Fabrication of nanocone arrays by two step metal assisted chemical etching method

AUTHOR NAMES

Tomohiro Shimizu, [1,*] *Norihiro Tanaka,* [1] *Yoshihiro Tada,* [2] *Yasuhiro Hara,* [1] *Noriaki Nakamura,* [3] *Junichi Taniuchi,* [3] *Koichi Takase,* [4] *Takeshi Ito* [1] *and Shoso Shingubara* [1]

AUTHOR ADDRESS

[1]Graduate School of Science and Engineering, Kansai University, Yamate-cho 3-3-35, Suita, Osaka 564-8680, Japan

[2]Muroran Institute of Technology, Mizumoto-cho 27-1, Muroran 050-0071, Japan

[3] Tanaka Kikinzoku Kogyo K.K., Wadai 22, Tsukuba, Ibaraki 300-4247, Japan

[4] College of Science and Technology, Nihon University, Kanda-surugadai 1-8,Chiyoda 101-8308, Japan

CORRESPONDING AUTHOR: Tomohiro Shimizu

AUTHOR EMAIL ADDRESS: shimi@kansai-u.ac.jp

Abstract

This work develops a novel method for preparing a moth eye structure, which has a sub-wavelength periodical Si nanocone structure on Si (100) substrate, using two-step metal assisted chemical etching (MACE). The 1st and 2nd MACE were respectively performed with the intention to form perpendicular Si nanowire arrays on a Si substrate and sharpening the Si nanowire arrays. We found the inhomogeneous absorption and aggregation of Au particles used as a catalyst for 2nd MACE was important to obtain the nanocone shape. The obtained Si nanocone arrays showed superior anti-reflecting properties especially in wavelength below 600 nm compared to the Si nanowire arrays. A possible mechanism involved in the formation of the nanocone structure by the 2-step MACE is discussed in this paper.

1. Introduction

Existing in nature, several unique surfaces based on high aspect ratio nanostructure arrays possess special features[1–7]. For instance, the surface of cicada wings[2–4] and moth eyes[5,6] consist of nanoscale cone-like structure indicate a killing action on bacteria and a quite low reflectance in visible range, which are potentially considered applications as an anti-bacterial coating and an anti-reflection layer for the photovoltaic cells. Therefore, reproduction of nanocone structure using an artificial method is one of the interesting issues on the biomimetic field. In the previous study, there are several methods have been demonstrated to prepare Si nanocone structures using top-down and bottom up techniques, such as conventional dry etching[8,9], vapor liquid solid growth (VLS)[10] and chemical etching method[11,12]. Among of them, the metal assisted chemical etching (MACE) is one of the promising method for mass production of Si nanostructures because it is a simple and low cost method to fabricate nanostructures with controlled shape[13,14]. There are many reports about formation of Si nanowire arrays[6,15–17] but few studies report the fabrication of Si nanocone structure using MACE[11]. The previous report about preparation of nanocone mainly focused on the modification of etching solution during MACE process. In this study, we focused on morphology of etching catalyst for MACE, and demonstrated a new approach to prepare Si nanocone arrays by 2 step MACE technique using Au nanoparticles.

2. Sample Preparation

The Si nanocone arrays were prepared by a two - step MACE technique. We used Si (100) substrates (*p*-type, 1-10 Ω cm) cut into 30 x 30 mm^2 in the experiments. At first,

the Si substrates were degreased with acetone and propanol using an ultrasonic bath for 10 min, respectively. Then, the Si substrates were immersed for 30 min in piranha (volume ratio 4:1= H_2SO_4 : H_2O_2) and RCA (volume ratio 1:1:5=NH_3 : H_2O_2 : H_2O) solution maintained at 75 ^oC to form a hydrophilic surface. Subsequently, the Si substrates were rinsed several times in deionized water.

Fig1 (a)-(g) show schematics of the sample preparation procedure. The 1st MACE was performed to form vertically aligned Si nanowire arrays on a Si substrate with anti-dot patterned Au catalyst, which was prepared by PS spheres lithography technique[16]. The PS sphere with average diameter of 500 nm were used in this experiments (Polysocience Inc. Polybead Polystyrene Microspheres 2.5% Solids-Latex: 3.64 × 10^{11} / ml). The PS sphere solution was dropped on the hydrophilic Si surface and dried at room temperature, and a close-packed PS monolayer array was formed on the Si substrate (Fig. 1(a)). The average diameter of PS spheres was reduced from 500 nm to 300 nm by reactive ion etching (RIE) treatment under O_2 flow of 30 sccm and power of 30 W for 85 sec. Thus a space was created between the shrunk PS spheres as shown Fig.1 (b). 30 nm of Au was deposited on the PS arrays on Si substrate by DC sputtering, and Au anti-dot pattern was formed on the Si substrate using PS sphere arrays as a sputter mask (Fig. 1 (c)). For the MACE process, a mixture of hydrofluoric acid (HF), hydrogen peroxide (H_2O_2) and deionized water with volume ratio of 15: 2: 83 was used. The 1st MACE was carried out for 12 min at room temperature, and vertical nanowire arrays were formed on Si substrate (Fig. 1 (d)). After 1st MACE, the Au anti-dot pattern and PS spheres were selectively etched away (fig. 1(e)) by doubling diluted aqua regalis (volume ratio 1:3:4 = HCl : HNO_3 : H_2O) and piranha solution, respectively.

The 2nd MACE was conducted for the Si nanowire arrays with Au nanoparticles. Polyvinylpyrrolidone (PVP) coated and uncoated colloidal Au nanoparticles with average diameter of 20 nm were used as an etching catalyst. For comparison, the Si nanowire arrays prepared by 1st MACE were immersed into the two kinds of colloidal Au nanoparticle solutions for 30 min at room temperature, respectively. Then the Si nanowire arrays were decorated with Au nanoparticles (Fig. 1 (f)). Subsequently, 2nd MACE was carried out with the same solution used in 1st MACE for 10 min at room temperature, and the Si nanocones arrays were obtained (Fig. 1(g)).

The morphology of the samples was observed by scanning electron microscopy (SEM: JEM-7500F, JEOL) with an energy dispersive X-ray analysis (EDX) measurement system. A UV- vis spectrophotometer (Jasco, V-650) was used to measure the reflectance properties of samples. The incident angle of light for reflectance measurements was 5^{o} tilted from normal to the surface of the substrate, and 5 x 5 mm^2 area on the sample surface was measured. The reflectance measurements were performed five times at different area on the each sample.

3. Results and Discussion

Fig. 2 (a) and (b) show SEM images of Si nanowire arrays after 1st MACE and selective dissolution of the PS spheres. Self-standing Si nanowire arrays with average diameter of about 300 nm were observed in Fig.2 (a), and each wire showed perpendicular to the Si (100) substrate. In Fig. 2 (b), hexagonally ordered Si nanowire arrays with average diameter of about 300 nm were observed. An inter-wire distance, which is a center to center distance of a nearest neighbor of the Si nanowires, were 500 nm.

The cross-sectional SEM images of the Si nanowire arrays after absorption of Au nanoparticles are shown in Fig. 3. For comparison, we used two types of Au nanoparticles with and without PVP. PVP is commonly used as a dispersing agent to avoid aggregation of metal nanoparticles [18,19]. In Fig. 3 (a) and (b), most of adsorbed Au particles without PVP were concentrated around top of the nanowires, and they were strongly aggregated each other. In contrast, the adsorbed Au nanoparticles with PVP were widely distributed along the length of the Si nanowires, although density of the nanoparticle gradually decreased from top to bottom of the Si nanowires, as shown in Fig. 3(c) and (d). During the Au adsorption process, the Au particles were supplied from above the nanowire arrays, and preferred to adsorb around the top of the nanowire. This tendency was observed in both samples with exception of a certain difference.

Fig. 4 shows SEM images of Si nanowire arrays after 2^{nd} MACE using Au nanoparticles (a) without and (b) with PVP as catalysts for the etching. Although the etching duration of 1^{st} and 2^{nd} MACE for both samples was the same, a distinct difference was observed in their morphology. The Si nanowires etched with Au particle without PVP were strongly tapered especially at the tip section and exhibited a cone-like shape. The aggregated Au nanoparticles were observed at the top of nanocone structure indicated as arrow in the Fig. 4 (a). Moreover, the tapered angle of the nanocone gradually changed along the length direction, and the tapered angle got lager near the top of the nanocone. On the other hand, the samples using Au particles with PVP appeared slightly tapered nanowires but many nanopores were observed on the surface as shown in Fig. 4 (b). Additionally, the diameter at the bottom part of nanocone was decreased after 2^{nd} MACE. These morphological differences between the two samples imply that etching shape of Si during MACE strongly depends on the condition of

adsorbed Au nanoparticles.

Generally, MACE can be explained as a microscopic electrochemical cell at the Si surface with metal a catalyst a particle in the mixture of HF and H_2O_2 solution. [13,14,20]. Fig. 5 (a) and (b) show scheme of the the MACE process using Au nanoparticles on a Si substrate. The MACE process is initiated by the reduction of H_2O_2 at a cathode.

$$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+ \qquad (1)$$

Due to high catalytic activity at the metal particle compared with Si surface, the reaction mainly occurs at the surface of the metal particle. The electrons are transferred from surface of the metal particle to H_2O_2 in the solution as a result of the reaction (1),

At the anode, the Si substrate is oxidized and dissolved. The reaction can be expressed as follows,

$$Si + 4h^+ + 6HF \rightarrow SiF_6^{2-} + 6H^+ \qquad (2)$$

For successive oxidation and dissolution of Si, a continuous supply of charges and chemicals to the etching point is necessary. The electrons in the Si substrate are transferred into the metal particle, and the reaction (1) consumes electrons at the surface of the metal particle. Then, holes injection occurs into the Si substrate at the surface under the metal, since the oxidative dissolution of Si surface preferentially occurs, consuming holes, near the interface between Si and metal. Most of holes are consumed at the Si surface under metal due to oxidative dissolution of Si indicated as reaction (2).

However, some excess holes, which are not consumed at the Si surface under metal diffuse in the Si substrate. The diffused holes are used for oxidative dissolution of Si, away from meal catalyst[13]. The diffused holes usually increased with increased in reaction (1) using etching solution containing high concentration oxidant agent of H_2O_2[11].

In our experiments on the 2nd MACE using Au nanoparticles without PVP, the nanoparticle adsorbed inhomogeneously and aggregated each other on the Si nanowires as shown in Fig.6 (a). The degree of aggregation of Au nanoparticles at the top of the nanowires is higher than at that bottom. The aggregated Au particles exsist larger surface ratio (Au surface area per surface area of Si beneath the Au) than the isolated single nanoparticle due to the 3-dimentional porous structure. This large surface ratio of Au catalyst allows a larger amount of the chemical reaction indicated as equation (1) per unit area of Si surface, and the number of injected positive holes into the Si substrate is also increased under the aggregated Au particles as shown in Fig. 5(b). Therefore, reaction (2) could be enhanced and etching speed was accelerated at the Si surface under the aggregated Au particles. In fact, a previous study also reported a faster etching speed of Si using aggregated Au particles than with the use of single particle [13]. The Si etching would occur not only in length direction but also in the diametrical direction of the nanowire. Then, the gold particles was further aggregate around top of the nanowire during 2nd MACE, and finally only one large aggregate of Au particles at the top of nanocone was observed as shown in fig. 4(a). Moreover, the aggregated Au particle has produced many excess injected holes in the Si nanowire, and the holes diffused from top downward. The diffused holes etched the Si nanowire in the diametrical direction, away from the aggregated Au nanoparticles. The concentration of

the injected holes gradually decrease from top to bottom as shown Fig.6 (a), and the etching rate of Si in the diametrical direction also gradually decreased depending on the distance from the aggregated Au particles around the top of the nanowire. Therefore, tapered cone shapes and aggregated Au particle on the top of the nanocone were finally formed, as shown in Fig. 6 (b). In the case of 2nd MACE with Au particles with PVP, the adsorbed Au particles were widely distributed on the surface of the Si nanowire. The differential of concentration of injected holes along the length direction would be smaller, and the taper angle of the nanocone was finally small.

The each sample with the nanostructure showed homogenous dark color at the surface, and reflectance spectra measured at different part on the sample indicated almost similar. Fig 7 shows the typical optical reflection spectra of Si (100) with various structure on the surface. The reflectance spectra at the different point. The length and diameter of the Si nanowires were 1.5 μm and 300 nm. The measured Si nanocone arrays were prepared using Au nanoparticles without PVP, and the length and diameter at the bottom were 1.2 μm and 300 nm, respectively. Both of nanowire and nanocone samples exhibited lower reflectance the whole measured wavelength region than the polished Si substrate. In addition, the reflectance of the Si nanocone arrays especially showed superior anti-reflecting property in the wave length region below 600 nm compared with Si nanowire arrays. These results indicated that the nanocone arrays prepared by 2 step MACE method were equipped with anti-reflecting function as a moth eye structure. However, the reflectance of the nanocone arrays is still higher than the reflectance of previously reported Si nanowire arrays in visible range[21,22]. The optimization of size and shape of the nanocone arrays is necessarily to realize further low reflectance.

4. Conclusions

In conclusion, with the present work we demonstrated the formation of Si nanocone arrays by a 2 step MACE method using Au nanoparticles as the catalyst for the 2nd MACE. Inhomogeneous adsorption and aggregation of Au nanoparticle on the surface of nanowire arrays was important to determine a morphology of nanocone arrays. The nanocone arrays exhibited lower reflectance compared to nanowire arrays, especially at shorter wavelength.

Acknowledgements

This work was supported by KAKENHI Grant Numbers 25790024, 25600048 and 15K04602 from the Japan Society for the Promotion of Science (JSPS), Strategic Project to Support the Formation of Research Bases at Private Universities: Matching Fund Subsidy from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), and Kansai University Subsidy for supporting Young Scholars 2013.

Reference

[1] A. Marmur, Langmuir 20 (2004) 3517–3519.

[2] E.P. Ivanova, J. Hasan, H.K. Webb, G. Gervinskas, S. Juodkazis, V.K. Truong, A.H.F. Wu, R.N. Lamb, V.A. Baulin, G.S. Watson, J.A. Watson, D.E. Mainwaring, R.J. Crawford, Nat. Commun. 4 (2013) 2838.

[3] Y. Uang, Y. Jen, L. Chen, K. Chen, S. Chattopadhyay, ACS Nano 9 (2015) 301–311.

[4] S. Pogodin, J. Hasan, V.A. Baulin, H.K. Webb, V.K. Truong, T.H.P. Nguyen, V. Boshkovikj, C.J. Fluke, G.S. Watson, J.A. Watson, R.J. Crawford, E.P. Ivanova, Biophys. J. 104 (2013) 835–840.

[5] D.G. Stavenga, S. Foletti, G. Palasantzas, K. Arikawa, Proc. R. Soc. B 273 (2006) 661–667.

[6] S. Chattopadhyay, Y.F. Huang, Y.J. Jen, A. Ganguly, K.H. Chen, L.C. Chen, Mater. Sci. Eng. R Reports 69 (2010) 1–35.

[7] G.S. Watson, J.A. Watson, Appl. Surf. Sci. 235 (2004) 139–144.

[8] J. Liu, M. Ashmkhan, B. Wang, F. Yi, Appl. Surf. Sci. 258 (2012) 8825–8830.

[9] S.A. Boden, D.M. Bagnall, Appl. Phys. Lett. 93 (2008) 133108.

[10] Y. Wang, V. Schmidt, S. Senz, U. Gosele, Nat. Nanotechnol. 1 (2006) 186–189.

[11] T. Hwang, G. An, J. Lim, N. V Myung, Y. Choa, Jpn. J. Appl. Phys. 53 (2014) 05HA07.

[12] S.A. Boden, D.M. Bagnall, Prog. Photovolt Res. Appl. 18 (2010) 195–203.

[13] C. Lee, K. Tsujino, Y. Kanda, S. Ikeda, M. Matsumura, J. Mater. Chem. 18 (2008) 1015–1020.

[14] Z. Huang, N. Geyer, P. Werner, J. De Boor, U. Gösele, Adv. Mater. 23 (2011) 285–308.

[15] K.Q. Peng, Y.J. Yan, S.P. Gao, J. Zhu, Adv. Mater. 14 (2002) 1164–1167.

[16] Z. Huang, H. Fang, J. Zhu, Adv. Mater. 19 (2007) 744–748.

[17] Z. Huang, X. Zhang, M. Reiche, L. Ltu, W. Lee, T. Shimizu, S. Senz, U. Gösele, Nano Lett. 8 (2008) 3046–3051.

[18] M. Chen, Y. Xing, Langmuir 21 (2005) 9334–9338.

[19] S. Du, K. Kendall, P. Toloueinia, Y. Mehrabadi, G. Gupta, J. Newton, J. Nanoparticle Res. 14:758 (2012) 1–14.

[20] X. Li, P.W. Bohn, Appl. Phys. Lett. 77 (2000) 2572.

[21] K. Peng, Y. Xu, Y. Wu, Y. Yan, S.-T. Lee, J. Zhu, Small 1 (2005) 1062–1067.

[22] T. Yamaguchi, T. Shimizu, Y. Morosawa, K. Takase, T. Chen, Jpn. J. Appl. Phys. 53 (2014) 06JF10.

Figure captions

Fig. 1 Cross section schematics of sample preparation procedure. (a) PS sphere arrays on Si substrate. (b) PS spheres after O_2 plasma etching. (c) Formation of Au anti-dot pattern using the PS sphere arrays as a sputter mask. (d)1st MACE using anti-dot Au pattern as an etching catalyst. (e)Selective etching of Au and PS. (f)Au nanoparticle adsorption on Si nanowire arrays.(g)2nd MACE using Au nanoparticle as an etching catalyst.

Fig. 2 (a) cross-sectional and (b) top-view SEM images of Si nanowire array after 1st MACE and selective dissolution of the PS spheres.

Fig. 3 The cross-sectional SEM images of the Si nanowire arrays after adsorption of Au nanoparticles (a) without and (c) with PVP. Enlarged images of top of nanowires (b) without PVP and (d) with PVP

Fig. 4 Si nanowire arrays after 2nd MACE using Au nanoparticles (a) without and (b) with PVP as a catalyst for the etching.

Fig. 5 Cross-sectional scheme of etching process involving metal assist of etching on the Si substrate. (a)Initial stage of MACE with isolated Au nanoprticle. (b)Initial stage with aggregated Au nanoparticles. Arrow indicates direction of holes diffusion flow.

Fig. 6 Cross-sectional scheme of etching process of the Si nanowire with aggregated Au particles adsorbed around top of nanowire. (a)Initial stage of MACE and (b) after etching.

Fig. 7 Reflectance spectra for Si surface with various nanostructures.

Figures

Fig. 1

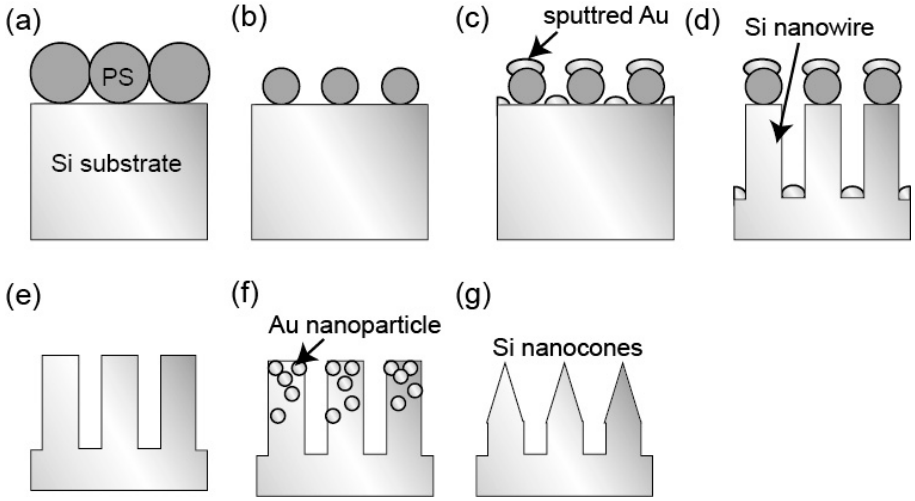


Fig. 2

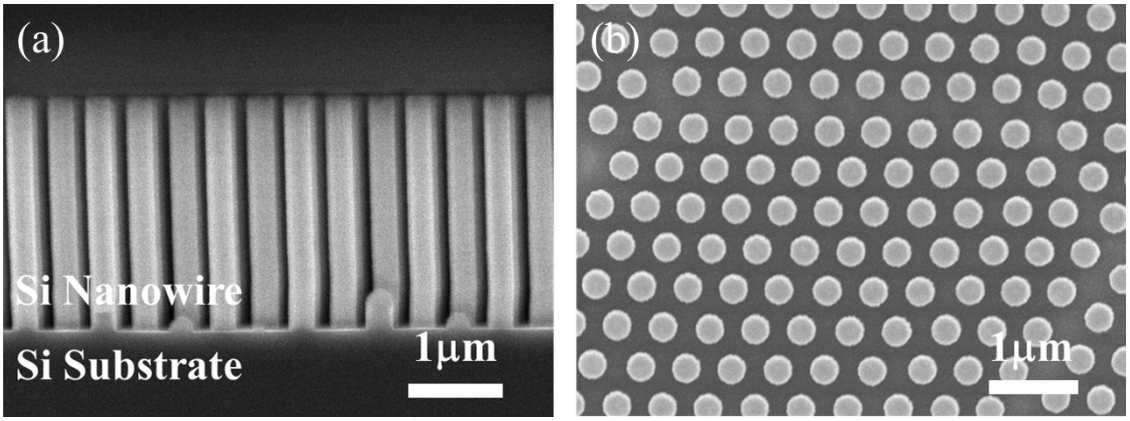


Fig. 3

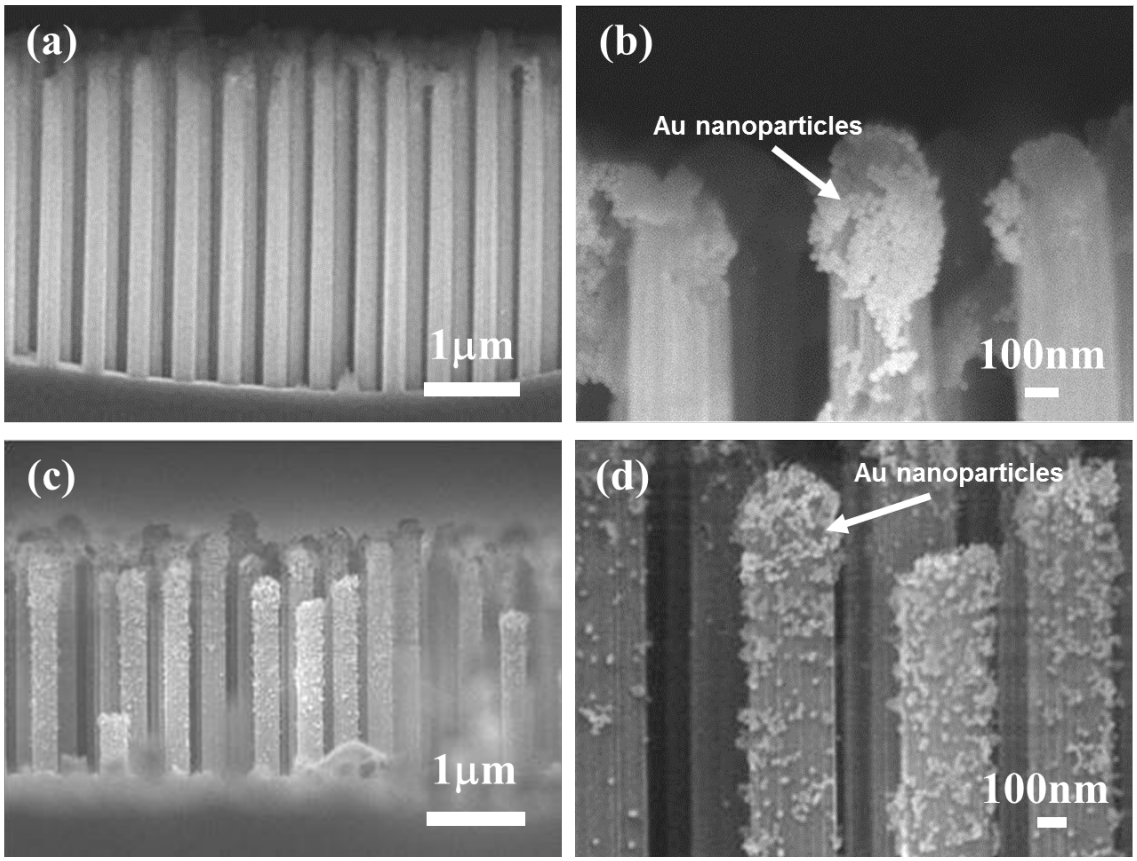

(a)
1μm
(b)
Au nanoparticles
100nm
(c)
1μm
(d)
Au nanoparticles
100nm

Fig4

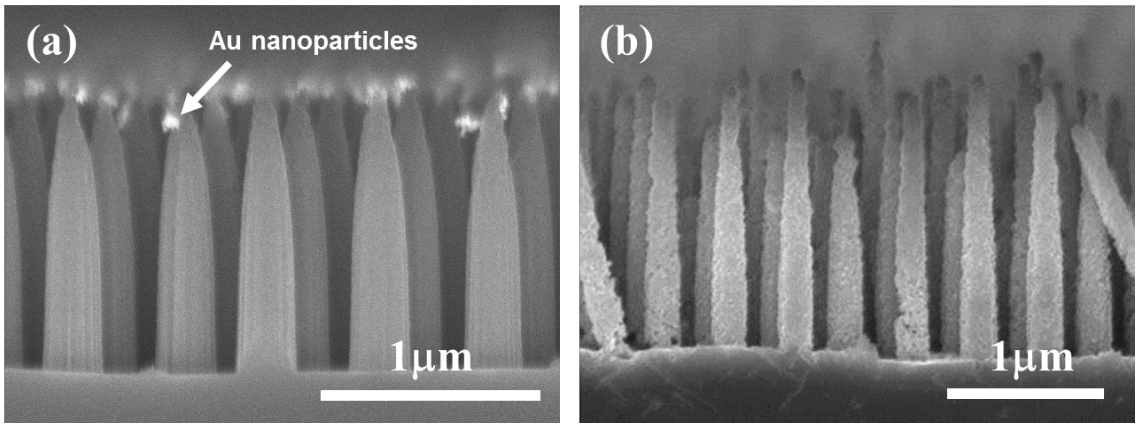

(a)
Au nanoparticles
1μm
(b)
1μm

Fig. 5

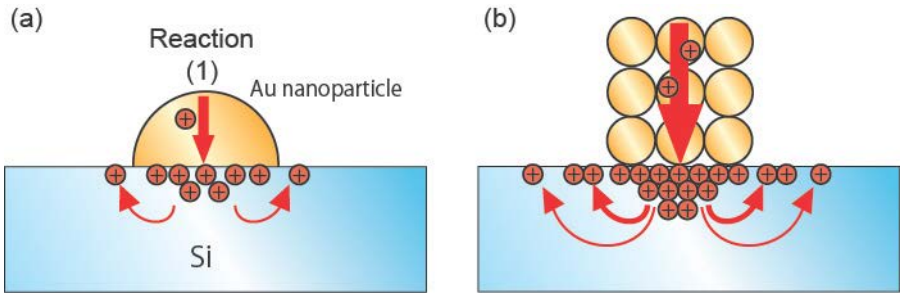

(a)
Reaction
(1)
Au nanoparticle
Si
(b)

Fig. 6

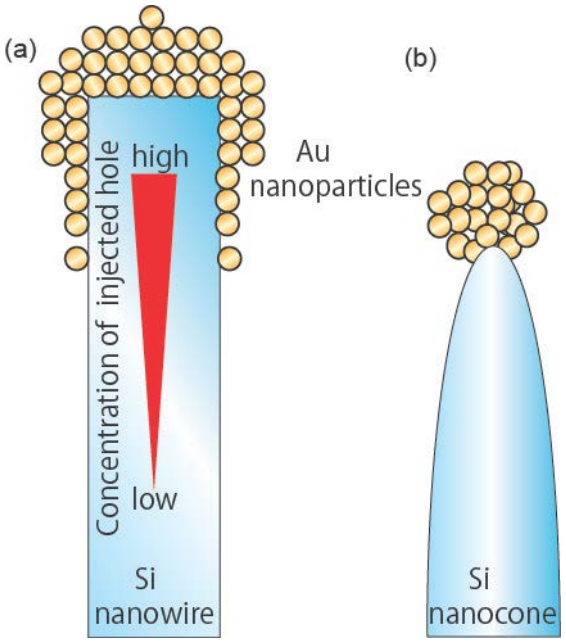
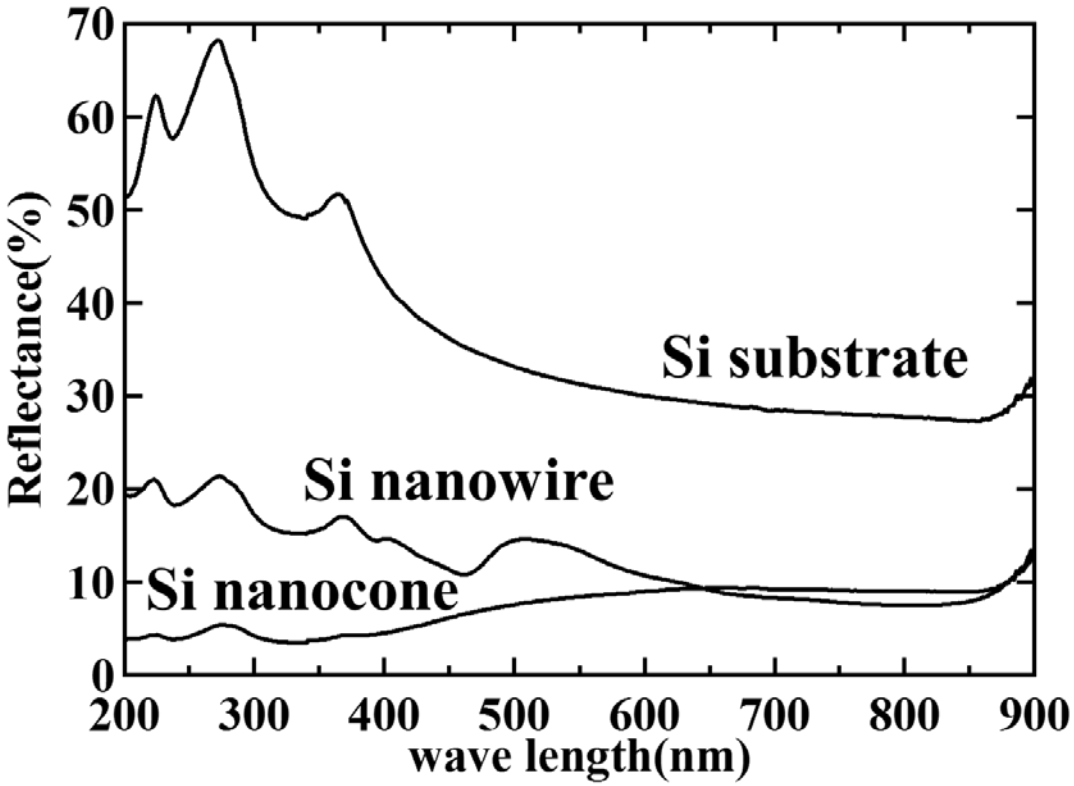

(a)
high
Concentration of injected hole
low
Si
nanowire
Au
nanoparticles
(b)
Si
nanocone

Fig. 7


Reflectance(%)
70
60
50
40
30
20
10
0
200
300
400
500
600
700
800
900
wave length(nm)
Si substrate
Si nanowire
Si nanocone