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Nitrogen Nanobubbles in a-SiO\textsubscript{x}N\textsubscript{y} Coatings: Evaluation of its Physical Properties and Chemical Bonding State by Spatially Resolved EELS

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ABSTRACT
Nanoporous silicon based materials with closed porosity filled with the sputtering gas have been recently developed by magnetron sputtering. In this work the physical properties (density and pressure) of molecular nitrogen inside closed pores in a SiO\textsubscript{x}N\textsubscript{y} coating are investigated for the first time using spatially resolved electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope. The paper offers a detailed methodology to record and process multiple EELS spectrum images (SIs) acquired at different energy ranges and with different dwell times. It is demonstrated an adequate extraction and quantification of the N-K edge contribution due to the molecular nitrogen inside nanopores. Core-loss intensity and N chemical bond state were evaluated to retrieve 2D maps revealing stable high density of molecular nitrogen (from 40 to 70 at./nm\textsuperscript{3}) in nanopores of different size (20 to 11 nm). This work provides new insights on the quantification of molecular N\textsubscript{2} trapped in porous nitride matrices that could be also applied to other systems.

I. INTRODUCTION
Silicon based materials are still nowadays key for the development of modern technology. Although significant basic research has been undertaken in the recent decades, the research in silicon oxynitride (SiO\textsubscript{x}N\textsubscript{y}) coatings is still a topic of high interest.\textsuperscript{1-4} The ability of modeling the optical and electrical properties by controlling the composition makes of SiO\textsubscript{x}N\textsubscript{y} a promising material for optoelectronic devices.\textsuperscript{5-7} A continuous change in its composition allows large refractive index ranges from 1.47 for pure silicon dioxide up to 2.3 for pure silicon nitride or even 4.75 for dense amorphous silicon coatings\textsuperscript{8} which is very appealing for low and high contrast index applications.

Among other deposition techniques SiO\textsubscript{x}N\textsubscript{y} coatings are most commonly grown by plasma enhanced chemical vapor deposition. Compositional changes are achieved by varying nitrous oxide (N\textsubscript{2}O) and silane (SiH\textsubscript{4}/N\textsubscript{2}) precursor ratios with optional addition of ammonia
(NH$_3$). However, the high hydrogen content in these plasma-enhanced chemical vapor deposition films in the form of Si-H or N-H bonds causes optical losses at wavelengths around 1500nm.$^{3-4,9}$ Additional annealing steps between 1000 and 1150°C, or plasma treatments at 300°C have been proposed to reduce the H content$^{3-4,10}$ however limiting the type of substrates to be used.

We have recently introduced a new bottom up methodology to produce silicon based porous coatings with controlled refractive index by magnetron sputtering.$^{8,11-13}$ This new approach gives the possibility to obtain tailored microstructures and refractive indexes based on the introduction of closed porosity, filled with the sputtering gas, in coatings produced by magnetron sputtering.$^{8,12,14-15}$ Si$_{x}$O$_{y}$N$_{z}$ coatings with similar composition and tailored refractive index$^{11-12}$ as well as pure or doped porous silicon layers$^{8,16}$ can be deposited without the incorporation of H. In addition to the advantages of easy scale-up of the magnetron sputtering process we have demonstrated the feasibility of producing silicon photonic structures by this procedure$^{16}$ on a wide variety of substrates from polymers to glass.

Similar closed pores microstructures can be found in ion-irradiated or ion-implanted thin films$^{17-23}$ which have been pointed out as fabrication routes for nanostructured materials and surfaces.$^{19-25}$ Generally these microstructures consist in few pores situated at a certain distance from the surface; while with our methodology, highly porous structures with uniform porosity from the substrate to the coatings surface are deposited, in a wide range of thicknesses (from 100 nm to few microns). From a fundamental point of view these new materials with embedded pores, filled with the sputtering gas, represent a new class of nanocomposite materials presenting on demand optical properties in comparison with the matrix film. To fully understand and control these properties and also for the stability and integrity of the coatings in possible applications, the physical parameters (density, pressure) defining the state of the gases inside the pores become an important issue.

In a recent work we have investigated the state of Helium gas inside the pores of magnetron sputtered amorphous silicon films, by spatially resolved electron energy-loss spectroscopy (EELS).$^{15}$ Through these 2D spectroscopic maps at the nanoscale, we have been able to demonstrate that He is located inside the nanopores of the coatings in a condensed state, with densities as high as tens of He atoms/nm$^3$ and pressure close to the GPa range.$^{15}$

The way to measure the He density consisted in extracting the intensity of the He-K edge (located at about 23 eV) and doing the quantification by considering the zero-loss intensity, the inelastic cross-section for He and the pore thickness.$^{15,18}$ The pressure was then evaluated using a suitable equation of state.$^{15}$ In principle, a similar approach could be used to quantify other elements trapped inside pores, like nitrogen in our case. However, contrary to the case
of nanobubbles or nanopores filled with helium for which quantification has already been achieved in various studies, only a few works attempted to evaluate the N\textsubscript{2} density and pressure inside closed cavities. Most of them were done in a semi-quantitative way based on the variation of the N-K edge intensity over the nitride matrix and over the pore. Indeed, the quantification of the nitrogen density inside small pores is a more challenging problem than for helium. The main reason is that the N-K edge position is quite far from the elastic peak and due to the limited dynamical range of the CCD detectors, the low-loss (LL) and core-loss (CL) energy range have to be recorded separately, with different dwell times. To our knowledge, only one work of the literature has reported the quantification of nitrogen density from EELS based on Ref. 18, but very few details of the analysis were given (in particular the way to record and process the EELS data to get the zero-loss and N-K edge intensities). In addition, this study was performed on an ideal case with a surrounding matrix free of nitrogen.

In this context, this article presents for the first time the extraction of the N-K signal due to molecular nitrogen and the quantification of the density and pressure of N\textsubscript{2} condensed inside small pores surrounded by an oxynitride matrix. The LL and CL EELS spectrum images were acquired consecutively and have been processed following the recent work by Bobynko et al. in Ref. 34. A better approach would have been to use the so-called DualEELS technique (not available in our study). However, as an alternative to DualEELS, we suggest here to acquire the LL and CL SIs separately and to realign them spatially during a post processing step. Our study will focus on nanopores filled with N\textsubscript{2} and formed in SiO\textsubscript{x}N\textsubscript{y} films deposited by magnetron sputtering according to our previous work. However, this approach may also be generalized to allow to study other systems, including nitride materials, and containing cavities filled with molecular nitrogen either formed during synthesis or nanostructuring processes like ion irradiation or implantation. Finally a comparison with macroscopic results obtained previously from Rutherford backscattering spectrometry (RBS) measurements will be presented to confirm our EELS quantification at the nanoscale.

II. EXPERIMENTAL METHODS

In order to have closed porosity filled with N\textsubscript{2}, the SiO\textsubscript{x}N\textsubscript{y} coating chosen for this study was deposited on Si (100) substrate, as described in Ref. 12, by reactive magnetron sputtering using a mixture of nitrogen and oxygen as sputtering gas (total pressure of 1.33 Pa, oxygen partial pressure of 1x10\textsuperscript{-4} Pa). A RF power source at 150 W was used to sputter a pure Si target (Kurt J. Lesker 99.999%). To obtain the largest pores according to our previous work, the
Transmission electron microscopy (TEM) experiments were carried out at the Advanced Laboratory of Nanosciences and Spectroscopies-LANE at the ICMS (Seville, Spain) using a FEI Tecnai F30 microscope operated at 300 keV. Cross-sectional TEM specimens were prepared by mechanical polishing and dimple grinding followed by Argon ion milling, until electron transparency was achieved. Just before insertion into the TEM, the specimen inside the holder was cleaned in O$_2$/Ar plasma. The coating morphology was studied by conventional bright field (BF) and high resolution TEM (HRTEM) imaging. To analyze the matrix and pores composition, electron energy-loss spectroscopy spectrum images (EELS-SIs) were recorded with a GATAN GIF Quantum energy filter using the scanning TEM high-angle angular dark field (STEM-HAADF) mode. The EELS spectra were recorded over 2048 channels with a dispersion of 0.25 eV/channel. The convergence and acceptance semi-angles were set to 12.4 mrad and 9.6 mrad, respectively and the probe current ranged between 50 and 90 pA. In order to measure the density of nitrogen trapped inside the pores, EELS-SIs were recorded consecutively in the CL and LL ranges, within a few minutes of interval. The energy ranges used to record the data (from -50 to 462 eV for the LL, and from 210 to 722 eV for the CL) were set to get a sufficient number of channels of overlapping energies for subsequent rescaling. Electron probe spacing of 1 to 3 nm with subpixel scanning (16x16) was used and different integration times in both ranges were set to avoid signal saturation on the CCD (typical values are 0.5 second/spectra for the CL and 0.02 second/spectra for the LL). The energy resolution of 1.5 eV was determined at the full width at half maximum of the elastic peak. During the acquisition, spatial drift correction was applied and the EELS data were corrected for the dark current and the gain variation of the CCD detector. Dark current correction was improved after each SI acquisition using the function provided by the GATAN Microscopy Suite 2.1.

The film bulk composition was determined by RBS using the 3 MV tandem accelerator of the National Centre for Accelerators in Seville (Spain). The spectra were measured with a 2 MeV He$^+$ beam and the detection angle was 165°. The experimental spectra were analyzed using the SIMNRA simulation code.$^{37}$

**III. RESULTS AND DISCUSSION**

*Microstructure, bonding and compositional information of the coating*

For this study a particular porous silicon oxynitride coating with a bulk composition Si:O:N = 35:20:45 at. % as given by RBS, presenting 26% of porosity and a refractive index of
1.60 was selected (more detailed characterization of this coating is presented in previous works\textsuperscript{11-12}).

The BF TEM image in Fig. 1a presents an overview of the SiO\textsubscript{x}N\textsubscript{y} coating microstructure where the porous structure can be seen in bright contrast. Pores from about 3 to 20 nm in size are observed. In the high magnification image shown in Fig. 1b it is possible to observe in more detail the round shape of the pores and the absence of crystal plane features.

The Si-L, N-K, and O-K edges provide useful information on the bonding state of these elements in the SiO\textsubscript{x}N\textsubscript{y} matrix and confirm the presence of molecular N\textsubscript{2} inside the pores. Figure 1c shows the energy-loss near-edge structures (ELNES) recorded across the matrix and across one pore compared to reference edges of amorphous SiO\textsubscript{2},\textsuperscript{38} Si\textsubscript{3}N\textsubscript{4},\textsuperscript{39} as well as O\textsubscript{2}\textsuperscript{40} and N\textsubscript{2}\textsuperscript{41}. These ELNES were extracted from the singular scattering distribution by fitting the signal prior to the edge with a power-law function. Prior to the edge extraction, the EELS-SIs were processed following the procedure described later in this work. As can be observed in Fig. 1c.1, the Si-L edges of the matrix and pore regions exhibit similar shapes, with four main features labelled `a1´, `a2´, `a3´ and `a4´ at about 105 eV, 113 eV, 127 eV, and 156 eV, respectively. Such features are close to the Si\textsubscript{3}N\textsubscript{4} reference and thus indicate that Si-N bonds dominate in the present SiO\textsubscript{x}N\textsubscript{y} coating. In SiO\textsubscript{2}, these features are slightly shifted towards the higher energies. Therefore, the larger peak widths observed for SiO\textsubscript{x}N\textsubscript{y} may also indicate the presence of Si-O bonds. The O-K ELNES recorded across the pore and the matrix does not present significant differences (Fig. 1c.3). The spectra present two main features identified as `c2´ and `c3´ at about 538 eV and 560 eV and have strong similarities with the SiO\textsubscript{2} reference, which indicates that oxygen atoms have similar local atomic environment than in silica. The shape of N-K edge changes significantly with the position of the electron probe (Fig. 1c.2). Across the matrix, the ELNES is very similar to the fingerprint in Si\textsubscript{3}N\textsubscript{4}, with two main broad features `b2´ and `b3´ at 405 eV and 422 eV. In the pore area an additional intense narrow peak `b1´ appears at the onset around 401 eV, corresponding to the signature of molecular nitrogen N\textsubscript{2} as observed previously in Ref. 12. These data confirm that the pores are filled with molecular nitrogen.

The composition of the SiO\textsubscript{x}N\textsubscript{y} matrix has been determined from these edges using the Digital Micrograph program. According to Ref. 42, an integration window of 25 eV was set for Si-L, while the N-K and O-K edges were integrated over 100 eV. An average matrix composition Si:O:N 33:25:42 at. % was calculated using Hartree-Slater cross-sections. It is worth to note that the composition obtained by quantification of the EELS spectra of the matrix is in quite good agreement with the bulk composition of the coating measured previously by Rutherford
backscattering spectroscopy. The value of the matrix composition by EELS quantification will be used later to calculate the inelastic mean free path of electrons in the specimen.

**EELS-SI data processing for compositional analysis**

The next sub-sections describe the steps necessary for processing the data in order to quantify the $N_2$ density inside the pores surrounded by the amorphous oxynitride matrix. An *Ad hoc* semi-automated code running with MATLAB has been developed to allow the data analysis over large datasets. It is available on demand. Prior to the analysis, X-rays spikes were removed from the SIs using the routine provided with the GATAN Microscopy Suite 2.1.

**Spatial and energy alignment of the SIs and noise reduction**

Since the LL and CL EELS-SIs were recorded separately, to ensure that each pixel of the two EELS-SIs corresponds to the same specimen area, the two datasets were first realigned spatially. For that purpose, the STEM-HAADF images recorded in the low-loss and the core-loss ranges were used as references and submitted to cross-correlation. More information about the spatial alignment of the LL and CL datasets can be found in the Supporting Information.

In a second step, the datasets were realigned along the energy axis. Figure 2a shows the STEM-HAADF signal of the porous coating acquired in parallel with EELS spectrum images. On this image, the intensity is proportional to the atomic number and the thickness of the sample, the dark areas correspond to phases with lower Z, and in this case the pores are darker than the surrounding matrix. Figures 2b-d present two examples of LL and CL spectra recorded across the matrix and across one pore after the alignment procedure. In the LL range, the spectra were shifted in order to get for each pixel position the zero-loss peak (ZLP) at the same channel corresponding to zero energy-loss (Fig. 2b). On Fig. 2b, the bulk plasmon can be seen at about 22.6 eV. An additional peak around 14 eV, attributed to the cavity plasmon, is also observed when the probe is located across the pore. An additional broad feature can be observed between 15 to 19 eV, which can be tentatively attributed to surface states of the $SiO_xN_y$ matrix. This feature is more important in the pores regions where the matrix layer is thinner than in the bulk matrix. The Si-L edge also appears in the LL range near 100 eV, see Fig. 2c. However, the N-K edge around 400 eV is not visible on the LL spectra due to the low exposure time. In the CL range, the spectra were shifted by aligning the onset of the O-K edge at reference energy of 532 eV. Figure 2d clearly shows the N-K edge, whose signature depends on the position of the electron probe: outside the pores, the N-K edge presents the two broad bands typical of the $SiO_xN_y$ matrix whereas the signal recorded across the pore has an additional narrow peak at the onset (401 eV) which is attributed to molecular nitrogen $N_2$.12
The choice of O-K instead of N-K as reference edge for the alignment was motivated by the fact that its shape remains unchanged whatever the position of the probe is.

As can be observed on the blue curves of Fig. 2, the EELS spectra contain a substantial noise component that can affect the background subtraction for further quantification. In order to reduce this contribution, principal component analysis (PCA) was applied on the LL and CL HL datasets after the alignment step. The signal was then reconstructed with a great care to avoid the loss of relevant spectroscopic information by keeping a limited (but sufficiently large) number of components, as shown on the red plots on Fig. 2. More details on PCA are given in the Supporting Information.

Splicing of the LL and CL spectra and multiple scattering deconvolution

As the LL and CL EELS data were recorded with different exposure times, the next step consists in splicing the spectra together pixel-by-pixel. This step has been performed with special care because residual noisy signal in the LL splicing region (due to low exposure time) may introduce additional errors in the determination of the scaling factor. An example of spliced spectrum and additional details related to the splicing procedure are given in the Supporting Information.

Electron multiple scattering can strongly affect the shape of the energy-loss near-edge structures (ELNES) especially when the specimen thickness increases. In the case of porous material with pores of several nm in size, changes in the specimen thickness crossed by the electron beam occur. In order to compare the edge shapes and intensities for different position of the probe, it is necessary to remove these plural scattering effects. For that purpose, multiple scattering deconvolution was applied to the spliced spectra using the Fourier logarithmic method (see FLOG routine in Ref. 45). An example of spectrum obtained after deconvolution is provided in the Supporting Information.

Quantification of molecular nitrogen inside the pores

In order to separate the two overlapping signals coming from the matrix and from pores, the N-K edges were beforehand extracted from the deconvoluted spectra by fitting the signal prior to the edge with a power-law function. Figure 3a illustrates the extraction procedure of the N$_2$ component. An average contribution of the matrix was first determined from a set of pixels outside the pore regions. The matrix spectrum was then scaled up to match the intensity of each extracted N-K edge spectrum in the dataset. To find the adequate scale factor, least square fitting was performed in two regions: before the edge (390 - 398 eV), and between 403.5 and 405.8 eV where the contribution of the molecular nitrogen to the N-K
edge spectrum is closed to zero. The scaled SiO$_x$N$_y$ matrix contribution was finally removed to obtain the molecular nitrogen component. In Fig. 3a, one can notice that the shape of the molecular contribution extracted from our sample is similar to the N$_2$ reference from McLaren et al.$^{41}$ Moreover, the N$_2$ contribution is negligible outside the pore while it is very strong across the pore, as expected. A contribution of the matrix is still present due to the SiO$_x$N$_y$ walls surrounding the closed pore. All these observations allow us to validate our extraction procedure. This approach was performed pixel-by-pixel and the intensities were integrated over 100 eV to return a 2D map representing the spatial distribution of each component. As can be seen on Fig. 3b, the amount of molecular nitrogen across the pore area is closed to 50% (blue region) indicating the presence of a high N$_2$ content.

The density of molecular nitrogen inside the pores $n_N$ can now be evaluated from an approach similar to that introduced in Ref. 18 using:

$$n_N = \frac{I_N}{I_0 \sigma_N h} \quad (1)$$

In equation (1), $I_N$ represents the integral intensity of the molecular contribution on the N-K edge. $\sigma_N$ is the angle-integrated cross-section for the N-K edge. It was calculated in our experimental conditions with the hydrogenic model using the SIGMAK3 routine.$^{45}$ Both $I_N$ and $\sigma_N$ were determined over an energy range of 100 eV starting at the edge onset. A large integration window was chosen to average out chemical bonding effects and maximize the signal, as suggested by Crozier and Chenna.$^{46}$ The parameter $h$ is the local pore (or cavity) thickness crossed by the electron beam, which was determined as the complement to the local thickness measurements of the matrix.$^{15, 26, 28}$ For that purpose, the absolute specimen thickness $t$ was computed by combining the calculations of the relative specimen thickness $t/\lambda$ with the inelastic mean free path $\lambda$. $t/\lambda$ was determined by the Log-ratio method.$^{45}$ $\lambda$ was obtained using the parametrized approach described by Malis et al.$^{47}$ taking into account the matrix composition determined previously. As the highest source of uncertainties certainly comes from the $h$ parameter, the pore thickness determination was cross-checked with the measurement of the pore size $d$ on the STEM-HAADF images assuming spherical pores. The integral intensity of the elastic peak $I_0$ was also determined and stored for each position during the calculation of $h$.

Figure 4 and Table I present the results obtained on the largest pore of the dataset (Pore#1 in the table). The 2D maps in Fig. 4a-d represent the normalized HAADF intensity, $t/\lambda$, $I_0$ and $I_N$ values. The nitrogen density map, shown in Fig. 4e, was calculated using $\sigma_N$=2427 barn and $\lambda$ =161 nm. An average density $n_N$=45 atoms/nm$^3$ was determined from a set of pixels in the pore center, which corresponds to about 23 N$_2$ molecules/nm$^3$ (1.04 g/cm$^3$ of
nitrogen) stored inside the pore. According to the $N_2$ pressure-density equation of state established at 300K in Ref. 48, the average nitrogen pressure $P_{N_2}$ inside the pore should be closed to 0.8 GPa. Similar analysis was applied to various pores in the sample with sizes ranging from 11 to 20 nm. The results are summarized in Table I. As the pores are not always perfectly round, a range of pore size is given in the table. It is worth to mention that the density values near the pores borders are slightly lower than at the pore center. Similar effects have already been reported for He bubbles by Taverna et al.\textsuperscript{26} and attributed to surface effects. In the present manuscript only pixels in the pore center were considered. This is a usual way to limit surface effects (see for example Ref. 28).

The $n_N$ values measured in the present work ranges from 40 to 72 at./nm$^3$ (0.93 to 1.67 g/cm$^3$). Even if some of them are slightly lower, these values are in the same range of magnitude than the nitrogen densities determined previously inside $N_2$ inclusions in GaN-based materials\textsuperscript{30-31} (1.9 g/cm$^3$ and 1.4 g/cm$^3$, respectively). According to the volume-temperature diagram determined by Mills et al.\textsuperscript{49} and assuming a temperature of 300K, our density values measured inside the nanopores of the SiO$_x$N$_y$ coating correspond to $N_2$ in a condensed state. In all the cases, nitrogen remains in the molecular state, which explain why we observe a similar ELNES signature than for the $N_2$ gas phase. Interestingly, an increase of the nitrogen density from 40 to 72 at./nm$^3$ (0.93 to 1.67 g/cm$^3$) was found as the pore size decreases. Assuming that pores are spherical of radius $r$ (with $r = h/2$, $h$ being the average pore thickness across the pore center) we obtained as a general trend a linear increase of the density $n_N = (403 \pm 105)/r + (4 \pm 14)$, as shown on Fig. 5. This behavior previously reported in helium bubbles\textsuperscript{18,26-27} can be attributed to the equilibrium condition of the surface energy of the matrix with the internal $N_2$ pressure of the pore. This point is actually under investigation in our laboratory for a future study.

It is known that in the case of He bubbles, a correlation exists between the density and the position of the He-K edge peak, producing a blue-shift for higher densities dominated by Pauli repulsion effect.\textsuperscript{50} In the present work the position of the molecular nitrogen K edge is however almost constant in the range of pore size and density measured here. Actually, for the two extreme nitrogen densities values of 40 and 72 at./nm$^3$, the mean position of the sharp peak of molecular nitrogen edge is found at 401.1 ± 0.1 eV and 401.0 ± 0.1 eV, respectively. In Fig. 4e, one can observe that the N density over the pore center is homogeneous, meaning that the nitrogen inside remains stable under the electron beam. The $N_2$ stability was verified by monitoring the evolution of the N-K edge for different times of residence of the probe across a pore of 25 nm diameter, the results are shown on Fig. 6. Notice that the spectra presented in Fig. 6 are raw data without PCA processing. As observed, the intensity of the
sharp peak corresponding to molecular $N_2$, integrated in the [399-403)eV range, does not decrease significantly with exposition to the electron beam, which indicates that in these conditions the $N_2$ inside the pore remains stable even after 60s of probe residence time.

**Comparison with macroscopic results**

Knowing the coating composition and porosity it is possible to determine an average value for the $N_2$ density inside the pores from the macroscopic results. Firstly one must assume that the pore distribution is homogeneous, which is supported by Fig. 1a. With a porosity $\phi = 26\%$ (see Ref. 12), to 1 nm$^3$ of the porous coatings corresponds 0.26 nm$^3$ of the pore volume (and 0.74 nm$^3$ of dense matrix). According the coating composition measured by RBS (35 at. % Si, 45 at. % N, and 20 at. % O), and considering the stoichiometry of pure phases ($SiO_2$ and $Si_3N_4$) one can consider for the oxynitride dense matrix the formula $(SiO_2)_{0.55}(Si_3N_4)_{0.45}$. This corresponds to a composition for the dense silicon oxynitride matrix of 35 at. % Si, 33.3 at. % N and 20 at. % O. The excess of nitrogen, 11.7 at. %, represents the percentage of atoms trapped as molecular nitrogen according to the macroscopic RBS measurements. Considering the density of crystalline $SiO_2$ and $Si_3N_4$ pure phases, an average density for the $SiO_xN_y$ dense matrix of 2.9 g/cm$^3$ is estimated (this value is likely overestimated due to the amorphous character of our $SiO_xN_y$ coating). From the results in the previous section, considering the molecular nitrogen to be trapped inside the pore volume, a final average density of 32.7 nitrogen atoms (or 16.3 $N_2$ molecules) per nm$^3$ of pore volume is obtained. This average value determined from macroscopic measurements is in good agreement with our mean values obtained at the nanoscale using EELS on different pores (see Table I).

**IV. CONCLUSION**

In this work, the state (density and pressure) of molecular $N_2$ inside closed nanopores in a $SiO_xN_y$ coating was determined for the first time using spatially resolved EELS. The procedure to record, process and quantify the EELS spectrum images acquired at different energy ranges and with different dwell times is described here in details. An adequate way to separate and extract properly the N-K edge contribution due to the molecular nitrogen inside the nanopores surrounded by a nitrogen-containing matrix is also reported. With this method, we were able to point out that these porous coating formed by magnetron sputtering can present a huge amount of $N_2$ inside nanopores of sizes ranging from about 11 to 20 nm. Nitrogen densities from 40 to 72 at./nm$^3$ were measured (20 to 36 $N_2$ mol./nm$^3$), which correspond to pressures ranging from 0.5 to 7.5 GPa. Measurements derived from
macroscopic techniques allowed to validate the $N_2$ quantification method inside the nanopores. Interestingly, a correlation between the pore size and the $N_2$ density and pressure was evidenced at the nanoscale: the smaller the pores, the higher the nitrogen density and pressure. In addition, these measurements demonstrated the very high stability of the porous coatings, since they were elaborated about 9 years before and still contain a high quantity of $N_2$. This quantitative approach can be easily extended to other nitride systems containing cavities filled with molecular nitrogen either formed during the growth or during processes like ion irradiation.

**SUPPORTING INFORMATION**

Spatial alignment of the LL and CL datasets using cross-correlation, Reduction of the noise contribution on the EELS data using PCA, Splicing of the LL and CL spectra, Multiple scattering deconvolution.

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39. The Si-L and N-K edges for silicon nitride were recorded on a Si$_3$N$_4$ powder (Sigma-Aldrich company, product number: 248622) in the same conditions than for the present SiO$_x$N$_y$ coating.


FIG. 1. (a) BF TEM image of the SiO$_x$N$_y$ coating showing the nanoporous structure (in bright contrast). (b) High magnification image recorded at the vicinity of various pores. The image was acquired in slight under-focused conditions in order to see the contour of the pores. (c) ELNES recorded across the matrix and across the pore of the SiO$_x$N$_y$ coating compared with references for Si$_3$N$_4$ and SiO$_2$, N$_2$ and O$_2$ (c.1) Si-L edge. (c.2) N-K edge. (c.3) O-K edge.
FIG. 2. (a) STEM-HAADF image recorded over various pores (in dark contrast) simultaneously with the EELS data. Labels (1) and (2) indicate the pixels chosen for plotting the aligned EELS spectra recorded across one pore and across the matrix, before and after PCA, in different energy ranges. (b) Low-loss range with the ZLP and plasmons contributions. (c) Middle-end of the low-loss range with the Si-L edge visible at about 100 eV. (d) High-loss range with the N-K and O-K edges visible at about 400 and 532 eV.
FIG. 3. (a) Extraction of the molecular contribution from the N-K edge (across the pore and across the matrix). The green areas indicates the energy ranges where the matrix contribution was scaled to the N-K edge. The N$_2$ reference spectrum shown for comparison was obtained from Ref. 41. (b) 2D map showing the ratio of intensities (integrated over 100 eV) of the two N-K components (molecular/matrix).
FIG. 4. 2D quantification of the molecular nitrogen inside one pore. (a) STEM-HAADF map, (b) relative specimen thickness map, (c) zero-loss intensity map, (d) molecular N-K intensity map, (e) nitrogen atomic density map. Each pixel on the maps corresponds to 2 nm.
FIG. 5. Evolution of the molecular nitrogen density as a function of the inverse of the pore radius $1/r$ (with $r = h/2$) assuming that the pores are spherical. The red dashed line represents the linear fit of the data.
FIG. 6. (a) Evolution of the N-K edge recorded in the center of a pore for different residence time of the electron probe. EELS-SIs were recorded consecutively over the same pore (about 25 nm in size) using an integration time of 0.5s/pixels. For comparison purpose, the edges were taken from the same pixel position across the pore and extracted by power-law fitting. Except the use of a dispersion of 0.1 eV/channel, the other experimental conditions are similar to that presented in Sec. II. The residence time of the probe was determined as the number of pixels recorded across the pore multiplied by the integration time per pixel, as proposed by David et al. (Ref. 29). (b) Variation of the integral intensity of the N-K edge in the [399-403]eV range.
TABLE I. Nitrogen density and pressure measured inside pores of different size. The pore size range $d$ was determined from the HAADF images. The mean values for $h$, $n_N$ and $P_{N_2}$ were estimated from STEM-EELS analysis over a set of pixels taken across the pore center. The errors correspond to the standard deviation.

<table>
<thead>
<tr>
<th>Pore</th>
<th>$d$ (nm)</th>
<th>$h$ (nm)</th>
<th>$n_N$ (at./nm$^3$)</th>
<th>$P_{N_2}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>18 - 20.5</td>
<td>18 ± 2</td>
<td>45 ± 3</td>
<td>0.8</td>
</tr>
<tr>
<td>#2</td>
<td>12 - 13.5</td>
<td>11 ± 2</td>
<td>72 ± 5</td>
<td>7.5</td>
</tr>
<tr>
<td>#3</td>
<td>13 - 14</td>
<td>14 ± 2</td>
<td>69 ± 6</td>
<td>6.3</td>
</tr>
<tr>
<td>#4</td>
<td>14 - 20</td>
<td>20 ± 4</td>
<td>40 ± 12</td>
<td>0.5</td>
</tr>
<tr>
<td>#5</td>
<td>11 - 15</td>
<td>16 ± 2</td>
<td>59 ± 10</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Table of Contents (TOC)

2D quantification of $N_2$ density and pressure inside nanopores
across the matrix

across the pore

extracted N-K edge

matrix contribution

molecular contribution

N$_2$ reference

Molecular/Matrix N–K intensity ratio

Energy loss (eV)

Intensity (a.u.)

N$_2$ reference

20 nm
The Journal of Physical Chemistry

(a) Integral intensity variation

(b) Residence time (s)

Energy loss (eV)

Intensity (a.u.)

1 0.5 1.0 1.5 2.0

0 20 40 60

t_{res} = 7.5s

t_{res} = 18s

t_{res} = 28.5s

t_{res} = 39s

t_{res} = 49.5s

t_{res} = 60s
2D quantification of N\textsubscript{2} density and pressure inside nanopores.