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Direct monitoring of broadband light absorbers

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Abstract

The final performances of manufactured thin film filters usually depend on to the monitoring strategy. Some optical monitoring systems provide transmittance measurements while others measure the reflectance. With our system, we are able to simultaneously measure both transmittance and reflectance over an extended spectral range [400 nm; 1000 nm]. This reflectance channel is necessary for direct monitoring of some kinds of filters like light absorbers. Indeed, in this case, transmittance is cancelled after the first metallic layer deposition. The optical system is also very useful for in situ characterization especially for metallic absorbing materials.

1. Introduction

Among the technical ways which allow to make light absorbers, black paints and surface anodization are efficient solutions. They can absorb all the light except only few percents for a low cost. These coatings are rather thick, from around 10 μm for anodization to around 100 μm for paints, but this is not problematic for most applications.

Thin film absorbers can offer a higher absorption level with a thinner coating (<1 μm). The transmittance cancellation can be easily obtained with an opaque metallic film. But the reflectance cancellation is more difficult. For monochromatic properties, one basic solution could consist in over-coating this opaque metallic layer, which can be considered as a metallic mirror, with an interferential dielectric mirror. We then obtain a Fabry–Perot cavity and an absorption peak is formed at a single resonant wavelength. However, the efficiency of this component is limited to a narrow spectral range. The spectral range enlargement requires a broadband antireflection stack coated on the opaque metallic layer. This antireflection structure consists in mixing metallic and dielectric layers to produce destructive interferences. For better results, a low dielectric index and a low reflective metal should be chosen [1]. These coatings only need few layers. But an accurate knowledge of the complex refractive index of metallic layers is required for high performances. In order to fulfil these necessary index determinations, a spectrophotometric characterization method has been developed for both opaque and semitransparent layers [2].

Our aim is to manufacture broadband absorbers compliant with space environment applications. First experiments were performed in our laboratory with nickel (Ni) as metal and cryolite (Na_3AlF_6) as dielectric material [2]. A 0.999 absorption level in the visible range was obtained. However, these coatings were manufactured with classical electron beam deposition technique and were consequently sensitive to moisture. To improve this point, we decided to use an ion assisted deposition technique, namely RLVIP (reactive low voltage ion plating) compliant with our needs [3,4]. At the same time we change the materials in the coating, using now Hf–SiO_2 instead of Ni–Na_3AlF_6. Several reasons lead to this choice [5]: first, cryolite as any fluoride material is not compatible with assisted deposition techniques. Second, Hf–SiO_2 are, respectively, a low reflective metal and low dielectric index as expected for

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light absorbers that can be easily evaporated since the machine is configured to deposit HfO_2–SiO_2 coatings. The only modification consists in suppress oxygen during Hf deposition.

Until now we worked with two monitoring systems: a quartz crystal micro-balance and a monochromatic optical monitoring. This optical control consists in measuring transmittance in real time and stopping the deposition when transmittance reaches its predicted theoretical value (level monitoring [6]) or when transmittance derivative versus thickness is cancelled at a specific wavelength (turning point monitoring [6]). However, for an absorber the first layer is an opaque metallic film which cancels transmittance. It is then impossible to perform optical monitoring on the absorber substrate directly. Indirect optical monitoring is possible with an other substrate introduced into the vacuum chamber after the first opaque layer deposition. All the following layers are controlled on this monitoring sample, inducing manufacturing errors without any compensation.

For few years, we have developed a spectrophotometric broadband optical monitoring [7]. It consists in associating two monitoring channels, respectively, in transmittance and in reflectance which allows to analyse both fluxes in real time on a large spectral range. The reflectance channel has been especially performed for applications like absorbers for which transmittance is cancelled. It ensures a direct monitoring of the component over a broad spectral band, and as a matter of fact, enables a better comprehension of signal shift linked to metallic layers oxidation phenomenon. With such broadband monitoring, the materials characterization stage is undoubtedly bettered with an improvement of the index refractive determination accuracy. And the absorber manufacturing stage is also improved since we have a complete information during deposition with a broadband optical monitoring.

2. Opaque metallic layer characterization

Classically, a dielectric layer characterization is performed with a thick layer deposited on a bare substrate. From transmittance and reflectance measurements we can find the different parameters: thickness, refractive index and extinction coefficient versus wavelength. An optimization algorithm is used to find the parameters which allow the best fit with measurements. In this case, spectral data shows some interference modulations giving enough information for characterization.

With a metallic layer the problem is more difficult mainly because spectral measurements show no modulation. To obtain additional information, the metallic layer can be over-coated with a dielectric one that provides the expected modulation of spectral curves. Results are more accurate with a high dielectric index so in our case, HfO_2 is used.

From both spectral curves of the single metallic film and over-coated with the dielectric layer, it is possible to extract the metallic film parameters. For that, the dielectric film parameters are supposed to be known. In case of an opaque film, the problem does not depend of the film thickness and the complex refractive index $n - ik$ can be determined from the two reflectance curves. Fig. 1 gives the measured and calculated reflectance curves. As can be seen the agreement is quite good.

The complex metallic index is determined from a polynomial law. For each law, $n(\lambda)$ and $k(\lambda)$, three free parameters are optimized. Results are given by the formulas (1) and (2) (the wavelength λ is in nanometer). Dispersion curves are given in Fig. 2.

$$n(\lambda)_{\text{Hf opaque}} = 4.7845 - \frac{3.1856 \times 10^5}{\lambda^2} + \frac{2.4810 \times 10^{10}}{\lambda^4} \quad (1)$$

$$k(\lambda)_{\text{Hf opaque}} = 3,8656 - \frac{5.0891 \times 10^5}{\lambda^2} + \frac{5.6774 \times 10^{10}}{\lambda^4} \quad (2)$$

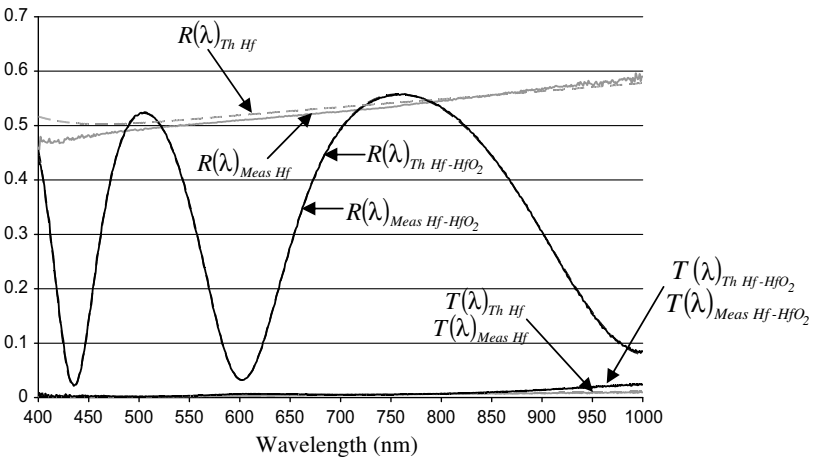

Fig. 1. Grey continuous curves: measurements after opaque metallic layer deposition (Hf). Grey discontinuous curves: theoretical curves after opaque metallic layer deposition (Hf). Black continuous curves: measurements after dielectric layer deposition (HfO_2). Black discontinuous curves: theoretical curves after dielectric layer deposition (HfO_2).

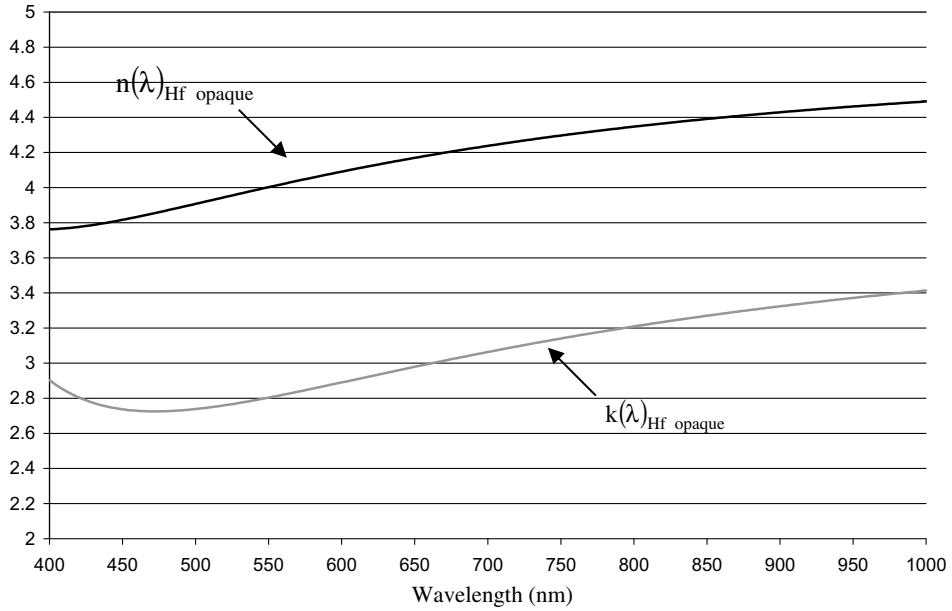

Fig. 2. Opaque metal refractive index and extinction coefficient.

3. Semitransparent layer characterization

For semitransparent films, the characterization method is almost the same as previously described except that now both the complex refractive index and the thickness must be determined. For this purpose we can benefit from additional information given by transmitted spectral curve.

3.1. Semitransparent hafnium layer deposition: oxidation phenomena

The film thickness in this case is very thin (less than 10 nm) and oxidation phenomena cannot be neglected concerning Hf films. Transmittance and reflectance measurements after the metallic layer deposition are presented in Fig. 3, curves 1. In most configurations the metallic layer is followed by a dielectric material deposition. This is the case for our specific light absorber application presented in the following section and for the metal index characterization presently investigated which requires the deposition of a thick HfO_2 layer over the metallic film. This dielectric material is obtained from evaporated hafnium (Hf) in a reactive O_2 atmosphere in the vacuum chamber ($\approx 8 \times 10^{-4}$ mbar). Immediately after this gas entrance the measured spectral profile shifts from curves 1 to curves 2 (Fig. 3). The hafnium layer is oxidized and it induces trans-

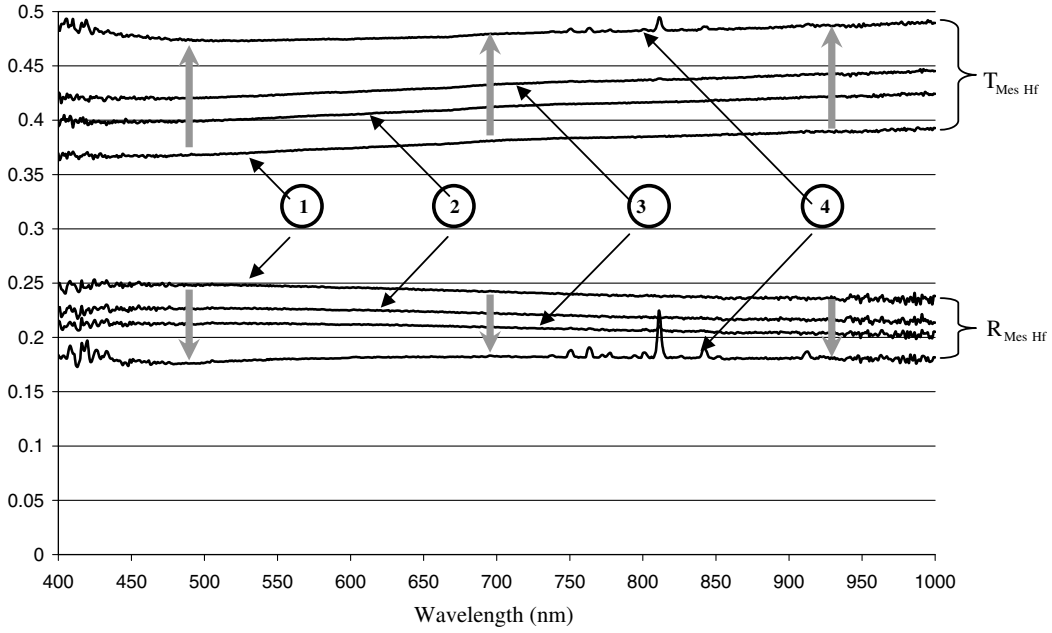

Fig. 3. Oxidation phenomena after metal deposition and before dielectric deposition.

mittance and reflectance level changes. After that, this phenomenon goes on but more slowly. Approximately 50 s after oxygen entrance the spectral response corresponds to the curves 3.

As mentioned in introduction these coatings are manufactured with an assisted technology. During deposition, an Argon plasma is created between a plasma source and the material that is melted inside crucible. The plasma induces an ionization of the evaporated material and reactive gases that can be introduced inside the chamber (oxygen). Ions are accelerated toward substrate holder which results in a densification of the film structure.

As soon as the plasma is created for the dielectric layer deposition, one can observe (approximately 5 s) a new translation of the measured curves (curves 4). This last one is not caused by material deposition because of the sudden occurring of the phenomenon. This surely corresponds to a second oxidation phase of the metallic layer. Note that one can see the plasma peaks at specific wavelengths.

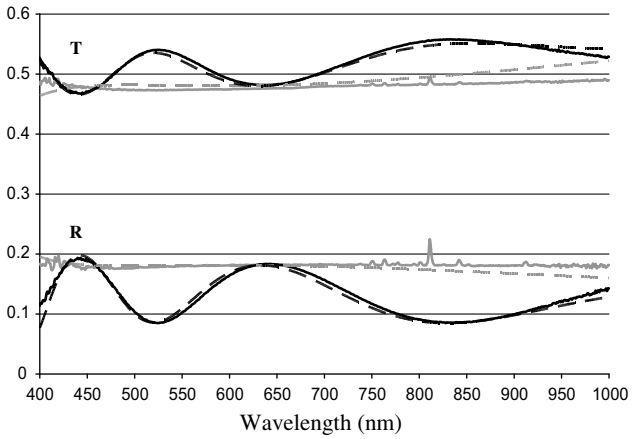

Fig. 4. Grey continuous curves: measurements after opaque metallic layer deposition (Hf). Grey discontinuous curves: theoretical curves after opaque metallic layer deposition (Hf). Black continuous curves: measurements after dielectric layer deposition (HfO_2). Black discontinuous curves: theoretical curves after dielectric layer deposition (HfO_2).

3.2. Dielectric material deposition: semitransparent hafnium characterization

At the end of the HfO_2 film deposition the transmittance and reflectance levels are shown in Fig. 4. One can see interference modulation which is necessary for hafnium characterization. From these spectral data we adjust index and thicknesses parameters to obtain the best fit between theory and measurements. But even if we can use transmittance data in this case, the adjustment is quite hard because of the complex oxidation phenomena which are difficult to investigate. The boundary between the metallic film partially oxidized, and the dielectric film perfectly transparent is not obvious. For this purpose we take advantage of the so called "potential transmittance" concept defined by the quantity $\frac{T}{1-R}$. This value is known to be stable as far as a non absorbing film is deposited over a coating. As a result, we follow the evolution of the potential transmittance during the deposition of the dielectric film. At the beginning, this one is decreasing due to potential oxidation of the metallic film and then tends to stabilize which allows an estimation of the beginning of the truly dielectric film. With this strategy, we can decide the spectral curves corresponding to the metallic film (partially oxidize) that must be used for characterization. These curves are given in Fig. 4 (grey continuous curves).

Even if the metal is partially oxidized and consequently non homogeneous, we use a homogeneous basic model to

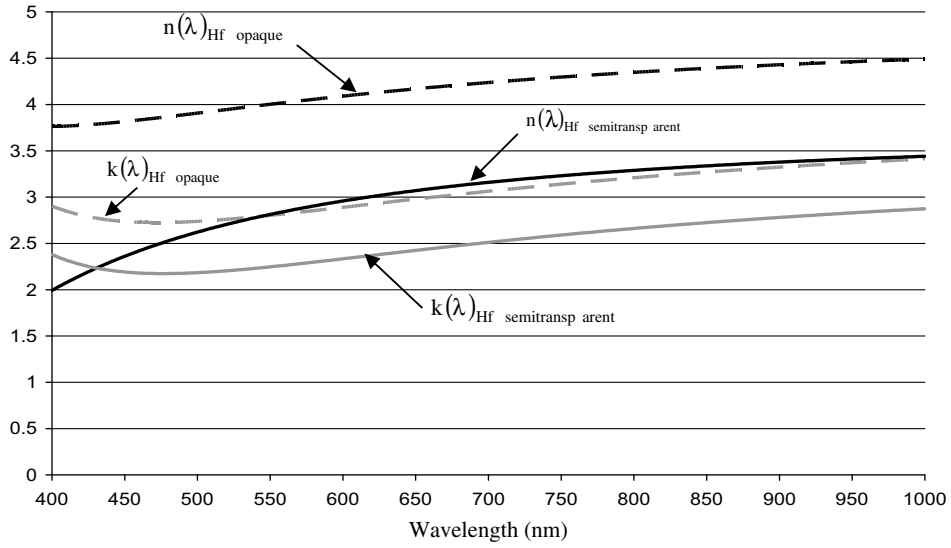

Fig. 5. Opaque and semitransparent metal refractive index and extinction coefficient.

describe it. The optimization procedure is performed using polynomial laws: $n(\lambda) = f(1/\lambda^2)$ and $k(\lambda) = g(1/\lambda^2)$, exactly as for opaque layers. The result combines all the observed phenomena: semitransparent metal deposition, oxygen introduction and plasma phenomena. For this particular metallic layer, the thickness is estimated to 7 nm. The reverse engineering fits are shown in Fig. 4 (discontinuous curves). Refractive index and extinction coefficient of the semitransparent metallic film are the following and they are presented in Fig. 5:

$$n(\lambda) = 3.7094 - \frac{2.6692 \times 10^5}{\lambda^2} - \frac{1.2311 \times 10^9}{\lambda^4} \quad (3)$$

$$k(\lambda) = 3.3459 - \frac{5.3224 \times 10^5}{\lambda^2} + \frac{6.0455 \times 10^{10}}{\lambda^4} \quad (4)$$

Table 1
Broadband absorber structure

	Thicknesses (nm)	Material	Monitoring	
			Monochromatic method	Monitoring wavelength, λ_0 (nm)
Layer 1	300	Hf_{opaque}	Reflectance level	657
Layer 2	38	SiO_2	Reflectance level	657
Layer 3	13	$Hf_{semitransparent}$	Reflectance level	657
Layer 4	62.8	SiO_2	Turning point monitoring	495
Layer 5	8.4	$Hf_{semitransparent}$	Reflectance level	584
Layer 6	92	SiO_2	Turning point monitoring	578

The opaque metal refractive index and extinction coefficient are higher than for the semitransparent metallic film. Notice that adjustments between theory and measurements slightly differ (Fig. 4). Oxidation phenomena are not problematic for opaque film characterization since reflectance levels are not modified. But they have to be taken into account for semitransparent film for which the effect is much larger. However, this problem is complex and a more precise model should be necessary. It would require a lot of complementary analyses. In this work we preferred to simplify the model as an homogeneous layer and mainly to focus on the coating manufacturing.

With the previous monochromatic optical system, it would have been practically impossible to see all these oxidation steps and characterization would not have been possible. The broadband optical measurement system allows in situ characterization and phenomena identification even if these last one are difficult to explain.

4. Absorber manufacturing

The previous metal index characterizations are necessary for a broadband absorber design and manufacturing. The coating presented here is a 6-layer stack (Table 1). Theoretical spectral response is shown in Fig. 6. The first opaque metallic layer cancels the transmittance and the others form an antireflective coating with silica and semitransparent hafnium layers. Fig. 7 presents the different measurements obtained layer after layer. For each layer a monochromatic stopping criterion is used (turning point monitoring or level monitoring). The semitransparent thin film depositions are the most difficult to monitor (layer 3

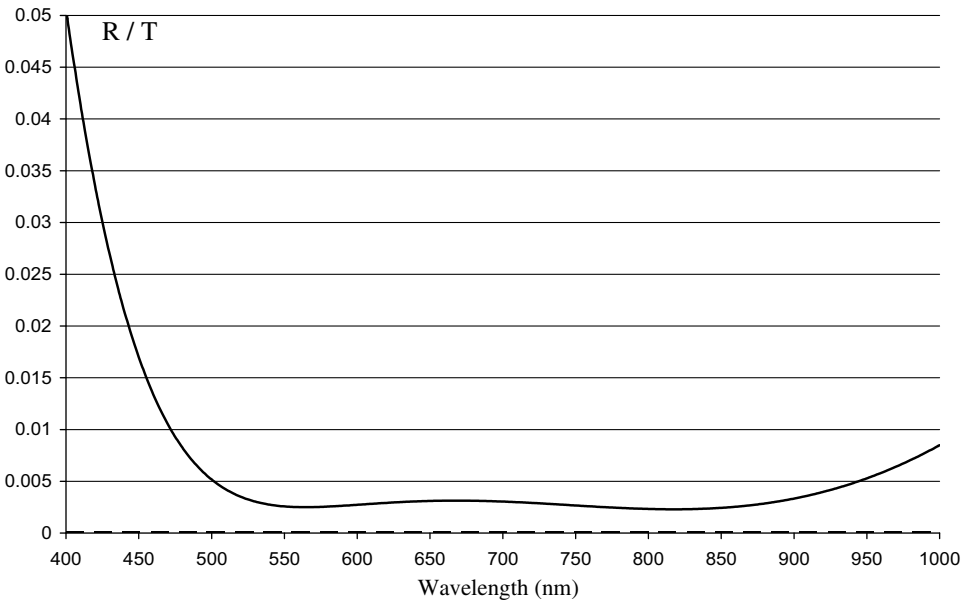

Fig. 6. Theoretical absorber reflectance (continuous curve) and transmittance (discontinuous curve).

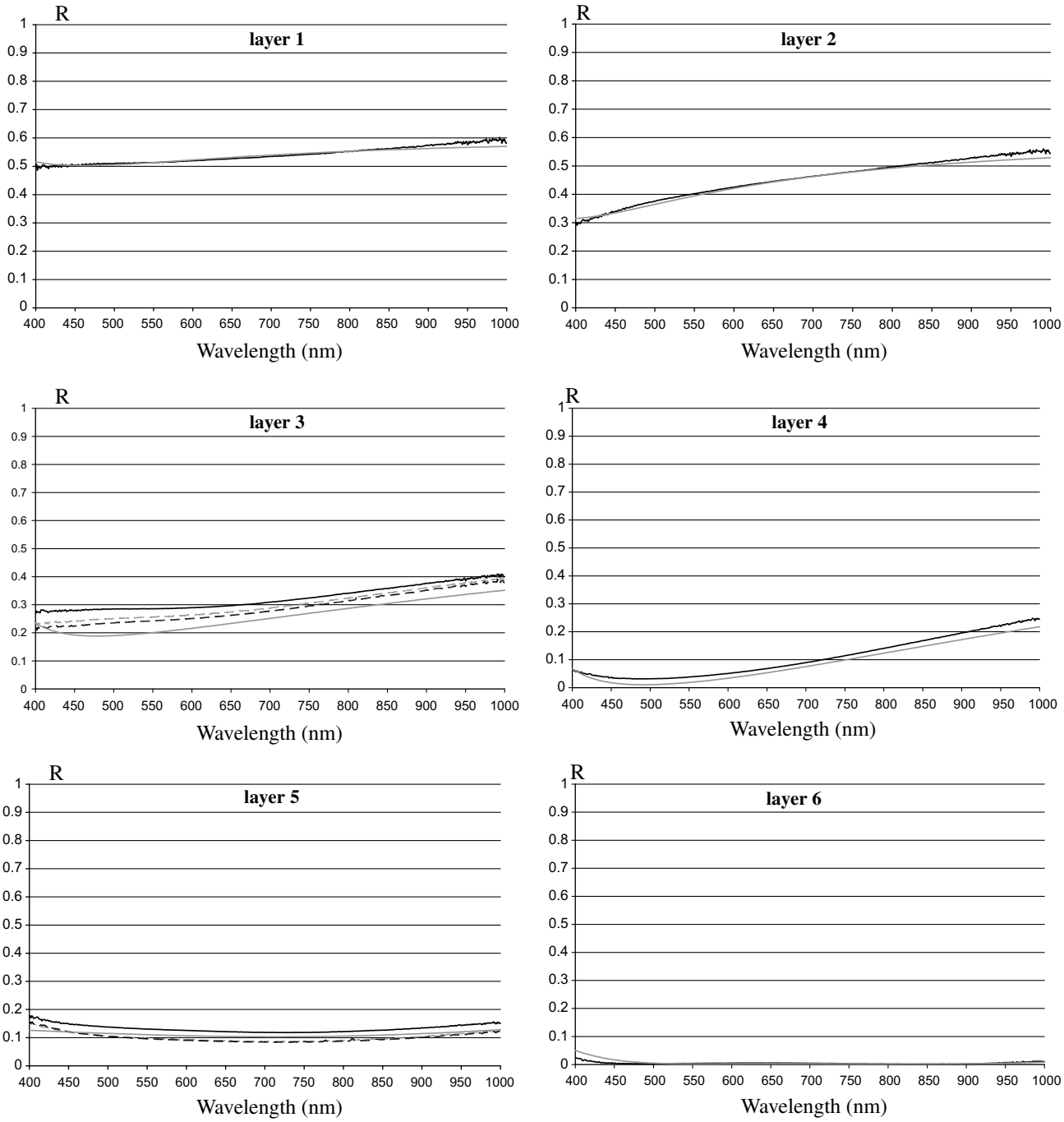

Fig. 7. Black continuous curves: measurements after each layer deposition. Grey continuous curves: theoretical values to reach after each layer deposition. Discontinuous curves: measurements after a semitransparent metallic layer deposition: grey – after oxygen introduction in the vacuum deposition chamber; black – after plasma creation and before the following layer deposition.

and 5). We have to stop the hafnium deposition for a higher reflectance than the expected level. After oxygen introduction and plasma creation, this one decreases and moves near the theoretical value (discontinuous curves). As we previously explained the depositions of layers 3 and 5 are quite difficult. We stop the material evaporation for a higher value than the expected level but the phenomenon reproducibility is not good. We can see that the layer 3 is probably too thin, on the contrary the layer 5 is probably too thick.

The final result with the transmittance and reflectance measurements is presented in Fig. 8. Compared to theoretical results the residual reflectance level is a bit higher with a slight spectral shift, but the absorber performances are rather good with an average residual reflectance about 0.005.

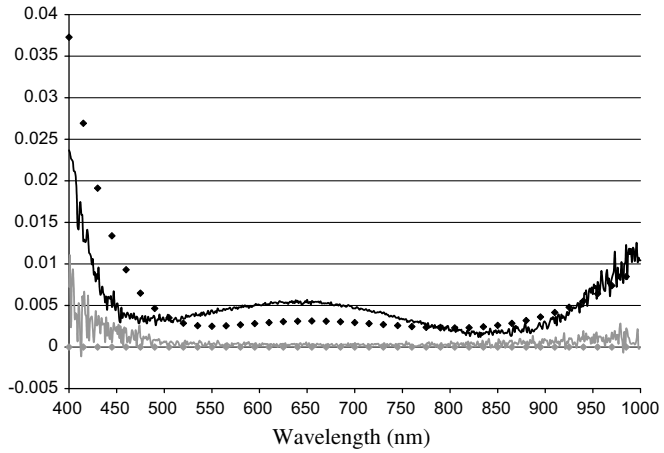

Fig. 8. Black and grey diamond pattern are, respectively, the theoretical reflectance and transmittance. Black and grey curves are, respectively, the reflectance and the transmittance measurements.

5. Conclusion

With classical optical system (monochromatic transmittance measurements) in situ characterization and direct monitoring of absorbers are impossible.

The optical system developed in our laboratory is very efficient for this stack. Broadband reflectance measurements are efficient for an in situ opaque metallic layer characterization. In the case of semitransparent hafnium layer, they allow to take into account complex oxidation phenomena for the characterization of this material. Finally we were able to manufacture high performance broadband absorbers with a direct monitoring.

Future work will be focused on monitoring strategy and metal characterization. For such coatings a stopping criteria based on the analysis of the whole spectral range could be interesting and a more precise model for metal layers seems necessary. These improvements should allow to manufacture absorbers with increasing performances.

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