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Nano/micro double texturing of antireflective subwavelength structures on inverted pyramids

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ABSTRACT

Antireflective Si subwavelength structures (SWSs) are fabricated after the texturing of nano-scale holes directly onto micro-scale inverted pyramid arrays. Thermally agglomerated Au catalysts and Au-assisted chemical etching adjusted the featured nanohole sizes that determined surface reflection. When nano-scale SWSs were textured into micro-scale inverted pyramids, the total reflectance was dramatically decreased to 2.9% in a wavelength region of 200–1100 nm. Additionally, the average specular reflectance value was below 3.6% up to the incident angle of 60°. The surface reflection was efficiently suppressed by combining the light trap of microstructures and anti-reflectance of nanostructures. This technique demonstrated the feasibility of nano/micro double textured structures for application in high-performance optical devices.

1. Introduction

Surface antireflective techniques have attracted increasing attention due to their potential applications in optical and optoelectronic devices such as solar cells (Rahman et al., 2015; Wang et al., 2012; Han et al., 2011), optical sensors (Lee et al., 2005; Glaser et al., 2005), and light-emitting diodes (Kim et al., 2008; Kanamori et al., 2002). Particularly, in solar cell applications, the high reflectance loss of incident light at the interface of air and Si substrates is a major issue of planar Si top surfaces. As Si has a high refractive index of 3.4, incident light exceeding 30% is scattered and reflected from the Si surface. The surface reflection loss limits the efficient utilization of sunlight.

Common methods for reducing surface reflection and high absorption light include using coating materials (such as SiOx, SiNx, TiOx, and ZnS) as an antireflection layer. This results in a graded drop in the effective refractive index from air to Si substrates. However, antireflective coating is effective only for light with narrow spectral range and special angle of incident (Martinet et al., 1997; Dobrowolski et al., 2002). Surface texturing is another efficient technique to reduce reflection. Micro-scale pyramid texturing is an important technology for improving the conversion efficiency of Si solar cells (Rosa et al., 2011; Hua et al., 2010; Zhao et al., 1999; Baker-Finch and McIntosh, 2011). However, its reflectance represents relatively high values in the entire wavelength region. Subwavelength structures (SWSs) are another type of surface texturing, which are inspired by the moth eye (Clapham and Hutley, 1973). SWSs effectively suppress surface reflections with the same effect as a stack of antireflective coatings (Raut et al., 2011). This leads to a graded drop in the effective refractive index from air to Si substrate.

Prior literature has examined various SWSs including nanowire (Zhu et al., 2008; Dai et al., 2010), nanopillar (Xu et al., 2008; Kiraly et al., 2013), nanopyramid (Han and Chen, 2010; Chen et al., 2007), and nanocone (Zhu et al., 2008; Wang et al., 2015) structures because of their strong light trapping capabilities. However, nanolithography techniques for fabricating SWSs using complex e-beam, interference, or nanoimprint lithography are very expensive and not suitable for the processing of a large area (Kanamori et al., 2005; Aydin et al., 2002; Yu et al., 2003). Furthermore, there are issues of mechanical fragility with the positive nanostructures mentioned above. This is due to the protruded shape from the substrates into free space. In contrast, negative shapes such as nanohole, inverted nanocone, and inverted nanopyramid structures are superior to positive structures in terms of mechanical robustness (Kim et al., 2014). However, these negative structures were rarely studied due to their limited fabrication methods.

In this study, negative shapes of random subwavelength nanohole arrays were fabricated on Si substrates using conventional wet etching and metal-assisted chemical etching (MacEtch). Micro-scale inverted pyramid arrays were first formed on Si substrates by anisotropic tetramethyl ammonium hydroxide (TMAH) etching. The inverted pyramids increased reflection path

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from two to three, which enhanced antireflection characteristics in comparison with upright pyramids (Baker-Finch and McIntosh, 2011). Then, nanoholes were textured onto inverted pyramids by the thermal agglomeration of Au thin films and metal (Au)-assisted chemical etching in a H_2O_2/HF aqueous solution. An agglomeration of the thin metal films is considered to be a simple and a cost-effective approach for forming metal nanopatterns over a large area (Lee and Kim, 2007; Leem et al., 2012; Song et al., 2009). Thermally agglomerated Au nanoparticles were used for etch catalysts of MacEtch, which is a simple and effective fabrication process for negative texturization on semiconductor substrates (Liu et al., 2013; Song et al., 2014; Lee et al., 2008). In addition, it mitigates the potential of ion-induced charging and crystal damage caused in the reactive ion etching process. During the etching process, the continual repetition of oxidation and removing cycle of Si substrates caused Au nanoparticles to be submerged into Si substrates. This produced random nanohole arrays. Clearly, agglomeration and MacEtch are simple, inexpensive, and efficient when compared with common methods for fabricating negative SWSs in nanoscales.

Nano/micro double texturing of Si substrates is very efficient in improving the absorption performance of incident light by enhancing its antireflection properties. In order to achieve desirable antireflective structures, agglomeration and MacEtch were used to adjust various dimensions and heights of the nanoholes. The double textured structures significantly reduced the surface reflection when compared to bare Si and simple nanohole structures. Their antireflection properties were systematically investigated to determine the optimal structures for solar cell applications.

2. Experiments details

Thermally oxidized SiO_2 of about 100 nm was grown on B-doped p-Si (100) substrates with resistivities in the range of 8–12 Ω-cm. Image reversal optical lithography was used to form periodic square mesh arrays of photoresist with 6 μm sides and 2 μm spaces. The exposed SiO_2 was then etched away by 7:1 buffered oxide etch (BOE, J.T. Baker) solution for 2 min. After removing the photoresist, TMAH etching was conducted for 35 min at 60 °C to fabricate regular square arrays of inverted pyramidal pits. The remaining SiO_2 was etched off in BOE. Fig. 1 shows the SEM images of (A) fabricated inverted pyramid arrays and (B) ~55° angle of {1 1 1} facets with respect to the {1 0 0} facets.

Nano-scale texturing was performed by MacEtch of agglomerated Au nanoparticles. Au thin films of 3, 5, and 10 nm thicknesses were thermally evaporated on textured Si substrates at a 0.3 Å/s deposition rate under a pressure of 10^{-6} Torr. The Au thin films were treated by rapid thermal annealing (RTA) at temperatures of 500, 600, and 700 °C for 100 s in a nitrogen environment. Then, films were changed to nanoparticles with the agglomeration process. Au nanoparticles were used as catalysts in the MacEtch. Hydrogen peroxide (H_2O_2) and hydrofluoric acid (HF) were stirred in deionized (D.I.) water for 30 min to prepare an etch solution. The substrates were immersed into a solution. Etching was then performed for various times of 5, 10, 15, and 20 min at room temperature. In the chemical etching process, the chemical reaction between the Au particles and the redox solution submerged Au catalysts into the Si substrates. This resulted in the direct fabrication of subwavelength nanohole structures onto micro-pyramidal arrays.

Field emission scanning electron microscopy (FE-SEM) was used to characterize Au catalyst distributions, etched profiles, depths, and surface morphologies of textured Si structures. ImageJ software was used to quantify the average sizes of the etched nanoholes (NIH, http://imagej.nih.gov/ij/). An UV–VIS–NIR spectrophotometer was used to measure the total reflectance and variable angle specular reflectance at angles of 20°, 30°, 40°, 50°, 60°, and 70° in order to evaluate the reflectance of nano/micro double textured Si structures.

3. Results and discussion

Fig. 2 shows the top view of the SEM images of subwavelength nanoholes on {1 0 0} facets of planar surface (2 μm spaces) between the inverted pyramid pits before (insets) and after MacEtch. Au thin films were thermally agglomerated with RTA at 600 °C for (A) 3-, (B) 5-, and (C) 10-nm-thick Au films. (E) 700 °C for 3-nm-thick Au film. In both cases, the Au thin films were changed to Au nanoparticles. Thermally agglomerated Au nanoparticles were used as catalysts for MacEtch. During the etching, the continual repetition of oxidation and reduction forced the Au nanoparticles to sink into the Si substrates, which resulted in the random subwavelength nanoholes. Since the chemical etching with Au nanoparticles formed nano-scale holes, the geometry of the nanoholes was strongly dependent on the initial thickness of the Au films and the agglomeration temperature. As the thickness of the Au films increased at 600 °C (A, B, C), the nanoholes and the correlation distance increased on average. For Au films with thicknesses of 3, 5, and 10 nm, the average nanohole sizes were 43.9, 77.2, and 216.6 nm and average correlation distances were 47.4, 78.5 and 218.2 nm, respectively. For thicker Au films, the nanohole dimensions and the correlation distances increased as nanoclusters merged together, thereby reducing the density. For the fixed Au film thickness of 3 nm (A, D, E), the size of Au nanoparticles gradually increased from 40.6 to 53.5 nm as the temperature increased

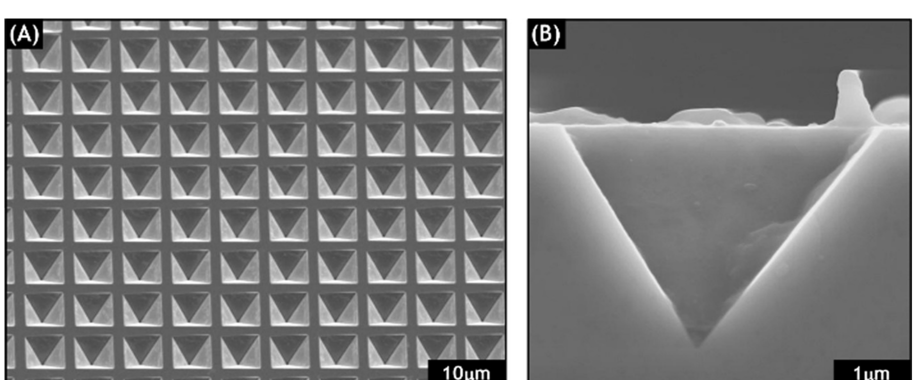

Fig. 1. (A) SEM image of inverted pyramid arrays with 6 μm sides and 2 μm spaces after TMAH anisotropic etching for 35 min at 60 °C. (B) The {1 1 1} facets of inverted pyramids have an angle of ~55° with respect to the {1 0 0} facets.