Rhenium Dichalcogenides: Layered Semiconductors with Two Vertical Orientations

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Supporting Information

ABSTRACT: The rhenium and technetium diselenides and disulfides are van der Waals layered semiconductors in some respects similar to more well-known transition metal dichalcogenides (TMD) such as molybdenum sulfide. However, their symmetry is lower, consisting only of an inversion center, so that turning a layer upside-down (that is, applying a C2 rotation about an in-plane axis) is not a symmetry operation, but reverses the sign of the angle between the two nonequivalent in-plane crystallographic axes. A given layer thus can be placed on a substrate in two symmetrically nonequivalent (but energetically similar) ways. This has consequences for the exploitation of the anisotropic properties of these materials in TMD heterostructures and is expected to lead to a new source of domain structure in large-area layer growth. We produced few-layer ReS2 and ReSe2 samples with controlled “up” or “down” orientations by micromechanical cleavage and we show how polarized Raman microscopy can be used to distinguish these two orientations, thus establishing Raman as an essential tool for the characterization of large-area layers.

KEYWORDS: rhenium diselenide, rhenium disulfide, ReSe2, ReS2, MoS2, transition metal dichalcogenide, phonon, Raman spectroscopy, asymmetry

The transition metal dichalcogenide (TMD) family has been well known since the 1960s and, particularly, since the seminal work of Wilson and Yoffe.1 Rhenium diselenide and rhenium disulfide (and their technetium analogues) are special among the 40 or so TMDs that were identified then since, in many respects, they do not behave as expected of typical TMDs. We focus on one important aspect of this, the lack of rotational symmetry in Re-based TMDs about any in-plane axis, and the use of Raman spectroscopy to identify the resulting orientation.

The TMD family has come to attention recently with the isolation of single layers of van der Waals bonded layered materials (graphene, h-BN, MoS2, WS2 and several others5). The isolation of single TMD layers leads to the well-known direct gap transition of MoS2,3 also to dramatic changes in dielectric properties,4 because the reduction of the effective dielectric constant for an isolated layer increases exciton binding energies, sometimes to the point that neutral and even charged exciton signals can be observed in optical spectroscopy at room temperature.5 In general, phonon frequencies are also modified in few- and monolayers.5 Finally, it is well established that gated electrical transport at high mobility can be achieved in single layers and heterojunctions, so that field effect transistor (FET) structures can be realized.7 Much interest is currently focused on heterostructures in which devices are built, layer by layer, from mixed graphene, h-BN and TMD layers to engineer new functionalities or improve existing material properties such as the electron mobility or the superconducting transition.2

In this context, the Re-TMDs will introduce features in a heterostructure that h-BN and the more well-known TMDs cannot. Their unusual nature arises from a Peierls distortion which moves the Re atoms away from the metal sites of the octahedral 1T structure into lozenges of four atoms, defined by Re–Re as well as Rechalcogen bonds.8 These groups of Re atoms form zigzag chains running along one crystallographic axis (usually defined as the b axis) in the layer plane, so that material properties are highly anisotropic in the layer plane.9–12 (these Re chains are illustrated in our table-of-contents graphic with the chalcogen atoms omitted, showing how rotation about an in-plane 2-fold axis reverses the orientation of the lozenges). More details of this and of the Re-TMD structures are shown in the Supporting Information, Figure S1. The in-plane anisotropy is clear in optical absorption and reflectance near the band gap13–21 and in Raman spectroscopy,22 but is also observed in electrical transport.17,19,23–26 It has been shown recently that transport measurements may be used to determine layer orientation26 as, of course, could transmission electron microscopy (TEM), and, though this is certainly true, we shall show that Raman spectroscopy provides this information nondestructively and without the need for any device fabrication steps.

From all optical experiments to date, it is clear that the interlayer interaction is particularly weak even for a van der Waals-bonded material, as shown by the rather small shifts in the frequencies of the vibrational modes observed in Raman
spectroscopy on going from bulk to monolayer samples.\textsuperscript{8,22,28,29} This is unfortunate, because the shifts in the Raman spectra of similar materials (graphene and MoS\textsubscript{2}, for example) allow useful measurements of layer thickness in the crucial region of mono-, bi-, and trilayers.

By contrast, the in-plane anisotropy of Re TMDs is very easily investigated via Raman spectroscopy and the results can be analyzed in terms of the fundamental Raman tensors \( R_{ij} \) for each vibrational mode. A detailed understanding of the angle-dependence of the Raman spectra leads to strategies for mapping variations in layer orientation independent of the dependence of the Raman spectra leads to strategies for each vibrational mode. A detailed understanding of the angle-dependence of the Raman spectra leads to strategies for each vibrational mode. A detailed understanding of the angle-dependence of the Raman spectra leads to strategies for each vibrational mode. A detailed understanding of the angle-dependence of the Raman spectra leads to strategies for each vibrational mode. A detailed understanding of the angle-dependence of the Raman spectra leads to strategies for each vibrational mode. 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Representative experimental Raman spectra of ReS\textsubscript{2} are shown in Figure 1; a low-resolution Raman spectrum of ReS\textsubscript{2} was apparently reported first in the RRUFF database,\textsuperscript{14} because ReS\textsubscript{2} occurs as a rare but naturally occurring mineral rhenite,\textsuperscript{32–34} the Raman spectra of ReSe\textsubscript{2} have also been presented earlier.\textsuperscript{22,35} The Re and Tc TMDs based on S and Se all have similar structures, though ReS\textsubscript{2} has been proposed to have a unit cell which is doubled along the normal to the layers and thus contains 24 instead of 12 atoms.\textsuperscript{12} This doubling results in an increase in the predicted number of \( \Gamma \)-point Raman-active modes, but (as confirmed by first-principles calculations) the modes of a monolayer have frequencies close to those of a thick layer,\textsuperscript{8,22,27,30} this appears to be true also for ReSe\textsubscript{2}.\textsuperscript{22} Here, we are not concerned with interlayer coupling and so we do not focus on few-layer flakes in this study; however, we used micromechanical cleavage to select single-crystal flakes of well-defined morphology. In all cases, these were of thickness greater than 100 nm, as was confirmed by AFM and by the absence of the silicon Raman peak at 520 cm\textsuperscript{-1} in the Raman spectra excited with 532 nm light. Figure 1a shows the Raman spectrum of a small bulk crystal of ReS\textsubscript{2} at low temperature using an excitation wavelength of 785 nm and with an experimental resolution sufficient to resolve completely all the detectable Raman signals (here, we see 16 out of the expected total of 18 \( A_g \) modes). Figure 1b shows the Raman spectrum of an exfoliated flake from the same bulk ReS\textsubscript{2} sample using 532 nm excitation in a Raman microscope at room temperature. The ReS\textsubscript{2} spectrum is now dominated by the 150, 160, and 211 cm\textsuperscript{-1} modes,\textsuperscript{28} as is shown in the Supporting Information (Figure S2). To analyze the effects of anisotropy, we define the Raman tensor for the scattering process due to a given mode as \( R \). If we consider only the in-plane components of the electric field, we can write \( R \) as

\[
R = \begin{pmatrix} u & v \\ v & w \end{pmatrix}
\]

(1)

When the polarization of the excitation is rotated by \( \theta \) with respect to the in-plane crystal axes, as already shown for ReSe\textsubscript{2},\textsuperscript{22} the intensity \( I(\theta) \) of a given Raman band varies with \( \theta \) as

\[
I(\theta) \propto u^2 \cos^2 \theta + v^2 \sin^2 \theta + u^2 + 2v(u + w) \sin \theta \cos \theta
\]

(2)

for detection of both scattered polarizations with equal sensitivity, or as

\[
I_p(\theta) \propto (ucos^2 \theta + 2vsin\theta cos \theta + vsin^2 \theta)^2
\]

given parallel detection and excitation polarizations or, finally, as

\[
I_L(\theta) \propto (v[cos^2 \theta - sin^2 \theta] + [w - u]sin\theta \cos \theta)^2
\]
for perpendicular excitation and detection polarizations. We showed elsewhere that $I_d(\theta)$ is a useful experimental quantity to consider because it has a simple mathematical form, and because it always carries information about all three non-equivalent (and, generally, nonzero) components of the 2D Raman tensor. 25 In a Raman mapping experiment aimed at highlighting areas of different orientation approximately independent of variations in thickness, for example, the ratio of $I_d(\theta)$ for two different peaks in the same spectrum can be plotted to obtain a false-color contrast that is dependent principally on $\theta$ and requires only one spectrum per pixel 22 (the extent to which layer thickness affects the polarization direction of modes III and V is addressed in the Supporting Information, Figure S7).

However, because Re-TMDs do not possess rotation axes in the layer plane, turning a layer upside-down is not a symmetry operation (see the Supporting Information, Figures S1 and S3 and Table S1) and, at least in principle, should affect the observed Raman intensities. In terms of the above expressions, for example, $u \rightarrow -u$, $v \rightarrow -v$, and $w \rightarrow w$ under rotation by $\pi$ about the in-plane laboratory $x$ axis, so that the measurement of $I_d(\theta)$ will now yield a result in which the sign of the final term in eq 2 is reversed (the derivation is given in the Supporting Information)

$$I_d(\theta) \propto u^2 \cos^2 \theta + w^2 \sin^2 \theta + v^2 - 2v(u + w) \sin \theta \cos \theta \tag{3}$$

This result can alternatively be viewed as the result of replacing $\theta$ by $-\theta$ and is quite general because rotation by $\pi$ about any other in-plane axis is equivalent to this in-plane rotation combined with an appropriate rotation around the plane normal. The expressions for $I_q(\theta)$ and $I_w(\theta)$ are modified by this transformation in similar ways. The appearance of the intensities predicted by eqs 2 and 3 is given in the Supporting Information, Figure S3.

We test these predictions as follows. If the bulk starting material for micromechanical cleavage has the ideal crystal structure, it should be straightforward to produce layers facing either way up by careful manipulation of the adhesive tape; fragments of the same crystal on opposite sides of the tape will deposit layers facing opposite ways up when transferred to the silicon substrate. Of course, this approach might fail if the starting crystals are twinned vertically, or if the cleavage or deposition process is disruptive enough that layers are overturned. We used thin cleaved layers because we could then identify flakes whose morphology gave an indication of the orientation of the crystal $b$ axis. This is, however, not always unambiguous, as shown in the Supporting Information, Figure S4. We therefore confirmed the orientation of the $b$ axis of the flakes used for the Raman measurements in each case by measurement of their optical reflectance under white light illumination in a polarizing microscope (see Supporting Information, Figure SS). Two band-to-band transitions are seen which are known from experiments 27 and first-principles modeling 28 to be orthogonally polarized along the $\Gamma$–$M$ and $\Gamma$–$K$ directions and to differ in energy by about $150 \text{ meV}$. The polarization direction giving the minimum energy is then unambiguously the direction of the $b$ axis 28 and this can be related to the cleavage edges of the flake imaged in the same microscope. The optical absorption or reflectance, however, does not discriminate between the two possible vertical orientations of a flake.

As the excitation polarization is rotated with respect to the laboratory and crystal axes, we expect to observe a variation in intensity of the Raman modes of a given single crystal flake; typical results are shown in Figure 2a, here for ReS$_2$ (equivalent data for ReSe$_2$ are shown in the Supporting Information, Figure S2). From the angle at which a given mode reaches its maximum, one can easily compare the relative orientation of different flakes produced in the same micromechanical cleavage process, whether or not their morphology is recognizable. This ability will be particularly useful when large area Re-based TMDs are grown by CVD or related techniques. In fact, the absolute orientation of a single flake with respect to the laboratory axes can also be determined. 27 We discuss this further by reference to data for ReS$_2$ in Figure 3, we plot only the peak intensity as a function of angle for the selected peaks specified above. Peak intensities were determined by fitting the spectra using mixed Lorentzian–Gaussian line shapes after careful background subtraction, taking into account also any overlapping peaks not in the required set.

Results are shown in Figure 3a and b for two large flakes of ReS$_2$ obtained from the same starting bulk crystal by micromechanical cleavage and deposition onto a standard silicon wafer with a $290 \text{ nm}$ oxide layer. The bright yellow-white color over most of the area of the flake indicates regions that are effectively bulk material. The direction of the crystallographic $b$ axis, which frequently (but not always) forms the longer edge of cleaved crystals, 26 is indicated on images of the samples in Figure 3c and d. First, it is clear that, as expected, the data are well described by fits according to eq 1 in all cases. Second, there is an approximate correspondence between the principal axis of the Raman tensor for the $211 \text{ cm}^{-1}$ mode V and the direction of the crystallographic $b$ axis, noted elsewhere. 27,36 This correspondence appears not to be exact and depends on layer thickness (see Supporting Information, Figures S6 and S7). More importantly here, we
Figure 3. Intensities as a function of angle with respect to the laboratory x axis of three peaks in the Raman spectra of large ReS₂ flakes (both of thickness >100 nm) which were cleaved from the same starting crystal but were facing (a) “upward” and (b) “downward”. Images of the corresponding flakes are shown in (c) and (d) respectively with a 20 μm scale bar (white) in each case; the inferred directions of the crystallographic b axes are indicated by the blue arrows. Spectra were recorded with unpolarized detection and the excitation polarization was rotated in 15° steps from 0° to 360° (bottom to top) in the same rotational direction in both cases. The peaks chosen are the 150, 160, and 211 cm⁻¹ modes III–V (black squares, red circles, and green triangles, respectively). The corresponding solid lines in each case show fits to the experimental data using the expression of eq 1 and the dashed lines show the orientation of the principal axis obtained from each fit.

Figure 3a into those of Figure 3b, as is clear also from the morphology of the chosen pair of flakes. The angles between the principal axes of the 150 cm⁻¹ mode III and the modes at 160 (IV) and 211 cm⁻¹ (V) are −45° and +39°, respectively in Figure 3a and are +45° and −36°, respectively in Figure 3b, with an estimated error of ±2°; the sequence of the peak maxima in angle is thus reversed in angle between Figure 3a and b, as already demonstrated by Figure 2 for the case of ReSe₂. This shows that Raman spectroscopy is able to distinguish the two possible orientations of Re-TMD layers and that there is no possible ambiguity between the effects of in-plane and vertical orientations in the angle-dependence of the Raman spectra.

This will be of great significance for large-area growth of materials of this low-symmetry family. In a CVD or similar growth technique, it is highly likely that different domains will be produced facing different ways up as well as having different in-plane orientations. Indeed, the in-plane orientation (that is, the direction of the b axis) will probably be more easily influenced by a suitable choice of substrate surface reconstruction or template than whether a layer faces “up” or “down”. However, this remains to be tested. Certainly, the fundamental chemical nature of the upper and lower chalcogen planes is the same since they are related by a center of inversion symmetry. This implies that the energy of interaction with the substrate of a particular domain within a growing layer will not depend strongly on whether its orientation is “up” or “down”. Although the vertical orientation may not influence the energetics of the layer significantly and may not be of importance for chemical processes at the surface (such as catalytic or sensing applications, for example), the coexistence of both types of domain within a growing monolayer introduces the new possibility of grain boundaries between “up” and “down” layers as well as between layers with different alignments of the b axis and, thus, may have a considerable impact on charge transport; recently, it has been shown that monolayers may be locally converted between “up” and “down” orientations under electron beam irradiation. First-principles calculations and high-resolution transmission electron microscopy are now needed to explore the possible configurations that result following growth on a typical hexagonal substrate. This combination of techniques has already proved powerful in analyzing the tilt and twin boundaries of, for example, CVD-grown MoS₂, where a variety of ring structures at the boundaries are found to form and which give gap states responsible for marked changes in the luminescence intensity and electrical conductance.

In summary, it has been shown that low symmetry of the distorted-1T transition metal dichalcogenides leads to two possible vertical layer orientations and that these can be produced in a controlled fashion by micromechanical cleavage. The vertical orientation of these layers can be identified easily by Raman spectroscopy. It was already shown in earlier studies that the in-plane orientation can be determined; here, it is shown that both vertical and in-plane orientation can be found simultaneously and unambiguously from the same spectra, though several polarization-dependent spectra per point on the sample surface must be measured in order to achieve this. This work paves the way for the investigation and characterization of few-layer samples grown by vapor-phase methods on supporting substrates.
carried out more extended studies, and D.W. and L.H. analyzed preparation and characterization of the samples, L.H. and D.W. conceived the investigation, S.D. and J.L.W. contributed to Performance Computing Facility. Data supporting this study provided by EPSRC grant EP/M022188. Computational of the Universities of Bath and Exeter, funded by the EPSRC This work was supported by the Centre for Graphene Science authors and all authors have given approval to the final version of the manuscript. S.H. carried out preliminary studies, D.W. conceived the investigation, S.D. and J.L.W. contributed to preparation and characterization of the samples, L.H. and D.W. carried out more extended studies, and D.W. and L.H. analyzed and interpreted the data.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

TMD: transition metal dichalcogenide; CVD: chemical vapor deposition

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