Generation of Ag–Ag₂O complex nanostructures by excimer laser ablation of Ag in water†‡

Zijie Yan,* Ruqiang Bao and Douglas B. Chrisey*

Pulsed laser ablation in liquid (PLAL) has been well established as a facile method to produce nanoparticles from bulk materials, but it is still insufficient for fabricating anisotropic and complex nanostructures, especially without the use of surfactants. Here, we demonstrate that silver (Ag) nanosheets can be produced by pulsed excimer laser ablation of bulk Ag in water via laser re-processing of the laser-produced primary clusters. We also show that by combining PLAL and drop evaporation, rice-shaped Ag–Ag₂O particles and their assemblies can be generated on Si substrates, because the interior flow of an evaporating colloidal drop could redistribute the laser-produced primary clusters, which results in the formation of complex nanostructures. These results show that PLAL is able to fabricate novel micro-/nanostructures while keeping its merit of “clean” fabrication.

1. Introduction

Pulsed laser ablation in liquid (PLAL) is a facile method to produce clean nanoparticles and colloidal solutions from bulk materials.1–3 By using a liquid without surfactants or precursors, such as water, the colloids can be made free of organic or ionic species.4 This merit is the cornerstone of this method founded about two decades ago,5 because surface cleanliness is important for some properties of colloids, such as surface-enhanced Raman scattering6 and antibacterial ability.7 On the other hand, using a “clean” liquid also decreases the probability of generating complex nanostructures, because the formation of anisotropic nanoparticles generally needs capping agents to control the growth of certain facets.8 As a result, the products from laser ablation of noble metals in water are usually spherical nanoparticles.9 However, PLAL provides another approach to fabricate anisotropic nanostructures, that is, via laser re-processing of the laser-produced primary clusters, such as laser welding/sintering of nanoparticles. Gold, silver (Ag) and platinum nano-chains or networks have been fabricated by PLAL via laser welding of the primary clusters (nanospheres),9–12 but generation of other metal nanostructures, especially nanostructures with well-defined growth behaviors, was seldom reported.

In this paper, we show that pulsed excimer laser ablation of bulk Ag in water can generate Ag nanosheets with large {111} facets, revealing that the laser re-processing could mediate the coalescence and growth of laser-produced clusters. We further show that a mixture of anisotropic Ag–Ag₂O nanostructures, including rice-shaped particles and flower-like assemblies of these particles, can be generated by crystallization of the laser-produced clusters via drop evaporation of the colloidal solution on Si substrates.

2. Experimental section

In a typical experiment, a silver metal target (99.99%) was placed on the bottom of a rotating glass beaker filled with 13 mL of distilled water. The laser beam of a KrF excimer laser (wavelength 248 nm, pulse width 30 ns, frequency 10 Hz) was focused onto the target surface with a fluence of ~8 J cm⁻² and an ablation time of 60 min. The concentration of Ag species in the resulting colloidal solution was ~0.06 mol L⁻¹ by weighting the mass loss of the Ag target after the laser ablation. The colloidal solution was dripped on a copper grid coated with holey carbon film to filter out the particles from the solution. The colloidal solution was also dripped onto n-type (phosphorus-doping) and p-type (boron-doping) (100) Si substrates. The volume of each drop was 3 μL with a diameter of ~4 mm on the substrates. The drops were evaporated in quiescent air at room temperature. Typical evaporation time was 12–15 min. For comparison, we also dripped the solution onto a glass coverslip.

Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy were conducted on a JEOL JSM-6330F field emission scanning electron microscope equipped with an EDX detector working at 10 kV. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were taken on a Philips CM12 transmission electron microscope at 120 kV. X-ray diffraction (XRD) patterns were collected on a X-ray
3. Results and discussion

3.1 Ag nanosheets formed by PLAL

By dripping droplets on a holey copper grid, we found that Ag nanoparticles (Fig. 1a) and nanosheets (Fig. 1b) were fabricated by the PLAL process. Fig. 1c is the SAED pattern of the nanoparticles, and the diffraction rings were from randomly dispersed Ag nanoparticles with face-centered cubic (fcc) structure. The nanosheet in Fig. 1b is assembled from irregular nanoplates. However, the corresponding SAED pattern in Fig. 1d is arranged in a six-fold rotational symmetry, indicating that the nanopieces have a face-centered cubic lattice with the (111) flat surface through oriented attachment. The intense spots [e.g., circled spot] are indexed as {220} Bragg reflections of Ag in the [111] zone axis with a lattice spacing of 1.44 Å, and the weak spots [e.g., boxed spot] originate from the 1/3{422} reflections with a lattice spacing of 2.50 Å. 13,14 The latter reflections are normally forbidden for perfect fcc structure, but the diffraction spots usually show up from plate-like Ag nanostructures and can be explained by a Ag (111) stacking fault (lying parallel to the (111) flat surface) model. 14 We also examined the colloidal solutions produced by PLAL with shorter ablation time, e.g., 15 min, and could only observe Ag nanoparticles, indicating that the laser re-processing of primary clusters is important for the generation of Ag nanosheets.

The formation of Ag nanosheets can be understood by considering the surface free energies of Ag crystals, which are in the order: γ_{110} > γ_{100} > γ_{111}. 15 Therefore, Ag clusters tend to crystallize into nanoplates with large {111} facets, and assemble with each other by coalescing the {110} lateral facets. 16 This growth behavior would result in sheet-like Ag nanostructures. However, for the nanocrystals, surface tensions generally overcome the surface free energies, and the resulting morphology of Ag nanocrystals would be spheres rather than plates or sheets. We consider that the formation of Ag nanoplates and the coalescence of the nanoplates are facilitated by the laser re-processing effects. The heating and surface sintering of the primary crystals promote the growth and coalescence of Ag nanoplates; for example, the boundaries and pores left by imperfect coalescence of nanoplates can be observed in Fig. 1b. Similar boundaries and pores due to laser-induced sintering and assembly were observed in permalloy colloidal solutions. 17

3.2 Ag$_2$O nanostructures formed by drop evaporation of the colloidal solution

We further found that the interior flow of an evaporating colloidal drop could redistribute the clusters, which also results in the formation of interesting nanostructures. Fig. 2 displays the SEM images of typical nanostructures observed on an n-type Si wafer by evaporating the laser-produced Ag colloidal solution on the wafer in air. The evaporation left deposits mostly in the central area surrounded by generally two evaporation rings as shown in the central panel of Fig. 2. The central area contains rice-shaped particles with lengths of ~1 μm and middle diameters of ~250 nm (Fig. 2a1 and a2). In the interior evaporation ring, flower-like structures assembled from similar micro-rice components (or petals) can be observed (Fig. 2b1, referred to as rice-flowers). A typical rice-flower is shown in Fig. 2b2, which has a complex three-dimensional structure. The rice-flowers could further assemble into chain-like structures in the nearby area as shown in Fig. 2c. Ag nanosheets can also be observed on the substrate, and their lateral sizes can be very large, for example, >10 μm, as seen in Fig. 2d1. Their surface is relatively smooth, as shown in Fig. 2d2, while the assembled subunits can still be identified on the edge; the image also shows nanoparticles on the substrate, with diameters less than 50 nm. The outmost evaporation ring is built up by irregular particles and nanocubes as shown in Fig. 2e.

Drop evaporation of the colloidal solution on a p-type (100) Si wafer generates similar nanostructures in the evaporation rings as those on the n-type Si wafer [Fig. S1, ESI†]. However, the central area of a p-type Si wafer contains disk-like structures as shown in Fig. 3a, instead of micro-rice. These disks are assembled from nanorice with lengths of ~100 nm (Fig. 3b). In the experiments, we produced arrays of drops (more than 10) on both kinds of Si wafers and found that the configurations of the deposits and the included nanostructures were similar for each kind of wafer. Bigger drops would generate larger evaporation rings (and require longer evaporation times), but the morphologies of the deposits were not affected. It is worth noting that the formation of these complex nanostructures depends on the substrate. When a glass substrate was used, only irregular particles were obtained although some of them had cubic morphologies [Fig. S2, ESI†].

The composition and structure of the deposits on both types of Si substrates were characterized by XRD and XPS. Fig. 4a shows the XRD patterns of the deposits. Three peaks at 2θ values of ~32.4°, 38.1° and 55.4° appear, which could be indexed to...
(111), (200) and (220) peaks of Ag$_2$O, respectively (JCPDS File No. 75-1532). The 38.1° peak may also originate from (111) diffraction of Ag (JCPDS File No. 04-0783), but the (200) peak of Ag which is the second most intense peak at 44.3° could not be identified, indicating that the content of Ag (i.e., in the form of nanoparticles and nanosheets) is much less than that of Ag$_2$O. The other peaks in the patterns come from the Si substrates (Fig. S3, ESI†). The XPS spectra in the Ag 3d binding energy range are shown in Fig. 4b. Compared with the Ag 3d$_{5/2}$ binding energy observed for pure Ag (368.3 eV, curve iii), the Ag 3d$_{5/2}$ peaks for the deposits shift to 367.9 eV by 0.4 eV. It is known that oxidation of Ag will cause the negative shift of the Ag 3d$_{5/2}$ peak.\textsuperscript{18–20} For Ag$_2$O, the shift is 0.3 eV to 0.5 eV.\textsuperscript{18–20} The increase of the FWHM of Ag 3d$_{5/2}$ peaks (1 eV) for the deposits compared to that (0.7 eV) for pure Ag also indicates the presence of Ag$^+$ ions.\textsuperscript{20} The XRD and XPS analyses show that deposits mainly contain Ag$_2$O.

An experimental phenomenon can also be used to distinguish Ag$_2$O and Ag, that is, Ag$_2$O tends to decompose into Ag nanoparticles under electron beam irradiation.\textsuperscript{7,21} Fig. 5a shows a rice-shaped particle after intense irradiation under SEM (at 10 keV for over 1 min); nanoparticles produced by irradiation-induced decomposition appeared on the surface. Similar nanoparticles are visible as well in the TEM image (Fig. 5b) of a micro-rice (or a petal from a rice-flower) scratched from the deposits on an n-type Si wafer. The decomposition can also be observed on petals of rice-flower (Fig. 5c)
and cubes (Fig. 5d) after intense electron beam irradiation. To further verify the composition of the deposits, we performed EDX measurements on some representative nanostructures and the results are plotted in Fig. 6. The scanned area for each curve is shown in the inset of each panel. For the rice-shaped particles (Fig. 6a), disk-like structures (Fig. 6b), and rice-flowers (Fig. 6c), oxygen can be detected from the surface, but for the nanosheet (Fig. 6d), only silver can be detected. These results suggest that the rice-shaped particles and the related assemblies are mainly Ag$_2$O while the nanosheets are Ag, which are consistent with the other characterizations.

Formation of Ag$_2$O nanostructures is related to the Ag$^+$ ions produced by the excimer laser ablation of Ag in water. The UV laser-produced Ag colloidal solution mainly contains Ag$^+$ ions and dissociative electrons from laser-produced plasma and/or due to photoionization of Ag clusters. Ag atoms could form by recombination of Ag$^+$ ions and electrons. The dissociative electron attachment to water molecules will generate hydroxide ions:

$$\text{H}_2\text{O} + e^- \rightarrow \text{OH}^- + \text{H},$$

and then Ag$_2$O clusters could form by the reaction:

$$2\text{Ag}^+ + 2\text{OH}^- \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O}.$$ (2)

Alternatively, the Ag species could react with O$_2$ from the air at the liquid–air interface, e.g., the contact line, and form Ag$_2$O. One may suggest that Ag$_2$O could also form in the laser-produced plasma which may contain oxygen ions and atoms, but Ag$_2$O starts to decompose into Ag at $\sim 360$ $^\circ$C, thus the formation of Ag$_2$O in the hot plasma is less likely.

We consider that the various nanostructures are produced by different evaporation modes of the Ag colloidal solution on Si substrates. Since evaporation behavior depends on surface properties of substrates, the different types of Si may induce different evaporation behaviors, thus in the uniform area Ag$_2$O formed different morphologies. Specifically, the evaporation ring deposits were formed by the pinned contact line mechanism, in which the drop maintained the liquid–substrate contact line during evaporation; deposits in the central area were formed by a constant contact angle mode, in which the height and radius of the drop decreased, or by a mixed mode of pinned contact line and constant contact angle. The (100) surface of Si is hydrophilic. During the liquid evaporation, the drop height contracted vertically. Due to the
decreasing height toward the perimeter, all the liquid at the contact line would be removed and the drop would shrink.\textsuperscript{23} In the pinned contact line mode, to prevent the shrinkage, a replenishing radial flow containing Ag species was driven to the perimeter that created a locally high concentration of Ag\textsubscript{2}O clusters. Self-assembly of these clusters, which also results in the formation of anisotropic nanostructures; alternatively, the interior flow of an evaporating colloidal drop could redistribute the laser-produced clusters, which also results in the formation of anisotropic nanostructures facilitated by the ripening process. The latter approach indicates that the laser-produced colloids have potential applications in printable electronic devices and sensors by being incorporated into the inkjet printing technique. The study also shows that by combining with other fabrication methods, laser ablation in liquid can be used to explore novel micro-/nanostructures while keeping its merit of “clean” fabrication.

4. Conclusions

We have demonstrated that Ag nanosheets can be produced by pulsed excimer laser ablation of Ag in water via laser re-processing of laser-produced primary clusters. We also showed that rice-shaped Ag-Ag\textsubscript{2}O nanostuctures and their assemblies could be fabricated by drop evaporation of the laser-produced Ag colloidal solution on (100) Si substrates. Since no surfactant has been used in the experiments, these results demonstrate that laser re-processing during pulsed laser ablation in liquid can influence the coalescence and growth of laser-produced clusters to generate anisotropic nanostructures; alternatively, the interior flow of an evaporating colloidal drop could redistribute the laser-produced clusters, which also results in the formation of anisotropic nanostructures facilitated by the ripening process. The latter approach indicates that the laser-produced colloids have potential applications in printable electronic devices and sensors by being incorporated into the inkjet printing technique. The study also shows that by combining with other fabrication methods, laser ablation in liquid can be used to explore novel micro-/nanostructures while keeping its merit of “clean” fabrication.

References