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To cite this article: M Magnozzi *et al* 2019 *J. Phys.: Conf. Ser.* **1226** 012014

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Monitoring the solid-state dewetting of densely packed arrays of Au nanoparticles

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Abstract. We report a real time, *in-situ* spectroscopic ellipsometry study of the temperature-induced solid-state dewetting of Au nanowires into nanoparticles. Very large spectral variations are observed at different temperatures. Analysis of the key features in the acquired spectra reveals two different regimes: up to 300 °C the variation in the optical response is dominated by solid-state dewetting, while above that temperature, smaller variations not compatible with such mechanism are visible. Therefore our ellipsometry measurements allow us to determine in real time at which temperature the solid-state dewetting ceases and the morphology of our sample becomes stable. We point out that this observation is possible thanks to the higher sensitivity of ellipsometry with respect to reflectance/transmittance measurements.

1. Introduction

The drive toward the applications of metal nanostructures and nanoparticles calls for the availability of large-scale samples with uniform coverage and properties, that imply a high degree of spatial order. Among the bottom-up approaches commonly used to fabricate ordered nanostructures, the mechanisms which induce a self-organization of nanoparticles are subjected to a great deal of interest [1–5]. Self-organization means that nano-objects self-arrange in ordered structures (*e.g.* lattices, grids); for this reason, the fabrication process of self-assembled systems aims to control the driving forces causing the self-assembly, rather than the arrangement of single nano-objects [6].

Under proper conditions, solid-state dewetting can be exploited to induce the self-organization of nanoparticles. Solid-state dewetting causes agglomeration in thin films and nanostructures, at temperatures that are well below the melting temperature of bulk materials [7,8]. By exploiting nanopatterned substrates, it is possible to create ordered arrays of nanoparticles with tunable size and spacing [9]. Arrays of nanoparticles created by solid-state dewetting on our LiF nanopatterned substrates are characterized by high nanoparticles density ($\sim 10^{11}$ NPs/cm²) and few-nm interparticle distance [10]. This kind of system has been used to investigate the Localized Surface Plasmon Resonance (LSPR) of noble metals and aluminum under diverse experimental conditions [11–14]. So far, in our research we focused on the outcome of the samples fabrication process (that is, the arrays of nanoparticles); however, useful information can be obtained by monitoring *in-situ* and in real time the evolution of the optical (plasmonic) response of our samples during their fabrication. By performing spectroscopic ellipsometry (SE) measurements during the temperature-induced solid-state dewetting in high vacuum, we noticed



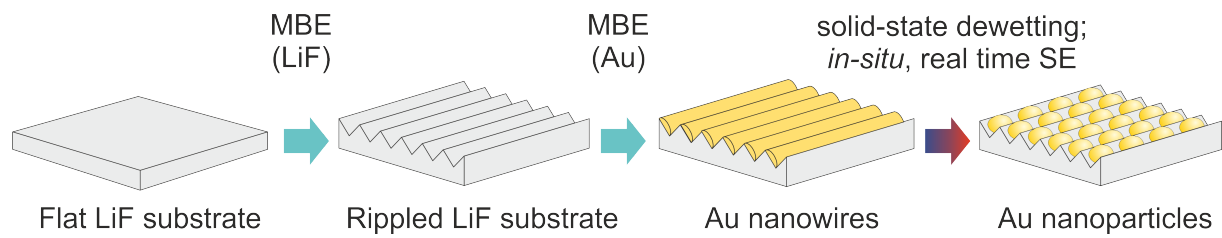


Figure 1: Sample preparation. From left to right: a crystal of LiF is rippled by depositing LiF *via* MBE; glancing angle MBE of Au creates disconnected Au nanowires; solid-state dewetting induces a transformation from nanowires to nanoparticles. This last process is monitored *in-situ* and in real time *via* spectroscopic ellipsometry.

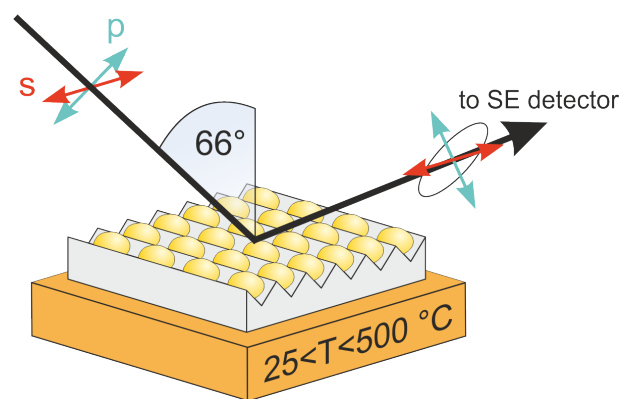


Figure 2: Sample orientation during the real time, *in-situ* SE measurements. Au NPs chains are parallel to the plane of incidence; angle of incidence is 66° . The sample is placed inside a high-vacuum chamber, and its temperature can be varied from 25 to 500 $^\circ\text{C}$.

a huge variation in the key features of the samples' spectra; in particular, a large blueshift, and a progressive narrowing and deepening of the features linked to the LSPR were observed. Interestingly, this trend is monotonous only up to $\sim 300^\circ\text{C}$; for higher temperatures, a small blueshift is still present, but the trend in the other two features is reversed. Therefore we identify two regimes: for lower temperatures, solid-state dewetting drives the variations in the optical response, while for higher temperatures, morphology remains largely stable and other effects become dominant.

2. Results and discussion

By following a well-established procedure, we fabricated a ($1 \times 1 \text{ cm}^2$) nanorippled LiF substrate (see Fig. 1) by depositing LiF *via* Molecular Beam Epitaxy (MBE) on a LiF (110) substrate in a dedicated high-vacuum chamber ("deposition chamber", base pressure $\sim 10^{-9}$ mbar) [11]; then in the same chamber, we deposited Au at glancing incidence to create Au nanowires as represented in Fig. 1. The sample was then extracted from the deposition chamber and immediately put inside a second high-vacuum chamber ("measurement chamber") to perform the real time, *in-situ* SE measurements. The measurement chamber has a base pressure of 10^{-7} mbar and allows the sample to be heated from room temperature to 500 $^\circ\text{C}$; more details about the measurement chamber can be found in Ref. [15]. The ellipsometer (J.A. Woollam Co., M-2000) has a spectral range between 245 and 1450 nm; the acquisition of a full spectrum requires just a couple of seconds. The sample was heated with a temperature ramp (heating

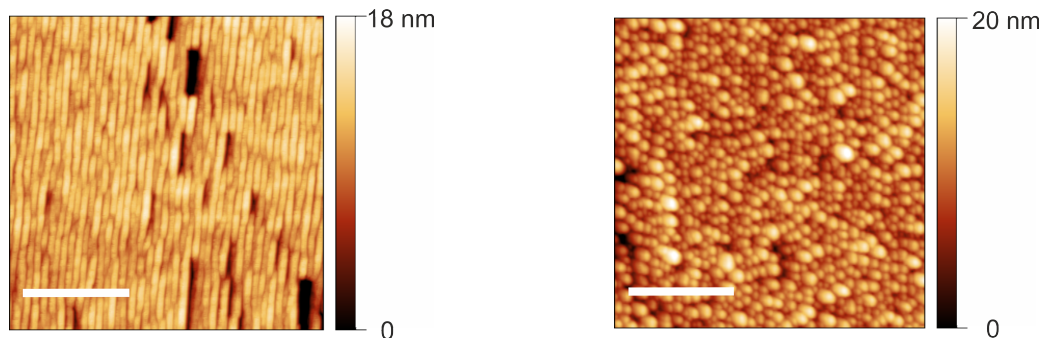


Figure 3: Left: representative AFM image of rippled LiF substrate. Right: Au nanoparticles as obtained after the solid-state dewetting of Au nanowires. White scale bar for both images is 400-nm long.

rate: 5 °C/min) and SE spectra were acquired from room temperature to 362 °C, at 12.5 °C interval. All SE measurements were performed at $\theta=66^\circ$, with the plane of incidence parallel to the direction of the ripples (see Fig. 2).

The morphology of our samples was investigated through Atomic Force Microscopy (AFM). AFM images were acquired in tapping mode using a Digital Instruments Dimension 3100 Atomic Force Microscope; image analysis was performed using the free software Gwyddion. Representative AFM images of our sample are shown in Fig. 3. On the left image is the rippled LiF surface; ripples periodicity is approximately 30 nm. The right image shows the sample surface after Au deposition and thermal annealing. Here we see nanoparticles aligned along the direction of the LiF ripples; mean interparticle distance is 33 ± 2 nm along the ripples and 37 ± 4 nm across them. As for the particles, their mean radius is 13 ± 1 nm along the ripples and 11 ± 1 nm across them. While AFM images are necessary to evaluate morphology, they are obtained only *before* or *after* the fabrication; this means that the intermediate variations induced on the sample by the thermal annealing are not accessible. In this regard real time, *in-situ* SE can provide a unique and valuable contribution.

The output of SE measurements is constituted by two angles called Ψ and Δ . In this work, we follow the definition

$$\rho = \tan \Psi \exp(i\Delta), \quad (1)$$

where $\rho = r_p/r_s$ and $r_{p,s}$ are the complex Fresnel reflection coefficients [16]. Thus $\Psi = \arctan(|r_p|/|r_s|)$ and $\Delta = \delta_p - \delta_s$, where $\delta_{p,s}$ are the phases of the p, s components of the reflected beam.

Real time, *in-situ* SE measurements are reported in Fig. 4 (panels A and B). Both Ψ and Δ spectra show macroscopic variations as the temperature rises. The most relevant feature in the Ψ spectrum at room temperature is the broad dip centered around 1000 nm, which is linked to the LSPR of the system [10]; for increasing temperatures, this dip steadily shifts towards shorter wavelengths and becomes deeper and narrower, meaning that the intensity of the LSPR increases. However, from 300 to 362 °C, this trend is reversed as the dip becomes significantly shallower and slightly broader (see Fig. 4A, inset). As far as Δ is concerned, at room temperature we observe a progressive rise in the Δ values when going from the visible to the IR; this becomes much sharper as temperature increases, until a phase inversion (i.e., Δ going to negative values) is observed.

An optical model is usually required to fully access the information contained in the Ψ and Δ spectra [16]. Modelling the system under investigation is a complex task that we discuss in detail elsewhere [17]; in this work, however, we present and discuss the useful information that can be extracted from our SE measurements without resorting to a model. Ψ and Δ spectra

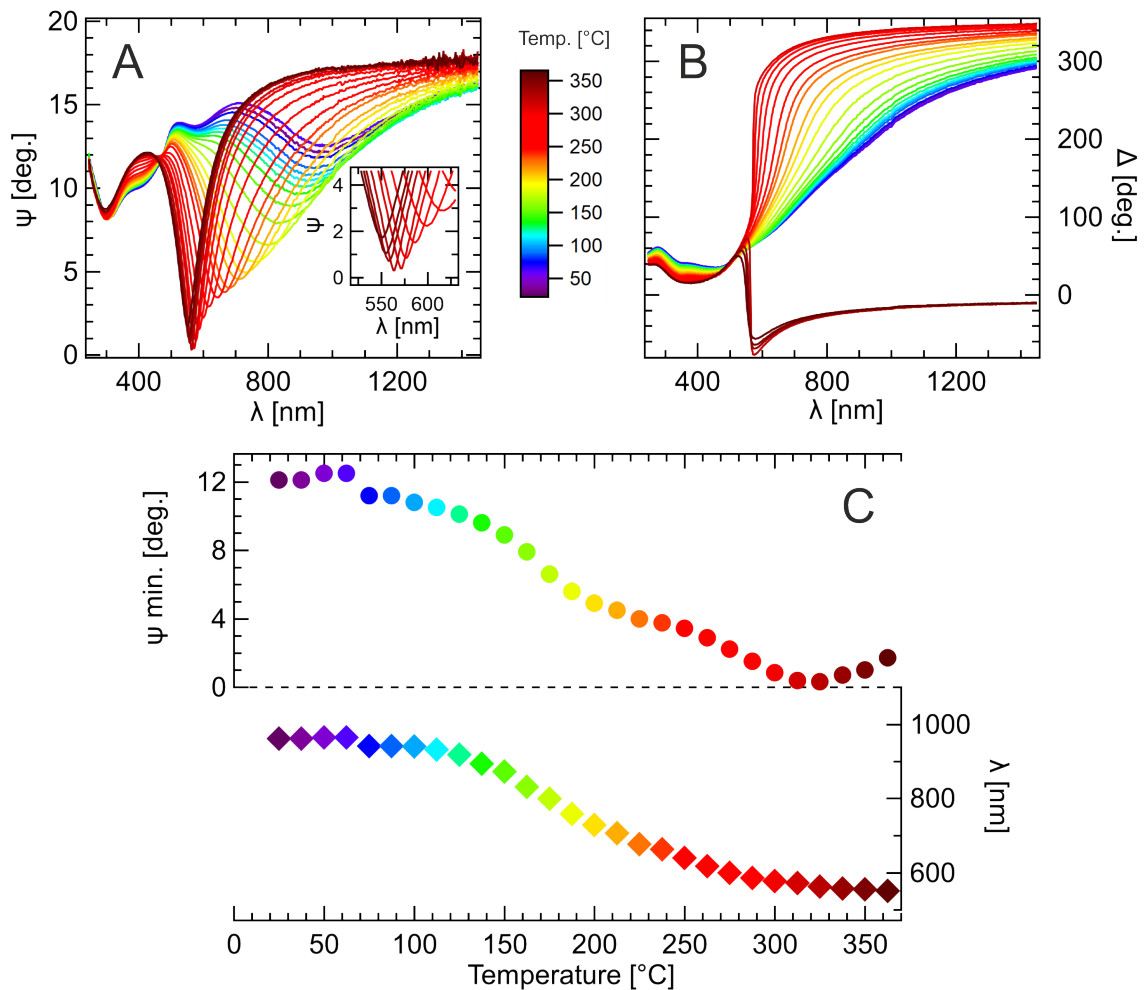


Figure 4: Panels A and B: Ψ and Δ spectra acquired *in-situ* and in real time during the dewetting of Au nanowires into nanoparticles. The color indicates the temperature, as shown in the color bar between the panels. Panel C: Left axis: intensity of the Ψ dip. Right axis: Spectral position of the Ψ dip.

are related to the complex Fresnel coefficients via Equation (1), therefore features linked to the LSPR can be seen in both spectra; however the dip in Ψ spectra offers a more intuitive way of understanding the morphological and physical changes induced in the sample by the thermal annealing. For this reason, in the following discussion we are going to focus on the Ψ dip.

In Fig. 4C we plot the spectral position and intensity of the Ψ dip. This plot reveals quantitatively the progressive blueshift of the LSPR, going from 960 nm at room temperature to 550 nm at 362 °C. Such a large spectral shift (410 nm) and all the other changes visible in Ψ and Δ spectra testify the major morphological change sustained by the system when Au nanowires dewet into densely-packed nanoparticles. We note that the blueshift is continuous as the temperature rises, and the largest variations occur approximately between 125 and 275 °C. However, the intensity of the Ψ dip does not follow a unique trend. We notice a very small rise at low temperatures, which is possibly due to desorption of ambient contaminants; then a continuous decrease from 11 degrees at 75 °C to almost 0 degrees at 300 °C; finally, from 300

to 362 °C, the trend is reversed as the minimum rises again. At the temperature where the dip in Ψ reaches its absolute minimum, Δ shows a sharp transition to negative values, assuming a wiggled shape.

A blueshift of the LSPR is observed in the longitudinal mode when plasmonic nanostructures reduce their aspect ratio [18]. In our case, the reduction in the aspect ratio occurs as a result of the solid-state dewetting of nanowires (high aspect ratio) into nanoparticles (low aspect ratio), as represented in Fig. 1 and 3. So we identify solid-state dewetting as the main cause of the large blueshift in the LSPR. However, solid-state dewetting cannot account for broadening and reduction of the Ψ dip (that is, a damping of the LSPR) at the highest temperatures; therefore, we have to invoke another mechanism that can explain such an inversion in the trend shown in Fig. 4. Surface melting, which is known to appear at temperatures much lower than the bulk melting [19, 20], increases the scattering rate of the free electrons, effectively damping the LSPR. The damping of the LSPR is opposite to the effect of solid-state dewetting; this means that at the temperatures where the damping is observed, the solid-state dewetting is no longer the main force driving the changes observed in the SE spectra. Solid-state dewetting may still be active from 300 to 362 °C, since there is a relatively small yet sizable (20 nm) blueshift of the dip in Ψ in that temperature range; however, subsequent heating/cooling cycles on the same sample showed that any further change in the SE spectra acquired at different temperatures is fully reversible, meaning that the morphology of our sample has found a stable configuration already at the end of the first thermal annealing.

3. Conclusions

We studied *via* real time, *in-situ* Spectroscopic Ellipsometry the evolution in the optical response of the sample during a thermal annealing, which induced a solid-state dewetting causing nanowires to transform into nanoparticles. By analyzing the spectral position, intensity and width of the Ψ dip related to the LSPR, we noticed two different trends in the evolution of the optical response of the sample. We identified solid-state dewetting as the main driver of change below 300 °C, while for higher temperatures, an opposite trend (damping of the LSPR) was observed in the SE spectra. In conclusion, from the analysis of the SE spectra we can determine the temperature at which the solid-state dewetting of Au is largely completed and our system becomes morphologically stable. In this way we can control in real time the fabrication of densely-packed Au NPs arrays. Lastly, we note that the observation of a clear difference between the two regimes discussed before is possible thanks to the fact that the LSPR feature in the SE spectra is very sharp and almost noise-free. Indeed, such an observation would have been virtually impossible in standard reflectance/transmittance measurements, because in that case the LSPR peak is much broader and noisy (see Ref. [10]).

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