sample. In an analogous manner, we also observed that there are selenium vacancies in our sample, as verified from scanning transmission electron microscopy. Thus it is reasonable to suggest that a similar mechanism also

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**Fig. 4** Electrical transport properties of patterned MoSe₂ grown by CVD ribbon channel. (a) $I$–$V$ characteristics of two-probe device at various temperatures; channel length 0.5 μm. Inset: optical micrograph of a typical patterned ribbon device. Scale bars: 100 μm (left) and 10 μm (right). (b) Arrhenius plot of the width-normalized conductance data. Black, broken straight line is a guide to the eye. (c) Temperature dependence of width-normalized conductance on a semi-log scale plotted with respect to $T^{-1/3}$. Inset: fitting parameter $T_0$ as a function of carrier density. (d) Temperature dependence of the field-effect mobility of electrons. Inset: simplified band diagram showing the position of localized states.
where \(N(E_F)\) is the density of states near the Fermi level.\(^{38}\) Given that eqn (1) in Mott-VRH is derived by assuming a nearly constant \(N(E_F)\) within the range of several \(k_B T\), then \(\partial n/\partial T = N(E_F)k_B\) at temperatures approaching 0 K. As a rough order of magnitude approximation\(^{15}\) we can take \(\partial n/\partial T \approx n(100 \text{ K})/100 \text{ K}\) to calculate \(N(E_F)\), which is about \(3 \times 10^{14} \text{ eV}^{-1} \text{ cm}^{-2}\). Thus, using eqn (2), we obtain \(\xi \approx 1 \text{ Å}\), lower than that assumed in MoS\(_2\) exfoliated flakes (6 Å) in previously published work.\(^{27}\)

A shorter \(\xi\) suggests that it is more difficult for charge carriers to hop across localized states distantly separated in space. This is consistent with the relatively low conductance and mobility of the MoSe\(_2\) film grown by CVD (an electron mobility\(^{17}\) reaching only 0.02 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 300 K). Although the MoSe\(_2\) film mobility seems low, the mobility value is within the typical values obtained for previously reported MoS\(_2\) films grown by CVD, which also contain numerous grains (~0.003–0.8 cm\(^2\) V\(^{-1}\) s\(^{-1}\)).\(^{4,6,39}\) The occurrence of VRH behavior at room temperature can also explain the performance of the MoSe\(_2\) FET, which has an on-off ratio of only 10\(^2\) at a 37.5 V gate overdrive. Considering that carrier localization induces states at the band gap (see Fig. 4d, inset), it is still possible for the charge carriers to contribute towards the electrical conduction across the device, although the gate voltage was tuned to position the Fermi level within the band gap of MoS\(_2\). The decrease in \(T_0\) at higher carrier concentrations is attributed to the increased screening effect, thus extending the localization length.

4. Conclusions

In conclusion, we have shown the patterning of 2D materials with SU-8 on MoSe\(_2\) grown by CVD. The success of the patterning was characterized optically and electrically. The patterning enables further study and the development of applications of MoSe\(_2\) grown by CVD in electronics, where the narrowing of the conduction channel area with SU-8 patterning is beneficial in significantly reducing the leakage current. We found that the film showed a variable range hopping behavior.

The SU-8 patterning method can be used as an alternative to an etching process with a pre-existing structure on the sample. For instance, it is possible to use the patterning method to create an array of openings on the sample for further fabrication steps, such as another growth step of the 2D material to stitch additional material into the patterned area. In this way, lateral heterostructures with more complex arrangements can be realized.\(^{40,41}\)

Although EBL was used in this study, we believe that it is also possible to use UV photolithography for SU-8 patterning because this method could also create similar cross-linking to induce stronger adhesion of the SU-8 to the 2D film. The use of photolithography will also help to improve the throughput of the patterning.

With respect to the materials used in the patterning, it is likely that other lithography resists could be used for a similar patterning approach, subject to adequate adhesion with the material to be patterned. However, considering that the patterning depends only on the strong adhesion of SU-8 to MoSe\(_2\) after exposure with EBL, with neither unique chemical reaction nor binding assumed, we also think that the method should be general and therefore also applicable to other 2D materials, including graphene, h-BN, MoS\(_2\), and WSe\(_2\).

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Notes and references