Tunable plasmon resonances of Ag nanoparticles obtained by photoelectric modification under room temperature

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Abstract

Stretched Ag nanoparticles (AgNPs) have been obtained by photoelectric modification with room temperature. Significant elongation occurs on partial AgNPs with diameters ranging from 50 to 120 nm. For AgNPs with diameters larger than 120 nm, protuberances with sizes about 10 nm have been observed after photoelectric modification. Simulations based on finite difference time domain method have been used to reveal the process of the photoelectric modification. Such morphology changes of AgNPs can be attributed to the plasmonic phase transition and electric induced migration of Ag atoms at AgNPs surfaces. Due to the stretching of AgNPs, tunable plasmon resonances in visible spectrum have been obtained. This work could provide a new technology for the metallic nanostructure modification under low temperature.

1. Introduction

Ag nanoparticles (AgNPs) with significant plasmon excitation within visible spectrum have attracted a lot of attention in recent years [1]. Many studies have focused on their applications, such as in optoelectronic devices [2, 3] for light managements, optothermal synergy therapies [4, 5], and SERS detectors [6]. It is well known that the plasmonic properties of AgNPs depend on their diameters and morphologies [7]. From the perspective of AgNPs’ fabrication, the most common way is hydrothermal synthesis and ripening of Ag nano-films recently [8, 9]. And the diameters and morphologies of AgNPs are mainly controlled by the guidance of their crystal growth [10]. More recently, a method of manipulating the morphology of nanoparticles by photon force has been reported [11]. However, only the morphology of single nanoparticles can be manipulated by this method, which makes it not suitable for the fabrication of AgNPs on large scales. As a result, a crystal growth independent way for large scale fabrication of AgNPs with various morphologies still remains a challenge.

Based on our previous study, photoelectric treatments have proved to be an efficient way for the tip engineering on the tip of single Ag nanowire (AgNW) with room temperature [12]. The significant deformation of the tip of AgNW is attributed to the plasmonic phase transition and electric migration of atoms on the tip of AgNW [13–16]. Similar results have been also obtained by Garnett et al they found that Ag nanowires can weld together by light illumination under temperature far below their melting point [17]. Obviously, photoelectric treatment provides us an efficient way for large scale fabrication of AgNPs with various morphologies beyond crystal growth limits.

Herein, photoelectric field has been exerted on AgNPs for their modification. In this case, AgNPs with various diameters are fabricated on silicon substrates (samples) by high temperature ripening of Ag nano-films with different thicknesses. After photoelectric modification, significant elongation occurs on AgNPs with diameters ranging from 50 to 120 nm. And protuberances with sizes about 10 nm formed on AgNPs with diameters larger than 120 nm. Finite difference time domain method (FDTD) simulations and ripening temperatures of AgNPs have been analyzed, which clarify the thermodynamics during the photoelectric modification process. Significant plasmon resonance shifts of AgNPs in visible spectrum have been found as
their elongation, which shows great potential application of these AgNPs in light management in solar cells, LEDs and even SERS detectors for their better performances.

2. Materials and methods

One-side polished n-type Si (111) wafers with area 0.3 cm$^2$ and thickness 0.5 mm were employed as substrates. AgNPs with different particle diameters on silicon surfaces were fabricated by sputter-anneal process. Ag nano-films were sputtered on silicon surface by magnetron sputtering (Q150TS, Quorum, United Kingdom). It is well known that the diameters of AgNPs fabricated by Ag nano-films ripening mainly depend on the thickness of nano-films [18]. To obtain Ag nano-films significantly different in thickness, the sputtering processes were sustained for 30 s and 60 s at a sputtering current of 30 mA. Then, samples were annealed in nitrogen at the temperature of 400 °C for 2.5 h. ITO glasses were used as transparent capacitor plates placed over the samples with a distance about 50 μm. 3V voltage was applied between samples and ITO glasses to offer electrostatic force on AgNPs. To avoid oxidation on AgNPs at atmosphere, the samples were negatively charged. Laser source (wavelength, 532 nm; power, 100 mW cm$^{-2}$) has been chosen to illuminate samples through ITO glasses. The morphology of the AgNPs was determined by field emission scanning electron microscopy (FESEM, JEOL Corp., Model JSM-6700F).

3. Results and discussions

As shown in figure 1, AgNPs with two diameter distributions on silicon surface are presented. A flow chart of the AgNPs preparation on silicon substrate has been also presented in figure 1(e). Before the photoelectric modification, the morphologies of AgNPs are mainly spherical for AgNPs with diameters ranging from 30 to 130 nm (figure 1(a)) in contrast to that of AgNPs with diameters ranging from 10 to 700 nm (figure 1(c)) which have island shaped irregular structures. The reason is that thinner films have higher surface tensions due to the increase of specific surface area of materials. And material reduces induced reduction of binding force in films causes the formation of the fractures of thinner films are more sufficient. Meanwhile, the fractures of thinner films have lower ripening temperatures. According to the Oswald ripening [18, 19], the fractures of thinner films reunion into spheres (which is just like the reunion of water droplet adhered on glasses) more easily due to their higher surface tension and low temperature needed. After 60 min photoelectric modification, significant elongation can be observed partially on AgNPs with diameter ranging from 50 to 120 nm, as shown in figure 1(b). And the detail morphology changes of the elongated AgNPs are presented in the inset. And the temperature increase of all samples is no more than 3 °C during the photoelectric modification. Obviously, the elongation of AgNPs is about 3 to 5 times than their diameters, which is quite different with the normal Oswald ripening of AgNPs under annealing process. For AgNPs mainly with diameters larger than 200 nm in figure 1(c), protuberances with sizes about 10 to 25 nm have been observed in the inset in figure 1(d) after photoelectric modification, which exhibits the roughness increase on their surfaces. Meanwhile, small particles dispersed among the large particles disappeared as shown in figure 1(d). Note that no obvious morphology changes of AgNPs with diameters smaller than 50 nm have been observed.

A schematic diagram is presented to illustrate the thermodynamics process of the photoelectric modification. As shown in figure 2(a), voltage and light were simultaneously applied on samples to offer heat and electrostatic forces to AgNPs. Apparently, the photoelectric stretching area which only depends on the electrode and light illuminated area can be very large, which provides uniform and large area action conditions for the elongation of AgNPs. The electrostatic force induce additional pressure $P_t$ on AgNPs can be simply deduced by $P_t = \varepsilon_0 U^2/2d^2$, where $U$ is the voltage applied between the electrodes, $d$ is the distance between the parallel plates and $\varepsilon_0$ is the vacuum permittivity. And from the deduction, the electrostatic force induced pressure is determined to be about 0.14 N m$^{-2}$ for all AgNPs. Apparently, the additional electrostatic force is more effective in AgNPs with larger diameters to overcome their surface tensions. Meanwhile, the light enhancement of AgNPs with larger particle diameters presents lower light enhancements, as shown in figure 2(b). Apparently, heat generation of AgNPs with larger particle diameters is less than that of the smaller particles. There is a balance for the photoelectric modification on AgNPs. As a result, the photoelectric stretching applied to all silver nanoparticles is more effective within a certain diameter range from 50 to 200 nm theoretically.

Models based on FDTD simulations have been applied to reveal the elongation process of AgNPs by photoelectric modification. In these models, all of the AgNPs have the same volume throughout the elongation process. In these models, the diameter of the bottom parts of AgNPs decreases following the increase of the upper parts. Considering the applications of sources applied in our case, plane wave polarized light with wavelength 532 nm were adopted in these models. The shaft section of the light enhancements of AgNPs with elongation of 0, 10, 20, 30, 40 and 50 nm have been presented in figure 3. And the typical cross sections of the
light enhancements of AgNPs (interval distances are 10 nm from the tip of a, b, c points; d points are across the diameter of the bottom) with elongation of 30 and 50 nm have been presented in figure 4. From figures 4(a) to (d), it can be found that the upper parts of AgNPs shows significant higher light intensity than that of the bottom. And AgNPs with longer elongation gain higher light intensity enhancement and hence could be driven more easily by applying electrostatic force during the elongation process. As a result, the upper parts of AgNPs can be continually elongated by photoelectric modification.

Note that the stretched Ag nanoparticles (AgNPs) obtained by photoelectric modification is under a relatively low temperature. To reveal the photoelectric stretching of AgNPs under such low temperature, the diameter-dependent ripening temperature (lowest temperature needs of atomic migration of materials) and additional pressure has been calculated [20] and provided in figure 5. As shown in figure 5(a), the ripening temperature of AgNPs significantly decreases with the deduction of diameters, which is far below their melting points. Meanwhile, plasmon excitation on the tips of AgNPs can provide above 13 times (about 1.3 W cm\(^{-2}\)) light intensity with that of the incidence based on above FDTD simulations, which provide enough energy for the atomic diffusion on AgNPs with proper sizes based on Oswald ripening [21]. The disadvantage of small
particles to the plasmonic modification is the diameter decrease induced additional pressures, as shown in figure 5(b). The significant increase of the additional pressures of AgNPs with diameters smaller than 50 nm could significant inhibition of electric field forces during the photoelectric modification process. As a result, no obvious morphology changes have been found on AgNPs with diameters smaller than 50 nm.

Tunable plasmon resonance from 400 nm to 600 nm of AgNPs can be obtained by photoelectric modification, as shown in figure 6. As shown in figure 6(a), the intrinsic absorption peak of AgNPs shifts from...
400 to 600 nm as the elongation increasing to 50 nm, which can be attributed to the damping effect of the elongations. Note that the peak around 450 nm of AgNPs should be attributed to the higher order oscillation caused by the morphology changes of AgNPs [22, 23]. Compared with that of the light absorption, the shifts of the extinction cross sections (light scattering and absorption) of AgNPs are also presented the similar rules. The height of the peak becomes higher from 400 to 600 nm, which is mainly attributed to the reduction of the absorption as the elongation increasing. Therefore, AgNPs modified by photoelectric treatment can easily realize the plasmon resonance tunable in visible spectrum and have great potential application in solar cells, LEDs and SERS detectors.

4. Conclusions

In summary, the morphology of AgNPs has been modified by photoelectric treatment. Significant elongations (about 3 to 5 times) have been found on partial AgNPs after 60 min photoelectric modification. And
protuberances with sizes about 10 nm have been observed on AgNPs with diameters larger than 120 nm. Note that not all AgNPs on the substrate have morphological changes. This phenomenon could be attributed to many reasons, such as the difference of adhesion force of AgNPs with silicon substrate, photoelectric field interferences between these AgNPs etc. More elongated AgNPs could be obtained by reducing the numbers of particles and improving the annealing process. The reasons of the elongation of AgNPs have been concluded by FDTD simulations and calculations of the rippling temperatures of AgNPs. The plasmon excitation induced low temperature phase transition and electric migration of atoms at AgNPs surfaces could be the main reasons for their morphology changes. Tunable plasmon resonance from 400 nm to 600 nm of AgNPs has also been obtained by photoelectric modification, which shows great potential application in light managements in many devices for better performances. This work not only offers a new way for the morphology changes of AgNPs, but provides a new approach for the deformation of all metallic nanostructures with low temperature.

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Conflicts of interest

The authors declare no conflicts of interest.

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Figure 6. (a) Light absorption of AgNPs with elongation of 0, 10, 20, 30, 40 and 50 nm in visible spectrum; (b) Extinction cross section of AgNPs with elongation of 0, 10, 20, 30, 40 and 50 nm in visible spectrum.
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