Structural and optical properties analysis of MoS$_2$ nanoflakes on quartz substrate as prepared by mechanical exfoliation

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Abstract. We study the structural and optical properties of MoS$_2$ nanoflakes on quartz substrate as prepared by mechanical exfoliation method. The structural and morphological properties of MoS$_2$ nanoflakes were characterized by SEM, EDS, and XRD, while the high-resolution spectroscopic ellipsometry (SE) with the photon energy of 1.27 to 6.53 eV is used to study its optical characteristics. As the results, SEM data shows that MoS$_2$ appears to be nanoflakes covering around 25-35% on the surface of quartz substrate, and XRD spectra shows the dominant orientation along c-axis (002). Based on spectroscopic ellipsometry analysis, the average thickness of MoS$_2$ nanoflakes is around 12 nm or about 6-8 layers. By using Tauc plot method, we confirm that MoS$_2$ nanoflakes have a semiconductor characteristic with the optical bandgap as high as 1.68 eV. Our study shows the important of structural and optical properties of MoS$_2$ nanoflakes that can be utilized for future optoelectronic devices and energy-harvesting purposes.

1. Introduction
Since 1859 scientists always failed to synthesize the two-dimensional materials, until finally graphene was found in 2004 with scotch tape by Novoselov and Constantine and it triggered the development of two-dimensional material [1–4]. Since that time, many potential materials such as MoS$_2$ were investigated further due to their potential merits in the future. MoS$_2$ is one of the TMDC (transition metal dichalcogenides) material that forms layered structure [1-3] with strong bonding (covalent bond) for each atom S-Mo-S in one layer or in one plane. MoS$_2$ has weak bonding (Van Der Waals bonding) for each layer which then can be detached into an individual plane or thin layers [4-6]. In the past, MoS$_2$ was usually used for lubricants in bulk size and its properties become interesting when it reaches nanosize, especially in two-dimensional material like graphene. The mobility reaches up to 410 cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature, while its high on/off ratio is about $10^9$. On the other hand, graphene has conductive properties low on/off ratio making less suitable for electronic devices. Additionally, MoS$_2$ has a sizeable bandgap that depends on the thickness. At monolayer thickness, it exhibits direct energy bandgap around 1.3 eV [7,8] resulted in the photoluminescence properties [9]. Therefore, it is very applicable for optoelectronic devices, namely solar cell and photodetector. At bulk structure, the band gap will turn into indirect around 1.8 eV [10] and it can be applied effectively for devices such as FET, memory, and battery.

Nowadays, the knowledge of optical properties and its correlated nanostructure of MoS$_2$ is still rarely investigated, especially in the broad energy spectrum. In this paper, we investigate the structural and
optical properties of MoS\(_2\) nanoflakes in the energy range of 1.27 to 6.53 eV. Spectroscopic ellipsometry (SE) was used to determine the dielectric function of MoS\(_2\). Dielectric function is the optical properties that can describe light-matter interactions and explain the excited-state properties of material. The dielectric function can also explain electronic structure of MoS\(_2\) and its potential application. Hence, it is crucial to determine the dielectric function to profoundly understand the potential of MoS\(_2\).

2. Method

Mechanical exfoliation is one of the top-down methods that is very handy and simple compared to any epitaxial synthesis, and this method is still reliable enough to represent the characteristic of the attached material. MoS\(_2\) bulk was peeled into nanoscale by adhesive tape [11-13]. Equalization or exfoliation process was repeated for 60-70 times or ten minutes every sample. Then it is pasted above quartz substrate as many as 10 times. For the comparison, we also attached bulk MoS\(_2\) upon silicon. The structural and morphological properties of MoS\(_2\) nanoflakes were characterized by SEM (scanning electron microscopy), EDS (Energy Dispersive X-Ray Spectroscopy), and XRD (x-ray diffraction) spectra. The high-resolution Spectroscopic ellipsometry (SE) with the photon energy of 1.27 - 6.53 eV was used to study its optical characteristics. SE measurements were carried out using an incident angle of 70° at room temperature. Amplitude ratio \(\psi\) and phase difference \(\Delta\) of the polarized light were directly obtained from this measurement. We used RefFit software to analyze the dielectric function of MoS\(_2\) by fitting both parameters using Drude-Lorentz model, as shown in equation 1. This model describes the free carrier absorption and electrical polarization of oscillated electron. The model is represented as

\[
\varepsilon(\omega) = \varepsilon_\infty + \sum_i \frac{\omega_p^2}{\omega_p^2 - \omega^2 - i\gamma_i\omega}
\]

where \(\varepsilon_\infty\) describes the infinite frequency, \(\omega_p\) describes plasma frequency, \(\omega_0\) describes the angular frequency and \(\gamma\) describes scattering rate [14]. From the generated model, it will produce the complex dielectric function that are mutually connected by Kramers-Kronig relation, as shown in equation 2 and 3. So, once we find the real part of the dielectric function, we can get the imaginary part simultaneously [15].

\[
\varepsilon_1(\omega) = 1 + \frac{2}{\pi} p \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'
\]

\[
\varepsilon_2(\omega) = -\frac{2\omega}{\pi} p \int_0^\infty \frac{\varepsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega'
\]

3. Results and Discussion

Based on the SEM image shown in figure 1, MoS\(_2\) is attached well with the coverage area around 25-35% on quartz substrate. The thickness of MoS\(_2\) is varied, which depends on its position. Figure 1(d) shows that the number of layers are around 2 layers. As we can see in figure 1, MoS\(_2\) is formed by multiple layers which is bounded by Van Der Waals force for each layer, like a stacking structure. The most important information from this microscopy images is that the MoS\(_2\) was not grown in the homogenous area, however it form a very small flake called as the nanoflakes.
Figure 1. SEM images of MoS$_2$ bulk on Si with magnification (a) 500 times and (b) 40,000 times. Nanoflakes MoS$_2$ shows the coverage area 25-35% on top of quartz with magnification 500 times and (d) 40,000 times.

EDS was used to determine the composition of the sample. If we compared between figure 2(a) and 2(b), there are still remain the molybdenum and sulfur characteristic in the different quantity. It is obvious that the elemental composition of bulk MoS$_2$ is more visible rather than the composition of MoS$_2$ nanoflakes, and confirm that the attached MoS$_2$ is not fully cover quartz substrate and consist of a small pieces of nanoflakes. Besides Mo and S, there are no others atomic element are identified, so we conclude that the attached material on quartz is pure MoS$_2$.

Figure 3 shows the XRD spectra of MoS$_2$ in bulk and multiple layer form. Bulk MoS$_2$ have many peak or miller indices. This indicates that MoS$_2$ in bulk form tend to be polycrystalline than in the nanoflakes form. The synthesized nanoflakes just have one peak (002) along c-axis. As the decrease of the composition, the miller indices will be decreased as well. By using equation 4, lattice parameters of hexagonal MoS$_2$ is obtained (a=b=3.160 Angstrom and c = 12.30 Angstrom). As compared to the reference [16], we find the error of a = b = 0.032% and c = 0.040%.

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}(h^2 + k^2 + hk) + l^2 \left(\frac{a}{c}\right)^2 \frac{1}{a^2}$$

Figure 2. EDS analysis (a) MoS$_2$ bulk (b) MoS$_2$ nanoflakes.
Figure 3. XRD data of bulk MoS$_2$ on Si (blue line) and nanoflakes MoS$_2$ on quartz (red line). The obtained lattice parameters of hexagonal structure are $a=3.16 \, \text{Å}$ and $b=12.3 \, \text{Å}$.

Because of Spectroscopic Ellipsometry is one of the indirect measurement, fitting $\psi$ and $\Delta$ data should be carried out to analyse the optical properties and its derivative. Drude-Lorentz model was chosen in the fitting process. In figure 4 (a) and (b), $\psi$ and $\Delta$ data of quartz substrate are almost reach 0° until having a peak around 6.2 eV. This peak indicates that substrate quartz is one of the isolator material. In Figure 4 (c) and (d), we can observe clearly the optical characteristic of MoS$_2$ nanoflakes. We assume that the resulted thickness is determined by the average of each nanoflake.

Fig 4. Fitting results of (a) $\psi$ (amplitude ratio) and (b) $\Delta$ (phase difference) of quartz substrate, and (c) $\psi$ and (d) $\Delta$ of MoS$_2$ nanoflakes. All of the data resulted by the incident angle of 70° from SE equipment.
From the best fit of experimenta data, we can extract optical constants of nanoflakes MoS$_2$, such as reflectance ($R$) and transmittance ($T$), as shown in fig. 5. Reflectance spectra represents the process of electromagnetic waves returned at the boundary of material, whereas transmittance represents the passage of electromagnetic waves through a material. Those $R$ and $T$ represent the specific character of MoS$_2$ nanoflakes attached above quartz substrate. From reflectance curve, MoS$_2$ have responses in visible region area. The unusual shape of the curve is caused by the absorbance responses of the excitation process in MoS$_2$[17,18], till the shape become constant at the high photon energy. Because the small intensity of reflectance and transmittance, MoS$_2$ nanoflakes is indicated to be one of the absorbing material and show the opaque characteristic material. In addition, the thickness of MoS$_2$ is around 15 nm or around 6-8 layers. From its layer, this MoS$_2$ nanoflakes must be an indirect type bandgap.

From the penetration depth parameters, Tauc-plot method is used to determine the optical bandgap. The obtained optical band gap is $\sim$1.68 eV. It was matched with the thickness of MoS$_2$ around 6-8 layers. This bandgap is suitable for the future devices, like electronic devices or optoelectronic devices.
4. Conclusion

EDS spectra and SEM images confirms that the nanoflakes MoS$_2$ is properly attached on the quartz substrate, and XRD spectra show that the crystallinity of MoS$_2$ is hexagonal with the lattice parameter $a = b = 3.160$ Å and $c = 12.30$ Å. More interestingly, $R$ and $T$ spectra of MoS$_2$ nanoflakes are small that indicates an opaque characteristic material and might be useful as an absorbing material. Based on the Tauc-plot method, the optical bandgap is $\sim$1.68 eV that come from the valence band to the conduction band transition. This study reveal the fundamental properties of MoS$_2$ nanoflakes that will be promising candidates for future optoelectronic devices and renewable energy application.

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