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Silica thin-films from perhydropolysilazane for the protection of ancient glass

Renzo Bertoncello[*1], Matteo Monti[1],[2], Cinzia Sada[3]

[1]*Dipartimento di Scienze Chimiche, Università degli Studi di Padova
renzo.bertoncello@unipd.it
[2] Dept. of Materials Science & Engineering, Stanford University mmonti@stanford.edu
[3] Dipartimento di Fisica, Università degli Studi di Padova cinzia.sada@unipd.it
Tel: +39.049.827.5204 Fax: +39.049.827.5829 E-mail: renzo.bertoncello@unipd.it

ABSTRACT

Silica coatings from polysilazane precursors were prepared to protect ancient glass from weathering. Polysilazane can be converted to silica by simple exposition to air or basic vapours and the properties of the synthesized film make this precursor a valuable choice to obtain solid, crack-free, highly adhesive and protective coatings. The coating is prepared starting from a Perhydropolysilazane precursor (20% PHPS in n-butyl ether) that allows to achieve high-quality thin-films of silica at room temperature. The obtained films are uncoloured, even in absence of strong heat-treatment. Perhydropolysilazane (PHPS) is a polymer of $[-SiH_2-NH-SiH_2-]_n$ units. When deposited on a soda-lime microscope slide, it reacts with atmospheric moisture (Si-H and Si-NH bonds are hydrolysed to Si-O) and a silica film is produced. The conversion to silica is completed in about 2.5 hours, using vapours of a 10 mol L^{-1} ammonia solution. The reaction is promoted with the application of a weak heat-treatment (45-50 °C), achievable using as heater a common tungsten filament lamp. The reaction of PHPS with atmospheric moisture produces a migration phenomenon of the mobile ions from the soda-lime glass to the film (in particular sodium, calcium and magnesium). The characteristics of the migration process vary according to the concentration of the precursor solution and the thickness of the film. Laboratory samples have been investigated by optical microscopy and surface techniques: XPS and SIMS. Preliminary evidences, obtained through the laser scanning confocal microscope (LEXT), on the application of such coatings at the surface of ancient stained glass are also discussed.
Keywords — PHPS, Silica, Coating, Ancient Glasses, weathering.

INTRODUCTION

Due to the scarce resistance of historical artistic glasses grisailles to weathering, the research on the preparation of new protective coatings to prevent further detachment of grisailles is a matter of great interest[1].

Previous investigations[2,3,4], in fact, show that the thin silica coatings do not change the appearance of artistic glasses when deposited on their surface but only act as a protective layer. Moreover, the film thickness is so small (around 200 nm) and its composition and structure so compatible with that of the original glass, that the coating is not distinguishable from the original glass. To slow down the phenomenon of weathering of ancient stained glass, the present work proposes the coating of glass with a silica film with the novelty given by the adoption of perhydropolysilazane (PHPS) as precursor for a silica protective film.

PHPS[5,6,7] is a polymer of $[-SiH_2-NH-SiH_2-]_n$ units, often used as precursor for a wide range of compounds (silicon-nitride, silicon-carbide). PHPS reacts with atmospheric moisture, the Si-H and Si-NH bonds are hydrolysed to Si-O bonds and the typical structure of silica is produced (Fig. 1)

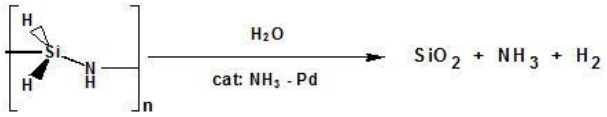

Fig. 1 Conversion reaction

To the authors knowledge, the complete mechanism of the reaction is unpublished. However, even if a complete study on the case is necessary, it is reasonable to hypothesise the interaction of a Pd coordination compound acting through the following reaction steps. The first step is supposed to be an oxidative addiction of Si-H bond to the palladium centre to break the silicon-hydrogen bond. Then a water molecule makes a nucleophilic attack on the silicon atoms coordinated to palladium. So palladium replaces the silicon with an hydrogen atom by a concerted reaction and the silanolic compound can be eliminated from the metal coordination sphere. The last step is the reductive elimination of the molecular hydrogen with the restoration of the original palladium catalyst. About the Si-N bonds, the reaction seems to be improved by hydroxyl ions derived from the sample exposition on ammonia solution. The first step is the nucleophilic attack of the hydroxyl group on silicon atom. Then the silicon-nitrogen bridge is broken and a silanolic group bonded to silicon is formed. The partial negative charge on nitrogen allows an acid-base reaction with water molecule with the retrieval of the initial hydroxyl group.

In order to obtain a quicker conversion a variation of the synthesis conditions is applied. Even if the process can be carried out at room temperature, the adoption of a very weak heat treatment (45-50°C, easily achieved with the use of a tungsten filament lamp) accelerates the reaction (from 66 to 2 hours). The heat treatment improves the formation of ammonia vapours and promotes the hydrolysis of Si-N bridges. The final result is a complete precursor conversion with a decreased ammonia exposition period.

Furthermore, the film showed excellent resistance to water environment, thus confirming the formation of an impermeable environmental barrier. The authors had demonstrated that thin films synthesized from PHPS can be used to coat ancient glasses, and that the obtained films are homogeneous with reduced ion migration[8]. The present paper focuses on the deposition of these films on historical glasses painted with grisailles.

In order to check the applicability of the coating to stained glass windows an original ancient glass tile was painted with a PHPS solution using a common paintbrush. The tile comes from the stained windows of the apse of the "*Basilica di SS. Giovanni e Paolo*" in Venice (Italy).

EXPERIMENTAL

General Procedures: The dipping solution is produced starting from commercially available PHPS polysilazane that is produced by ammonolysis of dichlorosilane[9] and is available as 20 wt% solution in dibutyl ether (PHPS NN120-20, formerly Clariant, Switzerland, now AZ Electronics Materials, Luxembourg).

The soda-lime substrates are dipped for 1 minute in the previous solution and then extracted at 1.5 cm min^{-1} speed, using different concentration of PHPS. In this work, the results of sample #1, also called P15H, (diluted) and samples #2, also called AG15M, (concentrated) are reported.

After the deposition, the samples are exposed to the vapours of an aqueous ammonia solution at room temperature. During this phase, different conditions have been tested, either changing the exposure time (2 - 4 hours) or the concentration of the ammonia solution (10 - 15 mol L^{-1}). Moreover, the effects of the application of a weak heating (43 – 45 °C) have been studied. The heating was carried out with a common tungsten filament lamp. In particular, in this work are reported the results for sample #1, whose conversion reaction was promoted by exposure to ammonia vapours (15 mol L^{-1}) for 2 hours at 43 °C, and for sample #2 exposed to ammonia vapours (10 mol L^{-1}) for 4 hours at 47 °C.

The sample #3 is composed of a part of an ancient stained-glass tile, dated around 1500 A.D., partially coated with the diluted solution. The tile comes from the stained windows of the apse of the "Basilica di SS Giovanni e Paolo" in Venice (Italy). The window is a typical venetian "rullo" window (fig. 2a), with 2 frames along the sides of the window. The first frame is characterised by a thin line of dark red glass tiles. The second line is characterised by green glass tiles with a vegetable decoration. The glass used for the experiment is a part of a green tile with the vegetable decoration (fig. 2b). The coating was deposited with a brush on the side with grisaille and no ammonia treatment was performed.

Fig. 2a part of the window Fig 2b the green glass tile

Instrumental Techniques: Morphological characterization of the samples has been performed in two steps: firstly, using an optical microscope (Axiotech 100 Zeiss) and a connected camera (Nikon Coolpix 5000) used to take photos; secondly, using a confocal laser microscope to obtain data both on the colour and on the three-dimensional morphology of the surface. The model of the instrumentation is Olympus LEXT OLS 3100 laser scanning confocal microscope (LSCM) designed for metrology in material science[10].

Surface quantitative analyses have been obtained by X-Ray Photoelectron Spectroscopy (XPS). Spectra have been collected by a *PERKIN ELMER 5600ci* spectrometer equipped with a double anode X-Ray Source (Mg/Al) and a monochromatic Al X-Ray Source. Anodes work with AlK (1486.6 eV) and MgK (1253.6 eV) sources at 20 mA and 14 kV. A CHA analyser (Concentric Hemispherical Analyser) has been used to collect the output signals. Analysed areas are circles 0.8 mm in diameter. Scan range is 0 – 1350 eV (AlK source) or 0 – 1150 eV (MgK source) according to the source adopted. Survey scan mode acquires spectra stepping every 1.0 eV, while multiplex scan mode requires 0.2 eV steps. A charge neutralizer has been used to avoid spectral shift in insulating samples and all spectra have been corrected according to charging effect, assigning to C1s peak 284.8 eV binding energy. Depth profiles have been taken using soft sputtering conditions. Surface has been sputtered with an ion gun using Ar^+ accelerated at 3-3.5 keV and 5 10^{-6} Pa pressure, with a raster size of 2 x 2 mm^2. In detail, the sputtering has been carried out at 3 keV for the first 75 minutes and 3.5 keV for the following minutes. The error in quantitative analyses can be estimated as ± 0.2%.

Secondary Ion Mass Spectrometry (SIMS) measurements were carried out by means of a IMS 4f mass spectrometer (Cameca, Padova, Italy) using a 14,5 KeV Cs^+ primary beam and by negative secondary ion detection. The charge build up while profiling the insulating samples was compensated by an electron gun without any need to cover the surface with a metal film. In order to define the best experimental conditions, the SIMS spectra were carried out at very low primary beam intensity (15 nA) rastering over a 150x150 μm^2 area and detecting secondary ions from a region close to 10x10 μm^2 to avoid crater effects. The primary beam intensity was chosen in order to reduce at minimum the erosion of the sample.

RESULTS

In a previous work[8], the complete conversion of the precursor to silica induced by ammonia solution has been followed by XPS technique. In the present work, in order to analyze the quality of the coating and the characteristics of the interface between the film and the substrate, XPS and SIMS depth profiles were performed.

The appearance of the deposited films is fine. The optical microscope shows that the coatings are homogeneous, transparent and uncoloured.

Figure 3 shows the XPS spectrum of the sample #1 (diluted solution and exposure to ammonia vapours 15 mol L^{-1} for 2 hours at 43°C).

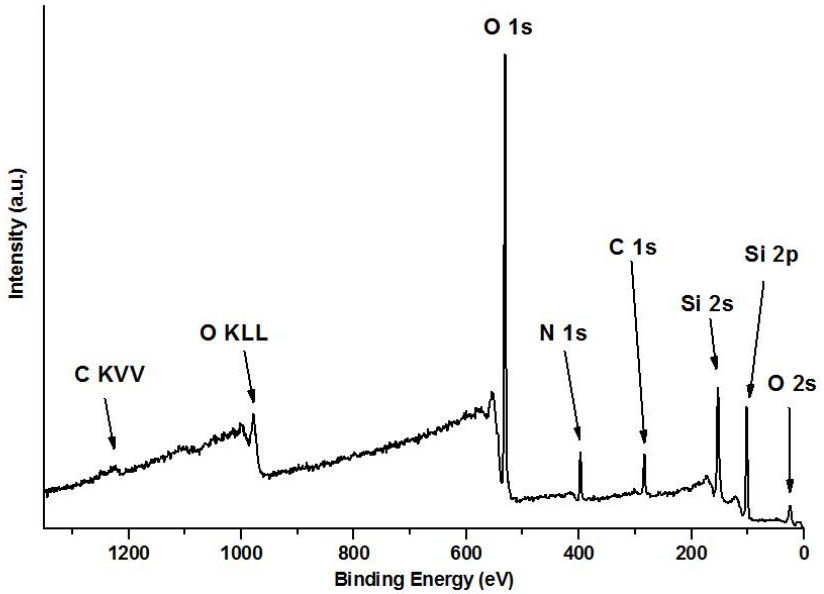

Fig. 3 XPS spectrum of sample #1 (P15H)

It shows the presence of N peaks, and in particular the atomic abundances of N, O and Si are 7.5, 47.2 and 33.3 respectively (atomic %, see table 1). The O/Si ratio measured does not correspond to that typical of the silica compound ratio (2:1). The conversion of PHPS to silica is not totally completed.

The SIMS in-depth profile of sample #1 (fig. 4) has been measured collecting several signals: H, Si, N, O, C and Na. In particular, N is typical of the coating; H, Si, O and C derive both from the coating and the substrate; Na is typical of the soda-lime substrate. The plot shows different regions. The first region (0 to 40 nm ca) is characterized by a composition typical of a still unconverted product, as can be inferred by the presence of the N signal and similar to the XPS results.

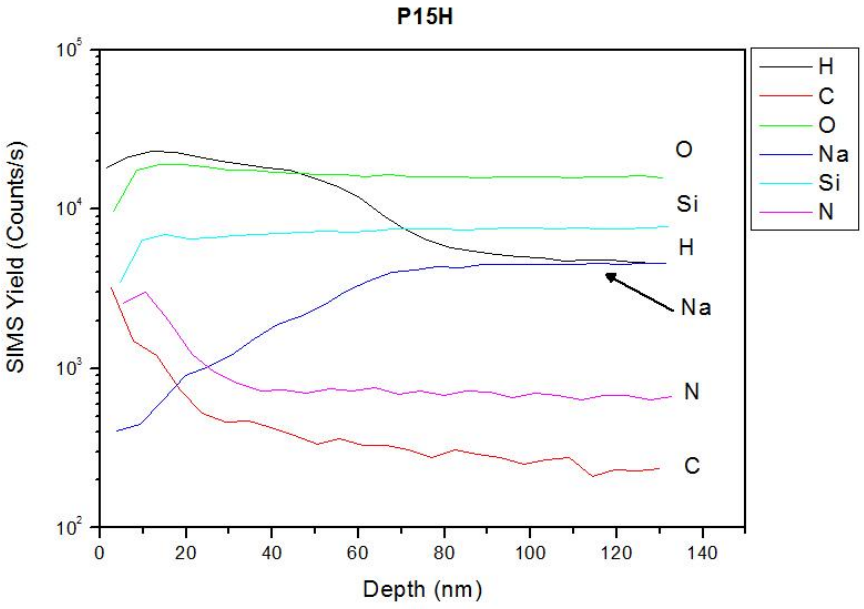

Fig. 4 SIMS depth profile of sample #1 (P15H)

The second region shows a change in composition. The N signal decreases and a particular behaviour of Na signal is remarkable. In fact, even if Na is a proper element of the substrate, its presence is partly visible in the coating. This fact suggests the occurrence of migration phenomena where Na coming from the soda-lime glass goes up to the deeper side of the coating region. Moreover, the interface is very broad. Figure 5 shows the XPS spectrum of the sample #2 (concentrated solution and exposure to ammonia vapours 10 mol L^{-1} for 4 hours at 47°C). Surface composition is typical of a silica layer. As a matter of fact, the presence of a very low N abundance (1.2 atomic %) indicates a nearly complete conversion of PHPS to silica. Si and O, are present with an abundance of 27.2 and 57.7 respectively (atomic %, see table 1).

Tab.1 XPS quantitative analyses of the samples (atomic %)

sample	O1s	Si2p	C1s	N1s
#1 (P15H)	47.2	33.3	12.0	7.5
#2 (AG10M)	57.7	27.2	13.9	1.2

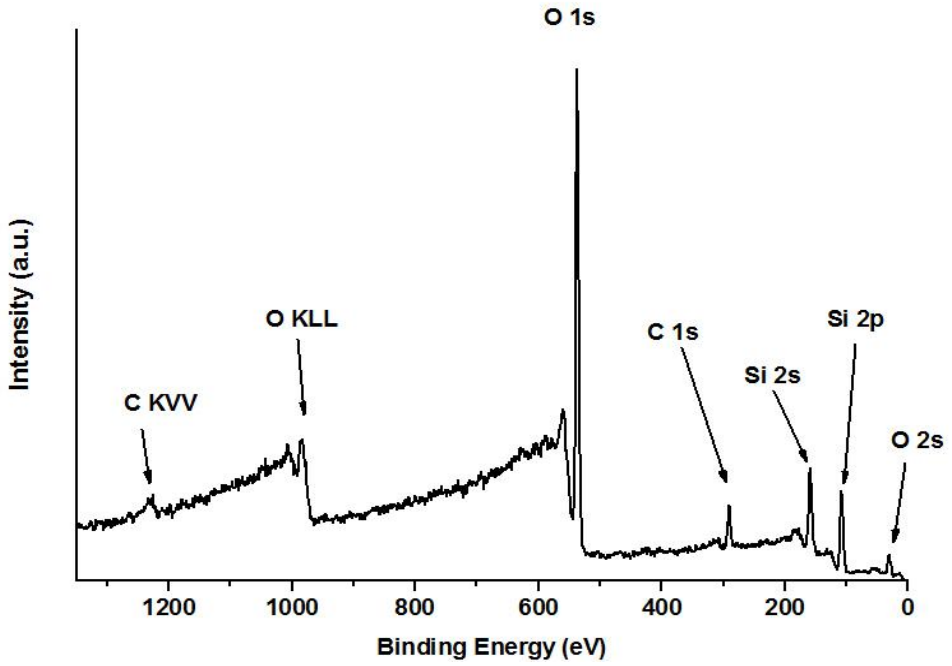

Fig. 5 XPS spectrum of sample #2 (AG10M)

SIMS depth profile of sample #2 (fig. 6) shows nine different signals. C, N and Pd properly relate to the precursor; Na, Mg, and Ca only relate to the soda-lime glass substrate and Si, H, and O relate to both. The depth profile shows a different behaviour if compared with the first sample. In particular the N signal, substantially absent close to the surface of the film, evidences two interfaces in depth: the first close to 40 nm, when it reaches its maximum value, and the second at 120 nm. After 120 nm N is no more revealed. This behaviour is confirmed by XPS analysis. Mg and Ca signals show a similar behaviour, but with a narrow interface: they are substantially absent at the surface up to the first interface (40 nm depth ca) where they rapidly increase to become constant only after 90 nm depth. Na signal behaviour is still different, showing a linear increase with depth in the whole film. This second

sample shows then a different composition trend from the first one. It is possible here to distinguish three regions. The first one (0 to 40 nm ca) is characterized by a composition comparable to silica and it indicates a high conversion degree. The second region (40 to 120 nm ca) is characterized by the presence of proper elements of soda-lime substrate (Na, Mg and Ca) with different tendencies to migrate, according to their different charge/radius rate.

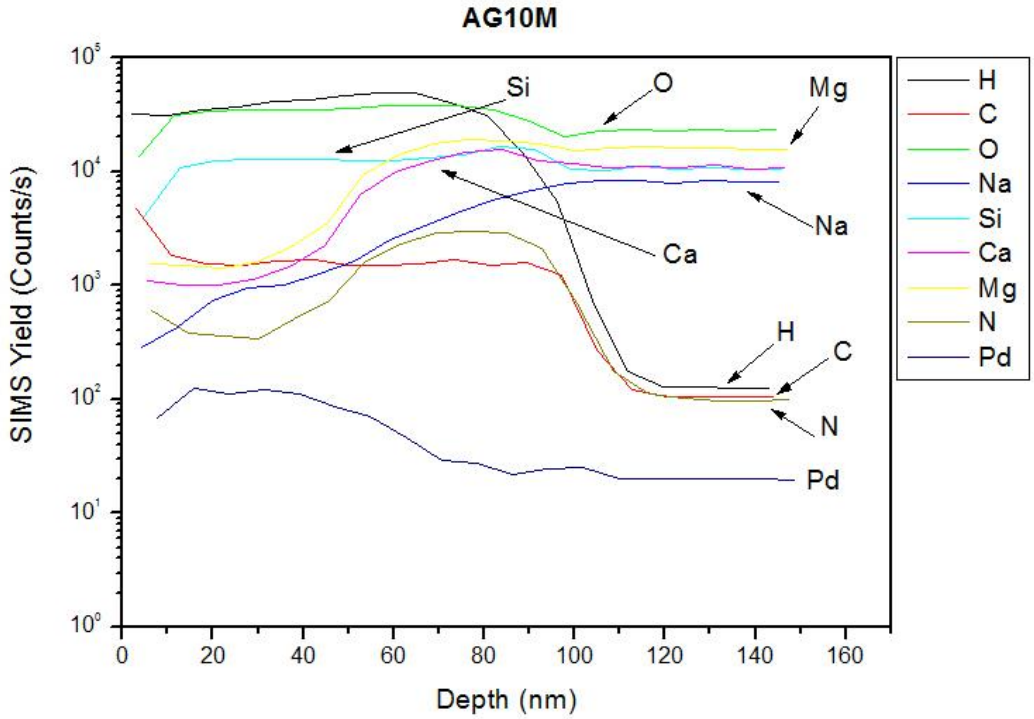

Fig. 6 SIMS depth profile of sample #2 (AG10M)

Moreover, the presence of N signal indicates a lower conversion degree compared to the most external area. The last region (more than 120 nm depth) presents a typical composition of the soda-lime substrate, with no N, Pd and H.

DISCUSSION

Comparing the data, it is clear that the migration of sodium from the substrate is not avoidable at this step of the research work. This migration increments the adhesion of the film to the substrate, therefore increases the performance of the coating. Also the magnesium and calcium migration are not avoided. However, a thicker film (sample #2) seems to be slower to convert, and still in modification. The progress of the reaction would influence the elimination of gases from the film, maintaining a clean coating surface in time even after the deposition. At this stage of the work is not possible to define what is the best kind of coating to protect ancient glass. The study of the properties of both coatings when exposed to ageing tests will be important in order to define which is the best performing coating. In order to obtain preliminary information about the ability to adhere of such coatings on historical samples - presenting a complex surface rich in bubbles and detaching grisailles - an ancient glass was coated with a PHPS thin-film. SIMS depth profile in this case was not performed, due to the non homogeneity of the surface. Also the use of a classical AFM (Atom Force Microscope) would be of scarce help, due to the high roughness of the sample. Therefore, a new technique for the definition of the surface appearance of the samples was used, the LSCM technique. The three-dimensional LSCM image of historical sample characterised by presence of grisaille are reported in Fig. 7.

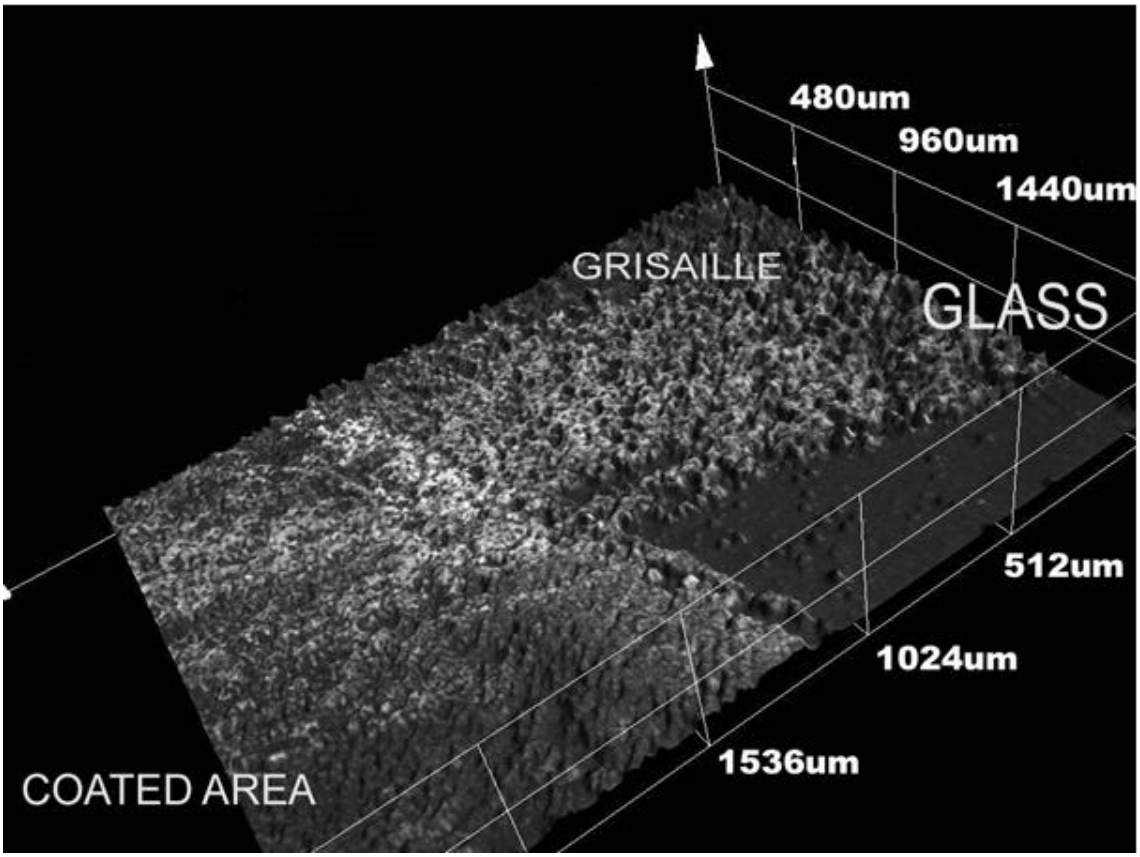

Fig.7 Tridimensional image of sample #3 (ancient stained window glass coated with PHPS thin-film). Image obtained with confocal laser microscopy

The image shows the surface sample, in particular, the interface zone. The right part shows the uncoated area. The surface appears very rough, unpolished and it is evident the presence of grisaille in the upper part. The left zone of image shows the coated area. The surface presents a lower roughness degree and the presence of grisaille is no more evident. Therefore the application of the coating allows a general smooth of the surface and a more cohesion of the grisaille layer, otherwise highly exfoliating from the glass substrate. More corrosion tests on similar samples are however necessary to define the resistance of the film to weathering attach, and its ability to maintain the adhesion of the grisaille to the glass.

CONCLUSIONS

Pursuance of the past work[8] gives another important information about the PHPS behaviour as precursor to deposit silica thin film on glass substrates. In particular, SIMS results underline the presence of elements proper of substrate in the coating in a sort of inter-diffusion process. The formation of different composition part is explained by migration effect typical of metal ions like sodium, potassium, calcium and magnesium. The formation of a particular interface area between external part of the coating and the soda lime substrate is recognizable. This gradual composition changing could favour good adhesive properties of the protective coating to the substrate. The conversion of PHPS to silica allows to obtain an external thin film comparable to SiO_2. This result is potentially exploitable to protect the substrate from external attacks and to smooth the pauperisation of the substrate metal ions due to migration phenomena.

The qualitative features obtained from LSCM technique show the applicability on historical sample of PHPS like protective coating. In particular, it's exploitable to prevent detaching effect of grisaille, due to ageing, and to improve its adhesion degree.

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