

Nanofabrication technology for single-crystalline metal nanoparticle ensembles using nanotemplate-guided thermal dewetting

Kyohei Okubo^{*1,2}, Yusuke Niimura², Naoto Oonishi², Loan Le Thi Ngoc³, Edwin T. Carlen^{2,4}

¹ Tokyo University of Science, ² University of Tsukuba, ³ Quy Nhon University, ⁴ Aichmis Technologies

*E-mail: kyohei.okubo@rs.tus.ac.jp

1. Introduction

Metal nanoparticle (NP) research has made significant progress over the past few decades, and now a wide range of materials with well-controlled size and dispersity are available [1]. However, far less progress has been achieved in realizing techniques for controlling the spatial position of NPs in ensembles with predefined arrangements. This is especially important for nanoplasmonics applications, where the optical response of metal NP ensembles is governed by the spatial arrangement of NPs [2,3].

Here, we report a hybrid nanofabrication technology for realizing single-crystalline (SC) metal NP ensembles, such as trimers, heptamers, and periodic arrays. Top-down engineered nanotemplates results in the deterministic formation of isolated polycrystalline (PC) gold islands with precise volume and position, which are transformed into SC NPs using bottom-up self-assembly based on nanotemplate-guided thermal dewetting.

2. Experimental

Thermal dewetting of metals is a simple bottom-up method to produce SC NPs from a PC-metal thin film [4], which is especially attractive for combining with top-down methods [5]. Figure 1 shows a schematic of the hybrid nanofabrication technology. Electron-beam lithography and reactive-ion etching are used to form the silicon nitride (SiN) nanotemplates and anisotropic wet etching is used to create the isolation trenches, as shown in Fig. 1 (a, i). The isolated PC-Au islands are transformed into SC-Au NPs by the dewetting process, shown in Fig. 1 (a, ii and iii). Complex patterns, such as dimers, trimers and heptamers, shown in Fig. 1 (b), can be realized. Figure 2 shows scanning electron microscope (SEM) images of SC-Au NP ensembles.

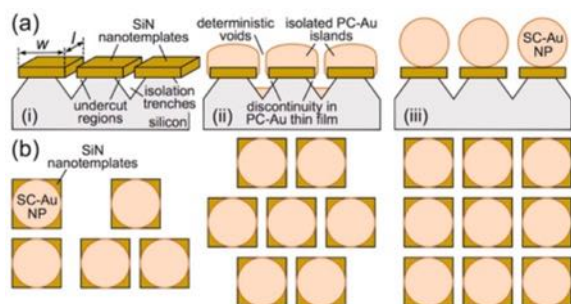


Fig. 1 Nanofabrication of SC-Au NP ensembles. (a) Process flow: (i) SiN nanotemplates, (ii) Deposition of isolated PC-Au islands, (iii) Transformation of PC-Au islands into SC-Au NPs by thermal dewetting. (b) Examples of SC-Au NP ensembles.

Figure 2 (a) and (b) show a heptamer nanotemplate and its array, respectively, prior to PC-Au deposition and thermal dewetting. Figs. 2 (c-f) show four SC-Au NP ensembles following sputter deposition of 30 nm-thick isolated PC-Au islands and thermal dewetting. These images demonstrate that the capability of the hybrid nanofabrication technology for realizing SC-Au NP ensembles with high precision.

From Fig. 2, it is clear that the residual PC-Au deposited in the v-shaped isolation trenches between adjacent SC-NPs is no longer present. We discovered that the PC-Au in the trenches *flow* to regions of greater depth during thermal annealing, which will be discussed in detail at the presentation.

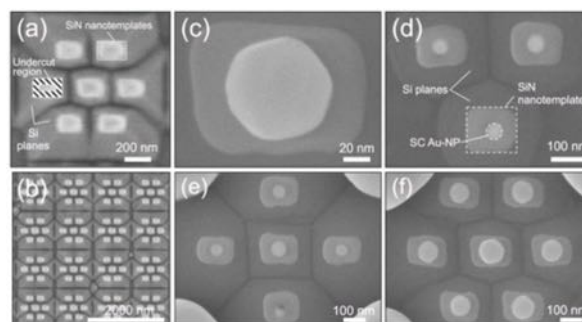


Fig. 2 SEM images of fabricated SC-Au NP ensembles. (a) Heptamer nanotemplate. (b) Array of heptamer nanotemplates. (c) NP monomer formed on $100 \times 140 \text{ nm}^2$ template. (d) NP trimer, (e) NP pentamer, and (f) NP heptamer formed on $140 \times 170 \text{ nm}^2$ template, respectively.

3. Conclusions

We will present a low-cost hybrid nanofabrication technology for realizing SC-Au NP ensembles that is based on techniques from top-down nanolithography and bottom-up nanotemplate-guided thermal dewetting of thin films. This approach facilitates the realization of high-precision SC NP ensembles without directly etching or milling the polycrystalline gold thin film. Many different NP ensemble patterns can be realized and we demonstrate the flexibility of the technology with gold nanoparticle dimers, trimers, pentamers, and heptamers, as well as periodic arrays.

References

- [1] Y. Sun and Y. Xia, *Science* **298** (2002) 2176.
- [2] M. Hentschel, et al., *ACS Nano*, **5** (2011) 2042.
- [3] P. Genevet, et al., *Optica*, **4** (2017) 139.
- [4] C. V. Thompson, *Annu. Rev. Mater. Res.*, **42** (2012) 339.
- [5] L-X. Lu, et al., *Sci. Rep.* **21** (2016) 32398.