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1 TiO₂-SiO₂ Nanocomposite thin films deposited by
2 Direct Liquid Injection of colloidal solution in an
3 O₂/HMDSO low-pressure plasma

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11 **Keywords:** low-pressure plasma processing, direct-liquid injection, colloidal solution, TiO₂
12 nanoparticles, TiO₂-SiO₂ nanocomposite thin films

13 **Abstract:** TiO₂ nanoparticles (NPs), 3 nm in size, were injected inside a very-low-pressure O₂
14 plasma reactor using a liquid injector and following an iterative injection sequence.
15 Simultaneously, hexamethyldisiloxane (HMDSO) vapor precursor was added to create a SiO₂
16 matrix and a TiO₂-SiO₂ nanocomposite (NC) thin film. Both the liquid injection and vapor
17 precursor parameters were established to address the main challenges observed when creating
18 NCs. In contrast to most aerosol-assisted plasma deposition processes, Scanning/Transmission
19 Electron Microscopy (S/TEM) indicated isolated (i.e. non-agglomerated) NPs distributed in a
20 rather uniform way in the matrix. The fraction of the TiO₂ NPs inside the SiO₂ matrix was
21 estimated by SEM, Spectroscopic Ellipsometry (SE), and X-ray Photoelectron Spectroscopy.
22 All techniques provided coherent values, with percentages between 12 and 19%. Despite the
23 presence of TiO₂ NPs, SE measurements confirmed that the plasma-deposited SiO₂ matrix was
24 dense with an optical quality similar to the one of thermal silica. Finally, the percentage of TiO₂
25 NPs inside the SiO₂ matrix and the effective refractive index of the NCs can be tuned through
26 judicious control of the injection sequence.

27

1. Introduction

Nowadays, there is an ongoing demand for smaller, faster, and low-cost integrated systems. Achieving this often requires new materials and structures that combine the more conventional ones. In this context, nanocomposite (NC) thin films formed of nanoobjects embedded in a matrix have gained great attention, as the properties of the resulting composite may be more likely to resemble those of the interface zones rather than those of the original constituents[1]. The high surface-area-to-volume ratio in NCs can also lead to enhanced macroscopic properties compared to the bulk materials.

One of the most significant challenge in the development of NC thin films is the control of the growth mechanisms, the final morphology and the incorporation of the nanoobjects using reproducible, versatile and low-cost processes. Several chemical and physical methods have been used in recent years. For example, sol-gel is a well-established process based on hydrolysis and condensation reactions.[2,3] The main drawback of this approach is the need of several steps to produce NC thin films. In addition, the toxicity of the nanoparticles (NPs) during the drying of the film[4] limits the industrialization. Vacuum processes such as PECVD or CVD have also demonstrated their ability to synthesize NC thin films by controlling the plasma- or thermally-activated reaction pathways.[5,6] In parallel, sputtering approaches have also been used to create metal, metal-oxide or metal-nitrides NC thin films. [4,7]

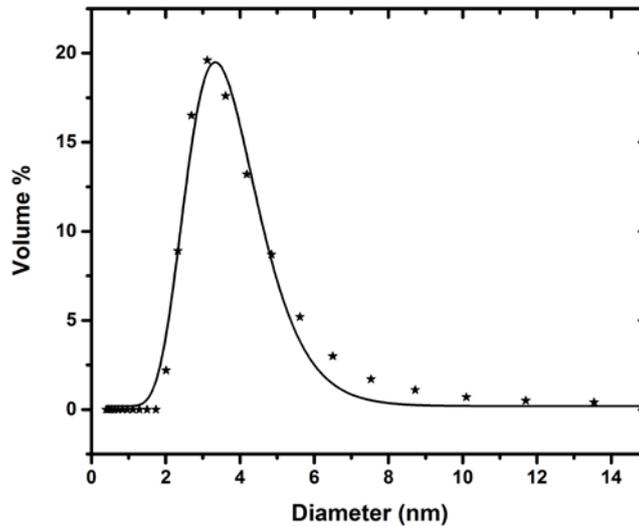
Recently, there have been some attempts using hybrid (aerosol-assisted, direct liquid injection etc.) approaches for the creation of NC thin films. Profili et al. [8] implemented a one-step approach for the deposition of ZnO-SiO₂ NC coatings on wood by the atomization of a stable suspension of ZnO dispersed in hexamethyldisiloxane (HMDSO) in an atmospheric pressure dielectric barrier discharge (DBD). Ross et al.[9] elaborated composite films using an ultrasonic atomizer and a PECVD system using Tetraethoxysilane (TEOS) as a matrix precursor and polystyrene nanoparticles with a mean size of 96 nm. The pressure in the specific system was varied between 100 and 500 mTorr. More recently, Kahn et al.[10] proposed a new method that allowed to synthesize NPs from organometallic precursor in a reactor-injector prior to their injection in a RF low-pressure plasma reactor at 750 mTorr. The resulted NC thin films consisted of small (6 ± 3 nm) and isolated ZnO NPs homogeneously dispersed in an amorphous hydrogenated carbon matrix. This increased interest in hybrid approaches led to the development of new direct liquid injection systems[11] and studies regarding the interactions of the liquid droplets with the low pressure plasma systems [12] (misty plasmas). As a general trend, most of these studies focus on the deposition of inorganic NPs-organic matrix NC film. The majority of the reposted works involve high-pressure and atmospheric-pressure plasma system. These systems have been thoroughly studied mainly because of the technically-challenging conditions existing at very low pressures (*e.g.* risk of contamination of the vacuum chamber, malfunction of the turbomolecular pump, fast liquid vaporization without reaching the substrate).[13,14] In most cases, however, the NPs in NC thin films are agglomerated, and their size is increased compared to the one in the colloidal solution before their injection in the plasma. [13,15–22]

72 The main bottlenecks for producing NC thin films are incorporating a high-volume fraction,
73 preventing the agglomeration of NPs and dispersing them homogeneously in the matrix. Using
74 a very-low-pressure system, the objective is to deposit thin films incorporating 3-nm TiO₂ NPs
75 in a high-quality inorganic SiO₂ matrix. This is accomplished by the direct liquid injection of
76 the 3-nm TiO₂ NPs colloidal solution without a carrier gas and the addition of HMDSO vapor
77 precursor in the very-low-pressure O₂ plasma. Furthermore, as several works involving
78 atmospheric-pressure plasma systems reported challenges to deposit in one-step and acquire
79 good quality NC films, the differences and prospects in using very-low-pressure hybrid systems
80 is investigated. The evaluation of the NC's quality, homogeneity and distribution of the TiO₂
81 NPs are achieved by various characterization techniques such as high-resolution Scanning
82 Transmission Electron Microscopy (HR-STEM), Energy Dispersive X-ray spectrometry
83 (EDX), Atomic Force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).
84 Finally, with this work, besides establishing this novel and versatile approach, the objective is
85 to identify experimental conditions for acquiring thin films oriented towards optical
86 applications. Therefore, the optical characteristics of the film, such as its effective refractive
87 index, are being extracted with Spectroscopic Ellipsometry (SE).

88 89 **2. Experimental Details**

90 91 **2.1 TiO₂ NPs colloidal solution**

92
93 The colloidal solution used for the injection of the TiO₂ NPs in the very-low-pressure plasma
94 has been synthesized following a specific protocol developed at the Institut des Matériaux Jean
95 Rouxel.[23,24] The NPs enclosed in the colloidal solution were well-defined and
96 monodispersed with an anatase crystalline structure. Their mean hydrodynamic diameter
97 (including species of the solvent surrounding the NPs to counterbalance surface charge)
98 obtained by Dynamic Light Scattering (DLS) with Zetasizer NanoZS (Malvern) was centered
99 on 3.7 nm (Figure 1). The double layer surrounding the NPs has been estimated at 1 nm.[24]
100 Therefore, the actual TiO₂ nanocrystallite diameter lay at 2.7 nm. As synthesized, the solvent
101 of this solution was a mixture of 4-methyl-1,3-dioxolan-2-one also known as propylene
102 carbonate (PC) and 1,2-propanediol or propylene glycol (PG), with a molar fraction of
103 27%:73% respectively. From previous studies of our group [23,25], we identified that some
104 solvent molecules remain attached to the surface of the NPs, creating an 4.7 Å hydroxylated
105 and organic shell around TiO₂ NPs.



107
 108 **Figure 1:** Hydrodynamic size distribution of the TiO₂ NPs inside the as-prepared (PC-PG)
 109 colloidal solution deduced from DLS. Line corresponds to a Log-Normal distribution fit, based
 110 on which the mean diameter size was extracted.

111 For the effective injection and evaporation of the colloidal solution in the very-low-pressure
 112 PECVD system, the dilution of the colloidal solution with a more volatile one was carried out.
 113 Therefore, the final colloidal solution used was a mixture of PC:PG:Methanol with a volume
 114 fraction of 20.25:54.75:25 . The size distribution of TiO₂ NPs in the diluted solution was
 115 verified with DLS and was not altered by either dilution or long-time storage..

116
 117 **2.2 Deposition of TiO₂-SiO₂ NC thin films using the hybrid approach**

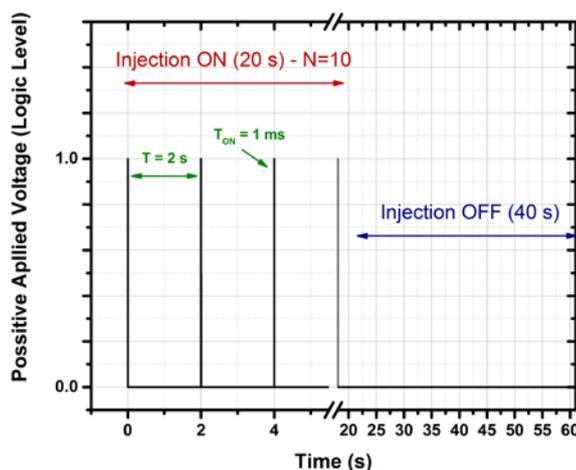
118
 119 For the elaboration of the TiO₂-SiO₂ NC thin film, the colloidal solution was injected in a
 120 very-low-pressure PECVD reactor. The schematic representation of the hybrid experimental
 121 setup is given in Figure 2. The reactor comprises a very-low-pressure high-density Inductively
 122 Coupled Plasma (ICP) source created at 13.56 MHz (400 W) in a fused silica discharge tube
 123 using a helicon antenna which is also connected to a matching network. A static magnetic field
 124 (50 G) is applied to the source in order to confine the electrons and densify the plasma. The
 125 plasma then expands into a stainless-steel processing chamber where the substrate holder is
 126 located. The substrate holder is 17 cm in diameter located in the middle of the processing
 127 chamber with a distance of 16.8 cm from the bottom of the ICP antenna. The Si substrates used,
 128 which were positioned in the middle of the substrate holder, were 1 cm x 2 cm in dimension
 129 and their temperature was measured at 400 K through temperature-sensitive labels located at
 130 the substrate's backside. In this system, plasma gases (95% O₂, 5% Ar here) are introduced at
 131 the top of the plasma source and the high-vacuum pumping system is located 11 cm from the
 132 bottom of the processing chamber. The outlet of the vacuum pumping system that includes also
 133 a cold trap, is 10 cm in diameter. In Figure 2b, its location related to the substrate holder and
 134 the liquid doser can be seen. More information about the reactor can be found in [26,27].

135
 136 For the deposition of the SiO₂ matrix, HMDSO vapor was introduced from a heated-
 137 container (at 35.8 °C) without any carrier gas through a distribution ring (indicated with blue
 138 in Figure 2), located 8 cm above the substrate. The injection of the TiO₂ colloidal solution was

170 extinguished remaining ignited during the total duration of the process. As a matter of fact, the
171 intensities of O and Ar lines (at 394.5 nm and 419.8 nm, respectively) measured by time
172 resolved OES are supplied as Electronic Supporting Information (ESI). These results, indicate
173 that during each injection (within the DLI-ON), the emission intensities of the Ar and O lines
174 are decreased trying to retrieve their steady state value within the pulses (Figure S1). This
175 variation, especially for the Ar emission intensity is related to the pressure variation. Both
176 intensities never reach a zero value verifying once more that the plasma remains ignited during
177 the total duration of the hybrid deposition process. Regarding the RF power supply, during the
178 droplet injection, a reflected power with a mean value of 2 W is provided by the CESAR RF
179 Power Generator.

180
181 For deposition experiments, the total sequence length was set at one minute (Figure 2). More
182 specifically, during the first 20 s, $N=10$ pulses of 1 ms ($T_{ON} = 1$ ms) were triggered each two
183 seconds ($T=2$ s). Thus, after this first-time lapse of $N*2$ s = 20 s, the valve remained closed for
184 $60-N*2$ s = 40 s (T_{OFF}). Such sequence was repeated for 50 minutes. The solvent mass rate was
185 estimated at 2.33 mg per pulsed injection and therefore 23.3 mg per minute for $N=10$ cycles.
186 During this intermittent mode of injection (Figure 3), the oxygen mass flow rate of the working
187 gas was set at 24 SCCM (standard cubic centimeters per minute) while the continuous mass
188 flow rate of HMDSO vapor was maintained at 0.11 SCCM. The fraction between HMDSO and
189 O_2 was chosen in a way to produce a silica-like matrix with a very low carbon content[29]. O_2
190 was also used to ensure the removal of solvent-based organic moieties surrounding TiO_2
191 NPs[30].

192



193
194 **Figure 3:** Description of the plasma deposition sequence including the first part of pulsed
195 injection of the colloidal solution (10 cycles of T_{ON} with an off time of 2 s between each pulse
196 for a total of 20 s) and the second part without liquid injection (for a total off time $T_{OFF} = 40$ s).

197 2.3 Characterization of the NC thin films

198
199 The cross section and distribution of the TiO_2 NPs inside the SiO_2 matrix were investigated
200 (Figure 4 a, b ,c) using transmission electron microscopy (S/TEM Themis Z G3, 300kV,
201 Thermo Fisher Scientific). A typical image of high-angle annular dark-field scanning
202 transmission electron microscopy (HAADF-STEM, 28.5 mrad, probe corrected) is reported in

203 Figure 4 d. The elemental mapping (Figure 4 e f g) was performed using EDX (energy
204 dispersive X-ray spectrometer) analysis. For the effective characterization of the samples
205 through TEM, the deposition was carried on Tin doped Indium oxide deposited on polyethylene
206 terephthalate (ITO (50 nm) / PET (125 μm), Sheldahl). Cross-sections of the sample were
207 prepared by using an ultramicrotome (Leica UC7/FC7) equipped with diamond knife
208 (Diatome). The morphological analysis of the $\text{TiO}_2\text{-SiO}_2$ NC film on Si was carried out through
209 Scanning Electron Microscopy (SEM) with a JEOL JSM 7600F, in a secondary electron mode,
210 operating at 5 kV. The chemical analysis by EDX was conducted with a SAMx SDD system
211 on a SEM JEOL JSM 5800LV. To increase the EDX signals, a dedicated thicker film was
212 prepared (224 nm). To ensure that no additional Si coming from the substrate would interfere
213 with the quantification of the silica matrix the dedicated thicker NC film was deposited on
214 ITO/PET substrate. To probe different thicknesses, EDX spectra were recorded at three
215 accelerating voltages: 15 kV, 10 kV and 7 kV and a magnification of X1000 ($2552 \mu\text{m}^2$) was
216 chosen to smooth any local anomalies of chemical concentrations. The software Stratagem was
217 used for EDX measurements because first the volume irradiated by the electron beam and
218 second the X-ray collected are related to a larger depth than the thickness of the top layer. [31]
219 The atomic percentages were determined by considering a theoretical model for the probed
220 zone [32]. For this, three layers were considered: first, 224 nm of NC (Ti, Si, O), second, 50
221 nm of ITO (In, Sn, O), and third, PET (C, O). The different atomic percentages were fitted to
222 reproduce the intensity of EDX signals as a function of the accelerating voltage, accounting for
223 the thicknesses of the NC and ITO and attenuation of signals throughout the different layers.
224 The determination of carbon and oxygen was not reliable because the corresponding signals
225 may come from ITO and PET underneath (one must also consider that the effective thickness
226 of PET analyzed by EDX depends on the accelerating voltage). However, the precautions taken
227 before acquisition and the good fit between theoretical curves generated by Stratagem and
228 experimental values make it possible to rely on the results concerning silicon and titanium
229 atomic percentages.

230
231 The optical characteristics and composition of the $\text{TiO}_2\text{-SiO}_2$ NC thin films deposited on
232 silicon substrates were also examined through a rotating compensator spectroscopic
233 ellipsometer (J.A. Woollam M-2000). The measurements were conducted in situ (i.e. during
234 plasma deposition) in the wavelength range of 245 to 1000 nm at 71.7° incident angle.

235
236 Atomic Force Microscopy (AFM) was used in tapping mode to investigate the nanostructured
237 topography and roughness of the NC thin films. AFM Nanowizard II (JPK Instruments), Al-
238 coated cantilever (PPP-NCHR-50 from NANOSENSORS) with a free resonance frequency of
239 330 kHz and a typical spring constant of about 42 N/m were used. The size distribution of the
240 NPs was deduced from the AFM scans by using the ImageJ software after adjustment of the
241 threshold and transformation in binary format.

242
243 Raman spectroscopy measurements were performed using a microconfocal Raman
244 microscope (Renishaw inVia). The instrument was equipped with a double edge filter to
245 eliminate the Rayleigh scattering and a charged couple device (CCD) camera working at a
246 temperature of 220 K with a 1024×256 pixel array. The setup was composed of a confocal

247 microscope that was equipped with an automated XYZ table and an X50 magnification
248 objective. The laser excitation source used was set at 514 nm and the focused power was
249 adjusted to avoid any degradation of the samples. Therefore, the power was fixed at 1.5mW
250 and a recording time of 1 s with an accumulation of 10 measurements was used.

251
252 The chemical characterization of the topmost surface was investigated with X-ray
253 photoelectron spectroscopy (XPS) on a Kratos Nova spectrometer with Al K α radiation at
254 1486.6 eV. Neutralization of the surface was applied to avoid differential charging effect.
255 Survey spectra were measured from 1200 to -2 eV (Binding Energy) using a pass energy of 160
256 eV whereas high-resolution spectra over specific regions of interest were recorded with a pass
257 energy of 40 eV. Short time measurements were recorded (dwell of 100 ms per 0.1 eV step-
258 scan for O1s, Ti 2p and 200 ms for C1s). After checking that no X-ray damage was induced,
259 the scans were summed up to increase the signal-to-noise ratio. The decomposition and fitting
260 of the measured XPS peaks was carried out using CasaXPS software [33]. After accounting for
261 the background using a U2-Tougaard background, Gaussian-Lorentzian (30-70%) functions
262 were selected to model the different components. The signals were calibrated in energy
263 according to the position of the C 1s band at the binding energy of 285 eV.

264
265 To be able to compare the results obtained from different characterization techniques, detailed
266 calculations have been achieved (which are supplied as Electronic Supporting Information) to
267 transform at% of elements to vol% of oxides.

268

269 **3. Results**

270

271 **3.1 Structural characterization of the TiO₂-SiO₂ NC thin films**

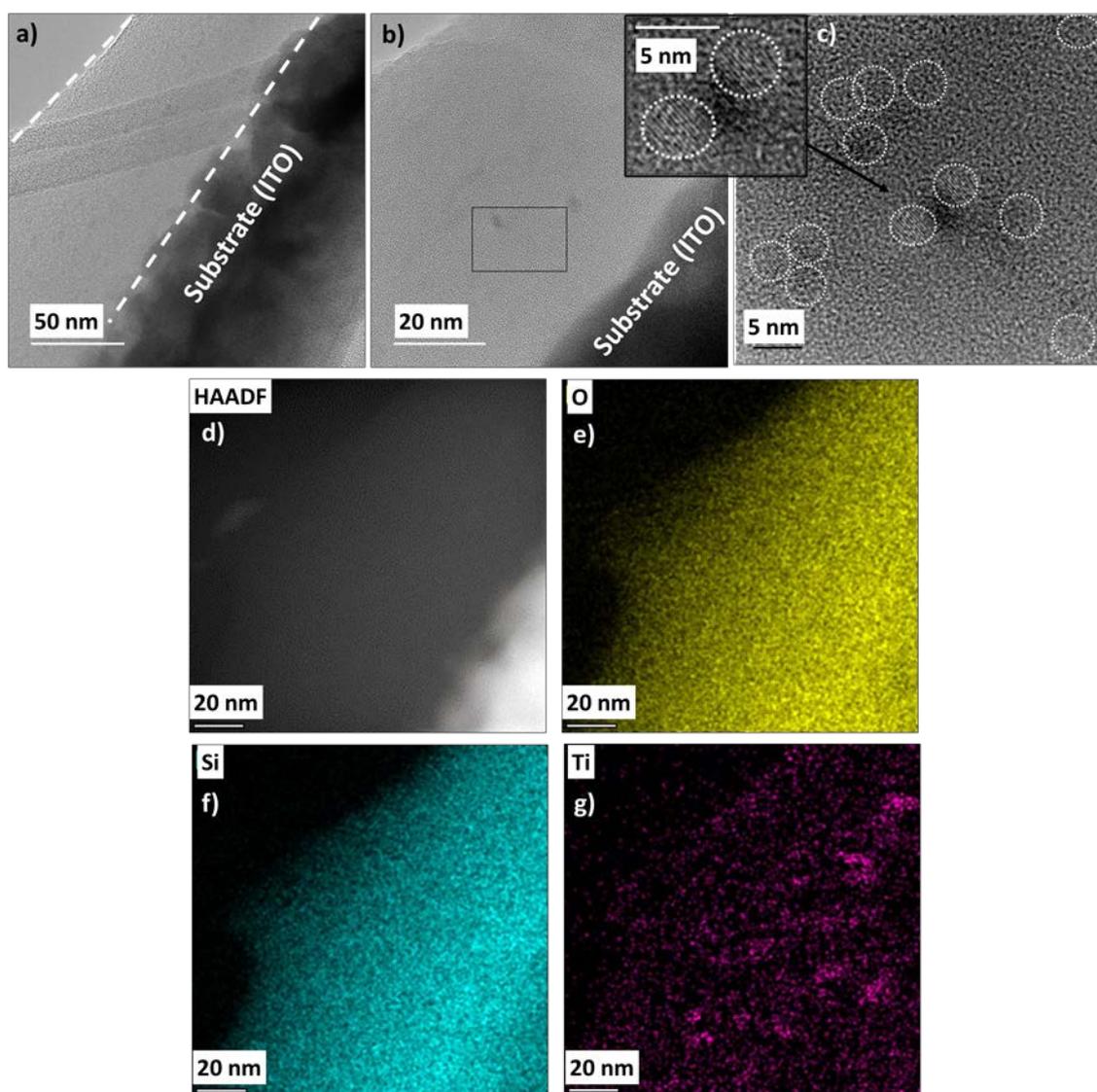
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273 Cross section structural analysis of the plasma-deposited NC thin film was performed using
274 TEM and STEM (Figure 4). Through multiple measurements on low magnification images (Fig.
275 4a), the thickness of the film was estimated at 85 +/- 6 nm (a growth rate of 1.7 nm/min for a
276 total plasma deposition time of 50 min). This value is comparable to the one achieved in
277 O₂/HMDSO plasmas without injection of the TiO₂ colloidal solution[29]. Using high-
278 resolution images on the rectangular area (black contour) shown in Fig. 4b and based on the
279 contrast between the amorphous matrix and the basal planes of the nanocrystals, some TiO₂
280 NPs can be identified (enlarged NPs as an inset in Figure 4) and stressed with white-rounded
281 contour shapes (Figure 4c). Interestingly, no agglomeration of these NPs is observed but rather
282 an assembly of small and isolated TiO₂ NPs in the SiO₂ matrix. Using ImageJ software, the
283 size of each of these NPs (14 nanoparticles identified in the specific zone probed by electron
284 microscopy) was extracted and their mean value was found to be at 2.7 ± 0.4 nm. By comparing
285 this value with the hydrodynamic diameter of TiO₂ NPs in the colloidal solution obtained by
286 DLS (2.7 nm + 1 nm, Figure 1), it can be confirmed that the NPs' size remains intact following
287 the aerosol formation and plasma deposition. This is a remarkable result with respect to other
288 experiments on hybrid plasma deposition of NC thin films for which agglomeration phenomena
289 were deemed unavoidable[13,15–22]. Moreover, TiO₂ NPs displayed in Figure 4c seem
290 dispersed in a rather random way in the SiO₂ matrix, with no evidence of preferential

291 incorporation sites. No cracking of the SiO₂ layers is visible, showing that the insertion of the
292 NPs does not strongly affect the growth of the silica layer.

293
294 The typical HAADF-STEM image given in the same figure confirms that no bright contrast
295 associated to possible agglomeration of the electronically denser TiO₂ NPs is detected,
296 indicating the homogeneity of the NPs dispersion, at this scale of observation. Moreover, EDX
297 elemental mapping also confirms that both oxygen and silicon (Fig.4 e,f) are homogeneously
298 distributed along the cross section of the NC thin film. On the other hand, Ti (Fig. 4g) signal,
299 which is only linked to the TiO₂ NPs, is identified with some small dots verifying the TEM
300 images (Fig. 4c) and their distribution inside the film. Since the data are a projection of 80 nm
301 thin sample, the reinforcement in contrast, (in some small parts of Fig.4g) may come from
302 particles distributed along this thickness.

303

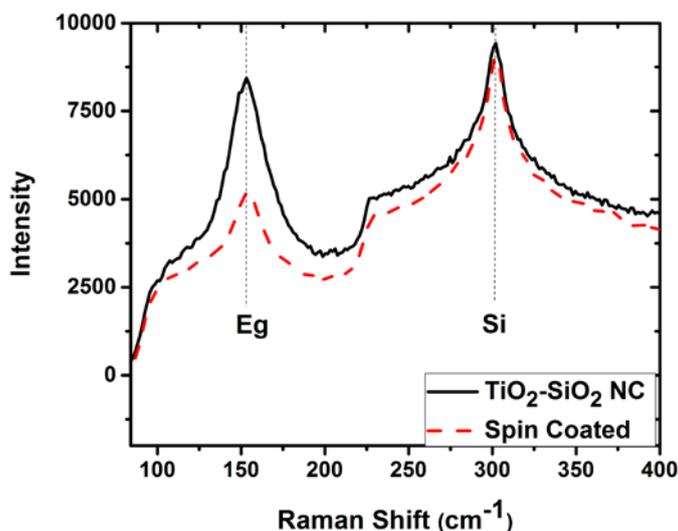


304
305 **Figure 4:** TEM cross section of the TiO₂-SiO₂ NC thin film a) in low magnification indicated
306 with white dashed lines, b) high magnification and c) higher magnification image focusing on
307 the distributed TiO₂ NPs inside the SiO₂ matrix. An inset is given with higher magnification

308 focusing on the basal planes of the anatase nanoparticles. d) Typical HAADF-STEM image of
309 the SiO₂-TiO₂ NCs in a selective area. Elemental mapping for e) O, f) Si and g) Ti.

310 The crystalline phase of the TiO₂ NPs was identified using Raman spectroscopy. Figure 5
311 presents the Raman spectra of the plasma-deposited NC thin film (black line) and the TiO₂ NPs
312 spin coated thin films (red line) using the as synthesized colloidal solution, with a focus on the
313 Eg anatase peak. The analysis was limited to using the peak positions since extreme caution is
314 required when using the Raman intensities of very thin films. Raman modes can be assigned to
315 the Raman spectra of the anatase crystal: 144 (Eg), 200 (Eg), 400 (B1g), 513 (A1g), 518 (B1g)
316 and 642 cm⁻¹ (Eg) [34,35]. In this figure, it can be observed that the Eg peak lies at 154 cm⁻¹, a
317 value shifted from the expected anatase peak at 144 cm⁻¹ [36,37]. It is well-established
318 experimentally that Raman spectra of low-dimensional semiconductor crystals are modified
319 when compared to the one of bulk crystals: (1) the Raman peaks are asymmetrically broadened
320 and (2) their positions are shifted [38,39]. The former is not observed mainly due to the size
321 distribution of the specific nanocrystals. This effect, results in masking the confinement effect
322 and averaging the Raman response [40]. However, the results presented in Figure 5 (black line)
323 confirm the strong shift of the Eg band that the plasma-deposited TiO₂ NPs embedded in the
324 SiO₂ matrix are anatase crystallites and in nanometric size. In addition to this, the Raman
325 spectrum of the TiO₂ NPs thin film through the spin-coated technique is given with red color.
326 The fact that for both cases the anatase peak is found in the same position (154 cm⁻¹) confirms
327 that upon the colloidal solution dilution, the TiO₂ NPs injection and the SiO₂ matrix deposition,
328 the nano crystallite is not affected.

329



330
331 **Figure 5:** Raman spectra indicating the Anatase Eg band at 154 cm⁻¹ and the second order Si
332 band peak at 303 cm⁻¹ for the TiO₂-SiO₂ NC thin film through the hybrid approach (black color)
333 and the spin coated TiO₂ NPs thin film using the as synthesized colloidal solution.

334

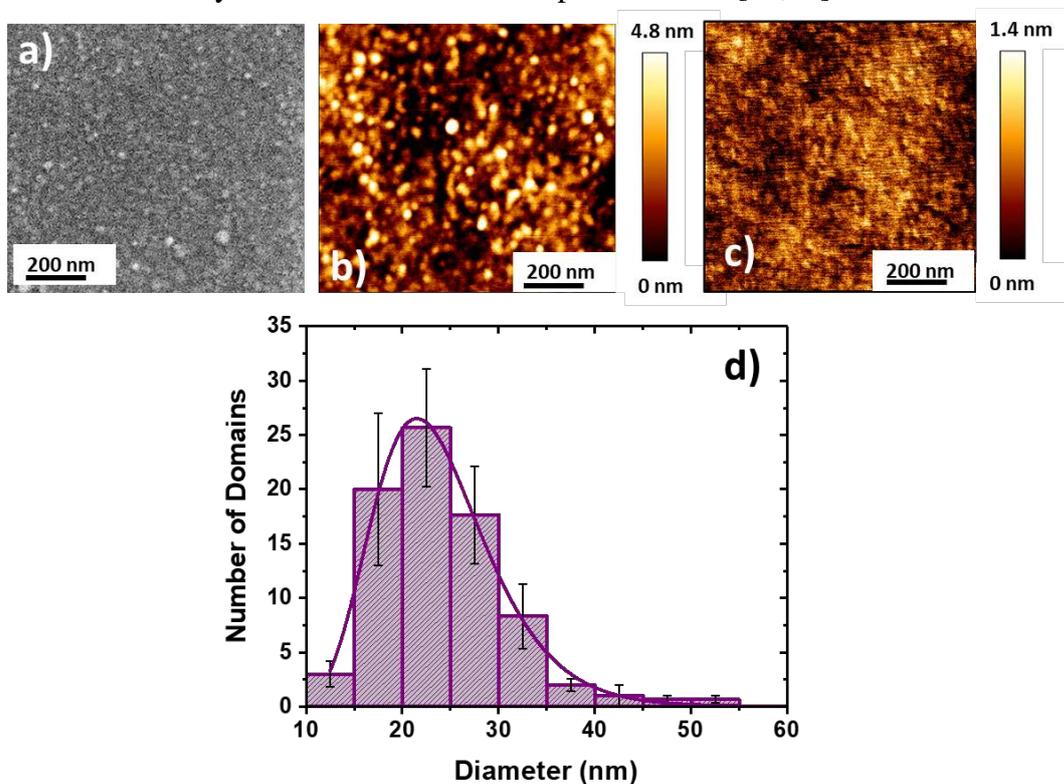
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336

337 3.2 Morphological analysis of the TiO₂-SiO₂ NC thin films

338

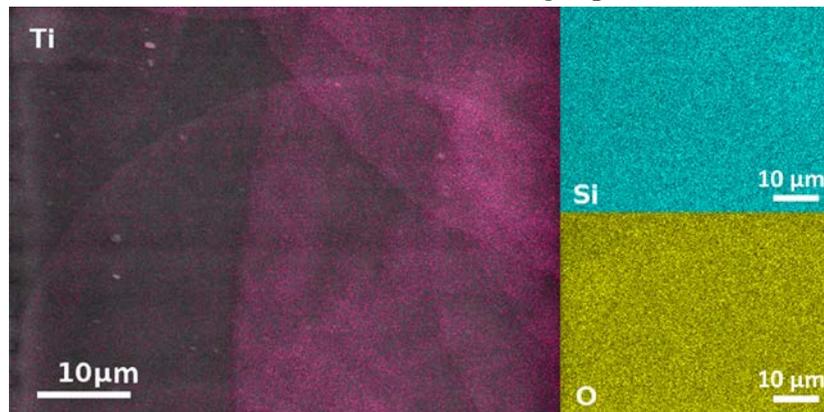
339 The surface morphological analysis of the TiO₂-SiO₂ NC thin film was investigated by SEM
 340 and AFM as shown in Figure 6. From the SEM top view image (Fig. 6a) in high magnification,
 341 the surface of the film is homogeneous and nanostructured, revealing some rounded domains.
 342 Since the resolution of the SEM is at 10 nm, one can understand that the exact identification
 343 and quantification of these domains is impossible. These same rounded domains are highlighted
 344 in the AFM measurements (bright yellow-white color in Fig 6b). They are located higher on
 345 the z axis and their size is higher than the one of the initial NPs in solution measured by DLS
 346 in Figure 1. From detailed analysis of multiple AFM scans at low and high magnification, the
 347 mean size of the domains was extracted and plotted as a histogram in Fig 6c. The fitting of a
 348 LogNormal distribution provided a mean size of 23 nm of these rounded domains and a standard
 349 deviation of 0.3 nm. The Rq (RMS) roughness of the NC film was also deduced. A value of 2
 350 nm was obtained, which was far different from the measured roughness of the silica thin film
 351 (Fig. 6c, Rq (RMS) = 0.3 nm) obtained by PECVD with the same reactor in comparable
 352 experimental conditions. The AFM scan for this case is given in Figure 6c, revealing the much
 353 smoother topography having a Rq (RMS) roughness lower than 5 nm. Since the deposition on
 354 flat silicon substrate should not lead to additional roughness or nanostructuration, especially for
 355 the deposition of amorphous SiO₂ (matrix), the nanometric pattern observed by AFM must be
 356 linked to the presence of TiO₂ NPs inside the SiO₂ matrix. It is worth highlighting, however,
 357 that the mean domain size displayed in Figure 6 (23 nm) is much larger than the mean size of
 358 TiO₂ NPs obtained from both DLS (Figure 1) and TEM (Figure 4a). This is because TiO₂ NPs
 359 are located at different locations across the thickness of the SiO₂ matrix (85 +/- 6 nm) and the
 360 PECVD process used in this study provides highly conformal plasma deposition.[41–45]
 361 Therefore, the deeper the particle is located inside the matrix, the larger is the size of the
 362 structure observed by SEM and AFM on the topmost surface[15,46].



363
 364

365 **Figure 6:** a) SEM secondary electron image of the surface, b) AFM scan (1 μm x 1 μm) of the
 366 $\text{TiO}_2\text{-SiO}_2$ NC thin films, c) AFM scan (1 μm x 1 μm) of SiO_2 only when deposited on Si
 367 substrate and d) size distribution of the rounded domains deduced from the AFM scans.

368 From the high-magnification and highly-localized analysis obtained both from TEM and
 369 SEM/AFM, the plasma-deposited $\text{TiO}_2\text{-SiO}_2$ NC thin films indicated a rather homogenous
 370 spatial distribution. To have an overall view of this film, low-magnification EDX mappings of
 371 the film's surface were recorded. To extract adequate resolution for each element, a thicker film
 372 was especially deposited on the ITO/PET substrate (224 nm). The results are presented in Figure
 373 7. While homogeneous distributions are observed for silicon and oxygen elements over the
 374 $2552 \mu\text{m}^2$ surface, abnormal rounded-ring shapes with diameters of several tens of micrometers
 375 can be seen for the titanium element. Such feature suggests the well-known coffee-ring effect,
 376 happening when the solute migrate in the edge of the evaporating droplet due to the formation
 377 of preferential flow and faster evaporation at this area. [47–49] Based on such large-scale SEM
 378 and EDX observations, it seems that TiO_2 species are provided to the substrate during growth
 379 as droplet and that evaporation and removal of organic species from the solvent[30] occur, at
 380 least partially, on the substrate surface rather than in the gas phase.



381 **Figure 7:** SEM backscattered electrons image and EDX map of Ti superimposed (left) and
 382 corresponding EDX maps of Si and O (right).
 383

384 A quantitative EDX analysis was conducted on the large region ($2552 \mu\text{m}^2$) avoiding an area
 385 exhibiting droplet traces such as the ones shown in Figure 7. In order to avoid all inhomogeneity
 386 aspects (in particular those related to the Ti element), only averaged values are shown in Table
 387 1. The results are presented only for Ti and Si due the weak energy of the carbon and oxygen
 388 EDX peaks and the strong interactions throughout the layers for these elements (see details in
 389 Sec. 2.2). From such analysis, 15% Ti and 85% Si is obtained (atomic %). Based on the
 390 calculations provided in the ESI, the volume percentage corresponding to 15 at% is estimated
 391 to reach 16 %.
 392

394 **Table 1:** Quantitative results by EDX on large surface ($2552 \mu\text{m}^2$ - magnification X1000).
 395

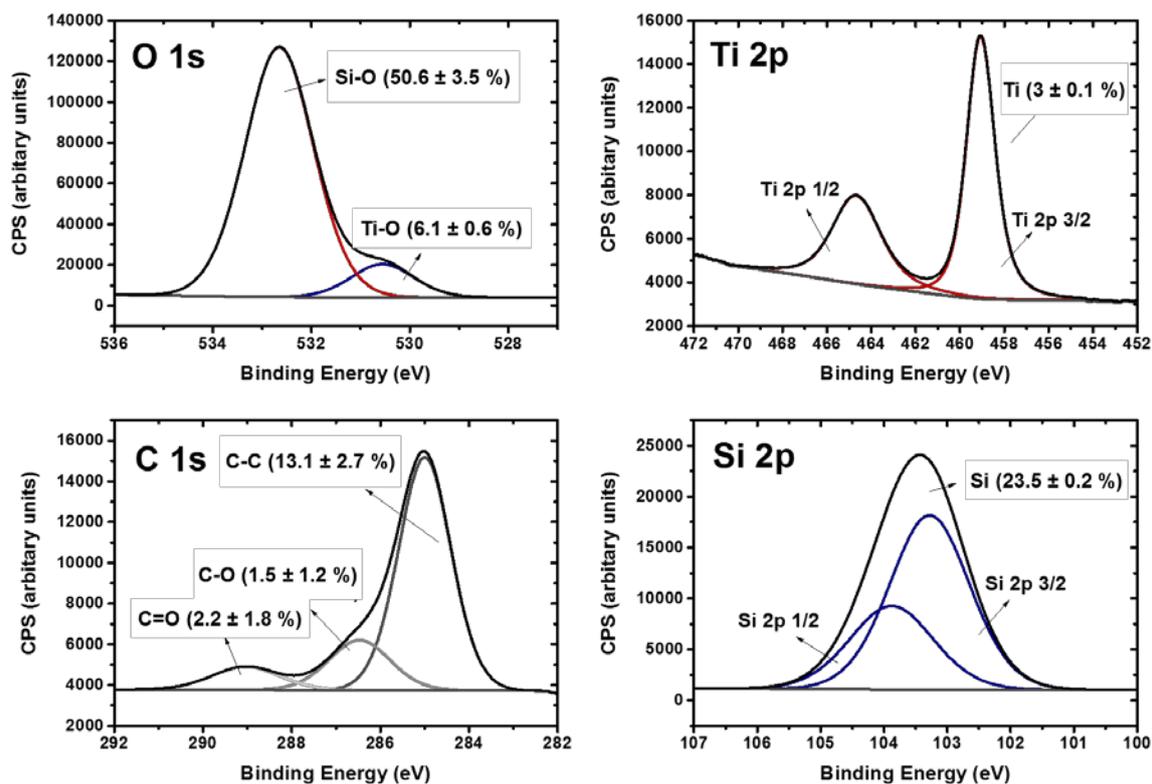
	Weight %	Atomic %
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Silicon	76.9	85
Titanium	23.1	15

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3.3 Surface chemical composition investigation of the TiO₂-SiO₂ NC thin films

The chemical analysis of the topmost surface of the TiO₂-SiO₂ NC thin films was carried out with XPS. Four different positions were measured on the same sample. Figure 8 represents the intensity of the O 1s, Ti 2p, C 1s and Si peaks. From these elementary spectra, the mean atomic concentration and the standard deviation in percentage is given by considering the components included in each atomic peak. The contribution of oxygen bonded to silicon atoms, noted as O-Si appears at the binding energy of 532.6 eV whereas the one corresponding to the bond with titanium, noted as O-Ti, at 530.5 eV. [6] A noteworthy observation in this figure is that no peak corresponding to Ti-O-Si (at 531.5 eV [50]) can be found, as expected for a NC, confirming that only two different phases are detected in the film.[50] As reported by many authors [24,51], the signal of titanium element in XPS results from two separated peaks that can be attributed to Ti_{2p3/2} and Ti_{2p1/2}. The 2p_{3/2} peak lies at 458.5 eV as expected for Ti⁴⁺ cations in TiO₂. Since the injected colloidal solution of TiO₂ NPs was synthesized in an organic solvent, the contribution of carbon element was investigated. Therefore, three components were identified in the C 1s peak. The first and most prominent one, at 285eV, is usually assigned to C-C bonds of both adventitious elemental carbon and the solvent, while the second, at 286.0eV, and the third, 288.5eV, can be related to -C-O bonds and C=O bonds, respectively. Finally, the Si 2p_{3/2} peak has a binding energy of 103 eV, which is related to the fully oxidized SiO₂ matrix [51]. Consequently, from the Ti2p and Si 2p signals only, the estimated atomic percentage in Ti is at 12 ± 0.004 % and for Si at 88 ± 0.004 %; these values are consistent with those obtained by EDX at the SEM (Table 1). The atomic percentage from XPS can be treated in the same manner as in Section 3.2 and the calculations provided in the ESI, leading to a volume percentage of 13 %.



422
 423 **Figure 8:** O 1s, Ti 2p, C 1s and Si 2p peaks of the TiO₂-SiO₂ NC thin film measured by XPS
 424 (mean atomic percentages and standard deviation of the components from 4 different positions
 425 in between brackets).

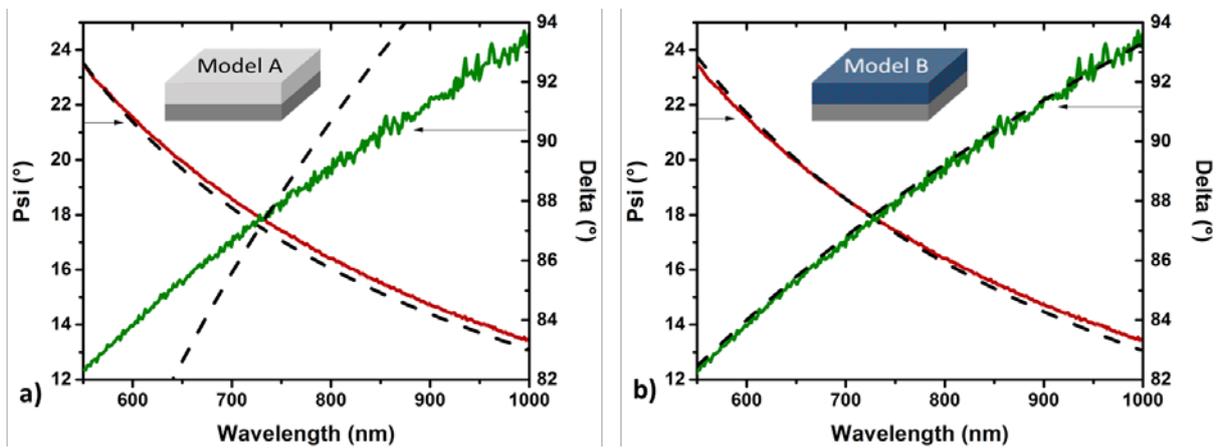
426 3.4 Spectroscopic ellipsometry of the TiO₂-SiO₂ NC thin films

427
 428 The investigation of the optical and physical characteristics was carried out with
 429 spectroscopic ellipsometry. The ellipsometric ratio $\rho = \tan(\Psi)\exp(j\Delta)$ is analyzed from
 430 the measured Ψ and Δ . To extract the structural and optical information from these data,
 431 the sample was modeled as a homogenous layer on silicon substrate, without any top-layer
 432 roughness. Due to droplet traces observed at low magnification in the Section 3.1, a more
 433 pronounced diffusion of the incident light was observed (in the measurement) at shorter
 434 wavelengths. Hence, the fitting was carried out in the limited range of 550 - 1000 nm. The
 435 validity of the model and therefore the evaluation of the accuracy of the fit was estimated by
 436 the Mean Square Error (MSE) factor. [52]

437
 438 Assuming the ellipsometry was not sensitive enough to detect the NC nature of the sample,
 439 the first ellipsometric model used was a one phase material with Tauc-Lorentz dispersion law
 440 (Figure 9a, Model A).[52] However, the experimental and simulated data show discrepancies,
 441 providing a high value of the error value (MSE=22). Therefore, a two-phase material (SiO₂ and
 442 TiO₂) was set up to account for the ellipsometric data of the TiO₂-SiO₂ NC thin films. First,
 443 the dispersion laws for the SiO₂ matrix and the TiO₂ NPs have to be assessed. Conducting an
 444 experiment of depositing the SiO₂ matrix while injecting the solvent without the NPs, using the
 445 same injection conditions as the plasma-deposited TiO₂-SiO₂ NC thin films, allowed us to
 446 acquire a reference SiO₂ matrix film and assess its quality, in the range between 550 and 1000

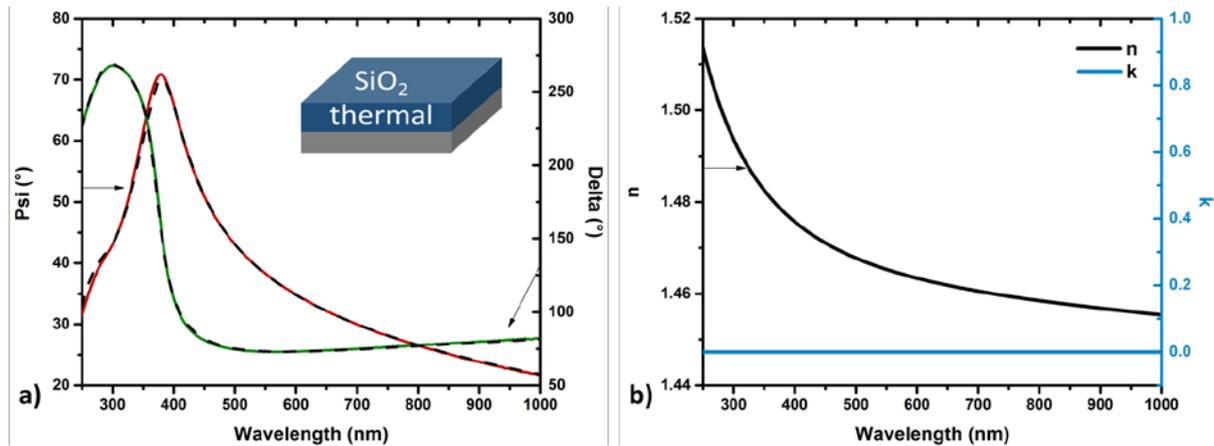
447 nm. The model used to fit the ellipsometry data of the matrix was the one of the classical thermal
 448 SiO₂ material, as expressed by Herzinger et al. [53] using the Sellmeier/Cauchy dispersion law.
 449 The measured and simulated Psi and Delta signals are given in Figure 10a. In this figure, the
 450 quality of the fit appears to be high and the MSE for all the wavelength range was given at
 451 MSE=10. In Figure 10b, the refractive index (n) and the extinction coefficient (k) of the SiO₂
 452 matrix are given. For the TiO₂ NPs, the Tauc-Lorentz dispersion law was used based on a spin-
 453 coated 50 nm TiO₂ NPs film. The effective refractive index for this spin coated film was found
 454 at 1.68 at 633 nm wavelength (as voids were evidenced in the film) and the optical bandgap
 455 (E_g) at 3.4 eV. The detailed results can be found in a very recent publication of the group.[25]
 456 The fit of the NC film using the second model (Model B), resulted in an improved error
 457 (MSE=4).

458 Then, based on the cross-section results obtained with TEM (Fig. 4, Section 3.1) for the
 459 nanocomposite film, the Bruggeman Effective Medium Approximation (BEMA) was used
 460 (Figure 9b, Model B) to model the TiO₂ NPs dispersed in the SiO₂ matrix. A much better
 461 agreement was observed between the experimental and the simulated data.
 462



463
 464 **Figure 9:** Psi (red) and Delta (green) results of the measured (continuous) and modeled
 465 (dashed) data with ellipsometry, based on Model A (a) and Model B (b).

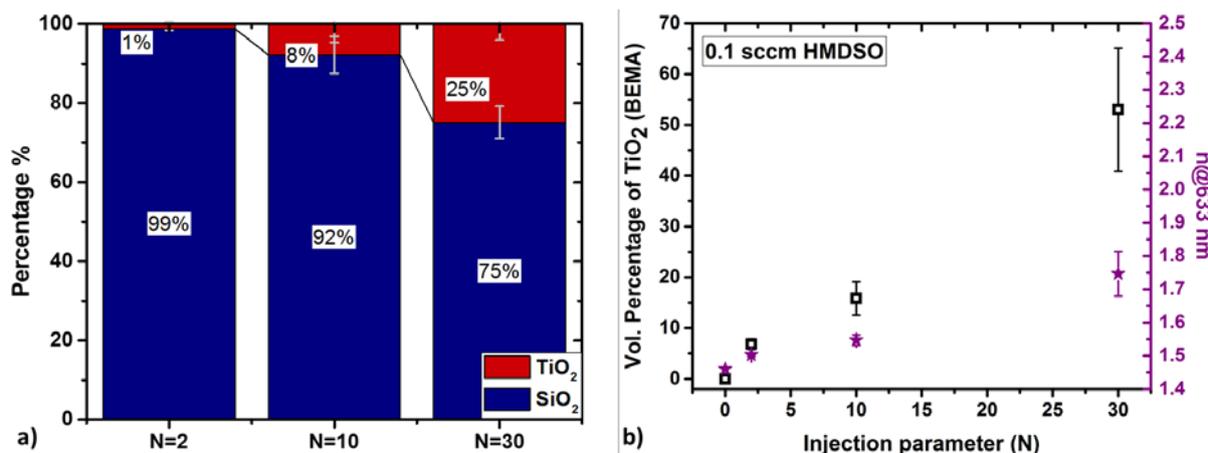
466 Additionally, from the BEMA, the volume fraction of TiO₂ NPs in the film could be deduced
 467 reaching 19 vol.% and 81 vol.% of SiO₂. This observation confirms the EDX and XPS results
 468 (Section 3.2), where no mixed (Ti-O-Si) bonding was observed. The optical TiO₂ energy gap
 469 is determined at 3.4 eV due to the nanometric size of the TiO₂ [54,55]. In addition, the effective
 470 refractive index at 633 nm wavelength was estimated at 1.59, an increased value compared to
 471 the SiO₂ matrix itself (1.46).



472
 473 **Figure 10:** a) Psi (red) and Delta (green) results of the measured (continuous) and modeled
 474 (dashed) data with ellipsometry of the matrix only fitted with SiO₂ thermal model.

475
 476 **3.5 Comparison with lower and higher TiO₂ NPs injection rate**
 477

478 To assess the agility of this hybrid process into acquiring NC thin films with different
 479 composition and optical characteristics, experiments with lower and higher injection rate were
 480 attempted. The N of the injection sequence (for deposition of TiO₂ NPs) was set either at N=2
 481 or at N=30 (instead of 10) and the flow rate of the HMDSO precursor (for deposition of the
 482 SiO₂ matrix) was kept at 0.11 sccm. The total deposition time was maintained at 50 min. Figure
 483 11a provides the stacked column (%) resulting from the XPS core level spectra fitting as
 484 explained in Section 3.3. In order to assess the reproducibility of the hybrid approach the XPS
 485 stacked column provide the mean value and the standard deviation (as error bars) for two to
 486 four different experiments in each condition (including the N=10). As expected, for lower N
 487 and therefore lower amount of TiO₂ NPs injected in a minute sequence, the atomic percentage
 488 of TiO₂ on the surface of the TiO₂-SiO₂ NC thin film was much lower than N=10 (1% for N=2
 489 and 8% for N=10). Additionally, for the highest TiO₂ NPs injection rate (N=30), we can observe
 490 a three times higher TiO₂ percentage (25% for N=30) than the N=10. Furthermore, using the
 491 data obtained by spectroscopic ellipsometry, and the Model B proposed in Section 3.4, the
 492 percentage of the TiO₂ NPs and the effective refractive index of the NC at 633 nm wavelength
 493 was obtained (shown in Figure 11b). Once more, to account for the reproducibility of this hybrid
 494 process, the results shown in Figure 11b are extracted from four different experiments for each
 495 condition. From these results, a clear dependency of the NC's characteristics on the injection
 496 parameters is observed. More specifically, for N=0 when no NPs are injected (SiO₂ matrix
 497 only) the refractive index is found at 1.47. As we start injecting a low amount of NPs, hence
 498 N=2, the NC film contains 7 vol.% of TiO₂ and reveals a refractive index of 1.50. In accordance,
 499 for higher injection (N=10), the NC film contains 16 vol.% and reveals an index of 1.54. For
 500 N=30, during the one minute sequence, pulses are applied on the injector constantly and
 501 consequently no DLI-OFF exists. Hence, this induces a strong pressure variation (from 16 to
 502 20 mTorr) and may produce less stable plasma conductions both the NPs deposition and the
 503 silica matrix. Therefore, the significantly higher error bars than the rest conditions could be
 504 explained. Nevertheless, for the highest amount of the injected NPs (N=30), the NC film can
 505 reach up to 53 vol.% in TiO₂ NPs leading to a refractive index of 1.74.



507
 508 **Figure 11:** a) Stacked columns (%) of the NC surface composition obtained from XPS for N=2,
 509 N=10 and N=30 with measurements obtained from two to four samples. b) Volume percentage
 510 of TiO₂ extracted from the BEMA and refractive index at 633 nm wavelength for N=0,
 511 N=2, N=10 and N=30 extracted from four samples.

512 4. Discussion

513

514 As demonstrated above, over the range of experimental conditions investigated, the deposition
 515 of TiO₂-SiO₂ NC thin films using a hybrid approach leads to small and isolated (non-
 516 aggregated) TiO₂ NPs well-distributed into a dense and inorganic SiO₂ matrix. Compared to
 517 other processes reported in scientific literature (mostly based on atmospheric-pressure
 518 systems)[15,22,46,56,57], the proposed method significantly limits agglomeration of the NPs
 519 and improves their dispersion in the matrix. An additional important factor leading to the
 520 limited agglomeration of the NPs could be the initially very small size of the NPs in the stable
 521 (over time and composition) colloidal solution. Changes in the agglomeration dynamics could
 522 partially be attributed to the differences affecting the aerosol formation dynamics between
 523 operating at low pressure compared to atmospheric conditions. In particular, at low pressure,
 524 the nature of the flow is mainly molecular flow whereas it is laminar or even turbulent at
 525 atmospheric pressure. [12,58,59] It could also be related to the low injection rates of the colloidal
 526 solution. Using a direct-liquid injection in a CVD system at low pressure, Varvaele et al. [11]
 527 have identified that low colloidal solution injection rates (as in this study) promotes the
 528 dispersion of the NPs whereas at higher rates, they tend to coalesce such that the mean size
 529 distribution shifts towards higher values.

530

531 Because of the overall good homogeneity of the film, the optical and dielectric properties of
 532 the films could also be deduced by proper modelling of the ellipsometric signals (especially
 533 between 550 and 1000 nm). This feature qualifies the process as suitable for the preparation of
 534 TiO₂-SiO₂ NC thin film for optical applications in this wavelength range. Despite the solvent
 535 injection, the plasma-deposited matrix proved to be of high quality as the fit with thermal silica
 536 was significantly accurate. This is a proof that carbon is not incorporated inside the matrix
 537 confirming its inorganic nature. By tuning the injection sequence, it was further possible to tune
 538 the effective refractive index, having the possibility to reach up to 53 vol% in TiO₂. To the best

539 of our knowledge, these results are unique compared to the reported approaches.
540 [12,15,22,46,56,60] Due to the set of experimental conditions used, the combination of adjusted
541 volatility of solvents, remarkable stability of the colloidal solution and condition of spraying in
542 a low-pressure plasma reactor resulted in an efficient transport of the droplets containing the
543 non-agglomerated NPs towards the substrate. The optimization of the injection sequence
544 permitted to keep the NPs protected inside the liquid droplets down to the substrate, thus
545 preventing them to aggregate following their interaction with the plasma species. A downside
546 of these liquid droplets as observed by the low magnification SEM-EDX images is the coffee
547 ring patterns of the TiO₂ NPs. Several works report the depiction of droplets due to the limited
548 volatility of the injected solution or the increased mean size (due to system limitations) of the
549 produced droplets [9,61,62]. Given that some of the produced droplets in the specific system (by
550 the direct-liquid injector) do not have enough time to evaporate (low volatility of the solvent),
551 the evaporation process happens at the surface of the film. Further works are under progress to
552 get better insight in the mechanisms involved during the process in terms of droplet formation,
553 droplet travel speed and evaporation of droplet solvents due to the interaction with the low-
554 pressure plasma. This will open a promising chapter for understanding the impact of low-
555 pressure plasma on the physical and chemical state of the liquid droplet during plasma
556 deposition of NC thin films.

557

558 **5. Conclusion**

559

560 In this work, the creation of TiO₂-SiO₂ NC thin films by injecting a colloidal solution in a
561 very-low-pressure O₂/HMDSO plasma was reported for the first time. The iterative injection
562 sequence was selected in a way to control and maintain in low levels the deposition rate of the
563 NC films. The pressure was maintained at 3 mTorr (with slight variations) leading to the
564 deposition of good-quality inorganic SiO₂ matrix. The cross section of the film revealed a fairly
565 homogeneous distribution of the NPs inside the matrix, at the local scale. The amount of these
566 3-nm NPs was evaluated by multiple characterization techniques and was estimated at 16 vol.
567 % at the SEM scale and 19 vol. % as deduced from ellipsometry *i.e.* on a larger area. The surface
568 composition revealed a slightly lower value (13 vol. %), which could be explained due to the
569 coating effect of the SiO₂ matrix (during the last second of the injection sequence). Notably,
570 not significant agglomeration of NPs was observed. Adjusting the parameters of the injection
571 sequence (from N=2 to N=30), NC films with lower and higher TiO₂ NPs content and thus
572 different optical properties could be achieved. Due to the originality of this work and its novelty,
573 large-surface area deposition has still to be improved. This requires conducting theoretical and
574 further experimental studies to understand the behavior and evaporation of the liquid droplets
575 inside low-pressure plasmas. Through these first results it is evidenced that potentially, an agile
576 approach like this could give the freedom to tune and adjust the NC's properties by adjusting
577 both the nature of the NPs and the matrix but also of the injection parameters reaching a large
578 range of NPs content inside the matrix.

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