ESRF	**Experiment title:** GISAXS analysis of Si_3N_4-capped Ag islands	**Experiment number**: 02-01-813
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Names and affiliations of applicants (* indicates experimentalists):

Mr. Vivek Antad*, Dr David Babonneau*, Dr Sophie Camelio*, Dr Jean-Paul Simon*, Dr Lionel Simonot, Mr. Elliot Vandenhecke*

Report:

The goal of this proposal was to perform *ex situ* and post-mortem GISAXS measurements in order to interpret *a posteriori* optical measurements performed *in situ* during the preparation of nanocomposite thin films by magnetron sputtering. Si_3N_4:Ag:Si_3N_4 trilayers consisting of Ag nanoparticles sandwiched between Si_3N_4 layers were fabricated by alternate sputtering of Si_3N_4 and Ag at 200°C onto glass substrates. GISAXS was used complementary to local TEM observations to obtain statistical and non-destructive information on the morphology and the organization of the Ag nanoparticles, which were possibly subjected to thermal annealing, plasma annealing, or O_2 exposure before their capping by Si_3N_4. The results constitute a significant part of the PhD thesis of V. Antad, which will be defended in October 2011.

GISAXS experiments were performed on the D2AM beamline at 9800 eV with an incidence angle $\alpha_i \approx 0.25°$. The sample-to-detector distance was varied between 715 mm and 1960 mm in order to give access to different *q* ranges depending on the average size of the nanoparticles. As a typical example, Fig. 1 shows the effect of the deposited Ag amount *t* on the 2D GISAXS patterns of Si_3N_4(20 nm):Ag(*t* nm):Si_3N_4(40 nm) trilayers. The quantitative analysis of the data, which is performed in the framework of the distorted

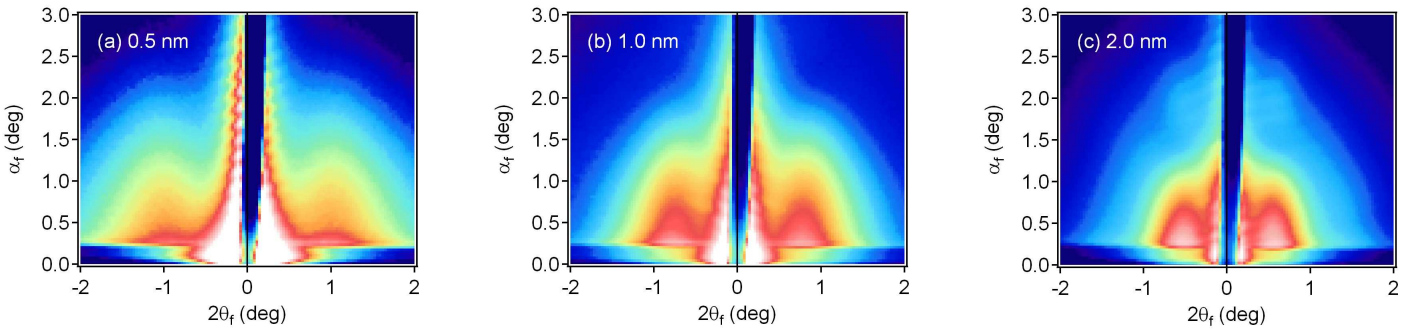

Figure 1: 2D GISAXS patterns of Si_3N_4(20 nm):Ag(t nm):Si_3N_4(40 nm) trilayers with different Ag amounts t.

wave-Born approximation assuming hemispheroidal nanoparticles, shows unambiguously that both the in-plane size D and the inter-particle distance Λ significantly increase with t as well as the height of the nanoparticles H, while their out-of-plane aspect ratio H/D decreases causing a red-shift of the surface plasmon resonance (SPR) as observed by *in situ* surface differential reflectance spectroscopy (SDRS).

Additionally, as seen in Fig. 2, the effect of different treatments on the morphology and the organization of the Ag nanoparticles was investigated in order to explain the corresponding optical variations detected by *in situ* SDRS. The main results are shortly described hereafter.

Thermal annealing

Thermal annealing (400°C) of the Ag nanoparticles before their capping induces a slight decrease of their in-plane size together with an increase of their out-of-plane aspect ratio and of the inter-particle distance (Fig. 2a). These effects are characteristic of a coalescence growth-type due to an increased Ag mobility at higher temperature, which lead to a prominent blue-shift and narrowing of the SPR.

Plasma annealing

Plasma annealing consisted in subjecting the Ag nanoparticles to a plasma of Ar^+ with the energy of the ionized species being varied between 25 eV and 50 eV (Fig. 2b). As observed in case of thermal annealing, plasma annealing results in an increase of the out-of-plane aspect ratio of the nanoparticles in agreement with a SPR blue-shift. However, in contrast to thermal annealing, it causes a more pronounced decrease of the in-plane size as well as a strong decrease of the interparticle distance. These results, associated to a damping of the SPR, suggest that sputtering/redeposition effects strongly contribute to the evolution of the nanoparticle assembly. Also, it is worth noting that *in situ* SDRS measurements show that both thermal and plasma annealing effects are irreversible, i.e. the morphology and organization of the nanoparticles does not evolve, even after decreasing the temperature to 200°C or after switching off the plasma.

O_2 exposure

Before their capping, the Ag nanoparticles were also subjected to a controlled O_2 atmosphere (10^{-4} mbar during 600 s). Surprisingly, *in situ* SDRS measurements show that although the optical response of the Ag nanoparticles is strongly modified during their exposure, the differences observed between non-exposed/exposed samples disappear during the very first stage of Si_3N_4 capping. These results are confirmed by our post-mortem GISAXS measurements, which show no obvious difference between non-exposed/exposed samples thus suggesting almost complete O_2 desorption during the deposition of the Si_3N_4 capping-layer above the Ag nanoparticles.

In conclusion, the GISAXS measurements of about 30 samples give valuable information to explain the temporal modifications observed in the *in situ* optical measurements as morphological and/or chemical changes, and to highlight the influence of the different deposition parameters on the final optical properties of the nanocomposite thin films.

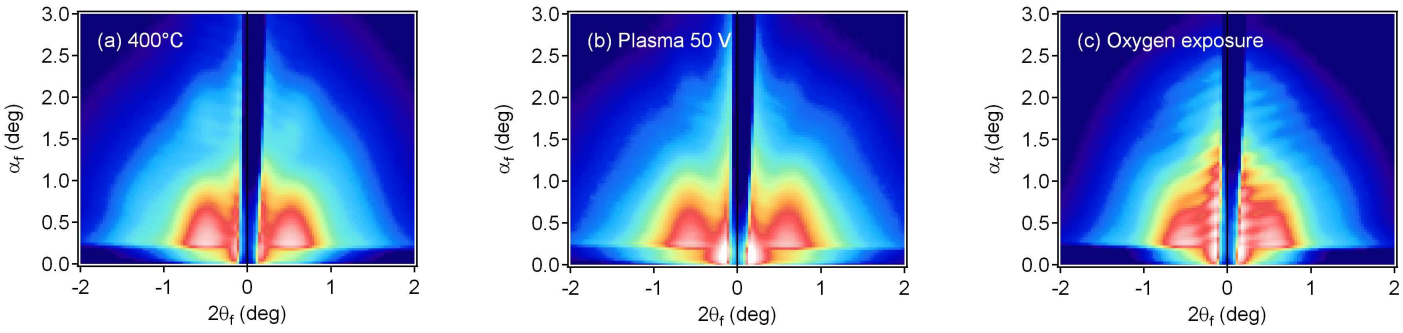

Figure 2: 2D GISAXS patterns of Si_3N_4(20 nm):Ag(2 nm):Si_3N_4(40 nm) trilayers. Before their capping by Si_3N_4, the Ag nanoparticles were subjected to (a) thermal annealing at 400°C, (b) plasma annealing at 50 V, and (c) exposure to O_2.