Controlled Synthesis of Gold Nanocomplex Arrays by a Combined Top-Down and Bottom-Up Approach and Their Electrochemical Behavior

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Patterned arrays of Au nanocomplexes with various features were fabricated over large areas by photolithography with electrochemical synthesis. This combined top-down and bottom-up approach eliminates the significant drawbacks (e.g., small areas, nonhomogeneity, nonuniform distribution) encountered with conventional bottom-up techniques. The effects of the applied voltage, the concentration of the HAuCl₄ solution, and the initial Au pattern size on a Au nanocomplex structure array were investigated. The results show that the Au nanocomplex array can be constructed according to different requirements. Electrochemical experiments clearly imply that the Au nanocomplex array electrode exhibits excellent electrochemical sensitivity and capacitance. A Au nanocomplex array on a large template prepared via the top-down and bottom-up approach can be applied to the areas of chemical sensing and optical signal processing in nanoelectronic devices.

1. Introduction

Currently, a great deal of research has focused on the fabrication of nano/microscale structured materials using bottom-up approaches such as self-assembly or chemical/electrochemical synthesis. With the aid of these approaches, the syntheses of metal particles including gold, platinum, and copper¹⁻⁴ have attracted widespread attention due to the unique optical, electrical, magnetic, and catalytic properties of these metals as well as their important technological applications.⁵⁻¹⁵ Recently, Cai reported the fabrication of Au flower-like nanoarchitectures¹⁷ as well as an ordered Au particle array on an indium tin oxide substrate based on an ordered alumina through-pore template.¹⁸ Raj et al. synthesized flower-like gold nanoparticles and studied their electrocatalytic activity to methanol and oxygen.¹⁹ Bottom-up approaches, however, cannot easily realize various perfectly ordered wafer-scale Au nanocomplex arrays according to different application requirements as chemical and physical forces directly determine their formation.

The photolithographic technique completely avoids the indiscriminate problems that occur with pure chemical processing. The most important advantage of this method is that the size, shape, and interparticle spacing of the structure is determined by the requirements of its end application rather than by the chemical and physical forces that direct its formation.²⁰⁻²² This study presents a lithographically patterned method that has high controllability in the construction of a Au nanocomplex array with a flower shape made up of a microscale structure with nanoscale flakes. Lithographically patterned nanocomplex array electrodeposition combines the attributes of photolithography with the versatility of bottom-up electrochemical synthesis. With a photolithographic pattern, a highly intricate gold nanocomplex array can be achieved on a silicon substrate. Photolithography defines the size, position, and density of a Au pattern on the silicon substrate, and these attributes are used for the growth of the Au complex. These parameters act as a “receptacles” that define the shape of an array during its electrodeposition. The electrodeposition duration, applied voltage, and concentration of the solution determine the growth of the nanocomplex structure. Considering that the Au nanocomplex array has some useful features for improving the performance of catalytic activity, such as a high loading, high active surface area, and long-term stability, and so on, cyclic voltammograms of a Au nanocomplex array system are investigated to confirm its application as a candidate for electrochemical sensors.

2. Experimental Section

Au-Patterned Si Substrate. Figure 1 shows the fabrication strategies for creating a Au nanocomplex array by combining a photolithographic technique with electrochemical synthesis. As
a starting substrate, a p-type 4 in. silicon wafer with a thickness of 525 μm was used. After a standard cleaning of the silicon wafer for 30 s using a 100:1 diluted HF solution, a 10 nm Cr layer and a 100 nm Au layer were deposited onto the silicon wafer by thermal evaporation. The role of the Cr layer is to improve the adhesion of the gold to the silicon. Following the formation of the Cr/Au layers, dot-shaped mask patterns were made on the Au surface using optical photolithography with a positive photoresist. This lithography step provided designed mask patterns with various sizes and densities of a dot pattern array. Through the use of G-line lithography with a wavelength of 436 nm, an AZ6612KE positive photoresist was patterned. The photoresist patterns served as a mask for a subsequent Au/Cr wet etching. A 100:1 diluted KCN solution transferred the photoresist patterns to the Au layer. This wet etching process was performed at 25 °C for 30 s. After Au etching, the remaining Cr layer was etched by a Cr etchant (CR-7) at 25 °C for 60 s. After Cr etching, the remaining photoresist patterns were then removed using acetone and a photoresist remover (AZ400T) at 50 °C for 1 h. Finally, the Au-patterned silicon wafer was washed using deionized water (DIW) and dried in nitrogen gas. Au nanocomplex arrays were grown in an aqueous solution using an electrochemical deposition process from the aforementioned Au-patterned silicon wafer.

**Synthesis of the Au Nanocomplex Array.** The Au nanocomplex array was synthesized in an aqueous solution containing HAuCl₄ (HauCl₄·H₂O, Sigma Aldrich) and 20 g·L⁻¹ polyvinylpyrrolidone (PVP, K 30, Fluka) using a two-electrode system. Prior to electrodeposition, the prepared wafer containing Au dot patterns was cleaned using acetone and DIW in order to include Au dot patterns. This wafer was employed as a working electrode. A clean graphite sheet served as the counter electrode. The applied potential was controlled using a triple-output DC power supply (Agilent, E3631A). After deposition, the sample was rinsed sequentially with acetone and DIW to eliminate any physically absorbed impurities that may have been present. It was then dried with high-purity nitrogen before further measurements were taken.

**Electrochemical Measurements.** Cyclic voltammetry measurements were performed with a CHI 600B electrochemical analyzer (CH Instruments, Inc.). All electrochemical experiments were carried out in a phosphate-buffered saline solution (PBS, pH 7.4) in a conventional three-electrode cell at room temperature. The silicon substrate with the size of 7 mm × 20 mm containing a gold nanocomplex array with the size of 3 mm × 3 mm was used as the working electrode. The working electrode was connected to the analyzer by a electronic clip which provided an electrical conduction path between the working electrode and analyzer. Ag/AgCl was used as a reference and Pt wire as a counter electrode (CH Instruments, Inc.).

**Materials Characterization.** Sample morphologies were analyzed using a Philips XL 30 AFEG field-emission scanning electron microscope (FESEM, Eindhoven, Netherlands) and a FEI NOVA 2000 dual-beam focused ion beam (FIB, Netherlands). TEM images were obtained from FEI Tecnai F20. Energy dispersive spectrometer analysis (EDS) was carried out using an EDAX system (Phoenix, EDAX International Corporation). The X-ray diffraction (XRD) spectrum analysis was carried out using a diffractometer (Philips X’pert PRO with Cu Kα radiation). The cyclic voltammogram was obtained using a CHI600B electrochemical analyzer (CH Instrument, Inc. U.S.A.).

**3. Results and Discussion**

Au nanocomplex structure arrays were grown in an aqueous solution containing HAuCl₄ and polyvinylpyrrolidone from a Au-patterned surface. The surface morphology of the as-grown nanocomplex structures was investigated via field-emission scanning electron microscopy (FESEM). A typical low-magnification SEM image (Figure 2a) shows that large-scale arrayed crystals are successfully fabricated onto a Au-patterned Si substrate, whereas no residue can be observed on the silicon surface, demonstrating that the synthesis exhibits high controllability. The crystals have similar sizes and structures. A high-magnification SEM image (Figure 2b) shows that these crystals have nanocomplex structures. Many leaf-like structured flakes with sharp edges and tips are interdigitatedly arranged on this structure. The diameter of the nanocomplex structure is approximately 3 μm, and the height is approximately 1.5 μm. As the physical and chemical properties of metal structures can be finely tuned by means of their shape, a Au nanocomplex array with unique surface morphologies can fulfill a number of important catalytic activities. Figure 2c shows the cross section of the Au nanocomplex structure (dual-beam FIB image). The figure suggests that each nanocomplex is a polycrystal. Further observations of the crystalline structure were made by a transmission electron microscopy (TEM, see Figure S1 for the details) measurement and selected area electron diffraction (SAED) pattern, as presented in Figure 2d and e. The TEM image shows that the nanocomplex includes many small grains that have independent orientations. SAED further reveals that the Au nanocomplex has polycrystalline structure. The structure of these arrayed crystals was further examined by XRD. Figure 2f shows the typical XRD pattern of Au arrays with regular nanocomplex morphologies. This figure reveals that the as-synthesized Au flowers in an array have a crystal, face-centered cubic lattice structure. The intensity ratio of the [200] and [111] diffraction peaks in the XRD pattern was measured at 0.33. This is lower than the bulk value (0.53), confirming that the Au structures in the nanocomplex array were abundant in the [111] planes and, hence, that their [111] planes tended to be preferentially oriented parallel to the surface of the patterned Au substrate. The Si {311} peak most likely originates from the silicon wafer.

An investigation of the effect of the applied voltage on the Au nanocomplex array at a constant concentration and deposition time was conducted. A voltage-dependent process that results in the formation of a desired nanocomplex structure with different surface features under one set of conditions was discovered. The results are shown in Figure 3. When applying 1.5 V, the pattern is crowded by many blocks of gold crystals, and the aggregated surface is covered by many ball-shaped particles and a number of leaf-like particles (Figure 3a). An enlarged SEM image shows that the ball-shaped structure contains many needle-like particles (Figure S2a). At 0.7 V, the Au patterns remain crowded by many blocks of gold crystals, but the surface morphologies are changed. The leaf-like particles in micrometers are clearly observed (Figure 3b); these can also be seen in a high-magnification SEM image (Figure S2b). When applying 0.5 V, a quite different array is obtained. Au crystals with nanocomplex surfaces are separately located on a Au-patterned Si substrate with few defects. The agglomerated Au particles disappear, and leaf-like particles interdigitatedly covering the surface can be clearly observed from the corresponding high-magnification image (Figure S2c). However, when a voltage of 0.1 V was applied, the perfect flower-like structure was replaced by various nanoparticle covering the Au-patterned surface (Figures 3d and S2d). Moreover, several nanoscale particles were found on the Si substrate; thus, it is suggested that the selectivity of the growth of the Au nanocomplex array
is not viable at a low applied voltage. From the above observations, it was concluded that the applied potential controls the nucleation rate and the particle shape. Cluster formations are associated with a higher potential, and leaf-like structures are associated with a lower potential.

Measurements were also made as a function of the concentration of HAuCl₄ at an applied voltage of 0.3 V and a deposition time of 60 min to probe the formation of the Au nanocomplex array, as reported in Figure 4. At a higher concentration of 40 mM, the Au pattern was covered by an aggregated structure.
FESEM. Figure 6 shows images of a Au nanocomplex synthesized on a patterned surface, the morphologies of Au nanocomplexes controlling the initial Au pattern size during the photolithography process. The other advantage of this technique is that Au nanocomplex arrays with different spacings or sizes were grown by controlling the initial Au pattern density or size. From the SEM images, the evolution of the Au nanocomplex with different spacings or sizes was clearly distinguished, and the physical attributes of the grown nanocomplex could be clearly distinguished, and the diameters increased compared to those at previous stages (Figure 6a, b, and c). Thus, the stage shown in Figure 6c is a very important intermediate structure. After a 60 min deposition time, the expected structure continued to grow and eventually expanded into a fully developed flower-like structure (Figure 6f).

Owing to the very rough structure of micro/nanoparticles, many researches have demonstrated that they exhibit better enhancement in surface-enhanced Raman spectroscopy compared to other analogous micro/nanoparticles with smooth surfaces. For some applications, such as in vivo measurements or with fuel cells, electrodes with a high active surface area are very useful. In order to investigate whether the Au nanocomplex array can be used as an electrode, the electrochemical behavior of ferriyanide, which is widely used as an electrochemical probe, was investigated on the surface. Figure 7a shows the cyclic voltammograms obtained for a Si substrate, a pure Au pattern array with a dimension of 4 µm and a spacing of 32 µm (4 × 32), and Au nanocomplex array electrodes of 0.1 mM Fe(CN)₆³⁻. First, no signal can be observed for the Si substrate; hence, the signals at the other two electrodes are considered to be from the patterned Au and Au nanocomplex arrays on the Si substrate. Second, and importantly, the catalytic and anodic peak current for the Au nanocomplex array electrode is enhanced much more than that for the pure Au pattern, showing that some reactions are more favorable at the nanocomplex electrode. The voltammetric features of the Au nanocomplex array electrode are due to the presence of a large surface area and sharp edges or tips on the complex surface. Additionally, the results in Figure 7a show that the electrochemical capacitance of the Au pitches’ array electrode had increased substantially by the introducing of a nanocomplex structure. The capacitance was calculated from the cyclic voltammogram curves, with $C = \frac{i}{\Delta V}$, where $i$ is the current and $\Delta V$ is the scan rate (V·s⁻¹). At a potential of 0.208 V, as an example, the effective capacitance is over 20 times larger than that of the pure Au pattern array electrode. This high capacitance, which is consistent with the large surface area, demonstrates that the Au nanocomplex array electrode can provide a larger surface area for the electrochemical reaction. Figure 7b shows cyclic voltammograms of a Au nanocomplex array system at different concentrations. As the bulk concentration of Fe(CN)₆³⁻ increases, the voltammetric response is stably enhanced, demonstrating that there is no dissociation of gold debris from the structure surface. Therefore, we concluded that the Au nanocomplex array exhibits high stability and does not easily peel off from the Si substrate when placed in a solution. The typical plots of the response current versus concentration for the Au nanocomplex array system are shown in Figure 7c. It is found that the calibration plot has a slope of 4.82 µA·mM⁻¹ (sensitivity) and a correlation coefficient of 0.998. We suggest therefore that the higher responses are obtained with a nanocomplex structure. Furthermore, this structure provides a higher surface area, which can accommodate many more reactant molecules.
molecules in a given region. Consequently, we can expect a high level of sensitivity.

In order to investigate the electrochemical behavior of the Au nanocomplex array electrode further, a comparison of this
type of complex arrayed surface with different patterns was carried out. The results are shown in Figure 8. It is worthwhile to note that no signal was observed at the (2−16) complex arrays electrode. Figure 8 shows cyclic voltammograms of complex arrays of (4−16), (4−32), (8−16), and (8−32) at different scan rates. It was found that no anodic and cathodic peak current can be observed at high scan rates of 0.1 V·s⁻¹ for the four types of arrays. However, a clear redox peak current appears at a low scan rate of 0.005 V·s⁻¹. This case may be due to the semiconductive property of the Si substrate (surface-controlled process) or may have resulted from the diffusion-controlled electrode process kinetics. At a high scan rate, although a reduction reaction occurs at the arrayed electrode surface, it was not possible to record the signal due to the semiconductivity of the Si substrate. To rule out this possibility, a comparison experiment was run in which good electrical contact was made from underneath of the nanocomplex electrode via a gold wire. The cyclic voltammograms feature of the as-prepared electrode was nearly identical to that without the gold wire contact, suggesting that the behavior is controlled by the diffusion process. Fitting the data in Figure 8d, the peak currents are proportional to the square root of the scan rate. This indicates a diffusion-controlled electrode process. At relatively high scan rates, the rate of diffusion of the redox couple is slower than that of the scan rate on this kind of arrayed electrode; this is why the cyclic voltammograms change so obviously. Another aim of Figure 8 is to demonstrate the effect of the dimension and spacing of the arrays on the electrochemical behavior. It is worthwhile to emphasize that if the spacing between the complex (each complex can be considered as an individual microelectrode) is narrow, the diffusion layers of adjacent microelectrodes may start to overlap, resulting in a situation where the solution on the “overlapping region” is similar to a macroelectrode. If the spacing between the complex is so wide that each overlaps with its own undisturbed diffusion layer, the arrayed electrode still presents the behavior of a microelectrode. These results will guide the design of a reasonable array for electroanalysis. Smaller is not always better, and it is necessary to optimize the parameters of the Au nanocomplex array electrode. As previously reported, electrode activation can improve the signal-to-noise ratio for selectivity against interfering species; the methods include electrochemical means, mechanical polishing, abrasive roughening, or heating. A piranha solution (7:3 v/v 98% H₂SO₄/30% H₂O₂) was chosen here for Au nanocomplex electrode activation. The cyclic voltammograms of the electrode before and after activation are reported in Figure 9. Clearly, the activation improves the electrode response, and cathodic and anodic peak currents can be observed. These results clearly substantiate that a Au nanocomplex array can function as an electrode of an electrochemical sensor.

4. Conclusion

In summary, an effective approach that combines top-down photolithography and bottom-up electrochemical synthesis is presented. This approach can be used to grow a large-scale position-controlled Au nanocomplex array, and its possible application in electrochemical sensors is demonstrated. The proposed technique uses a Au pattern produced via photolithography to realize controllability; that is, it guides the growth of the Au nanocomplex onto a designed Au-patterned surface. This feature of controllability has certain advantages for many applications that require optimized structures. Additionally, the applied potential was shown to control the nucleation rate and the particle shape. Cluster formations are associated with a higher potential, and leaf-like structures are associated with a lower potential. The formation of the Au nanocomplex structure is a stoichiometry-dependent process. Due to the very rough surface of the structure (confirmed by a larger capacitance), the complex array electrode exhibits a high level of sensitivity (4.82 µA·mM⁻¹). Detailed experimental results show that the electrochemical behavior is different for different arrays. These results provide an opportunity to understand the sensing behavior...
of the microelectrode array further. They may also be useful in a variety of biosensing applications, that is, they can be an ideal matrix for enzyme immobilizations.

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Supporting Information Available: FESEM images. This material is available free of charge via the Internet at http://pubs.acs.org

References and Notes

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