

Shift-free narrowband filters for the UV-B region

Hein Uhlig, Uwe B. Schallenberg, Norbert Kaiser

Fraunhofer-Institute of Applied Optics and Precision Engineering, Department of Optical Coatings,
Schillerstr. 1, D-07745 Jena, F.R.G.

ABSTRACT

Monitoring of stratospherical ozone depletion by filter radiometers calls for narrowband filters with outstanding parameters. At filter wavelengths down to 300 nm narrow bandwidth, high peak transmittance together with high out-of-band blocking especially at longer wavelength are demanded. Furthermore, filters have to be completely free of wavelength shift caused by humidity. Conventional interference filters suffer from such shift because of the water sorption of the evaporated layers.

By using plasma ion assisted deposition (Advanced Plasma Source - APS, Leybold) of zirconia and silica layers we succeeded in manufacturing blocked two-cavity filters with full width at half maximum (FWHM) of 1.7 nm and peak transmittance of 17% at the center wavelength in the UV-B region. Outside the transmission band from UV to NIR (≥ 1000 nm) optical density is at least 6. There was no decrease in wavelength of such filters (without hermetisation) by changing relative humidity from 100% to 0%. Corresponding conventional filters shifted 4.5 nm under the same conditions. The filter performance achieved allows use for the development of sensitive and specific instrumentation for environmental, climate, and meteorological research.

1. INTRODUCTION

Progressive stratospheric ozone depletion increases solar UV-B (285 nm - 325 nm) irradiances on earth. Instrumental requirements for UV-B irradiance monitoring are spectroradiometers of high accuracy and filter instruments as control radiometers. The detection of future trends in ozone depletion requires more sensitive measurements, careful calibration and long time stability of the instruments¹⁻⁵.

A generalized radiometric configuration consists of entrance optics (diffuser or integrating sphere), monochromator (prism, grating or filter), detector, amplifier, and control unit. Filters can be much more advantageous if only a few fixed wavelengths have to be isolated from the spectrum, which is typical for control radiometers. Filters give much more energy throughput (ratios >100 are possible⁶) than prism or grating monochromators of the same spectral resolution. Other powerful arguments for favouring the use of filters are size, weight, costs, and mechanical stability. Especially, where volume and weight are at a premium, in air- and space-borne instruments for example, they are probably favourable.

Figure 1 shows solar spectral irradiance vs. wavelength at the earth's surface⁷. Solar radiation in the UV-B region plays a dominant role in the photochemistry of the atmosphere. The steep absorption edge of solar radiation in the UV-B region is caused by ozone. The gradient is (15 - 20) $\mu\text{W}/\text{cm}^2$ per each nm of solar irradiance⁸.

A minimal 0.1 nm spectral shift of a UV-B filter with FWHM of 1 nm along the UV-B edge would cause a change in intensity of about 5%⁷. Consequently, FWHM of the filters has to be as narrow as 2 nm or less and the edges of their transmission bands must be as steep as possible. Because of the low solar radiation irradiance at 300nm (logarithmic scale in Fig. 1) and losses of two orders of magnitude due to the diffusor, filters with the highest possible transmittances are required. On the other side, solar irradiance at longer wavelengths is two to three magnitudes higher in IR than in UV. Consequently, blocking of the filters in this spectral region must be virtually complete.

A primary requirement of global trend monitoring of ozone depletion is radiometric accuracy. A long-term stability of calibrations of better than 2% are recommended. Long-term stability demands the elimination of the well known humidity shift⁹ of the optical thickness of the conventionally deposited layers. Ion assisted deposition is one method to increase coating's packing density and to reduce moisture influences¹⁰. On the other hand, ion assisted deposition tends to raise optical losses in comparison to the layers evaporated by classical vapour deposition¹¹. The problem of ion assisted induced optical losses is most serious in the UV. From the point of view of interference optics the need for a highly transmissive interference filter with small FWHM corresponds to the demand for low optical losses of the interference layers.

The main focus of that paper is to present results about shift-free ultra-narrow band filter configurations with enhanced peak transmittance for the UV-B.

2. SPECIAL FILTER DESIGN

First attempts to deposit dense layers of ZrO_2 and SiO_2 by ion assisted deposition (IAD with an END-Hall ion source) failed. The filter was not free from humidity shift. In order to avoid this inherent problem we searched for a new Fabry-Perot filter design, which prevents humidity shift without using IAD. It is known, that MgF_2 ¹² and Al_2O_3 ¹³ can form layers, which are almost completely free from humidity shift, if they are conventionally evaporated at 300° C substrate temperature.

Figure 2 shows the design of a Fabry-Perot filter which takes advantage of this fact. The central layers consist of MgF_2 and Al_2O_3 exclusively. Humidity sensitive layers of ZrO_2 are used only in the outer layers of the filter where changes in optical thickness have little effect on filter wavelength.

Figure 3 shows the measured shift of such a filter in comparison to a corresponding conventional filter consisting of ZrO_2 and SiO_2 ¹⁵. All layer stacks were measured after storage in air first at 20° C and second at 120° C, respectively. Heating caused both the negative humidity shift as a consequence of water desorption and a positive thermal shift due to increase of the layer thicknesses and the refractive indices of the layer materials. The wavelength of the $\text{ZrO}_2/\text{SiO}_2$ -filter decreased 3.7 nm because humidity shift was much stronger than thermal shift. On the other hand the wavelength of the filter made of MgF_2 and Al_2O_3 as central layers and $\text{ZrO}_2/\text{MgF}_2$ as outer layers shifted 0.35 nm to higher wavelengths due to the fact, that the

positive thermal shift exceeded the amount of the negative humidity shift. After measuring the thermal shifts separately we estimated the water-desorption shift of the filter made of Al_2O_3 , MgF_2 and ZrO_2 to be $< 1/20$ of the water-desorption shift of the $\text{ZrO}_2/\text{SiO}_2$ -filter.

We made a blocked UV-B filter consisting of two low-shifting Fabry-Perot filters, dielectric blocking filters and colored glass. The performance of the filter (Fig. 4) has been measured with high spectral resolution near 300 nm and the optical density of the same filter with low spectral resolution from 200 nm to 900 nm. The optical density is >5 , the transmittance at 301 nm is 24% and the FWHM is as small as 1 nm. During one year of observation the wavelength shift was < 0.1 nm. Fig. 5 shows the construction of the complete filter.

3. PLASMA ION ASSISTED DEPOSITION (PIAD)

Unfortunately, low shift filters corresponding to the special design described in the previous chapter can only be made for short wavelengths. At longer wavelengths or when using multi-cavity designs, filters fail because of the large mechanical stress of MgF_2 . Therefore, we used PIAD (APS 904, Leybold Systems GmbH¹⁴) technique for preventing moisture shifts. There is a high power Advanced Plasma Source (APS) at the bottom of the coating chamber. During evaporation of the layers by an electron gun accelerated plasma ions and other plasma particles strike on the substrate surface and densify the growing layers. The plasma gets a positive self bias voltage relative to the chamber walls and the substrate holder. The higher this bias voltage the higher is the acceleration of the plasma ions. So the bias voltage is an essential parameter of PIAD. Another essential parameter is the deposition rate.

For our first filters deposited with APS (APS filters) consisting of ZrO_2 and SiO_2 we chose the following parameters: bias voltage ZrO_2 -135 V, SiO_2 - 130 V; evaporation rate ZrO_2 - 0.4 nm/s, SiO_2 - 1.4 nm/s. First during short-time observation these filters seemed to be free from humidity shift. Venting or heating did not cause positive or negative shifts of the filter wavelength as opposed to conventionally evaporated filters. But after some weeks of storage in air under suitable monochromatic illumination we observed moisture penetration patches on the area of the filters as shown in figure 6.

Such patches have been already observed in zinc sulfide and cryolite multilayer filters⁹. They appear in "semidense" layer stacks, where one of the two alternating substances does not absorb water but the second does. The watertight layers act as a barrier. Unfortunately, this kind of hermetisation works only for short periods - weeks are typical. There are always defects such as dust particles or nodules on the coated surface where the watertight layers are leaking. Fig. 7 illustrates the principle of water penetration into a "semidense" layer stack.

Since lateral diffusion distances are very long in comparison to layer thickness, water sorption is a very slow process. In the case of our first filters we found that ZrO_2 layers did not absorb water but SiO_2 did. We verified this facts by measuring the 2.9 μm -transmission of single layers and by measuring the shifts of transmittance of single layers. Because the wavelength at the patches was about 2.5% larger than outside, we estimated, that our APS-silica layers absorbed at least as much water as SiO_2 layers which were evaporated conventionally on heated substrates.

The filter stack was coated over with an opaque aluminium layer and the surface profile imaged by white-light interferometry. The result is shown in figure 8. There are hillocks on the surface of the filter stack. Positions and extensions of these hillocks correspond to the moisture patches which have been observed before Al-overcoating. It is assumed that penetrating water not only occupies existing voids in the volume of the silica layers but additionally causes an increase (water-swelling) of layer thickness.

Increasing the APS-bias voltage to 180 V (the given upper limit) and decreasing the evaporation rate to 0.5 nm/s it was possible to deposit completely dense SiO₂ layers. It was not possible to detect water penetration patches on filters which were stored for months without any hermetisation. By using this high power APS-technique, 2-cavity narrowband UV-B-filters, blocked dielectrically and with colored glasses were produced. The narrowband filter consist of APS-deposited ZrO₂ and SiO₂ layers completely free from humidity shift. Figure 9 shows transmittance in the UV-B and optical density from 200 nm to 850 nm. At the center wavelength of 306.3 nm transmittance is 17.2 % and FWHM 1.8 nm. The optical density outside the transmission pass is > 6 .

In comparison to the conventional non-APS-filters, as shown in Figure 5, the transmittance of the APS-filter is smaller and the FWHM is larger. This is because of the increase of optical losses in the layers as a consequence of the application of APS technique. On the other hand the general blocking and the steepness of the edges of the bandpass of the APS-Filter are superior and the FWHM is small enough for many applications.

4. CONCLUSIONS

The APS technique makes possible the production of very low loss and dense ZrO₂/SiO₂ Fabry-Perot narrowband filter for the UV-B spectral region. These filters are completely insensitive against moisture penetration and therefore shift-free at constant temperature. They can be used for a new generation of filter radiometers for monitoring ozone depletion.

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6. REFERENCES

1. B. L. MacKenzie, P. V. Johnston, M. Rotkamp, A. Bitta, and J. D. Hamlin, "Solar ultraviolet spectroradiometry in New Zealand: Instrumentation and sample results from 1990", *Applied Optics*, Vol.31, 6501-6509, 1992
2. J. Staehelin, H. Schill, B. Höger, P. Viatte, G. Levrat, A. Gamma, "Total ozone observation by sun photometry at Artos, Switzerland"; *Optical Engineering*, Vol. 34, 1977-1986, 1995
3. S. R. Wilson, B. W. Forgan, In situ calibration technique for UV spectral radiometers", *Applied Optics*, Vol. 34, 5475-5484, 1995
4. G. Seckmeyer, S. Thiel, M. Blumthaler, P. Fabian, S. Gerber, A. Gugg-Helminger, D. -P. Häder, M. Huber, C. Kettner, U. Köhler, P. Köpke, H. Maier, J. Schäfer, P. Suppan, E. Tamm, and E. Thomalla, "Intercomparison of spectral-UV-radiation measurement systems", *Applied Optics*, vol. 33, 7805-7812, 1994
5. N. Kaiser, H. Uhlig, "Narrowband interference filter for use in UV-B spectral region", *Proc.SPIE*, vol.1782, p.245, 1992
6. H.A. Macleod, *Thin film optical filters*, Adam Hilger Ltd, Bristol, 1986
7. J. Metzdorf, A. Sperling, V. Bentlage, H.-C. Holstenberg, "Trendmessungen der bodennahen solaren UV-B-Strahlung: Eine Herausforderung an die Spektroradiometrie", *Kleinheubacher Berichte*, Bd. 38 (1995)
8. Landoldt Börnstein, New series Group V, vol. 4, Metrology, Subvolume b, *Physical and Chemical Properties of the Air*, Ed. G. Fischer, Springer-Verlag Berlin, Heidelberg 1988; Chapter 6; Bakan, Hinzpeter, p. 112
9. H.A. Macleod, " Influence of microstructure on the properties of optical thin films; *Vide les couches minces* 39, vol.223, p.347-51, 1984
10. U.J. Gibson, "Ion Beam Processing of Optical Thin Films," *Physics of Thin Films*, vol.13, p.109, 1987
11. A. Starke, H. Schink, J. Kolbe, J. Ebert, "Laser induced damage thresholds and optical constants of ionplated and ion beam sputtered Al_2O_3 and HfO_2 coatings for the ultraviolet," *Proc. SPIE*, vol.1270, p.299, 1990
12. H.K. Pulker, *Coatings on Glass*, Elsevier, Amsterdam, Oxford, New York, Tokyo, 1984
13. I. Emmer, Z. Hajek, P. Repa, "Surface adsorption of water vapour on hydrated layers of Al_2O_3 ", *Surface Science* vol. 162, p.303-309, 1985
14. A. Zöller, R. Götzelmann, K. Matl, "Shift free interference coatings deposited with plasma ion assisted deposition", *Proc. of: Optical Interference Coatings, Topical Meeting*, Tucson, Arizona, USA, June 5-9, 1995
15. Interferenzbandpaßfilter, applied for *German Patent*, P 44 44 786.8-51

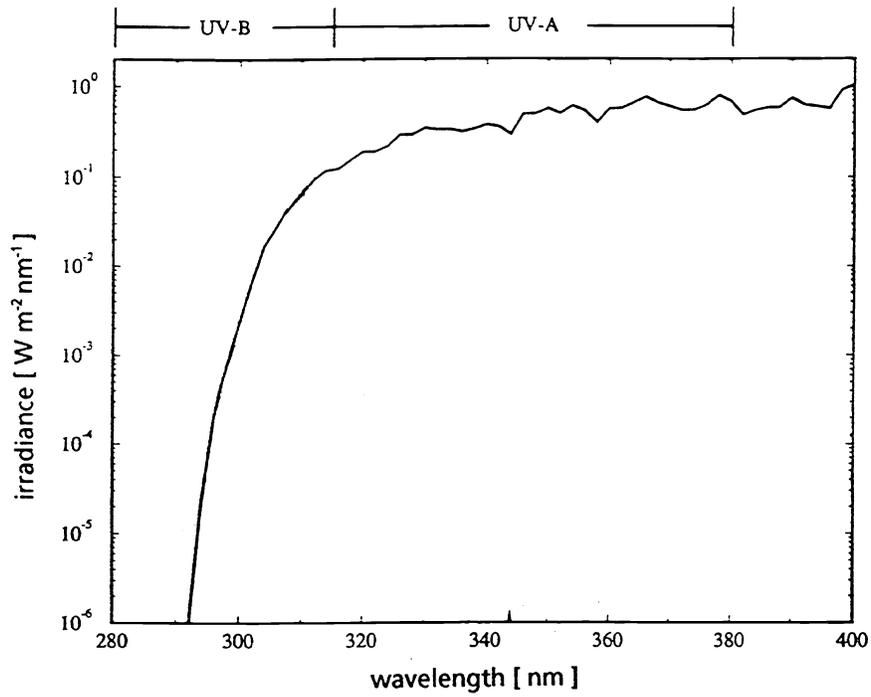


Fig. 1. Global solar irradiance vs. wavelength ⁷

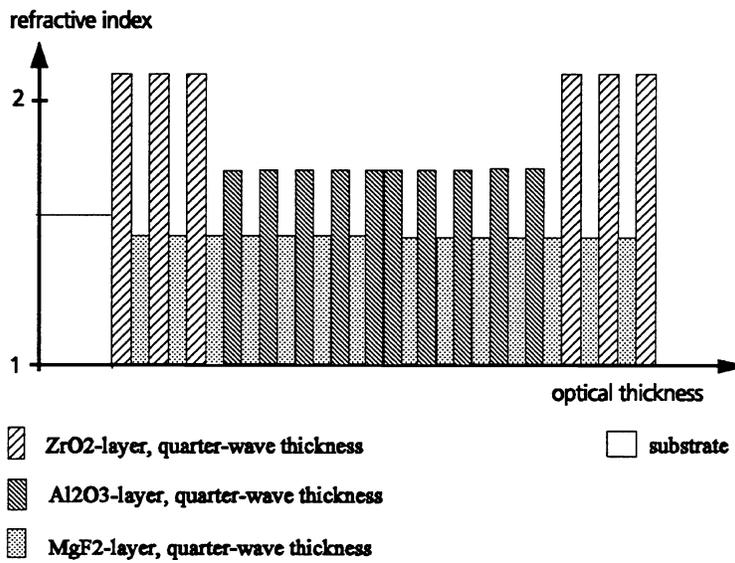
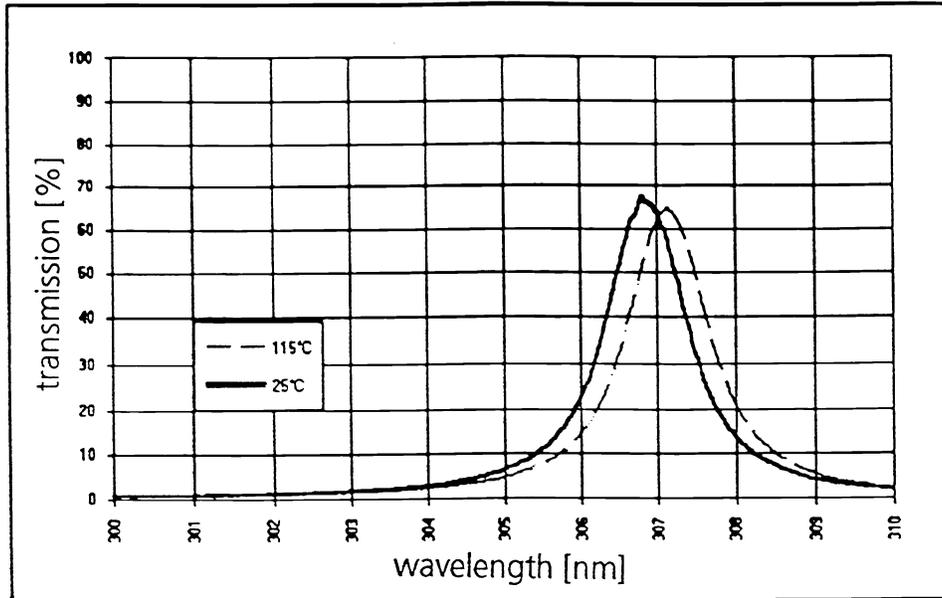
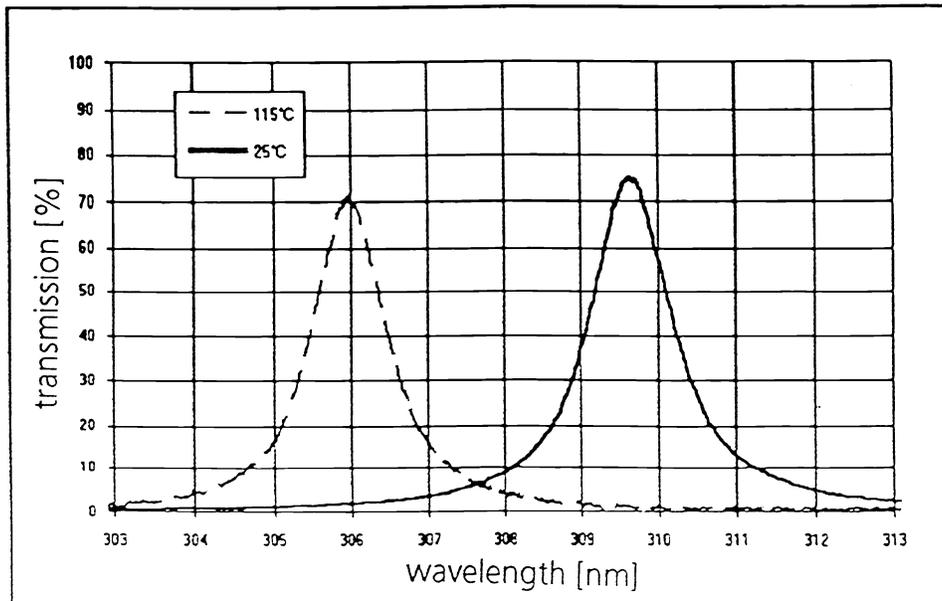


Fig. 2: The design of a humidity stable Fabry-Perot filter¹⁵



a



b

Fig. 3: Spectral shift of filter transmittance during heating from 20°C to 115°C:
 a) humidity stable filter with MgF_2 and Al_2O_3 as central layers and ZrO_2/MgF_2 as outer layers
 b) shift sensitive ZrO_2 and SiO_2 filter

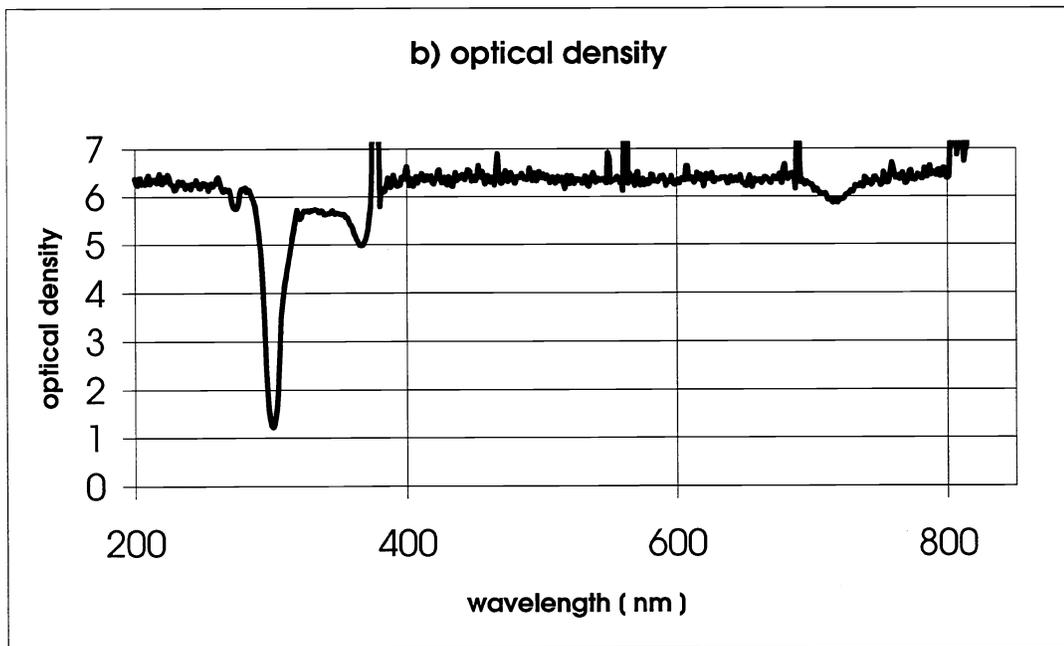
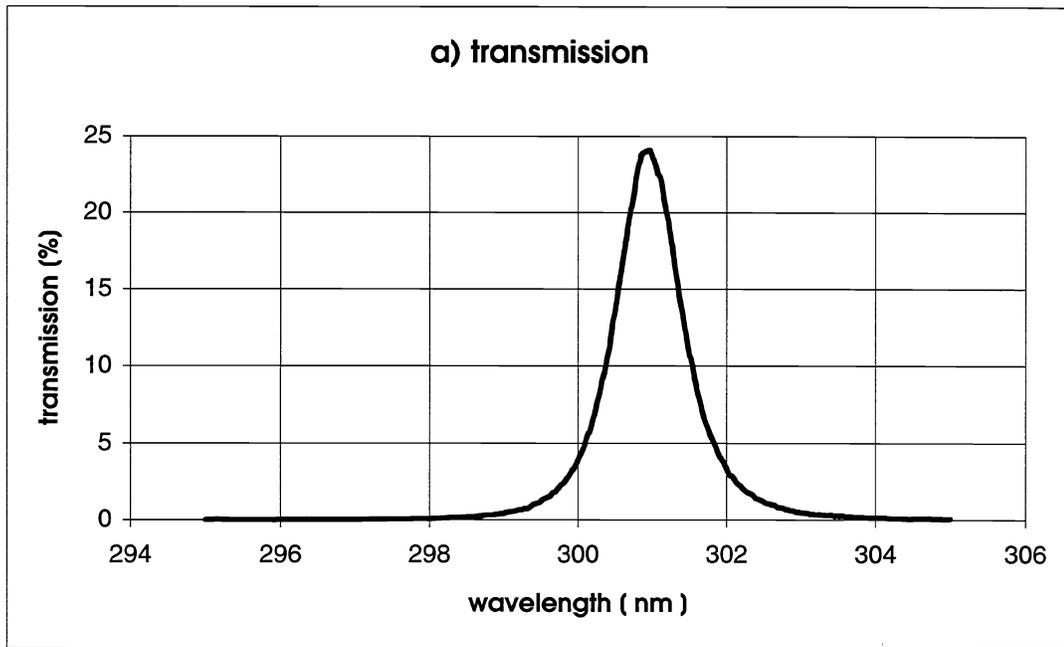


Fig. 4: Performance of a humidity stable filter with MgF_2 and Al_2O_3 as central layers and ZrO_2/MgF_2 as outer layers. a) Transmittance vs. wavelength; b) optical density vs. wavelength (detection limit is at optical density >6).

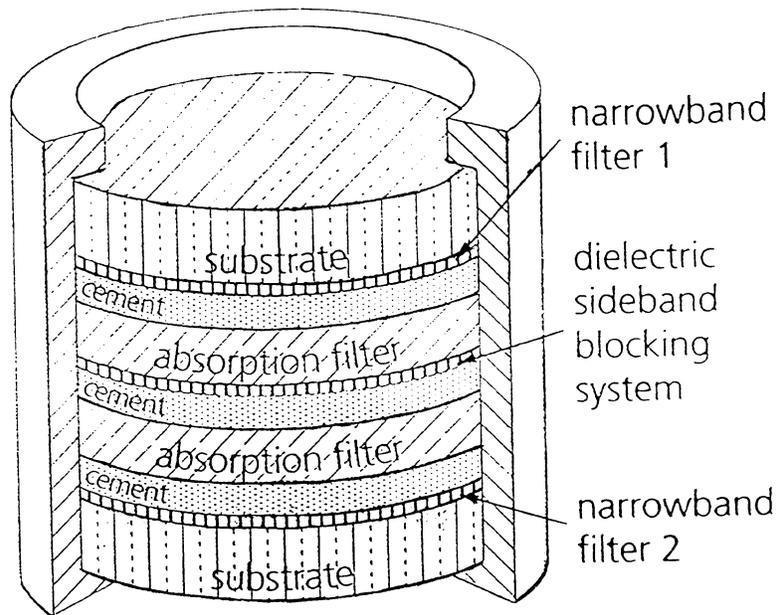


Fig. 5.: Construction of a complete UV-B filter consisting of two low-shifting Fabry-Perot filters, dielectric blocking filters and colored glass

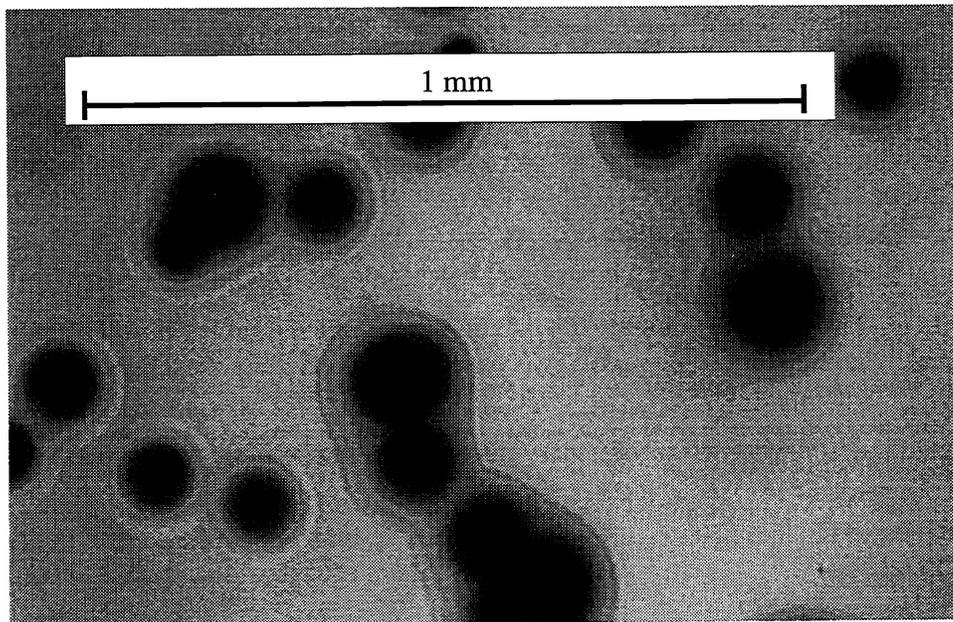


Fig. 6: Light micrograph of moisture penetration patches in a Fabry-Perot filter with center wavelength of 574 nm taken in transmission with a microscope-spectrophotometer at 574 nm. By moisture penetration detuned patches appear dark.

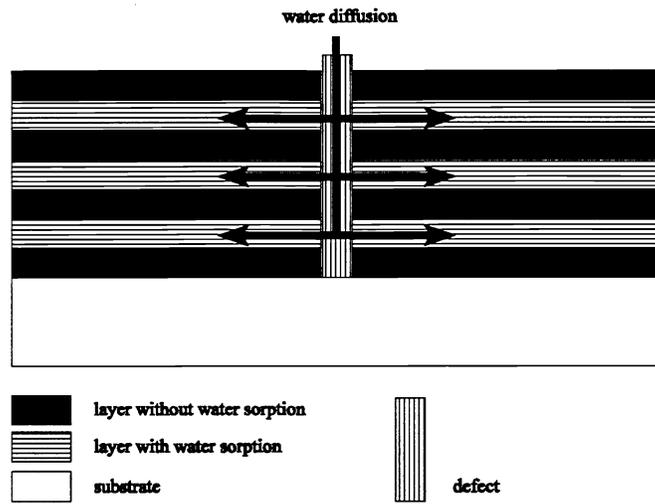


Fig. 7: Principle of water penetration into a semidense layer stack

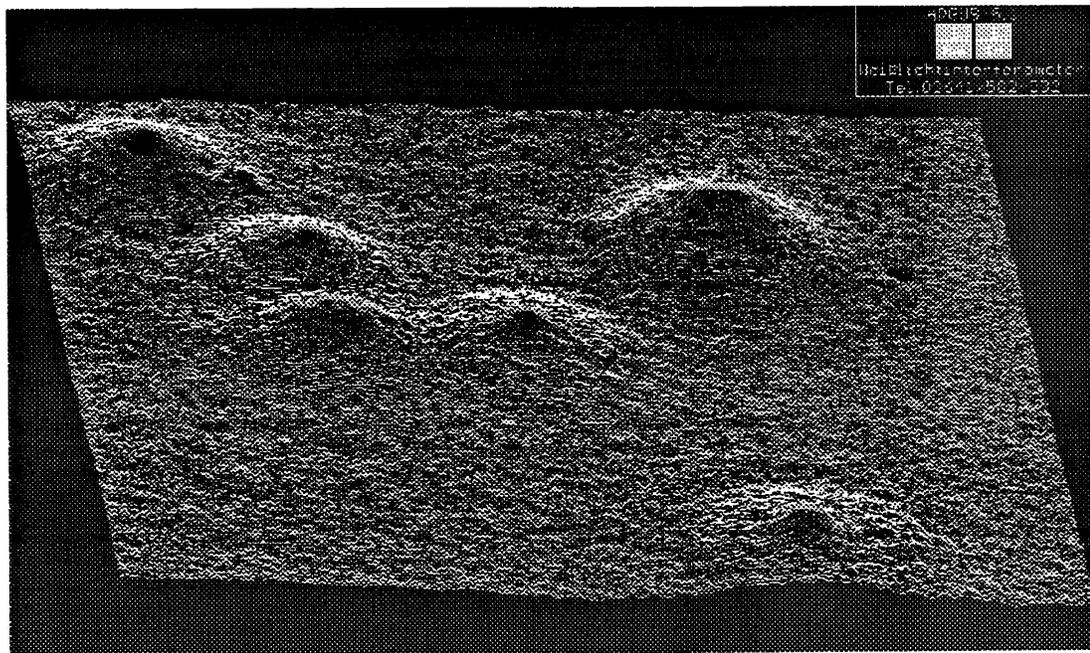


Fig. 8: White-light interferometric micrograph of moisture patches in ZrO_2/SiO_2 layer stacks (Al overcoated). At moisture penetration patches the geometric thickness of the layer stack is increased by about 50 nm.

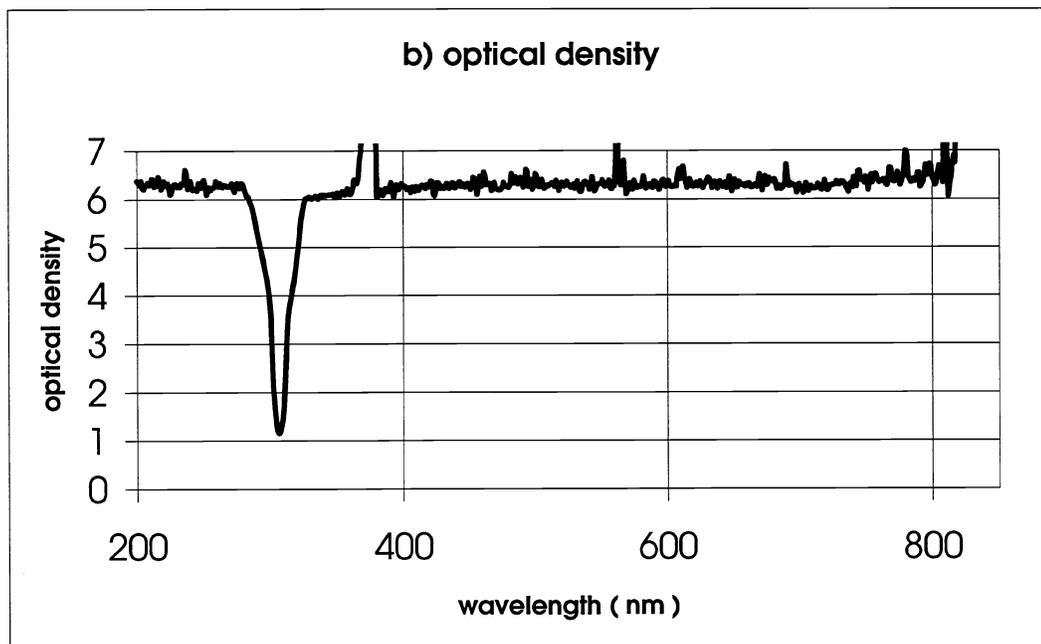
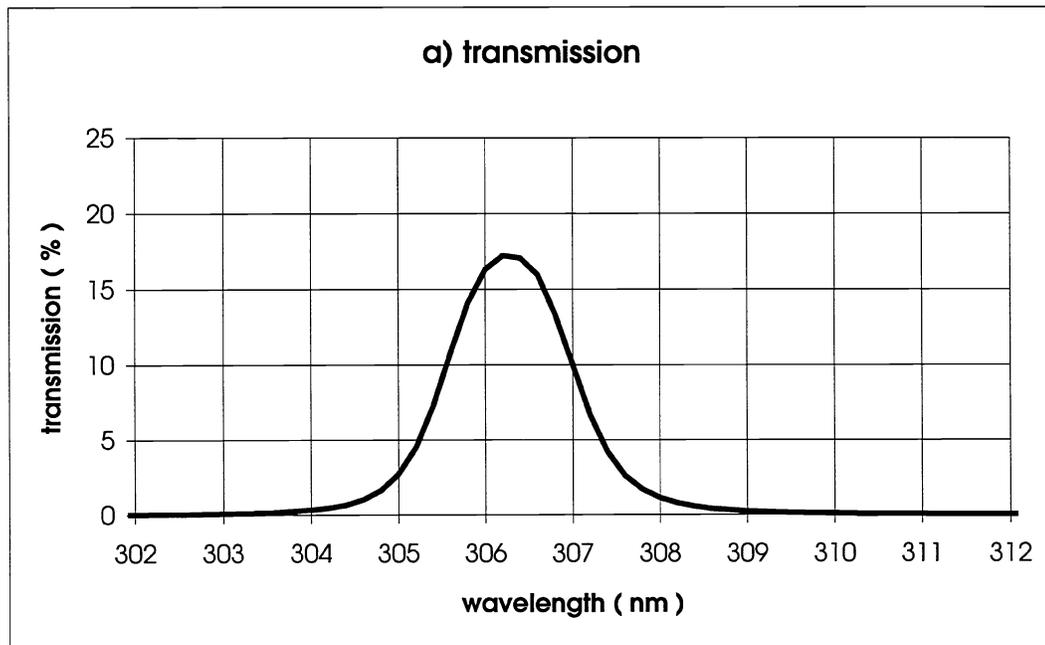


Fig. 9: Performance of a completely blocked humidity stable APS-filter (ZrO_2/SiO_2) . a) Transmittance vs. wavelength; b) optical density vs. wavelength (detection limit is at optical density > 6).