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journal homepage: www.elsevier.com/locate/solmatThe nature of the photochromism arising in the nanosized MoO₃ filmsAlexander Gavriluk^{a,*}, Ulf Tritthart^b, Wolfgang Gey^b^a A.F. Ioffe Physical-Technical Institute of Russian Academy of Sciences, Polytechnicheskaya Street 26, 194021 Sankt-Petersburg, Russia^b Institute of Applied Physics of Technical University of Braunschweig, Mendelssohnstrasse 2, 38106 Braunschweig, Germany

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ABSTRACT

We carried out the experiments which show unambiguously that not one, as it was commonly accepted, but three optical absorption bands corresponding to different color centers arise in the nanosized MoO₃ films due to hydrogen atoms. Varying the conditions for the photoinjection of hydrogen into the MoO₃ films, it is possible to change drastically the correlation between the concentrations of different arising centers, which in turn yields the great difference in the optical absorption spectra. Our findings are crucial for understanding of the nature of electrochromism and photochromism not only in MoO₃ films but also in the series of the transition metal oxide films.

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1. Introduction

MoO₃ is a famous multifunctional material regarding hydrogen atoms. It efficiently catalyzes reactions of detachment of hydrogen atoms from hydrogen donor molecules adsorbed on its surface. At the same time, MoO₃ is capable of accommodating and transporting great amounts of hydrogen atoms. When hydrogen atoms are inserted into MoO₃, molybdenum bronzes H_xMoO₃ are formed, which are under intensive long-term investigations due to numerous interesting properties ([1] and references therein).

MoO₃ is related to, the so called “chromic” materials changing their optical properties under the action of either light or electric field, which is the reason for their wide investigation in electrochromism and photochromism [2–5].

The conventional photochromism occurring in MoO₃, WO₃, and V₂O₅ films, when the oxide surface is excited by photons with energy exceeding the oxide forbidden energy gap [6–10], is due to hydrogen atoms detached from hydrogen-containing molecules (water and organics) uncontrollably adsorbed on the oxide surface either during film preparation, or from ambience [11,12].

It can be enhanced dramatically via adsorption of specially selected organic molecules (hydrogen donors) on the oxide surface [13–19]. The photochromism due to hydrogen atoms detached from organic molecules under the action of light and inserted into MoO₃ thin films, i.e., photoinjection of hydrogen (PIH), yields the drastic changes in the optical parameters of the MoO₃ films.

The aims of ongoing investigations concerning the PIH involve the production, storage, and transport of hydrogen for different functions, e.g. as a fuel, dopant, or catalyst, which may find applications in science and technology, especially in hydrogen energetics, biology, and medicine.

The mechanism of the PIH in the nanosized oxide films was described in detail elsewhere [18] and was determined as tunneling proton-coupled electron transfer (PCET) [20].

The photochromism arising with the PIH is a unique phenomenon. It is not connected with intrinsic defects of solids, the defects being injected from outside: one can achieve a record-breaking value of color centers using the PIH.

Here we report on the very important aspect of the photochromism, namely, the formation of color centers arising due to hydrogen atoms inserted into the MoO₃ nanostructured films, in other words, on the nature of the optical absorption.

The detached hydrogen atoms donate their electrons to molybdenum Mo⁶⁺ cations, forming lower-valency Mo⁵⁺ cations, whereas protons are bonded to oxygen atoms by hydrogen bonds [2]. The photochromism is attributed to an optical absorption band arising due to light-induced electron transfer between non-isovalent neighboring cations Mo⁶⁺ and Mo⁵⁺. The mechanism of the absorption arising in the transition metal oxides due to guest atoms was described in general with the help either of the intervalence electron transfer model [21] or the small polaron model [22]. However, the most important problem, namely, whether only one or several color centers arise due to the injection of hydrogen atoms remains unsolved. This problem is crucial for understanding of the process of the hydrogenation not only in MoO₃, but also in the whole series of electrochromic and photochromic materials (WO₃, V₂O₅, Nb₂O₅, etc.) [2–4]. The main

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task of the present research was to prove the formation of several color centers with the PIH.

2. Film preparation and characterization

Highly disordered nanostructured MoO₃ films were prepared by evaporating MoO₃ powders in dimethylformamide (DMFA – (CH₃)₂NCHO) vapor as described elsewhere [13,14–19]; DMFA playing the role of a hydrogen donor. These films were investigated and characterized in detail [18,19] and we present here a brief summary on the film characterization to provide understanding of our research.

The highly disordered nanostructured MoO₃ films were prepared by evaporating a MoO₃ powder of 99.999% purity from a tantalum boat onto substrates from molten quartz. The evaporation temperature was between the limits of 950 and 1050 °C. The substrates were not heated during evaporation and the temperature did not exceed 30 °C. An evaporation chamber was pumped to a 2×10^{-5} mbar pressure and then ventilated by DMFA vapors at a pressure within the limits $6\text{--}8 \times 10^{-4}$ mbar, which was maintained during evaporation. The average growth rate, controlled by a quartz monitor, was 20–30 Å/s.

Film morphology was studied with the help of a “Smena-B” atomic force microscope (NTMDT-Company). The atomic microscope images of the film surface were presented before in [18,19]. The films were found to be nanocomposites with a high porosity with an average of ~100 nm pore diameter; an average pore depth determined as a peak to valley difference exceeding ~100 nm; the surface is essentially heterogeneous, which pre-determines different chemical reactivity for different surface reaction centers [18,19].

The film thickness was varied within the limits from 0.7 up to 1.5 μm and was measured with the help of an interference microscope. Then the optical inspection of the interference fringes of the oxide films made it possible to determine the value of the refractive index [23], which amounted to $n=2$. The film density was 3.3 g/cm³ as against 4.7 g/cm³ for the bulk material.

Analyses of micro-quantities of the organic molecules adsorbed on the film surface were carried out on the cyclotron of the A.F. Ioffe Institute with the help of the nuclear resonance reaction ³He (²D, p)α, the method being described in [24]. DMFA, containing deuterium with an isotope exchange exceeding 99% in all hydrogen groups, was used. Analysis gave the number of the adsorbed DMFA molecules per transition metal atom at 0.75–0.9. These values refer to the whole film thickness.

The film structure was investigated with the help of IR spectroscopy. IR spectra were registered with the help of a double-beam spectrometer “Specord” 75 IR (Carl Zeiss, Jena). The MoO₃ films evaporated in the DMFA vapor exhibit well resolved absorption bands in the range of the metal–oxygen vibrations (1000–400 cm⁻¹). Besides the absorption bands observed in the range 400–900 cm⁻¹ and related to the –Mo–O–Mo– stretching vibrations, two pronounced bands are observed at $\nu=950$ and 915 cm⁻¹ in the optical density spectra, which are related to the Mo=O stretching vibrations [18]. The vibrations of the Mo=O and W=O double bonds are often observed in MoO₃ and WO₃ films with the help of Raman and IR spectroscopy in the range between 900 and 1000 cm⁻¹ [25,26]. It is reported that MoO₃ films deposited by conventional evaporation have a meta-stable β perovskite-like type structure with a six-fold coordination [27]. To preserve a valency of 6 for molybdenum cations on the surface, the molybdenyls (double bonded oxygen atoms) arise on the film surface, which yields a single band in the spectra in the range between 900 and 1000 cm⁻¹ due to the Mo=O stretching vibration in five-fold clusters. According

to [28], the reason for the appearance of a doublet instead of a single band, which we observe in the present case, is that the oxide structure is highly irregular at the molecular level; polymerization, which usually prevails in these films, is strongly hampered due to DMFA molecules on the oxide surface, which yields a high concentration of the Mo=O groups. The evaporated species of MoO₃ are reported to be cyclic molecules, the dominating one being Mo₃O₉, and evidence also have been found for Mo₄O₁₂ and Mo₅O₁₅ [29–31]. In these molecules the molybdenum-oxide tetrahedrons are connected into cycles. Each molybdenum-oxide tetrahedron contains two bridging and two terminal oxygen atoms. Thus, some elements of the evaporated species are maintained in the MoO₃ film. On the other hand, the appearance of other multiple bands in the spectra hints that the film structure consists of several phases. Partial polymerization and formation of molybdenum oxygen octahedrons can occur in the grain nuclei, whereas the tetrahedral coordinated clusters are formed at the grain periphery. The highly disordered (quasi amorphous) WO₃ and the MoO₃ films contain the framework structure with higher coordination number and the periphery structure with Mo cations with lower coordination number [32,33].

3. Experimental details

The samples prepared had been stored under a non-oxygen atmosphere before the experiments started. Hydrogen atoms injected into the films were detached from the adsorbed DMFA molecules under the action of photons with energy exceeding the oxide forbidden band-gap ($E_g \sim 3.2$ eV) and transfer of surface excitation to the adsorbed molecules [13–19].

The films prepared in one technological run were illuminated by the full output of a 250 W mercury lamp through a water filter either under a $p=10^{-2}$ mbar vacuum, or in air w at ~100% relative humidity.

The illumination was carried out in a gas-flow cryostat “Oxford instruments” with quartz windows at room temperature (RT). The samples were illuminated by the full output of a 250 W mercury lamp through a water filter to get rid of the infra-red part of irradiation. The spectral characteristics of the lamp are given in [34].

The distance between the sample and the lamp was 35 cm. Special measures were undertaken to prevent heating of the samples; the highest temperature not exceeding 45 °C during illumination. With the help of the special semiconductor dosimeter worked out in A.F. Ioffe Institute [35], the power of the UV irradiation per cm² of the surface of the film was measured and amounted to 35 mW cm⁻². Optical density spectra were recorded with the help of a Hitachi-2000 double-beam spectrophotometer. The optical density is defined as:

$$D = \log_{10}(I_0/I)$$

where I is the intensity of light at a specified wavelength λ that has passed through a sample (transmitted light intensity) and I_0 is the intensity of the light before it enters the sample or incident light intensity (or power) (the definition is taken from Wikipedia). The reflection losses were not taken into account since they are relatively small as compared with the absorption.

4. Results and discussion

The optical density D spectra for 0.8 μm thick films are shown in Fig. 1. One can see the interference fringes in the spectra registered before the illumination. Since the surface roughness for

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