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

Mehdi Rouhani^a, Jonathan Hobley^{b,†}, Gomathy Sandhya Subramanian^b, In Yee Phang^b, Yong Lim Foo^c, Sergey Gorelik^{b,†,*}

^a Advanced Institute of Manufacturing with High-tech Innovation (AIM-HI), National Chung Cheng University, 168 University Road, Ming-Hsiung Township, Chia-Yi 62102, Taiwan (R.O.C.)

^b Institute of Materials Research and Engineering, Agency for Science, Technology And Research, 3 Research Link, Singapore, 117602

^c Singapore Institute of Technology, EFG Bank Building, 25 North Bridge Road #03-01 Singapore 179104

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.

*Corresponding Author: E-mail Address: goreliks@imre.a-star.edu.sg. Tel:+65-6874-7992; Fax: +65-6774-1042

† These authors contributed equally

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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

1 the Mo^{5+} site to the Mo^{6+} site via inter-valence charge transfer (IVCT) upon absorption of
2 visible to near infra-red light. Neither of these models requires the presence of oxygen
3 vacancies for photochromism. The models of this category have been widely accepted by
4 many authors. The model of double insertion/extraction of ions and electrons is certainly
5 valid to explain the electrochromism of TMO and photochromism of TMOs in presence of
6 water or other protic molecules. However, further expansion of these models onto
7 photochromism of TMOs is in contradiction of a range of experimental facts, such as the
8 photo-coloration is less efficient for the films with more stoichiometric composition, the
9 photo-coloration is more efficient in an atmosphere without oxygen and the color of initially
10 photo-colored films bleaches when the films are heated in presence of oxygen in the
11 atmosphere. Although the efficiency of the photochromic response increases in the presence
12 of water, molybdenum oxide films still remain photochromic even when water cannot be
13 detected in the films [21,22]. Therefore, it could be suggested that, the mechanism of
14 photochromism of TMOs is more sophisticated and involves more processes than those
15 described in the models of this category and in particular in the model of double
16 insertion/extraction of ions and electrons.

17 In contrast, models such as the color center formation model rely on the presence of
18 oxygen vacancies in the films. In this model, it is assumed that oxygen vacancies are often
19 present in the films due to the various preparation methods. These oxygen vacancies can be
20 envisioned as two Mo^{5+} atoms lacking a bridging oxygen atom between them. This vacancy's
21 energy lies in the valence band [20]. Upon UV-irradiation, this vacancy donates an electron
22 to the conduction band. At the same time the color center is formed: one of the Mo^{5+} turns
23 into Mo^{6+} and the energy of the state that forms is raised into the band gap. This color center
24 can then absorb a visible photon. Upon absorption of a visible photon the electron from the
25 remaining Mo^{5+} can transfer to an adjacent Mo^{6+} through the IVCT transition or it can be

1 excited to the conduction band, in which case the energy of the state that forms, with two
2 Mo^{6+} , will lie in the conduction band [20]. Electrons excited to the conduction band can be
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4 trapped by this state, by other low energy Mo^{6+} atoms or contribute to the molybdenum
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6 bronze formation via mechanisms described in the small polaron model and the model of
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8 double insertion/extraction of ions and electrons. All these pathways of electron trapping will
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10 lead to Mo^{5+} formation. Therefore, in these cases, when only oxygen vacancies absorb UV-
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12 light photons, the overall Mo^{5+} content will not change and this model can be assigned to the
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14 second category. The experimental facts that are contradictory to the models of the first
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16 category as listed above are in good agreement with this model however, as in the case of the
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18 models of the first category, the color center formation model fails to explain some
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20 experimental observations and it has been criticized for a number of reasons. Firstly, in
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22 particular cases the density of color centers required for coloration is estimated to be much
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24 higher than the density of existing oxygen vacancies [14]. Secondly, conclusive evidence for
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26 color centers is lacking in the optical spectra [23]. Thirdly the photochromism of MoO_3 films
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28 is temperature dependent and inhibited by lowering the temperature, which is inconsistent
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30 with the electronic basis of the suggested model [24]. Additionally, although the models of
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32 this category explain the dependence of photochromic behavior on oxygen presence in the
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34 ambient atmosphere, they fail to explain the influence of presence of water or other proteic
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36 molecules on the photochromism.
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46 We assume that the models described above may all be correct but have their
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48 limitations in that each may only be appropriate within its limited set of conditions.
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50 Therefore, various experimental observations described in the literature [16, 19] may simply
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52 suggest that the photochromism in these metal oxide films cannot be explained by applying
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54 just one of the proposed mechanisms (*vide supra*). Many previous works have studied a
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56 particular type of film prepared under a certain set of conditions. However we assume that the
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1 preparation method may itself affect the mechanism of photochromism. In view of the
2 discussion above, the concentration of oxygen vacancies can be considered as a potentially
3 very important parameter and it is therefore important to study photochromism of films with
4 significant variation of initial oxygen vacancy concentration. This variation can be achieved
5 by deposition of the films with essentially different stoichiometries. Therefore, the main goal
6 of this work is to study the photochromism of molybdenum oxide amorphous films with
7 essentially different initial stoichiometries from the point of view of applicability of the
8 models described above. The change in the Mo^{5+} relative content during UV-irradiation is
9 considered to be a key parameter to distinguish between the models.
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11 In our previous work [21] the oxidation state of Mo in molybdenum oxide films of
12 essentially different stoichiometry and its change as a result of UV-irradiation were studied
13 using an X-ray Photoemission Spectroscopy (XPS), as the most direct method of probing
14 oxidation states, and Raman spectroscopy. It has been shown that the changes in Raman
15 spectra correlate very well with the XPS data and can thus be used as an in situ probe of the
16 molybdenum oxidation state. At the same time, optical spectra of these films and their
17 evolution with UV-irradiation time have been studied in detail and these changes have been
18 correlated to the Mo oxidation state changes. In addition, sensitivity of Raman spectroscopy
19 to Mo oxidation state had been justified independently by other research groups [22, 25, 26].
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21 Therefore, in the current study we use Raman spectroscopy to monitor, in situ, the
22 detailed evolution of the Mo oxidation state during the full course of UV-irradiation of
23 molybdenum oxide films of different stoichiometry. Films were irradiated with the UV light
24 at room temperature in air.
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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-inch 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 250W) 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.

Table 1

Four different sets of essential deposition parameters used to deposit MoO_{3-x} sample films with different stoichiometry.

Parameters	Film ‘ α ’	Film ‘ β ’	Film ‘ γ ’	Film ‘ δ ’
P_{O_2} (mTorr)	3.84	3.84	0	0
R.F. power (W)	100	250	100	250
Deposition time (min.)	825	120	165	60
Bias Voltage (V)	243-235	356-375	214-160	198-195
Thickness (nm)	165	125	170	250

2.2. Characterizations

Raman spectra of the virgin films were measured using a Raman microscope (Witec confocal Raman microscope, Alpha 300s). Virgin films were irradiated under the same microscope **at room temperature in air** through a microscope objective, 40x, NA 0.6, using a Witec DPSS 355nm 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, 80x80 μm^2 each, was created on each film. Each square consists of 10x10 UV-irradiated spots with the same time of irradiation. This spot irradiation time was different for different squares varying from 1 to 90s. The intensity of the laser radiation was kept constant (0.3mW) for all the measurements. The diameter of the resulting photo-converted spot was about 8 μm , as measured optically using the same microscope and a CCD camera.

Raman spectra of the squares were measured **at room temperature in air** using a Witec 532 nm Nd-YAG CW laser as a probe. The intensity of the laser radiation was kept sufficiently low (0.6 mW) to avoid annealing MoO_3 films by laser induced heating. For each UV-irradiated square, Raman spectra were averaged over a 60x60 μm^2 area (60x60 scan points), with 100ms integration time for each point. Squares of the same dimensions were scanned in a non-irradiated area to obtain corresponding Raman spectra of virgin portions of the films.

The UV-Vis transmittance spectra of the virgin films in the range 300 to 1200nm were measured using a UV-Vis spectrometer (UV-2450, SHIMADZU).

In order to assess color change in the UV-irradiated squares of such a small size an optical microscope can be used. In our previous work, evolution of optical spectra of the same sample films with UV-irradiation time was studied [21]. The spectra of the UV-irradiated films were essentially broad and covered the whole visible - NIR spectral range, in agreement with other studies [12, 13, 16, 27]. In the current work we logically assumed that,

the spectral changes of the films induced by the UV-irradiation are the same as in these previous works. Therefore, for simplicity, we used an integral transmission of white light through the UV-irradiated squares to estimate the absorbance change during the photochromic coloration. To achieve this, images of the UV-irradiated squares in transmission were recorded using an upright optical microscope (Nikon Eclipse 50i Pol) equipped with a CCD camera, a 5x objective lens and a tungsten lamp as a source of white light illumination. The brightness of the images of the squares was analyzed. The average absorbance for each square was simply calculated as $\log(I_0/I)$, where I_0 is the value of brightness in the non-irradiated area just outside the square and I is the value of brightness inside the irradiated square. In other words, the absorbance variation with wavelength is disregarded throughout the whole spectrum of the white light used as it is in any case broad and featureless.

3. Results and discussion

3.1. As-deposited virgin films

Films with four different sets of deposition conditions were deposited as described in experimental section. In our previous study, the Mo oxidation state in the films was examined [21]. Different deposition conditions resulted in different relative concentrations of Mo^{5+} and Mo^{6+} . No Mo^{4+} was detected in any of the deposited films. The Mo^{5+} relative concentration of the films deposited with the four different sets of deposition parameters measured in our previous study [21] are given in Table 2 together with the film stoichiometries calculated assuming that the stoichiometry is directly related to the Mo^{5+} relative concentration (as determined by XPS).

Table 2

Stoichiometry of four types of MoO_{3-x} films corresponding to four different sets of deposition parameters listed in Table 1.

Film	$[\text{Mo}^{5+}]/([\text{Mo}^{5+}]+[\text{Mo}^{6+}])$	Ratio of O to Mo, MoO_y (y)
α	0 ± 0.02	3 ± 0.01
β	0.03 ± 0.02	2.985 ± 0.01
γ	0.15 ± 0.02	2.925 ± 0.01
δ	0.35 ± 0.02	2.825 ± 0.01

The Mo^{5+} relative concentration increases from 0 to 35% from film α to film δ . We assume that, Mo^{5+} in as-deposited films is directly related to the presence of oxygen vacancies. Therefore, oxygen vacancy relative concentration $[\text{Vo}]/[\text{O}]$ can be estimated as increasing from 0 to 6% from film α to film δ .

Optical UV-Vis transmittance spectra of the as-deposited films are shown in Fig. 1. The spectra are very similar to those measured in our previous study [21] which indicates the good reproducibility of the deposition method. The as-deposited films are intrinsically colored depending on the concentration of the oxygen vacancies – the higher the concentration, the stronger the coloration. For films ' α ' and ' β ' the spectra appear to be affected by interference. However, the spectral features of films ' γ ' and ' δ ' clearly result from the absorption in the films. For defect free MoO_3 only absorption above the optical bandgap should be observed in the spectra with absorption edge at about 400nm [13]. All other absorption bands observed in visible to near infrared (NIR) spectral region should be attributed to the presence of oxygen vacancies and related Mo^{5+} . These bands in the spectra of all the films are broad, covering nearly the whole visible-NIR spectral range, with maxima at ~800-900nm. With increasing the oxygen vacancy concentration, from ' α ' to ' δ ' these spectral bands become broader. At the same time, spectral maxima shift towards shorter

wavelength. Similar spectral features were observed for virgin molybdenum oxide amorphous films deposited by R.F. sputtering using different oxygen flow [3] and deposited using thermal evaporation under high vacuum [28]. Dieterle et al studied diffuse reflectance spectra of polycrystalline MoO_{3-x} powders [26]. They concluded that, two absorption bands contribute the most to the absorption spectra of their samples: (1) at around 950nm ($\sim 1.3\text{eV}$) corresponding to the IVCT transition involving hexacoordinated Mo^{5+} and (2) at around 600nm ($\sim 2\text{eV}$) corresponding to the IVCT transition involving pentacoordinated Mo^{5+} which is attributed to the oxygen defect state. They have demonstrated that the contribution of (2) increases with increasing oxygen defect concentration, in agreement with [29,30]. The sample films in the current study are amorphous and fabricated using a method which is different from that used in [26] (e.g. heating above 670K is involved in fabrication of the samples [26]). However the 'blue' shift and broadening of the spectra of the films in the current study with increasing oxygen defect concentration are consistent with [26,29,30]. Therefore, we assume that in the current study both, pentacoordinated and hexacoordinated Mo^{5+} is present in the as-deposited films with relatively high oxygen vacancy concentration in films ' γ ' and ' δ '. The origin of hexacoordinated Mo^{5+} in the films deposited under current study as well as in [26] is not clear. We could suggest that, hexacoordinated Mo^{5+} is formed via electron transfer from pentacoordinated Mo^{5+} during the deposition process or due to immediate rearrangement of MoO_3 polyhedra resulting in the elimination of oxygen vacancies as suggested in [31].

Fig.1. UV-Vis transmittance spectra of virgin films ‘α’ – ‘δ’.

The surface topography of the as-deposited films was examined using AFM. Resulting AFM topography images are shown in the supplementary information (Fig. S1). The root mean square surface roughness (R_{RMS}) of the films derived from AFM data is also given in supplementary information (Table S1). All of the films are smooth, although films ‘β’ and ‘γ’ show some needle-like features. However, no obvious correlation between film topography and deposition conditions can be seen.

Fig. 2 shows Raman spectra of virgin films ‘α’ – ‘δ’. The spectra are broad as compared to the Raman spectra of crystalline MoO_3 [22, 26] indicating the absence of crystalline structure in the films. Raman spectra of virgin films ‘α’ and ‘β’ show two broad bands centered at ~ 830 and 950 cm^{-1} and a broad shoulder at $700\text{--}750 \text{ cm}^{-1}$. In our previous work [21], these bands were assigned to the doubly connected bridge-oxygen ($\text{O}=\text{Mo}^{6+}=\text{O}$) stretching mode at 830 cm^{-1} , the terminal oxygen ($\text{Mo}^{6+}=\text{O}$) stretching mode at 950 cm^{-1} and the triply connected bridge-oxygen ($\text{Mo}^{6+}_3=\text{O}$) stretching mode at $\sim 750 \text{ cm}^{-1}$ in agreement with the assignment of Raman bands of amorphous MoO_3 reported by Ajito *et al* [25]. In contrast to the spectra of films ‘α’ and ‘β’, the Raman spectrum of film ‘γ’ has a broad peak centered at $\sim 850 \text{ cm}^{-1}$ with two shoulders at $\sim 945 \text{ cm}^{-1}$ and $\sim 750 \text{ cm}^{-1}$ and the Raman spectrum of film ‘δ’ shows a peak centered at $\sim 890 \text{ cm}^{-1}$ with a pronounced shoulder

at $\sim 750 \text{ cm}^{-1}$. Based on the detailed analysis of the Raman spectra of these films in [21], the observed difference in Raman spectra of films ‘ γ ’ and ‘ δ ’ as compared to the spectra of films ‘ α ’ and ‘ β ’ should be attributed to the higher Mo^{5+} content for these films. The detailed analysis of Raman spectra of the virgin and UV-irradiated films will be described below.

Additionally, a peak (shoulder) in the range $\sim 400\text{-}450 \text{ cm}^{-1}$ can be seen in the spectra of films ‘ γ ’ and ‘ δ ’, while it is absent in the spectra of films ‘ α ’ and ‘ β ’. It is reported that this peak is a signature of Mo^{5+} [22]. This statement is confirmed in our previous study [21] using XPS and Raman spectral analysis.

The spectra presented in Fig. 2 are overall in good agreement with the spectra reported in our previous study [21], the small differences in the spectra can be attributed to the slight differences in the optical configuration: in [21] a 50x 0.55 NA objective was used and in current work a 40x 0.6 NA UV objective was used for the Raman spectra collection. These slight changes can result in different transmission characteristics as well as potentially altering the proportions of polarized to depolarized peaks being collected. This is because polarized and depolarized peak intensities are angle dependent relative to the incident probe beam and different objective lenses have different numerical apertures.

Fig. 2. Raman spectra of virgin films ‘ α ’ – ‘ δ ’. The spectra are vertically shifted for better visualization.

3.2. UV-irradiated films

Fig.3 shows transmission optical microscope images of squares created using different UV-irradiation time for film ' α ' - ' δ ' as described above in the experimental section.

Fig. 3. Transmission optical microscope images of series of squares created using different UV-irradiation times for (a) film ' α ', (b) film ' β ', (c) film ' γ ' and (d) film ' δ '.

The corresponding evolution of the average absorbance change with UV-irradiation time for films ' α ' - ' δ ' are shown in Fig. 4. The average absorbance change is determined from brightness analysis of the optical transmission microscopy images (Fig. 3) as described in the experimental section. During the early stages of UV-irradiation the absorbance of film ' α ' rises sharply, but after that it rapidly plateaus. Similar behavior can be seen for films ' β ' taking into account the thickness difference. For film ' γ ' there is an initial rapid absorption change, similar to films ' α ' and ' β ', after which the absorption change does not plateau but continues rising until the end of the time-course.

Fig. 4. Dependence of the average absorbance change on the UV-irradiation time for (a) film 'α', (b) film 'β', (c) film 'γ' and (d) film 'δ'.

For film 'δ' the absorbance increases slowly throughout the whole irradiation time-course. Note that the final average absorbance change for film 'δ' is about 2 times larger than for all other films which cannot be explained even taking into account the difference in film thicknesses (table 1). These findings are fully consistent with the evolution of absorption spectra of the films observed in our previous study [21] although the timescale is different due to the different UV-irradiation sources.

Fig. 5. Normalized Raman spectra of the UV-irradiated square arrays corresponding to different UV-irradiation times for (a) film ‘ α ’; (b) film ‘ β ’; (c) film ‘ γ ’; (d) film ‘ δ ’. Raman spectra corresponding to different UV-irradiation times are vertically shifted for better visualization. Black vertical arrow indicates direction of the UV-irradiation time increase (0 - 90 s).

Fig. 5 shows the normalized Raman spectra of films ‘ α ’ – ‘ δ ’ at different UV-irradiation times. To visualize changes in the Raman spectra, difference spectra at different UV-irradiation times relative to the corresponding initial spectra of virgin films are plotted in Fig. 6. In Fig. 5 and Fig. 6 the main spectral changes can be seen at two different regions: $\sim 400\text{-}450\text{ cm}^{-1}$ and in the range $500\text{-}1000\text{ cm}^{-1}$. The changes in these two spectral regions will be analyzed below in detail. In both spectral regions changes in Raman spectra of films ‘ α ’ and ‘ β ’ upon UV-irradiation are relatively large and can be easily seen: the changes in Raman spectra for film ‘ γ ’ are significantly smaller than those for films ‘ α ’ and ‘ β ’ and for film ‘ δ ’ the spectral changes are of the order of the noise level.

Fig. 6. Difference Raman spectra of films ‘ α ’ – ‘ δ ’ for different UV-irradiation times.

The relative intensity of the Raman band in the spectral region $\sim 400\text{-}450\text{ cm}^{-1}$ is plotted against UV-irradiation time for films ‘ α ’ – ‘ δ ’ in Fig. 7. It rises sharply for films ‘ α ’ and ‘ β ’ at the early stage of UV-irradiation and then plateaus. In contrast, the intensity of this shoulder in the Raman spectra of films ‘ γ ’ and ‘ δ ’ is almost constant throughout the whole time-course of UV-irradiation; just slightly decreasing. These observations are consistent with our previous study [21].

Fig. 7. Changes of the intensity of the Raman band in the spectral region $\sim 400\text{-}450\text{ cm}^{-1}$ with UV-irradiation time for films ‘ α ’ (black squares), ‘ β ’ (red stars), ‘ γ ’ (green triangles) and ‘ δ ’ (blue circles). The corresponding lines are guide to the eye. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

As discussed above, this Raman band is a signature of Mo^{5+} [21, 22]. Comparing the time evolution of this band in Fig. 7 with the average absorbance change evolution shown in Fig. 4 we can conclude that for films ‘ α ’ and ‘ β ’ Mo^{5+} formation directly correlates to the color change while for films ‘ γ ’ and ‘ δ ’ there is no correlation and further we can conclude that the Mo^{5+} content does not change despite of the pronounce color change for these two films.

Fig. 8 shows the dependence of the difference in the maximum peak to valley displacement on the UV-irradiation time estimated from difference Raman spectra shown in Fig. 6 for films ‘ α ’ – ‘ δ ’ in the spectral region $500\text{-}1000\text{ cm}^{-1}$. Raman spectra of films ‘ α ’ and ‘ β ’ in this spectral range change very sharply at the very early stage of UV-irradiation and then continue changing, albeit significantly slower, until the end of the UV-irradiation time-course. Changes in the Raman spectra of film ‘ γ ’ are again substantially smaller and changes in the Raman spectra of film ‘ δ ’ are comparable with the experimental error.

Fig. 8. Amplitude of the maximum difference of the difference Raman spectra in the region 500-1000 cm^{-1} plotted against UV-irradiation time for films ‘ α ’ (black squares), ‘ β ’ (red stars), ‘ γ ’ (green triangles) and ‘ δ ’ (blue circles). The corresponding lines are guide to the eye. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

From comparison of Fig. 8 with Fig. 4 the same trend can be seen as from comparison of Fig. 7 with Fig. 4: direct correlation of absorbance change with change in Raman spectra for films ‘ α ’ and ‘ β ’ and no correlation for films ‘ γ ’ and ‘ δ ’.

To further analyze the changes in the Raman spectra of these films resulting from UV-irradiation, in the spectral region 500-1000 cm^{-1} , we used the same Gaussian fitting approach as described in our previous study [21]. As in [21] in total 6 Gaussians were used to represent Raman bands of 3 Mo^{6+} —O stretching modes and Raman bands of 3 Mo^{5+} —O stretching modes in this spectral region. The peak center positions and widths of the Gaussians were kept constant for all of the fitted spectra. At first, assuming that virgin film ‘ α ’ does not contain any Mo^{5+} , its Raman spectrum was fitted with initial three Gaussians, centered at 754, 849 and 952 cm^{-1} , corresponding to the triply connected bridge-oxygen (Mo^{6+}_3 —O) stretching mode, the doubly connected bridge-oxygen (O— Mo^{6+} —O) stretching mode and the terminal oxygen (Mo^{6+} =O) stretching mode respectively, as discussed above (Fig.2 and related discussion) and consistent with our previous study [21]. These Gaussians were used to represent Raman bands of Mo^{6+} stretching modes in Raman spectra of all the films before and

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after UV-irradiation. Raman spectra of films ‘ α ’ after UV-irradiation as well as the spectra of films ‘ β ’, ‘ γ ’ and ‘ δ ’ before and after UV-irradiation could not be fitted using just these three Gaussians. Additional Gaussians, centered at 738, 895 and 980 cm^{-1} , were required. These bands were assigned to stretching modes of the bonds involving Mo^{5+} and could be further assigned to the triply connected bridge-oxygen ($\text{Mo}^{5+}_3\text{—O}$) stretching mode at 738 cm^{-1} , the doubly connected bridge-oxygen ($\text{O—Mo}^{5+}\text{—O}$) stretching mode at 895 cm^{-1} and the terminal oxygen ($\text{Mo}^{5+}\text{=O}$) stretching mode at 980 cm^{-1} . The results of fitting for films ‘ α ’ – ‘ δ ’ before and after 90 sec of UV-irradiation time are shown in Fig. 9. As in our previous work [21] the Raman spectrum of virgin film ‘ α ’ could be fitted using only three Gaussians centered at 754, 849 and 952 cm^{-1} , all other films could be fitted using different combinations of 6 Gaussians indicating different Mo^{5+} and Mo^{6+} content.

Fig. 9. Gaussian fitting of Raman spectra in the spectral region $500\text{cm}^{-1} - 1000\text{cm}^{-1}$ for (a) film ' α' ', (b) film ' β' ', (c) film ' γ' ' and (d) film ' δ' ' before (left) and after (right) 90 sec of UV-irradiation. The dot (black) lines represent the experimental data (after subtracting the baseline), solid (blue) lines show Gaussian functions representing Raman bands of stretching modes of bonds involving Mo^{6+} , dashed lines (red) show Gaussian functions representing stretching modes of bonds involving Mo^{5+} and solid (orange) lines show the fitting envelopes of the Gaussian peaks. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

Fig. 10. (a) Ratio of maximum values of Gaussians representing Raman bands associated with doubly connected bridge-oxygen stretching mode involving Mo^{5+} at $895cm^{-1}$ to that involving Mo^{6+} at $849cm^{-1}$ (I_{895}/I_{849}) against UV-irradiation time, (b) sum of the ratios of the maxima of all of the Gaussians representing Raman bands related to Mo^{5+} to those related to Mo^{6+} ($(I_{738}/I_{754}) + (I_{895}/I_{849}) + (I_{980}/I_{952})$) against the UV-irradiation time for films 'α' (black squares), 'β' (red stars), 'γ' (green triangles) and 'δ' (blue circles). The corresponding lines are guide to the eye. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

Fig. 10(a) shows the ratio of maximum values of Gaussians representing Raman bands associated with doubly connected bridge-oxygen stretching mode involving Mo^{5+} at $895cm^{-1}$ to that involving Mo^{6+} at $849cm^{-1}$ (I_{895}/I_{849}) plotted against UV-irradiation time. The ratio is the highest for the as-deposited film 'δ' (UV-irradiation time 0) but does not significantly change throughout the whole UV-irradiation course. For film 'γ' this ratio is also significantly high from the beginning and again does not change. This is consistent with Figs.5, 6 above and is in agreement with the XPS and Raman data from our previous study

[21] showing that these sample films have high Mo^{5+} content from the beginning. For film 'α' the ratio increases sharply at early stages of UV-irradiation then plateaus. The ratio for film 'β' follows a similar trend: it sharply rises at early times of UV-irradiation and then plateaus. Again, this ratio for films 'α' and 'β' follows similar trend as the intensity of the Raman band at $\sim 400\text{cm}^{-1}$ in Fig. 5.

The sum of the ratios of the maxima of all the Gaussians representing Raman bands related to Mo^{5+} to those related to Mo^{6+} ($(I_{738}/I_{754}) + (I_{895}/I_{849}) + (I_{980}/I_{952})$) is plotted against the UV-irradiation time in Fig. 10(b). For each film the sum of the ratios follows the similar trend as the single ratio (I_{895}/I_{849}) shown in Fig. 10(a) and hence the same trend as the intensity of the Raman band at $\sim 400\text{cm}^{-1}$ in Fig. 5. This, again, indicates that at early stages of UV-irradiation Mo^{5+} content is increasing sharply for films 'α' and 'β', while it almost constant for 'γ' and 'δ' throughout the whole UV-irradiation course.

In summary, we can conclude from the Raman spectra analysis (Figs. 5 - 10) that during UV-irradiation films 'α' and 'β' follow a different trend to films 'γ' and 'δ' in terms of the correlation of the Mo^{5+} formation to the color change (Fig. 4). For films 'α' and 'β', with very low initial Mo^{5+} content, the color change is clearly associated with relatively large increases in the Mo^{5+} content of the film, whereas for films 'γ' and 'δ', which have initially higher Mo^{5+} content, presumably due to pre-existing oxygen vacancies, there is no increase in the Mo^{5+} content of the films even though the films become significantly more colored during irradiation.

Recall back to our initial aim. We wished to determine under what conditions the color change is associated with changes in Mo^{5+} concentration, which is consistent with the first category of models disregarding the presence of oxygen vacancies in the material. We also aimed to establish under what conditions the color changes are not associated with changes in Mo^{5+} content, which is consistent with the second category of models based on the

1 presence of oxygen vacancies. It seems from this work that the first group of models is
2 appropriate for films with initially low Mo^{5+} content (and low numbers of oxygen vacancies)
3
4 and the second group of models is appropriate for coloration of the films with an initially
5
6 high Mo^{5+} content.
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10 Note, that Mo^{5+} concentration during UV-irradiation of film 'δ' previously reported
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12 [21] was found to be significantly decreased as measured both with XPS and Raman
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14 spectroscopy, while in current work no significant changes in Mo^{5+} concentration was
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16 detected. This discrepancy might come from the fact that in our previous study a UV-lamp
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18 was used as a source of UV-irradiation and subsequently much longer UV-irradiation times
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20 (up to 3 hours) [21]. The spectrum of radiation of this UV-lamp contains wavelengths
21
22 significantly shorter than 355nm used in the current study. This deep UV portion of light
23
24 could form ozone and other reactive oxygen species from the oxygen in the atmosphere
25
26 which could cause surface oxidation of the molybdenum oxide films. And since film 'δ' has
27
28 the highest oxygen vacancy concentration, significantly higher than the other films, it can be
29
30 more susceptible to the oxidation.
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39 **4. Conclusion**

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41 The results presented in this work clearly show that mechanisms of photochromism
42
43 for MoO_{3-x} films are different for films with different initial stoichiometry. Coloration for the
44
45 films with more complete stoichiometry is fully correlated to conversion of Mo^{6+} to Mo^{5+} ,
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47 while coloration of the sub-stoichiometric films is controlled by another mechanism, which
48
49 does not involve conversion of Mo^{6+} to Mo^{5+} . Hence, the mechanism of photochromism of
50
51 films with low oxygen vacancy concentration (more complete stoichiometry) is consistent
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53 with the group of models such as the model of double insertion/extraction of ions and
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55 electrons, small polaron model, etc. which disregard the role of oxygen vacancies in the
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1 starting films whilst the mechanism of photochromism of films with high oxygen vacancy
2 concentration (sub-stoichiometric films) is consistent with models which rely on the presence
3 of oxygen vacancies such as color center formation model.
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7 Whereas previous authors have attempted a one-model-fits-all approach we can show
8 that this is clearly not an appropriate approach. This may to some extent explain the apparent
9 controversies in the literature since the contributions from different models may be involved
10 to different extents depending on the film preparation method and more specifically on the
11 initial oxygen defect content.
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Figure captions:

Fig. 1. UV-Vis transmittance spectra of virgin films ‘α’–‘δ’.

Fig. 2. Raman spectra of virgin films ' α ' – ' δ '. The spectra are vertically shifted for better visualization.

Fig. 3. Transmission optical microscope images of series of squares created using different UV-irradiation times for (a) film ' α ', (b) film ' β ', (c) film ' γ ' and (d) film ' δ '.

Fig. 4. Dependence of the average absorbance change on the UV-irradiation time for (a) film ' α ', (b) film ' β ', (c) film ' γ ' and (d) film ' δ '.

Fig. 5. Normalized Raman spectra of the UV-irradiated square arrays corresponding to different UV-irradiation times for (a) film ' α '; (b) film ' β '; (c) film ' γ '; (d) film ' δ '. Raman spectra corresponding to different UV-irradiation times are vertically shifted for better visualization. Black vertical arrow indicates direction of the UV-irradiation time increase (0 - 90 s).

Fig. 6. Difference Raman spectra of films ' α ' – ' δ ' for different UV-irradiation times.

Fig. 7. Changes of the intensity of the Raman band in the spectral region $\sim 400\text{--}450\text{ cm}^{-1}$ with UV-irradiation time for films ' α ' (black squares), ' β ' (red stars), ' γ ' (green triangles) and ' δ ' (blue circles). The corresponding lines are guide to the eye. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. Amplitude of the maximum difference of the difference Raman spectra in the region $500\text{--}1000\text{ cm}^{-1}$ plotted against UV-irradiation time for films ' α ' (black squares), ' β ' (red stars), ' γ ' (green triangles) and ' δ ' (blue circles). The corresponding lines are guide to the eye. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

Fig. 9. Gaussian fitting of Raman spectra in the spectral region $500\text{ cm}^{-1} - 1000\text{ cm}^{-1}$ for (a) film ' α ', (b) film ' β ', (c) film ' γ ' and (d) film ' δ ' before (left) and after (right) 90 sec of UV-irradiation. The dot (black) lines represent the experimental data (after subtracting the baseline), solid (blue) lines show Gaussian functions representing Raman bands of stretching modes of bonds involving Mo^{6+} , dashed lines (red) show Gaussian functions representing stretching modes of bonds involving Mo^{5+} and solid (orange) lines show the fitting envelopes of the Gaussian peaks. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

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Tables:

Table 1

Four different sets of essential deposition parameters used to deposit MoO_{3-x} sample films with different stoichiometry.

Parameters	Film 'α'	Film 'β'	Film 'γ'	Film 'δ'
P _{O₂} (m Torr)	3.84	3.84	0	0
R.F. power (W)	100	250	100	250
Deposition time (min.)	825	120	165	60
Bias Voltage (V)	243-235	356-375	214-160	198-195
Thickness (nm)	165	125	170	250

Table 2

Stoichiometry of four types of MoO_{3-x} films corresponding to four different sets of deposition parameters listed in Table 1.

Film	[Mo ⁵⁺]/([Mo ⁵⁺]+[Mo ⁶⁺])	Ratio of O to Mo, MoO _y (y)
α	0 ± 0.02	3 ± 0.01
β	0.03 ± 0.02	2.985 ± 0.01
γ	0.15 ± 0.02	2.925 ± 0.01
δ	0.35 ± 0.02	2.825 ± 0.01