

A facile direct deposition of silver nanoparticles on silicon surface by silver mirror process

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The Ag nanoparticles with different morphology are directly prepared on Si surface by a facile silver mirror reaction without capping agents and shape-controlling seeds. Ag nanoplates and Ag polyhedrons are produced on the Si surface by controlling the reaction temperature. Ag nanoplates are easily obtained at the low temperature, which are the products controlled by kinetics pathway. Ag polyhedrons are produced at the high temperature under the combined action of the surface energy and strain energy. Through the catalysis of Ag nanoplates and Ag polyhedrons, different nanoporous structures on the Si surface are obtained using the same etching process, which are useful for the antireflection layers in solar-cell devices.

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1. Introduction

In silicon solar-cell applications, nanostructures can enhance the antireflection of Si surface so as to improve the efficiency of solar-cell devices. Recently, a metal-assisted chemical etching technique (MacEtch) has been used to prepare nanostructures on the Si surface [1–11]. In the MacEtch process, the final etching nanostructures are related to the morphology of catalytic metal particles on the Si surface [4,5,10]. Therefore, it is possible to adjust the nanostructures on the Si surface by varying the morphology of the metal particles. Silver is one of the most popular catalysts for the MacEtch process because of its good catalytic properties and low cost. In previous studies, Ag nanoparticles (Ag-NPs) in a variety of shapes were synthesized successfully and their nucleation and evolution mechanisms were proposed [12–21]. However, in most synthetic processes, silver ions are reduced into Ag-NPs with many shapes through introduction of stabilizing agents or shape-selected seeds. When being used in MacEtch, these Ag-NPs act as catalysts and they must be centrifuged, redispersed and recoated on the Si substrate. The processes seem complex and do not constitute a one-step deposition on the substrate. Additionally, stabilizing agents might deactivate catalytic sites. Therefore, in this paper we propose a simple, direct and reproducible synthetic method to control the morphology of Ag-NPs on the Si substrate for etching nanostructures.

Recently, the silver mirror reaction has caught the attention of researchers and was used to produce Ag-NPs, silver surfaces and core-shell structures on substrates for extensive applications [22–27]. The reaction is an “old” chemical route, which was used to quickly generate reflective mirrors on solid surfaces in the past [28]. In this work, Ag-NPs were prepared on a Si surface in a single synthetic step by a silver mirror reaction without any stabilizing agents and shape-controlling seeds. The morphology of Ag-NPs was controlled by varying the reaction temperature.

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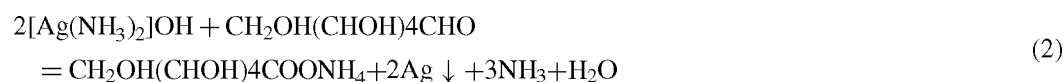
2. Experimental procedure

p-Si (100) single crystal wafers with resistivities of $\rho \sim 7\text{--}13 \Omega \text{ cm}$ were purchased from Emei Semiconductor Factory, China. Single-polished wafers were cut into $1.0 \times 1.0 \text{ cm}^2$ pieces and used for the experiments. Silver nitrate (AgNO_3), glucose ($\text{CH}_2\text{OH}(\text{CHOH})_4\text{CHO}$), aqueous ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28–30% NH_3), hydrofluoric acid (HF, 40%) and hydrogen peroxide (H_2O_2 , 30%) were purchased from Sinopharm Chemical Reagent Beijing Company. All these chemicals were reagent grade and deionized water was used to prepare all the aqueous solutions.

Solid state AgNO_3 powders were dissolved in water and ethanol to form AgNO_3 solutions. The $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ solutions were prepared by continuously dripping aqueous ammonia into the AgNO_3 solution while stirring until the mixtures became colorless. The reaction between AgNO_3 solution and aqueous ammonia is as follow:



The concentrations of $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ aqueous solutions were controlled at 0.02 M. As is well known, the silver mirror reaction actually is a redox reaction, in which the oxidizing $[\text{Ag}(\text{NH}_3)_2]^+$ are reduced to Ag-Nps by glucose with $-\text{CHO}$ aldehyde groups, as shown in Equation (2).



Square polished p-type Si (100) samples of $10 \times 10 \times 0.5 \text{ mm}^3$ were cleaned by dipping in CP-4A solutions (the volume ratio of HF, HNO_3 , CH_3COOH and H_2O is 3:5:3:22.) and sonicating in deionized water. There are many residual defects on Si substrate after cleaning process, which make the Ag-Nps preferentially nucleate on Si substrate. After that, the clean dry Si sample was put into the $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ aqueous solution. Then the glucose (0.01 M) was added into the $[\text{Ag}(\text{NH}_3)_2]\text{OH}$ aqueous solution while carefully stirring to ensure complete mixing. The reactions were kept at the temperature of 4 °C and 60 °C temperature by a water-bath. Thereafter, the Si samples were taken out and washed with deionized water. The morphologies of Ag-Nps on the Si surface were characterized by scanning electron microscope (SEM, FEI Quanta 200F). After characterization, the Si samples with Ag-Nps were immersed into a mixing solution composed of HF, H_2O_2 and H_2O (1:5:2, volume ratio) for 5 minutes at ambient temperature. After the etching process, the Si samples were rinsed with deionized water and then immersed into concentrated HNO_3 for 10 minutes to remove residual silver. After MacEtch process, the Si nanostructures were obtained and then observed by SEM.

3. Results and discussion

The morphology of the Ag-Nps on the Si surface deposited at different temperature were observed by SEM. Figure 1 shows the SEM images of Ag-Nps on the Si surface obtained at 4 °C. Through EDS (Energy Dispersive Spectroscopy) analysis, the bright particles and dark areas in Figure 1 were defined as Ag particles and Si substrate, respectively. When the reaction time was 5 min, most the products were dominated by some small Ag nanoplates, as shown in Figure 1(a). Though the size of Ag nanoplates was not uniform which was ranged between 50–150 nm, the obvious hexagonal and triangular shape can be distinguished from Figure 1(c), (d) and (e). With increase of reaction time, the nanoplates became larger and thicker, as shown in Figure 1(b). In past research, the five-fold twinned rods were prepared on Si surface by the silver mirror reaction at ambient temperature [29]. In the present work, the reaction was controlled at a lower temperature of 4 °C. It is considered that the driving force of different shaped Ag-Nps is growth rate of different crystal facet controlled by different temperature. Obviously, the reaction rate at the low temperature is lower compared with that at ambient temperature. When the reduction is considerably slow, the atoms tend to form nuclei and seeds through random hexagonal close packing (rhcp), together with the inclusion of stacking faults [30]. Inclusion of stacking faults and/or twin planes can lead to the formation of a plate-like seed, which is covered by $\{111\}$ facets at the top and bottom surfaces. Figure 1(f), (g) and (h) show that the typical Ag hexagonal plates with a single twin plane. The reaction pathways of hexagonal and triangular plates are schematically depicted in Figure 3(a). The total free energy of a plate-like seed is intensely high because of the lattice strain energy caused by defects [20]. Therefore, to obtain plate-like seeds, both nucleation and growth must divert from a thermodynamically controlled to kinetically controlled.

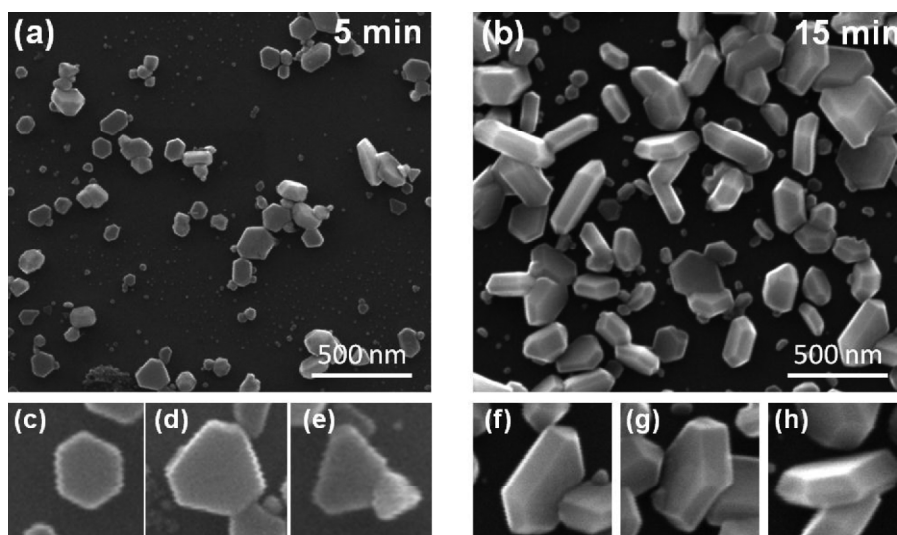


Fig. 1 The morphology of Ag nanoplates on Si surface synthesized at the lower temperature (4 °C). (a) reaction time is 5 minutes; (b) reaction time is 15 minutes; (c)(d)(e) hexagonal and triangular shaped Ag nanoplates; (f)(g)(h) larger and thicker hexagonal Ag nanoplates.

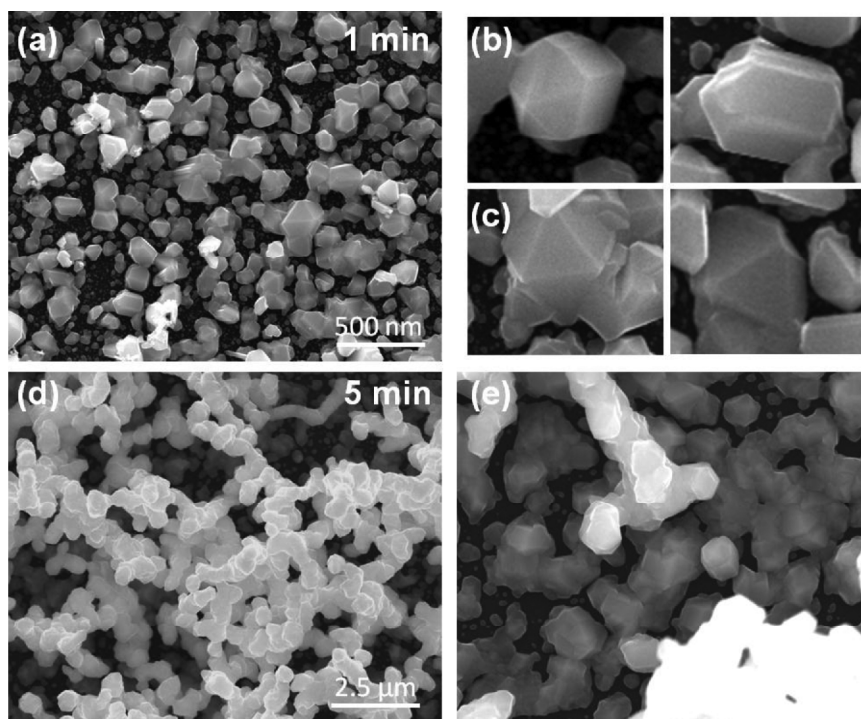


Fig. 2 The morphology of Ag polyhedrons and Ag film on Si surface synthesized at the higher temperature (60 °C). (a) reaction time is 1 minutes; (b) and (c) magnified image of flocculent Ag polyhedrons; (d) reaction time is 5 minutes; (e) magnified image of bottom of Ag film.

pathway. In this paper, as an important factor of kinetics, the decrease of the reaction rate at the low temperature is the reason of plate-like Ag-Nps.

Figure 2 shows the morphology of Ag-Nps on Si surface synthesized at 60 °C using silver mirror reaction. The reaction rate is very high at the high temperature. When the reaction time was one minute, many Ag polyhedrons were obtained quickly, as shown in Figure 2 (a). From magnified images, it was found that the particles were five fold twinned rods (see Figure 2(b)) and five-fold twinned decahedrons (see Figure 2(c)). Through the analysis:

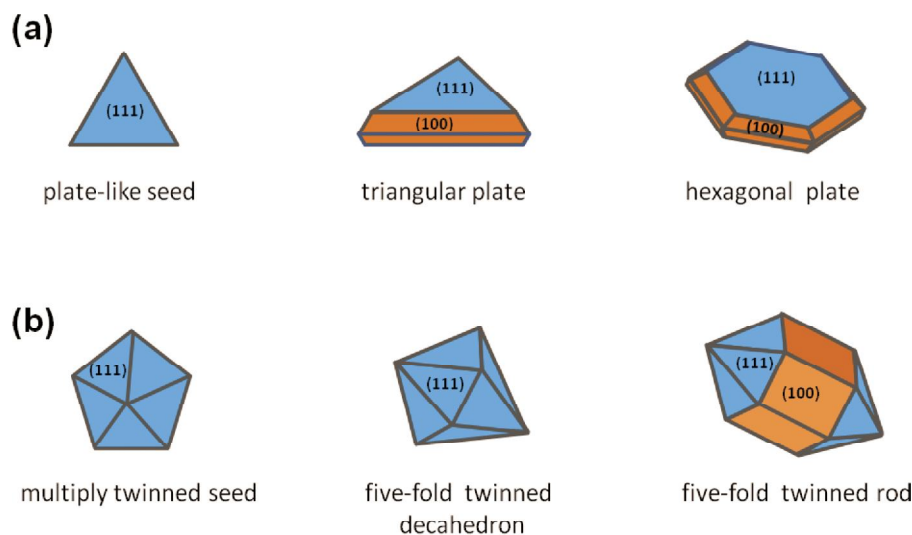


Fig. 3 The schematic image of reaction pathways of Ag nanoplates and Ag polyhedrons. (a) triangular plate and hexagonal plate formed from plate-like seed; (b) five-fold twinned decahedron and five-fold twinned rod formed from multiply twinned seed.

reaction pathways and SEM observation, it is considered that the Ag five-fold twinned rods and five-fold twinned decahedrons are derived from multiply twinned seeds. The schematic images of reaction pathways of five-fold twinned rods and decahedrons are shown in Figure 3(b).

Different from the plate-like seeds, multiply twinned seeds are favored by thermodynamics because they have more {111} planes with the lower surface energy [20]. At the higher temperature the seeds can grow rapidly in size. On one hand, during rapid growth, the multiply twinned seeds prefer to grow along {100} to become rod shape, which can relax the strain energy induced by lateral growth. Therefore, the five-fold twinned rods were observed at the high temperature, as shown in Figure 2(b). On the other hand, the strain energy during lateral growth can be decreased by the higher temperature, resulting in the particles can grow laterally continuously to become five-fold twinned decahedrons. Hence, the shape of Ag-Nps is determined by increase and relaxation of the strain energy induced by lateral growth at the high temperature, which result in the formation of mixture of five-fold twinned rods and five-fold twinned decahedrons, as depicted in Figure 2(c). When the reaction time was increased to 5 minutes, the flocculent Ag film with a slight thickness was observed, as shown in Figure 2(d). Through the observation of the bottom of Ag film, we found that the film was the product of agglomeration of many Ag polyhedrons, as presented in Figure 2(e).

Nanoporous and nanowires on Si surface are as the antireflection layer of solar-cell devices, which can be obtained by Ag-NPs assisted etching. In etching procedure, the nanostructure can be controlled by varying the morphology of catalytic Ag-Nps on substrate [4,5]. In this work, the effect of morphology of Ag on etching structures on Si surface was also investigated. The nanoporous structures etched by Ag nanoplates and Ag polyhedrons were shown in Figure 4. The results show that round porous structures were obtained by etching Ag nanoplates and some transverse grooves were also observed at the surface of round porous structures, as shown in Figure 4(a). From cross-section observation, the most nanoporous were helical along the longitudinal etching direction, as shown in Figure 4(b). Figure 4(c) shows that the quasi-square porous structures were obtained by etching Ag polyhedrons. At the same time, the cross-section shape of quasi-square porous was cone. From above observation, it is found that the morphology of Ag-Nps make a difference to form unique different Si nanostructure when the etching process is the same. The phenomenon is reproducible in our many experiments. The catalytic mechanism of different nanostructures etched by Ag-Nps with different morphology will be intensively studied in the future.

4. Summary

In summary, Ag nanoplates and Ag polyhedrons can be directly deposited on a Si surface by a simple silv mirror reaction at different temperatures without any stabilizing agents or shape-selected seeds. The results shc

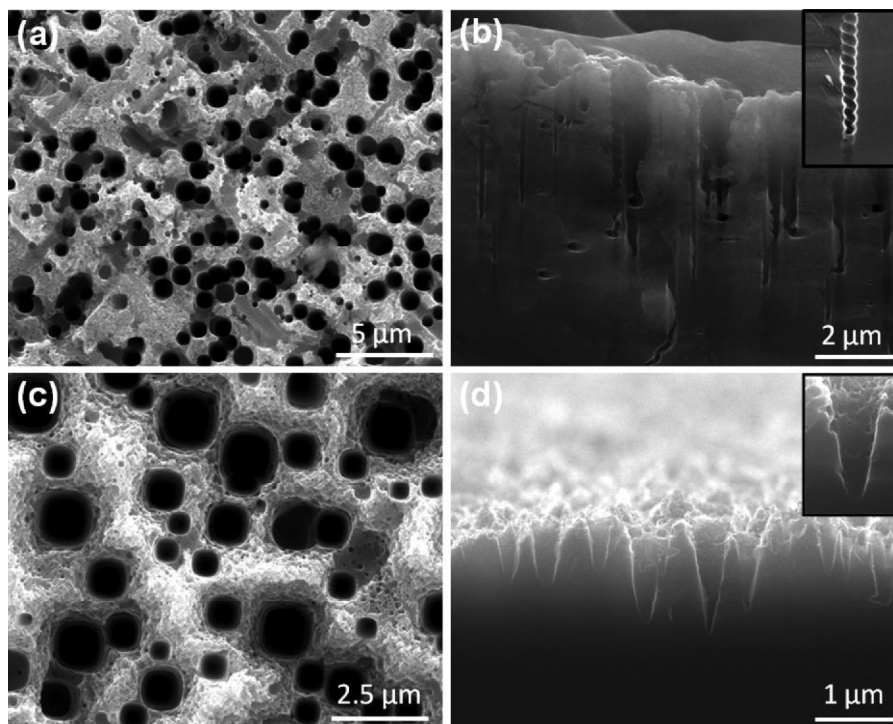


Fig. 4 The SEM images of the nanostructures etched by different Ag NPs. (a) round nanoporous etched by Ag nanoplates; (b) the cross-section of round nanoporous; (c) quasi-square porous etched by Ag polyhedrons; (d) the cross-section of quasi-square porous.

that the morphology of Ag-NPs could be controlled by varying the reaction temperature. Ag nanoplates were easily obtained at 4 °C, while multiply twinned seeds grew to five-fold twinned rods and five-fold twinned decahedrons at the high temperature of 60 °C. The formation of Ag nanoplates was ascribed to the kinetically controlled pathway due to the slow growth at the low temperature. At the high temperature, the surface-energy minimization and strain relaxation of twinned planes led to the formation of five-fold twinned rods and five-fold twinned decahedrons. This paper has provided a simple synthetic process of Ag-NPs with different morphology, which has many advantages, including the one-step chemical procedure, without stabilizing agents or shape-selected seeds, and direct quick deposition on the Si surface. Moreover, the experimental results show that the morphology of the Ag-Nps affected the etching nanostructures on the Si surface. The round helical porous and cone quasi-square porous structures were obtained by etching different Ag-Nps. Different nanostructures can be used to adjust the antireflection properties of the Si surface in solar-cell devices.

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References

- [1] X. Li and P. W. Bohn, *Appl. Phys. Lett.* **77**, 2572 (2000).
- [2] F. Bai, M. Li, R. Huang, D. Song, B. Jiang, and Y. Li, *Nanoscal Res. Lett.* **7**, 1–5 (2012).
- [3] F. Bai, M. Li, D. Song, H. Yu, B. Jiang, and Y. Li, *J. Solid State Chem.* **196**, 596–600 (2012).
- [4] Z. Huang, N. Geyer, P. Werner, J. de Boor, and U. Gosele, *Adv. Mater.* **23**, 285–308 (2011).
- [5] X. Geng, M. Li, L. Zhao, and P. W. Bohn, *J. Electron. Mater.* **40**, 2480–5 (2011).
- [6] H. Park, S. Choi, J.-P. Lee, and S. Park, *J. Mater. Chem.* **21**, 11996–2000 (2011).
- [7] H. Chen, R. Zou, H. Chen, N. Wang, Y. Sun, Q. Tian, et al., *J. Mater. Chem.* **21**, 801–5 (2011).
- [8] S. Yae, Y. Morii, N. Fukumuro, and H. Matsuda, *Nanoscale Res. Lett.* **7**, 352 (2012).

- [9] Z. Huang, X. Zhang, M. Reiche, L. Liu, W. Lee, T. Shimizu, et al., *Nano. Lett.* **8**, 3046–51 (2008).
- [10] M. K. Dawood, S. Tripathy, S. B. Dolmanan, T. H. Ng, H. Tan, and J. Lam, *J. Appl. Phys.* **112**, 073509–8 (2012).
- [11] K.-Q. Peng, X. Wang, and S.-T. Lee, *Appl. Phys. Lett.* **95**, 243112–3 (2009).
- [12] J. Bonsak, J. Mayandi, A. Thøgersen, E. Stensrud Marstein, and U. Mahalingam, *Phys. Status Solidi (c)* **8**, 924–7 (2011).
- [13] J. Zeng, X. Xia, M. Rycenga, P. Henneghan, Q. Li, and Y. Xia, *Angew Chem. Int. Ed. Engl.* **50**, 244–9 (2011).
- [14] B. J. Wiley, Y. Chen, J. M. McLellan, Y. Xiong, Z. Y. Li, D. Ginger, et al., *Nano Lett.* **7**, 1032–6 (2007).
- [15] D. Yu and V. W.-W. Yam, *J. Phys. Chem. B* **109**, 5497–503 (2005).
- [16] H. Liang, H. Yang, W. Wang, J. Li, and H. Xu, *J. Am. Chem. Soc.* **131**, 6068–9 (2009).
- [17] B. Wiley, Y. Sun, B. Mayers, and Y. Xia, *Chemistry* **11**, 454–63 (2005).
- [18] K. A. Eid and H. M. Azzazy, *Int. J. Nanomedicine* **7**, 1543–50 (2012).
- [19] M. M. Mariscal, J. J. Velázquez-Salazar, and M. J. Yacaman, *CrystEngComm* **14**, 544 (2012).
- [20] Y. Xia, Y. Xiong, B. Lim, and S. E. Skrabalak, *Angew Chem. Int. Ed. Engl.* **48**, 60–103 (2009).
- [21] M. Baia, L. Baia, S. Astilean, and J. Popp, *Appl. Phys. Lett.* **88**, 143121–3 (2006).
- [22] R. Dondi, W. Su, G. A. Griffith, G. Clark, and G. A. Burley, *Small* **8**, 770–6 (2012).
- [23] X. Li, J. Shen, A. Du, Z. Zhang, G. Gao, H. Yang, et al., *Colloids Surf., A* **400**, 73–9 (2012).
- [24] Y. Saito, J. J. Wang, D. N. Batchelder, and D. A. Smith, *Langmuir* **19**, 6857–61 (2003).
- [25] L. Shen, J. Ji and J. Shen, *Langmuir* **24**, 9962–5 (2008).
- [26] T. V. Bukreeva, I. V. Marchenko, B. V. Parakhonskiy, and Y. V. Grigor'ev, *Colloid. J.* **71**, 596–602 (2009).
- [27] Z. Xu, J. Hao, F. Li, and X. Meng, *J. Colloid Interface Sci.* **347**, 90–5 (2010).
- [28] A. G. Ingalls. *Amateur Telescope Making (Book One)*. New York: Scientific American Inc. (1981).
- [29] B. Jiang, M. Li, F. Bai, H. Yu, T. Mwenya, Y. Li, et al., *AIP Advances* **3**, 032119–7 (2013).
- [30] V. Germain, J. Li, D. Ingert, Z. L. Wang, and M. P. Pileni, *J. Phys. Chem. B* **107**, 8717–20 (2003).