Using self-assembled nanoparticles to fabricate and optimize sub-wavelength textured structures in solar cells.

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ABSTRACT

In this study, we demonstrated the textured structure on silicon surface by metal assisted etching method, using Au nanoparticles as catalysts in HF and H_2O_2 solution. The size and density of the nanoparticles could be tuned easily. The porous layers filled with cylinder- or cone-shaped were uniformly formed by immersing the gold deposited silicon wafers in a mixed solution containing HF and H_2O_2 under different etching conditions. The optimized textured structure was close-packed pyramids-like surface in subwavelength scale and showed the lowest reflectance less than 0.5% over whole visible and near IR wavelengths. The large reduction of reflectance was attributed from the gradient refractive index of the silicon surface with the depth along the light propagation.

Keywords: antireflective layer, silicon solar cells, gold nanoparticles, acidic wet etching, subwavelength textured surface.

1. INTRODUCTION

Nowadays, it becomes more and more important to develop new substitute energy technologies because of the shortage of energy. It should be noted that current production of solar cells is dominated by crystalline silicon modules because of their mature fabrication techniques and relatively high efficiency; however, due to the high refractive index of silicon, more than 40% of incident light is reflected back, which greatly reduces the conversion efficiency of photovoltaic devices. Thus, light trapping is an important method of increasing the efficiency of crystalline silicon solar cells. Several techniques such as the surface antireflection coating thin films (ARC) and textured structures have been used for the same purpose.[1] Previously some techniques for texturing silicon have been demonstrated. Some have focused on the use of dry etching process.[2], [3], either in conjunction with a mask to achieve large, regular features [4], or without a mask to produce much smaller and more random texture. We also previously reported that combining subwavelength-scale monolayer and bilayer polystyrene spheres with a one-step RIE process, to fabricate optimized pyramid- and honeycomb-shaped antireflection structures.[5] However, most of these existing techniques are expensive to implement, impeding development of solar cells that can be made truly economically competitive with fossil fuels.

Other approaches have been based on wet etching processes. Texturization by anisotropic etching with an alkaline solution, such as KOH or NaOH, is generally used for the fabrication antireflection structure in single crystalline silicon.[6], [7] Anisotropic etching cannot uniformly form optimal textured structures in multicrystalline silicon, which is the main material of present solar cells. Wet acidic processes including of chemical etching using solutions containing HF/HNO_3 or electrochemical anodic etching under anodic bias that tend to etch isotropically can result in features with rounded or cylinder-like porous surfaces.[8]-[10] Except these, metal-assisted etching has been studied as another method for production of porous structures in multicrystalline silicon.[11]-[15] In this method, fine metal particles loaded on silicon wafers are used as catalysts for etching of silicon in aqueous solutions containing HF and oxidants such as H_2O_2 without the need of external electrical power. Because of the simplicity of this method compared to the common techniques described above, the method is promising for application to mass production if efficient control of the geometrical structure is achieved.

Recently, Yae *et al.* reported the porous silicon as an antireflection layer of solar cells was fabricated by metal assisted chemical etching in a pure HF solution for 24 hours.[11], [12] The size and particle density of the platinum particles loaded on silicon wafers by electroless displacement deposition were 20-240 nm in diameter and about only 10

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particles μm^{-2}. This method successfully reduced the reflectance of the silicon wafer to 6%. However, the optimization of antireflective structures was difficult due to the limitation of electroless displacement deposition. Moreover, etching by pure HF solution makes the reaction time too long for massive industry application. Here, we report the optimization of the porous textured structures on silicon wafers using presynthesized Au nanoparticles as catalysts in HF/H_2O_2 solution. We also control the density of Au nanoparticles by varied deposition time of that and etching conditions to obtain minima reflection.

2. EXPERIMENTAL

In the experiments, the following materials were obtained from ACROS: $HAuCl_4 \cdot 3H_2O$, trisodium citrate dihydrate, (3-aminopropyl)trimethoxysilane (APTMS), 30% H_2O_2, 50% HF aqueous solution. Si (100) wafers obtained from Summit-Tech Co. The wafers were cut into 1 X 1 cm pieces as test samples and were cleaned by following procedures. The samples were immersed in sulfuric acid-hydrogen peroxide mixture (97% H_2SO_4:30% H_2O_2 = 4:1, in volume) for 10 min, then rinsed with ultrapure water (UPW >18 MΩ cm) for 10 min. Au nanoparticles were prepared by sodium citrate reduction of $HAuCl_4 \cdot 3H_2O$ [16]. Typically, in a 1 L round-bottom flask equipped with a condenser, 50 mL of 1 mM $HAuCl_4$ was brought to a rolling boil with vigorous stirring. Rapid addition of 5 mL of 38.8 mM sodium citrate to the vortex of the solution resulted in a color change from pale yellow to burgundy. Boiling was continued for 10 min; the heating mantle was then removed, and stirring was continued for an additional 15 min. After the solution reached room temperature, it was filtered through a 0.2 μm Gelman membrane filter and stored at 4 °C. The solution of colloidal particles was characterized by an absorption spectrum and found maximum at 520 nm. Derivatization of silicon substrates with APTMS was accomplished in the following manner: clean substrates were immersed in a 2% (v/v) solution of APTMS in boiling anhydrous ethanol for 45 min. The substrates were removed and rinsed profusely with methanol to remove unbound monomer from the surface. At this point, silanized substrates were stored in methanol until needed. Prior to derivatization with colloidal Au, the substrates were rinsed with UPW; they were then immersed in vials of colloidal Au for 15, 30, 60 min. Then, Au nanoparticles-deposited substrates were spun at 3000 rpm for removing excess nanoparticles. A final UPW rinse concluded the derivatization process. The substrates were dried and stored in atmosphere until be further use. After the deposition of Au nanoparticles, the silicon samples were rinsed in UPW for 2 min, then etched in aqueous solutions containing HF and H_2O_2 for 5, 20, 40, 60 min. We used a mixed solution of 50% HF, 30% H_2O_2, and H_2O at a volume ratio of 2:1:8. Etched samples were successively rinsed with UPW, ethanol, each for 3 min, and dried in air. All the processes were performed at room temperature and the etching were carried out in the dark. Morphologies of the samples were observed with a scanning electron microscope (SEM), (JEOL, JSM-6500F). The cross-sectional views were obtained for the surfaces which were exposed by mechanically cleaving the sample after having scribed the back side with a diamond scriber. The optical properties were measured using an optical spectrometer (Hitachi, U-4100).

3. RESULTS AND DISUSSION

Au nanoparticles were deposited on the silicon wafer, which was modified with alkoxysilane molecules with NH_2 end group, via chemical adsorption after immersing the silicon wafer in the colloid solution. Colloidal Au nanoparticles can be prepared by sodium citrate reduction method with high monodispersity. The density of Au nanoparticles on the silicon surface was varied by tuning the immersion time. Fig. 1(a)~(c) show the SEM images of Au nanoparticles deposited on silicon wafers before wet etching. The size of Au nanoparticles was between 10 and 50 nm and the density was about 280, 350 and 450 /μm^2 with immersion time of 15, 30 and 60 minutes respectively. Fig. 1(a) shows that Au nanoparticles were massively adsorbed on silicon surface with slightly long distance between each other, when the immersion time was only 15 minutes. As increasing the immersion time to 30 minutes, more Au nanoparticles were adsorbed with shorter distance between them (Fig. 1b). As shown in Fig. 1c, the amount of Au nanoparticles was almost saturated however no aggregation of particles were seen. It indicated that most Au nanoparticles were located with all the others closely but separately after immersion for 60 minutes. After loading the silicon wafers with Au nanoparticles, they were etched in aqueous solution containing of HF and H_2O_2. Fig. 1(d)~(f) show the SEM top-view images of these textured silicon surface, a similar porous layer with pore sizes of a range between 100 and 2000 nm was observed in all images. It is interesting that the size of these pores were ten folds to hundred folds larger than the size of Au nanoparticles pre-deposited on silicon wafers. Moreover, tens of Au nanoparticles aggregated and remained on the surface or in the shallow pores (see Fig. 1d), through they were isolated before being immersed in the etching solution.

In addition, Fig. 1d shows that the surface morphology between the pores was slightly rough, because the space in between Au nanoparticles, as catalyst, was somewhat large. However, close-packed Au nanoparticles would result in the pores strongly overlapping to form drastically rough surface as shown in Fig. 1e-f.

In order to realize the relation between the morphology of the textured silicon surface and metal-assisted etching process, we fixed the immersion time in the Au nanoparticles solution and studied the change of morphologies with varied etching time in the HF/H_2O_2 solution. Fig. 2 shows the SEM images of these textured silicon surface with varied etching time. When a sample was etched in the HF/H_2O_2 solution for 5 minutes (see Fig. 2a), two kinds of pore sizes were observed over the sample surface, including of micropores similar to the isolated Au nanoparticles (< 50 nm), and mesopores a few folds larger than the former ones (~ 100 nm). For the longer etching time (20 minutes), micropores disappeared observably and mesopores connected with the each others, further forming larger macropores (100-500 nm) as shown in Fig. 2b. It should be noted that some sharp peaks of silicon, located in the connect spots between the macropores, and few aggregative/isolated Au nanoparticles were observed. As shown in Fig. 2c (etching for 40 minutes), no micropores and Au nanoparticles appeared, however some deeper mesopores and a few shallower macropores still exhibited. It seems likely that these Au nanoparticles sunk into these pores. Finally, when a sample was etched for 60 minutes, the mesopores were apart from the each others and the macropores were too trivial to be identified (see Fig. 2d).

For further understanding the mechanism of forming the porousstructure, the SEM cross-section images of the above samples were extremely useful and necessary (see Fig. 3). Fig. 3a shows that two kinds of pore sizes were observed such as in Fig. 2a, and the depths of these micropores and mesopores were both less than 200 nm. Two Au nanoparticles were found in the bottom of the micropores; the position of the particles is indicated by an arrow, which was indicative of that the mechanism of forming the porous layer is compatible with the literature reported[13-15]. Moreover, the morphologies of these pores with varied depths contained cylinder- and cone-shaped concavities. A typical cone-shaped concavity was observed in Fig. 3c, which had the bottom diameter less than 50 nm, the top diameter of a range between 100 and 500 nm, and the depth of a range between 100 and 1000 nm. It is noteworthy that the vertexes of silicon with diameter less than 50 nm were formed due to a few neighbor and close cone-shaped concavities. On the other hand, it is considered that the dense and overlapping cone-shaped concavities showed the pyramid-like textured subwavelenth structure, which was consistent with the observation in Fig. 2b. As shown in Fig. 3c, bowl-shaped holes with depth of about 500 nm were observed, rather than cone-shaped, so that the top diameter of the pyramid-like structure and the curvature diameter of the bowl-shaped holes both increased. The pores in Fig. 3d appeared loosely with depth less than 200 nm.

In this study, we proposed a mechanism for formation of cone-shaped concavities. During the initial stage of etching silicon using Au nanoparticles in a solution containing HF and H_2O_2, the Au nanoparticles gradually sank into silicon forming micropores with diameters ranging from 10 to 50 nm, which were comparable to those of Au nanoparticles. After that the walls between the micropores collapsed without difficulty due to the very short distances between Au nanoparticles, which resulted in the aggregation of those Au nanoparticles. In our cases the etching solution containing lower concentration of HF than in general etching methods was determined, so that the silicon/gold interface may be covered with a thin silicon oxide layer. In such a case, the injected positive holes are expected to diffuse into the bulk of silicon and oxidize silicon at places apart from the Au nanoparticles. They will generate the cone-shaped concavities in the porous layer.[14]And then these cone-shaped macropores form pyramid-like textured subwavelenth structures over the silicon surface. When over-etching occurring, neighbor macropores will strongly overlap and be combined into wide and shallow holes, forming lower and flatter pyramids rather than sharper ones.

It is well known that the close-packed pyramidal arrays is a optimal antireflection layer on solar cells due to a refractive index gradient between air and silicon interfaces.[6] Furthermore our previously research indicated that the subwavelenth pyramidal structures display lower reflectance. Fig. 4 shows the reflectance curves of pyramid-like textured silicon wafers by metal-assisted chemical etching. Observably, reflectance dramatically decreased with the increasing etching time until 20 minutes and reached the minimalreflectance, less than 0.5 % in whole wavelength ranging from 300-800 nm in Fig. 4a. At this stage, the pyramid-like structures in sub-wavelength scale appear and display the most optimized result. However with longer etching time, reflectance increased slowly due to the bowl-like not pyramid-like structures, which it is comparable to the general porous antireflection layer using HF etching method. Fig. 4b-c both show similar results to the above, the lowest reflectance reached less than 2% and 1.5%, respectively.

The general porous silicon structures using isotropic acidic etching method mainly compose of cylinder holes, which mean that the antireflection layer has a specific refractive index between air and silicon, not real gradual refractive index with the depth form the surface of the silicon wafer. However the subwavelenth pyramid-like textured structure using modified metal-assisted chemical method, which is equivalent to that composed of multilayer thin films with gradual refractive index ranging from air to silicon, could reduce the reflectance more effectively. In addition, single-crystal silicon solar cells are generally textured with random pyramids in micrometer scale, which are produced by etching in an alkaline solution such as KOH or NaOH. The random nature of the crystal orientation of multicrystalline silicon wafers makes such techniques much less effective for this material because only a handful of grains are properly orientated. It is worthy to note that the subwavelenth pyramid-like textured structures could be applied to the multicrystalline silicon solar cells due to the etching solution containing of HF and H_2O_2 catalytically by Au nanoparticles is an isotropic enchant.

4. CONCLUSION

Antireflection is one key technology for the manufacture of efficient silicon solar cells. In this study, we demonstrated textured structure of the silicon surface by metal assisted etching method, using Au nanoparticles as catalysts in HF and H_2O_2 solution. The surface morphologies changed with the etching conditions such as distribution density of Au nanoparticles and etching time. The mechanism of the formation of the random but dense pyramid-like feature in subwavelength scale from cone-shaped concavities filled with the porous layer was proposed. Furthermore, the relation between the reflectance and the antireflection layer with gradient refractive index in the direction of light propagation was studied. Finally, the reflectance of the silicon wafer was reduced to less than 0.5% in the solar cell working-wavelength regime.

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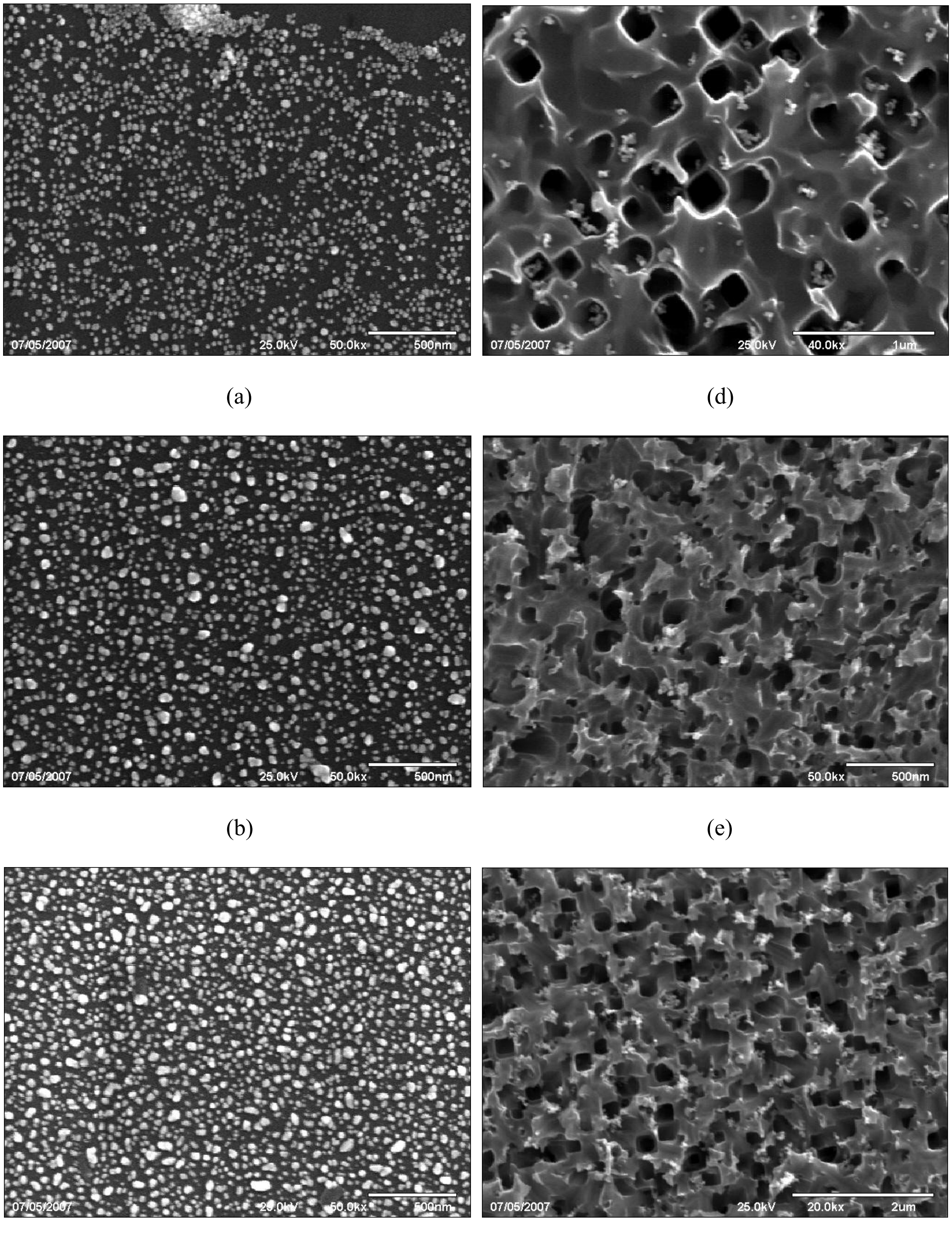
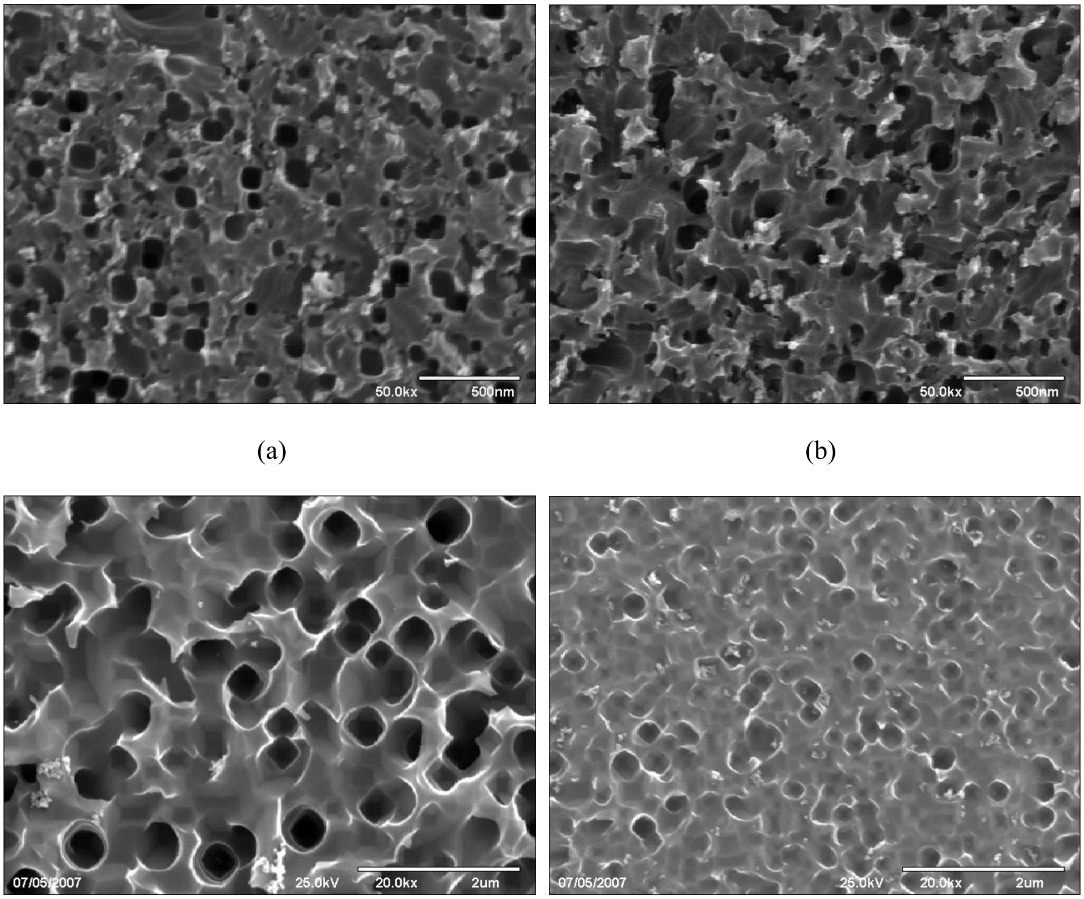


(a) (d)

(b) (e)

(c) (f)

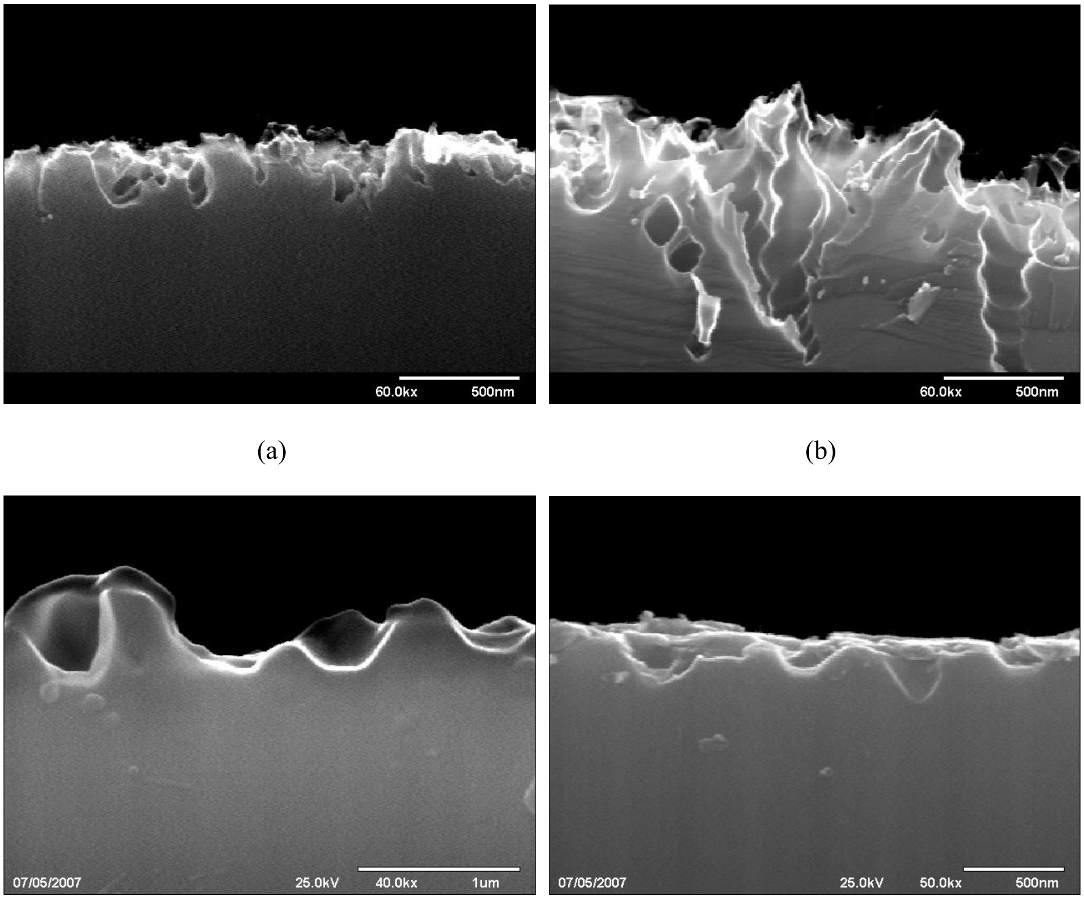
Figure 1 Top-view SEM images of silicon wafers loaded with Au nanoparticles for (a) 15, (b) 30 and (c) 60 min; (d)-(f) those after immersion in the etching solution for 20 min in the dark, respectively. The etching solution contained 50% HF, 30% H_2O_2, and H_2O at a volume ratio of 2:1:8.



(a) (b)

(c) (d)

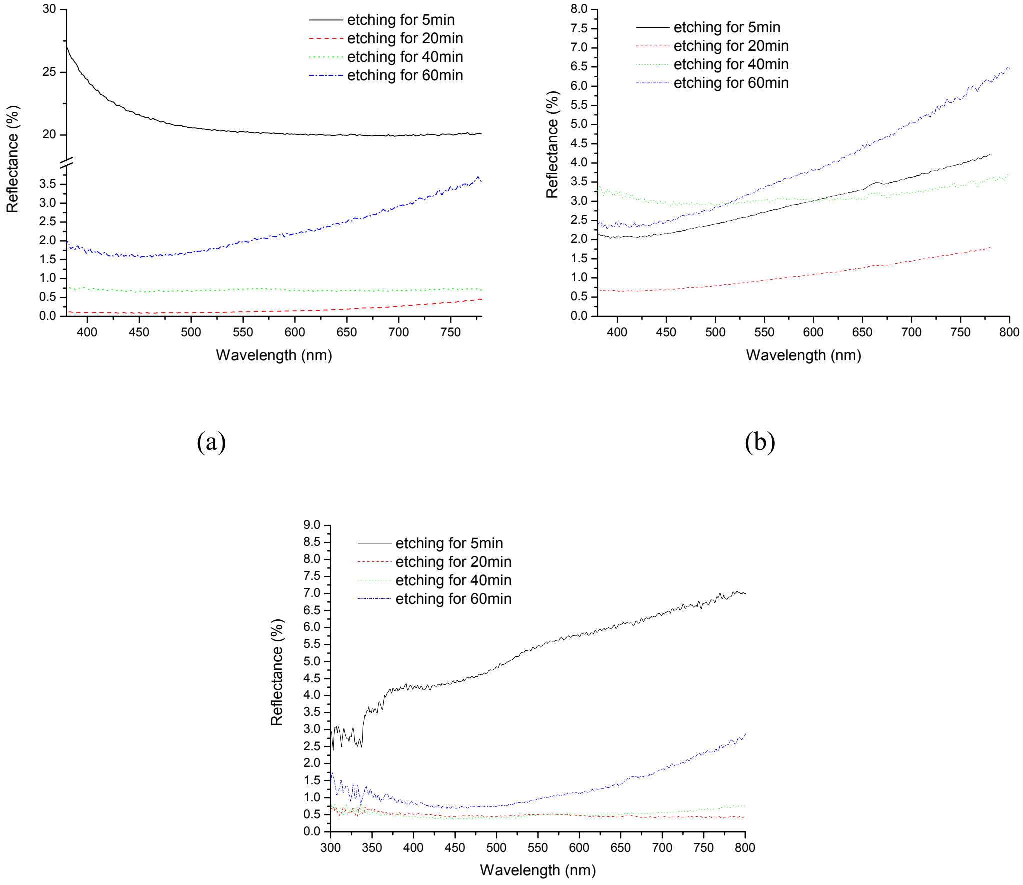
Figure 2. Top-view SEM images of Au nanoparticles deposited silicon wafers after immersion in the etching solution for (a) 5, (b) 20, (c) 40 and 60 min in the dark, respectively. The Au nanoparticles were adsorbed for fixed 30 min before immersion.



(a) (b)

(a) (b)

Figure 3. Cross-section SEM images of Au nanoparticles deposited silicon wafers after immersion in the etching solution for (a) 5, (b) 20, (c) 40 and 60 min in the dark, respectively. The Au nanoparticles were adsorbed for fixed 30 min before immersion.



(a)

(b)

(c)

Figure 4. Reflectance measurements of subwavelength textured silicon surface wafers. The silicon wafer were deposited for (b) 15, (a) 30 and (c) 60 min and further immersed in HF/H_2O_2 solutions for 5(solid), 20(dash), 40(dot) and 60(desh dot) min in the dark.