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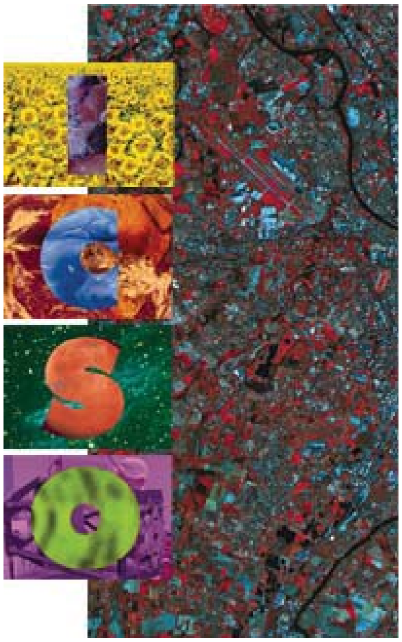

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THIN FILM OPTICAL COATINGS FOR THE ULTRAVIOLET SPECTRAL REGION

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ABSTRACT - *The applications and innovations related to the ultraviolet field are today in strong growth. To satisfy these developments which go from biomedical to the large equipment like the Storage Ring Free Electron Laser, it is crucial to control with an extreme precision the optical performances, in using the substrates and the thin film materials impossible to circumvent in this spectral range. In particular, the reduction of the losses by electromagnetic diffusion, Joule effect absorption, or the behavior under UV luminous flows of power, resistance to surrounding particulate flows... become top priority which concerns a broad European and international community.*

Our laboratory has the theoretical, experimental and technological tools to design and fabricate numerous multilayer coatings with desirable optical properties in the visible and infrared spectral ranges. We have extended our expertise to the ultraviolet. We present here some results on high reflectivity multidielectric mirrors towards 250 nm in wavelength, produced by Ion Plating Deposition. The latter technique allows us to obtain surface treatments with low absorption and high resistance.

We give in this study the UV transparent materials and the manufacturing technology which have been the best suited to meet requirements.

Single UV layers were deposited and characterized. HfO_2/SiO_2 *mirrors with a reflectance higher than 99% at 300 nm were obtained. Optical and non-optical characterizations such as UV spectrophotometric measurements, X-Ray Diffraction spectra, Scanning Electron Microscope and Atomic Force Microscope images were performed.*

1 – INTRODUCTION

The aim is to design and realize high-quality and high-reflectivity UV coatings. Concerning the properties which define "high-quality" films, we consider low absorption in the wavelength range of interest, smooth interfaces with low levels of light scattering, high laser damage thresholds and films densities approaching that of the bulk material (in order to prevent absorption of water vapor when exposed to atmosphere). Various Physical Vapor Deposition (PVD) technologies may be used. However film porosity occurs when the depositing atoms arrive at the substrate with a relatively low energy ($\triangleright$ 0.1 eV). This happens by Electron Beam Deposition (EBD). Therefore, we have to use Ion Assisted Deposition (IAD) [Leh 91, Alv 99], Plasma Ion Assisted Deposition (PIAD) [Thi 98], Ion Beam Sputtering (IBS) [Pon 87] or Ion Plating (IP). IAD and PIAD facilities bombard the substrate with energetic ions (50-100 eV) from an auxiliary ion source, whereas during IP deposition, ions are accelerated in an electric field (5-100 eV) towards a negatively charged substrate. This latter technique has been used in our laboratory and is reported here.

IP process allows us to get advantages such as good adhesion between film and substrate (due to the plasma etching before evaporation), high density of the film (which could reach the bulk value), hardness, uniform coating (concerning thickness uniformity along the sample and homogeneity in z axis of the coating), high deposition rate (typically between 10 and 12 Å/s) and substrate heating during coating process (> 250°C). Previous authors have reported that some oxide coating materials in evaporated IP thin films are good candidates for UV applications [Wal 93]. We present here high-reflectivity and degradation resistant interference multilayer coatings in the UV spectral region with hafnia and silica combination.

2 - FABRICATION OF UV COATINGS BY ION PLATING

The Reactive Ion Plating System employed is a Balzers BAK 800. This IP set-up is assisted with a specially adapted UV in-situ optical monitoring device to control the multilayer thickness with required accuracy and sensitivity. This control is based on the real-time calculation of the derivative of transmission versus time. The experimental set-up is described on figure 1. An electron beam gun is used to evaporate the materials. Base pressure is approximately 5.10^{-7} Torr and deposition pressure is about 10^{-4} Torr when oxygen is introduced to oxidize evaporants. A plasma arc (> 50A) is produced between the plasma chamber and the crucible while a bias voltage is applied between the crucible and the substrate holder ($V^+ - V^- > 70V$). Therefore ions originating from the evaporated materials (M^+) or from the reactive gas species (Ar^+, O_2^+…) are accelerated towards the substrate during the deposition process. The plasma allows us to densify coating by increasing the packing density of the films. The silicon and metal hafnium starting evaporation materials were prepared in granule form by Balzers Materials Company.

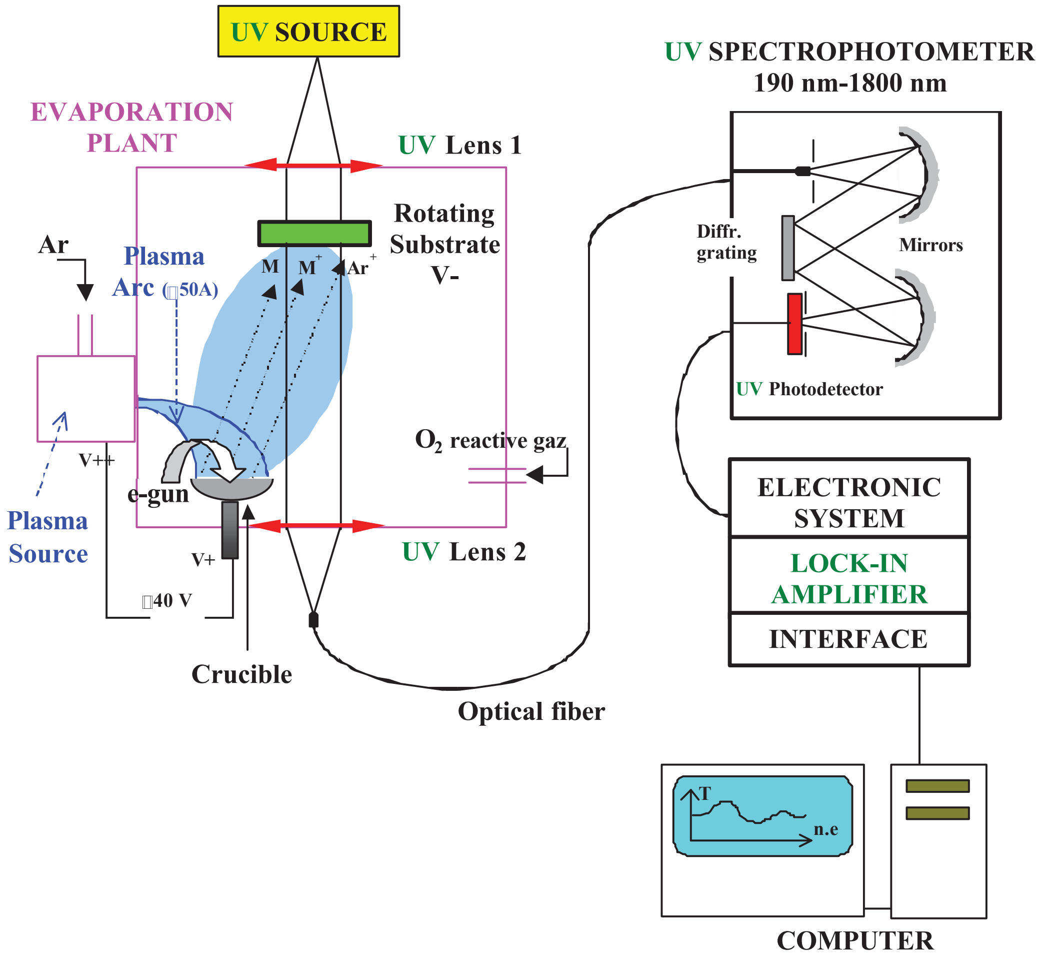


Fig. 1 : Experimental set-up.

3 - SPECTRAL MEASUREMENTS RESULTS

Spectrophotometric measurements are carried out by a Lambda 18 Perkin Elmer 185-800 nm. A V-W attachment is added for measuring high reflectance levels. Accuracy is around ± 0.25%.

3.1 - Substrates

Transmittances of bare substrates are plotted on figure 2. We present here spectral curves from UV-B16® (Corning), Suprasil® (Heraeus) and UV-Silica. Suprasil 1 and 2 are samples coming from 2 different batches. We clearly observe the cut-off wavelength of each substrate. Currently, we use UV-Silica EQ 96 (fused silica) substrates for our single layers and mirrors at 300 nm. However, for coatings towards 200 nm, we will use Suprasil substrates.

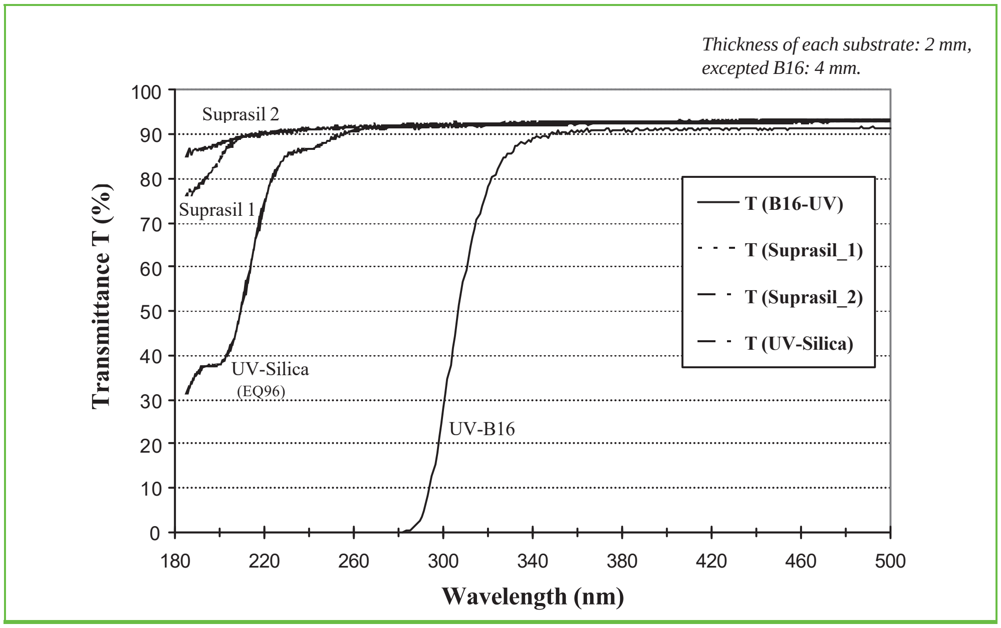


Fig. 2 : Transmittance of bare substrates.

3.2 - SiO_2 and HfO_2 single layers

Investigations on single layers enable us to evaluate thin film properties (refractive index, extinction coefficient, structure, and film density) in function of deposition process parameters in order to find parameter set for producing high-quality multilayer coatings.

In the following paragraph, Tc, Rc and Lc will be respectively transmittance, reflectance and losses (deduced from the relationship: Lc = 100% - Rc - Tc) from the coating only (i.e. the substrate parameter is removed). Besides H and L will be respectively high and low index quarter-wave optical thickness (QWOT) layers. Figure 3 shows transmittance, reflectance and losses curves of a 350 nm silicon oxide single layer ($6\lambda/4$ optical thickness at $\lambda = 350$ nm), by IP. We measure very low levels of losses, even in the UV-range. Thus SiO_2 is suitable as low refractive index material for producing HR-mirrors down to 200 nm wavelength.

Spectral measurements of a 210 nm hafnium oxide single layer (6H optical thickness at 300 nm) by IP, are plotted on figure 4. The measured λ_c cut-off wavelength about 230 nm is in good agreement with the well-known gap energy of HfO_2 at 5.4 eV. Hafnia has relatively low levels of losses down to 230 nm and hence can be selected as high refractive index material for manufacturing multilayer mirrors at 300 nm and 250 nm wavelengths.

Beside this optical behavior, this material is also suitable for low stress application. The low tensile stress of hafnia is useful to compensate compressive stress of silica in multilayer coating [Zöl 96].

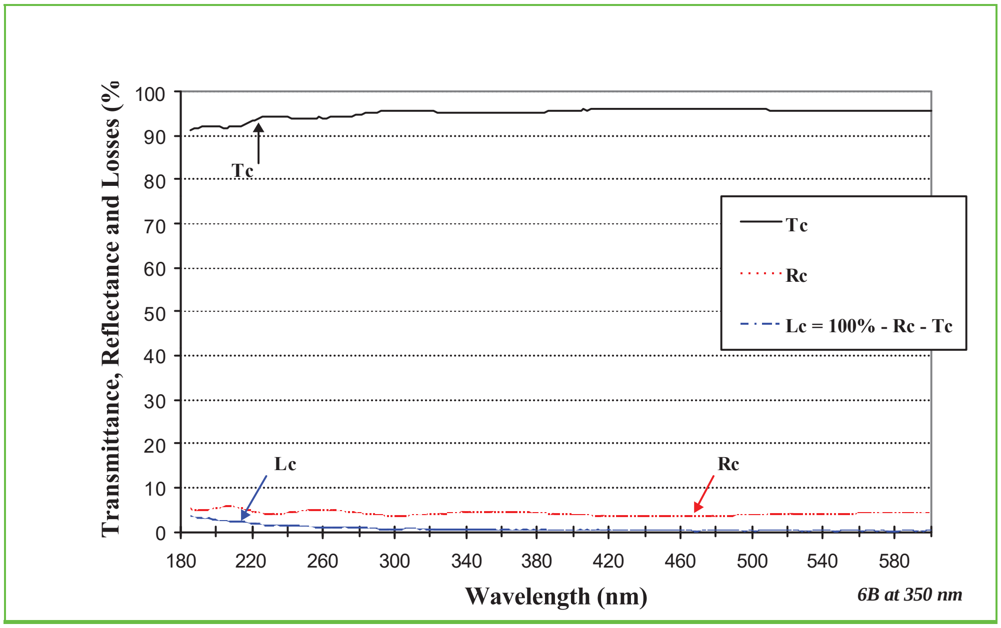


Fig. 3 : Transmittance, reflectance and losses of a 350 nm SiO_2 single layer by IP.

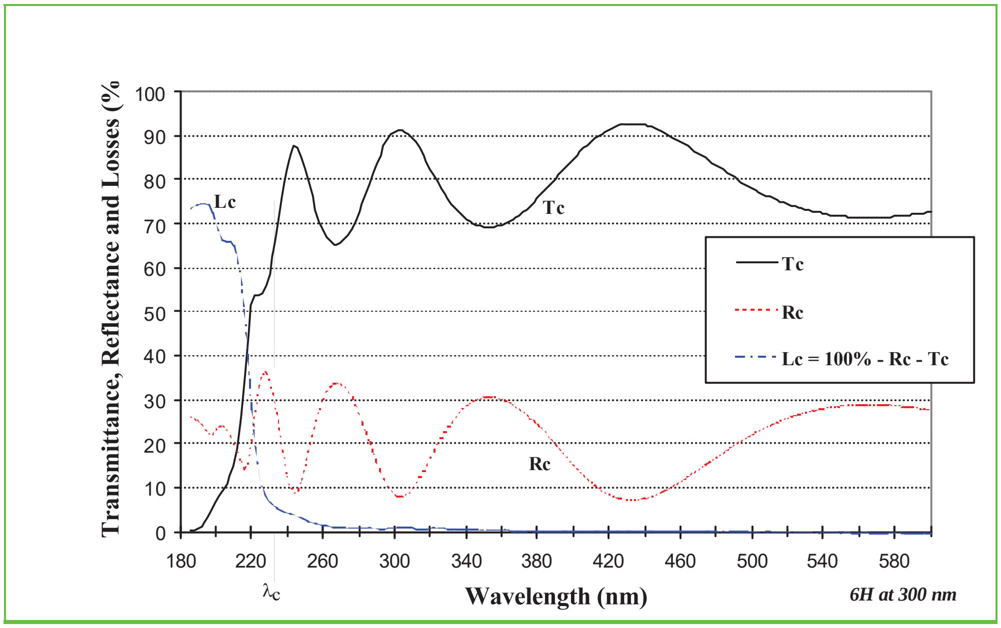


Fig. 4 : Transmittance, reflectance and losses of a 350 nm HfO_2 single layer by IP.

3.3 - Thin film HfO_2 refractive index and extinction coefficient

Optical constants are determined by numerical treatment to fit calculated data to experimentally measured spectral curves. The refractive index *n* dispersion of HfO_2 film deposited by IP is shown on figure 5. Ion Plating results in dense films with index close to that from the bare substrate. The extinction coefficient *k* of HfO_2 film deposited by IP is given on figure 6. The increasing value of k below 230 nm is due to the HfO_2 energy gap.

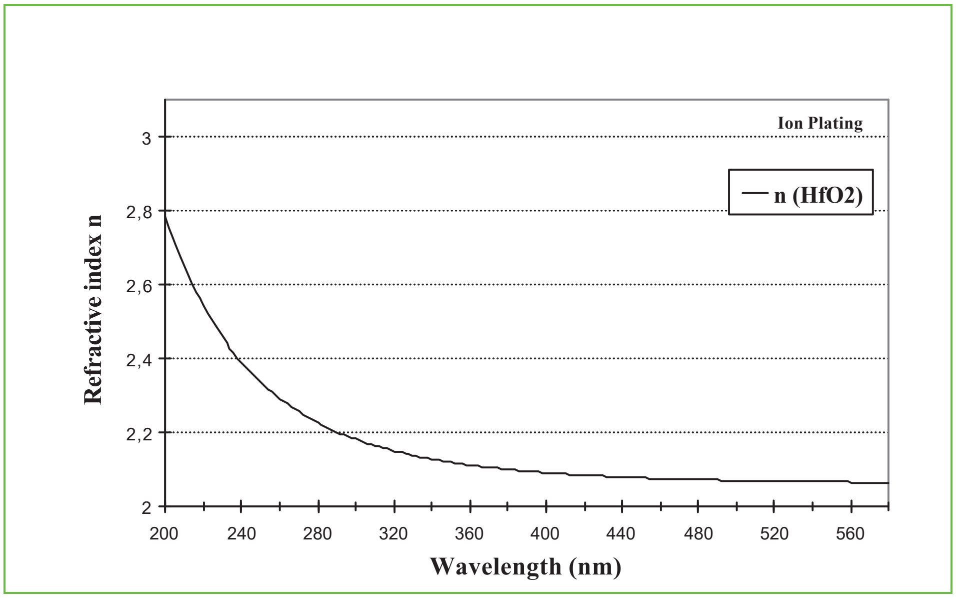


Fig. 5 : Refractive index of HfO_2 film deposited by IP.

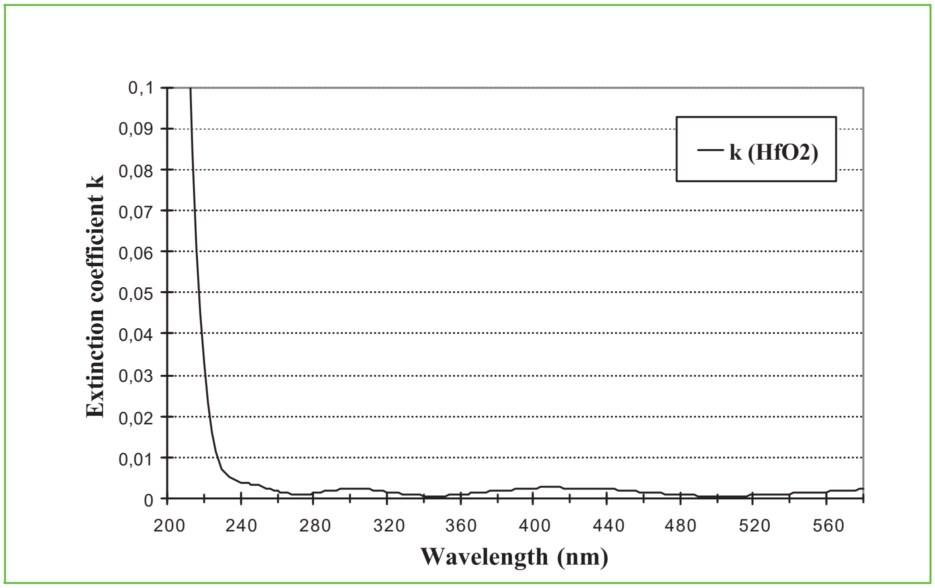


Fig. 6 : Extinction coefficient of HfO_2 film deposited by IP.

3.4 - High Reflecting-Mirrors deposited by IP technology

High-reflecting mirrors are performed with the alternated hafnia/silica material combination. "Substrate / $(HL)^{11}H$ / air" conventional mirror design is employed, where H and L are respectively high and low index QWOT layers. Reflectance R, transmittance T and losses L, deduced from the relationship: $L = 100\% - (R + T)$, of the global component (i.e. substrate and coating included) are plotted on figure 7 in λ-range 185-600 nm. The 23-layer stack total thickness is about 1.1 µm. Reflectance is higher than 99% and losses are lower than 1% at the wavelength of 300 nm. Besides, maximum reflectance is found for wavelength values ranging between 275 and 320 nm.

Coatings produced by IP process at high substrate temperature show very steady optical properties with no relevant spectral shift between air and vacuum due to water adsorption or desorption.

This is an evidence of high-density layers. Several depositions were performed to check the experimental repeatability.

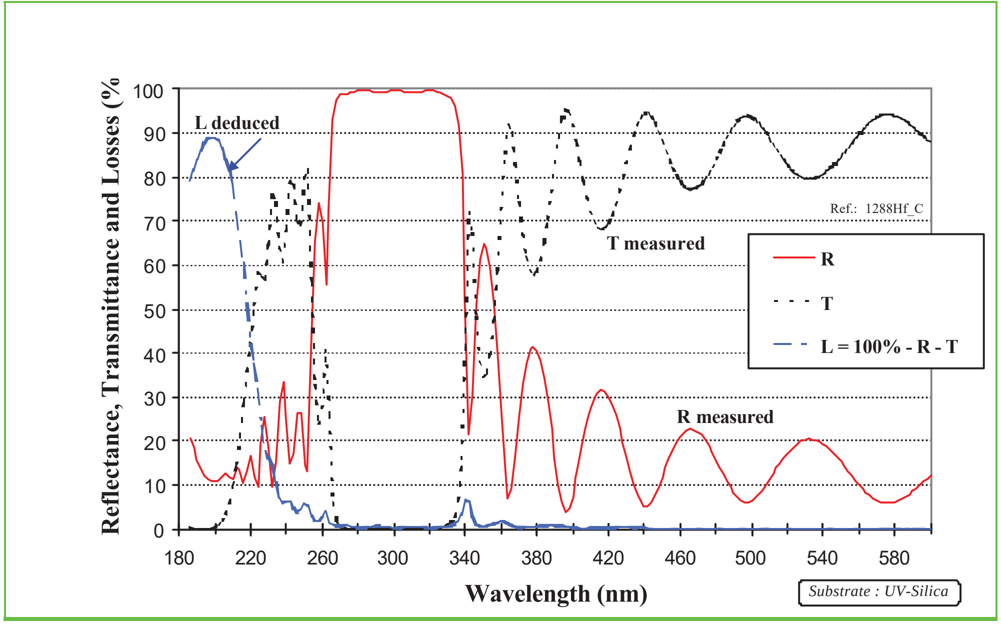


Fig. 7 : Measured reflectance, transmittance and losses from a 23-layer HfO_2/SiO_2 IP mirror centered at 300 nm wavelength.

4 - CHARACTERIZATIONS OF UV-COATINGS

4.1 - X-Ray Diffraction measurements

X-Ray Diffraction (XRD) spectra are obtained with Philips MPD and MRD systems and the CuK_{α} radiation at 1.5405 Å. Figure 8 presents XRD scans in Bragg-Brentano reflection geometry (θ-2θ) from a HfO_2 single layer (on the left side) and from a HfO_2/SiO_2 mirror (on the right side), both deposited by IP.

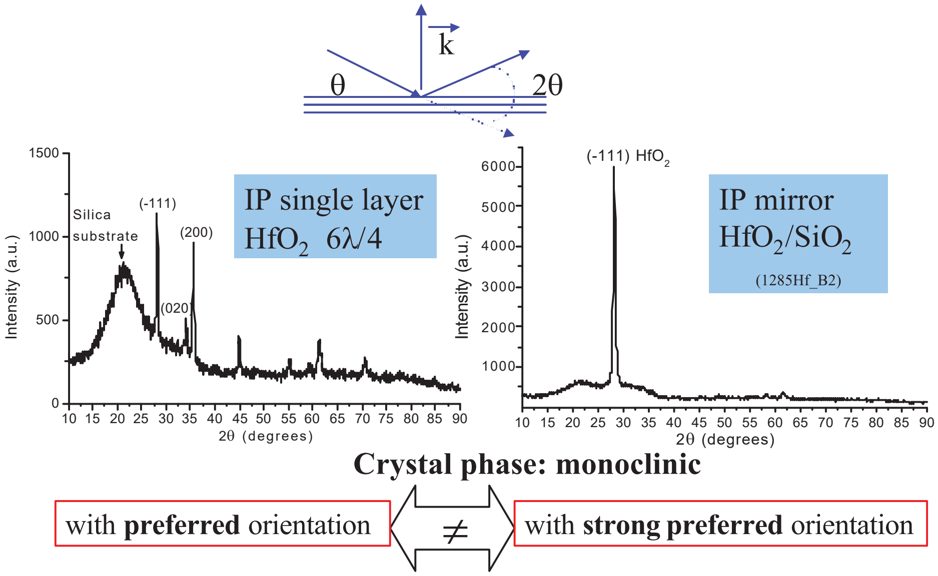
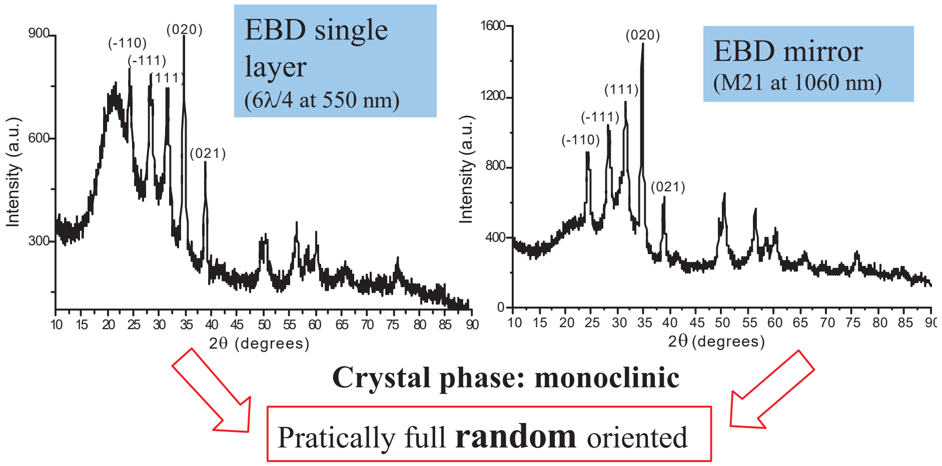


Fig. 8 : XRD (θ-2θ) spectra of a single layer and a mirror deposited by IP.

A x-ray amorphous spectrum is found for the fused silica substrate while a well-defined polycrystalline structure appears for both coatings. The spectra show a monoclinic crystalline phase with a preferred orientation for the single layer and a strong preferred orientation (-111) for the mirror. In fact, the diffraction scan of the mirror exhibits an intense peak at 2θ = 28.3° due to the crystal planes of the monoclinic phase [Joi 96]. The scan of the single layer presents several supplementary peaks, all caused by monoclinic phase crystal planes.

As a comparison, figure 9 shows XRD patterns from a single layer and a mirror deposited by EBD. Spectra exhibit a monoclinic crystalline phase practically full random oriented.

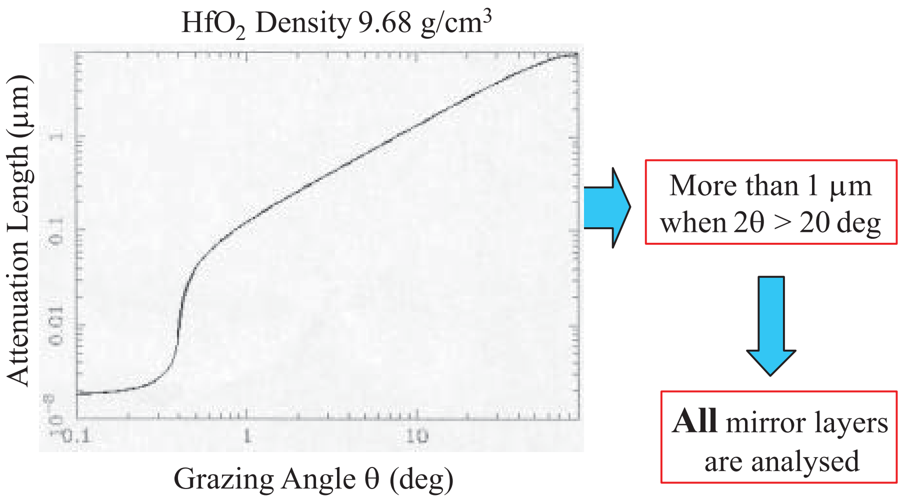


Crystal phase: monoclinic

Pratically full **random** oriented

Fig. 9 : XRD (θ-2θ) analysis of a single layer and a mirror deposited by EBD.

The figure 10 shows X-Ray Penetration Depth of a HfO_2 film. It proves that all mirror layers are analyzed by XRD. As the x rays penetrate through all the film, the XRD spectra average the crystal structure of the whole film thickness. The HfO_2 layers within the mirror present a columnar grain structure, as shown on figure 11.



More than 1 μm when 2θ > 20 deg

All mirror layers are analysed

Fig. 10 : X-Ray Penetration Depth of HfO_2 film.

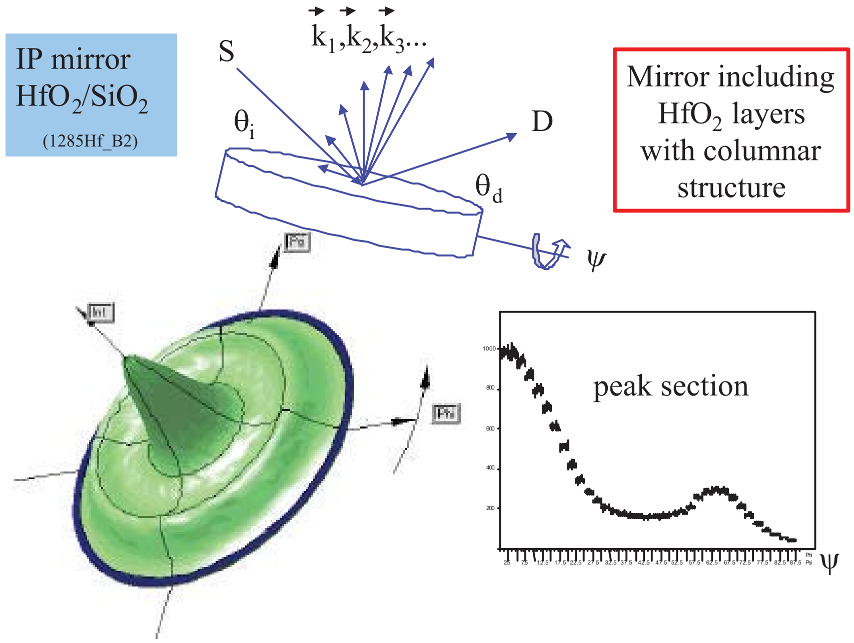


Fig. 11 : XRD – Texture.

4.2 - Annealing

In order to improve mirror quality, we have studied the influence of an air annealing at 400°C for 8 hours. Figure 12 shows the influence of the annealing on a HfO_2/SiO_2 mirror by IP. We observe an increasing of the reflectance and a decreasing of the losses after annealing especially below 300 nm. In the same time, the (-111) preferred orientation of the diffraction peak is enhanced.

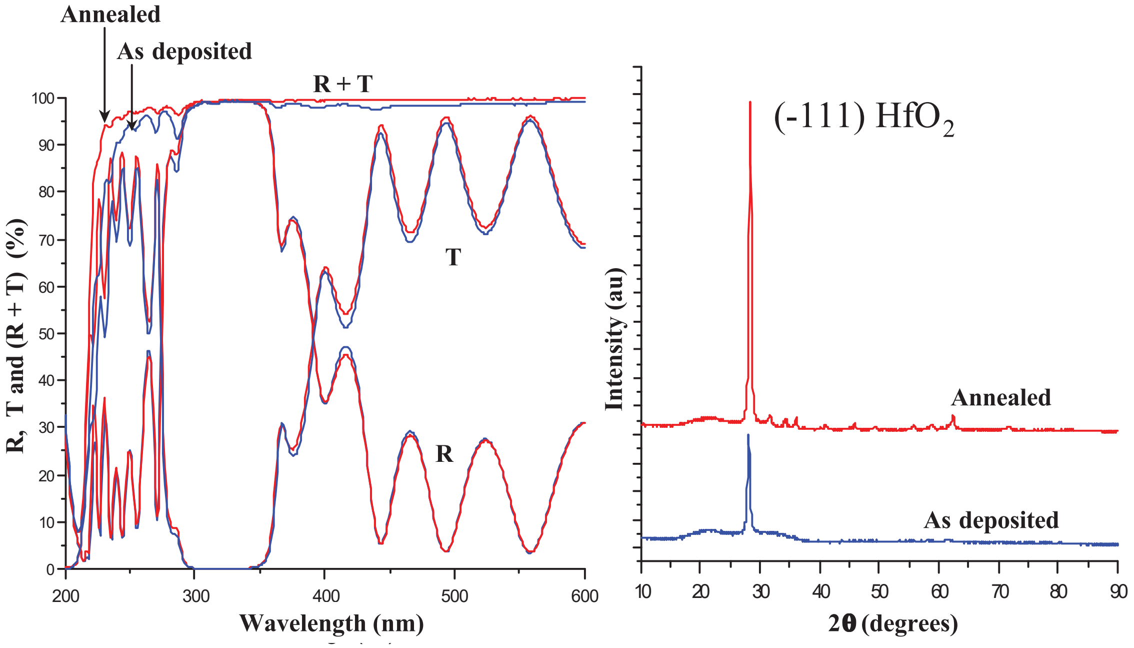


Fig. 12 : Optical and XRD spectra of IP HfO_2/SiO_2 mirror before and after annealing in air at 400°C for 8 hours.

4.3 - Atomic Force Microscopy

Atomic Force Microscopy (AFM) images are stemmed from a TopoMetrix TMX 2000 System 3.05 operating in contact mode with a silicon nitride tip. This facility investigates film surface topography over a 5 µm by 5 µm or a 1 µm by 1 µm area. AFM images show a very smooth surface upon a HfO_2 single layer by IP (figure 13). The calculated root-mean-square (rms) surface roughness is very low (0.3 nm), not so far from the bare substrate (0.2 nm). Smooth surface and low roughness are preserved in the 23-layer mirror (figure 14).

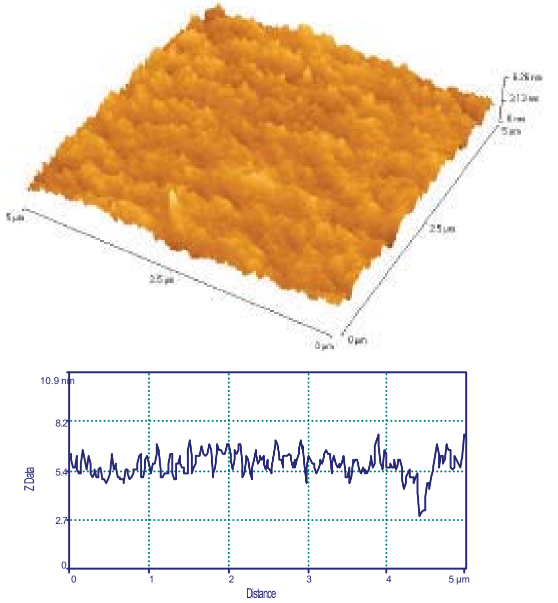


Fig. 13 : IP HfO_2 single layer AFM image (5 x 5 μm^2 mapping) and height profile.

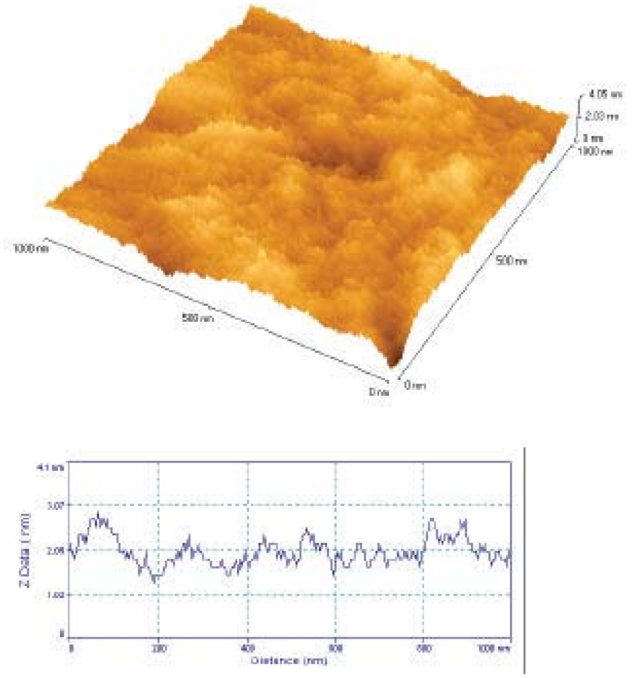


Fig. 14 : IP HfO_2/SiO_2 mirror AFM image (1 x 1 μm^2 mapping) and height profile.

4.4 - Scanning Electron Microscopy

The device is a Philips SEM 515 equipped with Energy Dispersive X-Ray spectroscopy (EDX). Scanning Electron Microscopy micrographs are obtained from a mirror manufactured by IP (figure 15). Hardness of IP layers is confirmed by the sharp break of a fractured film cross-section.

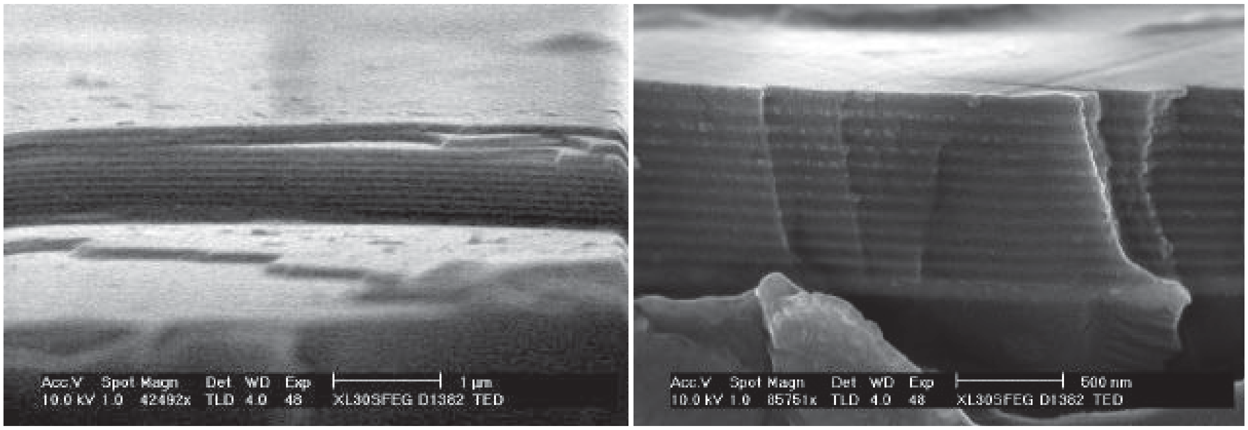


Fig. 15 : Cross-sectional SEM secondary electron image of IP HfO_2/SiO_2 mirror (left: 1µm-scale; right: 500 nm-scale).

5 – CONCLUSION

It has been shown that Ion Plating process has succeeded in manufacturing high-reflectivity and resistant degradation coatings in the UV spectral region. Single layers of silicon and hafnium oxides have been deposited by IP upon fused silica. The very low optical losses of both materials allow us to perform dense UV interference coatings. Multilayer HfO_2/SiO_2 mirrors with reflectance higher than 99 % at 300 nm wavelength have been performed.

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