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# **Role of SiC substrate surface on local tarnishing of deposited silver mirror stacks**

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## **Abstract**

The role of the SiC substrate surface on the resistance to the local initiation of tarnishing of thin-layered silver stacks for demanding space mirror applications was studied by combined surface and interface analysis on model stack samples deposited by cathodic magnetron sputtering and submitted to accelerated aging in gaseous H<sub>2</sub>S. It is shown that suppressing the surface pores resulting from the bulk SiC material production process by surface pretreatment eliminates the high aspect ratio surface sites that are imperfectly protected by the SiO<sub>2</sub> overcoat after the deposition of silver. The formation of channels connecting the silver layer to its environment through the failing protection layer at the surface pores and locally enabling H<sub>2</sub>S entry and Ag<sub>2</sub>S growth as columns until emergence at the stack surface is suppressed, which markedly delays tarnishing initiation and thereby preserves the optical performance. The results revealed that residual tarnishing initiation proceeds by a mechanism essentially identical in nature but involving different pathways short circuiting the protection layer and enabling H<sub>2</sub>S ingress until the silver layer. These permeation pathways are suggested to be of microstructural origin and could correspond to the incompletely coalesced intergranular boundaries of the SiO<sub>2</sub> layer.

Keywords: Mirror layers; protection layers; silver; silicon dioxide; atmospheric corrosion; tarnishing mechanism; surface analysis; ToF-SIMS; XPS; AFM

## Introduction

Space telescopes are equipped with mirrors consisting of thin-layered stacks including a reflecting metallic layer and a protection dielectric layer [1-4]. Silver is used as reflecting layer for its highest reflectivity in the visible and lowest emissivity in the infrared [5,6] while  $\text{SiO}_2$  [7,8]  $\text{Al}_2\text{O}_3$  [9,10]  $\text{Si}_3\text{N}_4$  [11,12] or  $\text{SiN}_x$  [13-15] overcoats have been developed for confinement of the silver layer and protection from degradation in earth atmosphere. Despite this protection, silver space mirrors are susceptible to local degradation by tarnishing during indoor qualification and storage phases, limiting their long-term environmental durability after satellite assembly and before launching.

Silver sulfide ( $\text{Ag}_2\text{S}$ ) is the predominant tarnish product of silver found in indoor atmospheres as a result of corrosion by organosulfur compounds or  $\text{H}_2\text{S}$  pollutants [16-22] and  $\text{H}_2\text{S}$  is the most used corrosive agent to study silver sulfidation in laboratory [23-27]. It has been shown that a  $\text{H}_2\text{S}$  concentration as low as 0.2 ppb is sufficient to initiate silver sulfidation [28]. Degradation studies performed on space silver mirrors mostly addressed the efficiency of the protection layer and the effect of environmental aging on the optical properties [10,15,25,29-31], and more seldom their tarnishing mechanism [32-35].

In a recent work [35], we studied model stack samples consisting of thin silver layers covered by  $\text{SiO}_2$  coatings deposited by cathodic magnetron sputtering on SiC, a substrate already in use in light weight all-SiC telescopes assigned to scientific or earth observation missions. These stacks were submitted to accelerated aging in  $\text{H}_2\text{S}$  gas and studied by combined surface and interface analysis using Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS) and Time-of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). It was shown that local tarnishing is initiated by the formation of  $\text{Ag}_2\text{S}$  columns emerging above the stack surface.  $\text{Ag}_2\text{S}$  growth was promoted at high aspect ratio defects (surface pores) of the SiC substrate as a result from a failing protection by the covering  $\text{SiO}_2$

layer. It was proposed that, in the failure sites, permeation channels connect the silver layer to its environment through the deposited protection layer, like observed with silicon dioxide barrier layers on polymer substrates [36-38], and would enable local H<sub>2</sub>S entry and Ag<sub>2</sub>S growth until eruption at the stack surface.

Here we bring new insight on the improved local resistance to tarnishing observed on a SiC substrate pretreated by chemical vapor deposition so as to suppress the high aspect ratio defects (surface pores) promoting degradation. Model stack samples consisting of thin silver mirror layers covered by SiO<sub>2</sub> overcoats with adhesion interfacial layers were analyzed by AFM, ToF-SIMS and XPS before and after accelerated ageing in gaseous H<sub>2</sub>S environment in order to study the beneficial effect of the SiC substrate surface pretreatment.

## Experimental

Two types of Boostec® SiC samples (10 x 10 x 1.5 mm) were purchased from Mersen. The samples hereafter denoted SiC were specified to have an optical surface polish with a nominal rms roughness of 4.4 nm. Those hereafter denoted SiC+CVD had one face pretreated by chemical vapor deposition (CVD) at Mersen so as to deposit a high purity SiC layer, ~200 μm thick, in order to suppress surface pores as specified by Mersen. Their nominal rms roughness was 1.2 nm after surface polish.

All layers in the stacks were prepared by cathodic magnetron sputtering using the PACA2M deposition platform installed in clean room at CILAS Marseille [39-41]. The platform is equipped with an *in situ* broadband optical monitoring of the optical performance and deposited thickness [40]. Base pressure and working pressure during deposition were of 10<sup>-7</sup> mbar and 10<sup>-3</sup>-10<sup>-2</sup> mbar, respectively. The deposited stacks consisted of (i) an adhesion interlayer of metallic nickel and chromium, about 10 nm thick, (ii) a silver mirror layer, 100

to 200 nm thick, (iii) an adhesion interlayer<sup>a</sup>, and (iv) a dielectric protection layer of silicon dioxide, from 140 to 200 nm thick depending on the targeted optical performance. Prior to deposition, the target cathode surfaces were pretreated by Ar sputtering in order to minimize their surface contamination. After preparation the stack samples were taken out to clean room atmosphere and enclosed in membrane boxes under ambient pressure before shipping to CNRS-Chimie ParisTech for surface and interface analysis and accelerated aging tests.

Accelerated atmospheric aging was performed in gaseous H<sub>2</sub>S selected as most corrosive indoor atmospheric agent of silver. The accelerated aging tests were performed at 1000 mbar H<sub>2</sub>S and 75°C for 24, 48 and 96 h, like previously described [35]. The sulfurized samples were transferred through air for surface analysis.

AFM imaging was performed in intermittent contact (tapping<sup>®</sup>) mode in air, using an Agilent 5500 microscope. A silicon cantilever with a resonance frequency in the range 200-400 kHz and a force constant in the range 25-75 Nm<sup>-1</sup> was employed. The silicon tip had a nominal radius < 10 nm. Sets of images were recorded over areas of 50 × 50 μm<sup>2</sup>, 20 × 20 μm<sup>2</sup> and 5 × 5 μm<sup>2</sup> for each sample at different surface locations to ensure for surface homogeneity. Densities were estimated from the local images recorded over 50 × 50 μm<sup>2</sup> and 20 × 20 μm<sup>2</sup> areas and extrapolated to 1 cm<sup>2</sup>.

ToF-SIMS analysis was performed at a pressure of approximately 10<sup>-9</sup> mbar with an IonTof 5 spectrometer. For depth profiling analysis, a pulsed 25 keV Bi<sup>+</sup> primary ion source delivering a target current of 1.2 pA over a 100 × 100 μm<sup>2</sup> area was interlaced with sputtering performed with a 2 keV Cs<sup>+</sup> ion gun delivering 100 nA of target current over a 300 × 300 μm<sup>2</sup> area. These conditions were reproduced for all samples allowing direct comparison of the relative secondary ions intensities. For chemical imaging, a pulsed 25 keV Bi<sup>+</sup> primary ion source was employed, delivering 0.15 pA of current over a 100 × 100 μm<sup>2</sup> area analyzed with

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<sup>a</sup> Thickness, material and chemical composition of this interlayer cannot be disclosed

a resolution of about 150 nm. Data acquisition and post-processing analyses were performed with the Ion-Spec software.

XPS analysis was performed at an operating pressure of about  $10^{-9}$  mbar with a VG ESCALAB 250 spectrometer calibrated against the reference binding energies (BE) of clean Cu (932.6 eV), Ag (368.2 eV) and Au (84 eV) samples. Survey spectra and high resolution spectra of the C 1s, O 1s, Si 2p, S 2p and Ag 3d core level regions were collected at 90° take-off angle and with a pass energy of 100 and 20 eV, respectively, using an Al K $\alpha$  monochromatized X-ray source ( $h\nu = 1486.6$  eV).. Data processing (peak fitting and decomposition) was performed with the Advantage software provided by Thermo Electron, using a Shirley-type background, component peaks defined by BE, Full Width at Half Maximum (FWHM) and Gaussian/Lorentzian envelopes combined at a fixed ratio of 70/30. BEs of the component peaks were corrected with reference to the C 1s peak for -CH<sub>2</sub>-CH<sub>2</sub>- bonds set at 285.0 eV. Atomic concentration ratios were calculated from the intensities of the component peak assuming a homogeneous semi-infinite material and using the calibrated transmission factors of the spectrometer, Scofield photoionisation cross sections and values of the photoelectron attenuation lengths calculated using the method of Tanuma et al. [42].

## **Results and Discussion**

### ***SiC substrate and stack surface morphology***

Figure 1 shows typical AFM topographic images of the bare substrates and stacks for the SiC and SiC+CVD samples. They confirmed that the surface porosity characterizing the SiC substrate and originating from the material production process is suppressed by the CVD surface treatment like specified by the provider. On the SiC substrate (Figure 1(a,b)), the lateral dimensions (0.5-6  $\mu\text{m}$ ), depth (0.05-0.4  $\mu\text{m}$ ) and density ( $\sim 1.6 \times 10^6 \text{ cm}^{-2}$ ) of the surface

pores remain essentially unchanged after deposition of the stacks, showing that the pores remain incompletely filled and that the surface still exhibits high aspect ratio topographic sites as discussed previously [35]. On the SiC+CVD substrate (Figure 1(d)), the pores have been filled by the deposition of the ~200  $\mu\text{m}$  thick CVD SiC film. The images show the presence of polishing grooves with a local depth reaching 3 nm. This is indicative of the subsequent polishing treatment performed by the provider and suppressing all traces of the initial surface pores that may subsist in case of conformal growth of the CVD film. The measured rms roughness is 0.8 nm, in good agreement with the nominal value of 1.2 nm and significantly lower than that (3.7 nm) measured on the SiC substrate (nominal value of 4.4 nm). At higher magnification, a granular morphology characterizes the surface of the SiO<sub>2</sub> protection layer, both on the SiO<sub>2</sub>/Ag/SiC (Figure 1(c)) and SiO<sub>2</sub>/Ag/SiC+CVD (Figure 1(e,f)) stacks. The grains have lateral dimensions of 50-150 nm on both substrates, as measured from Figure 1(c) and Figure 1(e). This morphology appears compact on both substrates revealing no detectable pores or pinholes of sub-micrometer dimension.

### ***Depth profiling of as-received stacks***

ToF-SIMS elemental depth profiles of the as-received SiO<sub>2</sub>/Ag/SiC and SiO<sub>2</sub>/Ag/SiC+CVD stacks are shown in Figure 2(a) and (b), respectively. The intensities of the selected ions are plotted on a logarithmic scale *versus* sputtering time. Starting from the outer surface, they allow us defining the following five regions (all marked): the protection layer region (using the SiO<sup>-</sup> and <sup>18</sup>O<sup>-</sup> ions), the adhesion interfacial layer I<sub>a</sub>, the silver mirror layer and the adhesion interfacial layer I<sub>b</sub> regions (all three using the Ag<sup>-</sup> ions) and the SiC substrate region (using the SiC<sup>-</sup> and C<sup>-</sup> ions). The I<sub>a</sub> and I<sub>b</sub> interfacial layer regions can also be defined using their respective ions as reported previously [35].

In the protection layer region, the SiO<sup>-</sup> and <sup>18</sup>O<sup>-</sup> ions profiles exhibit plateaus of increasing intensity with in-depth progress on both substrates, confirming on the SiC+CVD



sample the observation made on the SiC sample [35] and suggesting a density of the SiO<sub>2</sub> layer increasing with in-depth progress, i.e. decreasing with on-going deposition from the I<sub>a</sub> interface, independently of the presence of SiC surface pores. In this protection layer region, the ions characteristic for the substrate (SiC<sup>-</sup> and C<sup>-</sup>) and silver layer (Ag<sup>-</sup>) are detected at trace level on the SiC+CVD sample. Carbon contamination during deposition and silicium-carbon combination during analysis can be an explanation for the detection of the SiC<sup>-</sup> and C<sup>-</sup> ions. Silver contamination of the target cathode during deposition of the previous layers could explain the detection of the Ag<sup>-</sup> ions. The presence of Ag in the protective SiO<sub>2</sub> layer could also result from photo-enhanced diffusion during deposition promoted by oxygen adsorption on silver, as previously proposed for a TiO<sub>2</sub> protection layer [43]. Still the pronounced decrease in intensity of these ions measured on the SiC+CVD sample compared to the SiC sample appears to be a direct effect of the suppression of the substrate surface pores, as confirmed by the AFM data, and thus of the channels in the protection layer exposing the underlying silver layer and substrate at the surface pores. This conclusion is also supported by the comparison of the profiles of the Cl<sup>-</sup>, <sup>34</sup>S<sup>-</sup> and CN<sup>-</sup> ions, characteristic of atmospheric contamination by chlorine-, sulfur- and nitrogen-containing pollutants, respectively. Their trace level measured in the protection layer region of the SiC+CVD sample could originate from residual contamination during deposition (except for sulfur which is not detected in the protection layer region). However, the marked increase on the SiC sample is consistent with the presence of penetration pathways (i.e channels), associated with the presence of the substrate surface defects (i.e. pores) and enabling the permeation of the contaminants from the atmosphere [36-38].

Like previously discussed [35], the peak of the Ag<sup>-</sup> ions profile in the I<sub>a</sub> interfacial region is consistent with the formation of a discontinuous adhesion interlayer forming islands [2,13], possibly as a result of silver diffusion during deposition [43] and promoting the

nucleation of a protection layer of decreased permeability [29,32,44]. This peak is also observed on the SiC+CVD sample, however with a much steeper increase at the approach of the I<sub>a</sub> interfacial region. This is consistent with the formation of a sharper interface induced by the suppression of the substrate pores. In the silver layer region, the Ag<sup>-</sup> ions profile exhibit a plateau consistent with the formation of a continuous metallic layer. On the SiC+CVD sample, all other ions drop down in intensity as expected but much more than on the SiC substrate. Again, this is consistent with the suppression of the substrate holes and the associated decrease in roughness. Like in the SiO<sub>2</sub> protection layer region, the extremely low intensity level of the Cl<sup>-</sup>, C<sup>-</sup> and CN<sup>-</sup> ions in the silver layer region is indicative of trace level contamination possibly occurring during deposition.

In the I<sub>b</sub> interfacial region (NiCr), the Ag<sup>-</sup> ions drop down in intensity like expected, which coincides with a peak in the NiCr<sup>-</sup> ions profile (not shown here) [35]. The SiC<sup>-</sup> and C<sup>-</sup> ions increase in intensity until reaching a plateau in the SiC substrate region. Again the intensity increases are steeper on the SiC+CVD sample because of the smoother interface formed after suppression of the substrate pores. In the I<sub>b</sub> interfacial region, peaks are observed in the SiO<sup>-</sup>, <sup>18</sup>O<sup>-</sup>, CN<sup>-</sup>, Cl<sup>-</sup> and <sup>34</sup>S<sup>-</sup> ions profiles which are better defined on the SiC+CVD sample because of the smoother interface on the pore-free substrate surface. They are indicative of contamination of the substrate surface by oxygen, nitrogen, chlorine and carbon prior to the stack deposition. In the substrate region, the Ag<sup>-</sup>, SiO<sup>-</sup>, <sup>18</sup>O<sup>-</sup>, CN<sup>-</sup>, Cl<sup>-</sup> and <sup>34</sup>S<sup>-</sup> ions profiles drop down in intensity as expected but much more markedly on the SiC+CVD substrate. This is further evidence for the suppression of the substrate surface pores.

### ***Improved resistance to Ag<sub>2</sub>S formation***

The XPS survey and Ag 3d core level spectra for the SiO<sub>2</sub>/Ag/SiC and SiO<sub>2</sub>/Ag/SiC+CVD stacks subjected to accelerated aging in H<sub>2</sub>S for 96 h are shown in Figure 3. The survey spectra are characteristic of a silicon dioxide surface contaminated by carbon

and evidence the presence of silver only on the SiC sample (Figure 3(a)). For both samples, the C 1s spectra recorded at high resolution exhibited one major component peak set at 285 eV BE (1.8 eV FWHM) and one minor component peak at  $287.4 \pm 0.1$  eV BE (1.8 eV FWHM) corresponding to  $-\text{CH}_2-\text{CH}_2-$  and C=O and/or O-C=O bonded carbon, respectively, which is typical of oxide thin films exposed to ambient air and contaminated by organic pollutants [45-47]. The high resolution Si 2p spectra could be fitted with one single component peak at  $103.2 \pm 0.1$  BE (1.7 eV FWHM) and the O 1s spectra by one single component peak at  $533.1 \pm 0.1$  eV BE (1.7 eV FWHM), like expected for silicon dioxide [48,49]. The intensity ratio of these components yielded an O/Si atomic ratio of  $1.9 \pm 0.2$  corresponding to the  $\text{SiO}_2$  stoichiometry.

The XP Ag 3d core level spectra show two peaks assigned to the  $3d_{5/2}$ - $3d_{3/2}$  spin orbit doublet. On the SiC sample (Figure 3(a)), the  $3d_{5/2}$  and  $3d_{3/2}$  components are positioned at BEs of 367.8 and 373.8 eV (0.8 eV FWHM), respectively, which does not allow discriminating the Ag(0) metallic state from the Ag(I) oxidized state. However, the Auger parameter  $\alpha'$ , calculated from the kinetic energy of the Ag  $M_{4NN}$  Auger transition (1129.6 eV) and binding energy of the Ag  $3d_{5/2}$  core level, is 724.8 eV, which is in good agreement with values reported for  $\text{Ag}_2\text{S}$  [50-53] and thus shows a Ag(I) oxidation state. The S 2p region for the SiC sample also supports the formation of  $\text{Ag}_2\text{S}$  with its  $2p_{3/2}$ - $2p_{1/2}$  spin orbit doublet positioned at BEs of 160.7 and 161.9 eV, respectively, in good agreement with those reported for silver sulfide [50,52,54-57]. As previously discussed [35], these data characterize the formation of  $\text{Ag}_2\text{S}$  columns emerging at the surface of the  $\text{SiO}_2$  layer and in contact with the conductive silver layer of the stack through the dielectric protection layer.

On the SiC+CVD sample (Figure 3(b)), the high resolution XPS Ag 3d core level region exhibits a signal undetected in the survey spectra because of its low intensity. Two Ag  $3d_{5/2}$ - $3d_{3/2}$  spin orbit doublets are resolved. The  $3d_{5/2}$  and  $3d_{3/2}$  components of the minor

intensity doublet are positioned at BEs of 367.8 and 374.0 eV (1.8 eV FWHM), respectively, in good agreement with those measured on the SiC sample. Consistently, they are also assigned to the formation of Ag<sub>2</sub>S columns emerging at the surface of the dielectric SiO<sub>2</sub> layer, but in trace quantity compared to the SiC sample. The 3d<sub>5/2</sub> and 3d<sub>3/2</sub> components of the major intensity doublet are shifted to higher BE at 369.9 and 375.9 eV (1.8 eV FWHM), respectively, which is assigned to an electrical charging effect, as previously observed on the as-received SiC sample prior to sulfidation [35]. This higher BE Ag 3d doublet is thus assigned to the residual presence of silver also at the surface of the dielectric SiO<sub>2</sub> layer but electrically isolated from the conductive mirror layer, so that there is no compensation of the charge during photoelectron emission. This residual contamination by silver of the surface of the as-received stacks is confirmed by the ToF-SIMS depth profiles that show a peak on the Ag<sup>-</sup> ions in the very first seconds of sputtering (Figure 2(b)). It most likely occurred in the cathodic magnetron sputtering chamber after deposition of the SiO<sub>2</sub> protection layer. In the Ag M<sub>45</sub>NN Auger transition region, the signal was below the detection limit precluding the determination of the Auger parameter  $\alpha'$  and thus the identification of Ag<sub>2</sub>S. Likewise no S 2p<sub>3/2</sub>-2p<sub>1/2</sub> spin orbit doublet could be discriminated from the background on the SiC+CVD sample sulfurized for 96 h, also because of an intensity below the detection limit. Still the sulfidation of these silver surface traces is most likely after accelerated aging in H<sub>2</sub>S for 96 h and proven by ToF-SIMS data presented further on.

The Ag/(Si+O) atomic ratio calculated from the component peak intensities is  $1.8 \times 10^{-2}$  for the SiC sample but only  $0.1 \times 10^{-2}$  for the SiC+CVD sample, demonstrating the markedly improved resistance to sulfidation brought by the suppression of the substrate surface pores. If one excludes from the calculation the silver surface contamination of the protection layer of the as-received SiC+CVD sample (higher BE Ag 3d<sub>5/2</sub> and 3d<sub>3/2</sub> components), this ratio drops down to  $\sim 0.03 \times 10^{-2}$ , i.e. a factor of 1/60 compared to the SiC sample, showing that the

formation of Ag<sub>2</sub>S columns emerging at the surface of the protection layer is nearly suppressed in our severe accelerated aging conditions.

### ***Residual local initiation of tarnishing***

AFM topographic images of the stacks after 24 h accelerated aging in H<sub>2</sub>S are shown in Figure 4. On the SiC sample (Figure 4(a)), local protruding features replace most of the surface pores as judged from their respective densities estimated to  $\sim 1.4 \times 10^6 \text{ cm}^{-2}$  and  $\sim 1.6 \times 10^6 \text{ cm}^{-2}$ , respectively, confirming that Ag<sub>2</sub>S columns have grown from the silver layer and through the protection layer, locally failing at the substrate pores, to erupt above the protection layer. On the SiC+CVD sample (Figure 4(b)), local protruding features are also observed but with a density reduced by a factor of at least 1/10 as judged from these AFM observations. Their lateral dimensions (0.5-2  $\mu\text{m}$ ) and height (0.1-0.3  $\mu\text{m}$ ) are also markedly lower than on the SiC sample (0.4-6  $\mu\text{m}$  and 0.1-1  $\mu\text{m}$ , respectively), confirming the markedly improved resistance to the local initiation of tarnishing brought by the suppression of the SiC substrate surface pores. Combined with the XPS data, these AFM data also show that the residual initiation of tarnishing measured on the SiC+CVD sample is local and corresponds to the formation of Ag<sub>2</sub>S hillocks protruding from the protection layer surface. It is unclear from these XPS data alone if the Ag<sub>2</sub>S hillocks observed correspond to the sulfidation of the silver residual surface contamination and or to the emergence at the surface of Ag<sub>2</sub>S columns growing from the silver mirror layer.

ToF-SIMS elemental images ( $100 \times 100 \mu\text{m}^2$ ) of the surface of the stacks after 24, 48 and 96 h accelerated aging in H<sub>2</sub>S are shown in Figure 5. They were obtained after removal of the organic carbon contamination from exposure to ambient air by light sputtering of the surface. Superimposed O<sup>-</sup>+S<sup>-</sup> ions images are displayed with O<sup>-</sup> and S<sup>-</sup> images color-coded in green and red, respectively (color online). The images for the SiC sample (Figure 5(a)) have been discussed previously [35] and are reproduced here for the sake of comparison. They

show that sulfidation is local and dispersed ( $S^-$  ions) and coincides with the presence of defects in the protection oxide layer ( $O^-$  ions). With increasing accelerated aging time, the silver sulfide spots corresponding to  $Ag_2S$  columns grow in number and size eventually leading to coalescence. On the SiC+CVD sample (Figure 5(b)), not all surface defects of the protection layer are sulfurized which suggests that the protection layer can remain an isolating barrier even if defective at the surface. With increasing accelerated aging time, the density of sulfide spots increases as measured from these  $100 \times 100 \mu m^2$  images, however to much lower extent than on the SiC sample thus confirming a markedly improved resistance to the initiation of local tarnishing. Besides, only a fraction of the observed sulfide spots correspond to the emergence at the surface of  $Ag_2S$  columns growing from the silver mirror layer according to the XPS data.

Figure 6 shows the specular reflectance spectra of the stacks prior to and after 24, 48 and 96 h accelerated aging in  $H_2S$ . All curves show reflectivity drops at 315 and 375 nm related to plasmon absorption by the Ag layer and by the silicon dioxide protection layer, respectively. The decrease of reflectivity caused by the protection layer and its adhesion layer above 330 nm was estimated to about 3% by comparison of stacks with and without the silicon dioxide overcoat on reference glass and silica substrates. Comparing the as-received SiC (Figure 6a) and SiC+CVD (Figure 6b) samples shows that the gain of specular reflectivity brought by the suppression of the SiC substrate surface pores and associated defects in the deposited stack is about 5%. Accelerated aging in  $H_2S$  leads to the failure of the optical performance on the SiC sample as shown by the pronounced loss of reflectivity already observed after 24 h and amplified after 48 and 96 h. Clearly, it is caused by the development the silver sulfide spots corresponding to  $Ag_2S$  columns invading the reflective stack. On the SiC+CVD samples, no reflectivity loss is observed after 24 and 48 h of accelerated aging, confirming the markedly improved resistance to sulfidation of the stacks.

For the sample aged for 96 h (and its reference), the reflectivity is lower in the 350-550 nm range owing to some variation of the protection layer thickness of the as received stacks. Above this spectral range, the loss of specular reflectivity is only about 2% with respect to the as-received sample, markedly lower than that measured after aging the SiC sample for 96 h (33%) and even 24 h (7%). The reflectivity of the SiC+CVD sample after 96 h aging is also observed to be higher than that of the SiC sample before aging, showing that the suppression of the SiC substrate surface pores improves the resistance to the initiation of tarnishing as well as the optical properties.

### ***Sub-surface penetration of sulfur and initiation of tarnishing***

Comparative ToF-SIMS depth profiles of the SiO<sup>-</sup>, minor isotope <sup>34</sup>S<sup>-</sup> and AgS<sup>-</sup> ions measured before (0 h) and after 24, 48 and 96 h accelerated aging in H<sub>2</sub>S are shown in Figure 7 for the SiO<sub>2</sub>/Ag/SiC+CVD stacks. The interfaces are marked for the 24 and 96 h samples with variations that reflect some dispersion of the as received multilayer stacks, mostly of the protection layer thickness. As discussed above, the SiO<sup>-</sup> ions profiles are characteristic for the protection layer and for the residual oxide contamination of the substrate surface prior to deposition of the stack. Their steep intensity variations in the I<sub>a</sub> and I<sub>b</sub> interfacial layer regions are indicative of the sharpness of the interfaces of the stack improved after suppression of the SiC surface pores. After accelerated aging up to 96 h in H<sub>2</sub>S, the SiO<sup>-</sup> ions profiles are identical showing that the structure of the stack and sharpness of its interfaces are essentially unchanged and thus that very little if any sulfidation took place underneath the protection layer.

Prior to accelerated aging in H<sub>2</sub>S, the <sup>34</sup>S<sup>-</sup> ions profile peaks in the I<sub>b</sub> interfacial region, which is also indicative of surface residual contamination of the substrate by sulfur, most likely from ambient air, prior to deposition of the stack. No intensity is measured in the protection layer, I<sub>a</sub> interfacial and silver layer regions. After 24 and 48 h accelerated aging,

the  $^{34}\text{S}^-$  ions profiles are identical in the protection layer region. Looking further in-depth, their intensity increases regularly before dropping at zero in the  $\text{I}_a$  interfacial and silver layer regions. These profiles reveal that sulfur entered and progressed in the protection layer where it accumulated until reaching saturation level because further progress in the stack was blocked by the  $\text{I}_a$  interfacial and silver layer regions.  $\text{H}_2\text{S}$  has been shown to molecularly adsorb on  $\text{SiO}_2$  [58] and it is inferred that, in our accelerated aging conditions where water, that can promote  $\text{H}_2\text{S}$  dissociation is absent, sulfur entered and accumulated in the protection layer as molecular  $\text{H}_2\text{S}$ . The regularly increasing intensities of the measured profiles with in-depth progress in the protection layer are not characteristic for inward solid state diffusion from the outer surface, for which a profile decreasing in intensity should be observed [59]. This suggests the presence of pathways for  $\text{H}_2\text{S}$  penetration in the protection layer and thus the presence of defects, possibly of microstructural origin and corresponding to incompletely coalesced intergranular boundaries of the  $\text{SiO}_2$  layer since AFM revealed a granular surface morphology of this layer. These microstructural defects would connect to form the pathways short circuiting the protection layer and enabling  $\text{H}_2\text{S}$  ingress. The regularly increasing intensities of the  $^{34}\text{S}^-$  ions profile could then be explained by an increasing density of these channels with in-depth progress in the  $\text{SiO}_2$  layer. However, this is not supported by the  $\text{SiO}^-$  ions profiles also regularly increasing with in-depth progress and suggesting an increasing density of the  $\text{SiO}_2$  layer. Outgassing of  $\text{H}_2\text{S}$  from the penetrating pathways in the UHV conditions of the ToF-SIMS measurements cannot be excluded.

Figure 7 also shows that the  $\text{AgS}^-$  ions profile have quite low intensities and peak concomitantly with the  $^{34}\text{S}^-$  in the interfacial  $\text{I}_b$  region and/or  $\text{Ag}^-$  ions profiles in the interfacial  $\text{I}_a$  region (shown in Figure 2 prior to accelerated aging). The combination of silver and sulfur secondary ions during analysis is a possible explanation. After 24 and 48 h accelerated aging, the intensities of the  $\text{AgS}^-$  ions are still extremely low but slightly increase



at the extreme surface of the stack and during the first 100-200 seconds of sputtering before vanishing. This is a clear indication that, at this stage of sulfidation, silver sulfide is not yet formed in the silver layer region and in the deeper part of the protection layer, and thus that the formation of  $\text{Ag}_2\text{S}$  columns growing from the silver layer is not yet initiated despite the penetration of sulfur in the  $\text{SiO}_2$  layer, in contrast to what occurs in the presence of the SiC substrate pores. The local spots of sulfidation revealed by AFM (Figure 4) and ToF-SIMS imaging (Figure 5) are then those characterized in XPS by higher BE-shifted Ag  $3d_{5/2}$ - $3d_{3/2}$  doublets and corresponding to the sulfidation of the silver contamination traces initially present at the surface of the stacks after deposition and/or of those present in the bulk of the protection layer and possibly segregating to the surface during accelerated aging performed at  $75^\circ\text{C}$ .

After 96 h accelerated aging, both the  $^{34}\text{S}^-$  and  $\text{AgS}^-$  ions profiles increase in intensity in all regions of the stacks, including in the  $\text{I}_a$  interfacial, silver and  $\text{I}_b$  interfacial layer regions until then unaltered. This shows that sulfidation of the silver mirror layer has been initiated below the protection layer following its exposure to  $\text{H}_2\text{S}$  penetrating through the channels short circuiting the protection layer. The  $^{34}\text{S}^-$  ions profile shows a peak increase in the interfacial  $\text{I}_b$  region underneath the silver mirror layer.  $\text{Ag}_2\text{S}$  growing by cationic outward diffusion of  $\text{Ag}^+$  ions [60-62], this suggests that short circuits for sulfur penetration underneath the silver layer have been created by the formation of  $\text{Ag}_2\text{S}$ . Porosity has been previously reported to develop in a silver layer following the formation of  $\text{Ag}_2\text{S}$  by cationic transport [63] and it is possible that in our case pores were formed in the silver mirror layer in the vicinity of the sites of local growth of  $\text{Ag}_2\text{S}$  and subsequently connected to open channels for the penetration of sulfur through the silver layer until the interfacial  $\text{I}_b$  layer.

At this stage (96 h) of accelerated aging,  $\text{AgS}^-$  ions are detected all throughout the protection layer region (Figure 7). This is consistent with the growth of  $\text{Ag}_2\text{S}$  columns from

the silver layer and until emergence at the surface of the stack as inferred from the XPS data that show a Ag 3d<sub>5/2</sub>-3d<sub>3/2</sub> doublet non shifted in binding energy in contrast to that corresponding to Ag<sub>2</sub>S formation at the surface of the protection layer. The growth of these Ag<sub>2</sub>S columns is local as confirmed by the ToF-SIMS (Figure 5) data. It has been shown that Ag<sub>2</sub>S does not grow as a continuous layer but rather forms local hillocks that coalesce in advanced stages of sulfidation [64-66]. In our case, the growth of Ag<sub>2</sub>S as columns results from the presence of the channels enabling the penetration of H<sub>2</sub>S through the protection layer and it is local because of the most likely discontinuous distribution of these pathways short circuiting the protection layer. The Pilling-Bedworth ratio for the formation of Ag<sub>2</sub>S from metallic silver being 1.65 as calculated from the molar volume of Ag<sub>2</sub>S (33.82 cm<sup>3</sup>) and Ag (10.27 cm<sup>3</sup>), swelling of the silver mirror layer underneath the protection layer can be expected to result from its local sulfidation. This volume increase would generate mechanical stress that could eventually crack the protection layer above. Newly formed cracks, presumably of nanoscale dimensions since not observed by AFM (Figure 4) nor ToF-SIMS imaging (Figure 5), would then open new permeation pathways, promoting the penetration of H<sub>2</sub>S in the protection layer and thereby explaining the increased intensity of the <sup>34</sup>S<sup>-</sup> ions profile measured in the protection layer region after 96 h accelerated aging in H<sub>2</sub>S.

## Conclusions

AFM, XPS and ToF-SIMS measurements were combined in a comprehensive approach to bring new insight on how to improve the pre-launch long-term environmental durability of thin-layered silver stacks supported on light-weight SiC substrates for space mirror applications. Model stack samples consisting of a thin silver layer and a SiO<sub>2</sub> protection overcoat, with adhesion interfacial layers, and deposited by cathodic magnetron sputtering, were submitted to severe accelerated aging in H<sub>2</sub>S gas at 1000 mbar and 75°C.

The results show that markedly improved resistance to local tarnishing and preservation of the optical properties is obtained for stacks supported on a SiC substrate pretreated by CVD so as to deposit a  $\sim 2 \mu\text{m}$  thick SiC film. The CVD surface treatment suppresses the surface pores resulting from the bulk SiC material production process and thereby eliminates the high aspect ratio surface sites that are imperfectly protected by the SiO<sub>2</sub> overcoat after the stack deposition, and thus more susceptible to the initiation of tarnishing. As a result the preferential tarnishing mechanisms, involving channels connecting the silver layer to its environment through the protection layer and enabling local H<sub>2</sub>S entry and Ag<sub>2</sub>S growth as columns until emergence at the stack surface, is shut down and tarnishing initiation by degradation of the silver layer is markedly delayed and optical performance preserved.

After 96 h accelerated aging at 1000 mbar and 75°C, only trace sulfidation was observed on the CVD pretreated samples. It resulted for its majority from the reaction with H<sub>2</sub>S of silver contamination traces initially present at or near the surface of the stack from the deposition process. The minority tarnish traces revealed a degradation mechanism, essentially identical in nature to the preferential mechanism with Ag<sub>2</sub>S growing as columns through the protection layer, but involving different pathways short circuiting the protection layer and enabling H<sub>2</sub>S ingress until the silver layer. These pathways are suggested to be of microstructural origin and could correspond to the incompletely coalesced intergranular boundaries of the SiO<sub>2</sub> layer.

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## Figure captions

*Figure 1 (color online) Top view AFM topographic images of the SiC (a,b,c) and SiC+CVD (d,e,f) substrates: (a,d) uncoated samples, (b,c,e,f) stack samples prepared by cathodic magnetron sputtering.  $\Delta z$  range is 150 nm (a), 100 nm (b), 25 nm (c,f); 20 nm (e) and 7 nm (d) and color-coded from dark/black to light/white with increasing  $z$  (surface height).*

*Figure 2 (color online) ToF-SIMS elemental depth profiles of the stacks on the SiC (a) and SiC+CVD (b) substrates and consisting of the silver mirror layer (marked Ag) deposited on the NiCr layer (marked  $I_b$ ) grown on the SiC substrate and covered by the silicon oxide protection layer (marked Protection) with an interface layer (marked  $I_a$ ). Selected negative secondary ions are marked.*

*Figure 3 (color online) XPS survey and Ag3d core level spectra for the stacks on the SiC (a) and SiC+CVD (b) substrates after 96 h accelerated aging in  $H_2S$  at 1000 mbar and 75°C.*

*Figure 4 (color online) Top view AFM topographic images for stacks on the SiC (a) and SiC+CVD (b,c) substrates after 24 h accelerated aging in  $H_2S$  at 1000 mbar and 75°C.  $\Delta z$  range is 100 nm (a) and 20 nm (b,c) and color-coded from dark/black to light/white with increasing  $z$  (surface height). (c) is an enlarged new image of the local region marked in (b).*

*Figure 5 (color online) ToF-SIMS elemental images for the stacks on the SiC (a) and SiC+CVD (b) substrates after 24, 48 and 96 h accelerated aging in  $H_2S$  at 1000 mbar and 75°C. Superimposed  $O^-+S^-$  images are shown with the  $O^-$  and  $S^-$  ions color-coded in green and red, respectively.*

*Figure 6 (color online) Specular reflectance spectra for the stacks on the SiC (a) and SiC+CVD (b) substrates before and after 24, 48 and 96 h accelerated aging in H<sub>2</sub>S at 1000 mbar and 75°C..*

*Figure 7 (color online) ToF-SIMS depth profiles of the SiO<sup>-</sup>, AgS<sup>-</sup> and <sup>34</sup>S<sup>-</sup> ions for the stacks on the SiC+CVD substrate prior to (0 h) and after 24, 48 and 96 h accelerated aging in H<sub>2</sub>S at 1000 mbar and 75°C.*

**Figure 1**

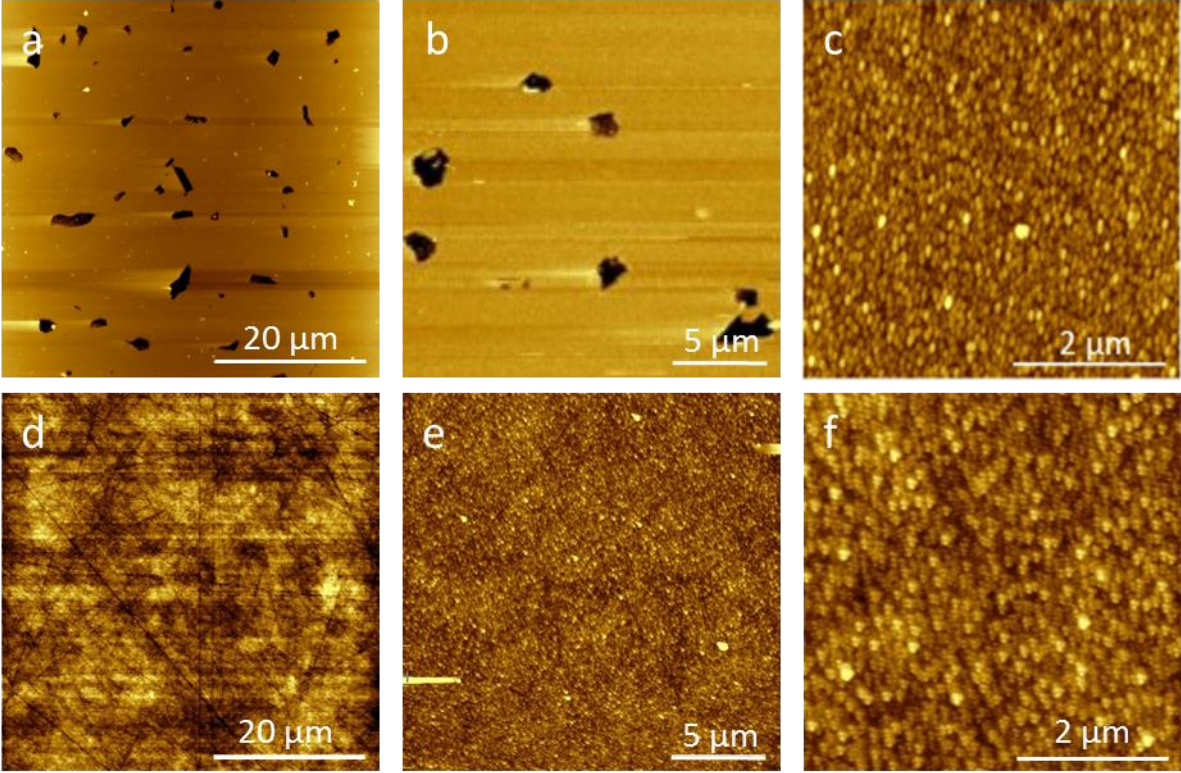
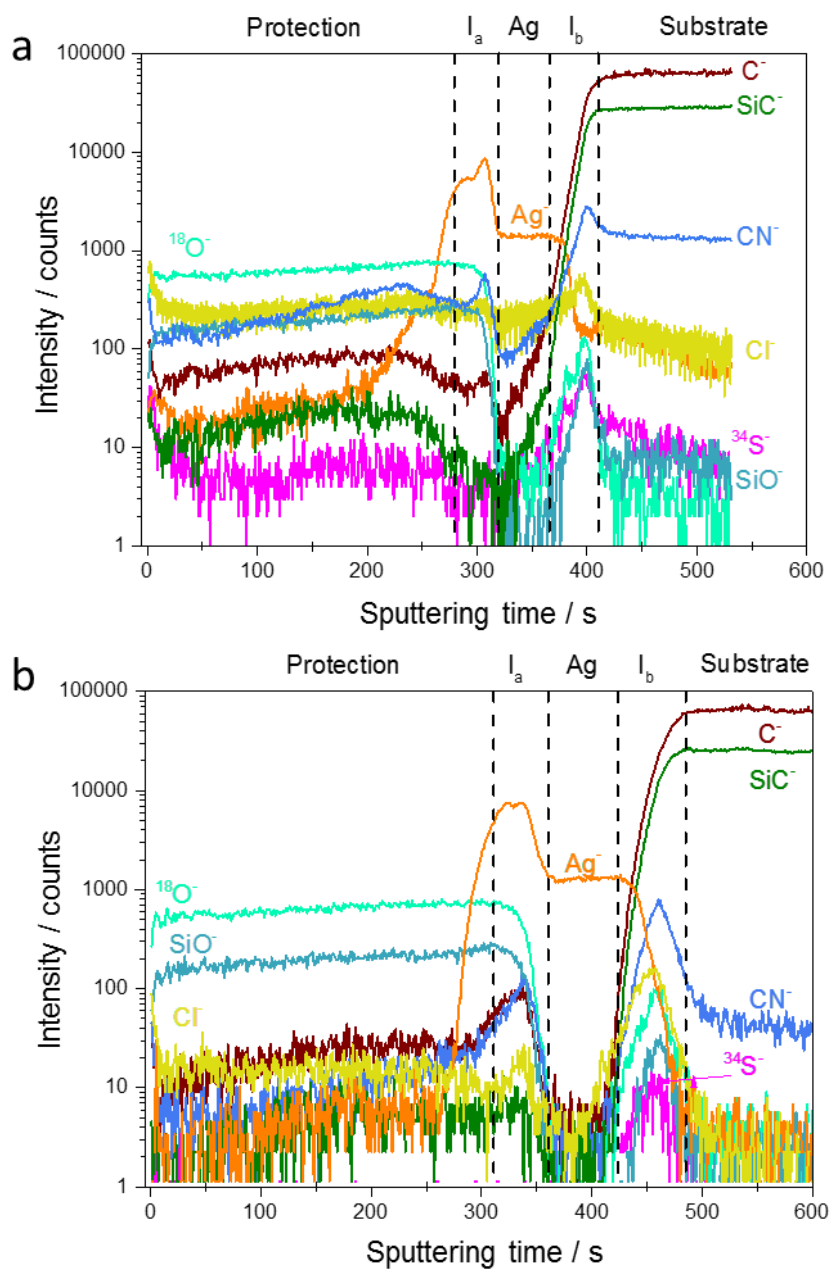
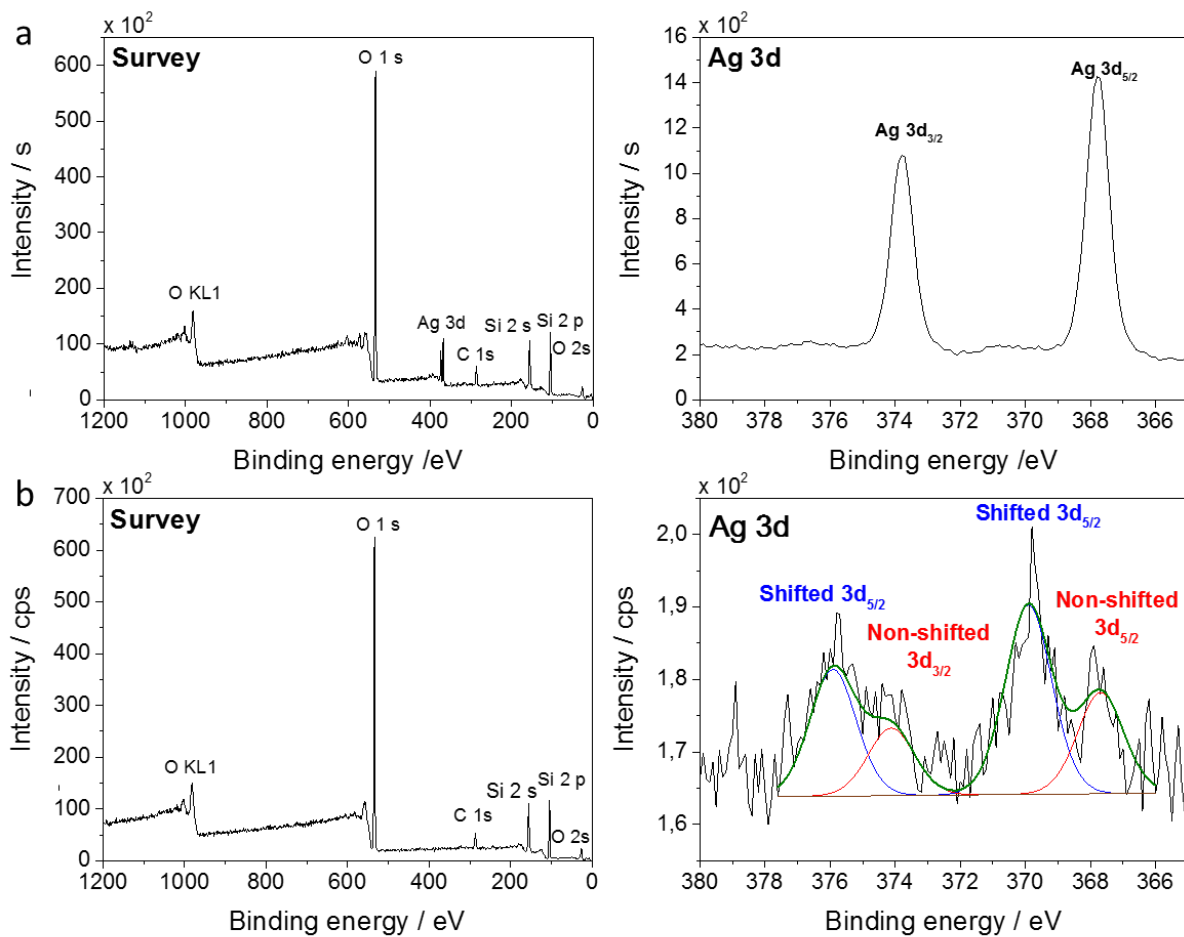


Figure 2



**Figure 3**



**Figure 4**

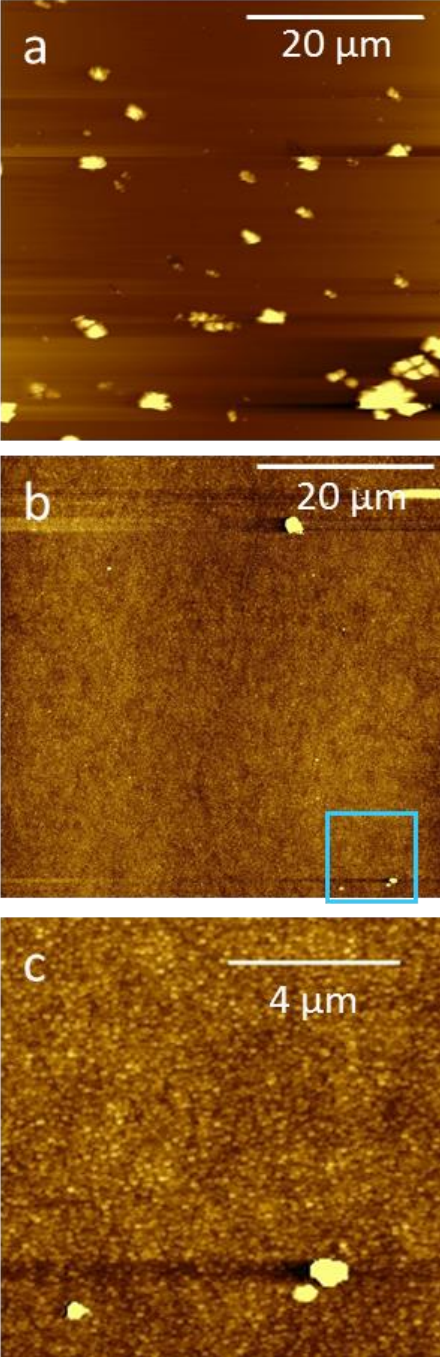
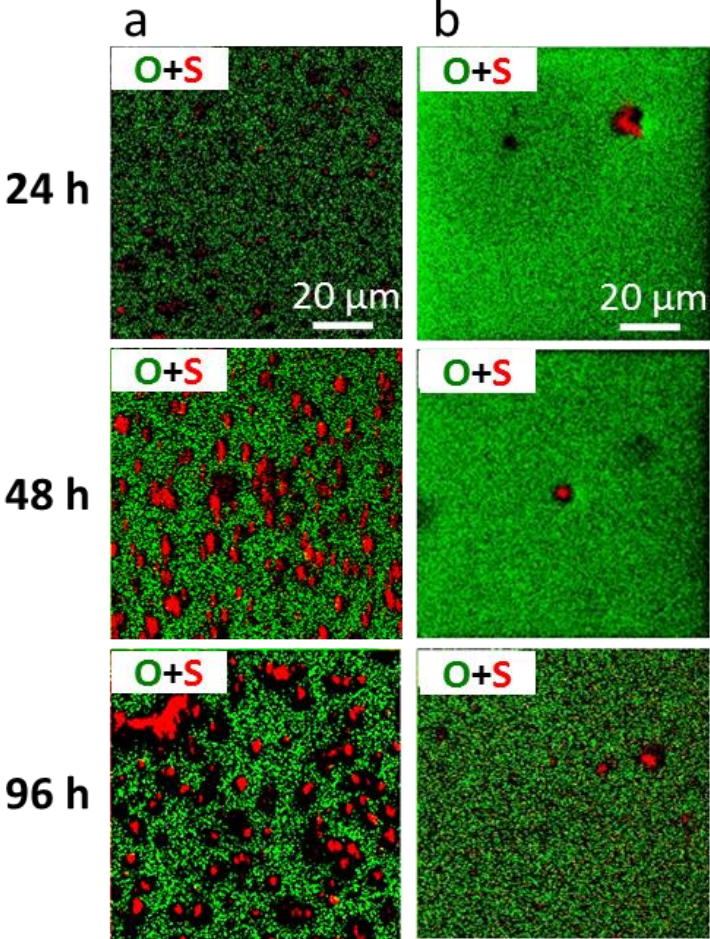




Figure 5





**Figure 6**

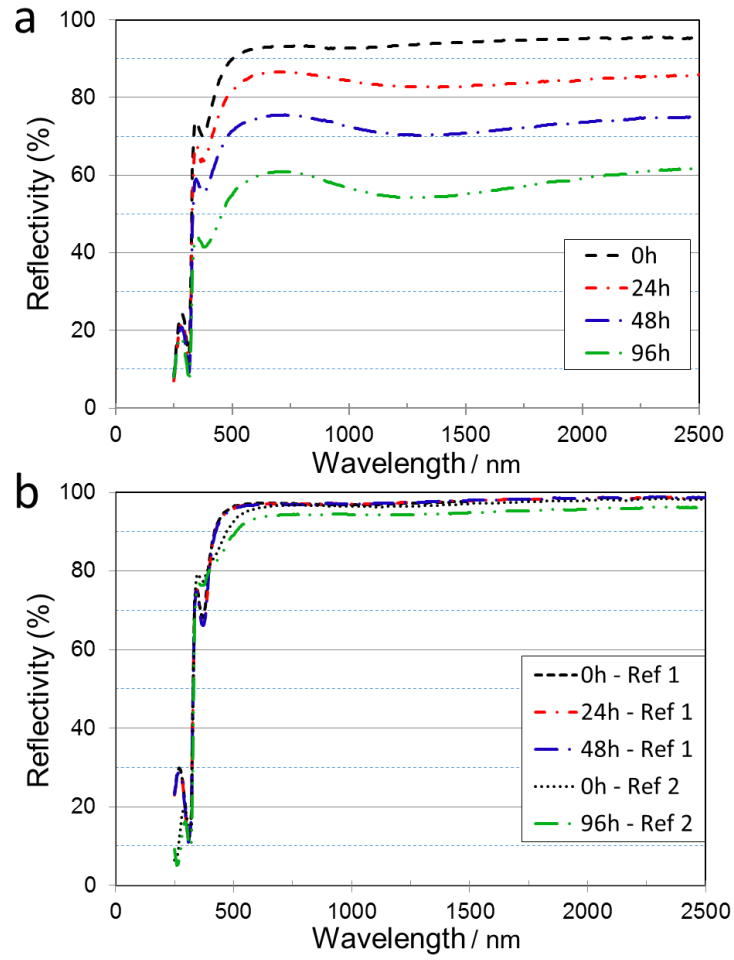


Figure 7

