PHYSICAL PROPERTIES OF MOLYBDENUM AND ITS OXIDES IN FILM FORMATION

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Abstract. *This article examines the requirements of modern electronics, the need for new materials and technologies to meet these requirements, and the challenges of creating heat-resistant alloys, including refractory alloys. The solution to these problems was the production of film structures based on molybdenum oxide, followed by a study of their properties using electrical and optical methods.*

Modern electronics require materials that can withstand increasingly harsh operating conditions, including elevated temperatures and aggressive environments. Traditional alloys often fail to meet these stringent requirements because of their limited thermal stability and mechanical strength. This challenge has driven the search for novel materials and advanced technologies capable of delivering enhanced heat resistance without compromising other essential properties of the material. Among the promising solutions are refractory alloys, which are known for their high melting points and resistance to deformation at elevated temperatures; however, their practical application is hindered by difficulties in fabrication and performance optimization.

To address these challenges, research has focused on developing film structures based on molybdenum oxide, which offers a versatile platform for tailoring the electrical and optical properties of modern electronics. The production of these films involves precise control over their composition and microstructure, enabling improved heat resistance and functional performance. Subsequent characterization using electrical and optical methods provides critical insights into their behavior under operational stress, facilitating the optimization of these materials for practical applications. This approach represents a significant step toward overcoming the limitations of conventional heat-resistant alloys and advancing the development of next-generation electronic components.

Keywords*: electron shell, valence, film structure, molybdenum oxide, molybdenum foil.*

Introduction

One of the significant challenges in modern microelectronics is the search for new material. Despite the rapid and significant development of silicon technology, the range of requirements and challenges facing modern electronics is so broad that new materials and technologies are required to meet them. From a practical perspective, transition metal oxides are promising materials. Owing to their unfilled electron shells, transition metals exhibit variable valence and form a wide range of compounds with oxygen.

The current development of modern technology (primarily in the rocket, space, and aviation industries) places several demands on alloys capable of operating at high temperatures, where traditional nickel-based alloys cannot be used.

Molybdenum plays a significant role in modern technologies. Of all the molybdenum consumed by the industry, up to 80% is used in the ferrous metallurgy industry for the production of heat-resistant, heat-resistant anti-corrosion, tool, high-speed, magnetic, and structural steels, as well as heat-resistant and heat-resistant cast irons. Molybdenum increases the strength of steels at low temperatures, promotes their retention at high temperatures, improves the heat resistance of steels and cast irons, and improves their hardenability. One part by weight of Mo increases the strength of steel equivalent to 2-2.5 parts by weight of wolfram.

Niobium, wolfram, and molybdenum oxides are known to possess electrochromic and photochromic properties. Nearly all transition metals exhibit the properties of electronic switches when combined with oxygen and undergo a metal-insulator phase transition [1].

The switching effect is associated with the formation or reversible electrical breakdown, which forms a conducting channel in the dielectric matrix of the base material. Despite intensive research, the study of switching phenomena continues, and the accumulation of experimental data contributes to the development of stable technical designs based on film structures with switching and memory properties. Furthermore, the study of switching phenomena is of interest for solving several problems related to the mechanism of the metal-semiconductor phase transition [2].

The relevance of this work lies in the search for new materials for practical applications, as well as the research and accumulation of experimental data in the field of phase transitions in solids.

The goal of this study was to obtain film structures based on molybdenum oxide, followed by an investigation of their physical properties using electrical and optical methods.

Properties of simple substances. The appearance of metallic Mo depends on the production method. Compact molybdenum (in the form of ingots, wire, sheets, or plates) is a fairly light but dull metal, whereas molybdenum obtained in a mirror-like form by decomposition, for example, of carbonyl, is shiny but gray. The molybdenum powder was dark gray. The density of Mo was 10,280 kg/m3. Its melting and boiling points are 2623 and 4639°C, respectively. Only one crystalline modification of the metal is known (at normal pressure), with a body-centered-cubic lattice. In its pure state, compact Mo is ductile and malleable, and can be stamped and rolled fairly easily. At high temperatures (but not in an oxidizing atmosphere), the strength of Mo exceeds that of most other metals. When contaminated with carbon, nitrogen, or sulfur, Mo, like Cr, becomes brittle and hard, significantly complicating its processing. Hydrogen is sparingly soluble in molybdenum and therefore cannot significantly affect its properties. Molybdenum is a good conductor of electricity, being only three times inferior to silver in this regard. Its electrical conductivity is greater than that of platinum, nickel, mercury, iron, and many other metals.

Under normal conditions, molybdenum is stable, even in humid air. Its reactivity depends on the degree of grinding, and fine powder still slowly oxidizes in humid air, producing the so-called molybdenum blue. Molybdenum begins to vigorously react with water vapor at 700°C and with oxygen at 500°C.

$Mo + 2H_2O = MoO_2 + 2H_2$

$2Mo + 3O_2 = 2MoO_3$.

Molybdenum burns in a fluorine atmosphere at 50–60 °C, and reactions with other halogens occur at higher temperatures.

$Mo + 3F_2 = MoF_6$

$2Mo + 5Cl_2 = 2MoCl_5$.

Dilute and concentrated mineral acids dissolve Mo when heated, but concentrated HNO_3 passivates it. At elevated temperatures, Mo reacts with sulfur, Se, As, nitrogen, carbon, and many other nonmetals.

The main industrial method for producing metallic Mo is the reaction of MoO_3 with hydrogen:

$MoO_3 + 3H_2 = Mo + 3H_2O$.

This process occurs in two or three stages. First, molybdenum anhydride is reduced to MoO_2 and then to a free metal. The first stage of reduction occurred at 550°C. If the second stage occurs below 900°C, the resulting metal contains a significant amount of oxygen, requiring a third stage of reduction at 1000–1100°C or higher. The metal obtained in this manner is suitable for processing using powder metallurgy methods.

For a long time, it was not possible to obtain molybdenum in a compact state, and a method for producing molybdenum wire was proposed only in 1907. The metal powder was mixed with an organic adhesive (sugar syrup) and forced through the die holes to form filaments. A direct electric current with a small potential difference was passed through the filaments in a hydrogen atmosphere. This generates intense heat, burning the organic material and sintering the metal particles to produce the wire.

Powder metallurgy techniques are now used to produce compact molybdenum, allowing ingots to be produced at temperatures significantly lower than the melting point of the metal. Powdered Mo was pressed in hydraulic presses in steel dies, heated in a hydrogen atmosphere at 1100–1300°C, and sintered at 2200°C in a hydrogen atmosphere in thick-walled Mo boats. Another common method is melting molybdenum in a vacuum using an electric arc generated between a rod of pressed molybdenum powder and a cooled copper electrode at a current of 7000 A and a small potential difference. Melting using a focused electron beam or argon plasma is sometimes used.

Molybdenum(II) oxide, $MoO_{0.93\text{-}0.97}$. When potassium vapor reacts with molybdenum oxygen compounds, a series of products containing $K_{1.5}MoO_3$ and $K_{0.6}MoO_2$ are formed. When exposed to water or alcohol, these products are converted to soluble molybdate, oxygen, and a black, sparingly soluble precipitate with strong reducing properties and a composition that is intermediate between $MoO_{0.93}$ and $MoO_{0.97}$.

Molybdenum(III) oxide, Mo_2O_3. A matte black powder. Density is 7.07 g/cm^3. It is slightly soluble in water. It is obtained by the dehydration of molybdenum(III) hydroxide and the reduction of molybdenum trioxide with liquid potassium or hydrogen.

Molybdenum(IV) oxide, MoO_2. It is a gray amorphous powder or violet-brown paramagnetic monoclinic crystal. Density is 6.47 g/cm^3. Stable in air, it slowly sublimes in a vacuum at 1100°C. It exhibits semiconducting properties. It is slightly soluble in water, acids, and alkali. It dissolves in oxidizing acid solutions. It is obtained by oxidizing metallic Mo with a mixture of water and hydrogen vapor at 700-800°C, gently heating the powdered metallic Mo in air, and reducing molybdenum trioxide with hydrogen, zinc, and Cd upon heating.

Molybdenum(V) oxide, Mo2O5. It is obtained in the form of a dark purple powder by the dehydration of molybdenum hydroxide in a stream of gaseous CO_2 (or nitrogen), as well as by the decomposition of compounds $Mo_2O(SO_4)_2$ and $Mo_2O(C_2O_4)_2$ in a stream of nitrogen.

Molybdenum(VI) oxide (MoO3). Weakly paramagnetic, birefringent, white, shiny, snow-like (yellowing when heated), and orthorhombic crystals with a layered structure. mp = 795°C, bp = 1255°C, density = 4.69 g/cm^3. It is soluble in water, excess alkali solutions, and alkali metal carbonates. It is obtained by calcining Mo in air at 570°C.

In addition, oxides with compositions intermediate between MoO_3 and MoO_2 have been obtained: Mo_8O_{23}, Mo_9O_{26}, Mo_4O_{11}, and $Mo_{17}O_{47}$. The bonding in the oxides is primarily ionic and partially covalent. MoO_2 is more refractory and thermodynamically stable than MoO_3.

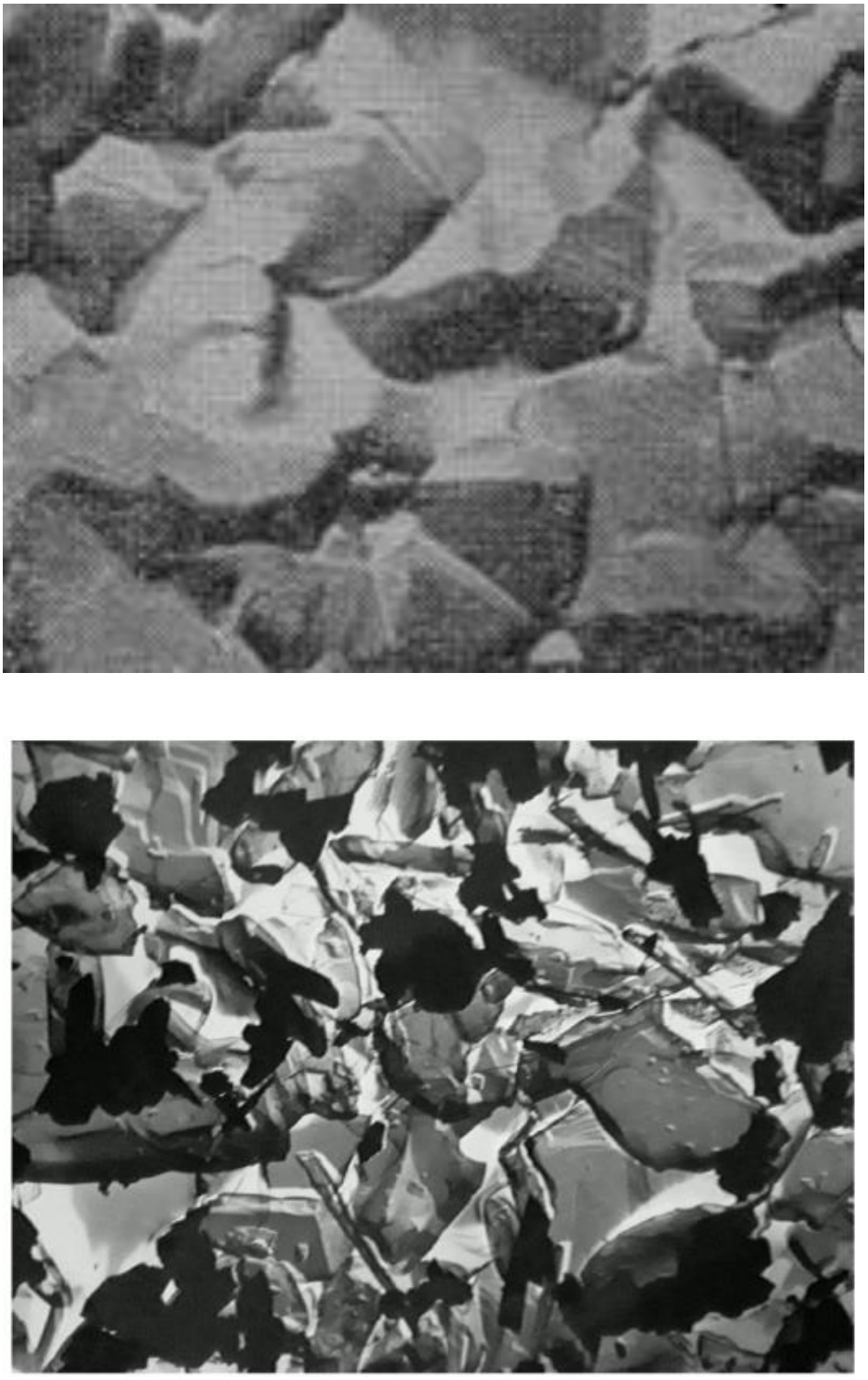
As molybdenum is a metal, its oxides should exhibit basic properties. However, the oxides MoO_3 and MoO_2 are acidic rather than basic. They form a series of compounds with general formulas of H_2MoO_4 and H_2MoO_3. The oxide Mo_2O_3 exhibits basic properties.

In terms of chemical properties, the oxide exhibits more basic properties, and the greater the electronegativity difference between the element and oxygen. The Pauling electronegativity of Mo is 1.8, whereas that of oxygen is 3.5. As can be seen, the electronegativity difference between the elements is 3.5 – 1.8 = 1.7.

The basic properties of molybdenum oxides can be confirmed by their interactions with acidic and alkaline solutions.

MoO_3 Films. Thin MoO_3 films have attracted considerable attention owing to their interesting structural, chemical, electrical, and optical properties [3-5]. These layers have wide applications in batteries, electrochromic devices, solar cells, gas sensors, and optoelectronic devices. Owing to its wide bandgap (Eg), MoO_3 can only absorb the short-wavelength portion of the solar spectrum, which limits its photovoltaic and photoelectrochemical applications. Along with these oxides, molybdenum oxide (MoO3) also has a wide band gap from 2.8 to 3.2 eV.

In works [6, 7], molybdenum foil Mo was pre-oxidized in nitric acid HNO_3, then the oxide was removed in hydrofluoric acid HF, followed by rinsing in distilled water. In addition, the substrate was subjected to gas etching for 30 min in the chamber of the gas deposition reactor at a temperature higher than the deposition temperature in a hydrogen flow, H_2. The temperature of the source T_i and the substrate T_p varied in the range of 850 ÷ 900 ^{0}C, and the cooling rate was in the range of the cooling rate of 10^{-5} deg/min. Structural analysis of the "substrate Mo-MoO_3" boundary was carried out using X-ray diffraction with an MIM-7 microscope and a Cameka microanalyzer. An amorphous structure with a columnar shape was clearly visible in the MoO_3 films (Fig. 1).



(a) ***(b)***

Fig. 1. Mo foil film without surface treatment (magnification 1500) (a); MoO_3 film on the surface of Mo substrate (magnification 3500) (b).

The XRD patterns of MoO_3 (000) thin films showed that Mo^{+5} in the film accounted for only 3% of the total Mo_{3d} peak, indicating that the film was predominantly in the Mo^{+6} oxidation state, that is, stoichiometric. AFM analysis of pure MoO_3 films showed the highest transmittance in the visible region of the spectrum, where the absorption edge shifted toward higher wavelengths of the solar spectrum [7]. The absorption coefficient (α) of the obtained films was determined from the transmittance spectrum values (T) using the ratio

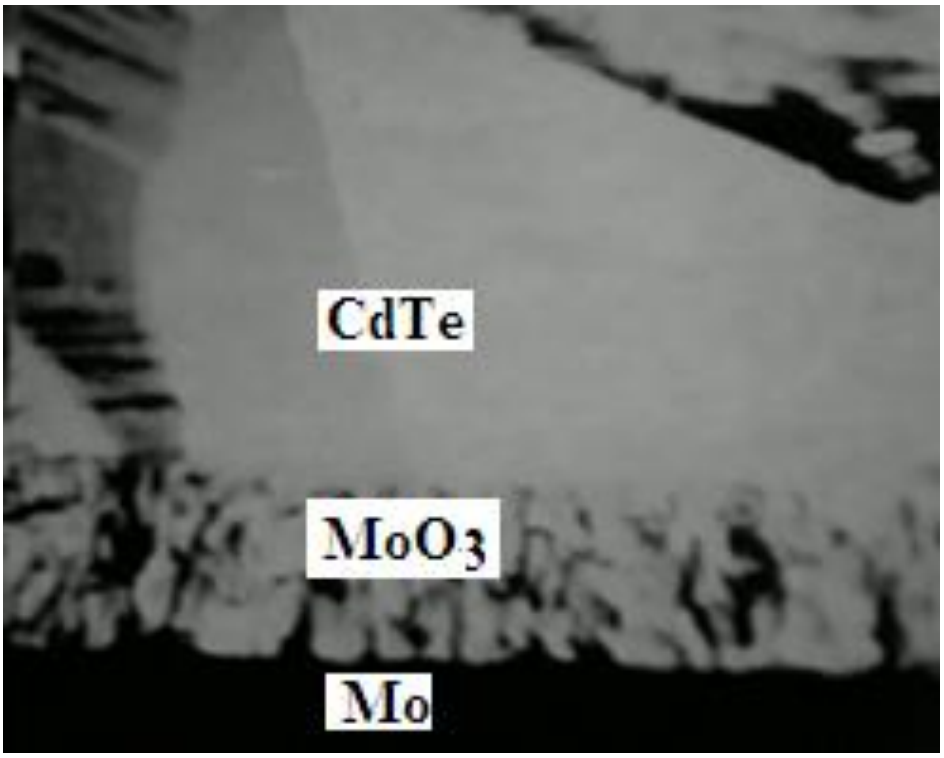
$$T = exp\ -\alpha\ d \qquad (1)$$

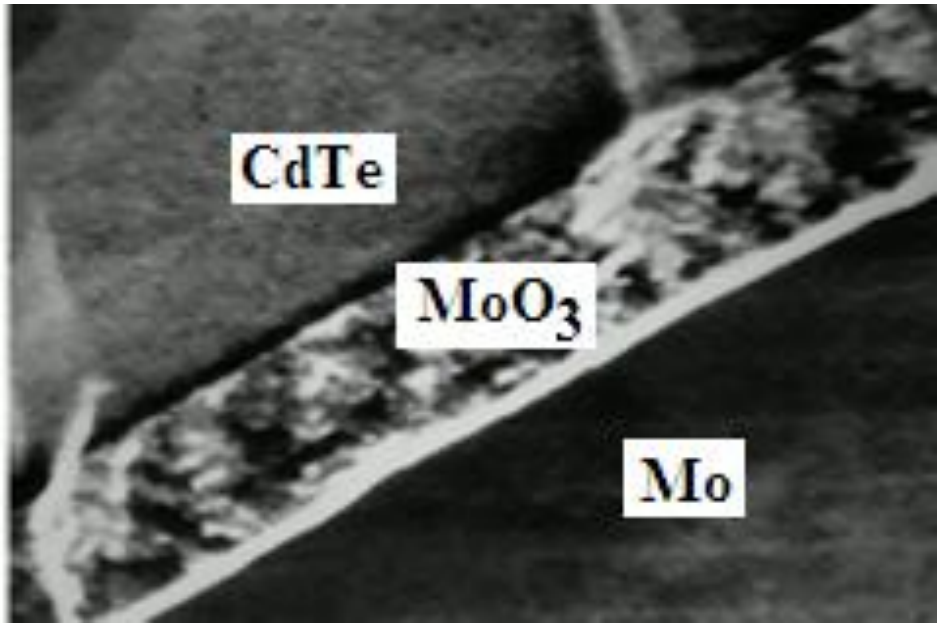
where d is the film thickness, and

CdTe is a highly absorbing material with a high optical absorption coefficient (~10^5 cm^{-1}) in the visible region of the solar spectrum. These results indicate the potential of CdTe-doped MoO_3 films for efficient light absorption in solar cells.

In our case, CdTe films were formed on a Mo substrate in a single process cycle [8,9]. The substrate is a Mo-molybdenum foil with a thickness of ~300 μm, which is pre-oxidized in HNO3, then the oxide is removed in HF, followed by rinsing with distilled water. Before deposition, the Mo substrate was placed in the deposition zone for 1 h and subjected to gas etching in an atmosphere of hydrogen carrier gas. The source and substrate temperatures varied in the ranges of 750–950 °C and 500–700 °C, respectively.

To study the structure of the Mo – CdTe interface, the CdTe film was separated from the Mo substrate, and the surfaces of the Mo and MoO_3 films adjacent to the CdTe and the substrate adjacent to the film were studied separately (Fig. 2 a, b), as well as the X-ray diffraction pattern of the structure.





a) *b)*

Fig. 2. Micrograph of the interface between Mo and CdTe (a) magnification 980 M: 1 cm–10.2 μk) and the interface between Mo and CdTe (b) magnification 1750 (M: 1 cm–3.7 μk).

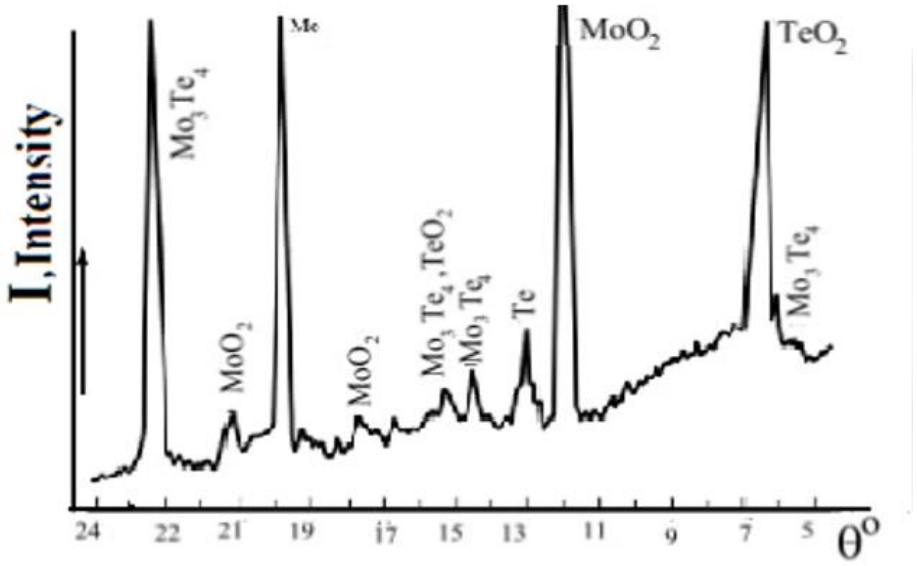


Fig. 3. Actual structure of Mo–CdTe interface.

Based on the obtained micrograph and X-ray phase analysis results, it was confirmed that the original high-purity Mo substrate did not contain any oxides on its surface. The oxide MoO_3 is formed during the synthesis process, in contact with the heated Mo substrate, as a result of a chemical interaction with the residual O_2 in the system.

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