

# Thermotransformations in Nanosize Aluminium – Molybdenum (VI) Oxide Systems

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**Abstract – By spectrophotometric method is investigated thermotransformations in Al–MoO<sub>3</sub> systems depending on Al and MoO<sub>3</sub> film thickness, temperatures and heat treatment time. As a result of the contact photo electromotive force, a contact potential difference the contact nature of effects of change with aluminium of MoO<sub>3</sub> film thermotransformation speed is confirmed. The diagram of power zones is constructed, the thermal transformation model of Al–MoO<sub>3</sub> systems is offered.**

## 1. Introduction

Heterogeneous system reception, finding-out of the nature and laws of the processes proceeding in them under action of various power factors, represent for physics and chemistry of a firm body multilateral interest [1–6]. Among various inorganic materials, the special place occupies molybdenum (VI) oxide [7–14]. It is known also, that optical and physical properties of various material thin films substantially depend on their thickness, conditions of reception, substrate material. Practical value, and also absence by present time in the domestic and foreign literature of the information on regular researches of dimensional effects influence on aluminium – molybdenum (VI) oxide system optical properties put lawful and duly a problem of complex research of individual and two-layer nanosize molybdenum (VI) oxide and aluminium layer optical properties.

In the present work results of a cycle of the researches directed on finding-out of the nature and laws of processes, proceeding in atmosphere conditions an in individual and two-layer nanosize various thickness molybdenum (VI) oxide and aluminium layers depending on temperature and are submitted to heat treatment time.

## 2. Objects and research techniques

Samples for researches prepared a method of thermal evaporation in vacuum ( $2 \cdot 10^{-3}$  Pa) by drawing thin (2–95 nm) MoO<sub>3</sub> and Al layers on substrates from a glass, using a vacuum universal post “VUP-5M”. Al–MoO<sub>3</sub> heterosystems prepared by consecutive drawing layers MoO<sub>3</sub> (on preliminary put on substrates from a glass) for layer Al. As substrates from photographic plates, optical transparent preliminary cleared [6, 15] glasses served in a range of 300–1100 nm. Al and MoO<sub>3</sub> film thickness determined by spectrophotometric, ellipsometric, microscopic and gravimetric meth-

ods. Samples subjected to thermal processing in a drying case “Mettler BE 300” in a temperature interval 373–600 K. Samples placed on heated up to the corresponding temperature a porcelain plate and subjected to thermal processing within 1–140 min in atmospheric conditions. Registration of effects before thermal processing researched samples carried out by gravimetric, microscopic and spectrophotometric (in a wave length range of 190–1100 nm, using spectrophotometer “Shimadzu UV-1700”) methods. Photo electromotive force ( $U_p$ ) measurements carried out on highly vacuum experimental complex including electrometric voltmeter V7-30. Contact potential difference (CPD) between aluminium, molybdenum (VI) oxide and platinum comparative electrode is measured, using Calvin modified method.

## 3. Results and discussion

As a regular research result of nanosize MoO<sub>3</sub> and Al film optical properties, and two-layer Al–MoO<sub>3</sub> systems before thermal processing in atmospheric conditions it has been established, that absorption and reflection spectra of samples substantially depend on thickness of each of MoO<sub>3</sub> and Al layers before heat treatment. At thermal processing Al films irrespective of their thickness reduction of optical density [16] takes place. On a measure of increase in heat treatment temperature and reduction of aluminium film thickness the increase in oxidation process speed is observed.

At thermal processing MoO<sub>3</sub> different thickness films the increase, reduction, increase and the subsequent of reduction of optical density [17] is established. With increase in temperature and reduction of MoO<sub>3</sub> film thickness transformation speed grows. Limiting after thermal activation MoO<sub>3</sub> optical density in spectrum long-wave area increases.

In Fig. 1 representative absorption spectra of Al–MoO<sub>3</sub> systems with various sublayer thickness before heat treatment are resulted.

By comparison Al, MoO<sub>3</sub> films and Al–MoO<sub>3</sub> systems absorption spectra it has been established, that on absorption spectra of systems (Fig. 1) reflexes individual Al and MoO<sub>3</sub> films in the degrees corresponding to a parity of sublayer thickness are shown.

Mainly in the field of 500–1100 nm (Fig. 1, curves 3, 4) in the greater degree are shown aluminium film reflexes.

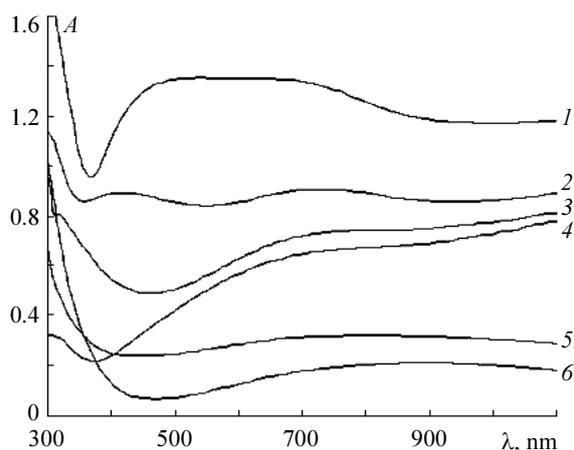


Fig. 1. Absorption spectra of Al-MoO<sub>3</sub> samples with thickness: 1 -  $d(\text{Al}) = 95$  nm,  $d(\text{MoO}_3) = 61$  nm; 2 -  $d(\text{Al}) = 85$  nm,  $d(\text{MoO}_3) = 44$  nm; 3 -  $d(\text{Al}) = 55$  nm,  $d(\text{MoO}_3) = 22$  nm; 4 -  $d(\text{Al}) = 38$  nm,  $d(\text{MoO}_3) = 8$  nm; 5 -  $d(\text{Al}) = 19$  nm,  $d(\text{MoO}_3) = 23$  nm; 6 -  $d(\text{Al}) = 7$  nm,  $d(\text{MoO}_3) = 40$  nm

The kind of curves in spectrum short-wave area is determined characteristic for MoO<sub>3</sub> films absorption that are to the greatest degree shown for systems with Al sublayer thickness less than 20 nm (Fig. 1, curves 5 and 6).

For finding-out of possible interaction between Al and MoO<sub>3</sub> films during Al-MoO<sub>3</sub> systems preparation experimental absorption spectra of systems have been compared to the absorption spectra of received by summation of absorption spectra of individual Al and MoO<sub>3</sub> films of similar thickness. It is established, that settlement and experimental curves for all investigated samples do not coincide. On experimental curves the wide absorption strip with a maximum is shown at  $\lambda \approx 870$  nm which presence, probably, is connected to formation at system preparation of additional amount of  $[e(V_a)^{++}e]$  centers [17]. As a result of thermal processing Al-MoO<sub>3</sub> different thickness systems in temperature interval 373–600 K in atmospheric conditions absorption and reflection spectra of samples undergo essential changes. Observable changes of absorption and reflection spectra, and limiting values of optical density in strip maxima of absorption after thermal processing samples depend on initial Al and MoO<sub>3</sub> film thickness, temperatures and heat treatment time.

All investigated Al-MoO<sub>3</sub> systems on character of optical properties change of samples during thermal processing have been classified with division into 4 groups. To the first group samples for which the individual MoO<sub>3</sub>, Al films, and also two-layer Al-MoO<sub>3</sub> systems optical density during thermal processing decreases have been referred. Such behavior is typical of systems, MoO<sub>3</sub> film thickness for which makes  $d \leq 20$  nm, irrespective of Al film thickness. To the second group have been referred samples for which during thermal processing the increase in optical density of individual MoO<sub>3</sub> films and reduction of Al films and two-layer Al-MoO<sub>3</sub> samples optical den-

sity is observed. To the given group the systems having MoO<sub>3</sub> film thickness of 20–30 nm and Al of 15–200 nm are referred. Samples for which the optical density MoO<sub>3</sub> films, Al-MoO<sub>3</sub> systems as a result of thermal influence grows and optical density of Al film decreases have been included in third group. To the fourth group the samples having «thermochromic effect» have been referred. During thermal processing for these systems the symbate increase and reduction of optical density with similar changes of optical density for MoO<sub>3</sub> films is observed. For Al films, reduction of optical density is observed. Conditions of thermochromic effect (TCE) display the following: Al film thickness less than 10 nm, distinction in layer thickness  $\approx 30$  nm, temperature of processing  $> 473$  K.

For finding-out of laws of course of thermal transformation process in systems kinetic dependences of transformation degree  $\alpha = f(\tau)$  (where  $\tau$  is thermal processing time) have been designed and constructed at various wave lengths and heat treatment temperatures.

It has been established, that Al-MoO<sub>3</sub> system transformation degree depends on initial thickness of Al, MoO<sub>3</sub> layers, temperatures and thermal processing time. On a measure of heat treatment time increase the transformation degree of Al-MoO<sub>3</sub> systems grows. The heat treatment temperature increase (at constant Al and MoO<sub>3</sub> film thickness) results in increase of thermal transformation speed. On a measure of Al film thickness reduction (at constant thickness of MoO<sub>3</sub> layer) in Al-MoO<sub>3</sub> system at heat treatment constant time the transformation degree in all the investigated interval of temperatures grows.

For finding-out of a power structure of contacts molybdenum (VI) oxide with aluminium and the reasons causing observable changes by metal of optical properties MoO<sub>3</sub> in different spectral areas for Al-MoO<sub>3</sub> heterosystems  $U_p$  and values CPD between MoO<sub>3</sub>, Al and platinum comparative electrode have been measured. As  $U_p$  measurement result in range  $\lambda = 300$ –1100 nm have been established, that during light irradiation  $U_p$  positive potential on the part of MoO<sub>3</sub> layer is formed. From the analysis of  $U_p$  and CPD (Table) measurement results it has been established, that in the field of molybdenum (VI) oxide with aluminium contact antishut-off layer is formed. Received in the present work and earlier [8–12, 14, 15] results of researches testify to the contact nature of effects of change by aluminium thermal transformation speed of MoO<sub>3</sub> film.

Observable MoO<sub>3</sub> and Al work function difference (Table) testifies to an opportunity at formation of dense contact and an establishment in Al-MoO<sub>3</sub> system conditions of thermodynamic balance of electron stream from aluminium in molybdenum (VI) oxide.  $U_p$  formation for Al-MoO<sub>3</sub> heterosystems directly testifies to nonequilibrium carrier division of a charge into border of the unit. We believe, that at creation of molybdenum (VI) oxide contact with aluminium as a result of electronic transitions contact MoO<sub>3</sub> layer is

Table. CPD between samples and platinum comparative electrode at  $T = 293$  K

| Sample                                      | CPD, V                |                          |                           |
|---|-----------------------|--------------------------|---------------------------|
|   | $P = 1 \cdot 10^5$ Pa | $P = 1 \cdot 10^{-5}$ Pa | $P = 1 \cdot 10^{-5}$ Pa* |
| Al film $d = 250$ nm on glass               | +1.10                 | +1.10                    | +1.40                     |
| Al film $d = 56$ nm on glass                | +1.10                 | +1.10                    | +1.60                     |
| Al film $d = 250$ nm on a platinum plate    | +1.2                  | +1.2                     | +1.50                     |
| MoO <sub>3</sub> film $d = 220$ nm on glass | +0.2                  | +0.71                    | +0.66                     |

\* After preliminary thermal processing at  $T = 550$  K within 180 min.

charged negatively. The diagram of Al–MoO<sub>3</sub> hetero-system power zones at which construction results of  $U_p$  spectral distribution researches, CPD (Table) are used, it is resulted in Fig. 2.

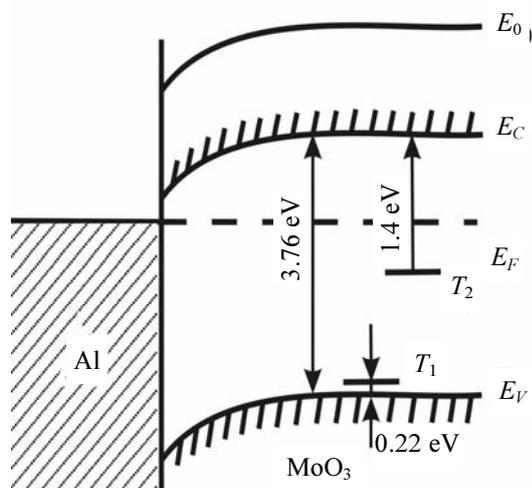
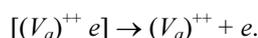


Fig. 2. The diagram of Al–MoO<sub>3</sub> heterosystem power zones:  $E_V$  – level of a ceiling of a valent zone;  $E_C$  – level of a bottom of a zone of conductivity;  $E_F$  – Fermi level;  $E_0$  – level of vacuum;  $T_1, T_2$  – capture centers

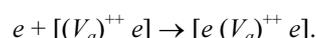
By authors [18] it has been established, the absorption strip at  $\lambda = 350$  nm for MoO<sub>3</sub> monocrystals is connected to a maximum with stoichiometrical lack of oxygen and caused by oxygen vacancies with one seized electron  $[(V_a)^{++} e]$  (analogue of the F-center). This center, probably, is formed during preparation of MoO<sub>3</sub> layers of various thicknesses. Depth of occurrence of  $[(V_a)^{++} e]$  center makes  $E_F^1 = 3.54$  eV. We believe, that absorption maximum reduction at  $\lambda = 350$  nm, and absorption maximum formation at  $\lambda = 870$  nm during MoO<sub>3</sub> layer thermal processing are interconnected processes and grow out transformations of  $[(V_a)^{++} e]$  center.  $[(V_a)^{++} e]$  center transformation at MoO<sub>3</sub> thermal excitation can be carried out:

A) by electron translation from a level of occurrence the center on free levels near to a bottom of a conductivity zone with clearing anionic vacancies  $(V_a)^{++}$ :



For maintenance of this process energy  $E_F^1$  is required.

B) by electron translation from levels located near to a ceiling of a valent zone anionic by the nature on a level of the  $[(V_a)^{++} e]$  center with the neutral  $[e (V_a)^{++} e]$  center formation:

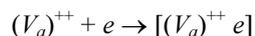


For maintenance of this process energy  $E = E_g^T - E_F^1$  ( $E_g^T$  is thermal width of MoO<sub>3</sub> forbidden zone) is required. Thermal width of MoO<sub>3</sub> forbidden zone according to [18] makes  $E_g = 3.54$  eV (on 0.2–0.3 eV it is less, than optical width of MoO<sub>3</sub> forbidden zone  $E_g = 3.76$  eV).

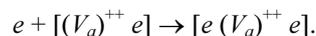
We shall estimate an opportunity of realization of the specified transitions at MoO<sub>3</sub> thermal excitation in real experimental conditions. Phonons do not monoenergetic. Their energy distribution submits to Boltzman equation [19]. According to Boltzman equation always there is a probability of that in temperature interval  $T = 373$ – $600$  K (the area of temperatures at which heat treatment of MoO<sub>3</sub> samples was carried out) will exist quantum with energy equal  $E_F^1 = 3.28$  or  $E = 0.26$  eV. (For maintenance of thermally labilized transitions of an energy expense will make 0.2–0.3 eV from optical [18].)

Values for speeds of thermal electron excitation processes from  $[(V_a)^{++} e]$  center levels on levels near to a bottom of a zone of conductivity or thermal electron excitation from levels near to a ceiling of a valent zone on  $[(V_a)^{++} e]$  center levels will make  $W_1 \approx 2 \cdot 10^1$  and  $W_2 \approx 6 \cdot 10^{26} \text{ cm}^{-3} \cdot \text{c}^{-1}$  accordingly. From here follows, that speed of thermal electron excitation process from levels near to a ceiling of a valent zone on  $[(V_a)^{++} e]$  center levels is great enough to provide the further MoO<sub>3</sub> layer transformations.

Thus, during preparation, thermal processing of MoO<sub>3</sub> layers electron transition from a valent zone with hole (p) formation on levels anionic vacancies with formation  $[(V_a)^{++} e]$  center takes place



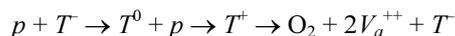
and on  $[(V_a)^{++} e]$  center levels with  $[e (V_a)^{++} e]$  center formation



Holes can be grasped own  $(V_k^{6-})$  and extrinsic (T) defects

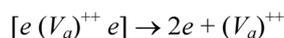


where  $V_k^{6-}$  and  $V_a^{++}$  are the cationic and anionic vacancies,

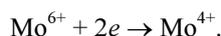


with oxygen allocation and clearing anionic vacancies.

Optical energy of  $[e(V_a)^{++}e]$  center ionization makes  $\approx 1.4$  eV. Thermal energy makes  $\approx 1.1$  eV. We believe, that during heat treatment  $[e(V_a)^{++}e]$  center thermal ionization, accompanying with electron transition in a zone of conductivity is possible



and interaction with  $Mo^{6+}$



The increase in electron concentration from  $MoO_3$  party in a condition of Al- $MoO_3$  heterosystem thermodynamic balance should result in increase in process speed of thermal transformation in  $MoO_3$ . Observable laws of  $MoO_3$  optical property change by aluminium correspond to the stated model of processes.

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