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Does N₂ gas behave as a surfactant during Ag thin-film sputtering deposition ? Insights from *in vacuo* and real-time measurements

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Abstract

Circumventing the thermodynamic trend of 3D growth of noble metals on dielectric substrates to form flat continuous ultra-thin films remains a challenge for many applications involving transparent conductive layers such as photovoltaic devices or smart windows. In this context, the use of gaseous species as "surfactants" during the sputtering deposition has attracted a lot attention in the past few years. The effect of N₂ on the Ag growth on amorphous SiO₂ is revisited herein in the light of film resistivity and UV-visible differential reflectivity real-time measurements combined with *in vacuo* x-ray photoemission spectroscopy. Increasing the N₂ content in the Ar gas flow (from 0 to 40%) gives rise to a drastic decrease of the percolation threshold thickness but at the expense of film conductivity. Photoemission suggests an apparent lack of chemistry between N and Ag with the absence of N

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in the bulk and at the surface of the Ag film despite a nitridation of the substrate due to activated species in the plasma. The plasmonic response of Ag nanoparticles evidences the dynamic presence of a N adsorbate that desorbs under vacuum once the growth is stopped. This latter decreases the metal surface energy thus inducing a flattening of islands before percolation as proved by optics. The adsorption is anisotropic between (111) and (100) facets. All of this explains (i) an earlier percolation resulting from flattened objects and a delayed coalescence, (ii) the change of film texture as seen by *ex situ* diffraction and (iii) the appearance of unfavourable grain boundaries for electrical transport in continuous films. By being immiscible in the bulk of Ag, by floating at its surface, by acting on metal surface energy and by desorbing at the end of the growth, nitrogen has all the characteristics of a "surfactant" for Ag growth.

Keywords: silver, nitrogen, thin film growth, sputtering deposition, surfactant effect, real-time monitoring, UV-vis plasmonics, photoemission

1. Introduction

The thermal insulation of buildings is a crucial lever to face the issue of global warming. In low-E or solar-control windows, complex stacks of layers are deposited by magnetron sputtering on one of the inside glass surfaces of the double-glazing [1, 2, 3]. The active layer for thermal infra-red reflection is a Ag film, the thickness (10-12 nm) of which should be well below the skin depth in the visible range to achieve optical transparency. According to the Hagens-Rubens relation [4, 5] $R = 1 - 2\sqrt{2\epsilon_0\omega\rho}$, the reflection coefficient R of a conductive medium at a given frequency ω is dictated by its resistivity ρ (ϵ_0

10 vacuum permittivity). For a fixed thickness, the remaining lever to improve
11 the heat regulation efficiency of glazings is the film resistivity and therefore
12 its microstructure *i.e.* the grain boundary and bulk defect densities and the
13 quality of its interfaces. A similar issue is also encountered for metallic elec-
14 trodes used in photovoltaics or optoelectronic devices such as flat display
15 panels [6]. In this context, research efforts have been directed towards a
16 fine tuning of the Ag deposition process to face the inherent thermodynamic
17 trend towards 3D growth on dielectric substrates, either polycrystalline or
18 amorphous. Mainly dictated at the first glance by the low adhesion energy of
19 Ag on poorly-interacting supports and the large metal surface energy, even
20 in the case of out-of-equilibrium deposition process, the so-called "Volmer-
21 Weber" 3D growth process follows a common scenario [7, 8]: (i) the homo-
22 geneous or heterogeneous nucleation of small clusters, up to a saturation
23 density (ii) their growth towards isolated 3D islands from direct impact or
24 by the capture of diffusing adatoms, (iii) the coalescence of islands upon im-
25 pingement with a more or less efficient recovery of equilibrium shape and
26 a decrease of particle density, (iv) the percolation with the formation of a
27 continuous path across the film and (iv) the filling of holes and the formation
28 of a continuous and homogeneous film. By acting upon the first steps of the
29 growth, it becomes possible to favour an earlier percolation and hinder the
30 3D growth. The relevant levers are (i) the change in nucleation density or in
31 surface/interface energetics, the latter having a direct impact on the island
32 equilibrium shape and (ii) the kinetics of coalescence between nanoparticles.
33 In this context, various strategies affecting the growth of the Ag film during
34 sputter deposition have been explored including the use of : (i) the kinetics

35 of deposition itself (flux and temperature) [9, 10], (ii) substrates or growth
36 layers (ZnO in the case of Ag [11, 12]), (iii) wetting or buffer layers of tran-
37 sition metals [13, 14, 15, 16], of the corresponding metal oxide [17], or of
38 Ge [18, 19, 20], (iv) film doping and alloying with metals such as Al [21, 22]
39 and (v) gaseous species, such as O₂ [23, 24, 25, 26, 6, 27, 28, 29, 30, 31, 32]
40 and N₂ [23, 33, 34, 35, 36, 37], during deposition.

41

42 This last strategy of gaseous "surfactants" has attracted much attention
43 in the past few years and was recognized as an efficient pathway for produc-
44 ing thinner continuous Ag films even on amorphous substrates. As shown in
45 many previous reports [24, 25, 26, 6, 27, 28, 38, 29, 30, 31, 32], O₂ addition
46 reduces drastically the Ag percolation thickness threshold but at the expense
47 of a film resistivity worsening due to O incorporation. This flaw can be par-
48 tially circumvented by the use of N₂ that produces similar overall effects but
49 without measurable chemical interaction with Ag [23, 33, 34, 35, 36, 37]. Nev-
50 ertheless, N₂ requires higher partial pressures to achieve the same change in
51 percolation thickness, presumably because of its lower dissociation efficiency
52 in the plasma due the strong triple N-N bond. Beside the presence of excited
53 N₂ molecules, plasma diagnostics actually confirm that only a small fraction
54 of molecules is actually dissociated into atomic N [39, 40, 41]. But surpris-
55 ingly, Ag films grown with N₂ addition were found free of N by *ex situ* pho-
56 toemission even when using pure N₂ gas during growth [23, 42, 34, 35, 36, 37].
57 Nonetheless, if these findings are in line with the chemical inertness of N₂ with
58 Ag and the lack of stable bulk Ag-nitride compounds [43], all first-principle
59 simulations [44, 45, 46, 47, 37] report on the energetically favourable ad-

60 sorption of atomic N at Ag surfaces. The concomitant drastic decrease of
61 surface energy was put forward to explain a better wetting and an earlier per-
62 colation [35, 37]. In parallel, aside from a low desorption temperature [48],
63 experiments pointed at an unusual efficient recombinative desorption of N by
64 direct impact (Eley-Rideal mechanism) [49, 50]. To circumvent the detrimen-
65 tal effect of N₂ on Ag film crystallinity while still benefiting from an earlier
66 percolation, Jamnig *et al* [36] proposed to inject the gas only during the first
67 stages of film growth before percolation. At last, N₂ was found to promote
68 the [100]-Ag film texture which is an unusual orientation on a surface energy
69 point of view for a face-centred cubic metal [42].

70

71 While N₂ appears as an efficient modifier of Ag growth leading to earlier
72 percolation [33, 34, 35, 36, 37], the apparent lack of N in the film questions
73 its actual floating-out surfactant behaviour that could have escaped to pho-
74 toemission measurements based on depth-profiling. Also, the observed wors-
75 ening of film resistivity and crystallinity remains unexplained. This work
76 proposes to revisit the question by a combination of *in vacuo* x-ray photo-
77 electron spectroscopy (XPS) and real-time measurements of film resistance
78 and of surface differential reflectivity spectroscopy (SDRS). Observations are
79 supplemented by *ex situ* x-ray diffraction (XRD) and scanning transmission
80 electron microscopy (STEM). The objective is to unveil the effects of N₂ ad-
81 dition at the different stages of sputtering deposition growth of Ag on silica
82 for a wide range of gas compositions and to discriminate between the possi-
83 ble origins of earlier percolation *i.e.* enhanced wetting, change in the particle
84 density and coalescence impediment. Plasmonics is used to probe directly

85 particle wetting and photoemission to scrutinize N chemistry, if any, at the
86 free surface.

87 **2. Experimental**

88 All experimental details regarding the film deposition and the employed
89 techniques can be found in Ref. [31] where a similar work was performed with
90 O₂ instead of N₂. Briefly, Ag films were grown by magnetron sputtering at
91 room-temperature on Si wafers (thickness 280 μm, n-doped, (100)-oriented),
92 the surface of which is covered by its ~ 2 nm-thick native amorphous SiO₂
93 oxide. The sputtering chamber (base pressure of < 2.10⁻⁸ mbar) includes
94 three different two inch targets equipped with a shutter, in front of which
95 the sample can be positioned by a manipulator. Ag depositions were car-
96 ried out at a power of 50 W and a total pressure of 2 μbar in direct current
97 mode with ultra-pure gas (< 50 ppm of impurities) at a target distance of
98 15 cm. During Ag deposition, the total flow of Ar and N₂ gases was kept
99 at 50 sccm while their ratio was varied via mass flow controllers. Hereafter,
100 x%N₂ will stand for the percentage of flow of N₂ in the total. As described
101 in Ref. [31], the deposition rates were carefully calibrated on thick films with
102 an uncertainty of ~ 1 %. For Ag, it ranged from 0.55 down to 0.45 nm.s⁻¹
103 when increasing %N₂ from 0% to 40%. Nominal thickness is systematically
104 used to designate the deposited amount of Ag all along this work.

105

106 Thanks to a direct connection under vacuum to an analysis chamber (base
107 pressure ~ 10⁻⁹ mbar) hosting an XPS apparatus, the chemistry of the free
108 surface could be analysed without exposure to air. This capability for such

109 a surface sensitive tool avoids any *ex situ* depth-profiling by sputtering of
110 capped samples that can bias the interpretation of photoemission spectra.
111 Right after deposition (~ 20 mins), samples were analysed by recording se-
112 lected core level regions (Ag 3d, N 1s, O 1s, C 1s, Si 2p). Besides a slight
113 presence of carbon of aliphatic nature at a binding energy of $E_B = 284.5$ eV,
114 no other contaminants, particularly implanted Ar and carbonates, were de-
115 tected. As Si wafers were used as received without specific surface treatment
116 prior to Ag deposition, the effect of plasma exposure on its surface chemistry
117 was also explored by XPS. To decouple it from Ag deposition, wafers were
118 exposed during 3 s to a plasma (pure Ar *i.e.* 0%N₂, and 40%N₂) ignited
119 in radio-frequency mode on an alumina target placed not inline of sight of
120 the sample. Due to the short duration of the substrate treatment (3 s) and
121 the low deposition rate of this material (0.007 nm.s⁻¹), no Al was found by
122 photoemission within the detection limit.

123

124 Real-time characterizations, namely electrical resistivity and UV-visible
125 SDRS, were carried out simultaneously on the same substrate during Ag
126 growth. Transport measurements allow determining (i) the electrical resis-
127 tivity $\rho(t)$ as the product of the sheet resistance R_{\square} and the film thickness t
128 *i.e.* $\rho(t) = t \times R_{\square}(t)$; and (ii) the thickness at the percolation threshold t_p .
129 Hereafter, the electrical resistivities of continuous films at a final thickness
130 of 20 nm will be systematically compared. During a SDRS measurement,
131 the relative variation of the sample reflectivity $\frac{\Delta R}{R}$ is recorded in the s and
132 p polarization states of light, corresponding, respectively to an electric field
133 perpendicular and parallel to the incidence plane. The incident angle was

134 fixed at 45° by the flanges of silica viewports of the deposition vessel [51, 52].
 135 SDRS is sensitive to film morphology through the excitation of localized plas-
 136 mon resonances [51, 53] in the Ag nanoparticles during the initial 3D growth
 137 stages (nucleation, growth, and coalescence). The intensities of the resulting
 138 peaks as well as their positions in energy, are driven, in a first approxima-
 139 tion, by the aspect ratio A_r (diameter/height) of the growing objects. As
 140 already shown in details [53], the integrated SDRS signal in s polarization
 141 once normalized to film thickness t :

$$\mathcal{I}_s(t) = \frac{1}{t} \int \frac{\Delta R_s}{R_s}(\omega, t) \frac{d\omega}{\omega} \propto A_r \quad (1)$$

142 is a reliable reporter of the A_r evolution as both quantities are proportional
 143 to the oscillator strength of the parallel plasmon oscillation. Finally, to help
 144 rationalizing SDRS evolution upon N adsorption/desorption, the optical re-
 145 sponse of a core-shell hemisphere [54] supported on SiO_2 has been simulated
 146 with the *GranFilm* code [55] and then renormalized to Si reflection coeffi-
 147 cient. While tabulated dielectric functions of Ag, SiO_2 and Si were used,
 148 the index of refraction of the shell was kept fixed at a value typical for ni-
 149 trides ($n = 2$) [56]. The basis of this modeling are fully described in previous
 150 works [57, 58, 59, 60, 61, 62, 63, 51, 53, 54] and technical details are given
 151 in Ref. [31]. Owing to the complexity of the quantitative description of the
 152 plasmonic response and of the involved morphologies and the dielectric model
 153 limitations, simulations were kept at a qualitative level to highlight the main
 154 trends of energy shift and of change in intensity of the plasmon resonances
 155 seen in SDRS as a function of morphology. They are not meant to be quan-
 156 titative in absolute values as no actual fit [60, 61, 62, 63] of SDRS spectra
 157 was attempted.

158

159 For *ex situ* measurements, Ag layers were capped with a 5 nm-thick Al-
160 doped ZnO (AZO) film deposited by direct current from a ceramic target
161 (target ZnO:2%Al₂O₃ in mass, power 50 W; distance 12 cm, 50 sscm and
162 2 μ bar of pure Ar) to protect them from ageing and oxidation by contact
163 with the atmosphere. While the AZO capping may damage the surface of
164 the Ag film, real-time resistivity of continuous Ag films, and therefore their
165 microstructure, do not change significantly upon capping. Thus, 20 nm-thick
166 Ag films were analysed *ex situ* by Cu-K α XRD in Bragg-Brentano and graz-
167 ing incidence geometries (Bruker D8 Advanced and Rigaku SmartLab devices
168 respectively); they were deposited on amorphous SiO₂ substrates (thickness
169 1 mm) to avoid any spurious diffraction signal from Si(100) wafer [64]. Also,
170 in order to more accurately determine the impact of %N₂ on the particle
171 density before film percolation, AZO-capped 0.6 nm-thick Ag films were
172 deposited on 15 nm-thick silicon nitride membranes and imaged in plane
173 view by Cs-corrected scanning transmission electron microscopy (STEM Ti-
174 tan Themis from Thermo Fischer Scientific) in high angle annular dark field
175 (HAADF) conditions. The oxidized surface of the membranes mimics that
176 of the Si wafer. A statistical analysis, based on a "Blob-log" treatment to
177 distinguish Ag nanoparticles from the Si wafer followed by a watershed al-
178 gorithm to find the precise edges of each object, was applied to all images.
179 All *ex situ* analyses were performed with the minimum delay after deposition
180 while samples were systematically stored in vacuum.

181

182 **3. Results**

183 *3.1. Real-time film resistivity*

184 The percolation threshold, *i.e.* the formation of a conductive path be-
185 tween electrodes but before film continuity, appears as a drastic drop in film
186 sheet resistance R_{\square} . Better determined as the maximum in a $\rho(t) \times t = R_{\square} \times t^2$
187 versus t plot [31], the corresponding equivalent thickness t_p decreases from
188 ~ 6 nm down to ~ 3 nm between 0%N₂ and 40%N₂ as shown in Fig. 1-
189 a. t_p even reaches a minimal value of 2.7 nm at 30%N₂ (Fig. 1-b, left
190 scale). Although never directly determined, such an early percolation is
191 in agreement with previous observations both for N₂ [34, 35, 36, 37] and
192 O₂ [26, 27, 28, 29, 30, 31] gas addition to Ar. The decrease in t_p occurs in
193 parallel to an increase in the continuous film resistivity at $t = 20$ nm from 6.7
194 to 8.5 $\mu\Omega$.cm (Fig. 1-b, right scale). Nevertheless, this 27 % increase remains
195 much more modest than that observed for Ar/O₂ mixtures, where a change
196 by an order of magnitude was observed between 0% to 40%O₂ (using similar
197 deposition conditions) [31]. For those films, the strong worsening of the final
198 film resistivity was mainly assigned to a complex formation of silver oxides
199 and of unfavourable grain boundaries due to a change of film texture.

200 *3.2. Photoemission analysis*

201 To explain the above resistivity findings, the chemistry of films grown
202 under Ar/N₂ was scrutinized using photemission. Fig. 2 shows the Ag 3d,
203 N 1s, O 1s and C 1s core level regions [65] of 20 nm-thick Ag films. Unlike
204 previous literature [35, 37, 36], the lack of capping layer gives direct access
205 to the chemistry of the free surface and avoids potential desorption of species

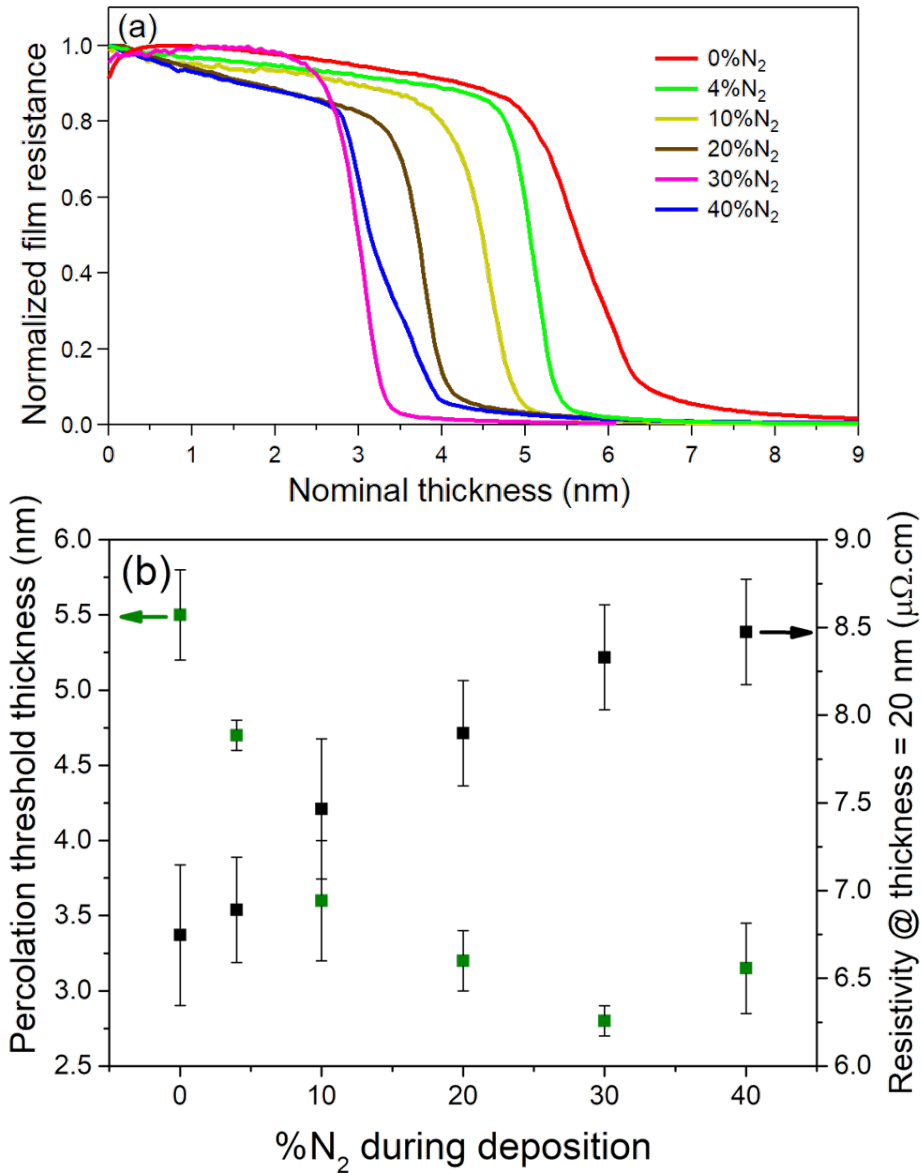


Figure 1: (a) Evolution of film sheet resistance R_{\square} during Ag deposition on SiO_2/Si substrates as a function of equivalent thickness for different $\%N_2$ in the gas flow. Data are normalized to the initial value before opening the shutter in front the target. The drop in R_{\square} corresponds to the formation of a percolated and conductive film. The slight increase in resistivity for some measurements at shutter opening is an artefact and does not compromise the interpretation of percolation threshold and final resistivity. (b) Percolation threshold thickness t_p (green squares, left axis) and film resistivity $\rho(t = 20 \text{ nm})$ (black squares, right axis). Values stand for an average over several (≥ 3) experiments and the error bars to the corresponding standard deviations.

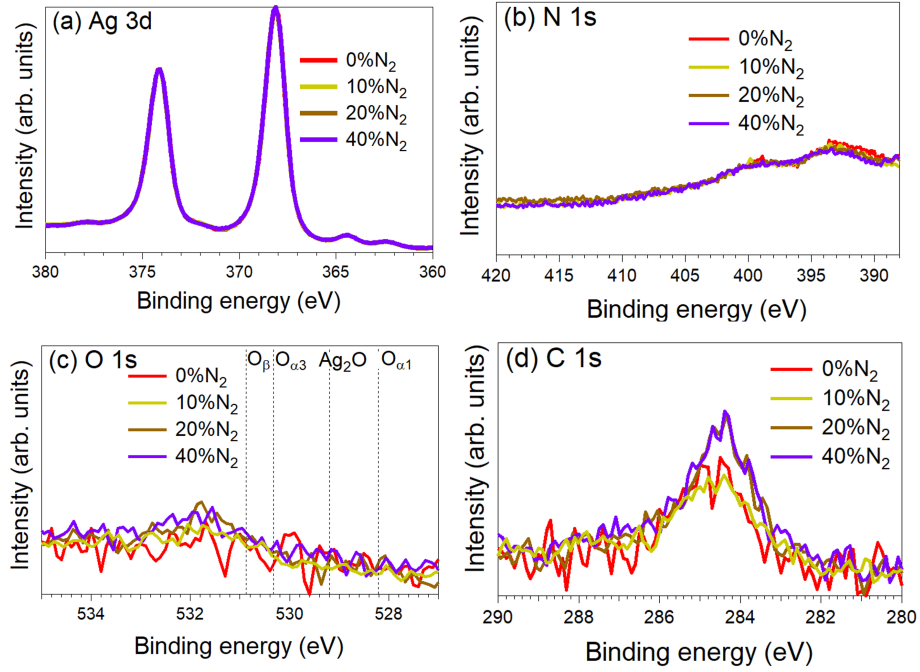


Figure 2: Photoemission analysis of 20 nm-thick Ag films after growth under different %N₂ conditions. Core level regions: (a) Ag 3d, (b) N 1s, (c) O 1s, (d) C 1s. The slight bump in Fig. b corresponds to a satellite plasmon of Ag 3d core level. In Fig. b, reported peak positions for Ag-O moieties are shown [31].

206 induced when depositing a protective layer. For all %N₂, the Ag 3d spectra
207 (Fig. 2-a) perfectly overlap, with no change in peak position or line shape
208 that would otherwise indicate an evolution in the chemical state of the metal.
209 In parallel, no peak is visible in the N 1s core level range (Fig. 2-b), ruling out
210 the presence of N in the film within the sensitivity of photoemission (*i.e.* a
211 few % of a monolayer). These *in vacuo* observations do confirm the apparent
212 inertness of Ag towards N suspected in previous reports [35, 37, 36] for depo-
213 sitions in similar conditions. It is worth noting that the plasmon multiple-loss
214 satellite of the Ag 3d core level peak at $E_B \simeq 398 - 400$ eV should not be
215 misinterpreted as the signature of residual traces of trapped N as done in
216 Ref. [35]. Nevertheless, x-ray or electron induced decomposition during pho-
217 toemission acquisition comparable to those observed for gold nitride [66] can
218 not be completely ruled out despite the much shorter time scale of the mea-
219 surement (a few minutes). In parallel, no significant O 1s signal that could
220 be due to gas impurities during growth is visible (Fig. 2-c) and, only adven-
221 titious carbon contamination of aliphatic nature at $E_B = 284.5$ eV (Fig. 2-d)
222 is present due to sample transfer (~ 20 min) despite high-vacuum conditions.
223 At the opposite, cracking/reaction with spurious C-containing molecules dur-
224 ing deposition would give rise to a distinct binding energy [65] characteristic
225 of graphitic carbon ($E_B < 284$ eV) or carbonates ($E_B = 287.6 - 288$ eV).
226 According to photoemission quantification with a model of thin film, this
227 surface contamination amounts to a fraction of Ag(111) monolayer at the
228 surface (see Ref. [31] for details).

229

230 Having a value of only a few nanometres at the studied photoelectron

231 kinetic energies [67], the probing depth of photoemission does not allow to
232 explore the interface with the substrate in the studied 20 nm-thick films.
233 To explore the chemical impact of the N₂-rich plasma on the wafer surface
234 itself before Ag film percolation, the substrate was exposed during 3 s to a
235 plasma ignited in front of an alumina target. As a reminder, such a duration
236 corresponds to an equivalent Ag deposited thickness of ~ 1.5 nm, well below
237 the percolation threshold. Fig. 3 summarizes the evolution before and after
238 plasma treatment with pure Ar (0%N₂) and 40%N₂. As seen by the shift of
239 Si 2p (Fig. 3-a) or O 1s (not shown) core levels, all gases induces an upward
240 band bending of about 0.4 eV. At the same time, the plasma reduces the
241 adventitious C 1s peak of the as-introduced substrate (Fig. 3-b); this "clean-
242 ing" effect of the monolayer-thick [31] carbon contamination is more efficient
243 with N₂ than with Ar. Similarly, at 40%N₂, a clear uptake of N is observed
244 in the N 1s core level region (Fig. 3-c); it parallels a broadening of the SiO₂
245 component of Si 2p on the low-binding energy side that is characteristic of
246 silicon nitride [65]. Quantification shows that such an uptake amount to
247 about one monolayer, *i.e.* an equivalent thickness of 0.2 nm. Regardless dif-
248 ferent plasma excitations (radio-frequency for alumina versus direct current
249 for Ag), this nitridation of the wafer demonstrates that activated N species
250 are actually present in the plasma and that they strongly interact with the
251 substrate surface during the time scale of film growth. This finding explains
252 the observation in previous works of an N signal at the substrate interface
253 by secondary ion mass spectroscopy that escaped the sensitivity of depth-
254 profiling *ex situ* photoemission [37, 36]. However, the exact nature of these
255 activated N-species (N atom, energetic N⁺/N₂⁺,...) remains unknown.

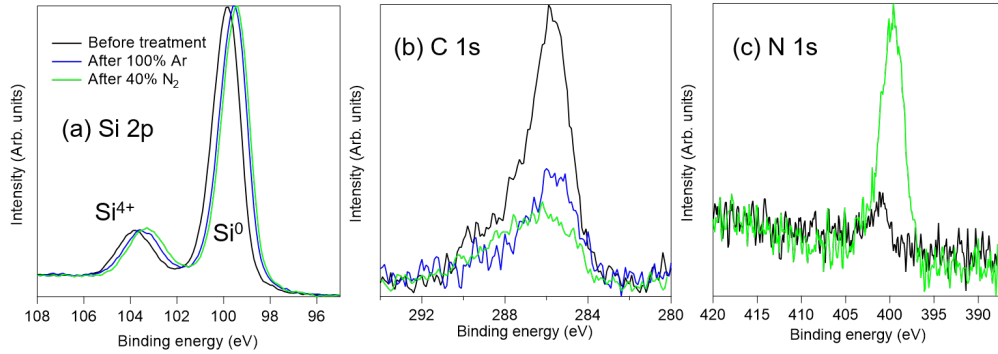


Figure 3: Evolution of Si wafer photoemission core levels after a 3 s treatment with a plasma ignited on a nearby alumina target for the indicated gas composition: (a) Si 2p, (b) C 1s, (c) N 1s.

256

257 3.3. *Ex situ* STEM-HAADF imaging

258 To get some direct insights on the influence of %N₂ in the stage of dis-
 259 continuous nanoparticle films, STEM-HAADF imaging was performed on
 260 AZO-capped 0.6 nm-thick Ag layers (Fig. 4). At such a thickness, all films
 261 are at the limit between growth at saturation density and the beginning of
 262 coalescence t_c that corresponds to the rise of the integrated SDRS signal
 263 $\mathcal{I}_s(t)$ [53, 31] as shown in the next section. Indeed, STEM images show the
 264 beginning of formation of elongated particles. At first sight, no clear-cut
 265 change in morphology shows up with %N₂ in the images of Fig. 4, in con-
 266 trast with previous reports devoted to the late coalescence regime [35, 37].
 267 Nevertheless, image analysis revealed an increase in particle density from
 268 $4.4 \cdot 10^{12}$ to $5.7 \cdot 10^{12} \text{ cm}^{-2}$ (Fig. 5). The difference could lie in the difference of
 269 substrate reactivity towards the active species in the plasma as demonstrated

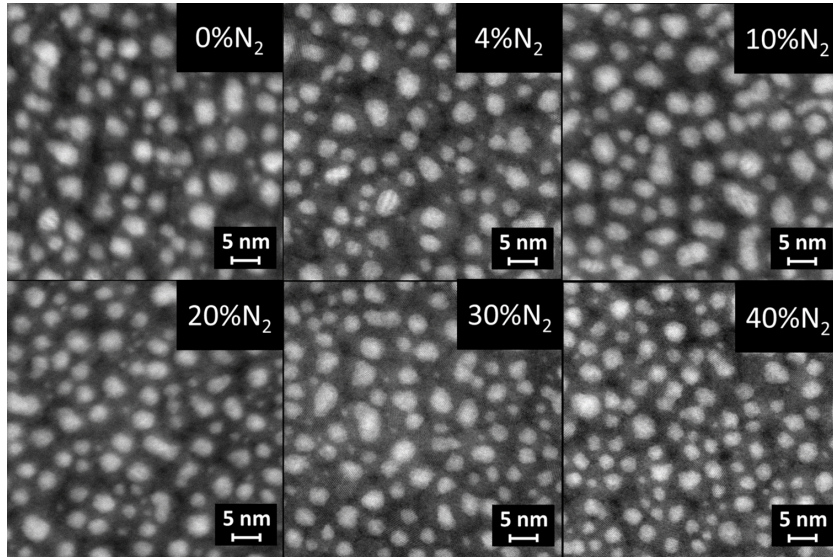


Figure 4: STEM-HAADF imaging of 0.6 nm-thick Ag films deposited on oxidized silicon nitride membranes at increasing %N₂. The scale bar corresponds to 5 nm.

270 above by photoemission (see Fig. 3-b). Further interpretation of STEM imag-
 271 ing, particularly the evolution of aspect ratio, was not pursued as it may be
 272 compromised by encapsulation and uncertainties in thickness due to shut-
 273 ter opening/closing, at the opposite to density. Instead, the sensitivity of
 274 real-time plasmonics to wetting was exploited.

275 3.4. Surface Differential Reflectivity Spectroscopy

276 In parallel to resistivity measurements, the growth process was followed
 277 using real-time SDRS to characterize Ag nanoparticles during the initial
 278 stages of film growth. Fig. 6 shows the integrated signal $\mathcal{I}_s(t)$ in s polar-
 279 ization (Eq. 1) for deposition under different Ar/N₂ mixtures. For all condi-
 280 tions, the value of $\mathcal{I}_s(t)$ is higher than under pure Ar. This quantity being a
 281 reliable reporter of the evolution of aspect ratio A_r [53], this finding consis-

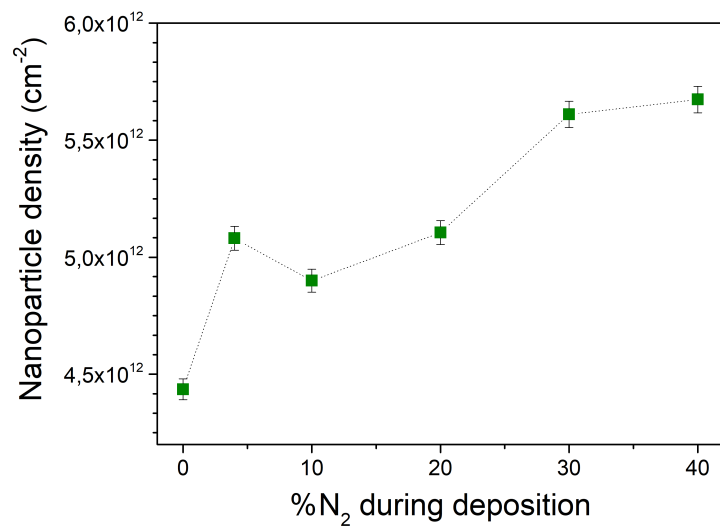


Figure 5: Evolution of the nanoparticle density with the fraction of N₂ in the gas flow. Values are deduced from STEM image analysis at the same equivalent thickness (0.6 nm). Error bars have been estimated over several images.

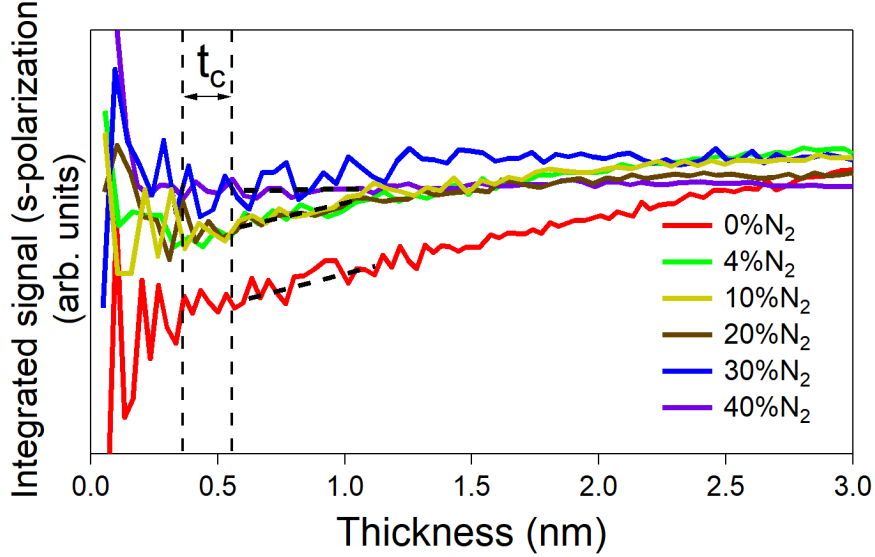


Figure 6: Integrated signal of s polarized SDRS spectra $\mathcal{I}_s(t)$ as a function of deposited equivalent thickness. The vertical line shows the approximate threshold for coalescence onset t_c while the dotted lines is a guide to the eyes showing the difference in slope in $\mathcal{I}_s(t)$ evolution.

282 tently indicates more flattened particles when N_2 is used despite the potential
 283 overall decrease of intensity due to the presence of an adsorbate shell (see
 284 simulations in references [31, 54] and below). Despite noise due to the divi-
 285 sion of two small quantities (see Eq. 1), this observation also holds before the
 286 onset of coalescence t_c that corresponds to the increase of the $\mathcal{I}_s(t)$ signal.
 287 Interestingly, with increasing % N_2 , $\mathcal{I}_s(t)$ reaches much faster the constant
 288 plateau value, which finds its origin in the competition between the increase
 289 of intensity (flattening) and the limited integration range of the red-shifted
 290 plasmon resonance [53]. The flatter particles grown with N_2 coalesce earlier
 291 than those grown without.

292 Fig. 7 shows the SDRS measurements in p polarization at three equiv-

293 alent thicknesses: 0.6 nm, 1 nm, and 2 nm. According to Figs 1 and 6,
294 such values roughly match (i) the end of the isolated particles growth regime
295 (0.6 nm), and (ii) more advanced particle coalescence (1 nm and 2 nm). The
296 observed spectra are characteristic of the excitation of plasmon resonances in
297 nanoparticles with (i) a negative dip at high photon energy associated to the
298 dipole perpendicular to the surface and (ii) a positive feature at low energy
299 associated to the parallel one. The latter being more sensitive to any evolu-
300 tion of morphology, in particular particle density, aspect ratio and formation
301 of a core-shell structure, the discussion will mainly focus on this feature.

302

303 General trends about morphology effects on the shift and change in inten-
304 sity of the plasmon resonances seen in SDRS were already predicted through
305 dielectric simulations of the optical response of truncated spheres (see Fig. 11
306 of Ref. [31] and references therein). The impact of a dielectric shell on a
307 metallic Ag core is also reminded in Fig. 8. To sum up Fig. 11 of Ref. [31],
308 at a constant amount of metal, the low energy plasmon peak red shifts and
309 its intensity increases upon particle flattening (*i.e.* increase of aspect ratio).
310 A similar impact, although less pronounced than upon flattening, is found
311 with a typical increase in particle density. The formation of a "core-shell"
312 morphology (consisting of a shell of dielectric nature and a metallic core)
313 strongly red-shifts the parallel resonance, whilst its intensity decreases if the
314 shell formation is at the expense of the metallic core (Fig. 8-a versus -b). The
315 effect is quite pronounced even for minute changes in shell thickness [31, 54]
316 (Fig. 8), in the range of a few percent of nanoparticle radius, a change that
317 would correspond to an atomic thickness for nano-sized particles. The shift

318 even strengthens with the index of refraction of the shell (not shown); its
319 value ($n = 2$) in the present simulations was chosen somehow arbitrarily to
320 mimic the effect a dielectric adsorbate. Thus, in principle, plasmonics is not
321 only sensitive to an actual change in chemistry (such as an actual surface
322 oxidation as observed in the case of O₂ [31]), but also to the presence of
323 adsorbates in the monolayer range.

324

325 For very thin Ag films (0.6 and 1 nm; Fig. 7-a,b), the addition of N₂
326 leads to a red-shift, an intensity increase and a broadening of the low-energy
327 resonance. Most of the change is nearly already set up at 4%N₂. According
328 to simulations [31], this energy shift is too large to be accounted for by the
329 change in particle density obtained from STEM pictures (Fig. 5) although
330 it may contribute to it. On the other hand, particle flattening can explain
331 the present plasmonic observation with %N₂ and, in turn, the decrease in
332 film percolation threshold as flattened particles with a more pronounced 2D
333 growth would impinge on each other and form a conductive percolated net-
334 work faster than more rounded 3D ones. The interpretation differs somewhat
335 at a thickness of 2 nm (Fig. 7-c). In this case, the addition of 4%N₂ red shifts
336 and enhances the low energy resonance while a further increase of %N₂ keeps
337 on shifting the peak but at the expense of its intensity and in a way nearly
338 independent of %N₂ for values greater than 10%N₂. This overall plasmonic
339 scenario with %N₂ matches with an increase in aspect ratio and the formation
340 of a core-shell structure, which relative impacts on the resonance intensity
341 are dictated by the N coverage. It also agrees with the decay on intensity of
342 the high energy resonance with %N₂ (Fig. 7 vs Fig. 8) although its red-shift

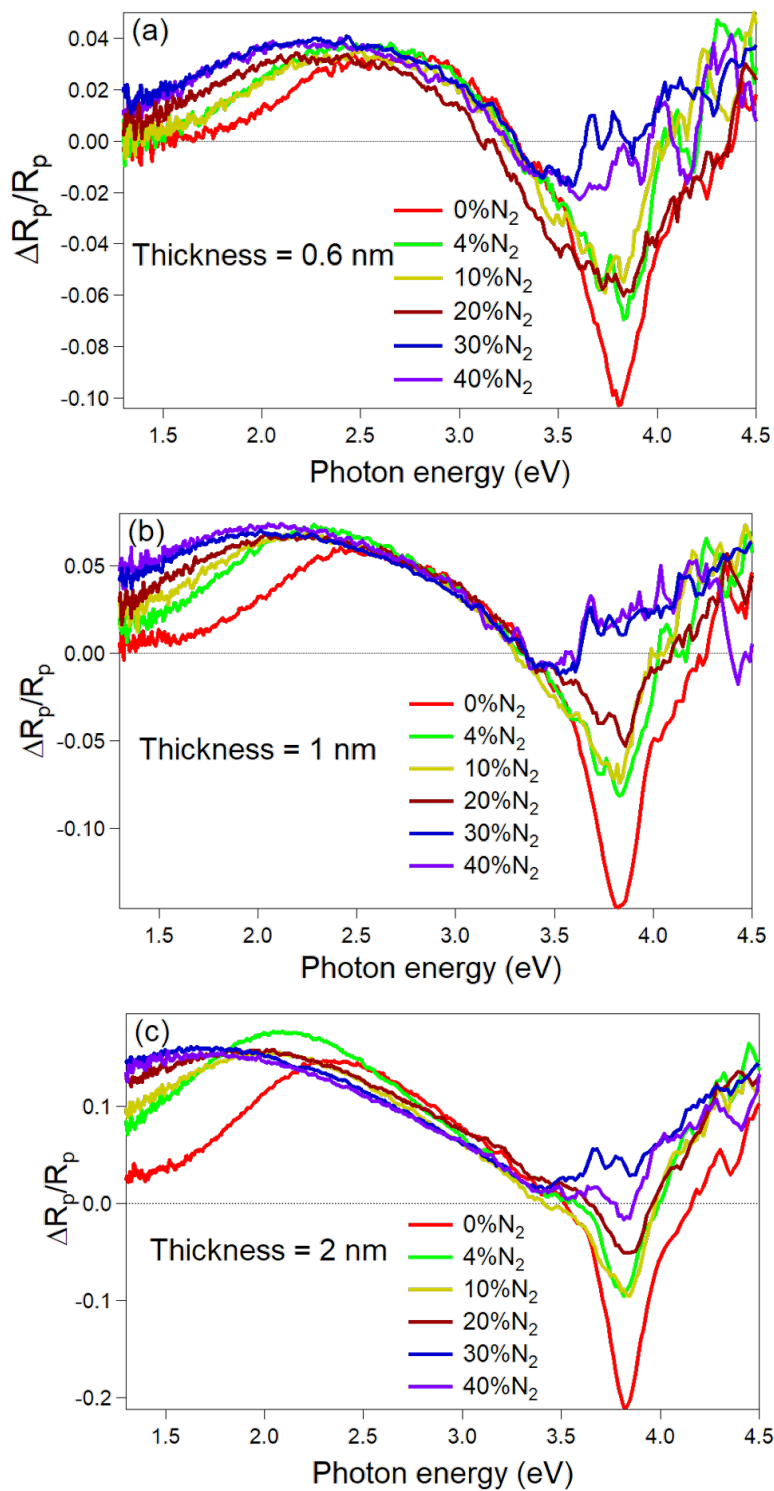


Figure 7: SDRS spectra in p polarization for different %N₂ during deposition, corresponding to a nominal equivalent thickness of (a) 0.6 nm, (b) 1 nm and (c) 2 nm.

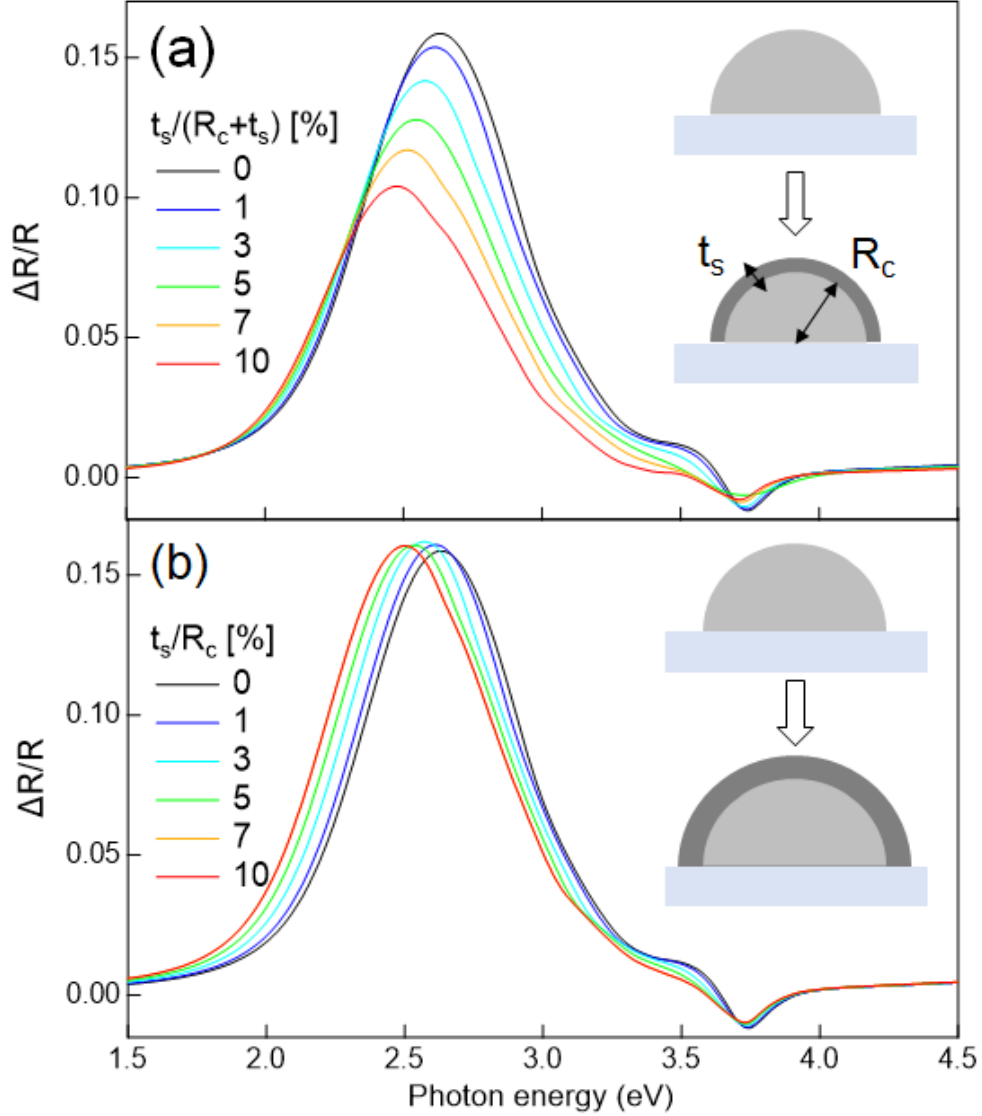


Figure 8: Simulated p polarized SDRS spectra for core-shell hemispheres arranged on a square lattice on SiO_2/Si . Evolution upon varying the shell thickness t_s at (a) the expense of the core size R_c and (b) at constant core size. The dielectric function of metallic bulk Ag was used for the core while the index of refraction of the shell was fixed arbitrarily at 2. The parallel plasmon is broadened by 0.3 eV to account for size-shape distribution and finite-size effects [31, 61, 62] and the particles are electrostatically coupled at quadrupolar order. The film thickness amounts to about 1.6 nm as in the ageing experiments of Fig. 9.

343 is less clear-cut due to noise. But the lack of any N 1s fingerprint for thick Ag
344 films makes this core-shell optical scenario unlikely unless adsorbed N at the
345 Ag surface is unstable once the growth is stopped. However, the nitridation
346 of the wafer surface unambiguously demonstrates the presence of activated
347 N species in the plasma, in the form of atoms or ions, that can react or be
348 implanted. To investigate this puzzle, in-vacuum post-deposition ageing of
349 deposits after the end of growth was investigated by SDRS.

350

351 Fig. 9 shows the evolution of SDRS spectra over an hour time scale under
352 vacuum after gas evacuation ($p \sim 5 \cdot 10^{-7}$ mbar). The cases of 1.6 nm-thick
353 Ag films deposited under pure Ar and 20 %N₂ conditions are compared. Note
354 that spectra were corrected from the drift of the light source using an ancil-
355 lary spectrometer [51]. The noticeable evolution of the spectra highlights the
356 post-deposition film instability that is often overlooked. For the film grown
357 under pure Ar, both resonances get closer in energy with time while their in-
358 tensities poorly evolve. These trends are characteristic of a slight dewetting
359 of nanoparticles, *i.e.* a decrease of A_r towards more rounded objects, al-
360 though the slight intensity increase of the low energy resonance (Fig. 9-a and
361 c) does not match fully theoretical expectations (see Figure 11 of Ref. [31]).
362 Argon adsorption is obviously ruled out and an evolution of particle density
363 by Ostwald ripening is unlikely owing to the short time scale of most of the
364 change observed after deposition under pure Ar (a few mins; Fig. 9-a). In
365 contrast, the evolution markedly differs at 20%N₂; both resonances increase
366 in intensity and come closer in energy but with a slower evolution after the
367 end of the growth than for 0%N₂. According to qualitative dielectric simu-

368 lations shown in Fig. 8-a (see Section 2 for all details), such a finding can
369 only be assigned to the desorption of a N species from the surface of the
370 nanoparticles. Indeed, dewetting cannot account, by any means, for the ob-
371 served increase in intensity for both resonances, although its presence cannot
372 be fully ruled out either. This conclusion is further reinforced by the increase
373 with time of $\mathcal{I}_s(t)$ (Fig. 9-c); pure dewetting (*i.e.* a decrease in A_r) would give
374 rise to the opposite (*i.e.* a decrease in \mathcal{I}_s). Moreover, according to Fig. 7-c,
375 the phenomenon occurs over a time scale of 15 mins; this duration is higher
376 than that required to transfer and analyze the sample by photoemission, thus
377 potentially explaining the lack of traces of N in the film. Finally, as shown
378 by comparing simulations for a shell growing at the expense of the metallic
379 core (Fig. 8-a) or not (Fig. 8-b), the observed change of SDRS intensity upon
380 N adsorption/desorption implies a charge transfer between Ag and N, or in
381 other words a change in the metallic character of Ag.

382 3.5. X-ray diffraction

383 Regarding film crystallography, XRD diffractograms (Fig. 10-a,b) only
384 show, for all of the studied %N₂, peaks corresponding to metallic face-centred
385 cubic Ag, wurtzite ZnO from the capping layer, and a large feature around
386 $2\theta = 22^\circ$ assigned to the amorphous SiO₂ substrate. Despite the out-of-
387 equilibrium conditions of sputtering deposition, no silver nitride formation
388 is observed in agreement with the lack of reported bulk structure [43, 37].
389 First of all, as seen in the Bragg-Brentano radial scans along the out-of-
390 plane direction (Fig. 10-a), the Ag films appears to be only [111]-[100] tex-
391 tured along the growth direction. Starting from the classical favoured (111)
392 stacking under pure Ar characterized by an intense (111) peak and a weak

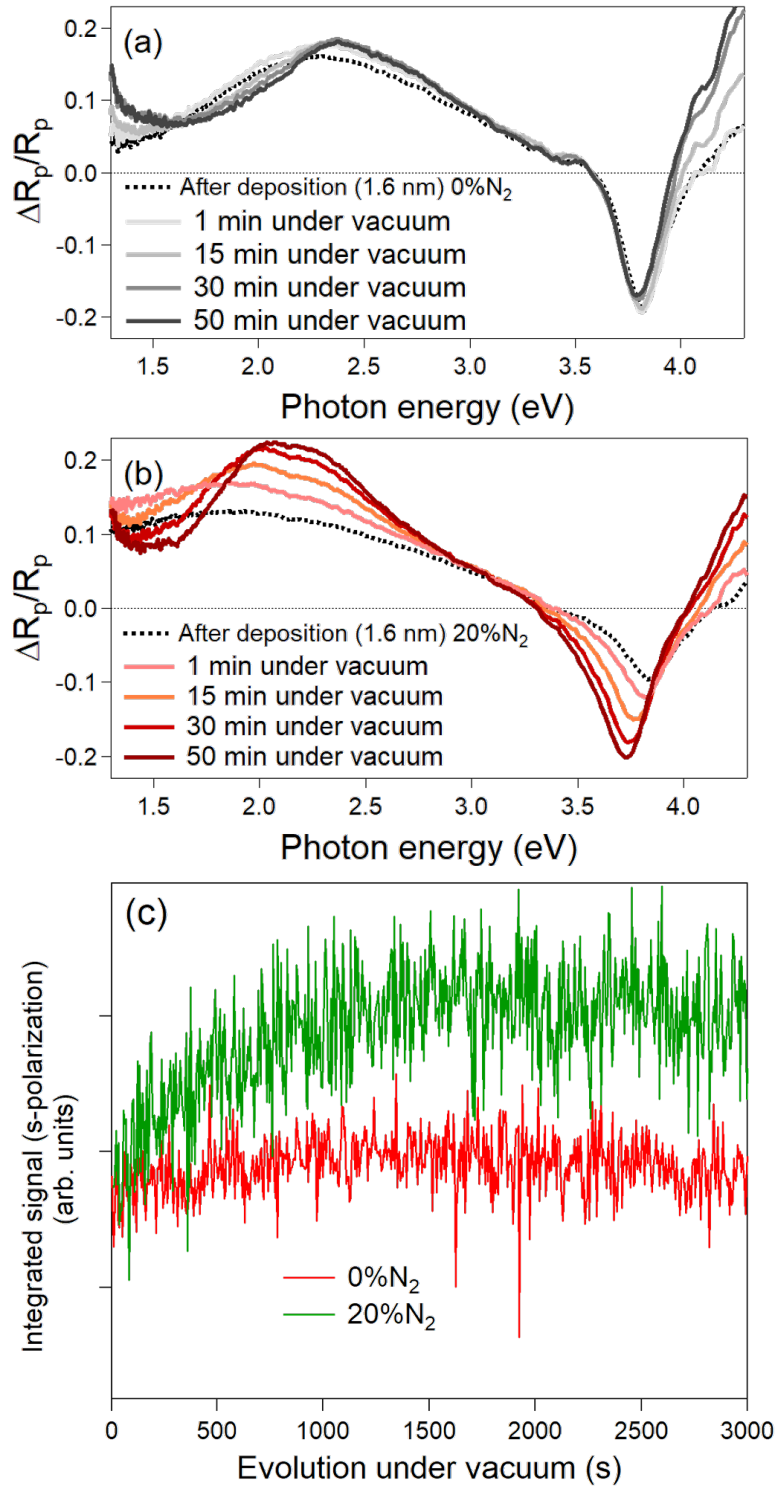


Figure 9: Post-deposition evolution under vacuum of p polarized SDRS spectra for 1.6 nm-thick Ag films deposited under (a) 0%N₂ and (b) 20%N₂. Duration after the end of the growth is indicated on figure. (c) Same evolution but for the integrated SDRS signal in s polarization (Eq. 1).

393 (200) reflection, the texture evolves with %N₂ towards more [100]-oriented
394 grains; this also reflects in the relative evolution of (220) and (200) peaks
395 in the grazing-incidence scans (Fig. 10-b). Owing to the inherent poor sen-
396 sitivity of Bragg-Brentano geometry at high-angles for a thin film, the lack
397 of (220) reflection does not rule out the presence of [110] out-of-plane ori-
398 ented crystallites, whose existence is supported by the (111) in-plane Bragg
399 peak. At last, regarding the crystallites corresponding with a (311) in-plane
400 Bragg peak (Fig. 10-b), it is impossible to assign their out-of-plane orien-
401 tation with only the present set of measurement geometries. No in-plane
402 preferential texture is expected for an amorphous substrate, a fact that is
403 partially supported by the presence of all Ag allowed reflections in Fig. 10-b.
404 This evolution was rationalized by fitting peaks with Voigt profiles to ob-
405 tain the corresponding Debye-Scherrer sizes from full-width at half-maximum
406 (Fig. 10-c) and an estimate of the crystallite volume fraction from peak ar-
407 eas (Fig. 10-d) after correction from the relative intensities as found for a
408 powder [68] (*i.e.* from structure factors, reflection multiplicity, Lorentz-
409 polarization factor and beam footprint). The out-of-plane Debye-Scherrer
410 size of [111] oriented-crystallites decreases at the expense of [100] ones; but
411 both are much smaller than the film thickness when N₂ is used thus show-
412 ing a worsening of film crystallinity. Meanwhile corresponding in-plane sizes
413 of those domains (derived from the widths of (220) and (200) Bragg peaks
414 which normal to the corresponding diffracting planes are perpendicular to
415 [111] and [100] directions) do not significantly change with %N₂ (Fig. 10-c).
416 In parallel to the size evolution, the film texture changes from a dominant
417 [111] out-of-plane orientation under pure Ar to a 40/60 % [111]/[100] mix

418 for 40%N₂ with a minor impact in-plane (Fig. 10-d). A parallel evolution is
419 observed in-plane on the volume fraction corresponding to (220) and (200)
420 peaks although less pronounced due to the presence of other reflections.

421 4. Discussion

422 The addition of N₂, even in small quantities, in the Ar plasma provokes a
423 spectacular decrease of percolation threshold (Fig. 1). Based on the previous
424 results, on literature data and on the comparison with a similar work with
425 O₂ [31], several aspects of this N₂ growth modifier effect can be discussed as
426 follows.

427 4.1. *N dynamic adsorption during growth*

428 N₂ molecule adsorption being excluded owing to its filled orbital structure
429 and its high bond energy, only species activated by the plasma and adsorbed
430 at the film surface can be at the origin of the phenomenon, most probably
431 atomic N. Indeed, N₂ ions would temporally implant as, once neutralized,
432 the resulting molecule would immediately desorb. The N-atom hypothesis is
433 supported by *ab initio* atomistic calculations that all predict (i) an energeti-
434 cally stable N adsorbate at the Ag surfaces with an adsorption energy above
435 2 eV/atom [44, 45, 46, 47, 37] and (ii) an energetically unfavourable dissolu-
436 tion in the bulk [37] in line with the strong positive enthalpy of formation of
437 Ag nitride (314 kJ.mol⁻¹=3.25 eV/atom [43]). Thus, while the nitridation
438 of the substrate testifies of the presence of such activated N species (Fig. 3-
439 c), the lack of any trace of N 1s signal on thick Ag films (Fig. 2-b) can be
440 explained only by a efficient recombinative desorption at room temperature.
441 Indeed, photoemission (not shown) does not evidence any trace of N at the

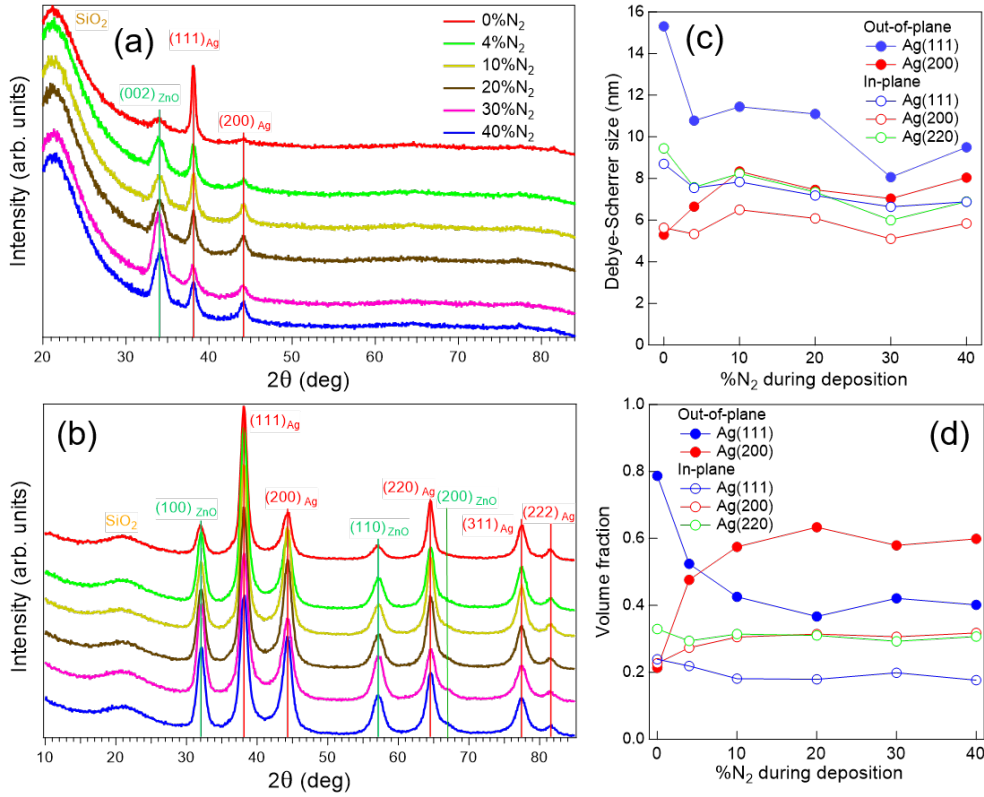


Figure 10: XRD diffractograms in (a) Bragg-Brentano and (b) grazing-incidence geometry of 20 nm-thick Ag films deposited under different %N₂. Vertical bars indicate the expected bulk positions of the diffraction peaks. (c) Debye-Scherrer sizes $D = \frac{0.9\lambda}{\cos(\theta)\Delta(2\theta)}$ from peak full-width at half-maximum $\Delta(2\theta)$. Similar sizes are derived from all in-plane diffraction peaks (not shown). (d) Film texture or volume fraction from ratio of the areas of all visible peaks after correction from intensities expected from a powder sample [68].

442 surface of a pure 20 nm-thick Ag film exposed to a 40%N₂ plasma ignited on
443 a alumina target during 90 s (*i.e.* more than two times the growth duration)
444 while a slight alumina coverage of 0.07 nm is estimated by photoemission in
445 these conditions. This points at an intrinsic N instability that is not only
446 related to the film growth process itself. The lack of N 1s fingerprint at the
447 Ag film surface apparently contradicts the only surface science experiment of
448 Carter *et al.* [48] and the atomistic calculations [44, 45, 46, 47, 37] on interac-
449 tion of atomic N with Ag(111) and Ag(100) orientations that all agree with
450 a favourable adsorption. Nevertheless, a quite low recombinative desorption
451 temperature of 350 K was found on Ag(111) [48] pointing at a poorly stable
452 adsorbate that could be present only dynamically at the surface of Ag in the
453 present experiments. This picture is supported by the large post-deposition
454 evolution of SDRS plasmonic signal (Fig. 9) indicating the disappearance of
455 a shell on top of a metallic core. In addition, the experiments of Carter *et*
456 *al.* [48] on N/Ag(111) showed that the process of desorption is not of second
457 order and therefore not limited by the surface diffusion of adsorbed N but
458 rather by the concerted lifting of N-induced surface reconstruction and N₂
459 molecule desorption. Thus, the dynamic N coverage expected during growth
460 is limited, of course by the amount of dissociation of N₂ in the plasma (*i.e.*
461 %N₂), but also by the surprisingly reported efficient desorption of N upon di-
462 rect impact of another N atom [49, 50] (*i.e.* Eley-Rideal mechanism). At last,
463 the major difference in chemistry between the O₂/N₂ gases partly explains
464 the much higher value of the final film resistivity at 20 nm for O₂ (80 μΩ.cm
465 at 40%O₂ [31]) than for N₂ (8.5 μΩ.cm at 40%N₂; Fig. 1-b). Thus, other
466 structural factors, such as film crystallinity, should be put forward to ac-

467 count for the worsening of film resistivity observed with N₂ as compared to
 468 pure Ar (Fig. 1-b).

469 *4.2. The origins of better percolation*

470 To rationalize the remarkable decrease of 51 % of the percolation thresh-
 471 old when adding N₂ (Fig. 1), the same reasoning developed for O₂ in Ref. [31]
 472 can be performed. Changes in particle saturation density ρ_s and aspect ratio
 473 A_r (diameter/height) or impeded coalescence can be put forward. Indeed,
 474 denser or flatter initial particles as well as delayed coalescence upon im-
 475 pingement all give rise to an earlier percolation. Assuming a scaling $t_p \propto t_c$
 476 between the onset in thickness t_c for coalescence between nanoparticles and
 477 the electrical percolation threshold t_p , one finds:

$$t_p \propto t_c \propto D_c^3 \rho_s / A_r \quad (2)$$

478 where D_c is the in-plane size of particles at coalescence start. Since particles
 479 are in contact with each other at coalescence, $D_c \propto \rho_s^{-1/2}$ so that:

$$t_p \propto 1/(\rho_s^{1/2} A_r). \quad (3)$$

480 Then, one can estimate the expected variation of t_p from the variation of A_r
 481 and ρ_s [31] as:

$$\frac{\Delta t_p}{t_p} = -\frac{\Delta A_r}{A_r} - \frac{1}{2} \frac{\Delta \rho_s}{\rho_s}. \quad (4)$$

482 Thus the change in density of $\frac{\Delta \rho_s}{\rho_s} = +28$ % from 0 to 40 %N₂ found by
 483 STEM (Fig. 5) accounts only for roughly one third of the observed evolution
 484 of t_p .

485

486 Assuming equilibrium shape before coalescence, particle shape can be
 487 tackled by thermodynamics of surface/interface energies. At such sizes of a
 488 few nanometers (see Fig. 4), the scalable regime of shape as predicted by
 489 Wull-Kaischew [69] or Young-Dupré construction is achieved and energetics
 490 is not size-dependent in particular on an amorphous substrate [60, 70, 53,
 491 71]. Unfortunately, at the opposite to evaporation [53], the SDRS signal-
 492 to-noise ratio prevents seeing the U-shaped variation of $\mathcal{I}_s(t)$, the bottom of
 493 which is characteristic of a growth at constant aspect ratio. Nevertheless, the
 494 comparison by plasmonics [63] between evaporation and sputtering growth of
 495 Ag on a similar poorly-interacting substrate (Al_2O_3) showed that equilibrium
 496 shape before coalescence is a reasonable hypothesis. Thus, the Young-Dupré
 497 equation for a truncated sphere

$$W_a = \gamma_m(1 + \cos \theta_c) \quad (5)$$

498 allows linking the variation of A_r to that of the contact angle θ_c , of the
 499 adhesion energy W_a and of the metal surface energy γ_m [31] through:

$$\frac{\Delta A_r}{A_r} = -\frac{\sin \theta_c \Delta \theta_c}{1 - \cos \theta_c} \quad (6)$$

$$\frac{\Delta W_a}{W_a} - \frac{\Delta \gamma_m}{\gamma_m} = -\frac{\sin \theta_c \Delta \theta_c}{1 + \cos \theta_c}. \quad (7)$$

500 Of course, forgetting cristallographic anisotropy of Ag surface energies by
 501 assuming a truncated sphere equilibrium shape [69] is a first approach of the
 502 problem that nevertheless grasps the present physics. This anisotropy

$$\left(\frac{\Delta \gamma}{\gamma}\right)_{ani} = \frac{\gamma_{(100)} - \gamma_{(111)}}{\gamma_{(111)}} \quad (8)$$

503 between (111) and (100) planes is modest on bare surfaces *i.e.* $\left(\frac{\Delta \gamma}{\gamma}\right)_{ani} \simeq$
 504 $+3 \%$ but strongly enlarges upon N adsorption *i.e.* $\left(\frac{\Delta \gamma}{\gamma}\right)_{ani} \simeq -50 \%$ [72, 37].

505 Starting from an equilibrium contact angle of $\theta_c \simeq 130^\circ$ for Ag/SiO₂ [53, 73]
 506 and assuming that adhesion energy is not modified by the interaction of
 507 N with the substrate ($\theta_c = 130^\circ$ for Ag/Si₃N₄ [74]), the calculated drastic
 508 decrease of Ag surface energy [37] of $\frac{\Delta\gamma_m}{\gamma_m} \simeq -75\%$ for both (111) and (100)
 509 planes with N coverage would lead to a modest $\Delta\theta_c = -20^\circ$ (Eq. 7) and
 510 $\frac{\Delta A_r}{A_r} = +16\%$ (Eq. 6). So

$$-\frac{\Delta A_r}{A_r} - \frac{1}{2} \frac{\Delta\rho_s}{\rho_s} = -30\% \quad (9)$$

511 accounts only for a fraction of the observed $\frac{\Delta t_p}{t_p} = -51\%$ (Eq. 4). Beyond ki-
 512 netic hindrance of reshaping that could be already present during the growth
 513 of isolated nanoparticles, a delayed coalescence should be invoked to explain
 514 the remaining part of the change in t_p . Evidence of this could be found in
 515 the much faster increase of $\mathcal{I}_s(t)$ towards a plateau value in the coalescence
 516 regime (Fig. 6) when comparing deposition with and without N₂.

517 4.3. Anisotropic N adsorption and change in film texture

518 Beside the modification of surface Ag diffusion by a N adsorbate, a likely
 519 explanation of delayed coalescence can be found in the competition between
 520 the growth of [111] and [100] oriented islands, as testified by the change in
 521 film texture although XRD gives information averaged over a comparatively
 522 thicker film (Fig. 10-c). As grain boundaries between such crystallites lead
 523 to a strong structural mismatch, this explains the worsening of the final film
 524 resistivity with %N₂ despite an earlier percolation (Fig. 1). Initially sug-
 525 gested by Kawamura *et al.* [42] to achieve films with the unusual [100] Ag
 526 orientation on an amorphous glass substrate by sputtering deposition, this
 527 surprising effect of N₂ on texture was also reported on SiO₂ upon increasing

528 (i) N_2 content in the gas flow in references [23, 35] or (ii) the film thickness
529 at constant $\%N_2$ in Ref. [37]; in Ref. [36], only a loss of out-of-plane [111]
530 texture was observed as the (200) peak is hardly visible. Assuming the dy-
531 namical presence of adsorbed N at the surface of Ag, this change in texture
532 with $\%N_2$ matches with the calculated reversal of surface energies between
533 N-covered (111) and (100) Ag surfaces with N surface concentration [37]. The
534 anisotropy goes from a small value of a few % in favour of (111) (that agrees
535 with the experimental microscopy observation of the Wulff-Kaischew equilib-
536 rium shape [72]) to around 50 % in favour of (100). Higher N_2 flow favours
537 an enhanced N_2 dissociation and therefore a larger dynamical coverage and
538 in turn a larger fraction of (100) facets as detected by XRD (Fig. 10-d).
539 Similarly, when N_2 is present, Yun *et al.* [37] observed a correlation between
540 this switch of texture and the onset of percolation. This might be explained
541 by a kinetic competition between (i) the metal-metal aggregation by diffu-
542 sion that favours an initial (111) stacking for a face-centred cubic metal, (ii)
543 the substrate decarbonation and nitridation (see Section 3.2) and (iii) the
544 starting of N adsorption on Ag(111) surfaces as theoretically expected on
545 a energetic point of view at low N coverage [37]. Thus, for the Ag growth
546 on ZnO films textured along the c-axis, N_2 gives rise to a surprising selec-
547 tivity towards [111]-oriented nanoparticles (before percolation) [37]. While
548 islands are larger in-plane due to N effect (see Section 3.4), the remarkable
549 Ag(111)/ZnO(0001) epitaxy [12, 75], its favourable interfacial energy and the
550 earlier percolation delay the growth of [100] orientation which is observed
551 only for thicker films compared to the growth on SiO_2 . But, during growth,
552 as the fraction of wafer surface covered by the metal and the availability of

553 N or of potential (100) facets for adsorption increase, the N-covered (100)
554 facets overcome the (111) ones. The impingement of islands with different
555 orientations results into incomplete coalescence and earlier percolation but at
556 the expense of poor grain boundaries for electrical transport. This scenario
557 shows the interest in the strategy of N₂ gas deployment at the beginning of
558 the growth to benefit from earlier percolation while avoiding the transition
559 between orientations that is detrimental to resistivity [36]. This drawback
560 can be turned into an advantage to grow Ag films on amorphous substrate
561 with the unusual [100] orientation [42] or to achieve epitaxial and continuous
562 films at very small thickness on substrates showing a cube/cube epitaxy such
563 as MgO(001) [76].

564 4.4. N₂ versus O₂ as "surfactants" of Ag growth

565 To conclude, N₂ appears to behave as a "surfactant" during sputtering
566 deposition of Ag. It is completely immiscible leading probably to an effi-
567 cient mechanism of spillover or segregation to the surface, as already put
568 forward in the case of O at low %O₂ [28, 29, 32]. But there is no equivalent
569 threshold of incorporation in the bulk [31] (*i.e.* of formation of subnitrides),
570 a phenomenon that is detrimental for electrical transport in the case of O.
571 Finally, as for O [77, 78], N adsorption decreases the surface energy of the
572 metal thus favouring wetting. Nevertheless, the origin of N impact on the
573 percolation threshold seems to results from a interplay between a better wet-
574 ting, a change in saturation density and a delayed coalescence in which the
575 orientation-dependent impact of N on energetics plays a decisive role.

576 **5. Conclusion**

577 The interpretation of the effect of N_2 during sputtering growth of Ag
578 on an amorphous substrate was revisited using a combination of real-time
579 and *in vacuo* measurements. Increasing the % N_2 in the gas flow led to
580 a sizeable decrease of the percolation threshold but at the expense of film
581 resistivity. According to *in vacuo* photoemission, N is absent from the film
582 and its surface. However, substrate nitridation and decarbonation prove the
583 presence of activated N species in the plasma, probably atomic N that covers
584 dynamically the metal but desorbs once the growth is stopped as indicated
585 by the evolution of the plasmonic response. This adsorbate decreases the
586 surface energy of the metal, thus inducing a flattening during the island
587 growth. However, this enhanced wetting cannot explain alone the observed
588 reduction of percolation threshold. It also involves a contribution from the
589 change in particle density and from a delayed coalescence. The latter is
590 assigned to the competition between [111] and [100] oriented particles that
591 ends up in an evolution of film texture and a worsening of film resistivity.
592 As a result, nitrogen displays all the characteristics of a "surfactant" for Ag
593 growth. It is immiscible in the bulk of the metal, decreases its surface energy
594 but stabilizes more (100) than (111) facets and finally desorbs easily after
595 growth. Nevertheless, these restrictive characteristics seem specific to the
596 case of N-Ag and could preclude, beyond the difficult dissociation of the N_2
597 molecule, the systematic use of such a gas as a surfactant with metals with
598 a stronger chemical interaction with N.

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