Self-consistent dielectric constant determination for monolayer WSe$_2$

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Abstract: Frequency-dependent dielectric constant dispersion of monolayer WSe$_2$, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, was obtained from simultaneously measured transmittance and reflectance spectra. Optical transitions of the trion as well as A-, B-, and C-excitons are clearly resolved in the $\varepsilon_2$ spectrum. A consistent Kramers-Kronig transformation between the $\varepsilon_1$ and $\varepsilon_2$ spectra support the validity of the applied analysis. It is found that the A- and B-exciton splitting in the case of the double-layer WSe$_2$ can be attributed to the spin-orbit coupling, which is larger than that in the monolayer WSe$_2$. In addition, the temperature-induced evolution of the A-exciton energy and its width are explained by model equations with electron-phonon interactions.

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1. Introduction

In contrast to graphene and boron nitride that can be categorized as a gapless Dirac material and wide gap insulator, respectively [1,2], transition-metal dichalcogenides (TMDCs) such as MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$, are semiconducting layered materials. Owing to the unique electronic and optical properties that TMDCs possess, they have attracted great interest from many fields [3–5]. Because of their finite energy gap, TMDCs can outperform graphene-based transistors in terms of the on/off ratio [6]. The large spin-orbit splitting in the case of MoS$_2$ or WSe$_2$ has led to long sustaining spin properties enabling novel functionalities in the field of valleytronics [7,8].

Because monolayer MoS$_2$ or WSe$_2$ are direct gap semiconductors with good radiative recombination efficiency, they can be utilized as light sources of atomic length scale. Due to large exciton binding energy light emission in TMDCs is featured by exciton states even at room temperature [4,9]. In the case of bulk crystals, the exciton binding energy can be determined using the following equation: $E_b = \frac{\hbar^2}{2m^*} \times 13.6 eV$, where $m^*$ is the reduced effective mass of electron and hole quasi-particles and $\varepsilon$ is the dielectric constant [10]. However, in case of monolayers, the substantial field intrusion out of the host material leads to a complicated change in the binding energy; it has been shown that a series of exciton sublevels in monolayer MoS$_2$ do not follow the Rydberg-type energy separation of the hydrogen atom, but they can be explained by field intrusion into the substrate [11]. Nevertheless, the dielectric constant and effective mass are still the most deterministic factors for the binding energy of two-dimensional (2D) monolayer excitons. While the effective mass can be obtained by measuring the energy band dispersion using angle-resolved photoemission spectroscopy [12,13], the dielectric constant can be obtained through optical characterizations.

The imaginary part of the dielectric constant, $\varepsilon_2(\omega)$, which is proportional to the optical transition probability, provides valuable information about the density of energy states,
including the excitons. Though the ellipsometry technique is used to obtain complex dielectric constants of monolayer MoS$_2$ and WSe$_2$ [14–16], it not only requires dispersion modeling, but also has difficulty in performing microscopic measurements. It has been proposed that the absorbance is proportional to the reflectance contrast in the case of atomically thin layers of graphene [17]. In the opaque spectral range, however, the complex dielectric constant cannot be completely determined based on the reflectance or transmittance individually, but values of both quantities are necessary for singular extractions. Several works have reported on the determination of the dielectric constant of monolayer TMDCs based on their reflectance and transmittance [18,19]. In particular, Morozov et al. reported on the dielectric constants of monolayer TMDCs obtained using concerted transmittance and reflectance measurements at room temperature [19].

In this study, we report on the frequency-dependent dielectric constants of monolayer WSe$_2$. By using the transfer matrix method (TMM), both real and imaginary components of the dielectric constant are obtained from the simultaneously measured reflectance and transmittance spectra. In addition, we study the temperature-induced evolution of the A-exciton and compare the dielectric constant of monolayer with that of the double layer WSe$_2$.

2. Sample preparation and methods

Monolayer WSe$_2$ was synthesized on a SiO$_2$ (300 nm)/Si substrate using the chemical vapor deposition (CVD) method. The synthesized monolayer film was then transferred onto a quartz plate via the poly(methyl methacrylate) (PMMA) support method in order to perform the transmittance measurement. The flake size of the monolayer was typically ~100 $\mu$m $\times$ 100 $\mu$m, but, it depended on the growth conditions. As indicated by the optical image in Fig. 1(a), in addition to pure monolayers, some double-layers were formed as well.

Fig. 1. Schematic diagram of the experimental setup for simultaneous reflection and transmission measurements. White light from the supercontinuum laser passes the monochromator and is focused onto WSe$_2$ layers using an objective lens. Transmitted or reflected beams are simultaneously measured using photodiodes. The optical microscope image of the WSe$_2$ layers is included in the figure.

A broadband white light source from a supercontinuum laser (Compact, NKT photonics) was passed through a monochromator, and the filtered beam was then focused using an objective lens onto the monolayer or double layer region of WSe$_2$. Both the transmitted ($T$) and reflected ($R$) intensities were simultaneously measured using silicon photodiodes. In addition, the $R_q$ and $T_q$ at adjacent quartz regions were measured, using which, the normalized reflectance ($R_n$) and transmittance ($T_n$), defined by $R_n = R / R_q$ and $T_n = T / T_q$, respectively, were obtained. The sample was mounted inside an optical cryostat in vacuum and the lock-in technique referenced by an optical chopper was applied to suppress the detection noise.
3. Results and discussion

Figure 2 shows the $R_n$ and $T_n$ spectra of monolayer WSe$_2$ measured at a temperature of 10 K. While $T_n$ is less than unity because of the absorption by the WSe$_2$ layer, $R_n$ is greater than one over the entire range. In previous works, it has been demonstrated that the reflectance contrast, defined as \( RC = (R - R_\infty) / R_\infty \), is positive and proportional to the absorbance in the case of graphene [17], indicating that $R_n$ is more than one in opaque regions. In many studies on monolayer TMDCs, the reflectance was analyzed to represent the optical transition probability or the absorbance. This can be attributed, in part, to the fact that transmittance could not be measured in samples with a silicon substrate. However, as shown in Fig. 2, there is a difference in the spectral shape of the $R_n$ and $T_n$ spectra. Furthermore, as shown in the inset of Fig. 2, the A-exciton peak near 1.75 eV in $T_n$ is slightly differentiated compared with that in $R_n$, which indicates that the reflectance alone cannot provide the precise position and shape of the exciton resonance, especially when the resonance is spectrally narrow.

In an optical system under study, the reflectance or transmittance is dependent on the dielectric constants of the constituent layers. In the opaque spectral region, the dielectric constant cannot be set based on reflectance alone. However, it can be unambiguously determined using both the $R_n$ and $T_n$ spectra. As previously mentioned, in order to obtain the dielectric constant from the measured $R_n$ and $T_n$ spectra, we applied the TMM approach [20–22]. According to the TMM approach, the matrix elements $ABCD$ representing the light propagation from air to quartz through the WSe$_2$ layer are presented as the multiples of the three sub matrices in Eq. (1), which correspond to the electric field transfer at the air/WSe$_2$ interface, through the WSe$_2$ layer, and at the WSe$_2$/quartz interface, respectively.

$$
\begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \begin{bmatrix} \frac{\sqrt{\varepsilon} + 1}{2} & \frac{\sqrt{\varepsilon} - 1}{2} \\ \frac{\sqrt{\varepsilon} - 1}{2} & \frac{\sqrt{\varepsilon} + 1}{2} \end{bmatrix} \times \begin{bmatrix} 1 & \exp(-\frac{i\sqrt{\varepsilon}\omega t}{c}) \\ \exp(-\frac{i\sqrt{\varepsilon}\omega t}{c}) & 1 \end{bmatrix} \times \begin{bmatrix} n_\infty + \sqrt{\varepsilon} & n_\infty - \sqrt{\varepsilon} \\ 2\sqrt{\varepsilon} & 2\sqrt{\varepsilon} \end{bmatrix}
$$

(1)

Here, $\omega$ is the angular frequency and $c$ is the speed of light. In addition, $\varepsilon$ and $n_\infty$ are the dielectric constants of WSe$_2$ and refractive index of quartz, respectively. With the $ABCD$ elements known, the reflectance and transmittance can be obtained using $R = |C / A|^2$ and
In this study, based on the measured $R_n$ and $T_n$ spectra, the TMM approach was used in reverse to obtain the dielectric constant of the WSe$_2$ layers. According to previous literature, $d = 0.65 \text{ nm}$ was assumed as the monolayer thickness [23]. We prepared a 2D array of $(\varepsilon_1, \varepsilon_2)$, covering a broad range of real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) components of the dielectric constant, and calculated the $(R_n, T_n)$ for each set. Then, for each photon energy, a set of $(\varepsilon_1, \varepsilon_2)$ was selected for which the deviation of $(\varepsilon_1, \varepsilon_2)$ from the measured values or $(R_n - R'_n)^2 + (T_n - T'_n)^2$ was the smallest.

Fig. 3. Real (a) and imaginary (b) spectra of the complex dielectric constant as a function of the photon energy for monolayer WSe$_2$ at 80 K with the plots in the right highlighting the region near the A-exciton position. The notations A, B, and C in $\varepsilon_1(\omega)$ indicate positions of A-, B-, and C-excitons, respectively. The Kramers-Kronig transformation of the $\varepsilon_1(\omega)$, $\varepsilon_{1,\text{KGR}}(\omega)$ in (a), is included for comparison with $\varepsilon_1(\omega)$. (c) $\varepsilon_{1,\text{KGR}}(\omega)$ spectrum in the low energy region below a photon energy of 1.4 eV obtained from the Kramers-Kronig transformation of $\varepsilon_1(\omega)$, and model fitting based on the Sellmeier single oscillator formula.

In Fig. 3, the extracted dielectric constant of $\varepsilon_1$ and $\varepsilon_2$ are plotted for the monolayer WSe$_2$ at 10 K. The $\varepsilon_1$ spectrum clearly exhibits resonant transitions at the A-, B-, and C-excitons. The A-exciton at 1.748 eV is quite sharp with an FWHM linewidth of 15 meV and a large peak value of $\varepsilon_2 = 58$. In contrast to the A-exciton, the B- and C-excitons are much broader with linewidths of ~35 and ~110 meV, respectively. In addition to neutral excitons, the signature of the trion or charged exciton is observed at left side of the A-exciton with an energy separation of ~30 meV consistent with the literature [9,24].

While the $\varepsilon_2$ spectrum is dominated by optical transitions at excitons, the $\varepsilon_1$ spectrum is closely correlated by those resonances through the Kramers-Kronig relation (KKR) [25]. A closer comparison of the $\varepsilon_1$ and $\varepsilon_2$ spectra near the A-exciton, as shown in Fig. 3(b), indicates an abrupt change of the $\varepsilon_1$ spectrum at the exciton peak, which is a typical signature
of the KKR. In order to verify this correlation in more detail, we generated the \( \varepsilon_{1\text{-KXX}}(\omega) \) through the Kramers-Kronig transformation of \( \varepsilon_{1}(\omega) \). In this transformation, in order to compensate for the high-energy optical transitions in WSe\(_2\) beyond the detection range, a single oscillator at 3.56 eV was added to \( \varepsilon_{1}(\omega) \). The consistency of the \( \varepsilon_{1\text{-KXX}}(\omega) \) with \( \varepsilon_{1}(\omega) \) presented in Fig. 3(a), thus satisfying the KKR, clarifies the validity of the \((\varepsilon_{1}, \varepsilon_{2})\) extraction procedure. In the low energy region below the A-exciton energy, where no electronic transitions are allowed, \( \varepsilon_{1}(\omega) \) can be produced through the Kramers-Kronig transformation of the measured plus compensational \( \varepsilon_{2}(\omega) \) at 3.56 eV. Figure 3(c) shows that transformed \( \varepsilon_{1}(\omega) \) attains a value of \( \sim21.1 \) in the zero-frequency limit. We find that the low-energy \( \varepsilon_{1} \) spectrum, which is indicated using a red line in Fig. 3(c), can be modeled by the Sellmeier single oscillator formula of \( \varepsilon_{1}(E) = 1 + A_{0} / (E^{2} - E_{0}^{2}) \) with \( A_{0} = 183.5 \text{ eV}^{2} \) and \( E_{0} = 3.02 \text{ eV} \) as a function of photon energy \( E \) in the eV unit [26]. Here, the energy of the Sellmeier oscillator is differentiated from the compensational oscillator because the optical transitions within our detection range contributes as well in the Kramers-Kronig transformation.

According to Eq. (1) the extracted dielectric constant depends on the choice of the monolayer thickness \( d \). As we varied the layer thickness from 0.5 to 0.8 nm it was found that the value of \( \varepsilon \times d \) did not change noticeably. We note that this multiplied value, through the relation of \( \sigma_{2D} = -i\omega\varepsilon_{0} \varepsilon_{D} \) with \( \varepsilon_{0} \) being the vacuum permittivity, corresponds to the 2D optical conductivity, which are widely used in order to explain the optical response of atomically thin monolayers [19,27,28].

![Fig. 4. \( \varepsilon_{1} \) and \( \varepsilon_{2} \) spectra of the double-layer WSe\(_2\) at 80 K compared with those of the monolayer WSe\(_2\) plotted with solid and dotted lines, respectively.](image)

The \((R_{\alpha}, T_{\alpha})\) measurement as well as the \((\varepsilon_{1}, \varepsilon_{2})\) extraction were repeated on the double-layer WSe\(_2\) region assuming a thickness of 2\( d \). Figure 4 shows a comparison of the \((\varepsilon_{1}, \varepsilon_{2})\) spectra of the double-layer WSe\(_2\) with those of the monolayer WSe\(_2\) at 10 K. It can be observed that, for the double-layer WSe\(_2\), the energies of the A- and B-excitons are 36 meV
and 8 meV lower than those of the monolayer WSe$_2$, respectively. The energy separation between the A- and B-excitons, which is larger in the case of the double-layer WSe$_2$, originates from the spin-orbit splitting of the valence band. It should be noted that the larger A-B splitting in the case of the double-layer over the monolayer was previously explained by the effect of interlayer interactions [29,30]. In contrast to the A- and B-excitons, the C-exciton experiences a greater energy shift of ~160 meV as the WSe$_2$ changes from monolayer to double-layer. There have been some controversial theories about the origin of the C-excitons—whether they are due to the transition between parallel bands or Van Hove singularities at saddle points in the band structure [31,32]. We believe that the layer number dependence of C-exciton energy in combination with the theoretical interpretation might help in addressing this issue. Though the $\varepsilon_1$ spectrum of the double-layer in Fig. 4 is accordingly differentiated from the monolayer, especially near the exciton resonances, the overall shape, including the low energy value of $\varepsilon_1 = 26$ at 1.5 eV, is similar to the monolayer.

As the temperature is increased, the electron-phonon interaction is accelerated and results in spectral broadening of the exciton resonances. We investigated the temperature dependence of excitons by measuring the dielectric constant at different temperatures. As is expected, the evolution of the $\varepsilon_1$ spectrum of the monolayer WSe$_2$ in Fig. 5 reveals a red shift and broadening of the A-, B-, and C-excitons with an increase in temperature. We plotted the temperature induced variation of A-exciton energy and width in the inset. From data fitting, we find that the energy shift follows the Varshni formula of $E_A(T) = E_{A0} - \frac{\alpha T^2}{T + \beta}$ with $E_{A0} = 1.749$ eV, $\alpha = 3.9 \times 10^{-3}$ eV/K and $\beta = 158$ K [33]. The temperature induced broadening, on the other hand, is well described by the Rudin’s relation of $\gamma(T) = \gamma_0 + \sigma T + \frac{\gamma'}{\exp(E_{LO}/k_BT) - 1}$ with the Boltzmann constant $k_B$ and fitting parameters of $\gamma_0 = 5.1$ meV, $\sigma = 0.038$ meV/K, and $\gamma' = 55.4$ meV [34], that takes into account the exciton interaction with longitudinal optical phonons ($E_{LO} = 31.25$ meV) and acoustic phonons.

![Fig. 5. $\varepsilon_2$ spectrum at different temperatures from 10 to 290 K. Inset shows the temperature dependence of the energy and width of A-exciton resonance, where the dotted lines represent the model fitting of the energy and width according to the Varshni formula and Rudin’s relation, respectively.](image-url)
4. Conclusion

In this study, by performing TMM analysis of simultaneously measured transmittance and reflectance, frequency-dependent dielectric constant of monolayer WSe$_2$ was obtained with self-consistency. The $\varepsilon_2$ spectrum exhibits clear optical transitions at A-, B-, and C-excitons as well as the trion resonance. The Kramers-Kronig transformation leads to a dispersion model $\varepsilon_1(E) = 1 + \frac{A_0}{(E^2 - E_0^2)}$ with $A_0 = 183.5$ eV$^2$ and $E_0 = 3.02$ eV in the transparent low-energy region below 1.4 eV. In addition, thermal shift and broadening of A-exciton resonance acquired from temperature-dependent measurements demonstrates significant exciton relaxation because of electron-phonon interactions. We expect that self-consistent dielectric constant extraction performed in this study will be useful in characterizing other ultrathin layered materials and provide valuable optical data for TMDC-based optoelectronic devices.

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