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Determining layer number of two-dimensional flakes of transition-metal dichalcogenides by the Raman intensity from substrates

Xiao-Li Li, Xiao-Fen Qiao, Wen-Peng Han, Xin Zhang, Qing-Hai Tan, Tao Chen and Ping-Heng Tan

State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, People’s Republic of China

E-mail: phtan@semi.ac.cn

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Abstract

Transition-metal dichalcogenide (TMD) semiconductors have been widely studied due to their distinctive electronic and optical properties. The property of TMD flakes is a function of their thickness, or layer number ($N$). How to determine the $N$ of ultrathin TMD materials is of primary importance for fundamental study and practical applications. Raman mode intensity from substrates has been used to identify the $N$ of intrinsic and defective multilayer graphenes up to $N = 100$. However, such analysis is not applicable to ultrathin TMD flakes due to the lack of a unified complex refractive index ($\tilde{n}$) from monolayer to bulk TMDs. Here, we discuss the $N$ identification of TMD flakes on the SiO$_2$/Si substrate by the intensity ratio between the Si peak from 100 nm (or 89 nm) SiO$_2$/Si substrates underneath TMD flakes and that from bare SiO$_2$/Si substrates. We assume the real part of $\tilde{n}$ of TMD flakes as that of monolayer TMD and treat the imaginary part of $\tilde{n}$ as a fitting parameter to fit the experimental intensity ratio. An empirical $\tilde{n}_{\text{eff}}$, namely, $\tilde{n}_{\text{eff}}$, of ultrathin MoS$_2$, WS$_2$ and WSe$_2$ flakes from monolayer to multilayer is obtained for typical laser excitations (2.54 eV, 2.34 eV or 2.09 eV). The fitted $\tilde{n}_{\text{eff}}$ of MoS$_2$ has been used to identify the $N$ of MoS$_2$ flakes deposited on 302 nm SiO$_2$/Si substrate, which agrees well with that determined from their shear and layer-breathing modes. This technique of measuring Raman intensity from the substrate can be extended to identify the $N$ of ultrathin 2D flakes with $N$-dependent $\tilde{n}$. For application purposes, the intensity ratio excited by specific laser excitations has been provided for MoS$_2$, WS$_2$ and WSe$_2$ flakes and multilayer graphene flakes deposited on Si substrates covered by a 80–110 nm or 280–310 nm SiO$_2$ layer.

S Online supplementary data available from stacks.iop.org/nano/27/145704/mmedia

Keywords: raman spectroscopy, two-dimensional materials, transition-metal dichalcogenides, layer number, refractive index, transfer matrix formalism, multiple reflection interference

(Some figures may appear in colour only in the online journal)

1. Introduction

With the advent of graphene and the exfoliation technique for preparing atomically thin sheets [1], layered materials (LMs) have sparked wide interest around the world [2]. Among the LMs, transition-metal dichalcogenide (TMD) 2H-MX$_2$ ($M = \text{Mo, W}; X = \text{S, Se}$) semiconductors have been widely studied due to their distinctive electronic and optical properties [3–5]. They have an X-M-X covalently bonded sandwich structure in each layer, and the layers are weakly stacked by...
van der Waals force. Such a stacked layer structure makes it possible to peel off different layers from bulk. The property of TMD flakes is a function of their thickness, or layer number (denoted as \(N\)) [3, 6–10]. For example, the band gap of MoS\(_2\), WS\(_2\) and WSe\(_2\) exhibits an indirect-to-direct transition from a few-layer to a monolayer (1L) thickness, [3, 6] enabling many applications in electronics and optoelectronics. Thus, how to determine the \(N\) of ultrathin TMDs materials is of primary importance for fundamental study and practical applications.

Several optical techniques have been developed to identify the \(N\) of the TMD flakes, such as photoluminescence (PL) and optical contrast [5]. PL can be used to distinguish 1L from multilayer (ML) because of its strong and narrow PL peak [3]. Optical contrast is not sensitive to the flake quality and the stacking structure of 2D flakes [11–13], and thus it has been widely used to identify the \(N\) of graphene flakes by comparing the experimental value with the theoretical one for different \(N\) thanks to almost identical complex refractive index (\(n\)) from 1L graphene (1LG) to ML graphene (MLG) [13, 14]. However, quantitative analysis of the optical contrast of ultrathin TMD flakes on SiO\(_2\)/Si substrate is difficult because there exist abundant features associated with optical transitions in the wavelength (\(\lambda\)) dependent \(n\) for TMD flakes and the \(n\) of TMD flakes itself significantly depends on \(N\) due to the indirect-to-direct transition from ML to 1L [15, 16].

Ultra-low Raman spectroscopy has been used to reliably determine \(N\) for MLG, TMD flakes and 2D alloy flakes [8, 17, 18]. However, this technique requires expensive adapters and a nonstandard equipment setup. Therefore, it is essential to look for the technique of \(N\) identification only by the standard Raman system. Recently, Raman mode intensity from substrates only requires \(\tilde{n}\) for TMD flakes due to the lack of unified \(n\) for TMD flakes from 1L to ML. However, the calculation of Raman mode intensity from substrates only requires \(\tilde{n}\) at the wavelengths of the laser excitation and the scattered photon, and thus, in this paper, we try to extend this technique for \(N\) determination of TMD flakes deposited onto the SiO\(_2\)/Si substrate. By fitting the experimental data of the intensity ratio between the Si peak from SiO\(_2\)/Si substrates underneath TMD flakes and that from bare SiO\(_2\)/Si substrates, we obtained empirical \(\tilde{n}\), namely, \(\tilde{n}_{\text{ef}}\), for ultrathin MoS\(_2\), WS\(_2\) and WSe\(_2\) flakes at different laser excitation wavelengths. The fitted \(\tilde{n}_{\text{ef}}\) of MoS\(_2\) has been used to determine the \(N\) of MoS\(_2\) flakes on Si substrate covered by 302 nm SiO\(_2\), which agrees well with that determined from their shear and layer-breathing modes [8].

2. Experimental details

Ultra-thin MoS\(_2\), WS\(_2\) and WSe\(_2\) flakes were mechanically exfoliated from bulk MoS\(_2\), WS\(_2\) and WSe\(_2\) (purchased from 2d Semiconductors, Inc.), and transferred onto Si substrates covered with SiO\(_2\) film with different thickness (\(h_{\text{SiO}_2}\): 100 nm, 89 nm or 302 nm). Raman measurements were performed at room temperature using a Jobin-Yvon HR800 micro-Raman system equipped with a liquid nitrogen-cooled charge couple detector (CCD), a \(\times 50\) objective lens with a numerical aperture (NA) of \(\sim 0.45\) and a 1800 lines \(\text{mm}^{-1}\) grating. The excitation energies (\(\varepsilon_L\)) are 2.09 eV from a He–Ne laser, 2.34 eV and 2.54 eV from a Kr\(^+\) laser. Plasma lines were removed from the laser beam by BragGrate bandpass filters. Measurements down to 5 cm\(^{-1}\) are enabled by three BragGrate notch filters with optical density 3 and with full width at half maximum (FWHM) of 8 cm\(^{-1}\) [8]. Both BragGrate bandpass and notch filters are produced by OptiGrate Corp. The typical laser power is about 0.4 mW to avoid sample heating.

3. Results and discussion

3.1. \(\tilde{n}_{\text{ef}}\) of MoS\(_2\) flakes fitted from \(N\)-dependent Si mode intensity

We denote a \(N\)-layer TMD flake as NL-TMD, such as NL-MoS\(_2\), NL-WS\(_2\) and NL-WSe\(_2\), and thus monolayer MoS\(_2\) is denoted as 1L-MoS\(_2\). 1–10L MoS\(_2\) flakes were pre-estimated by the Raman measurements of the ultra-low-frequency shear (C) and layer-breathing (LB) modes, as previously done for MoS\(_2\) and MoWS\(_2\) flakes [8, 18]. Figure 1(a) shows the high-frequency Raman spectra of 1–10L MoS\(_2\) along with Si mode from substrate which were measured by \(\varepsilon_L\) of 2.34 eV. Because of the different symmetry between even and odd NL-TMDs and bulk TMDs, the corresponding two Raman-active modes \(E_{2g}^{\text{NL}}\) and \(A_{1g}^{\text{NL}}\) in bulk TMDs should be assigned as the \(E'\) and \(A_{1g}'\) in odd NL-TMDs and the \(E_g\) and \(A_{1g}\) modes in even NL-TMDs [5, 20], respectively. However, to see the evolution from 1L to NL, \((N > 1)\), hereafter the two modes for all cases are simply labeled as \(E_{2g}\) and \(A_{1g}\), as is commonly done in the literature [5, 7, 21]. With increasing \(N\), the peak position difference between the \(E_{2g}\) and \(A_{1g}\) modes, \(\Delta \omega (A-E) = \text{Pos}(A_{1g})-\text{Pos}(E_{2g})\), increases from 17.4 cm\(^{-1}\) for 1L to 25 cm\(^{-1}\) for 10L, following the formula of \(\Delta \omega (A-E) = 25.8 - 8.4/N\) [5]. The peak area of the \(E_{2g}\) and \(A_{1g}\) modes, \(I(E_{2g})\) and \(I(A_{1g})\), increases with \(N\) up to \(N = 4\) and then gradually decreases with \(N\), as shown in figure 1(b), after being normalized by the peak area of the Si mode \((I_{\text{Si}}(\text{Si}))\) from bare substrate that is not covered by MoS\(_2\) flakes. Obviously, \(I(E_{2g})/I_{\text{Si}}(\text{Si})\) and \(I(A_{1g})/I_{\text{Si}}(\text{Si})\) cannot be used to identify \(N\) for few-layer MoS\(_2\).

Figure 1(a) shows that the peak area of the Si mode, \(I_{\text{Si}}(\text{Si})\), from the substrate underneath MoS\(_2\) flakes monotonously decreases with increasing \(N\). Now we focus on \(I_{\text{Si}}(\text{Si})\) itself. To exclude the effect of crystal orientation on the Raman intensity, \(I_{\text{Si}}(\text{Si})\) is normalized by \(I_{\text{Si}}(\text{Si})\). The maximum of \(I_{\text{Si}}(\text{Si})\) can be obtained by rotating the Si wafer and adjusting the focus of the laser beam onto the Si substrate, then, we directly moved the laser spot to MoS\(_2\) flake to measure \(I_{\text{Si}}(\text{Si})\) to ensure a good signal-to-noise ratio of \(I_{\text{Si}}(\text{Si})/I_{\text{Si}}(\text{Si})\). Figures 1(c), (d) and (e) depict the \(N\)-dependent \(I_{\text{Si}}(\text{Si})/I_{\text{Si}}(\text{Si})\) (squares) for NL-MoS\(_2\) flakes on SiO\(_2\)/Si substrate \((h_{\text{SiO}_2} = 100 \text{ nm})\) excited by \(\varepsilon_L\) of 2.54 eV, 2.34 eV, and 2.09 eV.
and 2.09 eV, clearly showing the monotonous decrease in intensity with increasing \( N \). The laser beam to Si substrate is initially adsorbed by the MoS\(_2\) flake and the Raman signal from Si substrate is adsorbed again by the MoS\(_2\) flake, similar to the case of MLGs [19, 22]. This makes \( I_{2D}(\text{Si})/I_{d}(\text{Si}) \) sensitive to \( N \) of MoS\(_2\) flakes, implying its possibility of \( N \) identification for MoS\(_2\) flakes.

\( I_{2D}(\text{Si}) \) can be calculated by using the multiple reflection interference method and transfer matrix formalism for multilayered structures [19], which can be expressed in air/NL-MoS\(_2)/\text{SiO}_2/Si\) four-layer structure as the following equation:

\[
I_{2D}(\text{Si}) \propto \int_0^{h_{\text{Si}}} \int_0^{\arcsin(\text{NA})} \int_0^{2\pi} \int_0^{\arcsin(\text{NA})} \int_0^{2\pi} \sum_{i,j=0}^{\infty} \sum_{j=0}^{\infty} |F_i(z, \theta, \varphi)F_j(z, \theta', \varphi')|^2 
\times \sin \theta \cos \theta \theta' \cos \varphi \theta' \cos \varphi' \text{d} \theta \text{d} \varphi \text{d} \varphi' \text{d}z,
\]

where the Raman intensity is given by integrating over the solid angle (arcsin (NA)) of microscope objective (\( \theta, \varphi \) for the laser beam and \( \theta', \varphi' \) for the Raman signal) and the penetration depth of laser excitation into Si layer (\( h_{\text{Si}} \approx 2 \mu m \)). Different from the case of normal incidence where \( \theta, \varphi, \theta', \varphi' = 0 \), the s-polarization (transverse electric field, \( \vec{E} \), perpendicular to the NL-MoS\(_2\) c-axis) and the p-polarization (transverse magnetic field, \( \vec{H} \), associated to electric field by \( \vec{H} = \vec{n}\vec{E} \) field components are considered separately for the oblique incidence, which are involved in the laser excitation enhancement factor \( F_L \) and Raman scattering enhancement factor \( F_R \). \( F_L \) and \( F_R \) are calculated by using transfer matrix formalism, in which complex refractive index (\( n \)) and thickness (\( h \)) of each medium should be known in advance. \( I_d(\text{Si}) \) can be obtained by setting the thickness of MoS\(_2\) flakes to be zero. The detailed derivation process can be found in the supplementary data stacks.iop.org/NANO/27/145704/medi.

\( I_{2D}(\text{Si})/I_d(\text{Si}) \) is expected to be sensitive to \( N \), NA of the objective used, \( \varepsilon_L \), and \( h_{\text{SiO}_2} \), as demonstrated in the case of MLGs [19]. A variation of 10 nm for can introduce a change on the N-dependent \( I_{2D}(\text{Si})/I_d(\text{Si}) \) [19], therefore, a precise determination of \( h_{\text{SiO}_2} \) is very important for \( N \) identification of NL-MoS\(_2\) flakes on SiO\(_2\)/Si substrates by \( I_{2D}(\text{Si})/I_d(\text{Si}) \). As a
simple, fast and nondestructive technique, optical contrast measurement can be used to determine with a typical micro-Raman confocal system [14]. It is found that an effective NA must be used to calculate optical contrast of multilayer graphene deposited on SiO2/Si substrates once the commonly used 100 × objective with NA of ~0.9 is used for the optical microscope [12, 13, 19]. In this work, the 50 × objective with NA of 0.45 is used to measure \( I_{2D}(\text{Si})/I_0(\text{Si}) \). In fact, as shown in the supplementary data stacks.iop.org/NANO/27/145704/mmedia, it is found that \( I_{2D}(\text{Si})/I_0(\text{Si}) \) is not sensitive to NA when NA \( \leq 0.5 \) and \( N \leq 10 \) for NL-MoS2 flakes on SiO2/Si substrates.

The unified \( \tilde{n} \) = \( n - ik \) for MoS2 flakes from 1L to ML is necessary to calculate \( n_{\text{eff}} \)-dependent \( I_{2D}(\text{Si})/I_0(\text{Si}) \), where \( n \) and \( k \) are the real and imaginary parts of \( \tilde{n} \), respectively. However, both \( n \) and \( k \) for MoS2 flakes are found to be sensitive to \( N \) in the visible region [15, 16]. \( \lambda \)-dependent \( \tilde{n} \) of 1L-MoS2 and bulk MoS2 are obtained according to their complex dielectric functions [15] using a formula of \( n^2 = \varepsilon \). If we apply \( \tilde{n} \) of 1L-MoS2 or bulk MoS2 to all the NL-MoS2 flakes, \( I_{2D}(\text{Si})/I_0(\text{Si}) \) can be calculated for the three \( \varepsilon_L \), as shown in figures 1(c), (d) and (e) by dash-dotted and dashed lines, respectively. Either of them fits well to the experimental data. When \( \varepsilon_L = 2.54 \) eV and 2.34 eV, the experimental data lie in-between the two theoretical curves. However, when \( \varepsilon_L = 2.09 \) eV excitation, the experimental data are larger than the two theoretical ones because they are under the near-resonant condition with the B exciton [3, 10].

In order to identify \( N \) by \( I_{2D}(\text{Si})/I_0(\text{Si}) \), it is necessary to adopt an empirical \( \tilde{n} \), namely \( n_{\text{eff}} \), for MoS2 flakes, to minimize the difference between the theoretical and experimental data. If we do not consider the multiple reflection interference effect, the difference between \( I_{2D}(\text{Si}) \) and \( I_0(\text{Si}) \) results from the adsorption of the laser beam and Raman beam when they pass through the MoS2 flakes, which is mainly dominated by the imaginary part (\( k \)) of \( \tilde{n} \) of MoS2, but not by the real part (\( n \)) of \( \tilde{n} \) of MoS2. Thus, we assume the real part of \( \tilde{n}_{\text{eff}} \), namely, \( n_{\text{eff}} \), of MoS2 flakes as \( n \) of 1L-MoS2. Also, as an approximation, we neglect the difference of \( n_{\text{eff}} \) between the wavelengths of laser excitation and Raman beam. Finally, we can obtain the imaginary part of \( n_{\text{eff}} \), namely \( k_{\text{eff}} \), of MoS2 flakes by fitting the experimental \( I_{2D}(\text{Si})/I_0(\text{Si}) \) by the theoretical ones for each excitation wavelength. We found that, indeed, the fitted \( k_{\text{eff}} \) can make the theoretical \( I_{2D}(\text{Si})/I_0(\text{Si}) \) agree well with the experimental ones, as shown in figures 1(c), (d) and (e) by solid curves. The fitted \( n_{\text{eff}} \) along with \( k_{\text{eff}} \) for MoS2 flakes are summarized in table 1 for \( \varepsilon_L \) of 2.54 eV, 2.34 eV and 2.09 eV. In this case, if we can calculate \( I_{2D}(\text{Si})/I_0(\text{Si}) \) based on the fitted \( n_{\text{eff}} \) for MoS2 flakes and compare them with the experimental one, \( N \) of MoS2 flakes can be determined. Based on the fitted \( n_{\text{eff}} \) for MoS2 flakes, we calculated \( I(E_{1s}^L)/I_0(\text{Si}) \) and \( I(A_{1g})/I_0(\text{Si}) \) as a function of \( N \) for \( \varepsilon_L = 2.34 \) eV, where adjustable parameters were introduced to take different efficiencies among \( E_{1s}^L \), \( A_{1g} \) and Si modes into account. The results are shown by solid curves in figure 1(b). The theoretical results basically are in agreement with the experimental ones, but there exists significant discrepancy for \( N < 5 \).

### Table 1

<table>
<thead>
<tr>
<th>Mode</th>
<th>( \varepsilon_L(\text{eV}) )</th>
<th>( n_{\text{eff}} )</th>
<th>( k_{\text{eff}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS2</td>
<td>2.54</td>
<td>2.34 2.09</td>
<td>1.85 1.20 1.22</td>
</tr>
<tr>
<td>WS2</td>
<td>5.29</td>
<td>4.85 4.58</td>
<td>1.10 0.48 1.86</td>
</tr>
<tr>
<td>WSe2</td>
<td>4.40</td>
<td>4.62 4.22</td>
<td>1.10 0.48 1.86</td>
</tr>
</tbody>
</table>

3.2. \( n_{\text{eff}} \) of NL-WS2 and NL-WSe2 flakes

Now we check the possibility of applying this technique to other TMDs, such as WS2 and WSe2. We obtain 1–8L WS2 and WSe2 flakes by mechanical exfoliation from bulk crystal and \( N \) is determined by the C and LB modes based on the method described in [18]. The C and LB modes and the \( E_{1s}^L \) and \( A_{1g} \) modes of 1–8L WS2 and WSe2 were measured by 2.54 eV laser excitation at room temperature, as depicted in figures 2(a) and (b), respectively. Pos(C) and Pos(LB) of 2–8L WS2 and WSe2 are summarized in figures 2(c) and (d), respectively. Besides a fan diagram [8], the \( N \)-dependent Pos(C) and Pos(LB) can also exhibit a sin diagram [23], which can be written as follows:

\[
\omega(C_{N,N-1}) = \sqrt{2} \omega(C_{21}) \sin \left( \frac{j\pi}{2N} \right)
\]

\[
\omega(LB_{N,N-1}) = \sqrt{2} \omega(LB_{21}) \sin \left( \frac{j\pi}{2N} \right)
\]

where \( j \) is an integer, \( j = N-1, N-2, \ldots, 2, 1 \). \( \omega(C_{21}) \) and \( \omega(LB_{21}) \) are the frequencies of the C and LB modes in 2L flakes, respectively. The measured C modes in bulk WS2 and WSe2 are located at 26.3 and 23.9 cm\(^{-1}\), and then the measured \( \omega(C_{21}) \) and \( \omega(LB_{21}) \) of 2L-WS2 and 2L-WSe2 are 18.4 (31.9) and 16.7 (27.8) cm\(^{-1}\), respectively. Each branch in equation (1) always decreases or increases in frequency with increasing \( N \). As indicated by the solid lines in figures 2(c) and (d), the branches of \( j = N-1 \) and \( j = N-3 \) are observed for the C modes, and the branches of \( j = 1 \) and \( j = 3 \) are observed for the LB modes.

The \( E_{1s}^L \) and \( A_{1g} \) modes of 1–8L WS2 and WSe2 are found to be insensitive to \( N \), as addressed in previous works [9, 24]. The \( E_{1s}^L \) mode of WS2 flakes is very weak and it can be clearly revealed under cross (HV) polarization configuration, as shown in figure 2(b). The frequency shift of both the \( E_{1s}^L \) and \( A_{1g} \) modes for NL-WS2 and NL-WSe2 is less than 3 cm\(^{-1}\), which makes it difficult for \( N \) determination.

\( I_{2D}(\text{Si})/I_0(\text{Si}) \) from Si substrate underneath WS2 and WSe2 flakes decreases with increasing \( N \), as shown in figures 2(a) and (b), similar to the case of MoS2 flakes in figure 1(a). This suggests that \( I_{2D}(\text{Si})/I_0(\text{Si}) \) can be used for \( N \) identification of WS2 and WSe2 flakes deposited on SiO2/Si substrate. \( I_{2D}(\text{Si})/I_0(\text{Si}) \) for NL-WS2 and NL-WSe2 flakes as a function of \( N (N = 1, 2, \ldots, 8) \) for \( h_{550} = 89 \) nm were measured for two excitations: \( \varepsilon_L = 2.54 \) eV and 2.34 eV. Indeed, \( I_{2D}(\text{Si})/I_0(\text{Si}) \) monotonously decreases with increasing \( N \) for
WS₂ and WSe₂ flakes excited by the two excitations. The corresponding experimental data were depicted in figure 3 by triangles and circles, respectively. Considering that the 2.09 eV excitation is almost resonant with the A exciton of 1L-WS₂ and B exciton of 1L-WSe₂, the 2.09 eV laser excitation is not used for WS₂ and WSe₂ flakes.

To understand the N-dependent $I_{2D}(Si)/I_D(Si)$ of WS₂ and WSe₂ flakes for their N determination, similar to the case of MoS₂ flakes as discussed above, we assume $n_{eff}$ of WS₂ and WSe₂ flakes as $n$ of 1L-WS₂ and 1L-WSe₂[15], respectively. $n_{eff}$ of WS₂ and WSe₂ flakes have been used as a fitting parameter to fit the experimental $I_{2D}(Si)/I_D(Si)$. The
of 2.54, 2.34 or 2.09 eV is obtained. The resulting $n_{\text{eff}}$ to $\varepsilon_L$ is summarized in Table 1. The calculated $I_{2D}(\text{Si})/I_0(\text{Si})$ based on the fitted $n_{\text{eff}}$ are shown by solid lines in Figure 3, which agree well with the experimental values.

### 3.3. Identifying layer number of MoS$_2$ flakes deposited on 302 nm SiO$_2$/Si substrate

As discussed above, the empirical $n_{\text{eff}}$ of MoS$_2$, WS$_2$ and WSe$_2$ flakes are obtained by fitting the theoretical $I_{2D}(\text{Si})/I_0(\text{Si})$ to the experimental data excited by different excitation energies. Once $n_{\text{eff}}$ for TMD flakes at specific $\varepsilon_L$ is available, one can compare the theoretical $I_{2D}(\text{Si})/I_0(\text{Si})$ with the corresponding experimental data excited by the same $\varepsilon_L$ to determine $N$ of the TMD flakes. As an example, we apply this technique to MoS$_2$ flakes on Si substrate covered by 302 nm SiO$_2$ film, where $N$ is precisely determined by the C and LB modes of MoS$_2$ flakes [8] and $N = 1, 3, 4, 6, 7$. Based on the fitted $n_{\text{eff}}$ for MoS$_2$ flakes, the theoretical $I_{2D}(\text{Si})/I_0(\text{Si})$ were calculated as a function of $N$ for $\varepsilon_L = 2.09, 2.34$ and 2.54 eV, as shown by crosses and solid lines in Figures 4(a), (b) and (c), respectively. They agree well with the experimental data, as depicted by squares in Figure 4. The $N$-dependent $I_{2D}(\text{Si})/I_0(\text{Si})$ of TMD flakes is found to be sensitive to $\varepsilon_L$, as demonstrated in Figures 1 and 3. Thus, the determined $N$ of TMD flakes by an excitation energy can be confirmed from further measurement by another excitation energy, which leads to an accurate $N$ determination of ultrathin TMD flakes by the Raman intensity from substrate.

### 4. Conclusions

In conclusion, a technique to determine the $N$ of TMD flakes such as MoS$_2$, WS$_2$ and WSe$_2$ deposited on SiO$_2$/Si substrate has been proposed by measuring $I_{2D}(\text{Si})/I_0(\text{Si})$, i.e. the intensity ratio of the Si peak from SiO$_2$/Si substrates underneath the 2D flakes of TMDs to that from bare SiO$_2$/Si substrates. The real part ($n_{\text{eff}}$) of the empirical $n_{\text{eff}}$ of TMD flakes is assumed as that of 1L TMD. The imaginary part ($\sigma_{\text{eff}}$) of the empirical $n_{\text{eff}}$ is a fitting parameter to the experimental intensity ratio between the Si peak from SiO$_2$/Si substrates underneath TMD flakes and that from bare SiO$_2$/Si substrates. The empirical $n_{\text{eff}}$ of MoS$_2$, WS$_2$ and WSe$_2$ flakes for $\varepsilon_L$ of 2.54, 2.34 or 2.09 eV is obtained. The resulting $n_{\text{eff}}$ of MoS$_2$ flakes has been used to identify $N$ of MoS$_2$ flakes deposited on 302 nm SiO$_2$/Si substrate. This opens the possibility of identifying the $N$ of ultrathin 2D flakes with a $N$-dependent complex refractive index by measuring Raman intensity from the substrate. For application purposes of $N$ identification of TMD and MLG flakes for the research community, $I_{2D}(\text{Si})/I_0(\text{Si})$ of TMD flakes deposited on SiO$_2$/Si substrate is provided in the supplementary data for commonly used excitation energies (2.34 eV and 2.54 eV) and SiO$_2$ thicknesses (80–110 nm and 280–310 nm), along with the corresponding data for MLG.

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### References