



ESR study of photoinjection of hydrogen in nanostructured MoO₃ thin films

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ABSTRACT

Formation of paramagnetic centers arising in highly disordered MoO₃ films due to photoinjection of hydrogen at room and liquid helium temperatures has been investigated. At room temperature the concentration of Mo⁵⁺ paramagnetic centers very quickly comes to a steady-state value, whereas at liquid helium temperature it grows continuously with exposure during the whole illumination time. Formation of free radicals forming due to the detachment of hydrogen atoms from the hydrogen-donor molecules has been observed at liquid helium temperature. Its reaction rate decreases twice during the illumination, whereas the formation rate of the Mo⁵⁺ centers decreases more than an order of the magnitude. This difference in behavior has been attributed to the pairing of the Mo⁵⁺ centers.

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1. Introduction

MoO₃ can change its optical properties dramatically under the action of either light or electric field. Since the pioneering works [1,2], MoO₃ thin films are widely investigated in electrochromism and photochromism [3–5].

Here we report on the injection of hydrogen into MoO₃ thin films under the action of light, photoinjection of hydrogen (PIH). The aims of ongoing investigations 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 PIH is always connected with the photochromism first observed in MoO₃ thin films in [1].

The nature of the photochromism arising in the MoO₃ thin films, when the oxide surface is excited by photons with energy exceeding the oxide forbidden energy gap, was attributed to the formation of F-centers: oxygen vacancies capture electrons, excited by light from the valence band into the conduction band of the oxide [1,2]; absorption of light arising due to electron optical transitions between these levels and the oxide conduction band. These transitions are caused by photons with energy less than the oxide forbidden energy gap and are observed in the visible and near infrared range. The hypothesis of F-centers was also applied for similar photochromism in WO₃ [6] and V₂O₅ thin films [7].

Later it has become clear that this model was not suited to explain the variety of experimental data. It was reported that the photochromic sensitivity of MoO₃ films quickly drops down to

zero upon lowering the temperature [8], which contradicts the model of a pure electronic mechanism of the color center formation. Furthermore, it has been shown that the photochromism in MoO₃ films, as well as in WO₃ and V₂O₅ thin films, can be enhanced drastically via adsorption of specially selected organic molecules on the oxide surface. Currently, it has become clear that the photochromism discovered in [1,2,6,7] is attributed to the “wild” PIH in MoO₃, WO₃, and V₂O₅ films, which arises due to hydrogen atoms detached from hydrogen-containing molecules (water and organics) uncontrollably adsorbed on the oxide surface during preparation, or from ambience [9,10]. Obviously, this effect is small compared with the “cultivated” PIH where specially selected hydrogen-donor molecules are adsorbed in great quantities on the oxide surface [11–20].

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. All said, the above makes it clear that one can achieve a record-breaking value of color centers using the PIH.

When hydrogen atoms are inserted into MoO₃ molybdenum bronzes H_xMoO₃ are formed, which are under intensive long-time investigations due to their various interesting properties [21 and refs therein]. H_xMoO₃ bronzes can be prepared by various methods, and it has been reported that *x* can reach the maximum value of ~2 [21,22], which corresponds to the concentration of the injected hydrogen atoms ~10²² cm⁻³.

Thus, in our case, we prepared H_xMoO₃ bronzes with the help of the PIH. The first report on the “cultivated” PIH in thin films of transition metal oxides was made in [23], which stimulated further investigations concerning various aspects of this phenomenon [11–20].

MoO₃ belongs to the family of “hydrogenphilics,” loving hydrogen materials, capable of accommodating and transporting great amounts of hydrogen atoms. Hydrogen atoms were

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detached from the adsorbed molecules as the result of excitation of the MoO₃ film surface by photons with the energy exceeding the oxide forbidden energy gap and transfer of surface excitation to the adsorbed molecules.

The adsorption mechanism for especially selected hydrogen-donor molecules (hydrogen donors) has been investigated. The great catalytic effect for the photochemical reaction of hydrogen atom transfer from the adsorbed organic molecules to the oxide surface is achieved due to the formation of donor–acceptor and hydrogen bonds, which perturbs both electronic and ionic systems of the molecules [18–20].

A non-zero low-temperature reaction rate limit for photo-triggered hydrogen transfer between adsorbed molecules and the surface of highly disordered nanostructured MoO₃ films was discovered [18–20], the reaction mechanism being determined as tunneling proton-coupled electron transfer (PCET) [24]. The fluctuative preparation of the barrier is achieved by the topological surface disorder (space fluctuations of the barrier parameters) since the oxide surface is essentially heterogeneous with large scattering of the energy barrier parameter for the hydrogen transfer reaction. The topological surface disorder provides the reactive sites with the highest degree of interaction between the adsorbate and the adsorbent, which yields the effective reduction of the barrier. Like in everyday life, where a chaos yields great possibilities, but only for a small minority of people, in the present case, the “creative” chaos on the film surface yields intriguing possibilities to carry out tunneling reaction, but only for small minority (~1%) of the reactive sites [18–20]. The tunneling in turn makes it possible to carry out the PIH at liquid helium temperatures. For this reason, one can achieve the low-temperature PIH only in these highly disordered films.

The time fluctuative preparation of the energy barrier is achieved by phonon stimulation. At very low temperatures, phonon modes are excited via the energy dissipated by the recombination of the electron photoexcitations, which provide the time fluctuation of the energy barrier; in the first turn, the C–H stretching vibration of DMFA molecules is excited [19]. These fluctuations, together with the space fluctuations, provide the hydrogen transfer at the reactive sites with the lowest energy barrier for the reaction.

Here we report on another aspect of photochromism concerning the type of color centers arising due to hydrogen atoms inserted into the MoO₃ nanostructured films. The detached hydrogen atoms donate their electrons to molybdenum atoms, forming lower-valency Mo⁵⁺ cations, protons being bonded to oxygen atoms by hydrogen bonds [3 and refs therein]. The photochromism is attributed to an optical absorption band arising due to light-induced electron transfer between non-isovalent neighboring cations Mo⁶⁺ and Mo⁵⁺ [3 and refs therein].

Earlier it has been reported that MoO₃ amorphous films have no photochromic sensitivity at liquid nitrogen and liquid helium temperatures, whereas under illumination at room temperature, the ESR signal very quickly reaches saturation with exposure [8]. The appropriate selection of the hydrogen-donor molecules and the original film preparation technology made it possible to achieve high photochromic sensitivity even at liquid helium temperatures and to carry out ESR investigations of the photochromism at very low temperatures.

2. Film preparation

The highly disordered nanostructured MoO₃ films were prepared by evaporating MoO₃ powders 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.

Dimethylformamide [DMFA—(CH₃)₂NCHO] was used, as described previously [11–20]. The structural formula of DMFA is presented in Fig. 3. A big mass of DMFA molecules makes it possible to inhibit polymerization (metal–oxygen–metal bond formation) in the growing MoO₃ film, the adsorption of organic molecules being carried on the film surface during evaporation. Being adsorbed on the oxide film surface, non-volatile DMFA molecules remain there for an indefinitely long time at both room and low temperatures, if an access of oxygen is prevented, otherwise the adsorbed DMFA molecules completely turn into volatile products during several months via surface oxidation reactions.

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.

The samples prepared had been kept under a non-oxygen atmosphere before the experiments started.

3. Film characterization

The films were found to be nanocomposites, whereas the absence of a long-range order was confirmed by X-ray analyses. For this reason, we characterize the films as ‘quasi-amorphous’.

Film morphology was studied with the help of a “Smena-B” atomic force microscope (NT-MDT-company). Fig. 1 shows three-dimensional (a) and two-dimensional (b) atomic force images, whereas Fig. 2 shows two-dimensional cross-sections in the XZ plane for ~1-μm-thick MoO₃ films. Heavy oxide particles, being deposited onto the unheated substrates, have small mobility, their sticking coefficient is close to unity, and the film nuclei arising are small. This provides a high probability to form a rough surface, since the deposition has an occasional character: the depositing particles are stuck to the surface at a first-impact point, especially since aggregation in an ordered structure is inhibited by DMFA molecules.

The films possess a high porosity with an average of ~100 nm pore diameter and ~200 nm depth, where the adsorbed molecules can freely move, rotate, and bond to the film surface (Figs. 1 and 2); the surface is essentially heterogeneous, which predetermines different chemical reactivities for different surface reaction centers. One can observe (Fig. 1b) that ~25-nm-diameter clusters have coalesced to form irregular-shaped ~100–200-nm-diameter grains in the MoO₃ films. Thus, the investigated films are macroporous with a rough and highly disordered surface.

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 He³ (D², p)α, the method being described in [25]. 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.

IR absorption spectroscopy was also used to investigate the film structure as well as the adsorption of DMFA molecules. IR spectra were registered with the help of a double-beam spectrometer “Specord 75 IR” (Carl Zeiss, Jena).

Fig. 3 shows an example of transmission spectra for the MoO₃ films evaporated onto the KBr substrate in DMFA vapors. The absorption bands in the range 1800–1000 cm⁻¹ are assigned to the adsorbed DMFA molecules [26,27], whereas the bands in the range 1000–400 cm⁻¹ are assigned to the metal–oxygen stretching vibrations. The band at 2930 cm⁻¹ is attributed to the C–H

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