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Ion-Plating Metal-Dielectric Coatings for Light Absorbers

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ABSTRACT

Ion Plating deposition technology is investigated for the manufacturing of durable metal-dielectric light absorbers that are compliant with space requirements. Coatings are manufactured using hafnium (Hf) and silica (SiO_2) for layer materials so that the deposition chamber can still be used without any modification for the manufacturing of standard dielectric coatings. Both monochromatic and broad band light absorbers are studied

1. INTRODUCTION

Light absorbers are of great interest to suppress stray light in optical systems. Classically, light absorbers are made with black paints or surface anodization [1]. These solutions are particularly advantageous when large achromatic black surfaces are required, at a reasonable cost. However, they are not appropriate for all cases, for example when the amount of non absorbed light must be as low as 0.1 %, when this residual stray light should rather be reflected in a specular way and not fully scattered, when the thickness of the coating should be less than a few micrometers or when absorption must occur at a single wavelength. For such particular cases, metal-dielectric light absorbers may be an efficient alternative solution.

These interferential coatings are made with alternated dielectric and semi-transparent metallic layers, the light being absorbed inside metallic layers. Most often, the total thickness of such coatings is less than one micrometer. The surface roughness of the coating is identical to the substrate roughness so that we can choose between specular or diffuse reflection of the residual stray light by a proper choice of the substrate. Generally, an opaque metallic layer is deposited first on the substrate so that the substrate is never illuminated. As a consequence, the choice of the substrate material (glass, metal,…) has no influence on the coating design, as illustrated on Fig. 1. According to the layer thicknesses, the interference pattern can be modified so that the light is absorbed at specific wavelengths only or over a wide spectral range.

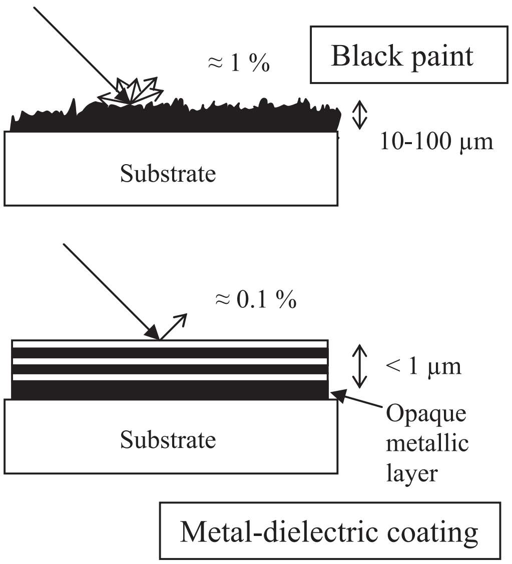

Fig. 1: Schematic representation and comparison of black paints and metal dielectric light absorbers.

More details about the coating design can be found in [2]. One important result concerning the choice of materials is that light absorbers are more efficient when using a low reflection metal and a low index dielectric material.

The major difficulty is that light absorbers are very sensitive to any design parameter, namely the refractive index and thickness of each layer. This difficulty is typical for antireflection coatings and light absorbers can be regarded as one kind of such coatings. As a consequence, we need an accurate knowledge of the refractive index of each material involved in the design. However, if this requirement can be achieved easily for the dielectric material, this is not the case for

the metallic one. Indeed very few results exist in the literature on metal optical constants and most of these results concerns high reflectance metals, such as gold silver or aluminum. More over, these results most often concern bulk materials and not thin films. As a consequence, we developed in the laboratory a new method for the index determination of metallic thin films. This method was applied successfully in the case of nickel and we manufactured several light absorbers using this metal and cryolite (Na_3AlF_6) for the dielectric material. These coatings were manufactured with classical electron beam. Fig. 2 gives the results obtained for the best sample, with an absorption level higher than 99.9 % in the whole visible range [3, 4].
However, electron beam deposition is a low energy deposition process which results in a low packing density of the layers. As a consequence, these coatings had mechanical properties that were not compliant with space requirements and optical properties were not stable with climatic conditions.

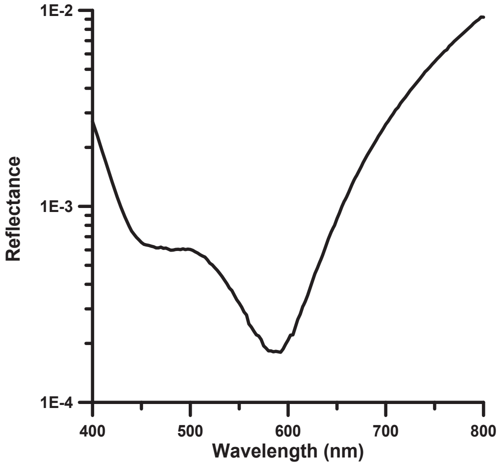

Fig. 2: Residual reflection measured on a Ni-Cryolite light absorber manufactured by electron beam deposition.

In this paper, we describe how this point can be improved using the Ion Plating deposition process which is known to provide high density layers. Section 2 briefly presents the Ion Plating process. Section 3 is devoted to the choice of the materials and section 4 describes the results we obtained concerning index determination for metallic layers. Section 5 concerns the manufacturing of light absorbers with this technology. Some of the coatings we manufactured were tested by CNES to evaluate their mechanical and climatic characteristics. This point is addressed in section 6.

2. DESCRIPTION OF THE ION PLATING PROCESS

The Ion Plating deposition technique is a high energy process which permits to compact the layer during its deposition by the mean of ionic assistance. In this technology, ions are generated by a plasma created in the vacuum chamber and accelerated toward substrates. One consequence is that the ionic assistance is uniform over the whole substrate surface. Another consequence of the plasma is that the deposition temperature rapidly increases up to 250 – 300 °C. For comparison, the Ion Assisted Deposition process (IAD) uses an ion gun which permits to reduce the temperature increase but also reduce the coating uniformity to the diameter of the ion beam. More precisely, the Ion Plating process we use in the laboratory is the Reactive Low Voltage Ion Plating developed by Balzers in its BAP 800 IP system [5]. As illustrated in fig. 3, the vacuum chamber (1 m^3 stainless steel box coater) is equipped with two electron guns with rotating crucibles that are insulated from the vacuum chamber. The rotating substrate holder is also insulated from the chamber.

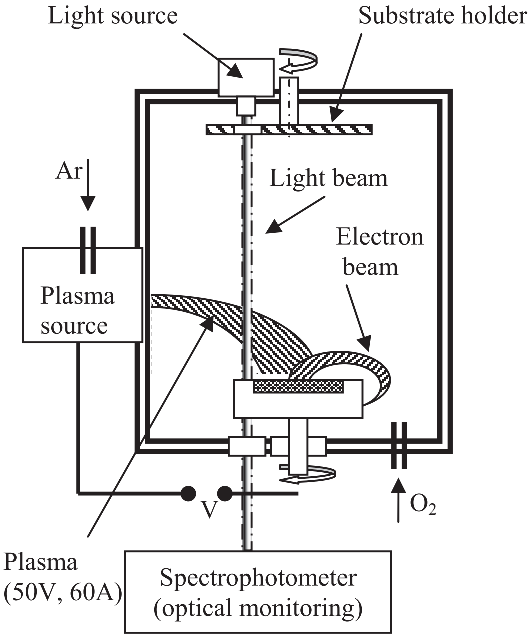

Fig. 3: Schematic representation of the Reactive Low Voltage Ion Plating process vacuum chamber.

During deposition, a plasma is created between the plasma source and the melted material evaporated from the crucible. This plasma takes place in the vacuum chamber and induces a strong ionization of all the gases that are in the chamber, especially oxygen introduced for reactive deposition of oxide materials. Escaping from the plasma, electrons are trapped in the vicinity of the insulated substrate holder. This creates a voltage bias between the plasma and substrates which induces ionic assistance. This Ion Plating process is mainly used in the laboratory to produce oxide materials, namely Ta_2O_5 and HfO_2 for high index materials, and SiO_2 as low index material.

The main parameters of the deposition process that can modify layers characteristics are the current and voltage of the plasma (≈ 50A, 60V), the anode voltage in the plasma source (≈ 40V), the argon pressure inside the plasma source (≈ 3 mbar), the argon and oxygen partial pressure inside the deposition chamber (≈ $2\ 10^{-4}$ and $8\ 10^{-4}$ mbar) substrate temperature and deposition rate. Layer characteristics also depends on the choice of the starting material since we can either choose a metallic (Ta, Hf, Si) or an oxidized material (Ta_2O_5, HfO_2, SiO_2).
The deposition rate is controlled by quartz crystal monitoring. Layer thicknesses can be controlled either by quartz crystal monitoring or optical monitoring. For this purpose, one sample is illuminated by a collimated white light beam from which we can deduce the evolution of the coating transmittance during deposition.
Notice that without using the plasma source, the deposition process corresponds to classical electron beam deposition.

3. CHOICE OF MATERIALS

As mentioned in the introduction, we need a low index dielectric material and a low reflection metal to design and manufacture high efficiency light absorbers. Obviously SiO_2 is the best choice in our case for the dielectric since it is a low index material that can be produced easily by Ion Plating.
Concerning the choice of the metal, as mentioned in the introduction, we started our first experiments using chromium and nickel for which reflectance is about 60%. Due to interface problems between the layer and the substrate, we did not succeed to determine accurately the complex refractive index of chromium. This explains why we finally used nickel. However, because of its magnetic properties, this material is not acceptable for all applications. In particular, this material cannot be used for some light absorbers we are studying in the frame of the atomic clock PHARAO. As a consequence, we had to look for another low reflectance metal. Among all potential candidates, hafnium and tantalum were obviously regarded as very interesting candidates since they can be used in the Ion Plating deposition chamber to produce HfO_2 and Ta_2O_5 high index dielectric layers. In that case, the vacuum chamber can be used to produce either metal dielectric coatings or more classical all dielectric coatings, without any modification. The only difference is that we introduce oxygen in the chamber to deposit dielectric layers while we do not to deposit metallic layers.
At last, we decided to use hafnium for two reasons. The first one is that tantalum has a very high melting point and is consequently rather difficult to evaporate. Most often, Ta_2O_5 layers are produced starting from Ta_2O_5 material and not Ta. The second reason is related to the index determination method we use for metallic layers. This method, as will be described in the following section, requires to deposit both a metallic and a high index dielectric layer and because of its lower absorption level, especially in the UV range, HfO_2 is more interesting than Ta_2O_5 for the dielectric layer.

As a conclusion, we selected Hf and SiO_2 for the manufacturing of metal-dielectric light absorbers using the Ion Plating deposition process.

4. CARACTERIZATION OF Hf LAYERS

4.1 Influence of the deposition process

In order to estimate the influence of the ionic assistance, we started by manufacturing of opaque hafnium layers with and without the help of the plasma source, which corresponds respectively to an Ion Plating process or to classical electron beam deposition. For each case, we used two different deposition rates, 0.4 and 0.1 nm / s, to see the influence of this parameter. Indeed light absorbers may require some very thin semi transparent metallic layers for which a low deposition rate would make the thickness monitoring easier. Fig. 4 gives the reflectance of the samples in the visible spectral range. As one can see, the reflectance is higher for the ion assisted layer deposited at 0.4 nm / s. For all other samples, manufactured with a low deposition rate or without ionic assistance, the lower reflectance level is probably due to a lower packing density.
The reflectance of these samples has been measured again three days later, to see the evolution of the optical properties of the film in ambient conditions. Fig. 5 gives the results for films manufactured with a 4 nm / s deposition rate, with and without ionic assistance. As expected, ion assisted layers are more stable.

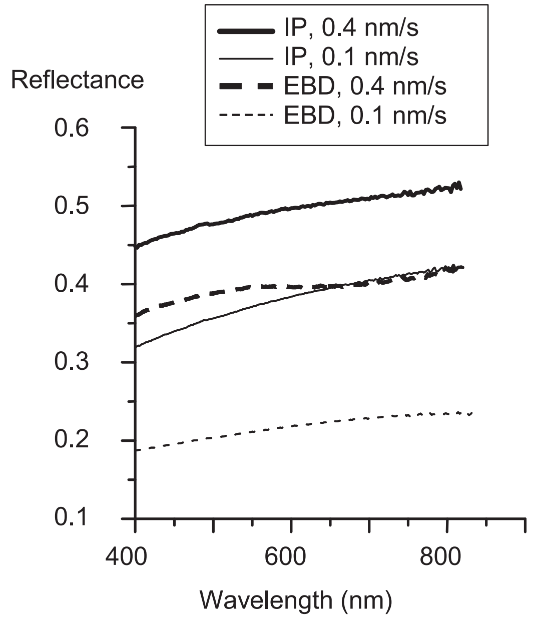

Fig. 4: Measured reflectance of opaque hafnium film manufactured with or without ionic assistance (Deposition rates 0.4 and 0.1 nm / s)

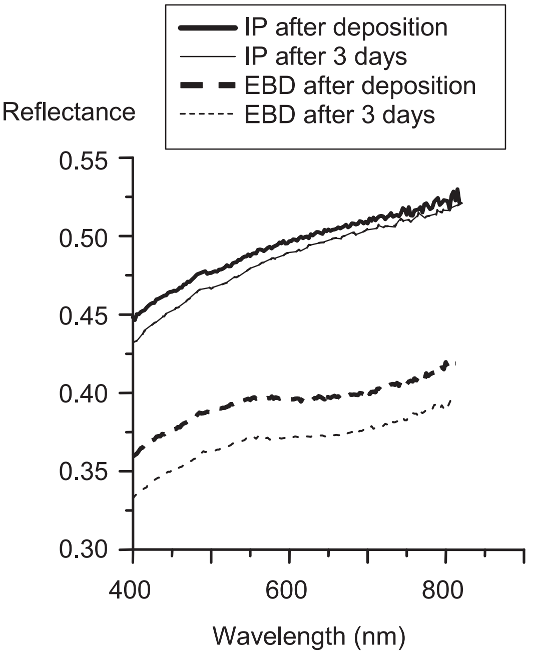

Fig. 5: Evolution of the reflectance after three days for opaque hafnium film manufactured with or without ionic assistance (Deposition rates 0.4 nm / s)

4.2 Index determination

In order to determine the complex refractive index of both opaque and semi transparent metallic layers, we developed a method based on reflectance and transmittance spectrophotometric measurements. This method is detailed in [4]. In this section, we will only give its principle and the result we obtained for opaque hafnium layers.

Considering an opaque metallic film, we aim to determine two unknowns that are its refractive index (n) and its extinction coefficient (k). For this purpose, we need at least two measurements. The first one is the reflectance of the bare metallic film. The second is the reflectance of the same sample after deposition of an additional dielectric film. This dielectric film is characterized alone on another sample so that we do not introduce new unknowns. Fig. 6 gives an illustration of these two measurements. From these two curves it is then possible to extract the metallic film index (n-ik) for any wavelengths except a few ones for witch the thickness of the dielectric layer is a multiple of a half wave. However, the accuracy of the determination, due to measurements uncertainty, is not constant and strongly depends on the wavelength, as can be seen on Fig. 7. Obviously, the film index can be interpolated from the results obtained in high stability spectral regions.

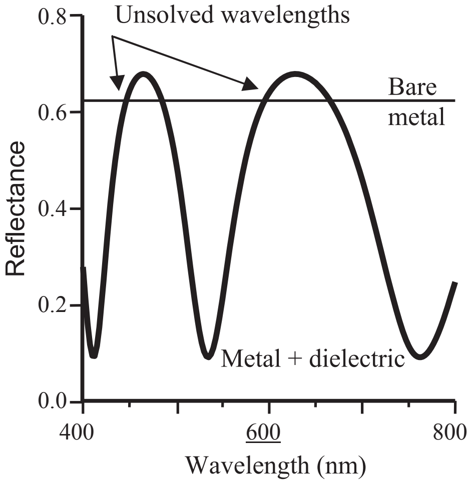

Fig. 6: Calculated reflectance of an opaque metallic film before and after deposition of a dielectric layer (metal index: 2-3.5i ; dielectric index:2.35; dielectric thickness 380 nm)

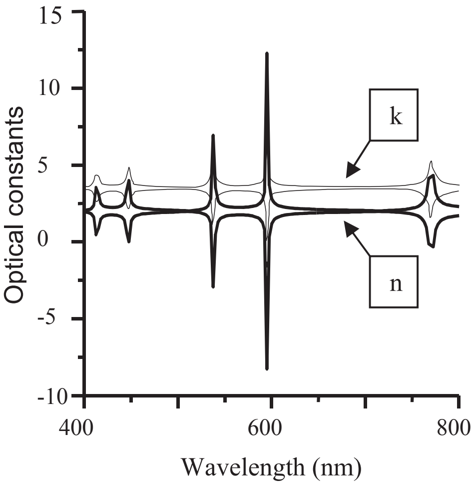

Fig.7: metallic film index (min and max values) determined from curves given in figure 6, assuming 0.2% relative uncertainty on reflectance values.

This method was applied to determine the complex refractive index of hafnium opaque layers manufactured with ionic assistance at depositions rates 0.1 and 0.4 nm / s. In both cases, the metallic layers were over coated with HfO_2 dielectric layers. Results are given in Fig. 8 and 9. As one can see, the change of the deposition rate mainly modifies the extinction coefficient.

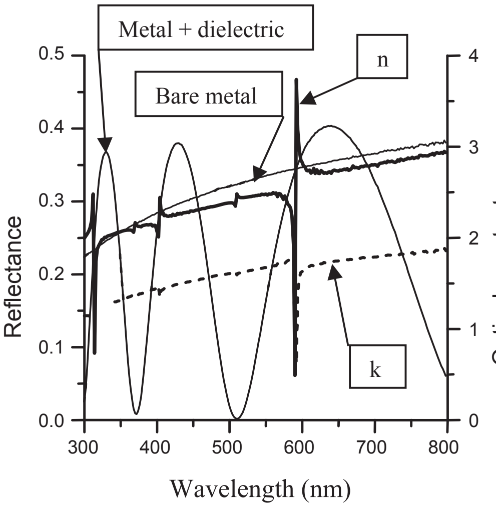

Fig. 8: Reflectance measurements and index determination for an opaque hafnium film manufactured with Ion Plating at deposition rate 0.1 nm / s.

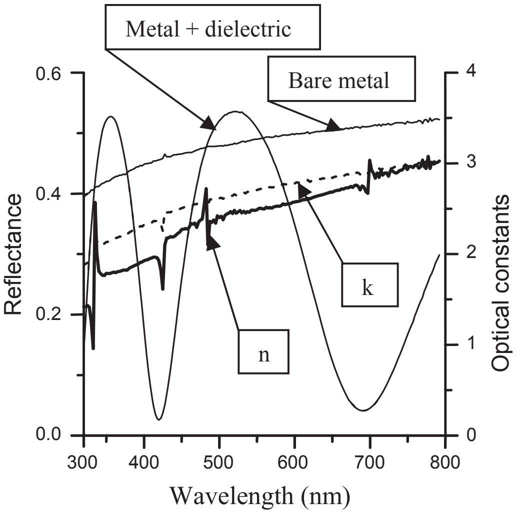

Fig. 9: Reflectance measurements and index determination for an opaque hafnium film manufactured with Ion Plating at deposition rate 0.4 nm / s.

In addition to these results it would be of interest to characterize not only opaque but also semi transparent films. Indeed, we need thin semi transparent layers to design light absorbers and we know that metallic film index strongly depends on the thickness at the early beginning of the deposition. In that case, we need to determine not only the index but also the thickness of the layer, which requires at least three independent measurements. For this purpose, we can use both reflectance and transmittance measurements. However, in the case of Hf semi-transparent films, we could measure an increase of the potential transmittance (T/1-R) after the deposition of the dielectric film while this quantity should remains constant while adding absorption free layers. This phenomenon is probably due to a partial oxidation of the metallic film during the deposition of the dielectric film, which reduces the absorption of the coating. As a consequence, we did not succeed to correctly characterize semi transparent films and we assumed that the metal index determined for opaque layers is valid for any thickness.

5 MANUFACTURING OF Hf-SiO_2 LIGHT ABSORBERS

The main difficulty concerning manufacturing is to deposit the required thickness for each layer. Indeed, since the goal of a light absorber is to cancel reflectance, any thickness error tends to increase reflectance and therefore, can rapidly reduce the coating efficiency. To address this problem, two thickness monitoring systems are at our disposal in the Ion Plating deposition chamber. The first one is a classical quartz crystal monitoring system. This system permits to measure independently the mechanical thickness of each layer. The second system is an optical monitoring system that permits a real time measurement of the coating transmittance. In that case the monitoring signal gives a measurement of the optical thickness of the layers. More over, this signal depends on the thickness of all the layers that are already deposited. As a result, the thickness error of any layer linked to the thickness errors of previous layers.

Better results were obtained using optical monitoring. However, as mentioned previously, the coating design starts with a first opaque metallic layer and this layer cancels transmittance so that optical monitoring cannot be used any more. To allow the optical monitoring of the following layers, a new test glass must be placed in the chamber, which requires to open the vacuum chamber after the deposition of the opaque layer. (Notice that in the case of quartz crystal monitoring coatings can be manufactured within a single deposition run)

In the case of dielectric layers, we used the transmittance turning points as stop criterion. For this purpose, optical monitoring is performed at a wavelength for which the end of the deposition corresponds to a turning point. For metallic layers, this criterion cannot be used since transmittance is always decreasing. Consequently, we simply stop the deposition when the transmittance reaches its predicted value for the monitoring wavelength. For more facility this wavelength is the monitoring wavelength used for the previous dielectric layer, as illustrated in Fig. 10.

Monochromatic and broad band light absorbers were manufactured with this monitoring process. Fig.11 gives the measured reflectance of a monochromatic light absorber for wavelength 852 nm. This coating was developed for the space atomic clock PHARAO. The design contains 6 layers and must operate at normal and oblique incidence, between 0 and 45 degrees. In that case the lack of knowledge concerning semi transparent film index can be compensated by layer thicknesses since only one wavelength is involved. The result is a reflectance level lower than 0.1 % at 852 nm.

The measured reflectance for a broad band coating is given in Fig. 12. This design contains only 4 layers for a reflectance level lower than 1% from 400 to 1200 nm. In that case an accurate index determination for semi transparent metallic layer is required improve the coating efficiency and reach for example a reflectance level of 0.1 %. Indeed, by the mean of thickness optimization, we can improve the result at some wavelengths only but not simultaneously on the whole spectral range.

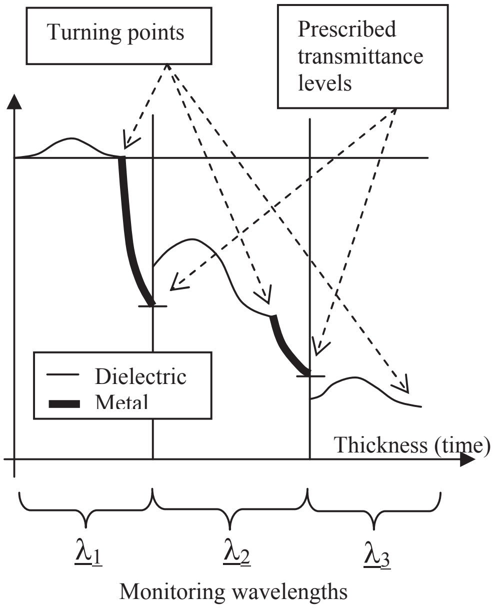

Fig. 10: Typical monitoring signal for layers deposited after the metallic opaque layer. Dielectric layers are stopped at turning points and metallic layers at prescribed transmittance levels.

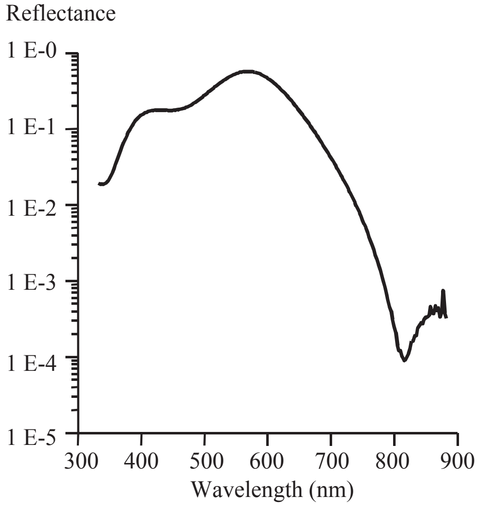

Fig. 11: Measured reflectance of a 6-layer monochromatic design at 852 nm

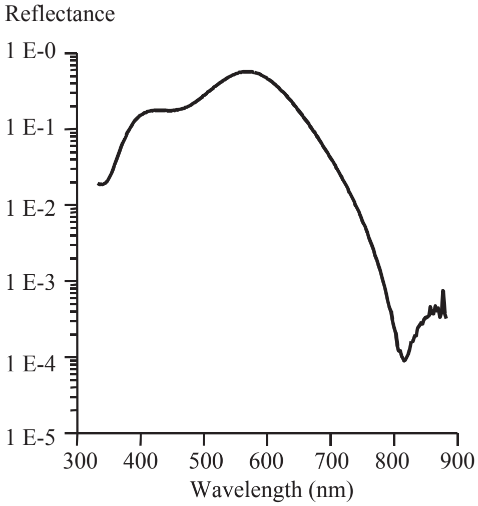

Fig. 12: Measured reflectance of a 4-layer broad band design.

6 ENVIRONMENTAL TESTS

Some of the samples we manufactured were tested at the Centre National d'Etudes Spatiales to evaluate their mechanical and climatic characteristics.

Samples suffered the following tests:
- 40°C, 90% relative humidity, during 24 hours.
- 4 thermal cycles between -50 and +50°C.
- 10 air / vacuum transitions.
- 80 thermal cycles between -35 and + 35 °C.
- adherence tests

At the end of these tests, no degradation was observed on coatings and after measurement, we could also observe no modification of their optical properties.
However, it must be mentioned that these samples where manufactured in a single deposition run using quartz crystal monitoring. Similar tests were performed on samples manufactured with optical monitoring. As mentioned in the previous section, this kind of monitoring requires to open the vacuum chamber during the manufacturing process. In that case, some samples showed poorer adherence characteristics.

7 CONCLUSION

In order to improve their mechanical and climatic resistance, we have shown that metal-dielectric light absorbers could be manufactured with a high energy deposition process, in our case Ion Plating Process. A great advantage of this process, for the manufacturer's point of view, is that, using Hf for metallic layers, no modification of the deposition chamber is required to manufacture either Hf-SiO_2 light absorbers or HfO_2-SiO_2 dielectric coatings.
In comparison with our previous results, optical efficiency is equivalent but mechanical and climatic characteristics are greatly improved since they are now compliant with space requirements.
However, several points still need to be improved. The first one concerns the index determination for semi transparent Hf films. The second one is linked to the monitoring process. Optical monitoring gives better optical properties, but requires to open the vacuum chamber during manufacturing, which results in poorer mechanical properties.
One solution that can help in both cases is to develop an optical monitoring system that works simultaneously upon reflection and transmission. Such a system should allows the index determination while keeping samples inside the vacuum chamber. It should also allows the manufacturing in a single step while improving the capabilities of optical monitoring.

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