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Characterization of two dimensional self-organized Au nanoparticles embedded in Si₃N₄

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Au/Si₃N₄ films have been prepared by gold and silicon nitride sequential sputtering with different Au thicknesses. The goal is to investigate the Au growth mode and to identify the regime where Au nanoparticles (NPs) can be prepared. The number of Au atoms, the bilayer thickness, the Au environment, the size, and the organization of the particles have been determined. Gold appears in metallic form. The thickest Au layer (8 nm) is continuous whereas the thinnest ones (with average values of 1–3 nm) are formed by nearly spherical Au NPs with diameters in the 5–7 nm range. Au NPs spatial self-organization is observed for average thickness of $t_{\text{Au}} = 2.9$ nm. These growth modes are discussed and compared with those observed for other metal/Si₃N₄ systems prepared in similar conditions. © 2010 American Institute of Physics. [doi:10.1063/1.3359705]

I. INTRODUCTION

Materials made of metallic nanoparticles (NPs) dispersed in dielectric matrices (nanocermets) exhibit specific properties particularly interesting for optical applications in the linear and nonlinear regime. In the case of noble metals, one can mention the existence of the surface plasmon resonance (SPR),¹ second,^{2,3} and third-order nonlinear susceptibility.^{4,5} These potentialities and the fundamental understanding still needed to interpret their properties, justify the efforts to build such nanocermets, efforts that must be associated with a precise characterization of their properties in terms of average size, size distribution, morphology, and organization in the matrix.⁶ In order to prepare samples with the optimized properties, growth mechanisms have to be understood.

Significant research has been done on Au NPs prepared by different techniques. Some of these techniques are based on chemical reduction processes.^{7,8} Others are based on physical vapor deposition. Magnetron sputtering has been used for example to prepare films to study nonlinear susceptibility^{9,10} and transport properties.¹¹ Electron beam evaporation¹² or cluster deposition¹³ allowed electron dynamics characterization. Ion beam techniques appeared to be successful in embedding metallic NPs in matrices.^{14–16} Au NPs are mostly embedded in oxide matrices such as SiO₂ and TiO₂.^{9,10,17} Thus, we have chosen to study Au NPs in another matrix, the transparent nitride Si₃N₄, and to use se-

quential sputtering, a tool that allows the experimentalists to vary parameters such as the total amount of deposited material, the layer thickness or the deposition rate. The refractive index of Si₃N₄, known to play a role on the SPR energy, is equal to 2 which is intermediate between the one of SiO₂ (1.5) and TiO₂ (2.7). We present here a structural study of samples fabricated by alternate Au and Si₃N₄ deposition. Several nondestructive techniques have been combined to get a fine description of the samples, such as x-ray absorption spectroscopy (XAS), grazing incidence small angle x-ray scattering (GISAXS), x-ray reflectometry (XRR), Rutherford Backscattering spectrometry (RBS), transmission electron microscopy (TEM), and atomic force microscopy (AFM).

In a recent paper, Garcia del Muro *et al.*¹⁸ showed that the NP growth is different for Au deposited on ZrO₂ as compared with Co and Ag. The final NP properties depend also strongly on the chemical environment of their surface atoms. Thus it is important to know whether Au NPs are surrounded by Si or N atoms. In order to answer this question, we compared the Au/Si₃N₄ system to others prepared with the same technique, i.e., Ni, Fe, Mn/Si₃N₄.^{19–21}

The goal of the present paper is to describe (i) the individual particles, i.e., their average size, size distribution, and morphology, (ii) the particle organization in the matrix, randomly distributed or self-organized, and (iii) the chemical NPs environment and finally to propose a growth process.

II. EXPERIMENTAL

Au/Si₃N₄ multilayered films were prepared by sequential sputtering of Si₃N₄ and Au on Si(100) substrates at room

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temperature. The sputtering system allows controlling automatically the movement of the sample-holder disk, the time it is placed on each sputtering (or presputtering) position, as well as the sputtering working gas. The residual pressure was near 1×10^{-7} mbar. Si_3N_4 layers were deposited by rf sputtering from a pure silicon target (99.99%) using N_2 as reactive sputtering gas. The deposition rate was about 2 nm/min for a rf power of 100 W. Au layers were grown from a gold target (99.999%) at 5.0×10^{-3} mbar pressure of pure Ar. The deposition rate was about 6 nm/min for a dc power of ~ 10 W. For all samples, multilayer structure fabrication began with a Si_3N_4 layer and a last additional layer (6 nm thick) was deposited on top. A series of five Au/ Si_3N_4 films, labeled as $[\text{Si}_3\text{N}_4(6 \text{ nm})/\text{Au}(t_{\text{Au}})]_n$, was prepared, keeping the Si_3N_4 layer nominal thickness constant in every sample (6 nm) and varying the Au thickness (t_{Au}) in the range of about 1–10 nm. The number of bilayers (n) was increased as t_{Au} values were reduced in order to maintain the Au total amount large enough to get reliable experimental data whatever the characterization technique.

To measure the period of the multilayers (i.e., the bilayer thickness Λ), low angle XRR measurements were carried out on a Bruker D8 x-ray diffractometer with a $\text{Cu K}\alpha$ source ($\lambda=0.154$ nm). Simulations of reflectivity data were done with the XREAL software developed in Ref. 22. In addition, AFM measurements were performed under ambient conditions using a commercial head from NanotecTM and commercial Nanosensors PPP-NCH-w tips with $k=42 \text{ Nm}^{-1}$ and $f_0=330$ kHz. Topographic characterization was performed in tapping mode and images and roughness analysis were studied with software from Nanotec.²³

RBS experiments were done²⁴ using a 1.2 MeV He^+ beam in order to get the number of Au atoms per layer (at./cm^2) and average Au/ Si_3N_4 composition. The experimental data were simulated by using the RBX code.²⁵

XAS experiments were carried out at the Au L_{III} -edge in total electron yield (TEY) detection mode at room temperature on the XAFS beamline at ELETTRA to characterize the atomic surrounding of the Au atoms. The double crystal monochromator was equipped with Si(111) detuned for harmonic rejection. Standard analysis of the XAS data was performed by means of the VIPER software.²⁶ XRD was performed with an x-ray imaging plate chamber using the $\text{Mo K}\alpha$ radiation ($\lambda=0.071$ nm) to get NPs average diameters when they exist. More precise information about the Au morphology and NPs dimensions was obtained by GISAXS measurements, carried out on the SWING beamline at SOLEIL synchrotron. The energy of the incident x-ray beam was set at 9.03 keV ($\lambda=0.137$ nm), the angle of incidence was slightly higher than the critical angle for total external reflection, θ_c , in order to achieve good surface sensitivity, and the sample-to-detector distance was varied between 1.305 and 2.425 m. The transmitted and specularly reflected beams were masked by a vertical beam stop and the scattered intensity was collected as a function of the in-plane ($2\theta_i$) and out-of-plane (α_f) exit angles with a two dimensional (2D) detector made of four charge-coupled devices cooled at -25°C , illuminated through a phosphor screen and a reducing optic fiber. The experimental data were analyzed with the

FIG. 1. XRR curves of $[\text{Si}_3\text{N}_4(6 \text{ nm})/\text{Au}(t_{\text{Au}})]_n$ multilayers (dots) and their simulations (solid lines). Curves have been vertically shifted for clearness.

home-made FITGISAXS package developed within the IGOR PRO analysis software (WaveMetrics, Inc.).

Electron microscopy studies were undertaken using a 200 kV JEOL2000FX TEM. Samples were prepared in plane-view using a GATAN656 dimpler grinder and a Fischione 1010 ion beam mill.

Before presenting the experimental results, it is necessary to compare the probed sample depths versus the different techniques. For RBS, the fact that the Si substrate is detected ensures that the whole stack is probed. When incident beams are x rays in the energy range of 10 keV, the incident path is a few microns. For GISAXS the recorded beam is still an x-ray beam, thus the information is also collected over a large path. The probed sample depth depends actually on the incident beam angle, θ_i , usually rather small for this technique. Typically the probed depth is 61 nm for $[\text{Si}_3\text{N}_4(6 \text{ nm})/\text{Au}(2.9 \text{ nm})]_{20}$ with $\theta_i=0.47^\circ$. The question arises also for XAS performed in TEY mode where emitted electrons are collected. From Girardeau *et al.*,²⁷ where the authors checked the electron escaping depth, one can expect depending on the Au concentration and the Si_3N_4 density that the sample thickness is totally probed in the thinnest samples and only partially in $[\text{Si}_3\text{N}_4(6 \text{ nm})/\text{Au}(2.1 \text{ nm})]_{40}$ and in $[\text{Si}_3\text{N}_4(6 \text{ nm})/\text{Au}(1.6 \text{ nm})]_{75}$. Thus for the thinner Au layer, we also prepared the $[\text{Si}_3\text{N}_4(6 \text{ nm})/\text{Au}(1.6 \text{ nm})/\text{Si}_3\text{N}_4(6 \text{ nm})]$ trilayer stack, in which a plane-view observation was carried out by TEM.

III. RESULTS

The XRR curves of the Au/ Si_3N_4 multilayer films are shown in Fig. 1. Satellite maxima corresponding to a heterostructure periodicity can be observed for all samples at $\theta = \theta_m$ ($m=1, 2, 3$, etc.) proving that they are actually formed by alternated Si_3N_4 and Au-rich regions with a vertical period Λ , given by $m\lambda=2\Lambda(\sin^2\theta_m-\sin^2\theta_c)^{1/2}$. Λ periodicities can be obtained from the slope of m versus $\sin\theta_m$ representation independently of the critical angle θ_c . The above expression, apart from the bilayer period (Λ), also accounts for the total thin film thickness (with $\Lambda'=n\Lambda+t_c$, considering an additional capping layer of thickness t_c and n being the number of repetitions).

TABLE I. Au time sputtering (s), critical angle (θ_c), bilayer thickness Λ (nm), and interface roughness (Interface R) as given by XRR, surface roughness (surface R) from the AFM images, and bilayer thickness from GISAXS.

Sample $[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(t)}]_n$	Au time sputtering (s)	θ_c (XRR) (deg)	Λ (XRR) (± 0.8) (nm)	Interface R (XRR) (± 0.2) (nm)	Surface R (AFM) (± 0.5) (nm)	Λ (GISAXS) (nm)
$[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(8.3 \text{ nm})}]_5$	88	0.8	12.9	1.0	...	14.0
$[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(4.7 \text{ nm})}]_{10}$	44	0.67	8.5	1.0	3.5	...
$[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(2.9 \text{ nm})}]_{20}$	22	0.48	10.1	1.1	2.5	9.8
$[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(2.1 \text{ nm})}]_{40}$	11	0.43	8.3	1.2	...	...
$[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(1.6 \text{ nm})}]_{75}$	7	0.42	6.4	1.5	3.0	7.7

In Fig. 1, only the $[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(8.3 \text{ nm})}]_5$ sample shows clearly both periodicities. Samples with large number of repetitions, as for instance more than 20 bilayers, provide a total thickness too large to exhibit the short oscillations corresponding to finite size film interferences. Simulations, also included in the figure, have been made in a simple way, using a short number of parameters in the calculated spectra to ensure a reliable determination of the bilayer thickness. The critical angle values (θ_c) and the obtained bilayer thicknesses Λ are gathered in Table I. The measured Λ are in agreement with the expected values within less than a 15% of deviation. The critical angle (θ_c) increases with the averaged Au concentration in the film, which gives an enhancement of the electronic density as well as of the refraction index at the x-ray frequencies. In this sense, the observed diminution of θ_c from 0.8° for samples with high Au layer thickness to about 0.4° for the $[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(1.6 \text{ nm})}]_{75}$ sample is in agreement with the reduction in the Au layer thickness obtained from the simulations to fit the bilayer periodicity. Furthermore, a first estimation of the roughness values can be also inferred. Interface roughness inferred from simulations, labeled in Table I as interface R, ranges from 1 nm, for the thinnest sample labeled as $[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(8.3 \text{ nm})}]_5$, to about 1.5 nm for the thickest one. Although these simple calculations do not completely reproduce the experimental data, the interface R values, which are average over the whole stack, can be understood as a lower limit to the actual value.

The surface roughness is given by AFM images of the samples named as $[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(4.7 \text{ nm})}]_{10}$, $[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(2.9 \text{ nm})}]_{20}$, and $[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(1.6 \text{ nm})}]_{75}$ (Fig. 2). The obtained surface rms roughness values (surface R in Table I) ranges between 2.5 and 3.5 nm, all of them being of the same order, indicating that the overall deposited thickness does not play a key role in the stack roughness. As expected, these values are larger than the interface R ones which are average ones. It is

FIG. 2. (Color online) AFM topographic images of samples (a) $[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(1.6 \text{ nm})}]_{75}$, (b) $[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(2.9 \text{ nm})}]_{20}$, and (c) $[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(4.7 \text{ nm})}]_{10}$.

important to comment also that both measured roughness correspond to different physical measurements. While AFM measures the surface roughness, surface R, at the length scale of the image dimension (of the one micron order), the XRR-obtained interface roughness, interface R, is related to the declination of the interfacial parallelism between layers evaluated at the x-ray coherence length scale (of the order of some tens nanometer).

Experimental data and simulations of the RBS spectra, done with the assumption of a Si/N ratio of 3/4, are shown in Fig. 3. The Au signal is well separated from the light atom ones, leading to a number of Au atoms/cm² per layer determined with an uncertainty of $\pm 1.5 \times 10^{15}$ at./cm², whereas the uncertainty on the number of Si and N atoms is rather $\pm 2 \times 10^{15}$ at./cm². The number of Au atoms/cm² per layer, the Au layer thickness calculated from the Au bulk density of 5.9×10^{22} at./cm³, and the film composition are given in Table II, where it appears that the Au relative concentration in the films ranges from 25% to 70%. The bilayer thickness, Λ (RBS), calculated as $\Lambda(\text{RBS}) = 6 \text{ nm} + \text{Au thickness}$ deduced from RBS, is in good agreement with Λ (XRR) presented in Table I. One notes that for samples with $t_{\text{Au}} = 2.1$ and 1.6 nm, the back edge slope of the Au signal indicates a

FIG. 3. RBS spectra corresponding to $[\text{Si}_3\text{N}_{4(6 \text{ nm})}/\text{Au}_{(t)}]_n$ multilayers. Simulation by using the RBX code is given for comparison (solid line).

TABLE II. Number of Au atoms per layer (10^{15} at./cm²), Au thickness per layer (nm), chemical composition, and Au relative atomic concentration as given by RBS. The bilayer thickness, Λ (RBS), is calculated as 6 nm+the Au thickness deduced from RBS.

Sample [Si ₃ N ₄ (6 nm)/Au(t) _n]	Number of Au atoms per layer (± 1.5) (10^{15} at./cm ²)	Au thickness per layer (± 0.3) (nm)	Atomic composition			[Au]/([Au]+[Si]+[N]) (%)	Λ (RBS) (nm)
			[Au]	[Si]	[N]		
[Si ₃ N ₄ (6 nm)/Au _(8.3 nm)] ₅	49	8.3	16	3	4	70	14.3
[Si ₃ N ₄ (6 nm)/Au _(4.7 nm)] ₁₀	27.5	4.7	8.9	3	4	56	10.7
[Si ₃ N ₄ (6 nm)/Au _(2.9 nm)] ₂₀	17.3	2.9	3.8	3	4	35	8.9
[Si ₃ N ₄ (6 nm)/Au _(2.1 nm)] ₄₀	12.6	2.1	3.0	3	4	30	8.1
[Si ₃ N ₄ (6 nm)/Au _(1.6 nm)] ₇₅	9.4	1.6	2.3	3	4	25	7.6

larger overall roughness than for samples with thicker Au layers in qualitative agreement with the interface R value decreasing from 1.5 to 1.0 nm when t_{Au} increases (Table I).

Au L_{III}-edge X-ray absorption near-edge structure (XANES) of several Au/Si₃N₄ multilayers and of a Au metal foil are displayed in Fig. 4. A direct comparison shows that Au is present in the metallic form. In order to obtain precise information on the local environment around Au, EXAFS oscillations were obtained after removing the atomic background by a cubic spline polynomial fitting, and the EXAFS signal ($\chi(k)$) was found by normalizing the magnitude of the oscillations to the edge jump. The pseudoradial distribution function around the absorber atoms has been calculated by Fourier transforming the k^2 -weighted EXAFS signal [$k^2 \cdot \chi(k)$] multiplied previously by a Hanning window. For all the samples, FTs were obtained over the same k^2 -weighted interval over a wave vector range from 2 to 14 Å⁻¹ (except for the thinnest Au layer where the range was 2–12 Å⁻¹), then fitted to the well-known EXAFS equation²⁸ by using amplitude and phase backscattering functions calculated by the FEFF6 code.^{29,30} The number of neighbors and distances is summarized in Table III. Simulations of the experimental data for four representative samples and a standard Au metal foil can be observed in Fig. 5. The Au–Au distances coincide with the Au metal reference, which justifies the use of Au bulk atomic density in the thickness calculations. Considering additional Au–N or Au–Si contributions in the simulations is not necessary since Au–Au simulations reproduce the experimental data. The

FIG. 4. XANES of several samples in comparison with the Au metal reference.

TABLE III. Au atomic surrounding as given by EXAFS. R, N, and σ^2 correspond to the atomic distance, number of neighbors, and the Debye–Waller factor.

Sample	EXAFS		
	R (Å)	N	σ^2 (10^{-3} Å ²)
Au foil	2.85 ± 0.01	12.0 ± 0.5	8.9 ± 0.5
[Si ₃ N ₄ (6 nm)/Au _(8.3 nm)] ₅	2.85 ± 0.01	10.5 ± 1.0	9.5 ± 1.0
[Si ₃ N ₄ (6 nm)/Au _(2.9 nm)] ₂₀	2.84 ± 0.01	10.4 ± 0.5	9.7 ± 0.5
[Si ₃ N ₄ (6 nm)/Au _(2.1 nm)] ₄₀	2.84 ± 0.01	10.2 ± 0.5	9.8 ± 0.5
[Si ₃ N ₄ (6 nm)/Au _(1.6 nm)] ₇₅	2.84 ± 0.01	10.6 ± 0.5	11.0 ± 0.5

FIG. 5. (a) k -space comparison between the experimental EXAFS signal (dots) and simulations (lines) for samples with $t=8.3$, 2.9, 2.1, and 1.6 nm and a Au foil. (b) Modulus and imaginary part of the Fourier transforms compared with the simulations (lines).

FIG. 6. (Color online) 2D GISAXS pattern of $[\text{Si}_3\text{N}_4(6 \text{ nm})/\text{Au}(t)]_n$ multilayers for (a) $t=8.3 \text{ nm}$, (c) $t=2.9 \text{ nm}$, (e) $t=1.6 \text{ nm}$, vertical cut for (b) $t=8.3 \text{ nm}$ or horizontal cuts for (d) $t=2.9 \text{ nm}$, (f) $t=1.6 \text{ nm}$. Dots are experimental data and lines are fits.

EXAFS results clearly indicate Au metal formation in all the sample series. However, it should be noted that the decrease in t_{Au} entails a slight increase in the amplitude loss factor S_0^2 . Moreover, it appears that for $t_{\text{Au}}=8.3 \text{ nm}$, the N value is strongly dependent on the σ^2 value. An uncertainty in the Au coordination number of the order of ± 1 is thus expected here whereas it is of ± 0.5 for the other samples.

The 2D GISAXS patterns of the multilayers with $t_{\text{Au}}=8.3$, 2.9, and 1.6 nm are shown in Fig. 6. For $t_{\text{Au}}=8.3 \text{ nm}$, only Bragg peaks characteristic of a rough multilayer³¹ can be seen in the vicinity of the vertical beam stop [Fig. 6(a)]. Thus the presence of isolated NPs is un-

likely. A vertical cut at $2\theta_i=0.32^\circ$ showing five Bragg peaks with a q -period of about 0.45 nm^{-1} [Fig. 6(b)] enables the period of the multilayer to be estimated as $\Lambda=14.0 \text{ nm}$, in agreement with the period of 13.2 nm determined by XRR. For $t_{\text{Au}}=2.9 \text{ nm}$, in addition to Bragg peaks indicating layering with a q -period of about 0.64 nm^{-1} corresponding to $\Lambda=9.8 \text{ nm}$ (also in agreement with the value determined by XRR), the pattern presents typical features of a distribution of isolated NPs with in-plane spatial correlation indicating that short-range order has taken place [Fig. 6(c)]. The quantitative analysis of the GISAXS intensity within the distorted wave Born approximation³² was performed on the basis of a

TABLE IV. Sample morphology from GISAXS. Au NPs average diameters (D , nm), diameter distribution (nm) and interparticle distance (nm). The values for C_{hs} and η_{hs} used in the calculations are also given. For comparison, the Au NPs average diameters (D , nm) from XRD. The Au NPs density calculated from the number of Au atoms obtained by RBS and D from GISAXS.

Sample	Au-NPs, D , XRD (nm)	Au-NPs, D , GISAXS (nm)	Distribution width (FWHM) GISAXS (nm)	Interparticle distance, GISAXS (nm)	C_{hs}	η_{hs}	Calculated Au-NPs density (NPs/cm ²)
[Si ₃ N ₄ (6 nm)/Au(8.3 nm)] ₅			Continuous layer				
[Si ₃ N ₄ (6 nm)/Au(2.9 nm)] ₂₀	7.5	6.9	3.2	8.7	1.23	0.23	1.7×10^{12}
[Si ₃ N ₄ (6 nm)/Au(1.6 nm)] ₇₅	6.7	5.1	2.1	11	1.99	0.05	2.3×10^{12}

horizontal cut at $\alpha_f = 0.19^\circ$ using the local monodisperse approximation³³ and assuming spherical NPs with no vertical correlation between NPs (i.e., each layer has a morphology which is completely independent from the adjacent layers).^{34,35} The structure factor of the assembly, which describes the interference effects between neighboring particles, was computed by the Percus–Yevick formula for interacting hard spheres. The diameter of the hard spheres, D_{hs} , was considered to be proportional to the diameter of the NPs, D , with a constant factor C_{hs} ($D_{hs} = C_{hs}D$), and the hard sphere volume fraction that characterizes the local arrangement of NPs relative to one another was η_{hs} .^{33,34} As seen in Fig. 6(d), the experimental data are well reproduced with a Gaussian size distribution of NPs with an average diameter $D = 6.9$ nm, a full width at half maximum (FWHM) of 3.2 nm, and an interparticle distance of 8.7 nm ($C_{hs} = 1.23$ and $\eta_{hs} = 0.23$). For $t_{Au} = 1.6$ nm, the pattern is typical of a distribution of isolated NPs with weak spatial correlation [Fig. 6(e)]. The horizontal cut at $\alpha_f = 0.29^\circ$ and fit taking into account spheres with a Gaussian size distribution leads to an average diameter $D = 5.1$ nm with a FWHM of 2.1 nm, and an interparticle distance of 11.0 nm [Fig. 6(f)]. In comparison with the sample with $t_{Au} = 2.9$ nm, the disappearance of the in-plane spatial correlation is confirmed by an increase in C_{hs} from 1.23 to 1.99 together with a decrease in η_{hs} from 0.23 to 0.05. A vertical cut at $2\theta_f = 0.32^\circ$ showing two Bragg peaks gives a q -period of about 0.82 nm^{-1} corresponding to $\Lambda = 7.7$ nm. The bilayer thicknesses measured with the GISAXS technique are satisfactorily compared with those obtained by XRR in Table I and RBS in Table II. Since GISAXS probes a thinner depth, this demonstrates that the bilayers remain similar in the growth direction whatever the sample overall thickness. Average NPs sizes given by GISAXS and average diameters determined from XRD measurements of the (111) Au reflection (not shown) by using the Scherrer formula are gathered in Table IV. It should be noted that both techniques do not measure the same magnitude since XRD gives the coherence length due to the Au(111) crystallographic planes along the perpendicular to the surface whereas GISAXS measures the average size. The agreement between these D values determined by both techniques is a fine indication that particles have a spherical shape. XRD also indicates that Si₃N₄ is amorphous. The areal density of NPs given in Table IV is equal to the total number of Au atoms/cm² measured by RBS divided by the number of atoms per NPs obtained from the volume calculated with the diameter, D , measured by GISAXS and the Au atomic density of $5.9 \times 10^{22} \text{ at./cm}^3$. The plane view image obtained

by TEM on the [Si₃N₄(6 nm)/Au(1.6 nm)/Si₃N₄(6 nm)] stack is shown in Fig. 7 where rather spherical NPs are seen generally isolated, but sometimes connected two by two, with average diameters of the order of 6 nm, in between values given in Table IV.

IV. DISCUSSION

Combining several characterizing techniques allowed us to describe the Au/Si₃N₄ stacks. Comparing data concerning different probed depths provides more precise information. For example, on one hand, the fact that the bilayer thickness is similar as measured by XRR which checks the overall thickness and by GISAXS which probes the upper part of the stack ensures the homogeneity on the growth direction of the sample. On the other hand, the fact that the NPs average diameter is similar for the thinnest Au layer in the trilayer as seen by TEM, in the last deposited bilayers as seen by GISAXS and on the overall sample as seen by XRD, demonstrates the homogeneity of the system.

Gold appears in a metallic form. No Au–Si bonds were detected although this silicide is likely to form in certain conditions.³⁶ The thicker Au layer, $t_{Au} = 8.3$ nm, is continuous whereas for $t_{Au} \leq 2.9$ nm, spherical Au NPs formation is observed. The NPs growth for metallic atoms deposited on an insulating surface is usually described by considering that the first deposited atoms diffuse on the surface and bind together acting as nuclei for cluster formation. The particles then grow by atomic aggregation up to a maximum size where percolation arises. For Au monolayers deposited at room temperature on TiO₂(110) in the range of thickness, t , from 0.22 to 12 nm,³⁷ three dimensional (3D) islands with diameter about 5 nm are observed for $0.22 \text{ nm} < t \leq 1 \text{ nm}$, then wormlike structures form until percolation is reached

FIG. 7. Plane view image obtained by TEM on the [Si₃N₄(6 nm)/Au(1.6 nm)/Si₃N₄(6 nm)] stack.

FIG. 8. (Color online) (a) Number of Au atoms/cm² per layer (RBS) and bilayer thickness values (averaged XRR- Λ and GISAXS- Λ) vs the sputtering time. Au NPs morphology for sample with (b) $t_{\text{Au}}=1.6$ nm and (c) $t_{\text{Au}}=2.9$ nm. Au/Si₃N₄ layered system is drawn in (d).

for $t=8.5$ nm. In our system, for $t_{\text{Au}}=1.6$ nm, the Au NPs diameter, D , is about 5 nm and the areal density of NPs is $2.3 \times 10^{12} \text{ cm}^{-2}$. Increasing the Au layer thickness up to $t_{\text{Au}}=2.9$ nm leads to slightly larger NPs with $D=7$ nm and to a decrease ($\sim 30\%$) in the areal density (see Table IV). To investigate more deeply the transition regime between NPs formation and continuous layer, we plotted in Fig. 8(a) the number of Au atoms/cm² per layer and the experimental bilayer thickness, Λ , versus the sputtering time given in Table I. Whereas the number of Au atoms/cm² per layer varies linearly with the sputtering time, two different slopes are observed for Λ , which indicates different growth modes, either continuous Au layers or NPs formation. Actually, one can show that the bilayer thickness, $t_{\text{Au}}+t_{\text{Si}_3\text{N}_4}$, versus t_{Au} grows faster in the second growth mode when NPs have constant diameter than in the continuous mode. The sample with $t_{\text{Au}}=4.7$ nm already belongs to the continuous regime-like sample with $t_{\text{Au}}=8.3$ nm and the transition is rather between 2.9 and 4.7 nm. Percolation thus occurs at a smaller thickness than observed in Ref. 37. The reasons are either the Au deposition mode which is different, and (or) the nature of the substrate and (or) a possible interlayer interaction present in our stacks. Indeed, a 6 nm thick gold monolayer deposited by electron-beam evaporation on Si₃N₄ is already in the percolation regime,³⁸ in agreement with the range determined here which underlines the role of the substrate.

Yu *et al.*³⁹ showed that for the same preparation tech-

nique under conditions similar to those used here, a Si₃N₄ film displays a surface roughness characterized by root mean square height variation, R_{RMS} , which depends on the sputtering time. For sputtering times in the range used here, R_{RMS} is no more than 0.2 nm, one order of magnitude smaller than the interface roughness or surface roughness measured here (see Table I). The interface roughness might thus be induced by the gold NPs. In addition, the largest roughness seen in the sample with the thinnest Au layer, $t_{\text{Au}}=1.6$ nm, corresponds to Au NPs randomly distributed in the Si₃N₄ matrix, whereas the sample with $t_{\text{Au}}=2.9$ nm, with a slightly decreased roughness, displays an in-plane correlation of the NPs, the in-plane interparticle distance being 8.7 nm as measured by GISAXS. For this sample, the NPs areal density of $1.7 \times 10^{12} \text{ at./cm}^2$ leads to an in-plane interparticle distance of 7.7 nm when one assumes a square arrangement, which differs by -13% only from the measured one. A possible explanation for the roughness decrease is to assume also a vertical correlation of the NPs where a row of Au NPs is shifted by half the interparticle distance from one layer to the other. Such a 3D NPs organization has already been observed for example in Ref. 40. Yet more observations are necessary to fully support this latter scheme. In Figs. 8(b)–8(d) we schematized the Au/Si₃N₄ stacks in different configurations. In Fig. 8(b), a drawing of sample with $t_{\text{Au}}=1.6$ nm is given with randomly distributed Au NPs. Figure 8(c) presents the sample for $t_{\text{Au}}=2.9$ nm with a possible layer interaction

leading to a better organization of the NPs and a roughness decrease. The scheme of the continuous Au layers is in Fig. 8(d).

NPs formation requires atomic diffusion and aggregation. To identify the main parameters playing a role on this initial stage, we can compare the behavior of the Fe/Si₃N₄, Mn/Si₃N₄, Ni/Si₃N₄, and Au/Si₃N₄ systems. They were prepared by the same sequential sputtering technique under the same experimental conditions. Indeed, in Ni/Si₃N₄,¹⁹ the role of the deposition velocity had been pointed out on the percolation threshold. The Fe/Si₃N₄, Mn/Si₃N₄, Ni/Si₃N₄, and Au/Si₃N₄ systems have been deposited with a rate in the range 2–2.5 nm/min. For the Mn/Si₃N₄ stack, a Mn₃N₂ compound is formed with no presence of Mn–Mn close neighbors.²¹ For Fe/Si₃N₄ (Ref. 20) and Ni/Si₃N₄,¹⁹ there is coexistence of metal–N and metal–metal bonds. To explain these different behaviors, one can look at the heat of formation, ΔH , of bulk metallic nitride. $\Delta H = -44$ kJ (mole of atoms)⁻¹ for Mn₅N₂, -31 kJ (mole of atoms)⁻¹ for Mn₄N, -16 kJ (mole of atoms)⁻¹ for Fe₄N, and $+0.2$ kJ (mole of atoms)⁻¹ for Ni₃N.^{41,42} Concerning Au/Si₃N₄, no heat of formation value for any gold nitride has been found in the literature. Yet, it has been shown that, for crystalline Si₃N₄,⁴³ the Au–Si₃N₄ interface is nonreactive, in agreement with our observation although the Si₃N₄ layer is amorphous here. The possibility to prepare Au₃N, demonstrated recently,⁴⁴ requires very specific conditions not met in the deposition process used here. Although we are dealing with first stages of layer deposition which could be seen as far from thermodynamical equilibrium process, the heat of formation for bulk nitride appears to be the key parameter in determining the initial chemical bounds. A question is why metallic nitrides are formed instead of silicides since these latter have sometimes more negative heat of formation than nitrides: ΔH for NiSi_x, whatever x, is about -25 kJ (mole of atoms)⁻¹ as compared to $+0.2$ kJ (mole of atoms)⁻¹ for Ni₃N.⁴² An answer could be given by considering that amorphous Si₃N₄ displays N dangling bonds and no Si dangling ones.

V. CONCLUSION

The deposition of Au layers sandwiched between Si₃N₄ using sequential sputtering of Si₃N₄ and Au has been studied. The deposition process with the stages of particle formation, percolation regime leading to continuous layer is observed as usual. For $t_{\text{Au}} \leq 2.9$ nm, Au NPs formed whereas for larger t_{Au} the Au layer is continuous. The percolation transition occurs for $2.9 \text{ nm} < t_{\text{Au}} \leq 4.7$ nm. By comparing to other Au deposited systems, we underline the role of the substrate and deposition parameters on the percolation transition.

The pure metallic Au NPs have spherical shape with average diameters in the range 5–7 nm, size distribution with a FWHM of 40%–45%, and high areal density of the order of $10^{12}/\text{cm}^2$. They are randomly distributed in the sample volume except for $t_{\text{Au}} = 2.9$ nm where an in-plane organized array is detected. The NPs volume density over the whole sample is controlled by the in-plane organization which depends on the metal wettability on Si₃N₄ and by the number

of layers which can be adjusted by the experimentalists. On the same substrate, Ni, Fe, and Mn have a different behavior which can be understood by considering the heat of formation of the metal nitride. This gives an indication that Si₃N₄ layers are terminated by N dangling bonds, so that Au NPs are surrounded by N atoms. Preparation of such well characterized samples with NPs of similar diameters and areal density but either randomly dispersed or spatially self-organized are interesting to study the consequences of order and disorder on the sample polarization, the Au SPR position and nonlinear susceptibility.

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