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Hard Coatings for Optically Bistable Interference Filters

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Abstract. We have fabricated optically bistable interference filters from layers of TiO_2 and SiO_2, vapour deposited on glass substrates. An experimental comparison with the more conventional ZnSe filters is presented. Our devices are superior in durability and switching contrast, equal in switching threshold, and slower in switching time.

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In view of their potential applications, there is an increasing interest in bistable interference filters. Detailed studies of filters have been made of a spacer of ZnSe, sandwiched between mirrors consisting of stacks with a structure $(ZnS/ThF_4)^4$ [1–6]. These structures are usually vapour deposited on a glass substrate. Unfortunately, the stability of optical properties is only marginal unless special measures are taken [2, 6]. Prominent among these is the replacement of the vapour deposition process with molecular beam deposition [6, 7]. It must be pointed out, however, that this does not change the fact that ZnSe films are so-called "soft coatings", a name alluding to their low mechanical and chemical durability.

We thus explored whether "hard coating" materials could be found that also exhibit thermal bistability with improved long term behaviour, with the additional benefit of vastly improved mechanical and chemical durability. We decided to produce filters consisting of a spacer of titanium oxide of thickness $k\lambda_c$, sandwiched between mirrors of alternating $\lambda_c/4$ layers characterized through $(TiO_2/SiO_2)^m$. The design wavelength λ_c was chosen as 515 nm in order to allow experiments with the 514.5 nm Ar^+ laser line. These structures were vapour deposited on BK 7 substrates in an in-house facility. We will demonstrate that our devices compare very favourably with ZnSe filters in most respects, with the notable exception of the switching time.

In a series of experiments we determined the best combination of spacer thickness and absorption and mirror reflectivities through variations of k, α (see below), and m. The first design goal in the optimization process was a low switching threshold; for this it is helpful if the mirror reflectivities are made very high. In practical terms, there is a fabrication limit at $m=4$, for which $R_f \approx 94\%$ and $R_b \approx 90\%$. For higher m, i.e. in even thicker stacks, several problems begin to become noticeable: the effective plane of reflection becomes increasingly ill-defined so that there are, in effect, several subcavities [5]; we indeed see extra peaks appear in the Airy function for $m>4$. Also, one begins to compromise the perfect durability which was our main objective. On the other hand, more layers do not necessarily improve the finesse because imperfections and the absorption in the mirrors will eventually become noticeable [5], and even an increased finesse will not necessarily improve the threshold while it renders fabrication tolerances in λ_c more critical.

With the mirror reflectivities fixed, one can obtain the optimum optical thickness of the spacer from [5]

$$\alpha D = (2 - R_f - R_b)/4$$

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** Present address: Institut für Quantenelektronik, Eidgenössische Technische Hochschule (ETH), CH-8093 Zürich, Switzerland which gives, in our case, $\alpha D = 0.04$. The effective absorption coefficient α of titanium oxide films can be controlled over a range from roughly $10\,\mathrm{cm}^{-1}$ to $2000\,\mathrm{cm}^{-1}$ (at 515 nm) by adjustment of the residual oxygen partial pressure during the vapour deposition because that controls the relative concentrations of TiO, Ti_2O_3, and TiO_2.

This gives us an additional design choice. We decided that α should be as low as possible, with a correspondingly larger D because that minimizes the thermal stress in the material. There are fabrication limits to the thickness of the spacer at about $k = 4$. It turns out that with this value, we get close to the above criterion when we minimize α by using an oxygen partial pressure $p(O_2) \approx 4 \times 10^{-4}$ mbar during deposition so that almost all titanium oxide is formed as TiO_2. This has the additional benefit that of all titanium oxides, TiO_2 is the most stable, and its properties are known well [8]. We arrive at a measured $\alpha D = 0.03$, with an estimated error of 20%. Filters of this design indeed worked best among the several alternatives we tried, and we will concentrate on these.

For comparison, we also fabricated ZnSe filters. We used the same kind of substrates and the same k and m [the mirrors were given the structure $(ZnS/LaF_3)^4$]. This resulted in a spacer absorption of approximately $\alpha D = 0.072$. Generally, we find that indeed the optical properties, like switching threshold, time, contrast, etc., agree well with numbers reported in the literature. To be more specific, let us discuss our experimental results in detail, with a view to a comparison of the two filter materials.

One specific advantage of TiO_2 is that, at least for bulk material, its absorption coefficient is nearly constant over a very wide spectral range from 500 nm to beyond 4 μm [9, 10]; thus the use of various light sources, including diode lasers, should be possible. The light source in our experiments, however, was an Ar^+ laser emitting the 514.5 nm line. The filters were tuned by tilting them with respect to the beam. At suitable angles, the typical hysteresis cycles of bistability were observed (see Fig. 1a and b). The upswitching threshold for TiO_2 was typically 20 mW for a spot size of $w = 50$ μm ($1/e^2$ intensity radius), corresponding to an intensity averaged over the spot of $220\,\mathrm{Wcm}^{-2}$. This value is virtually the same as for our ZnSe filters as can be seen from Fig. 2a and 2b; very similar values are reported in the literature [1, 3]. We also verified that for both materials, there is a linear relation between w and threshold for $w > 10$ μm, as obtained in [3].

Achieving the same threshold as for ZnSe is better than anticipated, because the absorption in ZnSe is about three to four times higher. Given the same substrate properties and similar mirror reflectivities, one must conclude that in TiO_2, the index change required for switching is reached at a lower absorbed energy and thus with a lesser temperature rise.

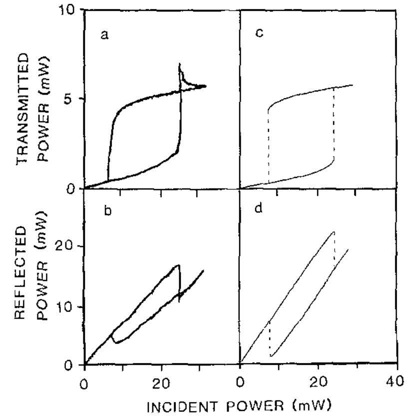

Fig. 1. Hysteresis loops for TiO_2 interference filters, in transmission (top) and reflection (bottom): observed (left), calculated (right). The spot size was 50 μm, and an absorption coefficient of $300\,\mathrm{cm}^{-1}$ for the TiO_2 spacer was assumed in the calculations

In order to examine this conclusion in more detail, we solved the heat diffusion equation for each material. Since the coatings are much thinner than the transverse spot diameter, the heat transport is provided almost exclusively by the substrate. Therefore the problem can be simplified by taking the thermal conductivities of the film equal to that of the substrate [3–5]. We assumed a semi-infinite body heated in the surface plane by a Gaussian profile thermal source, and solve numerically for the spot centre temperature. From the calculations we find that for reaching switching threshold the temperature has to rise by about 70 K in ZnSe. (Similar values were reported in [5, 6].) The model predicts that sapphire substrates with their (about ten times) higher thermal conductivities should yield correspondingly higher thresholds. This was indeed verified in an additional experiment on the ZnSe system. As expected, the model also gives a smaller temperature increase in the TiO_2 filters of only about 20 K. The uncertainties of both temperatures are estimated $\pm 20\%$, as for αD above.

We convinced ourselves that the index change for a given temperature change is indeed larger in the TiO_2 etalons. To this end, we mounted the filter on a heater block and performed a separate measurement of the index, obtained from the small signal peak reflection angle, as a function of temperature. This indicated a thermooptic coefficient of the TiO_2 spacer of $(1/n_0)dn/dT = -240 \times 10^{-6}\,\mathrm{K}^{-1}$, a value which is, besides of the opposite sign, indeed about three times higher than $(1/n_0)dn/dT = +90 \times 10^{-6}\,\mathrm{K}^{-1}$ for ZnSe [6]. Note, though, that a thermooptic coefficient that large is not expected from the bulk material with $(1/n_0)dn/dT = -14 \times 10^{-6}\,\mathrm{K}^{-1}$ [9]. It can also not be explained by an index change through thermal expansion given the respective coefficient for the bulk material, $(1/l_0)dl/dT = 9 \times 10^{-6}\,\mathrm{K}^{-1}$ [10]. In any case, however, we can be sure that the large thermooptic coefficient of the vapour deposited TiO_2 film reduces the temperature increase necessary in the switching process to about 20 K. Thus it is the key to the unexpectedly low threshold observed in our experiments. It also should be noted that, as a consequence, the thermal stress is reduced with respect to the ZnSe filters, and this may help to improve the long term stability.

An important quantity for a cascadability of devices is the switching contrast. We define the contrast as the ratio of the output intensities in both stable states taken at an input intensity in the middle of the hysteresis loop. Note that this tends to give smaller numbers than some other definitions, but we find this conservative method more realistic. One has to distinguish the contrast in transmission, c_t, and in reflection, c_r. For the mirror reflectivities used here, straightforward calculation shows an advantage for the contrast of the reflected beam for extremely low absorption in the filter, whereas for our αD values, the transmitted beam should have higher contrast. (Note that this is different when one mirror has 100% reflectivity [11].)

For TiO_2, we typically find contrasts c_t from 5 to 7 and c_r from 1.5 to 2 which compare favourably with our ZnSe values of c_t from 2 to 3 and c_r from 1.5 to 2. (These numbers depend on the detuning and thus vary with the angle of incidence). For ZnSe, similar values were reported in [1]. These numbers also agree well with our numerical analysis of the stationary heat diffusion problem. Figure 1c and d and 2c and d show examples of steady state hysteresis loops. For TiO_2 (Fig. 1) the shape of the experimental curves differs slightly from the calculated one. This can be attributed to the fact that, in the absence of forced cooling, the steady state is not quite reached during the experiment even at a scan rate of 0.01 Hz; thus a transient "overshoot" appears.

As for the long-term stability of the hysteresis cycles of the TiO_2 and ZnSe filters, we continuously ramped up and down the input power and monitored the width of the hysteresis. While for our TiO_2 devices the change in width was negligible even after 14 h (Fig. 3a), the hysteresis of the ZnSe devices narrowed rapidly and disappeared completely after 1–2 min (Fig. 3b). We then blocked the beam for intervals ranging from seconds to hours to check whether the hysteresis would reappear. There was no indication of a regeneration, though. So the stability is far from perfect [1, 2, 6], and the change is irreversible. The drift was attributed to moisture sorption in [2] and [6], with improvements being obtained by sealing the surface [2] or fabrication by molecular beam deposition [6, 7]. This latter technique reportedly improves the hysteresis stability of ZnSe filters up to 7 h but only at a fixed wavelength of 568 nm [7]. In contrast, our TiO_2 filters did not seem to degrade after even longer operation.

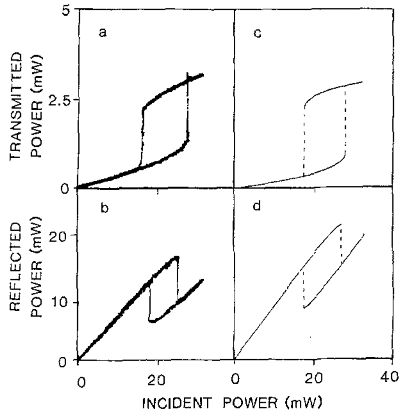

Fig. 2a, b. Hysteresis loops for ZnSe interferenc filters, in transmission (top) and reflection (bottom): observed (left), calculated (right). The spot size was 50 μm, and an absorption coefficient of 1200 cm^{-1} for the ZnSe spacer was assumed in the calculations. Even though **b** was measured immediately after **a**, the drift associated with the ZnSe filters gave rise to a noticeable change in hysteresis width

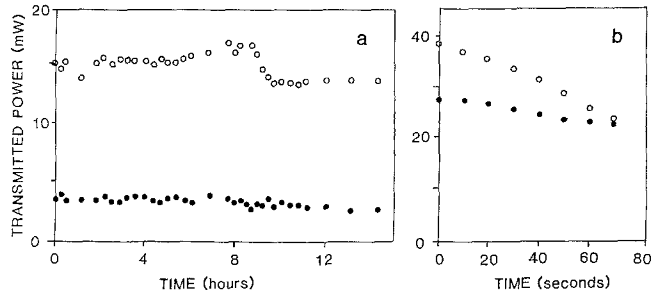

Fig. 3a, b. Upswitching thresholds (open circles) and downswitching thresholds (filled circles) as a function of time for TiO_2 **a** and ZnSe **b** filters. Note the different time scales. The ZnSe device was freshly fabricated while the TiO_2 device was 20 months old (see text)

We performed an even tougher test by letting the devices sit unattended in the shelf for an extended period of time. After 20 months, the longest period we tried to date, the ZnSe filters were totally destroyed by peeling off the substrates. (Note that filters with ThF_4 as low index material would be not quite as bad; ThF_4 is both toxic and radioactive, though.) In contrast, the TiO_2 filters still exhibited bistability if with reduced contrast. Heating the specimens up to 400 °C for about 15 min restored them so that the threshold intensity, contrast, etc. were virtually the same as measured

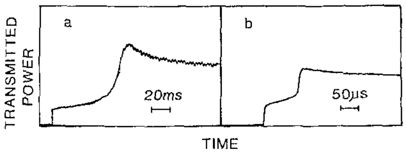

Fig. 4a, b. Response to a step of input power from 0 to a value P_{in} higher than the switching threshold P_{thr}. **a** TiO_2 filter ($P_{\text{in}}/P_{\text{thr}} = 1.2$), **b** ZnSe filter ($P_{\text{in}}/P_{\text{thr}} = 1.7$). Spot sizes were 50 µm

shortly after fabrication, that is, with no apparent degradation; they behaved just like new.

This demonstrates that the vapour deposited, unprotected TiO_2 films are superior in long-time stability to comparable ZnSe designs both during operation and during shelf life.

We now turn to a discussion of the switching time. One expects that switching times should be the same for both systems because in either case, the dynamics is expected to be governed by heat transport which, again, is governed by the substrate. The experiment shows, however, that the switching time is vastly different for the two materials. Only for ZnSe do our calculations of the time-dependent heat diffusion give a good agreement with experimental results; for TiO_2 they fail.

For a 50 µm spot radius, [4] reports a switching time for ZnSe of 400 µs at 1.5 times threshold power, consistent with our own experiments. Under the same conditions, our TiO_2 devices take 25 ms; they are thus nearly two orders of magnitude slower. Figure 4a and b illustrate the difference with examples of switching processes in the domain of critical slowing down.

This observation suggests that the mechanism for the index change in TiO_2 films is very different from that in ZnSe films. The unexpected thermo-optic coefficient points to the same conclusion. The mechanism will be treated separately in a forthcoming publication. Meanwhile, we find empirically that the hard TiO_2 coatings, which are superior in mechanical and chemical stability, beat comparable ZnSe devices in switching contrast and stability of thresholds, while they are equal in threshold power. Unfortunately they are very slow. However, they are still faster than the human eye so there may be applications in image processing, or in other cases where speed is not the prime demand.

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