Investigation on nonlinear optical properties of MoS$_2$ nanoflakes grown on silicon and quartz substrates

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Abstract

In this study, MoS$_2$ nanoflakes were directly grown on different substrates—Si/SiO$_2$ and quartz—by one-step thermal chemical vapor deposition using MoO$_3$ and sulfide powders as precursors. Scanning electron microscopy and x-ray diffraction patterns demonstrated the formation of MoS$_2$ structures on both substrates. Moreover, UV-visible and photoluminescence analysis confirmed the formation of MoS$_2$ few-layer structures. According to Raman spectroscopy, by assessment of the line width and frequency shift differences between the $E_{12}^g$ and $A_{1g}$, it was inferred that the MoS$_2$ grown on the silicon substrate was monolayer and that grown on the quartz substrate was multilayer. In addition, open-aperture and close-aperture Z-scan techniques were employed to study the nonlinear optical properties including nonlinear absorption and nonlinear refraction of the grown MoS$_2$. All experiments were performed using a diode laser with a wavelength of 532 nm as the light source. It is noticeable that both samples demonstrate obvious self-defocusing behavior. The monolayer MoS$_2$ grown on the silicon substrate displayed considerable two-photon absorption while, the multilayer MoS$_2$ synthesized on the quartz exhibited saturable absorption. In general, few-layered MoS$_2$ would be useful for the development of nanophotonic devices like optical limiters, optical switchers, etc.

Keywords: two-dimensional MoS$_2$ structure, TCVD, nonlinear optical properties

(Some figures may appear in colour only in the online journal)
photonic devices such as optical limiters, mode-lockers, and Q-switchers [34, 35].

For the growth of 2D-MoS₂, different methods have been reported including chemical vapor deposition (CVD) [36], hydrothermal synthesis [37], electrochemical synthesis [38, 39] and commercial atomic layer deposition (ALD) setup [40]. Among them, CVD has potential for large-scale, low cost manufacturing of 2D-MoS₂. Moreover, there are several reports on the effect of the substrate for growing 2D-MoS₂ by CVD. These suggest that the substrate has a significant effect on the growth of 2D-MoS₂ [41–43]. On the other hand, a wide range of research has been done on the nonlinear properties of few-layer MoS₂ structures including SA, nonlinear absorption (NLA), nonlinear scattering and nonlinear refraction (NLR) [21, 44, 45].

In this work, a simple method for growing MoS₂ nanoflakes through thermal evaporation of MoO₃ nano-powder along with sulfur on different substrates (Si/SiO₂ and quartz) was carried out using one-step thermal chemical vapor deposition (TCVD). The resulting nanoflakes were then characterized using scanning electron microscopy (SEM), micro Raman spectroscopy, x-ray diffraction (XRD), UV-visible and PL. Then, the nonlinear optical properties of the obtained nanoflakes were studied by the Z-scan technique. This technique is a sensitive method for nonlinear material characterization [46–49]. The real and the imaginary parts of the third-order nonlinearity were specified by means of the closed aperture (CA) and open aperture (OA) Z-scans.

2. Experimental setup

Growth of the nanoflakes was performed in a horizontal furnace with a two inch diameter quartz tube at atmospheric pressure. The schematic of our experiments is shown in figure 1. At the beginning, for removing native oxides, the silicon substrate was soaked in hydrofluoric acid (HF) (10%). Then,
200 nm SiO2 was sputtered on the silicon substrates using Radio Frequency (RF) magnetron sputtering (Nanostructured Coatings Co. DST3, Iran) at a power of 130 W and pressure of \(1 \times 10^{-2}\) mbar during the deposition. Then, before each experiment, both substrates (silicon and quartz) were sonicated in acetone, ethanol and deionized (DI) water, respectively, for a duration of 10 min and they were then dried for 3 min at 80 °C. A ceramic boat containing 500 mg of sulfur powder (TITRACHEM 99, 0%) was placed outside the hot zone at the lower-temperature entrance of the tube (150 °C–200 °C). Another ceramic boat containing 50 mg of MoO3 powder (MERCK 99.5%) was placed at the highest temperature of the tube (900 °C) where the reaction occurred (the distance between the ceramic boats was about 25 cm). Afterward, the substrate was placed face down on top of the boat containing MoO3 at the hot zone. Initially, the furnace was purged for 30 min with Ar gas with a flow rate of 400 sccm. The temperature of the furnace was gradually enhanced to 900 °C within 20 min (45 °C min\(^{-1}\)) in the Ar environment. The growth time was set at 60 min for all of the samples to react with the precursors through the Ar flow rate of 200 sccm as carrier gas and finally the temperature was ramped down to room temperature.

The obtained nanoflakes were analyzed by micro-Raman spectroscopy (confocal PerkinElmer spectrum version 10.03.06) with an exciting laser wavelength at 785 nm, XRD (X’Pert PRO MPD), SEM (XL30), UV-visible (stellarNet EEP-2000) (in the range of 200–800 nm) and PL (Perkin Elmer LS55) excited with a xenon lamp at a wavelength of 525 nm.

Moreover, the single beam Z-scan technique was used to investigate the nonlinear optical properties of the nanoflakes containing NLA and NLR. The experimental setup is shown in figure 2. A diode laser with a wavelength at 532 nm was used as the light source. The sample is scanned via a focused laser beam and its transitions at different positions (Z-position) are noted. Small changes in light transition can be easily detected using a highly sensitive photodiode. As the sample is translated through the focal region of the beam, the photodiode measures the fraction of intensity passing through the aperture, which is transmitted through the sample. For determining the NLA, the OA was employed, whereas the CA was utilized to determine the NLR of the nanoflakes. The intense laser beam was sent through a ‘long’ focal length lens with a focal length of 10 cm. While the sample was consecutively moved along the z-axis via the beam waist, the OA Z-scan measured total transmittance via the sample as a function of incident laser intensity and the photodiode measured the changes in the absorbance of light. For the CA Z-scan a small aperture with a 1.3 mm diameter was used to limit the transmitted incident beam on the detector. Finally, the technique gives the real and imaginary parts of the third-order susceptibility, \(\chi^{(3)}\).

For sample preparation (because of the intransparency of the silicon substrate), the nanoflakes grown on the silicon substrate were exfoliated by immersing the sample in a solution of ethanol (64%) and DI water (36%) and treating it with an ultrasonic homogenizer at a power of 15 W for 15 min. Then, the treated solution was drop casted on the glass substrate and dried in atmospheric conditions.
3. Results and discussion

3.1. Structure

The XRD patterns of the nanoflakes grown on the silicon and quartz substrates are shown in figure 3. It can be observed that both of the XRD patterns present three peaks at $2\theta = 14.4^\circ$, $29.2^\circ$ and $44.4^\circ$ (ref. code: 01-077-0341) which correspond to the (0 0 3), (0 0 6) and (0 0 9) planes of 3R-MoS$_2$, respectively. Further, three peaks are observed at $2\theta = 18.4^\circ$, $26.0^\circ$ and $37.3^\circ$ (ref. code: 01-086-0135) which are attributed to the (1 0 0), (0 1 1) and (2 0 0) planes of MoO$_2$, respectively. It is worth noticing that the peaks that correspond to MoS$_2$ are intensified for the sample grown on the quartz substrate as compared to the silicon.

SEM micrographs of the nanoflakes grown on both substrates are shown in figures 4(a) and (b). These images confirmed formation of the nanoflakes with most popular vertical direction growth. The nanoflakes grown on the quartz (figure 4(a)) are obviously bigger than those grown on the silicon substrate (figure 4(b)). However, the nanoflakes grown on the silicon substrate can be obtained with relatively uniform distributions.

For investigating the optical properties of the nanoflakes, UV-visible spectroscopy was carried out. Figure 5 shows the absorption spectra of the samples grown on both substrates. Two separate excitonic absorption peaks can be seen at 662 nm (1.87 eV) and 606 nm (2.04 eV) for the samples grown on the silicon substrate. Similarly, peaks are observed at 679 nm (1.82 eV) and 630 nm (1.96 eV) for the nanoflakes grown on the quartz substrate. These peaks are signs of the A and B exciton transitions and they are also reported as a direct transition at the K point of the Brillouin zone [50]. In addition, figure 5 shows C and D absorption peaks specified to the direct transition from the deep valence band to the conduction band at the $\Gamma$ point [51, 52] these peaks are associated with van Hove uniqueness [53, 54]. The existence of van Hove uniqueness makes the monolayer MoS$_2$ suitable for photovoltaic cells. Another peak, observed at ~553 nm, can be interpreted as the result of a direct transition from the valence band to the conduction band at the M point of the Brillouin zone [53]. The difference between the two exciton transitions, due to the spin–orbital splitting of the valence band, was found to be 0.17 eV for the silicon substrate which is consistent with the theoretical values for 2D-MoS$_2$ (monolayer MoS$_2$) [55]. This difference is 0.14 eV for the quartz substrate. Furthermore, the results demonstrate that the MoS$_2$ nanoflakes grown on both substrates have a direct band gap of about 1.8 eV.

Moreover, Raman spectra of the nanoflakes grown on both substrates are shown in figures 6(a) and (b). The two characteristic modes can be obtained from the spectra: the $A_{1g}$ mode corresponds to the out-of-plane vibration of sulfur atoms and the $E_{1g}$ mode is linked to the in-plane vibration of Mo and sulfur atoms [56–59]. The frequency shift difference between these modes ($\Delta K$) ($A_{1g}$ and $E_{1g}$) is related to the number of layers. As the number of layers is increased, the frequency shift difference is elevated. The $E_{1g}$ and $A_{1g}$ modes for the nanoflakes grown on the silicon substrate were observed at 386 cm$^{-1}$ and 406 cm$^{-1}$ ($\Delta K = 20$ cm$^{-1}$), respectively (figure 6(a)). Similarly, for the nanoflakes grown on the quartz substrate, those modes were observed at 385 cm$^{-1}$ and 410 cm$^{-1}$ ($\Delta K = 25$ cm$^{-1}$), respectively (figure 6(b)). In fact, according to the literature, the frequency shift difference ($\Delta K$)
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for the monolayer is found to be smaller than 20 cm$^{-1}$ while the one for bulk is higher than 25 cm$^{-1}$ [19, 58, 59]. In addition, in the TCVD process, at high temperature the MoO$_3$ powder was reduced by S vapor, and volatile suboxides (MoO$_3$-$x$) formed. Further reaction of these compounds with S vapor causes MoS$_2$ nanoflakes to form [60–62]. So, the molybdenum oxides were acquired accompanying the sulfide structures. Therefore, in the Raman spectra, lots of side peaks besides the $A_{1g}$ and $E_{2g}$ peaks were observed, illustrating that this region is oxisulfide (MoOS$_2$) which is in accordance with other research [63].

The PL spectrum of the nanoflakes grown on silicon substrate is presented in figure 7 to confirm the thickness of the MoS$_2$ nanoflakes. Two PL peaks A and B are fingerprints of the band edge emission of MoS$_2$ from valence band splitting due to the spin–orbit split [64] that can be found around 676 nm (1.83 eV) and 620 nm (2 eV), respectively.

### 3.2. Nonlinear optics

In general, the Z-scan is a relatively simple method to separately measure the sign and magnitude of both NLR and NLA. It has achieved rapid acceptance by the nonlinear optics community as a standard technique [46]. Figure 8 shows the normalized transmittance of CA and OA Z-scans of the nanoflakes grown on both substrates (silicon and quartz). As exhibited in figures 8(a) and (b), the nanoflakes demonstrated a pre-focal peak followed by a post-focal valley. Accordingly, the negative value of the nonlinear refractive index denoted obvious self-defocusing behavior in both samples. The magnitude of the phase shift can be specified from the change in the normalized transmittance between peak and valley, $\Delta T = T_p - T_v$, for calculating the nonlinear refractive index ($n_2$) using equation (1):

$$\Delta T_{p-v} = 0.406 (1 - S)^{0.27} \left| \Delta \varphi_0 \right|$$

$$n_2 = \left( \frac{\lambda}{2\pi} \right) \frac{\Delta T_{p-v}}{I_0 \Delta \varphi_0}$$

where $S$ is the fraction of the beam transmitted through the aperture which was determined to be approximately 0.128 by $S = 1 - \exp (-2r_a^2/w_a^2)$—$r_a$ displaying the radius of the aperture and $w_a$ demonstrating the beam radius at the aperture; $I_0$ is the intensity of the laser beam at the focal point which is equal to $I_0 = 7269.093$ W cm$^{-2}$ and $L_{eff} = [(1 - \alpha_0)/\alpha_0]$

| Sample          | $n_0$ | $\alpha_0$ ($\mu$m$^{-1}$) | $n_2$ (cm$^2$ W$^{-1}$) | $\beta$ (cm W$^{-1}$) | $|\text{Re} \chi^3|$ (esu) | $|\text{Im} \chi^3|$ (esu) |
|-----------------|------|---------------------------|------------------------|-----------------------|--------------------------|------------------------|
| Si/SiO$_2$/MoS$_2$ | 4.77 | 29.9                       | $-3.11 \times 10^{-4}$ | 31.18                 | $0.1798 \times 10^{-4}$  | $7.6383 \times 10^{-4}$ |
| Quartz/MoS$_2$  | 4.77 | 64.7                       | $-5.16 \times 10^{-4}$ | $-145.72$             | $0.2 \times 10^{-4}$    | $35.69 \times 10^{-4}$  |

### Figure 8. Z-scan results of the nanoflakes grown on both substrates. (a) Close-aperture (CA) Z-scan result of the nanoflakes grown on the silicon substrate; (b) CA Z-scan results of the nanoflakes grown on the quartz substrate; (c) open-aperture (OA) of the nanoflakes grown on the silicon substrate and (d) OA of the nanoflakes grown on the quartz substrate.
is the effective thickness with linear absorption coefficient 
\[
\alpha_0 = -\frac{1}{2}\ln(I/I_0)
\]
where, \(I\) is the thickness of the sample which is equal to 25 and 100 nm for the nanoflakes grown on silicon and quartz substrates, respectively and \(I_0\) and \(I\) are the intensity of the incident and the transmitted radiation, respectively. The linear absorption coefficient was measured by the conventional method in the linear regime of the experiment (table 1). The obtained outcomes of the nonlinear refractive indexes for the nanoflakes are tabulated in table 1.

The OA Z-scan curves of the nanoflakes grown on the silicon substrate (as shown in figure 8(c)), illustrated a minimum transmission when the samples achieved the focal point (\(Z = 0\)). Normalized transmittance peaks in figure 8(c), display an obvious TPA response (corresponding to positive sign NLA (\(\beta > 0\))). However, the curve in figure 8(d), related to the nanoflakes grown on the quartz substrate, illustrated a maximum transmission when the sample achieved the focal point and a normalized transmittance peak, demonstrating the presence of a SA response (corresponding to negative sign NLA (\(\beta < 0\))). Remarkably, in comparison with the monolayer MoS\(_2\) grown on the silicon substrate, the multilayer MoS\(_2\) grown on the quartz substrate demonstrates a SA response under the same excitation conditions. Several previous studies have announced that the few-layer MoS\(_2\) displays a SA response even when excited by photons with less energy than the bulk MoS\(_2\) band gap 1.2 eV [18, 64–66]. The normalized change in transmitted intensity (\(\Delta T(Z) = T(Z) - 1\)) can be estimated by using the equation (2):

\[
\Delta T (z) \approx \frac{q_0}{2\sqrt{2}} \left[ 1 + \frac{z^2}{Z_0^2} \right]
\]

where \(Z_0 = km_0^2/2\) is the diffraction length of the focused beam which was determined to be \(Z_0 = 4.7\) mm and also the laser beam radii at the focal point was found to be \(w_0 = 28.23\) \(\mu\)m. Same as the CA experiment, the laser beam intensity at a focal point of \(I_0\) was used. NLA coefficient, \(\beta\), can be defined using equation (3):

\[
q_0 = \beta I_0 L_{\text{eff}}
\]

The results of NLA coefficient \(\beta\) are displayed in table 1. The obtained results demonstrated that the NLA coefficient of multilayer MoS\(_2\) grown on the quartz substrate was impressively increased. Then, the real and imaginary parts of the third-order nonlinear optical susceptibility \(\chi^3\) are calculated using the following equations:

\[
\text{Re} \chi^3 \text{ (esu)} = \left(10^{-5} \varepsilon_0 c^2 n_0^2/\pi \right)n_2 \text{(cm}^2 \text{W}^{-1})
\]

and

\[
\text{Im} \chi^3 \text{ (esu)} = \left(10^{-2} \varepsilon_0 c^2 n_0^2/4\pi n_2^2 \right)\beta \text{(cm} W^{-1})
\]

where \(n_2\) is the linear refractive index, \(\beta\) is the NLA coefficient, \(\varepsilon_0\) is the vacuum permittivity, \(c\) is the speed of light in vacuum and \(m_0\) is the linear refractive index of the MoS\(_2\) which is equal to 4.77. Based on this theory, the results of experiments are used to compute \(\text{Re} \chi^3\) and \(\text{Im} \chi^3\), which are presented in table 1.

4. Conclusion

MoS\(_2\) nanoflakes were successfully grown by one-step TCVD on silicon and quartz substrates via thermal evaporation of MoO\(_3\) and sulfur powder. XRD patterns of the obtained nanoflakes grown on silicon and quartz substrates, confirmed the formation of crystalline structures of 3R-MoS\(_2\). Moreover, several peaks corresponded to MoO\(_2\). It seems that the peaks corresponding to MoS\(_2\) are intensified for the sample grown on the quartz substrate as compared to the silicon. By estimation of the line width and the frequency shift difference between the \(E_{2g}\) and \(A_{1g}\) in Raman spectroscopy and the nanoflakes’ band gap through UV-visible and PL analysis, it was affirmed that the nanoflakes grown on the silicon substrate were monolayer structures while the nanoflakes grown on the quartz substrate were multilayer. Moreover, the Z-scan technique was applied to study the nonlinear optical properties of the obtained nanoflakes grown on both substrates. OA and CA Z-scan techniques were employed to study NLA and NLR. Furthermore, the nanoflakes grown on both substrates were found to exhibit self-defocusing behavior (negative NLR index). The OA Z-scan curves of the MoS\(_2\) grown on the silicon substrate exhibit obvious TPA response. However, the multilayer MoS\(_2\) grown on the quartz substrate, displays the presence of a SA response. In summary, the results demonstrate SA performance in multilayer MoS\(_2\) nanoflakes grown on the quartz substrate and TPA performance in monolayer MoS\(_2\) nanoflakes grown on the silicon substrate under the same excitation conditions. Furthermore, the real and imaginary parts of the third-order nonlinearity were assessed by means of the CA and OA Z-scans.

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