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In situ measurements of thickness changes and mechanical stress upon gasochromic switching of thin MoO_x films

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Thin films of MoO_x coated with platinum as a catalyst were prepared by dc magnetron sputtering from a molybdenum target in an oxygen and argon atmosphere. The films were colored and bleached by exposure to diluted hydrogen gas and air, respectively. *In situ* measurements of x-ray reflectance and substrate curvature were performed during switching cycles. Upon hydrogen exposure a remarkable thickness decrease of 11% and a density increase of 6.5% are observed by x-ray reflectance measurements. Corresponding changes in optical transmittance and mechanical stress up to several hundreds of MPa are also observed. These changes are not fully reversible as revealed by measurements of multiple switching cycles. Both the change of thickness and density, as well as the change of optical transmittance and mechanical stress can be explained by the existence of a mixed phase of edge and corner sharing MoO_3 octahedra whereupon the first coloration the ratio between edge and corner sharing octahedra is changed. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1728309]

I. INTRODUCTION

Optically switchable coatings offer a wide range of promising applications, such as hydrogen sensors, nonglare rear view windows, displays, and smart windows.[1,2] The renewed interest in such materials is driven by the desire and need to develop energy saving solutions for architectural buildings as well as the recent discovery of a new class of materials, namely rare earth metals, which show optical switching.[2–4] The switching process involves the incorporation of hydrogen into the film, leading to a change of its optical properties. These optical changes are prompted by injection of charges (electrochromism) or gases (gasochromism). Gasochromic smart windows exploit switching under hydrogen exposure from a state which is transparent in the visible and near infrared to an absorbing state in the infrared region, which leads to a decreased transmission of the solar energy flux. In a recent paper we have shown in a comparison of several different classes of switchable coatings that WO_x should be the material of choice for many applications since the switching in this material is fully reversible and is accompanied by the smallest stresses observed in any material.[5] Other materials, such as simple metals, e.g., Mg and rare earth metals such as Gd are characterized by much larger mechanical stresses upon switching which lead to irreversible deformations.[5] While WO_3 shows the superior behavior in terms of mechanical stresses upon switching, the blue color the material obtains upon switching is considered a disadvantage for certain applications where color neutrality is a requirement. Molybdenum oxide is another oxide which exhibits chromogenic properties.[6,7] Upon coloration it shows a less pronounced color change, even though a sufficiently pronounced absorption occurs in the IR to render this material useful for smart window applications.

Although tungsten and molybdenum are very similar elements in terms of their electronic structure, molybdenum oxide has not been fully exploited as a window coating material and as a gas sensor.[6–9] This is due to the fact that switching of MoO_x films is more complicated due to the competition of several different phases which coexist in substoichiometric films. In order to exploit the potential of MoO_x as a gasochromic material and gas sensor, it is important that the physical processes that take place in the films when exposed to hydrogen are clearly understood. Of particular importance is the correlation between the deposition conditions and the resulting phases and their relation to the physical properties of these structures. This knowledge would also be important for the improvement of the long term cyclability and the switchability of the material. Suitably designed *in situ* techniques during hydrogen exposure could help clarify some of the microscopic processes involved in switching.

In this work, a combination of two complimentary techniques, namely, *in situ* x-ray reflectance measurements together with experiments to determine the change of mechanical stresses during switching in diluted hydrogen and air, respectively, have been used to study the physical changes that take place in thin MoO_x films. A possible mechanism for the observed changes is discussed.

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II. EXPERIMENT

A. Deposition

The samples were reactively deposited from a molybdenum target in an oxygen and argon atmosphere on unheated Si (100) wafers for x-ray reflectance (XRR) (thickness ≈525 μm), and glass substrates (thickness ≈150 μm) for wafer curvature measurements. The vacuum chamber has a background pressure of 10^{-6} mbar. In the present study, the nonstoichiometric MoO_x films were prepared at a constant pressure of 9.0 Pa at a cathode current of 800 mA while the oxygen flow was kept constant at 19 sccm. A 2 nm thin platinum layer was deposited from a platinum target in an argon atmosphere at a constant pressure of 0.8 Pa at a cathode current of 170 mA. The purpose of this Pt layer is to catalyze the dissociation of hydrogen and its incorporation in the film. In both cases, the substrates were placed at a distance of 78 mm from the target.

B. *In situ* stress measurements

Wafer curvature measurements[10] were employed to determine the mechanical stress induced in the film during the switching process in 2% hydrogen gas in argon. The wafer curvature is measured by a laser scanning technique using a rotating mirror. This method utilizes a position sensitive detector to determine the substrate curvature. An additional detector situated below the sample allows the determination of the transmittance changes of the film during the switching cycles. This makes the simultaneous monitoring of the stress and optical transmittance changes possible during coloration cycles. The stress change is determined from the Stoney equation[11]

$$\Delta\sigma = \frac{1}{6}\left(\frac{E_s}{1-\nu_s}\right)\frac{t_s^2}{t_f}\left(\frac{1}{R}-\frac{1}{R_o}\right), \tag{1}$$

where $E_s/(1-\nu_s)$ is the biaxial elastic modulus of the substrate, and t_s and t_f denote the thickness of the substrate and the film, respectively, while $1/R_o$ and $1/R$ represent the curvature of the substrate before switching and during switching, respectively.[12] Equation (1) applies to biaxial stresses in a film-substrate combination.[14,10] In using this equation here we neglect the 2 nm Pt layer on top. This is justified since previous work by Pedersen[21] has shown that a single 8 nm Pt film shows a stress change of about 200 MPa upon switching with hydrogen. Hence for a thickness of about 2 nm we can assume a maximum contribution to the stress of about 50 MPa. The loading with hydrogen is carried out in a gas cell equipped with windows to give the laser beam access to the sample. The intensity transmitted through the film and the substrate is determined at the laser wavelength of $\lambda = 632.8$ nm. The same setup is also used to measure changes in stress during the annealing process. For the wafer curvature measurements the samples on glass substrates were used, while the samples on silicon (100) were only used for XRR measurements.

C. *In situ* x-ray reflectance

The film thickness and density of the samples on Si (100) were determined by XRR, employing a Philips X'pert MRD system and a gas cell attached to the sample holder. The *in situ* gas cell consists of a polyethylene bag mounted on the goniometer and connected to a gas feed system. This bag can hold moderate overpressures of about 200 mbar of a gas mixture containing 1% H_2 in N_2. In this setup, the hydrogen/nitrogen mixture is preferred because of the lower loss of x-ray intensity as compared with an argon filled switching chamber. Simulations were performed to reproduce the measured data. The thickness of the films was determined from the intensity oscillations and the density was determined from the position of the total reflection edge.[12] The x-ray diffraction equipment was also employed to study the structure of the films.

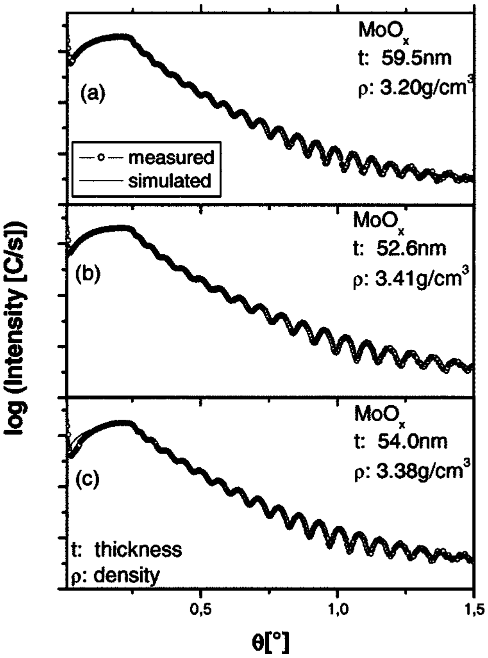

FIG. 1. XRR measurements of MoO_x film covered by a 2 nm Pt catalyst layer on a Si(100) substrate during the switching cycles. Measurements are first carried out with the film in ambient air in the gas cell (a), during the coloration process in 1% hydrogen in nitrogen (b), and after evacuating the gas cell and allowing in ambient air. Loading of hydrogen leads to a thickness decrease and a density increase which are not completely reversible.

III. RESULTS AND DISCUSSION

X-ray reflectance measurements and their simulation for an approximately 60 nm thick MoO_x film covered with a thin Pt catalyst at different stages of coloration and bleaching are shown in Figs. 1(a–c). Figure 1(a) displays the measured and simulated spectra for the system in the gas cell exposed to air prior to any exposure to hydrogen. The MoO_x film has a thickness of 59.5 nm and a density of 3.2 g/cm^3. This density is considerably lower than the bulk density of the crystalline α phase of MoO_3, which corresponds to about 4.71 g/cm^3. The low density is indicative for a porous structure of the amorphous film which is a prerequisite for switchable MoO_x films. The high pressure of 9 Pa employed during sputtering enabled the fabrication of the porous oxide films. Lower sputtering pressures lead to higher film densities and films that were considerably more difficult to switch. The thickness of the Pt layer was determined to be 2.5 nm, while a density of 5.66 g/cm^3 was measured. This density is much lower than the bulk density of Pt of 21 g/cm^3. This Pt layer is deposited at an Ar pressure of 0.8 Pa. Hence the low density of the Pt film is not a signature of a porous film but rather evidence for dispersed Pt clusters distributed on the MoO_x film surface.

Upon exposure to a mixture of 1% H_2 in N_2 with an overpressure of approximately 200 mbar the film thickness decreases by about 11% to 52.6 nm, while the density of the MoO_x film increases by 6.5% to 3.41 g/cm^3 [Fig. 1(b)]. These two changes are rather surprising. First of all, practically all other systems investigated so far[5,13] show an increase of film thickness upon exposure to hydrogen which is explained by the incorporation of hydrogen into the film. This incorporation typically leads to a decrease in density so that the product of density and film thickness is virtually constant. The latter finding is explained by the conservation of the mass of the film, where the rather small amount of incorporated hydrogen has a negligible effect on the entire mass. Upon subsequent evacuation of the cell, the film density and thickness do not return back to the initial values [Fig. 1(c)]. The film thickness is now 54 nm and a density of 3.38 g/cm^3 is reached. This implies that the switching process is not fully reversible. All changes noted above are neither observed in stoichiometric MoO_3 films nor for substoichiometric MoO_x films without the Pt catalyst. These observations imply that the switching process can only take place when atomic hydrogen is available and the MoO_x film contains sufficiently many oxygen vacancies before loading the film with hydrogen, which can be accomplished by producing substoichiometric films. These vacancies are important for the transport of oxygen atoms to the film or pore surface where oxygen atoms react to form H_2O. This leads to the formation of more vacancies which cause the subsequent film coloration. We note in passing that, as expected, the properties of the Pt catalyst do not show any significant change upon exposure to hydrogen and the subsequent evacuation of the gas cell.

To understand the behavior depicted in Fig. 1, we first compare our findings to the gasochromic switching of WO_x.[5] In this case perfect reversibility is observed upon multiple switching cycles both for the film transmittance and the mechanical stress. Furthermore, the observed thickness changes are below 1% for the switching of WO_x. This is in striking contrast to the behavior observed for MoO_x where thickness changes of more than 10% are observed for the first switching cycle. To fully comprehend this difference for two seemingly similar systems the change of optical transmission and the change of mechanical stresses have been monitored for MoO_x as well. Figure 2(a) shows changes in stress (full line) together with the transmitted intensity (dotted curve) during the coloration cycle of a 200 nm thin MoO_x film covered with 2 nm Pt catalyst layer. Vertical bars denote the different steps in the switching procedure. In a first step, in the left hand side of Fig. 2(a), the gas cell is evacuated before the hydrogen/nitrogen mixture is introduced. Evacuation leads to a high tensile stress of 170 MPa as the film tries to shrink [Fig. 2(a)]. We believe that this effect is caused by the emptying of microscopic pores in the film, which are now evacuated leading to a change of stress state. It should be noted that a similar behavior has been observed for WO_x films, where the amount of stress change upon evacuation scaled linearly with the film porosity.[5] This initial stress change, however, is not accompanied by a change in the transmitted intensity in agreement with our findings for WO_x films. During the first coloration cycle, which is performed by exposing the sample to a gas atmosphere consisting of 2% H_2/Ar at a total pressure of 0.6 bar, the stress initially becomes compressive but subsequently the stress change reverses direction to become slightly more tensile. Compared with the vacuum phase, a compressive stress change of approximately 50 MPa is observed after hydrogen exposure.

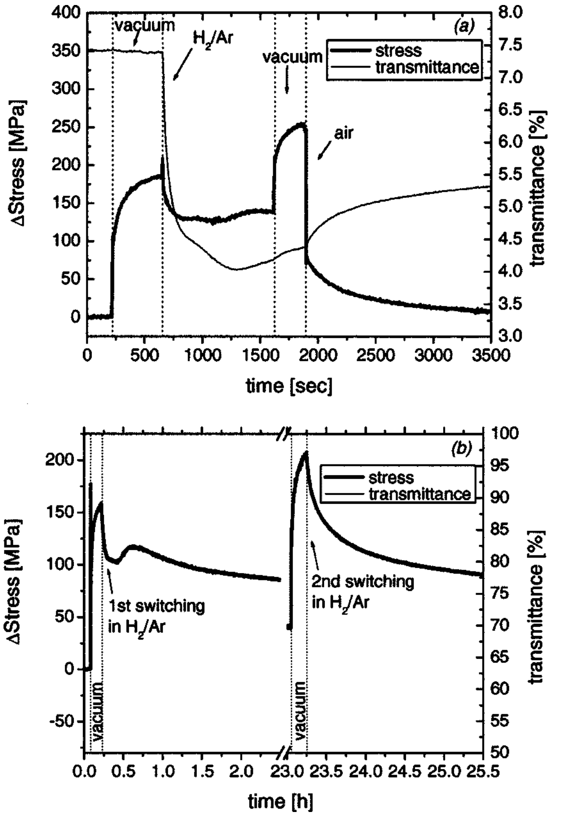

FIG. 2. Stress changes (full curve) and transmitted intensity (dotted curve) of a 200 nm MoO_x film coated with Pt on a 150 μm glass substrate during (a) short time switching cycles and (b) long time switching cycles. The transmitted intensity and stress changes were monitored during the vacuum phase, in 2% hydrogen in argon and back in air. A tensile stress is observed when air is sucked out of the film pores in the vacuum phase. The switching in hydrogen is first associated with a compressive stress change as the pores are filled with the hydrogen/argon mixture but later turns tensile. This change as well as the related increase of the transmitted intensity in the hydrogen phase can be explained by a structural transformation. In air a relaxation process in stress is observed as the film partly switches back. The long time measurement shows the changes in the transmitted intensity and stress in the hydrogen phase more clearly.

We first discuss the size of the stress change observed and then comment on the sign of the stress change. The irreversible change of the film thickness already implies that plastic processes proceed. This is in contrast to the behavior observed for WO_x. Further evidence for irreversible plastic behavior can be derived from the size of the stress change. Assuming an elastic volume change enables us to calculate the corresponding expected stress change. Using Hook's law we can calculate the change in mechanical stress for a purely elastic transition,

$$\Delta\sigma=\frac{E_f}{1-\upsilon_f}\varepsilon=\frac{E_f}{1-\upsilon_f}\frac{\Delta V}{3V_o}, \tag{2}$$

where $E_f/(1-\nu_f)$ is the biaxial modulus of the film, $\Delta V/V_o$ is the volume change of the phase considered, and ε is the change in film thickness upon switching.[14] ε is determined to be 0.11 from the observed change in film thickness for the first switching (the value of 0.11 for ε is even smaller than the difference between the bulk densities of α-MoO_x and β-MoO_x), while a value of 20 GPa is a reasonable estimate for the biaxial modulus. This leads to a calculated stress change of 2.2 GPa which is larger by a factor of approximately 40 than the observed stress change. This clearly demonstrates that the observed stress change must be related to a plastic deformation and hence an irreversible process in contrast to the behavior of WO_x where reversible elastic behavior was observed. To better understand the cause for the plastic, irreversible behavior observed for MoO_x, a second switching cycle, displayed in Fig. 2(b), was monitored as well, which reveals that the second switching cycle shows a monotonic decrease of transmission and stress with hydrogen exposure. The same holds for all further switching cycles (not shown). Hence only the first switching cycle shows an initial decrease of stress and transmission, followed by a subsequent increase of both quantities, which must be due to a process that is only observed upon the first switching in hydrogen. The irreversible process therefore already proceeds during the first exposure to hydrogen, while all further switching cycles show the characteristic features of reversible switching.

As already outlined in the Introduction, MoO_x has several metastable phases. This raises the question if irreversible behavior in the first cycle is caused by a structural transformation. Annealing is another approach to modify the film structure. We have followed the annealing of a MoO_x film with stress measurements, where the sample was heated to different temperatures as depicted in Fig. 3. Heating to 200 °C is not sufficient to induce a structural transformation as shown by the marginal stress change displayed in Fig. 3(a). Heating to 350 °C on the contrary shows clear evidence for irreversible changes of film properties. The tensile stress which starts to build up above 250 °C is clear evidence for film densification. Previous studies have shown that above 250 °C the transition from the β to the α phase proceeds.[1,15] This is confirmed by our x-ray diffraction experiments on the as-deposited samples, which show an amorphous structure of the porous film. Presumably, this amorphous structure is a mixture of nanocrystalline regions of α and β phase, which cannot be resolved by x-ray diffraction. This mixture then transforms to a multicrystalline state of α-MoO_3 after annealing above 250 °C. This α phase has a higher density than the β phase. The α phase involves distorted MoO_3 octahedra with a considerable amount of edge sharing.[11,16] The β phase on the other hand is based on distorted MoO_3 octahedra with a smaller amount of edge sharing. This explains why the films with α phase have the higher density. In addition, the α phase has a higher transmission than the β phase.[1,15]

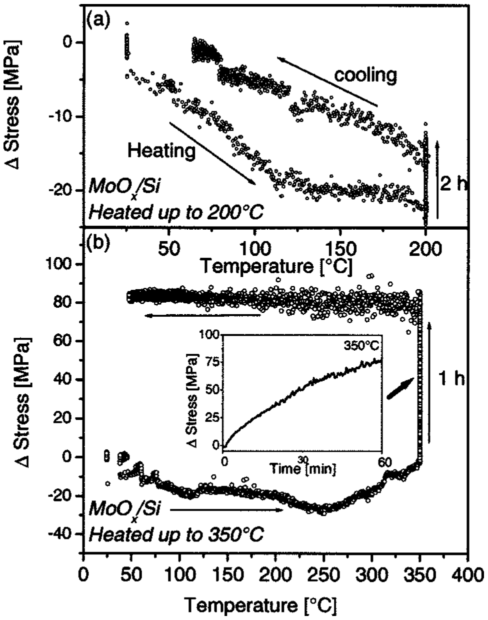

FIG. 3. Stress changes of 200 nm MoO_x film as a function of annealing temperature up to (a) 200 °C and (b) 350 °C and as a function of time (inset). Annealing at 200 °C does not lead to significant changes in stress and the film merely relaxes back upon subsequent cooling. At higher temperatures significant tensile stress arises, which is indicative of densification. This stress change is attributed to a structural change. In the inset, the change in stress as a function of annealing time at 350 °C is shown.

We can use the information provided above to better understand the behavior of the MoO_x film upon hydrogen exposure as already depicted in Fig. 1. When substoichiometric MoO_x is deposited, amorphous films are formed. Despite the fact that the present films are amorphous, as evidenced by the absence of diffraction peaks in the x-ray diffraction pattern, one may assume that the short range order observed in crystalline materials is maintained. This will give rise to a mixture of phases with corner and edge sharing octahedra, i.e., the so-called α and β phases, respectively. In the first hydrogen phase, when the stress changes from compressive to tensile, a phase transformation from the metastable β to the α phase takes place, which reduces the film thickness and increases the film density (Fig. 1). This scenario can also explain why the colored film becomes more transparent upon continued exposure to hydrogen, since the α phase is more transparent.[1,16,17] In Fig. 2 therefore, the increase in transmittance in the hydrogen phase points also to a phase transformation to the more transparent α phase. In the second hydrogen phase, the change in stress from tensile to compressive is not observed, nor the reduced transmittance in the hydrogen phase (Fig. 2), an indication that the change from β to α phase is not reversible and that the denser α phase is more difficult to color as evidenced by switching a film annealed above the phase transformation temperature (Fig. 4).

Hence subsequent coloration only affects the remaining film fraction with β phase. This phase, which closely resembles the structural arrangement observed in gasochromic

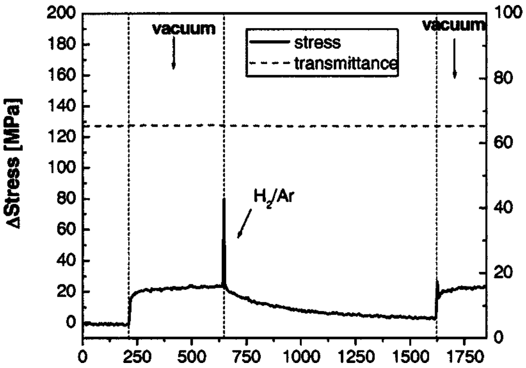

FIG. 4. Stress change (solid line) and transmitted intensity (dotted curve) upon exposure to different gas environments for a 200 nm MoO_x film after annealing at 350 °C. No significant changes in the transmitted intensity and stress are observed, indicating that the annealed films do not switch.

WO_x is either switching due the formation of color centers created by hydrogen incorporation into the film or by oxygen removal from the film, which causes water formation at the film pores and an increasing concentration of vacancies in the films. There is still considerable controversy which microscopic model is applicable for WO_x.[13,18–20] While our data do not enable us to make a decision about which model for the coloration of MoO_x is better suited to explain all data, the model which includes oxygen removal from the film and subsequent H_2O formation can both explain why upon switching the product of film density and thickness no longer remains constant as revealed in Fig. 1 and why water formation accompanies gasochromic switching. However, at present our data are insufficient to completely rule out hydrogen incorporation into the film as the atomic switching mechanism.[21]

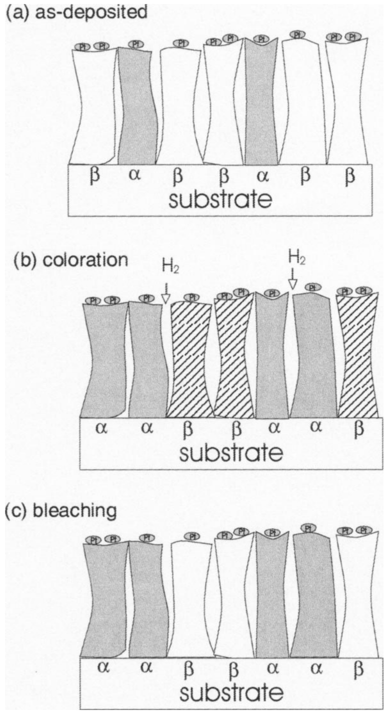

FIG. 5. A schematic side view of (a) the as-deposited MoO_x film having a mixed β and α phase and a Pt catalyst layer. Upon exposure to the hydrogen gas mixture, hydrogen is decomposed at the surface, the β phase is colored, and some of this phase is transformed to into the α-phase. (b) During the bleaching in air the β phase reverses back to the original transparent state while the fraction with the α phase remains unaffected.

IV. CONCLUSIONS

Substoichiometric MoO_x thin films were prepared by dc magnetron sputtering. *In situ* changes in stress and x-ray reflectance were observed during the switching cycles. During the first switching cycle there is a partial phase transformation from the β to the α phase as evidenced from a tensile stress and higher density. This also explains the higher transmitted intensity observed. The pure α phase obtained after annealing does not switch, presumably since the film is too compact to enable switching. The β phase, on the contrary, is responsible for the observed reversible switching and behaves like WO_x where both the transmittance and stress change are indicative for reversible and elastic behavior.[5] Figure 5 summarizes schematically the observed behavior and the assumed film morphology during the whole process.

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