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Does N_2 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 N_2 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 N_2 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 1. Introduction

The thermal insulation of buildings is a crucial lever to face the issue of 2 global warming. In low-E or solar-control windows, complex stacks of layers 3 are deposited by magnetron sputtering on one of the inside glass surfaces of 4 the double-glazing [1, 2, 3]. The active layer for thermal infra-red reflection 5 is a Ag film, the thickness (10-12 nm) of which should be well below the skin 6 depth in the visible range to achieve optical transparency. According to the 7 Hagens-Rubens relation [4, 5] $R = 1 - 2\sqrt{2\epsilon_0 \omega \rho}$, the reflection coefficient R of 8 a conductive medium at a given frequency ω is dictated by its resistivity ρ (ϵ_0 9

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

of deposition itself (flux and temperature) [9, 10], (ii) substrates or growth layers (ZnO in the case of Ag [11, 12]), (iii) wetting or buffer layers of transition metals [13, 14, 15, 16], of the corresponding metal oxide [17], or of Ge [18, 19, 20], (iv) film doping and alloying with metals such as Al [21, 22] and (v) gaseous species, such as O_2 [23, 24, 25, 26, 6, 27, 28, 29, 30, 31, 32] and N_2 [23, 33, 34, 35, 36, 37], during deposition.

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This last strategy of gaseous "surfactants" has attracted much attention 42 in the past few years and was recognized as an efficient pathway for produc-43 ing thinner continuous Ag films even on amorphous substrates. As shown in 44 many previous reports [24, 25, 26, 6, 27, 28, 38, 29, 30, 31, 32], O₂ addition 45 reduces drastically the Ag percolation thickness threshold but at the expense 46 of a film resistivity worsening due to O incorporation. This flaw can be par-47 tially circumvented by the use of N_2 that produces similar overall effects but 48 without measurable chemical interaction with Ag [23, 33, 34, 35, 36, 37]. Nev-49 ertheless, N_2 requires higher partial pressures to achieve the same change in 50 percolation thickness, presumably because of its lower dissociation efficiency 51 in the plasma due the strong triple N-N bond. Beside the presence of excited 52 N_2 molecules, plasma diagnostics actually confirm that only a small fraction 53 of molecules is actually dissociated into atomic N [39, 40, 41]. But surpris-54 ingly, Ag films grown with N_2 addition were found free of N by ex situ pho-55 to emission even when using pure N_2 gas during growth [23, 42, 34, 35, 36, 37]. 56 Nonetheless, if these findings are in line with the chemical inertness of N_2 with 57 Ag and the lack of stable bulk Ag-nitride compounds [43], all first-principle 58 simulations [44, 45, 46, 47, 37] report on the energetically favourable ad-59

sorption of atomic N at Ag surfaces. The concomitant drastic decrease of 60 surface energy was put forward to explain a better wetting and an earlier per-61 colation [35, 37]. In parallel, aside from a low desorption temperature [48], 62 experiments pointed at an unusual efficient recombinative desorption of N by 63 direct impact (Eley-Rideal mechanism) [49, 50]. To circumvent the detrimen-64 tal effect of N_2 on Ag film crystallinity while still benefiting from an earlier 65 percolation, Jamnig et al [36] proposed to inject the gas only during the first 66 stages of film growth before percolation. At last, N_2 was found to promote 67 the [100]-Ag film texture which is an unusual orientation on a surface energy 68 point of view for a face-centred cubic metal [42]. 69

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While N_2 appears as an efficient modifier of Ag growth leading to earlier 71 percolation [33, 34, 35, 36, 37], the apparent lack of N in the film questions 72 its actual floating-out surfactant behaviour that could have escaped to pho-73 to emission measurements based on depth-profiling. Also, the observed wors-74 ening of film resistivity and crystallinity remains unexplained. This work 75 proposes to revisit the question by a combination of *in vacuo* x-ray photo-76 electron spectroscopy (XPS) and real-time measurements of film resistance 77 and of surface differential reflectivity spectroscopy (SDRS). Observations are 78 supplemented by ex situ x-ray diffraction (XRD) and scanning transmission 79 electron microscopy (STEM). The objective is to unveil the effects of N_2 ad-80 dition at the different stages of sputtering deposition growth of Ag on silica 81 for a wide range of gas compositions and to discriminate between the possi-82 ble origins of earlier percolation *i.e.* enhanced wetting, change in the particle 83 density and coalescence impediment. Plasmonics is used to probe directly 84

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

87 2. Experimental

All experimental details regarding the film deposition and the employed 88 techniques can be found in Ref. [31] where a similar work was performed with 89 O_2 instead of N_2 . Briefly, Ag films were grown by magnetron sputtering at 90 room-temperature on Si wafers (thickness 280 μ m, n-doped, (100)-oriented), 91 the surface of which is covered by its ~ 2 nm-thick native amorphous SiO₂ 92 oxide. The sputtering chamber (base pressure of $< 2.10^{-8}$ mbar) includes 93 three different two inch targets equipped with a shutter, in front of which 94 the sample can be positioned by a manipulator. Ag depositions were car-95 ried out at a power of 50 W and a total pressure of 2 μ bar in direct current 96 mode with ultra-pure gas (< 50 ppm of impurities) at a target distance of 97 15 cm. During Ag deposition, the total flow of Ar and N_2 gases was kept 98 at 50 sccm while their ratio was varied via mass flow controllers. Hereafter, gc $x\%N_2$ will stand for the percentage of flow of N_2 in the total. As described 100 in Ref. [31], the deposition rates were carefully calibrated on thick films with 101 an uncertainty of ~ 1 %. For Ag, it ranged from 0.55 down to 0.45 nm.s⁻¹ 102 when increasing $\%N_2$ from 0% to 40%. Nominal thickness is systematically 103 used to designate the deposited amount of Ag all along this work. 104

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Thanks to a direct connection under vacuum to an analysis chamber (base pressure $\sim 10^{-9}$ mbar) hosting an XPS apparatus, the chemistry of the free surface could be analysed without exposure to air. This capability for such

a surface sensitive tool avoids any *ex situ* depth-profiling by sputtering of 109 capped samples that can bias the interpretation of photoemission spectra. 110 Right after deposition (~ 20 mins), samples were analysed by recording se-111 lected core level regions (Ag 3d, N 1s, O 1s, C 1s, Si 2p). Besides a slight 112 presence of carbon of aliphatic nature at a binding energy of $E_B = 284.5 \text{ eV}$, 113 no other contaminants, particularly implanted Ar and carbonates, were de-114 tected. As Si wafers were used as received without specific surface treatment 115 prior to Ag deposition, the effect of plasma exposure on its surface chemistry 116 was also explored by XPS. To decouple it from Ag deposition, wafers were 117 exposed during 3 s to a plasma (pure Ar *i.e.* $0\%N_2$, and $40\%N_2$) ignited 118 in radio-frequency mode on an alumina target placed not inline of sight of 119 the sample. Due to the short duration of the substrate treatment (3 s) and 120 the low deposition rate of this material $(0.007 \text{ nm.s}^{-1})$, no Al was found by 121 photoemission within the detection limit. 122

123

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

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

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

is a reliable reporter of the A_r evolution as both quantities are proportional 142 to the oscillator strength of the parallel plasmon oscillation. Finally, to help 143 rationalizing SDRS evolution upon N adsorption/desorption, the optical re-144 sponse of a core-shell hemisphere [54] supported on SiO_2 has been simulated 145 with the *GranFilm* code [55] and then renormalized to Si reflection coeffi-146 cient. While tabulated dielectric functions of Ag, SiO₂ and Si were used, 147 the index of refraction of the shell was kept fixed at a value typical for ni-148 trides (n = 2) [56]. The basis of this modeling are fully described in previous 149 works [57, 58, 59, 60, 61, 62, 63, 51, 53, 54] and technical details are given 150 in Ref. [31]. Owing to the complexity of the quantitative description of the 151 plasmonic response and of the involved morphologies and the dielectric model 152 limitations, simulations were kept at a qualitative level to highlight the main 153 trends of energy shift and of change in intensity of the plasmon resonances 154 seen in SDRS as a function of morphology. They are not meant to be quan-155 titative in absolute values as no actual fit [60, 61, 62, 63] of SDRS spectra 156 was attempted. 157

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For *ex situ* measurements, Ag layers were capped with a 5 nm-thick Al-159 doped ZnO (AZO) film deposited by direct current from a ceramic target 160 (target $ZnO:2\%Al_2O_3$ in mass, power 50 W; distance 12 cm, 50 sscm and 161 2 μ bar of pure Ar) to protect them from ageing and oxidation by contact 162 with the atmosphere. While the AZO capping may damage the surface of 163 the Ag film, real-time resistivity of continuous Ag films, and therefore their 164 microstructure, do not change significantly upon capping. Thus, 20 nm-thick 165 Ag films were analysed $ex \, situ$ by Cu-K α XRD in Bragg-Brentano and graz-166 ing incidence geometries (Bruker D8 Advanced and Rigaku SmartLab devices 167 respectively); they were deposited on amorphous SiO_2 substrates (thickness 168 1 mm) to avoid any spurious diffraction signal from Si(100) wafer [64]. Also, 169 in order to more accurately determine the impact of $\%N_2$ on the particle 170 density before film percolation, AZO-capped 0.6 nm-thick Ag films were 171 deposited on 15 nm-thick silicon nitride membranes and imaged in plane 172 view by Cs-corrected scanning transmission electron microscopy (STEM Ti-173 tan Themis from Thermo Fischer Scientific) in high angle annular dark field 174 (HAADF) conditions. The oxidized surface of the membranes mimics that 175 of the Si wafer. A statistical analysis, based on a "Blob-log" treatment to 176 distinguish Ag nanoparticles from the Si wafer followed by a watershed al-177 gorithm to find the precise edges of each object, was applied to all images. 178 All ex situ analyses were performed with the minimum delay after deposition 179 while samples were systematically stored in vacuum. 180

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182 3. Results

¹⁸³ 3.1. Real-time film resistivity

The percolation threshold, *i.e.* the formation of a conductive path be-184 tween electrodes but before film continuity, appears as a drastic drop in film 185 sheet resistance R_{\Box} . Better determined as the maximum in a $\rho(t) \times t = R_{\Box} \times t^2$ 186 versus t plot [31], the corresponding equivalent thickness t_p decreases from 187 \sim 6 nm down to \sim 3 nm between 0%N_2 and 40%N_2 as shown in Fig. 1-188 a. t_p even reaches a minimal value of 2.7 nm at 30%N₂ (Fig. 1-b, left 189 scale). Although never directly determined, such an early percolation is 190 in agreement with previous observations both for N_2 [34, 35, 36, 37] and 191 O_2 [26, 27, 28, 29, 30, 31] gas addition to Ar. The decrease in t_p occurs in 192 parallel to an increase in the continuous film resistivity at t = 20 nm from 6.7 193 to 8.5 $\mu\Omega$.cm (Fig. 1-b, right scale). Nevertheless, this 27 % increase remains 194 much more modest than that observed for Ar/O_2 mixtures, where a change 195 by an order of magnitude was observed between 0% to $40\%O_2$ (using similar 196 deposition conditions) [31]. For those films, the strong worsening of the final 197 film resistivity was mainly assigned to a complex formation of silver oxides 198 and of unfavourable grain boundaries due to a change of film texture. 199

200 3.2. Photoemission analysis

To explain the above resistivity findings, the chemistry of films grown under Ar/N_2 was scrutinized using photemission. Fig. 2 shows the Ag 3d, N 1s, O 1s and C 1s core level regions [65] of 20 nm-thick Ag films. Unlike previous literature [35, 37, 36], the lack of capping layer gives direct access to the chemistry of the free surface and avoids potential desorption of species



Figure 1: (a) Evolution of film sheet resistance R_{\Box} during Ag deposition on SiO₂/Si substrates as a function of equivalent thickness for different %N₂ in the gas flow. Data are normalized to the initial value before opening the shutter in front the target. The drop in R_{\Box} 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 $\%N_2$ 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].

induced when depositing a protective layer. For all $\%N_2$, the Ag 3d spectra 206 (Fig. 2-a) perfectly overlap, with no change in peak position or line shape 207 that would otherwise indicate an evolution in the chemical state of the metal. 208 In parallel, no peak is visible in the N 1s core level range (Fig. 2-b), ruling out 209 the presence of N in the film within the sensitivity of photoemission (*i.e.* a 210 few % of a monolayer). These *in vacuo* observations do confirm the apparent 211 inertness of Ag towards N suspected in previous reports [35, 37, 36] for depo-212 sitions in similar conditions. It is worth noting that the plasmon multiple-loss 213 satellite of the Ag 3d core level peak at $E_B \simeq 398 - 400$ eV should not be 214 misinterpreted as the signature of residual traces of trapped N as done in 215 Ref. [35]. Nevertheless, x-ray or electron induced decomposition during pho-216 to to emission acquisition comparable to those observed for gold nitride [66] can 217 not be completely ruled out despite the much shorter time scale of the mea-218 surement (a few minutes). In parallel, no significant O 1s signal that could 219 be due to gas impurities during growth is visible (Fig. 2-c) and, only adven-220 titious carbon contamination of aliphatic nature at $E_B = 284.5 \text{ eV}$ (Fig. 2-d) 221 is present due to sample transfer ($\sim 20 \text{ min}$) despite high-vacuum conditions. 222 At the opposite, cracking/reaction with spurious C-containing molecules dur-223 ing deposition would give rise to a distinct binding energy [65] characteristic 224 of graphitic carbon ($E_B < 284 \text{ eV}$) or carbonates ($E_B = 287.6 - 288 \text{ eV}$). 225 According to photoemission quantification with a model of thin film, this 226 surface contamination amounts to a fraction of Ag(111) monolayer at the 227 surface (see Ref. [31] for details). 228

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

kinetic energies [67], the probing depth of photoemission does not allow to 231 explore the interface with the substrate in the studied 20 nm-thick films. 232 To explore the chemical impact of the N_2 -rich plasma on the wafer surface 233 itself before Ag film percolation, the substrate was exposed during 3 s to a 234 plasma ignited in front of an alumina target. As a reminder, such a duration 235 corresponds to an equivalent Ag deposited thickness of ~ 1.5 nm, well below 236 the percolation threshold. Fig. 3 summarizes the evolution before and after 237 plasma treatment with pure Ar $(0\%N_2)$ and $40\%N_2$. As seen by the shift of 238 Si 2p (Fig. 3-a) or O 1s (not shown) core levels, all gases induces an upward 239 band bending of about 0.4 eV. At the same time, the plasma reduces the 240 adventitious C 1s peak of the as-introduced substrate (Fig. 3-b); this "clean-241 ing" effect of the monolayer-thick [31] carbon contamination is more efficient 242 with N_2 than with Ar. Similarly, at 40% N_2 , a clear uptake of N is observed 243 in the N 1s core level region (Fig. 3-c); it parallels a broadening of the SiO_2 244 component of Si 2p on the low-binding energy side that is characteristic of 245 silicon nitride [65]. Quantification shows that such an uptake amount to 246 about one monolayer, *i.e.* an equivalent thickness of 0.2 nm. Regardless dif-247 ferent plasma excitations (radio-frequency for alumina versus direct current 248 for Ag), this nitridation of the wafer demonstrates that activated N species 249 are actually present in the plasma and that they strongly interact with the 250 substrate surface during the time scale of film growth. This finding explains 251 the observation in previous works of an N signal at the substrate interface 252 by secondary ion mass spectroscopy that escaped the sensitivity of depth-253 profiling ex situ photoemission [37, 36]. However, the exact nature of these 254 activated N-species (N atom, energetic $N^+/N_2^+,\ldots$) remains unknown. 255



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.

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257 3.3. Ex situ STEM-HAADF imaging

To get some direct insights on the influence of $\%N_2$ in the stage of dis-258 continuous nanoparticle films, STEM-HAADF imaging was performed on 259 AZO-capped 0.6 nm-thick Ag layers (Fig. 4). At such a thickness, all films 260 are at the limit between growth at saturation density and the beginning of 261 coalescence t_c that corresponds to the rise of the integrated SDRS signal 262 $\mathcal{I}_s(t)$ [53, 31] as shown in the next section. Indeed, STEM images show the 263 beginning of formation of elongated particles. At first sight, no clear-cut 264 change in morphology shows up with $\%N_2$ in the images of Fig. 4, in con-265 trast with previous reports devoted to the late coalescence regime [35, 37]. 266 Nevertheless, image analysis revealed an increase in particle density from 267 $4.4\,10^{12}$ to $5.7\,10^{12}$ cm⁻² (Fig. 5). The difference could lie in the difference of 268 substrate reactivity towards the active species in the plasma as demonstrated 269



Figure 4: STEM-HAADF imaging of 0.6 nm-thick Ag films deposited on oxidized silicon nitride membranes at increasing $\%N_2$. The scale bar corresponds to 5 nm.

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

275 3.4. Surface Differential Reflectivity Spectroscopy

In parallel to resistivity measurements, the growth process was followed using real-time SDRS to characterize Ag nanoparticles during the initial stages of film growth. Fig. 6 shows the integrated signal $\mathcal{I}_s(t)$ in s polarization (Eq. 1) for deposition under different Ar/N₂ mixtures. For all conditions, the value of $\mathcal{I}_s(t)$ is higher than under pure Ar. This quantity being a 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 N_2 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.

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

292

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

alent thicknesses: 0.6 nm, 1 nm, and 2 nm. According to Figs 1 and 6, 293 such values roughly match (i) the end of the isolated particles growth regime 294 (0.6 nm), and (ii) more advanced particle coalescence (1 nm and 2 nm). The 295 observed spectra are characteristic of the excitation of plasmon resonances in 296 nanoparticles with (i) a negative dip at high photon energy associated to the 297 dipole perpendicular to the surface and (ii) a positive feature at low energy 298 associated to the parallel one. The latter being more sensitive to any evolu-290 tion of morphology, in particular particle density, aspect ratio and formation 300 of a core-shell structure, the discussion will mainly focus on this feature. 301

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General trends about morphology effects on the shift and change in inten-303 sity of the plasmon resonances seen in SDRS were already predicted through 304 dielectric simulations of the optical response of truncated spheres (see Fig. 11 305 of Ref. [31] and references therein). The impact of a dielectric shell on a 306 metallic Ag core is also reminded in Fig. 8. To sum up Fig. 11 of Ref. [31], 307 at a constant amount of metal, the low energy plasmon peak red shifts and 308 its intensity increases upon particle flattening (*i.e.* increase of aspect ratio). 300 A similar impact, although less pronounced than upon flattening, is found 310 with a typical increase in particle density. The formation of a "core-shell" 311 morphology (consisting of a shell of dielectric nature and a metallic core) 312 strongly red-shifts the parallel resonance, whilst its intensity decreases if the 313 shell formation is at the expense of the metallic core (Fig. 8-a versus -b). The 314 effect is quite pronounced even for minute changes in shell thickness [31, 54] 315 (Fig. 8), in the range of a few percent of nanoparticle radius, a change that 316 would correspond to an atomic thickness for nano-sized particles. The shift 317

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

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For very thin Ag films (0.6 and 1 nm; Fig. 7-a,b), the addition of N_2 325 leads to a red-shift, an intensity increase and a broadening of the low-energy 326 resonance. Most of the change is nearly already set up at $4\%N_2$. According 327 to simulations [31], this energy shift is too large to be accounted for by the 328 change in particle density obtained from STEM pictures (Fig. 5) although 329 it may contribute to it. On the other hand, particle flattening can explain 330 the present plasmonic observation with $\%N_2$ and, in turn, the decrease in 331 film percolation threshold as flattened particles with a more pronounced 2D 332 growth would impinge on each other and form a conductive percolated net-333 work faster than more rounded 3D ones. The interpretation differs somewhat 334 at a thickness of 2 nm (Fig. 7-c). In this case, the addition of $4\%N_2$ red shifts 335 and enhances the low energy resonance while a further increase of $\%\mathrm{N}_2$ keeps 336 on shifting the peak but at the expense of its intensity and in a way nearly 337 independent of $\%N_2$ for values greater than $10\%N_2$. This overall plasmonic 338 scenario with $\%N_2$ matches with an increase in aspect ratio and the formation 339 of a core-shell structure, which relative impacts on the resonance intensity 340 are dictated by the N coverage. It also agrees with the decay on intensity of 341 the high energy resonance with $\%N_2$ (Fig. 7 vs Fig. 8) although its red-shift 342



Figure 7: SDRS spectra in p polarization for different N_2 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 SiO₂/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. $\frac{22}{22}$

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

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Fig. 9 shows the evolution of SDRS spectra over an hour time scale under 351 vacuum after gas evacuation ($p \sim 5.10^{-7}$ mbar). The cases of 1.6 nm-thick 352 Ag films deposited under pure Ar and $20 \ \%N_2$ conditions are compared. Note 353 that spectra were corrected from the drift of the light source using an ancil-354 lary spectrometer [51]. The noticeable evolution of the spectra highlights the 355 post-deposition film instability that is often overlooked. For the film grown 356 under pure Ar, both resonances get closer in energy with time while their in-357 tensities poorly evolve. These trends are characteristic of a slight dewetting 358 of nanoparticles, *i.e.* a decrease of A_r towards more rounded objects, al-359 though the slight intensity increase of the low energy resonance (Fig. 9-a and 360 c) does not match fully theoretical expectations (see Figure 11 of Ref. [31]). 361 Argon adsorption is obviously ruled out and an evolution of particle density 362 by Ostwald ripening is unlikely owing to the short time scale of most of the 363 change observed after deposition under pure Ar (a few mins; Fig. 9-a). In 364 contrast, the evolution markedly differs at $20\%N_2$; both resonances increase 365 in intensity and come closer in energy but with a slower evolution after the 366 end of the growth than for $0\%N_2$. According to qualitative dielectric simu-367

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

382 3.5. X-ray diffraction

Regarding film crystallography, XRD diffractograms (Fig. 10-a,b) only 383 show, for all of the studied $\%N_2$, peaks corresponding to metallic face-centred 384 cubic Ag, wurtzite ZnO from the capping layer, and a large feature around 385 $2\theta = 22^{\circ}$ assigned to the amorphous SiO₂ substrate. Despite the out-of-386 equilibrium conditions of sputtering deposition, no silver nitride formation 387 is observed in agreement with the lack of reported bulk structure [43, 37]. 388 First of all, as seen in the Bragg-Brentano radial scans along the out-of-389 plane direction (Fig. 10-a), the Ag films appears to be only [111]-[100] tex-390 tured along the growth direction. Starting from the classical favoured (111) 391 stacking under pure Ar characterized by an intense (111) peak and a weak 392



Figure 9: Post-deposition evolution under vacuum of p polarized SDRS spectra for 1.6 nmthick Ag films deposited under (a) $0\%N_2$ and (b) $20\%N_2$. 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).

(200) reflection, the texture evolves with $\%N_2$ towards more [100]-oriented 393 grains; this also reflects in the relative evolution of (220) and (200) peaks 394 in the grazing-incidence scans (Fig. 10-b). Owing to the inherent poor sen-395 sitivity of Bragg-Brentano geometry at high-angles for a thin film, the lack 396 of (220) reflection does not rule out the presence of [110] out-of-plane ori-397 ented crystallites, whose existence is supported by the (111) in-plane Bragg 398 peak. At last, regarding the crystallites corresponding with a (311) in-plane 399 Bragg peak (Fig. 10-b), it is impossible to assign their out-of-plane orien-400 tation with only the present set of measurement geometries. No in-plane 401 preferential texture is expected for an amorphous substrate, a fact that is 402 partially supported by the presence of all Ag allowed reflections in Fig. 10-b. 403 This evolution was rationalized by fitting peaks with Voigt profiles to ob-404 tain the corresponding Debye-Scherrer sizes from full-with at half-maximum 405 (Fig. 10-c) and an estimate of the crystallite volume fraction from peak ar-406 eas (Fig. 10-d) after correction from the relative intensities as found for a 407 powder [68] (*i.e.* from structure factors, reflection multiplicity, Lorentz-408 polarization factor and beam footprint). The out-of-plane Debye-Scherrer 409 size of [111] oriented-crystallites decreases at the expense of [100] ones; but 410 both are much smaller than the film thickness when N_2 is used thus show-411 ing a worsening of film crystallinity. Meanwhile corresponding in-plane sizes 412 of those domains (derived from the widths of (220) and (200) Bragg peaks 413 which normal to the corresponding diffracting planes are perpendicular to 414 [111] and [100] directions) do not significantly change with $\%N_2$ (Fig. 10-c). 415 In parallel to the size evolution, the film texture changes from a dominant 416 [111] out-of-plane orientation under pure Ar to a 40/60 % [111]/[100] mix 417

for $40\%N_2$ with a minor impact in-plane (Fig. 10-d). A parallel evolution is observed in-plane on the volume fraction corresponding to (220) and (200) peaks although less pronounced due to the presence of other reflections.

421 **4.** Discussion

The addition of N_2 , even in small quantities, in the Ar plasma provokes a spectacular decrease of percolation threshold (Fig. 1). Based on the previous results, on literature data and on the comparison with a similar work with O_2 [31], several aspects of this N_2 growth modifier effect can be discussed as follows.

427 4.1. N dynamic adsorption during growth

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



Figure 10: XRD diffractograms in (a) Bragg-Brentano and (b) grazing-incidence geometry of 20 nm-thick Ag films deposited under different $\%N_2$. 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].

surface of a pure 20 nm-thick Ag film exposed to a $40\%N_2$ plasma ignited on 442 a alumina target during 90 s (*i.e.* more than two times the growth duration) 443 while a slight alumina coverage of 0.07 nm is estimated by photoemission in 444 these conditions. This points at an intrinsic N instability that is not only 445 related to the film growth process itself. The lack of N 1s fingerprint at the 446 Ag film surface apparently contradicts the only surface science experiment of 447 Carter et al. [48] and the atomistic calculations [44, 45, 46, 47, 37] on interac-448 tion of atomic N with Ag(111) and Ag(100) orientations that all agree with 449 a favourable adsorption. Nevertheless, a quite low recombinative desorption 450 temperature of 350 K was found on Ag(111) [48] pointing at a poorly stable 451 adsorbate that could be present only dynamically at the surface of Ag in the 452 present experiments. This picture is supported by the large post-deposition 453 evolution of SDRS plasmonic signal (Fig. 9) indicating the disappearance of 454 a shell on top of a metallic core. In addition, the experiments of Carter et455 al. [48] on N/Ag(111) showed that the process of desorption is not of second 456 order and therefore not limited by the surface diffusion of adsorbed N but 457 rather by the concerted lifting of N-induced surface reconstruction and N₂ 458 molecule desorption. Thus, the dynamic N coverage expected during growth 459 is limited, of course by the amount of dissociation of N_2 in the plasma (*i.e.*) 460 $\%N_2$), but also by the surprisingly reported efficient desorption of N upon di-461 rect impact of another N atom [49, 50] (*i.e.* Eley-Rideal mechanism). At last, 462 the major difference in chemistry between the O_2/N_2 gases partly explains 463 the much higher value of the final film resistivity at 20 nm for O_2 (80 $\mu\Omega$.cm 464 at 40% O₂ [31]) than for N₂ (8.5 $\mu\Omega$.cm at 40% N₂; Fig. 1-b). Thus, other 465 structural factors, such as film crystallinity, should be put forward to ac-466

count for the worsening of film resistivity observed with N_2 as compared to pure Ar (Fig. 1-b).

469 4.2. The origins of better percolation

To rationalize the remarkable decrease of 51 % of the percolation thresh-470 old when adding N_2 (Fig. 1), the same reasoning developed for O_2 in Ref. [31] 471 can be performed. Changes in particle saturation density ρ_s and aspect ratio 472 A_r (diameter/height) or impeded coalescence can be put forward. Indeed, 473 denser or flatter initial particles as well as delayed coalescence upon im-474 pingement all give rise to an earlier percolation. Assuming a scaling $t_p \propto t_c$ 475 between the onset in thickness t_c for coalescence between nanoparticles and 476 the electrical percolation threshold t_p , one finds: 477

$$t_p \propto t_c \propto D_c^3 \rho_s / A_r \tag{2}$$

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

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

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

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

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

485

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

$$W_a = \gamma_m (1 + \cos \theta_c) \tag{5}$$

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:

$$\frac{\Delta A_r}{A_r} = -\frac{\sin\theta_c \Delta\theta_c}{1 - \cos\theta_c} \tag{6}$$

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

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

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

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

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

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

517 4.3. Anisotropic N adsorption and change in film texture

Beside the modification of surface Ag diffusion by a N adsorbate, a likely 518 explanation of delayed coalescence can be found in the competition between 519 the growth of [111] and [100] oriented islands, as testified by the change in 520 film texture although XRD gives information averaged over a comparatively 521 thicker film (Fig. 10-c). As grain boundaries between such crystallites lead 522 to a strong structural mismatch, this explains the worsening of the final film 523 resistivity with $\%N_2$ despite an earlier percolation (Fig. 1). Initially sug-524 gested by Kawamura *et al.* [42] to achieve films with the unusual [100] Ag 525 orientation on an amorphous glass substrate by sputtering deposition, this 526 surprising effect of N_2 on texture was also reported on SiO_2 upon increasing 527

(i) N_2 content in the gas flow in references [23, 35] or (ii) the film thickness 528 at constant $\%N_2$ in Ref. [37]; in Ref. [36], only a loss of out-of-plane [111] 529 texture was observed as the (200) peak is hardly visible. Assuming the dy-530 namical presence of adsorbed N at the surface of Ag, this change in texture 531 with $\%N_2$ matches with the calculated reversal of surface energies between 532 N-covered (111) and (100) Ag surfaces with N surface concentration [37]. The 533 anisotropy goes from a small value of a few % in favour of (111) (that agrees 534 with the experimental microscopy observation of the Wulff-Kaischew equilib-535 rium shape [72]) to around 50 % in favour of (100). Higher N_2 flow favours 536 an enhanced N_2 dissociation and therefore a larger dynamical coverage and 537 in turn a larger fraction of (100) facets as detected by XRD (Fig. 10-d). 538 Similarly, when N_2 is present, Yun *et al.* [37] observed a correlation between 539 this switch of texture and the onset of percolation. This might be explained 540 by a kinetic competition between (i) the metal-metal aggregation by diffu-541 sion that favours an initial (111) stacking for a face-centred cubic metal, (ii) 542 the substrate decarbonation and nitridation (see Section 3.2) and (iii) the 543 starting of N adsorption on Ag(111) surfaces as theoretically expected on 544 a energetic point of view at low N coverage [37]. Thus, for the Ag growth 545 on ZnO films textured along the c-axis, N₂ gives rise to a surprising selec-546 tivity towards [111]-oriented nanoparticles (before percolation) [37]. While 547 islands are larger in-plane due to N effect (see Section 3.4), the remarkable 548 Ag(111)/ZnO(0001) epitaxy [12, 75], its favourable interfacial energy and the 549 earlier percolation delay the growth of [100] orientation which is observed 550 only for thicker films compared to the growth on SiO_2 . But, during growth, 551 as the fraction of wafer surface covered by the metal and the availability of 552

N or of potential (100) facets for adsorption increase, the N-covered (100)553 facets overcome the (111) ones. The impingement of islands with different 554 orientations results into incomplete coalescence and earlier percolation but at 555 the expense of poor grain boundaries for electrical transport. This scenario 556 shows the interest in the strategy of N_2 gas deployment at the beginning of 557 the growth to benefit from earlier percolation while avoiding the transition 558 between orientations that is detrimental to resistivity [36]. This drawback 559 can be turned into an advantage to grow Ag films on amorphous substrate 560 with the unusual [100] orientation [42] or to achieve epitaxial and continuous 561 films at very small thickness on substrates showing a cube/cube epitaxy such 562 as MgO(001) [76]. 563

564 4.4. N_2 versus O_2 as "surfactants" of Ag growth

To conclude, N₂ appears to behave as a "surfactant" during sputtering 565 deposition of Ag. It is completely immiscible leading probably to an effi-566 cient mechanism of spillover or segregation to the surface, as already put 567 forward in the case of O at low $%O_2$ [28, 29, 32]. But there is no equivalent 568 threshold of incorporation in the bulk [31] (*i.e.* of formation of subnitrides), 569 a phenomenon that is detrimental for electrical transport in the case of O. 570 Finally, as for O [77, 78], N adsorption decreases the surface energy of the 571 metal thus favouring wetting. Nevertheless, the origin of N impact on the 572 percolation threshold seems to results from a interplay between a better wet-573 ting, a change in saturation density and a delayed coalescence in which the 574 orientation-dependent impact of N on energetics plays a decisive role. 575

576 5. Conclusion

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

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