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The influence of initial stoichiometry on the mechanism of photochromism of molybdenum oxide amorphous films

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ABSTRACT

We investigate the role of oxygen vacancies in photochromism of molybdenum oxide amorphous films. MoO_{3-x} films with a wide range of initial stoichiometries are deposited using R.F. unbalanced magnetron sputtering. The evolution of visible light absorption in conjunction with Raman spectra for these films is studied in detail during the course of UV-irradiation to correlate the color change to the Mo^{6+} to Mo^{5+} conversion. For films which have an initially more complete stoichiometry, and hence lower oxygen vacancy concentration, the color change fully correlates with conversion of Mo^{6+} to Mo^{5+} . This behavior is consistent with the group of models of photochromism of transition metal oxides which disregard the presence of oxygen vacancies in the films. However, coloration of the films with initially greater deviation from complete stoichiometry, and hence higher oxygen vacancy concentration, is not accompanied by any significant conversion of Mo^{6+} to Mo^{5+} . This behavior is consistent with the group of models of photochromism of transition metal oxides which rely on the presence of oxygen vacancies. Overall, the reported results demonstrate the importance of the initial stoichiometry in the photochromism of MoO_{3-x} amorphous films, particularly in the initial stages of UV-irradiation.

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1. Introduction

The electrochromic and photochromic behavior of transition metal oxide (TMO) thin films has been the subject of many studies over the last 50 years [1–11]. Numerous efforts have been made to clarify the origin of the optical absorption band appearing in the TMO thin films upon UV-irradiation. Several models have been put forward to explain the mechanism of photo-coloration in WO_3 and MoO_3 : F-center model [12,13], the model of double insertion/extraction of ions and electrons [2,10,14–15], small polaron model [8,16–18] or variations of the above [19,20]. However, despite the decades of research in this field, there is no unifying model which can comprehensively explain all of the experimental observations associated with coloration in TMOs. As recently stated by Deb [19], one of the key challenges in these transition metal oxide systems is still to fully understand the mechanism of photocoloration.

The most accepted models of photochromism and electrochromism of TMOs are the color center formation model (via oxygen vacancies) [14], the model of double insertion/extraction of ions and electrons [10,14] and the small polaron model [16–17]. Note that, these models can be divided into two categories with respect to the formation of Mo^{5+} during the course of the coloration. The first of these categories involves Mo^{5+} formation and the second does not. The model of double insertion/extraction of ions and electrons and small polaron models belong to the first category. UV light excites electrons from the valence band (the oxygen p-orbital) to the conduction band (Mo^{6+} sites). Subsequently, these free electrons can be trapped forming molybdenum bronze as in the case of the model of double insertion/extraction of ions and electrons or by low energy Mo^{6+} sites as in small polaron model. Essentially, in both of these models during UV-irradiation, Mo^{6+} sites are reduced to Mo^{5+} . This results in the film becoming colored, because the electron can be transferred from the Mo^{5+} site to the Mo^{6+} site via inter-valence charge transfer (IVCT) upon absorption of visible to near infra-red light. Neither of these models requires the presence of oxygen vacancies for photochromism. The models of this category have been widely accepted by many authors. The model of double insertion/extraction of ions

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and electrons is certainly valid to explain the electrochromism of TMO and photochromism of TMOs in presence of water or other protic molecules. However, further expansion of these models onto photochromism of TMOs is in contradiction of a range of experimental facts, such as the photo-coloration is less efficient for the films with more stoichiometric composition, the photo-coloration is more efficient in an atmosphere without oxygen and the color of initially photo-colored films bleaches when the films are heated in presence of oxygen in the atmosphere. Although the efficiency of the photochromic response increases in the presence of water, molybdenum oxide films still remain photochromic even when water cannot be detected in the films [21,22]. Therefore, it could be suggested that, the mechanism of photochromism of TMOs is more sophisticated and involves more processes than those described in the models of this category and in particular in the model of double insertion/extraction of ions and electrons.

In contrast, models such as the color center formation model rely on the presence of oxygen vacancies in the films. In this model, it is assumed that oxygen vacancies are often present in the films due to the various preparation methods. These oxygen vacancies can be envisioned as two Mo^{5+} atoms lacking a bridging oxygen atom between them. This vacancy's energy lies in the valence band [20]. Upon UV-irradiation, this vacancy donates an electron to the conduction band. At the same time the color center is formed: one of the Mo^{5+} turns into Mo^{6+} and the energy of the state that forms is raised into the band gap. This color center can then absorb a visible photon. Upon absorption of a visible photon the electron from the remaining Mo^{5+} can transfer to an adjacent Mo^{6+} through the IVCT transition or it can be excited to the conduction band, in which case the energy of the state that forms, with two Mo^{6+} , will lie in the conduction band [20]. Electrons excited to the conduction band can be trapped by this state, by other low energy Mo^{6+} atoms or contribute to the molybdenum bronze formation via mechanisms described in the small polaron model and the model of double insertion/extraction of ions and electrons. All these pathways of electron trapping will lead to Mo^{5+} formation. Therefore, in these cases, when only oxygen vacancies absorb UV-light photons, the overall Mo^{5+} content will not change and this model can be assigned to the second category. The experimental facts that are contradictory to the models of the first category as listed above are in good agreement with this model however, as in the case of the models of the first category, the color center formation model fails to explain some experimental observations and it has been criticized for a number of reasons. First, in particular cases the density of color centers required for coloration is estimated to be much higher than the density of existing oxygen vacancies [14]. Second, conclusive evidence for color centers is lacking in the optical spectra [23]. Third the photochromism of MoO_3 films is temperature dependent and inhibited by lowering the temperature, which is inconsistent with the electronic basis of the suggested model [24]. Additionally, although the models of this category explain the dependence of photochromic behavior on oxygen presence in the ambient atmosphere, they fail to explain the influence of presence of water or other protic molecules on the photochromism.

We assume that the models described above may all be correct but have their limitations in that each may only be appropriate within its limited set of conditions. Therefore, various experimental observations described in the literature [16,19] may simply suggest that the photochromism in these metal oxide films cannot be explained by applying just one of the proposed mechanisms (vide supra). Many previous works have studied a particular type of film prepared under a certain set of conditions. However we assume that the preparation method may itself affect the mechanism of photochromism. In view of the discussion above, the

concentration of oxygen vacancies can be considered as a potentially very important parameter and it is therefore important to study photochromism of films with significant variation of initial oxygen vacancy concentration. This variation can be achieved by deposition of the films with essentially different stoichiometries. Therefore, the main goal of this work is to study the photochromism of molybdenum oxide amorphous films with essentially different initial stoichiometries from the point of view of applicability of the models described above. The change in the Mo^{5+} relative content during UV-irradiation is considered to be a key parameter to distinguish between the models.

In our previous work [21] the oxidation state of Mo in molybdenum oxide films of essentially different stoichiometry and its change as a result of UV-irradiation were studied using an X-ray Photoemission Spectroscopy (XPS), as the most direct method of probing oxidation states, and Raman spectroscopy. It has been shown that the changes in Raman spectra correlate very well with the XPS data and can thus be used as an in situ probe of the molybdenum oxidation state. At the same time, optical spectra of these films and their evolution with UV-irradiation time have been studied in detail and these changes have been correlated to the Mo oxidation state changes. In addition, sensitivity of Raman spectroscopy to Mo oxidation state had been justified independently by other research groups [22,25,26].

Therefore, in the current study we use Raman spectroscopy to monitor, in situ, the detailed evolution of the Mo oxidation state during the full course of UV-irradiation of molybdenum oxide films of different stoichiometry. Films were irradiated with the UV light at room temperature in air.

2. Materials and methods

2.1. Deposition of MoO_{3-x} films with different stoichiometry

Four types of thin film of MoO_{3-x} were deposited by R.F. reactive sputtering using an unbalanced magnetron sputtering machine (Nano Film Technologies International PTE LTD). Sputtering was done from a 4-in. diameter MoO_3 -target (99.9% purity, Super Conductor Materials, Inc.) in an atmosphere of Ar and O_2 . The chamber was first evacuated to a base pressure of 1×10^{-6} Torr before the deposition was started. For the deposition of MoO_{3-x} films, the total chamber pressure was kept between 3×10^{-3} and 4×10^{-3} Torr. Films were deposited using four different sets of deposition parameters. First, different flow rates of O_2 (0 and 20 sccm) and Ar (40 and 6) were used. Second, two different R.F. powers (100 and 250 W) were applied for each deposition atmosphere and the process was carried out at room temperature. Because the deposition rate strongly depends on the O_2 partial pressure (P_{O_2}) and the R.F. power, different deposition times were used in order to achieve similarity in the thicknesses of the films deposited under different deposition conditions. These four sets of deposition conditions were exactly the same as in our previous work [21] to deposit films with the same initial properties. The four sets of deposition parameters are listed in Table 1.

2.2. Characterizations

Raman spectra of the virgin films were measured using a Raman microscope (Witec confocal Raman microscope, Alpha 300 s). Virgin films were irradiated under the same microscope at room temperature in air through a microscope objective, $40 \times$, NA 0.6, using a Witec DPSS 355 nm CW laser as a source of UV-irradiation using different irradiation times, which was achieved as follows. A series of square arrays of the UV-irradiated spots,

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