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Title: Influence of the oxide thickness of a SiO$_2$/Si(001) substrate on the optical second harmonic intensity of few-layer MoSe$_2$

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Abstract

The nonlinear optical properties of few-layer MoSe$_2$ on a SiO$_2$/Si substrate were investigated with our optical second harmonic generation (SHG) microscope. Few-layer flakes were mechanically exfoliated from a single crystal onto a 90- or 270-nm-thick SiO$_2$-coated Si(001) substrate. The polar plot of the second-harmonic (SH) intensity from a mono- or trilayer MoSe$_2$ flake as a function of the rotation angle of incident polarization shows a threefold symmetry, indicating that the isolated few-layer flakes retain their single crystallographic orientation. SHG spectra were found to depend strongly on the oxide thickness of the substrate (90 or 270 nm), which was interpreted using the interference among the multiply reflected SH light beams in the system. By taking this interference into account, a resonant peak may be identified at a two-photon energy of equal to or less than 2.9 eV in an SHG spectrum. The spatial resolution of the SHG microscope was estimated as 0.53 μm.
1. Introduction
The family of monolayer transition-metal dichalcogenides TX$_2$ (T = Mo, W; X = S, Se) has attracted much attention because monolayer TX$_2$ could complement graphene in various applications that require thin, transparent semiconductors, such as optoelectronics [1-4]. These materials are direct-band-gap semiconductors that possess very different properties from graphene; monolayer MoS$_2$ transistors with a hafnium oxide dielectric gate showed a room-temperature single-layer MoS$_2$ mobility of up to 200 cm$^2$ V$^{-1}$ s$^{-1}$, similar to that of graphene nanoribbons, current on/off ratios of $10^8$, and ultralow standby power dissipation [4].

The linear optical properties of monolayer dichalcogenides have shown a marked increase in photoluminescence efficiency arising from the direct gap [5-7], where dielectric functions were obtained by the Kramers-Krönig constrained analysis of the reflectance spectra of monolayer TX$_2$ [8]. A laser system based on monolayer WS$_2$ was also demonstrated by harnessing the unique advantages of atomically thin crystals for coherent light generation [9].

The nonlinear optical properties of mono- and few-layer dichalcogenides have also been well investigated; in particular, optical second-harmonic generation (SHG) microscopy has become an indispensable tool for investigating electronic and nonlinear optical properties of few-layer TX$_2$, WS$_2$ [10-13,18], WSe$_2$ [10,13-15], MoS$_2$ [2, 3, 13, 16-18], and MoSe$_2$ [13, 19, 20]. The wavelength dependence of the SH intensity from mono- or few-layer TX$_2$ on a thick thermal oxide-coated Si substrate was also reported [2,11-13,15, 19, 20].

The layer number of a thin film is usually identified by the well-established procedure utilizing the optical contrast among the reflected beams in the thin film demonstrated for a 300-nm-thick SiO$_2$-coated Si substrate [21]. Graphene crystallites prepared on Si wafers with a certain SiO$_2$ thickness are visualized by optical microscopy based on the Fresnel law modeling of normal light incidence from air (refractive index $n_0 = 1$) onto a trilayer structure consisting of graphene, SiO$_2$, and Si [21]. The visual contrast sensitively depends on the SiO$_2$ thickness, light wavelength, and the thickness of graphene crystallites [21].

An anomaly in the G-band Raman intensity of graphene sheets on a 300-nm-thick SiO$_2$/Si substrate is explained by the interference effect of multiply reflected Raman light inside the graphene layer [22]. The strain-induced SHG intensity from a SiO$_2$/Si(111) interface was shown to change markedly as a function of oxide thickness ranging from 2 to 300 nm, owing to multiple reflections in the oxide film [23].
The SH spectra of few-layer TX2 on a SiO2/Si substrate are also likely to reflect the interference of multiple reflections. Thus, the interference effect must be carefully examined in the case of the wavelength dependence of SH light generated at few-layer MoSe2 on a thick thermal oxide-coated Si substrate [13,19,20].

In this study, we demonstrated that the wavelength dependence of the SHG intensity from mono- or few-layer MoSe2 on a 90- or 270-nm-thick SiO2-coated Si(001) substrate crucially reflects the interference among the multiply reflected fundamental and SHG light beams in SiO2 films. The SHG intensity increased steeply with the decrease in two-photon energy in the case of 270-nm-thick oxides, whereas there was a peak at a two-photon energy of equal to or less than 2.9 eV in the spectra in the case of 90-nm-thick oxides. Hereafter, we call the peak a peak at ≤2.9 eV. We followed the calculation method [22] by simply replacing the Raman light with the SHG light to take the interference effect into account in obtaining our SHG spectra. For monolayer MoSe2 at an oxide thickness of 270 nm, a very low SHG intensity is expected at around 3.1 eV owing to a destructive interference. For monolayer MoSe2 at an oxide thickness of 90 nm, the SHG intensity is determined to be less affected by the interference effects for the photon energy range studied, revealing a peak at ≤2.9 eV in the SHG spectra.

Yin et al. observed one-dimensional nonlinear optical edge states of a single atomic membrane of MoS2 [18]. To accurately investigate the electronic states at the edges, the microscope used is required to have a sufficient spatial resolution, which is yet to be obtained. Here, we estimated the spatial resolution of our SHG microscope to be 0.53 μm.

2. Experimental procedure

Mono- and few-layer MoSe2 flakes were mechanically exfoliated from a single crystal onto a SiO2 / Si(001) substrate. The crystal was grown by Br2 vapor transport [24]. We used a 90- or 270-nm-thick SiO2-coated Si(001) substrate. The layer number of a MoSe2 flake was identified by atomic force microscopy (AFM; Bruker Innova). For the SHG measurements, the fundamental pulse from a Ti-sapphire oscillator (Spectra Physics Mai Tai, pulse duration 80 fs, wavelength 740–880 nm, repetition rate 80 MHz, power 900 mW, mode quality M2 <1.1, beam divergence <1.2 mrad, beam diameter <1.2 mm) was guided through a Faraday isolator, a polarizer, and a low-pass filter, and then was reflected by a dielectric multilayer mirror in an Nikon optical microscope (Nikon Y-FL). The light beam was then focused by an objective lens (Nikon LU plan ×100, numerical aperture 0.9, focal length 2 mm) onto the sample at normal incidence. The light at the double frequency generated by the sample was allowed to pass through the objective lens,
the dielectric multilayer mirror, a high-pass filter, a polarizer, and a monochromator, and was finally detected by a photomultiplier tube. We obtained the SHG microscopy image by raster scanning the target position by controlling an automated X-Y stage (Sankei SAS-2V-XYF) with a minimum step size of 0.1 µm. We monitored the pulse durations of tunable fundamental light by using a spectrum analyzer (Ocean Photonics LSM-min) during the experiment. Varying the path length through the prisms inside the laser cavity, we control the amount of dispersion at each wavelength in order to keep the laser bandwidth at a fixed value.

3. Results and discussion

Figure 1(a) shows an optical microscopy image of a few-layer MoSe2 flake on a SiO2 (270 nm) / Si(001) substrate. The mono-, bi-, and trilayer regions are marked. Figure 1(b) shows the SHG image collected from the MoSe2 flake shown in Fig. 1(a). The SHG showed well-defined odd-even layer regions, which reproduced the previous results [2]. A strong SHG signal was observed from the monolayer and trilayer, whereas the signal disappeared in the bilayer region. This observation is usually explained by the symmetry of the crystals as follows. A bulk MoSe2 crystal with 2H stacking order belongs to the space group D6h, which is inversion-symmetric. Thus, its second-order nonlinear response should vanish [25]. The inversion symmetry is broken in a monolayer with D3h symmetry. However, in a bilayer with the space group D3d, the inversion symmetry is present again. In general, an even number of layers belong to the D3d point group, and an odd number of layers belong to the D3h point group [2, 16].

Figure 2 shows the intensity profile of the SH light obtained by scanning the irradiated position from left to right along the dotted line in Fig. 1(a). From this profile, the SHG intensity from the monolayer was about twice as high as that from the trilayer, whereas the intensity from the bilayer was almost three orders of magnitude lower than that from the monolayer.

A schematic of the lattice structure of monolayer MoSe2 is shown in Fig. 3(a). For the odd layer with D3h point-group symmetry, the nonvanishing second-order susceptibility tensors are \( \chi^{(2)}_{xx} = -\chi^{(2)}_{yy} = -\chi^{(2)}_{xy} = -\chi^{(2)}_{yx} \), where \( x \) and \( y \) are along the armchair and zigzag directions shown in Fig. 3(a), respectively [25]. SHG intensity as a function of the sample angle for a pump laser polarization parallel to the analyzer may be expressed as

\[
I \propto \cos^2(3\phi + \phi_0),
\]

where \( \phi \) is the angle between the input laser polarization and the x-direction, and \( \phi_0 \) is the initial crystallographic orientation of the MoSe2 sample [2]. Figure 3(b) shows polar plots of the SHG intensity from a monolayer
MoSe₂ flake as a function of the sample angle. The pattern clearly shows that the sample has a threefold rotational symmetry. Because the measurement is direction-insensitive, there is an arbitrariness of 60° in the definition of the x-axis. According to the plot, \( \phi_0 \sim -10° \) indicates the offset angle for setting the armchair (x) direction of MoSe₂ with respect to the input laser polarization.

Figure 3(c) shows the polar plots of the SHG intensity as a function of the sample angle from a trilayer MoSe₂ flake that lies next to the monolayer flake. The pattern of the SHG intensity from the trilayer has the same dependence on the sample angle as that from the monolayer in Fig. 3(a). This observation indicates that the few-layer MoSe₂ flakes that mechanically exfoliated from a sample retained the crystallographic structure of the layers in the bulk crystal.

Figures 4(a) and 4(b) show the wavelength dependence of the SH intensity for monolayer MoSe₂ on 270- and 90-nm-thick SiO₂-coated Si(001) substrates obtained with a fixed laser power of 0.5 mW without the polarizer for the SH light, respectively. The SHG spectra are normalized by a crystalline quartz reference placed at the sample position. The SH intensity corresponds to the \( \chi^{(2)}_{xxx} \) tensor element [25]. The SHG intensity increases steeply with the decrease in two-photon energy in Fig. 4(a), whereas a peak at \( \leq 2.9 \) eV is observed in the spectra in Fig. 4(b). The spectra of the MoSe₂ monolayer depending strongly on the oxide thickness of the substrate might be interpreted using the interference among the multiply reflected fundamental and SH light beams in the system. The strain-induced SH intensity at the SiO₂ / Si(111) interface was shown to change markedly as a function of oxide thickness, owing to multiple reflections in the oxide film [23]. The strain-induced SH intensity from our bare 90-nm-thick SiO₂-coated Si(001) substrate, however, may be expected to be low owing to the fourfold symmetry of the Si(001) interface where SHG is forbidden at normal incidence. Actually, it was almost of the fifth order of magnitude lower than that from monolayer MoSe₂ on the SiO₂/Si substrate.

Wang et al. [22] observed an unusually high G-band Raman intensity for monolayer graphene on a Si substrate with a 300 nm SiO₂ capping layer, and they explained their results by considering the multiple reflections of both the Raman light and the incident light in the graphene layer. We followed their calculation method [22] by simply replacing the Raman light with the SH light, and simulated the interference among the multiply reflected fundamental and SH light beams in the systems by using the optical constant of bulk MoSe₂ [26]. For monolayer MoSe₂ at an oxide thickness of 270 nm [Fig. 4(a)], the steep minimum intensity at around 3.1 eV and the increase in SHG intensity
towards a low photon energy are qualitatively reproduced (see supplementary data at http://stacks.iop.org/JJAP/55/085801/mmedia). For monolayer MoSe₂ at an oxide thickness of 90 nm, on the other hand, the calculation shows that the interference effects are less important for the photon energy range studied, and thus the raw SHG spectra in Fig. 4(b) would be sufficiently close to the unaffected SHG spectra. Therefore, the peak position at ≤2.9 eV identified in the SHG spectra in Fig. 4(b) may show the resonance enhancement in the electronic states of monolayer MoSe₂.

The SH intensity reported for monolayer MoSe₂ on a 285-nm-thick SiO₂/Si substrate [20] showed a minimum intensity at ~1.45 eV or its second harmonics at ~2.9 eV, which is clearly different from the minimum intensity at ~3.1 eV for our 270-nm-thick SiO₂/Si substrate. The energy for the minimum SH intensity reflecting the interference of the multiply reflected SH light beams may be inversely proportional to the oxide thickness [22, 27]. Thus, the thickness ratio of the two SiO₂/Si substrates applied to monolayer MoSe₂ at an oxide thickness of 285 nm would give a minimum intensity of about 2.9 eV. Then, the minimum at ~1.45 eV in Fig. 2 of Ref. 21 is likely to reflect this interference.

The dielectric function of MoSe₂ monolayers for photon energies from 1.5 to 3 eV was obtained by Li et al. from the reflection spectra by Kramers-Kröning constrained vibrational analysis [8]. They obtained the peaks labeled A and B in the photon energy range of 1.5–2 eV, which correspond to excitons from the two spin-orbit split transitions at the K point of the Brillouin zone. They also observed that the resonance energies labeled C and D peaks above 2 eV are modestly shifted from that of the corresponding bulk material, which has a very sharp strong peak near 3 eV and a somewhat weaker, although equally sharp structure near 4–5 eV for bulk MoSe₂ [26]. The C and D features are discussed to be associated with transitions away from the K point and involve a significant contribution from chalcogen orbitals [8].

The peak corresponding to the one-photon resonance with the A exciton transition may be expected at around 3.2 eV in Fig. 4(b); however, this is clearly not the case. The resonance may be attributed to the two-photon resonance with the C interband transition, which is reasonably expected above 2.5 eV [8]. Thus, we may conclude that the peak at ≤2.9 eV in the SHG spectra arises from the two-photon resonance with the C interband transition. Further identification of SHG resonance would require a detailed experimental study with a laser system having an extended wavelength tuning range.

The resolution of the SHG microscope was also estimated using a 16–84% criterion corresponding to twice the root mean square (RMS) width of a Gaussian function when convoluted with a step function [28]. By analyzing the steepness of the
intensity profile obtained by scanning the irradiated position with a step size of 0.2 \( \mu \text{m} \) as shown in the inset of Fig. 2, we estimated the resolution as 0.53 \( \mu \text{m} \). In the case of an ideal Gaussian-shaped beam (\( M^2 \sim 1 \)), the theoretical beam diameter at the focal point is estimated by \( 4\lambda f / \pi w_e \) [29], where \( \lambda \) and \( f \) are the wavelength and focal length, respectively. \( w_e \) is the laser beam diameter at the objective lens estimated as 3.4 mm. In our system, \( \lambda = 800 \text{ nm} \) and \( f = 2 \text{ mm} \) indicate the beam diameter at the focal point to be 0.60 \( \mu \text{m} \). For SHG, the spatial distribution of SHG intensity may be proportional to the square of the Gaussian as
\[
\exp\left(\frac{-(x^2)}{2\sigma^2}\right) = \exp\left(\frac{x^2}{2(\sigma / \sqrt{2})^2}\right),
\]
where \( x \) is the position of the beam profile and \( \sigma \) is the RMS width of the Gaussian distribution. Thus, the theoretical spatial resolution of the SHG microscope is obtained as 0.60 \( \mu \text{m} / \sqrt{2} = 0.42 \mu \text{m} \) by dividing the beam diameter at the focal point by \( \sqrt{2} \). The spatial resolution of our SHG microscope of 0.53 \( \mu \text{m} \) is sufficiently close to the theoretical spatial resolution.

4. Conclusions
We developed an SHG microscope and measured the SHG intensity from few-layer MoSe\textsubscript{2} on a 90 - or 270-nm-thick SiO\textsubscript{2} / Si(001) substrate as a function of the layer number, sample angle, and incident wavelength. The SHG microscopy images and intensity profile show that the SHG intensity from monolayer MoSe\textsubscript{2} was twice as high as that from trilayer MoSe\textsubscript{2}, whereas the intensity from the bilayer was less than three orders of magnitude lower than that of the monolayer. The sample angle dependence shows that the mechanically exfoliated few-layer MoSe\textsubscript{2} flakes retained the crystallographic structure of the layers in a bulk crystal. SHG spectra of the monolayer MoSe\textsubscript{2} depended strongly on the oxide thickness of the substrate, which was interpreted using the interference among the multiply reflected SH light beams in the system. A resonant peak may be identified at a two-photon energy of equal to or less than 2.9 eV in an SHG spectrum. The spatial resolution of the SHG microscope was estimated as 0.53 \( \mu \text{m} \) from the intensity profile.
References


Figure Captions

Fig. 1. (a) Optical microscopy image of a MoSe₂ thin film on a SiO₂ (270 nm) / Si(001) substrate. By measuring the height relative to the substrate by AFM, MoSe₂ was determined as monolayer (1L), bilayer (2L), and trilayer (3L). The scale bar is 5 µm. (b) Topographical representation of the SHG image obtained for the MoSe₂ flake in (a).

Fig. 2. Intensity profile of the SH light scanned from left to right along the dotted line in Fig. 1(a). The inset shows the intensity profile fitted by a step function of the scanned SH light obtained with a step size of 0.2 µm.

Fig. 3. (a) Lattice structure of monolayer MoSe₂. Polar plots of the SH intensity for (b) mono- and (c) trilayer MoSe₂ as a function of the sample angle. The solid curves serve as visual guides.

Fig. 4. SHG spectra of monolayer MoSe₂ on (a) 270- and (b) 90-nm-thick SiO₂-coated Si(001) substrates. The solid curve serves as a visual guide. The SHG spectra are normalized by a crystalline quartz reference placed at the sample position.
Figures

Figure 1

Figure 2