Vertical deposition of ultrafine silver particles on silicon surface out of solutions by silver mirror process

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ABSTRACT

Ultrafine silver particles are deposited on the surface not submerged in solutions by vertical deposition using mirror silver process. The size of particles on the surface out of solutions ranged from 10 to 40 nm. Compared with those on the surface in solutions, these ultrafine silver particles are monodisperse and display good uniformity in shape and size. The achievement of the ultrafine silver particles is attributed to the wetting effect of solid–liquid interface and evaporation of the ethanol solvent. The ultrafine porous silicon structures are obtained by catalysis etching of the ultrafine silver particles, and their reflectance near infrared wave band is decreased, which is useful for solar cell applications.

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1. Introduction

Metallic ultrafine particles (1–100 nm in diameter) have triggered a growing attention because they exhibit anomalous physical properties which are not observed in bulk solid phases [1]. Among them, ultrafine silver particles have been exclusively investigated in connection with surface-enhanced Raman spectroscopy (SERS), surface Plasmon renounce (SPR), catalyst, etc. [2–6]. Previously, silver particles have been successfully synthesized and their nucleation and growth mechanisms have been proposed [7–11]. Most chemical methods are not one-step deposition on substrate, and generally the substrate needs to be dipped into precursor solutions. Vertical deposition technique was proposed for the preparation of colloidal crystal and metal thin film with controlled thickness, in which the substrate was kept vertical to the surface of the solution [12–16]. The method relies on a balance between ethanol evaporation rate and particle sedimentation, and can produce high-quality single crystal with controlled thickness [15]. The silver mirror reaction has been used to prepare Ag-NPs, silver surfaces and core–shell structures on substrate for extensive applications [5,17–20]. In the present study, a facile vertical deposition method was used to prepare ultrafine silver particles on Si surface not submerged in the reaction solution by silver mirror reaction.

2. Experimental details

First, $AgNO_3$ powders were dissolved in a component solvent of ethanol and water (volume ratio was 1:1). Then, the $[Ag(NH_3)_2]OH$ solutions (0.2 M) were prepared by continuously dripping aqueous ammonia into the $AgNO_3$ solution while stirring until the mixtures became colorless. After that, the polished Si (100) samples of $20 \times 10 \times 0.5$ mm^3 were dipped vertically into the solutions, as shown in Fig. 1. One part of the sample was dipped in solutions and the other part was out of solution.

Then glucose (0.01 M) was added to the $[Ag(NH_3)_2]OH$ solutions while carefully stirring. The reactions were kept at ambient temperature for 2, 5 and 10 min and thereafter the Si samples were taken out and dried. The morphology of silver particles on the Si surfaces dipped in solutions and out of solutions was characterized by a scanning electron microscope (SEM, FEI Quanta 200 F). Finally, the silver particles were used for catalytic etching of Si nanostructures in mixing solutions composed of HF, H_2O_2 and H_2O (volume ratio was 1:5:2). Morphology of Si nanostructures was observed by SEM and the reflectance was measured by the ZoLix IPCE/QE system with integrating sphere.

3. Results and discussion

Fig. 2 shows the morphology of Si surfaces dipped in solutions and not in solutions after vertical deposition with different reaction times. The result shows that ultrafine silver particles were successfully deposited on the Si surface not submerged in

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solutions by this vertical deposition method. With the same reaction time, the quantity of the silver particles on the surface dipped in solutions was much more than that on surface not in solutions, as shown in Fig. 2(a)–(c). The quantity and size of particles increased with reaction time, regardless of whether the surface was in solutions or not. The size and coverage fraction of particles on the surfaces in solutions and out of solutions have been depicted in Table 1. It was found that with the same reaction time, the size of particles on the surface not in solutions was smaller than those in solutions. When the reaction time was short (2 min and 5 min), the particles deposited on the surface not in solutions were so little and small that they could hardly be observed (see Fig. 2(d) and (e)).

When the reaction time was increased to 10 min, the particles with the size of about 40 nm were obviously observed on the surface out of solutions, which were analogous to the particles on the surface dipped in solutions for 2 min. In Fig. 3(a), the silver particles on the surface dipped in solutions displayed irregular shapes, such as short rod, hexagon and triangle. Compared with those of Fig. 3(a), the ultrafine particles of Fig. 3(b) displayed some advantages including quasi-round shape, uniformity in size, monodisperse distribution and reduction of agglomeration. From the above results, ultrafine silver particles with uniformity in shape and size were more easily obtained on the surface not in solutions, which was useful in subsequent applications, i.e., catalysis.
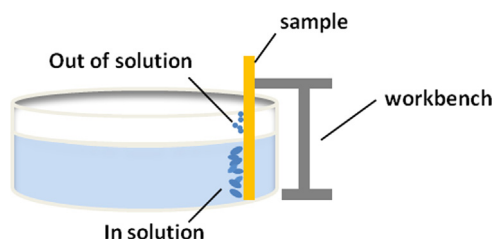

Fig. 1. The schematic image of vertical deposition on Si surface dipped in solutions and the Si surface out of solutions.

Vertical deposition of ultrafine silver particles on the surface not in solutions was considered to be related to wetting of solid–liquid interface and evaporation of ethanol solvent. The wetting effect results in very little precursor solutions being adsorbed slowly onto the surface out of solutions. The size and distribution of ultrafine particles can be influenced by the wetting force which depends on the surface state [16]. Moreover, in the initial stage of the reaction, the ultrafine particles can be taken out by the evaporation of ethanol solvent. In previous studies, the evaporation of ethanol solvent was usually used to explain vertical deposit colloidal crystals [12]. Therefore, in the present study, the ultrafine particles can be easily prepared on the surface not in solutions and their size and shape can be better controlled, which is attributed to the combined interaction of the wetting effect and evaporation of ethanol solvent. Moreover, the size and coverage of silver particles become smaller with increase of distance to the liquid surface. The effective deposition distance out of solution is about 1 cm. The deposition process and surface status play an important role on the distribution of these ultrafine particles, which will be intensively studied in the future.

The silver particles can be used for catalysis etching of nanostructures on Si substrate [21–23]. In solar cells applications, the Si nanostructures can increase the antireflection properties, which in turn improve the efficiency of solar cells. In this work, the catalytic effect of ultrafine silver particles on Si nanostructure was also investigated. Fig. 4 presents the morphology and reflectance of nanoporous Si structures etched by the particles deposited on the surfaces dipped in solutions and out of solutions for 5 min. In Fig. 4(e), the ultrafine porous Si structure etched by ultrafine silver particles out of solutions was smaller and more uniform. Meanwhile, it can be seen from Fig. 4(a) that the ultrafine porous Si decreased the reflectance in the near infrared range, which was attributed to better light scattering of ultrafine porous Si due to the increase of the optical absorption path lengths [24,25]. The effect of scattering on the reflectance is determined by many details of the nanostructure, such as porosity, thickness of the porous layer, the shape of pores, interface roughness and surface area. The results show that the reflectance of the ultrafine porous Si was below 1.6% in the 400–1000 nm range, which is excellent antireflection
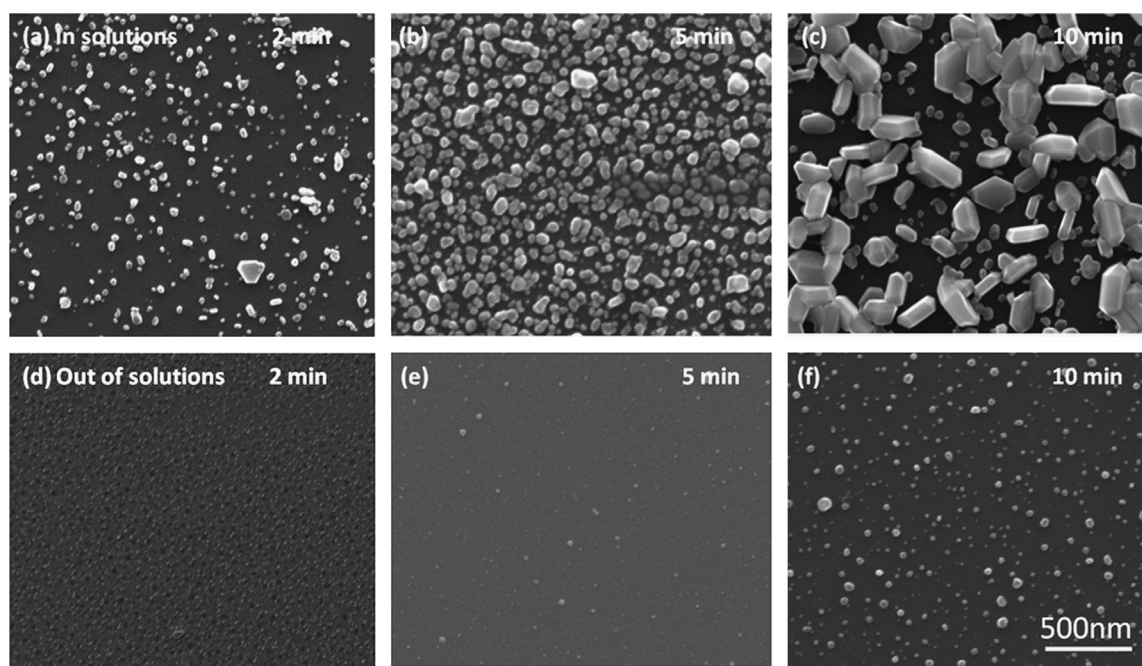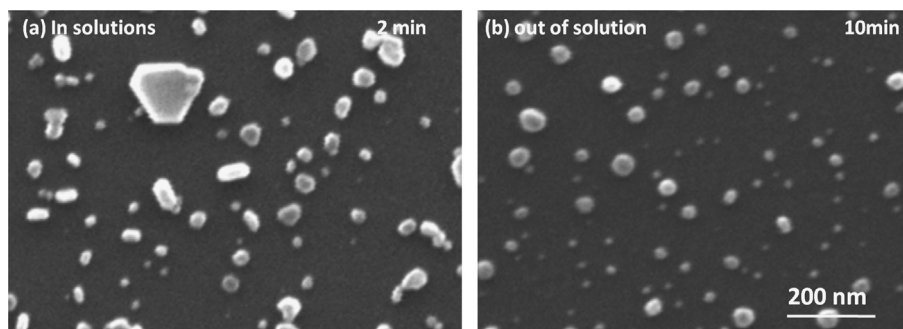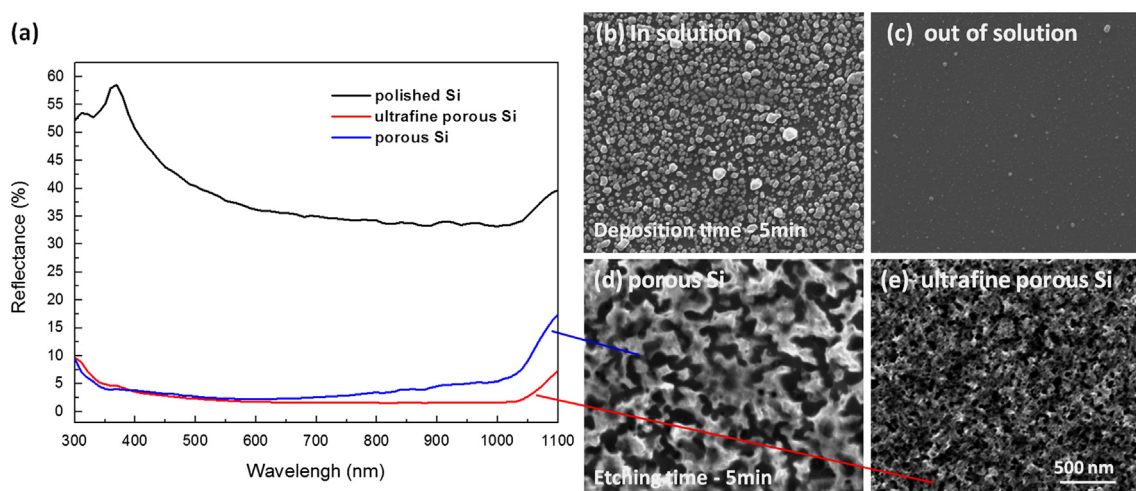

Fig. 2. Morphology of silver particles on Si surface in solutions and out of solutions after vertical deposition. (a)–(c) in solutions for 2 min, 5 min, 10 min and (d)–(e) out of solutions for 2 min, 5 min, 10 min, correspondingly.

Table 1
The size and coverage fraction of particles on the surfaces in solutions and out of solutions.

Deposition time (min)	Surface out of solutions		Surface dipped in solutions	
	Size (nm)	Coverage fraction (%)	Size (nm)	Coverage fraction (%)
2	5–10	2	50	20
5	20	13	70–100	25
10	40	22	200–300	30

Fig. 3. Analogous silver particles on Si surface dipped in solutions and on Si surface not in solutions (a) irregular shaped particles and (b) quasi-round particles.

Fig. 4. The morphology and reflectance of porous Si structures etched by silver particles on the surface dipped in solutions and not in solutions for 5 min (a) the antireflection properties of polished Si, porous Si and ultrafine porous Si and (b)–(e) morphology of silver particles and their corresponding Si nanostructures.

properties in a broader spectral range. For 2 min and 10 min deposition, the obtained nanostructures have the similar antireflection properties. It is considered that the shape and uniformity of particles play an important role in the etching of nanostructures, resulting in the difference in antireflection properties.

4. Conclusions

In summary, the ultrafine silver particles were deposited on Si surface out of solutions by the vertical deposition method. These ultrafine particles were monodisperse, without agglomeration and exhibited uniform size and shape. The facile method can be used in the deposition of silver particles on the surface of materials that cannot be entirely dipped into precursor solutions. In this method, the deposition of ultrafine particles out of solutions was related to the wetting and evaporation of ethanol solvent. The ultrafine porous Si etched by these ultrafine particles displayed better antireflection properties in a broader spectral range, which is useful for improvement of the efficiency of solar cells.

Acknowledgment

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