

Investigation of Energy Action Influence on $\text{WO}_3(\text{MoO}_3)$ – Metall Systems

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Abstract – By spectrophotometric and gravimetric methods influence of a photo and heat treatment on optical properties nanosize layers of metals (Cu, Al, Pb), oxides (WO_3 and MoO_3) and metal – oxide heterosystems investigated

1. Introduction

Reception of perspective materials, creation on their basis of multilayer heterogeneous systems, finding-out of correlation between composition, structure and properties of compounds depending on conditions of their preparation, studying of the nature and laws of the processes running under action of various power factors represent significant interest both for physics and chemistry of solidity and the common theory of a contact catalysis, and in connection with necessity of development of substantial systems with a controlled level of various external influences sensitivity.

Among the major metals the special place is occupied with copper, aluminium and lead. Due to special properties they have found wide application in the modern industry. Copper, aluminium and lead fall into to group of semimobile metals which have positive value of a free energy at passing reaction of ionization only in absence of oxygen [1, 2]. Expansion of ranges of metals application lifts requirements to conditions of products [3]. Oxides of wolframium (VI), molybdenum (VI), system on their basis due to a complex of positive properties also draw attention of researchers various of a profile. Devices on the basis of oxides of wolframium (VI) and molybdenum (VI) are recommended to use as electrochromic and photochromic displays (systems of the information displaying in which there are convertible decolorations of a material under action of an electric current or radiation [4 – 6]), electrochromic mirrors or light redistribution filters (the devices, allowing to operate a reflection or absorption factor) [7], sensors for the control of the contents of oxides of nitrogen in the atmosphere [8, 9].

In the present work, results of researches of light radiation and heat treatment influence on optical properties thin (3 ... 100 nanometers) films of metals (Cu, Al, Pb), oxides (WO_3 , MoO_3), metal (Cu, Al, Pb) – oxide (WO_3 , MoO_3) and oxide (WO_3 , MoO_3) – metal (Cu, Al, Pb) heterostructures on glass substrates are submitted.

2. Objects and research techniques

Samples for researches prepared by a method of thermal evaporation in vacuum ($2 \cdot 10^{-3}$ Pa) layers of metals (Cu, Al, Pb), oxides (WO_3 , MoO_3), metal (Cu, Al,

Pb) – oxide (WO_3 , MoO_3) and oxide (WO_3 , MoO_3) – metal (Cu, Al, Pb) heterostructures and precipitations on substrates from a glass, using vacuum generalpurpose post VUP-5M. As an evaporator used the floating troughs made of molybdenum by thickness $d=3 \cdot 10^{-4}$ m. The optimal distance from a floating trough-evaporator up to a substrate are 8 ... 9 sm. Substrates from photoplates thickness of $1 \cdot 10^{-3}$ m and the area $2 \cdot 10^{-4}$... $4 \cdot 10^{-4}$ m² which subjected to pretreatment in concentrated hydrogen nitrate, in a solution of bichromate of potassium in concentrated sulfuric acid, in boiling soap water, washed out in distilled water and dried [6,10]. The processed substrates optically are transparent in a range 300 ... 1100 nanometers. Thickness of films determined by spectrophotometric, microscopic and gravimetric methods [1,10]. Samples subjected to heat treatment in drying chambers Memmert "BE 300" and "SPT-200", in a muffle "Tulyachka-3P" in an interval of temperatures 373 ... 600 K. Thus samples seated on a porcelain plate heated to the relevant temperature and subjected to heat treatment during 1 ... 120 minutes in atmospheric conditions. As a light source used lamps DRT-220 and DKsSH-1000. Actinometry of light sources carried out by radiating thermal cell RT0589. Time of light action on samples are 1 ... 111 minutes. Registration of effects after heat treatment and influences of light on researched samples carried out by gravimetric, microscopic and spectrophotometric in a range of wavelengths of 300 ... 1100 nanometers (using a spectrophotometer "Shimadzu UV-1700") methods.

3. Results and discussion

As a result of the analysis of research results of optical properties of thin layers of metals, oxides of wolframium and molybdenum, metal – oxide and oxide – metal structures on glass substrates it has been established, that absorption spectrums essentially depend on their thickness. In Fig. 1 (as an example) absorption spectrums of different thickness copper films in a range ($d=3 \dots 100$ nanometers) are submitted. It is visible, that for samples with thickness more than 30 nanometers are possible to bleed with absorption bands characteristic for copper [10]. For films of copper thickness of ($d < 4 \cdot 10^{-9}$ m) observes unstructured absorption.

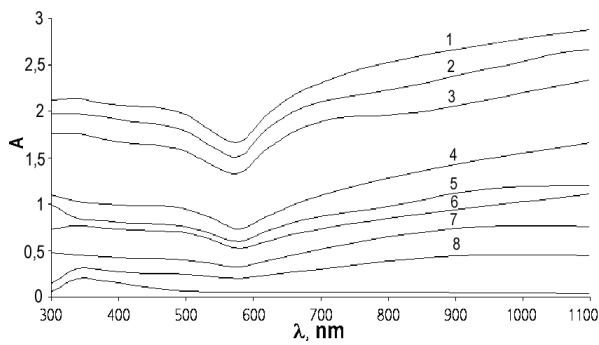


Fig. 1. Absorption spectra of films of copper thickness of: 1) 112, 2) 100, 3) 88, 4) 62, 5) 47, 6) 40, 7) 31, 8) 18, 9) 3 nm

It is established, that optical properties of all examined groups of the objects subjected to influence of power factors (light radiation of a various spectral range and intensity, heat) in atmospheric conditions, undergo significant changes (Fig. 2–5).

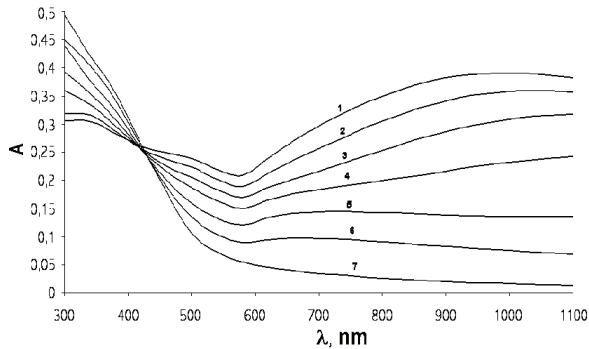


Fig. 2. Absorption spectra of films of copper thickness of 16 nm before and after preliminary heat treatment at 373 K: 1) 0 (initial), 2) 2, 3) 5, 4) 10, 5) 20, 6) 30, 7) 60 min

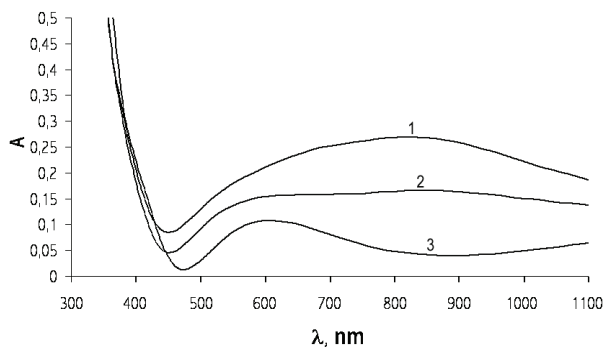


Fig. 3. Absorption spectra of MoO₃ before and after of heat treatment (T=473 K). Treatment time: 1) 126, 2) 16, 3) 0 (initial) min

And, speed of transformations essentially depends on type of object, its thickness, sequence of drawing of layers, on a kind and time of power influence.

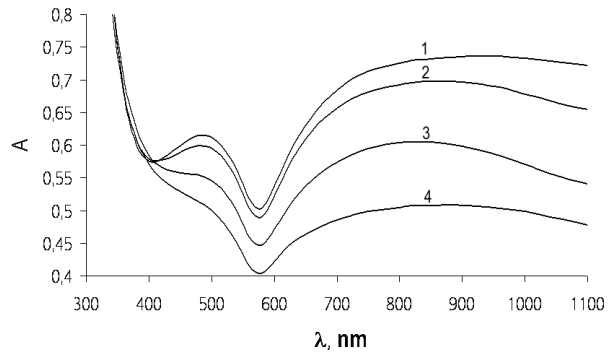


Fig. 4. Absorption spectra of WO₃-Cu before and after action of light. Action time: 1) 0 (initial), 2) 6, 3) 51, 4) 111 min

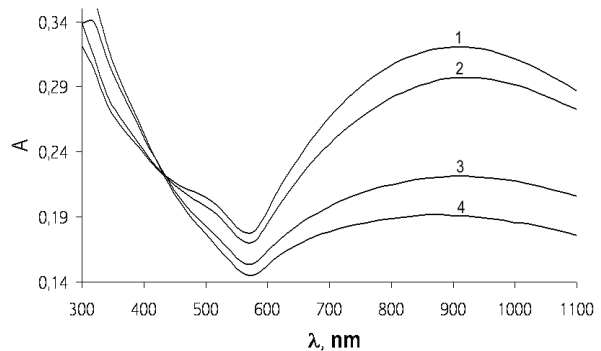


Fig. 5. Absorption spectra of Cu – WO₃ before and after action of light. Action time: 1) 0 (initial), 2) 6, 3) 51, 4) 111 min

As a result of the analysis of results it is established, that change of optical and gravimetric properties of oxide – metal heterosystems is consequence of change of individual objects properties, in particular, adsorptions and interactions of gaseous ingredients of an environmental atmosphere with a surface of samples, and also interactions making heterosystems layers of metals and oxides of wolframium and molybdenum. We shall note, that observable changes are not additive in an examined spectral range of lengths of waves. For metal films alongside with reduction and increase in different spectral areas of samples optical density the absorption spectrum of new substances is formed. Appreciated, for example, for films of copper on a long-wavelength threshold of absorption, which is at $\lambda=560\dots570$ nanometers (see Fig. 2), the optical bang gap of formed substance makes $E=2.17\dots2.21$ eV. Received value of band gap of substance well coincides with band gap of copper oxide (I) ($E=2.18$ eV) [11,12]. Therefore, the assumption has been made, that at heat treatment of copper films by a main product of their interaction with ingredients of an environment is copper oxide (I). Similar laws of corresponding oxides formation are observed at thermal and photochemical processing films of aluminium and lead.

With increase in temperature at which heat treatment of films of metals and oxides of identical initial thickness was carried out, and intensity of an incident light the increase in effects of optical density change takes place. In accordance with magnification of thickness of films of metals and oxides (up to 100 nanometers) at constant heat treatment temperature (in an interval 373...600 K) and intensity of an incident light, serial reduction of effects of optical density change of samples in all the investigated spectral range is observed.

For finding-out of laws of interaction process passing of films of metals, oxides and oxide – metal heterosystems with active ingredients of an environment and between contacting components (using results of measurements of different thickness films absorption spectrums before influence of power factors) kinetic dependences of a transformation degree $\alpha=f(\tau)$ have been designed and constructed at various wavelengths. In Fig. 6 as an example kinetic curves of a degree of transformation of copper films baked at 473 K depending on initial thickness of samples are given. It is visible, the degree of thermal conversion of copper films depends on initial thickness, temperatures and time of heat treatment and in accordance with magnification of thickness of copper films the increase in time of achievement of a degree of transformation of equal unit is observed.

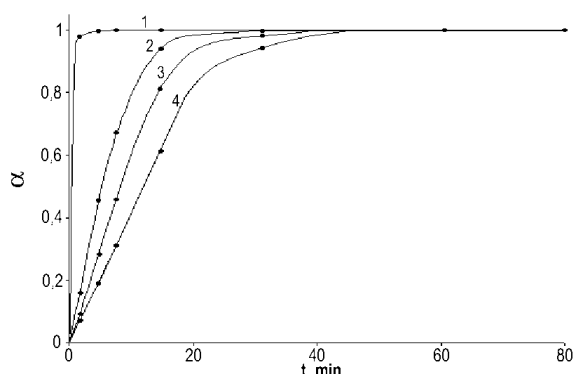


Fig. 6. Dependence of a degree of transmutation on thickness of films of copper at 473 K: 1) 4, 2) 37, 3) 41, 4) 47 nm

For films of copper thickness of ($d < 16$ nanometer) in the investigated interval of temperatures the degree of transformation achieves unit for $t = 1 \dots 5$ minutes. Kinetic dependences of a degree of transformation of copper films thickness $d < 4$ nanometer (at 373 and 423 K), $d < 50$ nanometer (473 K), $d < 60$ nanometer (523 K), $d < 140$ nanometers (300 K) in result of heat treatment down to maintenance of full oxidation of copper films up to copper oxide (I) are practically linear. At increase in temperature of heat treatment angle of lean of a straight line in coordinates $\alpha=f(\tau)$ grows. Similar laws are displayed at a photo and heat treatment of films of all metals, oxides and metal – oxide heterosystems. In accordance with magnification of films thickness, temperature, intensity of an incident light and time of

processing kinetic curves of a degree of transformation also are well described within the framework of linear, parabolic or logarithmic laws.

It is known [1, 2], that one of the basic requirements describing ability of formed initial layer of yields of interaction of ingredients of an environment with metal to brake the further oxidizing of metal is continuity of a an obtained oxide film. The formed oxide film will interfere with infiltration of agents participating during oxidation and thus to brake its further propagation. According to Pilling and Bedwantes criterion [1] which for aluminium, copper and lead makes 1.28, 1.64, 1.31 accordingly, it was necessary to expect formation of continuous oxide layers considerably braking the further passing of process of oxidation and, as consequence, in a theoretical case – the parabolic law of metal films oxidation process limited diffusion of corresponding ions through oxide layer to its surface [1, 2]

$$L^2 = K\tau + A,$$

where L – film thickness, τ – time of an oxidizing, K – kinetic constant of an oxidizing, A – integration constant.

It is established, that growth rate of an oxide film (see higher) on surfaces of metal films (down to maintenance of their full oxidation) remains practically constant – as it takes place for alkaline and Earth metals, for which Pilling and Bedwantes criterion less unit [1]:

$$dL / d\tau = K,$$

or after integration

$$L = K\tau + A.$$

Thus, thickness of an oxide layer formed on a surface of metal films (the established sizes and subjected photo or heat treatment at corresponding intensity of incident light and temperatures) will be proportional to time of oxidation. From here follows, that $V_{Ox}/V_{Me} > 1$ criterion (where V_{Ox} – volume of oxide, V_{Me} – volume of metal) [1] is not carried out, the oxide layer, apparently, has a loose structure with weak protective properties and a limiting stage of process of oxidation, probably, is immediately chemical reaction of interaction metals with oxygen of an environment.

In accordance with magnification of metal films thickness as a result of a photo or heat treatment at different temperatures kinetic curves of their oxidation are well described within the framework of parabolic or logarithmic laws. Thus, on a surface of metal films with $d > 50$ nanometers as a result of chemical corrosion will be formed by thickness continuous oxide layers and process of corrosion will be braked by diffusion of corresponding ions through an oxide layer one's further propagation will be retarded by increase in its thickness [1, 2]. According to results of measurements of contact potential difference (CPD) in systems metal-oxide is formed double electric layer of a negative mark from the side of oxide. During a photo and heat treatment of systems metal-oxide CPD field stimulates process of moving of corresponding ions through an oxide layer.

Models of objects optical properties change at the various power influences, including stages of formation of double electric layer between contacting partners, formation of surface-bound charge in the oxides, stimulating adsorption of gases, diffusion of ions, generation and redistributions of nonequilibrium carriers of a charge in a contact field and their participation in the processes responsible for changes of optical performances of explored objects are offered.

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