MoS$_2$ thin films spectrophotometry

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Abstract. Molybdenum disulphide (MoS$_2$) thin films deposited on silicon substrates by magnetron sputtering spectrophotometry study results are presented. Graphical-calculated method for MoS$_2$ thin film samples bandgap values determination was used.

1. Introduction
In recent years two-dimensional materials such as MoS$_2$, for example, attract increasing attention as promising materials group for using in a new generation of nanoelectronic devices because of its unique properties as high electron mobility, excellent current ON/OFF ratio and etc. [1]. MoS$_2$ thin films as semiconductor has tunable bandgap, that varies with a thickness. As known, bulk MoS$_2$ has an indirect band-gap, however, with reducing their thickness to monomolecular layer, formed by two sulfur atoms and one molybdenum atom, electronic structure of it transformed to the direct bandgap [2]. The effectiveness of the molybdenum disulphide using at the digital electronics area stayed actual due to the presence of a bandgap, whose width reaches 1.8 eV value for a monolayer film [2]. And the using such films in the field-effect transistors prototypes provides a high ratio of currents through the channel at the open / closed states (ON/OFF), which are 6-8 orders of magnitude.

To study and measure the spectral characteristics and properties of promising two-dimensional materials are widely used optical methods, including, based on the reflectance spectrum detection, implemented at simple equipment. The reflection spectroscopy method can be used to study thin films with the thicknesses in the range from 1 nm to 1 mm [3]. Transmittance $T$ and reflectance $R$ optical coefficients values using allow with a much more accuracy determinate optical absorption coefficient ($\alpha$) at the region around the optical gap, and rest upon the equations of $\alpha$ as a wavelength $\lambda$ function can be implemented bandgap energy. Group of Miika Mattinen et. al 2017 [4] produced by ALD method MoS$_2$ thin films at borosilicate glass substrates and determine bandgap by applying Tauc graphical method, using absorption spectrum recalculated from the transmission spectrum. At report [6] also shown that the bandgap of thin films TiO$_2$ can be obtained by using Tauc method from the absorption coefficient, derived from the diffuse reflectance.

MoS$_2$ thin films optical properties at the different thickness measuring by spectrophotometer «Epsilon» and its bandgap estimation by using Tauc method results is presented at this work.

2. Experimental
MoS$_2$ thin films at silicon substrates were prepared by magnetron sputtering MoS$_2$ target at $10^{-3}$ Pa argon pressure. Substrate surfaces before the deposition passed preliminary preparation with two stages: cleaning at ultrasonic bath in alkaline solution and ethanol consistently, and surface treating
with argon ions bombarding from an independent ion source in a single vacuum, immediately before the material target sputtering. The substrate temperature for different process parameters was set at the range from 200 to 300 °C. The thicknesses of the samples were determined by masking part of the substrate surface during deposition in order to have a sharp step between coated and uncoated zone, and then measuring the height profile.

MoS$_2$ thin films measurements were carried out at atomic force microscopy (AFM) "Solver-NEXT" by "NT-MDT". And the "Epsilon" spectrophotometer with the wavelength range 380-1100 nm was used for the diffuse reflectance spectral characteristics at prepared samples with coatings optical measurements.

The "Epsilon" spectrophotometer that used at this work provides spectral reflectance $R$ for flat optical components and coatings on the substrate measurements. An optical scheme equipped with a white light source collected the reflected light signal from the sample. An optical fiber used to selectively couple part of the reflected light signal into a spectrophotometer. At the device optical system the spectral reflector uses fixed angle (90°) to a surface and carry out spectroscopic measurement that scans the frequency of the probe light. Conditionally, the elementary diagram for MoS$_2$ thin films on Si substrate reflectance spectrum measurements is shown in Figure 1. At transmittance spectrums registration except components of light which as it is shown in Figure 1, has passed through a substrate and researched layer, it is possible to evolve some component which has passed through film layer, but it was reflected from the film-substrate border. This component spectrum in the general stream of the light reflected from the researched sample represents resulting reflectance-absorption spectrum, taking into account absorbed light.

![Figure 1. Scheme for the spectral reflection measuring of MoS$_2$ thin films on Si substrate.](image)

The most widespread approach to the light behavior theoretical analysis in the dispersing medium consists in the decision first-order differential equations system that describes an intensity decreasing in a sample own due to the arising phenomena from absorption and scattering. On this approach based P. Kubelka and F. Munch, and also M. Gurevich have positioned interrelation between absorption coefficients $\alpha$, medium dispersion $S$, and diffusive reflectance quotient ($R$) which can be received experimentally:

$$ F(R) = \frac{(1-R)^2}{2R} = \frac{\alpha}{s} $$

(1)

Function $F(R)$ (1), is the absorption function which is in proportional dependence with a layer material absorption coefficient, therefore, having executed spectrum registration at a diffusive scattered radiation and plotted absorption function from the light wave length dependence it is possible to receive actually investigated material absorption spectrum. Its difference from a real absorption spectrum will consist only at a difference value of a light dissipation factor $S$ at a sample surface.

To estimate materials optical bandgap modified Kubelka–Munk function can be applied by receiving function $F(R)$ on photon energy $hv$ multiplication, using the corresponding coefficient ($n$) that associated with an electronic transition, as follows:

$$ (F(R) \times hv)^n $$

(2)

By extrapolating equation (2) as an energy function in eV, the semiconductor films bandgap can be obtained. It is known that the monomolecular MoS$_2$ layer has a direct bandgap, and two or more MoS$_2$
layers have an indirect gap, so for the calculations performing the corresponding value of the semiconductors indirect gap coefficient \( n = \frac{1}{2} \) is using.

To determine the optical bandgap in accordance with the Tauc method [5], that based on relation (3), \((F(R) \times hv)^{1/2}\) from \(hv\) dependences were plotted and then extrapolated to the \(hv\) axis (Figure 3b) with photon energy value that corresponding to the bandgap \((E_g)\) value.

\[
(F(R)hv)^{1/2} \approx (hv - E_g)
\]  

(3)

3. Results and discussion

In experiments series five samples \(\text{MoS}_2\) thin films on Si substrates with a difference in the thickness and surface roughness have been prepared. The measured values of a thickness and average square roughness \(R_a\) are resulted in table 1. Figure 2 shows the reflection spectra of \(\text{MoS}_2\) films for samples A, B, C, D, E, and also for an initial silicon substrate.

Figure 2. \(\text{MoS}_2\) films samples on Si substrate spectra’s.

Figure 3. Graphical representation of \(F(R)\) spectra – absorbance coefficient from the light wavelength dependences (a); Graphical representation of \((F(R)hv)^{1/2}\) from \(E_g\) dependences for \(\text{MoS}_2\) samples (b).
Based on the dependence (1) and using the obtained reflection coefficient values for different wavelengths, the values for the absorption function \( F(R) \) were determined.

The calculated absorption coefficient values were used to plot the dependence \( (F(R)hv)^{1/2} \) from \( hv \), whose fragment for the energy range of wavelengths from 1.2 eV to 3.3 eV is shown in figure 3(b). Subsequently, by extrapolation at the linear sections of the plots, the bandgap values for each MoS\(_2\) sample were determined.

Using the Tauc method were obtained bandgap values for MoS\(_2\) films samples at different thickness and roughness results are summarized in table 1. For D and E samples with the same thickness but deposited at different parameters, were observed a difference in \( E_g \) values that can be caused by differences in a films structure, which reflected on a surface roughness.

### Table 1. MoS\(_2\) films on Si substrates geometric characteristics and bandgap \( E_g \) experimental values.

| MoS\(_2\) samples | Thickness, nm | Roughness \( R_a \), nm | Bandgap calculated value \( E_g \), eV |
|------------------|--------------|-------------------------|-------------------------------------|
| A                | 500          | 3.688                   | 1.33                                |
| B                | 530          | 4.265                   | 1.31                                |
| C                | 680          | 4.856                   | 1.3                                 |
| D                | 20           | 1.201                   | 1.38                                |
| E                | 20           | 0.974                   | 1.4                                 |

### Conclusions

At the present results shows that for MoS\(_2\) films with a more than 600 nm thickness, the observed bandgap values had compatibility with the MoS\(_2\) bulk crystals characteristic literature data’s (1.3 eV). With the films thickness decreasing to 530 nm or less, bandgap values increasing and reaching 1.4 eV at a 20 nm film thickness is observed.

### References

[1] Radisavljevic B et al. 2011 *Nature Nanotech* **6** 147–50
[2] Mak K F et al. 2010 *Phys Rev Lett* **105** 136805
[3] *Filmetrics* https://www.filmetrics.com/ellipsometry
[4] Mattinen Miika 2017 *Adv Mater Interfaces* **4** 1700123
[5] Tauc J 1972 *Journal of non-crystalline solids* **10** 569–85
[6] Murphy A B 2007 *Solar Energy Materials & Solar Cells* **91** 1326–37