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Large-area and high-density gold nanoparticle arrays with sub-10 nm gaps

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Abstract

Electrochemical techniques are widely used for the fabrication of nanostructured materials, yet a desired high-density nanoparticle arrays remains a challenge. Here large-area and high-density gold nanoparticle arrays with sub-10 nm gaps have been, for the first time, synthesized on Si(1 0 0) substrate within an electrochemical deposition system via the application of an unusually high over-potential. The extremely high over-potential contributes to the relatively small critical island size and high nucleation rate. It is believed that this method can be extended to the electrochemical fabrication nanoparticle arrays of other materials.

Keywords: Gold nanoparticle arrays; Electrochemical deposition; High-density; Over-potential

1. Introduction

Noble metal nanoparticles (e.g., Au and Ag) with their associated strong plasmon resonance have generated great interest in fields such as nanoscale photonics and biological labeling [1,2]. Theoretical and experimental studies indicate that the strong plasmon resonance is likely to be related to the so-called "hot-spots" effect, which strongly depends on the interparticle spacings or nanostructural gaps [3,4]. A great challenge that remains is to develop effective ways to organize the nanoscale particles into functional structures and devices. Of particular interest is a general method for fabricating high-density nanoparticle films with controllable sub-10 nm spacing on solid substrates [5].

Recently, silver nanoparticle arrays with controlled sub-10 nm gaps have been achieved by some routes such as porous anodic aluminum oxide (AAO) nanochannels, Langmuir–Blodgett (LB) technique or solvent evaporation [6–8]. However, the fabrication process is complicated for the AAO method; and the uniformity in a large-scale, controlled by polymer shrinkage for the LB and solvent evaporation route still requests further improvements. Moreover, the adhesion strength between particles and substrate obtained by the above methods is relatively low. Meanwhile, the introduction of an organic solvent is disadvantageous for the studies of some properties such as biological sensitivity.

Electrochemical deposition of metals and alloys onto metallic or semiconductors substrates plays an important role in many modern technologies such as copper printed circuit boards, through-hole plating, multilayer read/wire heads and thin film magnetic recording media. Electrochemical deposition techniques are cheap, versatile, and allow a wide range of parameters to be adjusted for obtaining desired nanostructures. The unique feature of electrodeposition is the ability to control the driving force or departure from equilibrium of the deposition process by simply controlling the applied potential [9]. The departure from equilibrium is determined by the electrode over-potential, η. The over-potential is the difference between the applied potential, E, and the equilibrium potential, E_{eq} (that is, $\eta = E - E_{eq}$). In many cases, deposition of metals onto semiconductors follows a 3D island growth (Volmer–Weber) mechanism

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due to the weak interaction energy between the adsorbed metal atom and the semiconductor. In general, the over-potential dependence of the critical cluster size, N_{crit}, is given by the following relation [10]:

$$N_{crit} = 8BV_m^2\sigma^3/27(e|\eta|)^3 \quad (1)$$

where B is a geometrical factor (36π for a sphere, 6^3 for a cube), V_m is the atomic volume and σ is the average specific surface energy. The rate of nucleation can be represented by the classic Volmer–Weber equation:

$$J_{nucl} = A_{3D}\exp[(-4BV_m^2\sigma^3)/27kT(e|\eta|)^2] \quad (2)$$

where the pre-exponential factor A_{3D} is only weakly dependent on the over-potential and can be neglected. In these regards, a desired nucleation rate and critical island size can be achieved by adjusting the over-potential during electrochemical deposition.

Recently, gold nanoparticles were deposited on various substrates such as indium tin oxide (ITO) film coated glass [11], highly oriented pyrolytic graphite (HOPG) [12–14], glassy carbon (GC) [14], and Au(1 1 1) single-crystalline substrate [14]. Compton et al. prepared gold ultra-microelectrode arrays by electrodeposition route, where the individual gold particles are organized in a hexagonal arrangement [15]. In this article, we demonstrate, for the first time, a novel electrochemical deposition condition for the fabrication of large-scale, very uniform and high-density gold nanoparticle arrays on a conventional silicon substrate. The gold nanoparticle arrays with tunable sub-10 nm gaps are achieved by the control of 3D island nucleation and growth.

2. Experimental

$HAuCl_4$ was purchased from Aldrich and *ortho*-phenylenediamine from Beijing Chem. Co. All reagents were used as received without further purification. The water used was purified through a Millipore system. In a typical experiment, the Si(1 0 0) plate was first treated by hydrochloric acid to remove surface contamination and rinsed by distilled water. The electrochemical deposition of gold QDs was carried out in a two-electrode cell on a Si(1 0 0) substrate. The Si(1 0 0) plate was mounted as a cathode with a graphite rod as the anode. The applied potential (E) was controlled at 100 V with the constant potential mode by a DC voltage-stabilized power supply. Following deposition, the samples were rinsed with ethanol and characterized with FEG-JSM 6335 field-emission scanning electron microscope (FE-SEM) and D/Max 2500V/PC X-ray diffractometer using Cu (40 kV, 200 mA) radiation.

3. Results and discussion

Fig. 1A and Fig. S1 present SEM images of gold nanoparticles synthesized under an applied potential of 100 V and 0.1 mM aqueous $HAuCl_4$ solution for 3 min of reaction

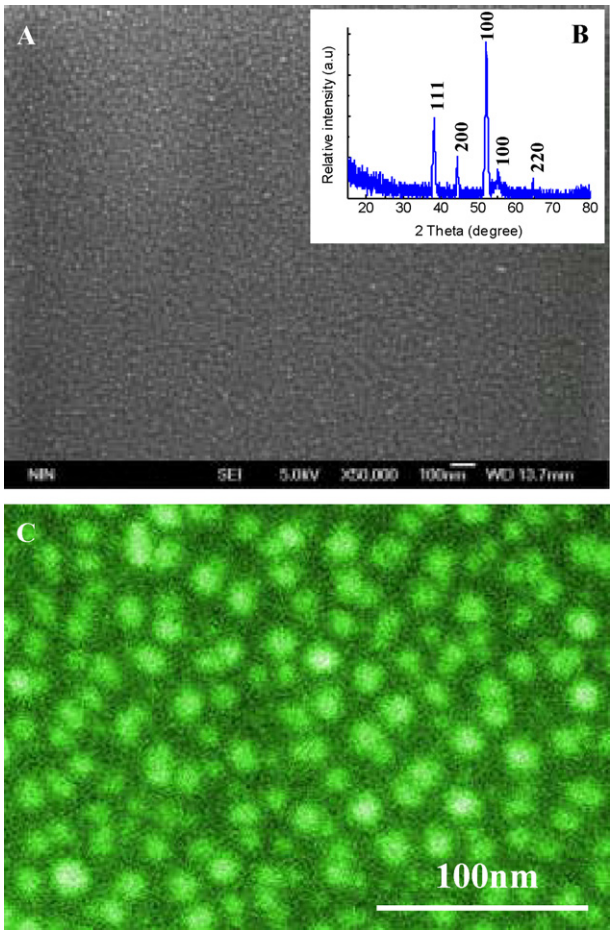

Fig. 1. (A) SEM image of gold QDs that were synthesized at 100 V applied potential and 0.1 mM aqueous $HAuCl_4$ solution for 3 min reaction time. (B) XRD pattern of sample (A). (C) The magnified SEM image of image (A).

time. As shown in these images, a very uniform gold nanoparticles film is obtained at a large-scale area. A typical X-ray diffraction (XRD) pattern of the product is shown in Fig. 1B. The peaks are assigned to the diffraction of (1 1 1), (2 0 0), and (2 2 0) planes of fcc gold accordingly. The two peaks located at about 52° and 55° correspond to the Si(1 0 0) plane because the thin layer XRD scanning mode is adopted. Fig. 1C is a magnified image of Fig. 1A, demonstrating high-density gold nanoparticle arrays with an average size of 10 nm and interparticles spacing of 5–10 nm. The results indicate that it is possible to fabricate gold nanoparticle arrays with sub-10 nm gaps.

To get deep insight into the details of island nucleation and coarsening, the interval samples are analyzed at different stages of the reaction performed under 100 V applied potential and in 0.1 mM aqueous $HAuCl_4$ solution (Fig. 2). At $t = 1$ min (Fig. 2A), the sample is composed of small gold nanoislands with an average 8 nm size distribution and 15% standard deviation (Fig. 3A_1). The interparticle gaps in this case are relatively wide (mainly at about 35 nm), exhibiting three peaks (Fig. 3A_2). As the reaction proceeds to $t = 3$ min, the gold islands grow up