Study of the parameters of molybdenum oxide films by optical methods

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Abstract. In this work, the physical properties of molybdenum oxide films obtained by reactive magnetron sputtering were studied. Based on the experimental transmission and reflection spectra for samples at different currents in the fundamental absorption region, the optical band gap was determined, and in the visible range, the thickness of the films was defined. The studied films had the values of optical parameters that were observed by other authors. However, the dependence of the optical band gap width on the thickness of the films is not found in the literature and can be associated with the influence of the flux density of the substance sputtered from the target surface on the structure of the film.

Films based on oxide materials gained popularity last years (in particular, molybdenum oxide) due to their properties, which include high optical transparency, good mobility of electrical carriers and resistance to mechanical stress.

The ability to customize their physical properties resulting in various electronic and geometric structures that can have metallic, semiconducting or insulating properties makes this class of materials unique. This increases their importance as potential materials in a wide range of applications, including transparent electronics, optoelectronics, magnetoelectronics, photonics, spintronics, thermoelectric, piezoelectric, energy harvesting, hydrogen storage, and environmental waste disposal. In particular, flat 2D materials can be a promising area of application for molybdenum oxide, which may be ideal candidates for channels for future field-effect transistors [1].

There are several methods for producing MoO$_3$ thin films, including physical sputtering, chemical vapor deposition, pulsed laser sputtering, spin coating, spray pyrolysis, atomic layer deposition and printing [2]. In particular, reactive magnetron sputtering is considered as the most suitable method for producing a uniform thin film.

In [3–5] the optical properties of molybdenum oxide films were determined under various deposition conditions. Under standard conditions, films have poor absorption in the visible wavelength range. It was found that the optical band gap width varies from 2.5 to 4.0 eV, the refractive index varies from 1.55 to 2.50 and the optical transmission of the films reaches 95 percent.

In this work, molybdenum oxide films were synthesized by reactive magnetron sputtering in an Ar + O$_2$ environment. The volume of the vacuum chamber was $8 \times 10^{-3}$ m$^3$, a planar magnetron with a molybdenum target 60 mm in diameter was installed inside. The deposition of films on a glass substrate took place within 20 minutes, while the Ar pressure was 6 mTorr. The O$_2$ consumption was chosen so that the oxide mode of operation was observed during sputtering. The films were deposited at three current values (0.6, 1.1 and 1.5 A).
When recording experimental transmission spectra in the range of 200–1000 nm, an ISM3600 spectrometer was used with an absolute error of wavelength no more than 0.5 nm. The obtained spectra were processed using the Aspect2010 program. A halogen lamp in the range of 400–1000 nm and a deuterium lamp in the range of 200–400 nm were used as sources of optical radiation.

The results of measurements of the experimental transmission spectra of films that were produced at different currents can be seen in figure 1. Oscillations occurring in the visible range are explained by the interference of incident and reflected waves from the film-substrate interface. There is a known technique for calculating the parameters of films based on transmission spectra and making it possible to determine their thickness, refractive indices and absorption [6, 7].

In this work, we used a simpler method for calculating the film thickness and refractive index, in which calculations are carried out from the reflection spectra at two angles of incidence of the light wave (see figure 2). When the angle of incidence changes, the position of the extrema is shifted. From these displacements through the difference in the path of the rays and the Snell equation, the required parameters are calculated. The calculation technique is based on a set of formulas:

\[
d = \frac{\sqrt{\Delta^2 - (\Delta')^2}}{\sin \alpha}, \quad n = \sin \alpha \left[1 - \left(\frac{\Delta'}{\Delta}\right)^2\right]^{1/2},
\]  

(1)

where \(d\) is the film thickness; \(\alpha\) is the angle of incidence of the light wave; \(n\) is the refractive index and:

\begin{align*}
\Delta &= \lambda_1 - \lambda_2, \\
\Delta' &= \lambda_1 - \lambda_3,
\end{align*}

(2)

\begin{align*}
\lambda_1 &= \text{wavelength for maximum transmission,} \\
\lambda_2 &= \text{wavelength for minimum transmission,} \\
\lambda_3 &= \text{wavelength for another extremum.}
\end{align*}

Figure 1. Experimental transmission spectra of MoO\(_3\) films: \(a\) – in the UV range; \(b\) – in the visible range at discharge current values (A): \(1\) – 0.6; \(2\) – 1.1; \(3\) – 1.5.

Figure 2. Reflection spectra of a film deposited at a discharge current of 1.5 A at \(\alpha\): \(1\) – 0°; \(2\) – 30°.

Figure 3. Dispersion of the refractive index of a film deposited at a discharge current of 1.5 A.
where \( \lambda \) and \( \lambda' \) – the positions of the extrema max and min at \( \alpha = 0^\circ \) and \( \alpha = 30^\circ \), respectively. The results of calculations by formulas (1) and (2) are summarized in table 1 and shown in figure 3.

The refractive index in the visible range has a normal dispersion characteristic (table 2). Unfortunately, the method for calculating the dispersion characteristic \( n(\lambda) \) for other samples cannot be calculated by this method due to the small number of extrema in the spectra.

**Table 1. Films thickness.**

| Discharge current, A | Film thickness, nm |
|---------------------|-------------------|
| 0.6                 | 270               |
| 1.1                 | 420               |
| 1.5                 | 650               |

From the UV transmission spectra in figure 1, it can be seen that the fundamental absorption edge shifts to longer wavelengths with increasing current. This indicates an increase in the width of the optical bandgap \( E_g \) of the film.

Fundamental absorption is determined by the configuration of the energy bands, and all films can be divided into two main types [8]. The first of them have vertical or direct transitions of electrons to the conduction band, their probability depends on the photon energy so that the intrinsic absorption coefficient \( \alpha \) can be expressed in the following way:

\[
\alpha = \begin{cases} 
A(h\nu - E_g)^{1/2} & h\nu > E_g \\
0 & h\nu \leq E_g 
\end{cases}
\]

(3)

where \( A \) is the coefficient of proportionality; \( h\nu \) is the photon energy.

In films of the second type, indirect (non-vertical) transitions occur, which are carried out with the emission or absorption of phonons. Neglecting the phonon energy, which is usually more than an order of magnitude smaller than the gap width, the intrinsic absorption coefficient for indirect transitions is expressed by the formula

\[
\alpha = \begin{cases} 
B(h\nu - E_g)^2 & h\nu > E_g \\
0 & h\nu \leq E_g 
\end{cases}
\]

(4)

where \( B \) is the coefficient of proportionality.

From (3) and (4) it follows that if only one type of transition (direct or indirect) occurs in the film, then only one of the dependences can be a first-order polynomial:

\[
\alpha^2 = f(h\nu) \quad \text{and} \quad \sqrt{\alpha} = f_1(h\nu),
\]

(5)

respectively. To determine what type of transition is implemented, both dependencies are approximated by this polynomial. The type of transition is determined by the best agreement of the approximating straight line with the experimental points. By extrapolating the selected straight line to the intersection with the photon energy axis, the value of \( E_g \) is determined. The results of calculations using formulas (5) are shown in figure 4, which shows that indirect transitions occur in the studied films. The numerical values of \( E_g \) are summarized in table 2.
In conclusion, we note that the films under study have values of optical parameters that were also observed by other authors. However, the dependence of the width of the optical bandgap on the thickness of the films is not found in the literature and may be associated with the influence of the flux density of the substance sputtered from the target surface on the structure of the film.

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