Photoactive periodic media

Tahar Ben-Messaoud, Jason Riordon, Alexandre Melanson, P. V. Ashrit, and Alain Haché[a)]

Department of Physics and Astronomy, Thin Films and Photonics Research Group, Université de Moncton, Moncton, NB E1A 3E9, Canada

Photoactive (photochromic) multilayers of MoO_3/SiO_2 are studied optically before and after UV excitation. Enhancement in photochromic activity is observed over a wide spectrum and in particular near the photonic band edges where optical changes are up to 25 times greater than in similarly prepared bulk, nonperiodic samples. Applications to light-sensitive devices are discussed. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3095478]

Transition-metal oxides such as molybdenum oxide (MoO_3) and tungsten oxide (WO_3) exhibit photochromic (PC) coloration under UV excitation.[1–4] The process is based on electron trapping at oxygen vacancies and the formation of color centers.[5] These light-sensitive materials have enabled the development of smart windows,[6] electrochromic display devices,[7,8] and high-density memory.[9] The insertion of metallic layers such as Au or Pt (Refs. 10 and 11) or semiconductor layers such as CdS (Refs. 12 and 13) enhances these effects even further. With metals, coloration is aided by the Schottky barrier at the metal semiconductor which favors long electron-hole pair lifetimes; with CdS, the semiconductor was found to facilitate electron injection into oxygen vacancies at color centers. Work on WO_3 has yielded similar results.[14,15]

In this letter, we report PC enhancement by control of the material properties at the photonic level. By stratifying PC material to the scale of visible wavelength, we show that UV-induced optical changes are greater for multilayered structures than for bulk material of equal thickness. Whereas previous work has dealt with enhancements at the material level, here we examine the collective effect of many layers, effectively studying transition metal oxides in the context of a one dimensional photonic crystal. Optical periodic media are known to produce stop bands and field-enhancement effects.[16] As a result, their optical properties near the photonic stop band are particularly sensitive to local changes in absorption and refractive index, both of which are affected by photochromism. To examine the interplay between the photonic band and the PC effect, we studied multilayers of SiO_2 with MoO_3 as well as with WO_3.

MoO_3 is a wide band gap ($E_g \approx 3.2$ eV) (Refs. 17 and 18) n-type semiconductor that is photoactive under UV excitation. The process is conventionally explained as follows:[19,20] holes from photogenerated electron-hole pairs react with surface-adsorbed species such as H_2O, causing the formation of protons. Through the double insertion of these freed electrons and the protons blue-colored hydrogen molybdenum bronze or H_xMoO_3 is formed.

Reactive magnetron sputtering was used to deposit thin films of MoO_3 and SiO_2 onto glass substrates. MoO_3 layers were fabricated from a circular (3 in. diameter) MoO_3 target at 150 W, an O_2:Ar pressure ratio of 1:7.14, and a deposition rate of 15 nm/min; SiO_2 layers were fabricated from a p-doped circular (3 in. diameter) Si target at 440 W, an O_2:Ar pressure ratio of 1:8.33, and a deposition rate of 3 nm/min. Pressure was maintained constant at 5 mT throughout deposition. Several samples were grown at once so vacuum was breached every five or ten pairs of layers. The samples therefore contain either 5, 10, or 20 pairs of layers and form quarter-wave stacks with a photonic stop band near 650 nm. Although similar results, as reported here, were obtained in structures containing more than 20 pairs of layers, they were deemed too diffuse and not uniform enough to be used in this study. Atomic force micrographs revealed all films to be uniform on a scale of $\geq$100 nm and Raman spectroscopy confirmed the amorphous nature of MoO_3.

The PC response of multilayers was measured using a standard pump-probe setup. Both the probe and pump beams illuminated the sample over a spot size of 3 mm at ~5° angle relative to normal incidence. A spectrally filtered high-pressure mercury-xenon lamp provided a UV pump beam with a spectrum centered at 380 nm and with a 50 nm bandwidth. Irradiance at the sample surface was measured to be 20 mW/cm². After 1 h of UV exposure, films acquired a dark bluish tint from their initial transparent yellowish color. A halogen-deuterium white light source was used as a probe beam and was analyzed spectrally in reflection and transmission.

Light-induced coloring is accompanied by changes in optical transmittance T and reflectance R that can be quantified with relative measurements $\Delta T/T = (T_a - T_b)/T_b$ and $\Delta R/R = (R_a - R_b)/R_b$. Here indices b and a refer to samples before and after excitation, respectively. In order to measure the role of the photonic stop band on PC optical changes, measurements were made on multilayers as well as on reference samples containing the same amount of MoO_3, prepared under the same conditions, but in the form of a single layer only. This way, it is possible to single out the effect of stratification on the PC response.

The photonic band structure of MoO_3/SiO_2 multilayers before and after UV exposure is shown in Fig. 1. With a refractive index contrast of $MoO_3/SiO_2 = 2.1/1.5$, a deep stop band appears between 625 and 700 nm. After 1 h of UV excitation (fluence of 450 J/cm²), the change in transmittance is measured. The relative changes in transmittance and reflectance are plotted in Fig. 2. Optical changes also increase with the number of layers with sharp features appear-

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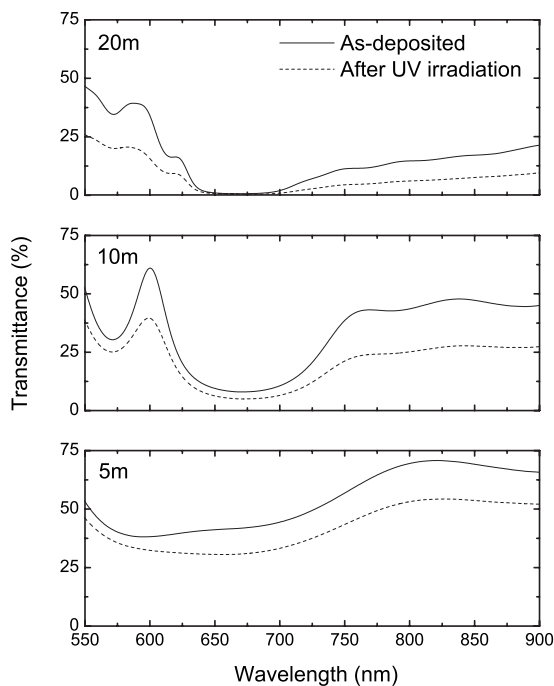
FIG. 1. Transmittance spectra of MoO_3/SiO_2 multilayers before and after the films were irradiated with UV light for 1 h. Samples have 5, 10, and 20 pairs of layers (5m, 10m, and 20m).

FIG. 3. Calculated relative change in transmittance assuming the same increase in absorption ($\Delta\kappa = 0.04$) in all samples.

ing on the lower edge of the photonic band. Using samples with thicker layers revealed that this peak shifts along with the position of the stop band: it is solely due to the periodic nature of the structure, not a material effect per se. This bandgap-induced effect can be attributed to a slight shift in refraction index during coloration.

Based on the results on the sample with five pairs of layers, it is possible to calculate the local change in refractive index (real and imaginary) and thus make theoretical predictions for samples with 10 and 20 pairs. Figure 3 shows the
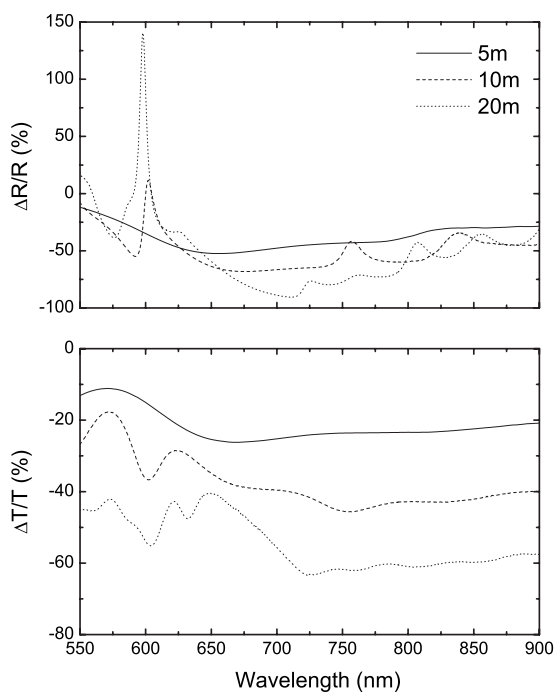

FIG. 2. Relative changes in transmittance and reflectance in MoO_3/SiO_2 multilayers exposed to UV light for 1 h.

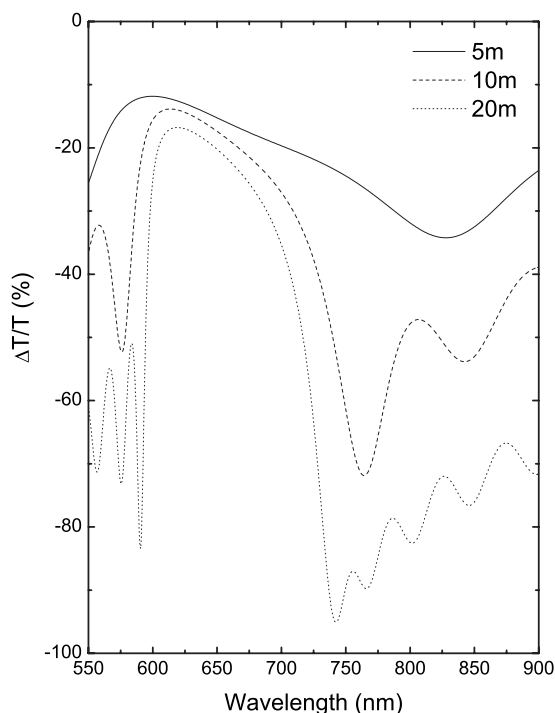calculated relative optical changes and assumes the same coloration in the thicker samples as in the five pairs. Because calculations follow the same general trend as the experiment, it suggests that coloration is uniform throughout all samples. This could appear surprising at first since PC coloration depends on the availability of structural water, which might change during deposition. However, since the vacuum is broken periodically during fabrication, it is likely that layers at various depths are exposed to similar levels of ambient water. During subsequent UV irradiation and optical analysis, MoO_3 layers are shielded from atmospheric humidity due to neighboring SiO_2 layers. Fabrication conditions are thus of great importance.

Measurements on single bulk layers of MoO_3 are presented in Fig. 4. Here, samples 5s, 10s, and 20s have the same amount of MoO_3 as in multilayer samples 5m, 10m, and 20m and were UV irradiated for 1 h under the same conditions. Results show a clear dependence on thickness with thinner films exhibiting more PC sensitivity. This can be attributed to proportionally better H_2O adsorption into thinner films: the role of H_2O adsorption at the surface trumps that of structural H_2O for single MoO_3 layers. More importantly, comparing Figs. 2 and 4, $\Delta T/T$ and $\Delta R/R$ are up to 25 times larger in multilayers than in their single layer counterparts near the photonic stop band and up to six times larger elsewhere. The fact that multilayers show enhancement over the whole spectrum and not just near the stop band indicates that the PC effect may be aided by contact with SiO_2. As mentioned earlier, such interfacial effects have been observed with other materials. We performed PC recovery (relaxation) measurements on all samples and found a half-life time of ~11 days and approximately the same in both stratified and nonstratified samples (measurements were made at 900 nm away from photonic band gap effects). However, multilayers initially exhibit a much faster (and partial) recovery time of ~1 day, something not observed in a single layer.
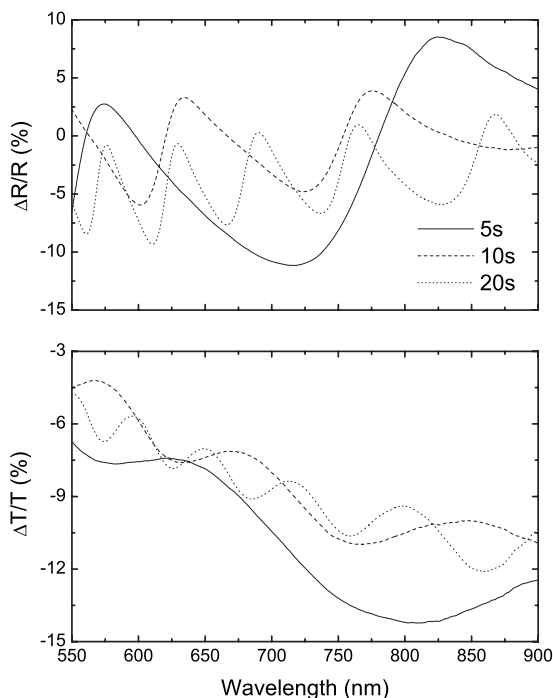
FIG. 4. Relative change in transmittance and reflectance for a single layer of MoO_3 after 1 h of UV exposure. Film thicknesses are 415 nm (5s), 830 nm (10s), and 1660 nm (20s).

This suggests that an interface mechanism is involved in coloration. Further tests were done on single layers of MoO_3 with and without a layer of SiO_2 on top. Measurements are presented in Fig. 5 and show comparable optical changes in both cases, and this is in spite of the fact that the SiO_2-capped layer has no access to surface-absorbed water
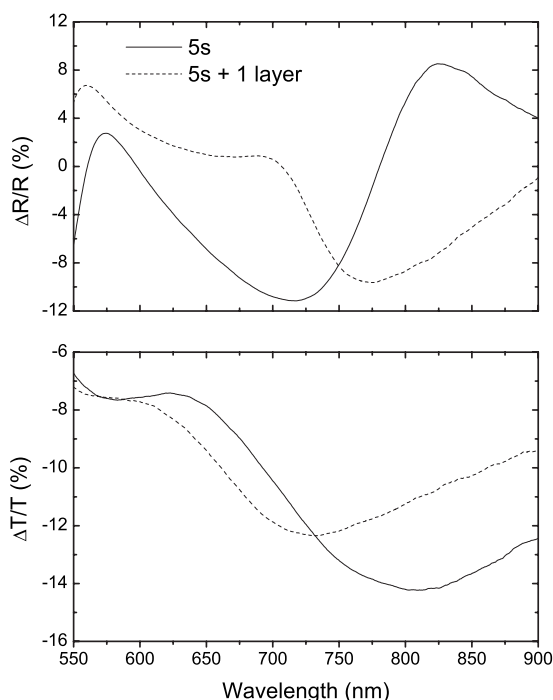

FIG. 5. Transmittance and reflectance relative change for bulk MoO_3 with and without a single layer of SiO_2 for 1 h UV irradiation.

during coloration. It appears that contact with SiO_2 is itself an enhancement factor.

A set of PC WO_3/SiO_2 multilayers (9 and 19 layers) were obtained from commercial sources (Dominar Inc., USA) and tested under identical conditions for comparison purposes. As with MoO_3 multilayers, relative optical changes increase with the number of layers and are especially pronounced at the edges of the photonic stop band.

In conclusion, by using periodic structures of various thicknesses, we have shown that the progressive introduction of a photonic stop band in a PC material heightens its effects. After UV excitation, optical changes in both transmission and reflection are more pronounced in a material that is periodic with sharper features appearing at the band edges. Near the stop band of MoO_3 periodic structures, relative changes in reflectance are up to 25 times higher than in the same material in bulk form. In addition, the multilayer structure itself leads to heightened effects well outside the stop band due to the MoO_3/SiO_2 interfaces. Similar enhancements were observed in WO_3/SiO_2 multilayers.

These findings suggest possible applications for PC materials in the form of photonic crystals. In the past decade, optical control of photonic crystals has been a domain of intense activity, but it typically relies on nonlinear optics (typically χ^2 and χ^3 effects) requiring strong laser beams. With photochromic materials, similar control and switching applications may be possible with ultralow levels of light intensity.

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