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Improved antireflection properties and optimized structure for passivation of well-separated, vertical silicon nanowire arrays for solar cell applications

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ABSTRACT

Large-area, well-separated, and vertically aligned silicon nanowire (SiNW) arrays with excellent antireflection properties were fabricated through a combination of anodic aluminum oxide template and metal-assisted chemical etching, followed by supercritical drying. Less than 1% reflectance was achieved over the wavelength range of 200–600 nm, and 23% reduction in average reflectance was observed over the 200–1000 nm range, compared with the conical-frustum structure array by natural drying. Furthermore, the well-separated SiNW arrays considerably facilitated the conformal coating of the plasma-enhanced chemical vapor deposited amorphous silicon layer on the SiNW surface, which could result in effective passivation of surface states. Therefore, such well-separated and vertically aligned SiNW arrays are highly promising for solar cell application.

1. Introduction

Device physics has demonstrated the potential of radial homo- or heterojunction nanowires to achieve high energy conversion efficiency with low-quality materials because this structure decouples the light absorption and minority charge carrier diffusion lengths by orthogonalizing the direction of light absorption and charge separation [1]. Therefore, more attention has been given to silicon nanowires (SiNWs) for photovoltaic application because of their unique structural, electrical, and optical properties [2–9]. Various methods using top-down or bottom-up approaches have been reported for the fabrication of the SiNWs. Among these methods, metal-assisted chemical etching of Si provides a simple and low-cost approach that enables the fabrication of large-area SiNWs with uniform and controllable height [10–13]. The fabricated SiNW arrays showed enhanced absorption of incident light because of the suppressed reflection, and improved light scattering and trapping in between the arrays [6,7,9,14–17]. Despite excellent optical property, the solar cells based on such SiNW arrays have significantly lower efficiency than conventional bulk silicon solar cells [6,7,9,16]. The serious recombination of photogenerated carriers mediated by the surface states is recognized as a dominant factor responsible for the low efficiency because of the high surface-to-volume ratio of SiNWs [3–5], which makes surface passivation extremely important for these nanowire-based solar cells. Amorphous silicon (a-Si) film has been demonstrated to effectively passivate the surface states of crystal silicon (c-Si), and a-Si/c-Si planar heterojunctions have already achieved great success in HIT (heterojunction with intrinsic thin layer) solar cells [18,19]. Therefore, conformal coating of a-Si:H (or a-SiN_x:H) on SiNWs is expected to effectively passivate the surface states of SiNWs and consequently improve the performance of SiNW-based solar cells [20,21]. However, SiNW arrays fabricated by wet chemical process typically resemble a sheaf-like structure that results from the agglomeration of nanowires at the tips because of the capillary forces present during drying [10,12,22]. Such a structure may lead to difficulty in conformal coating of a-Si on each SiNW surface because of the shadow effect.

To circumvent the aforementioned problem, we conducted supercritical drying on SiNW arrays fabricated by combining anodic aluminum oxide (AAO) template and metal-assisted chemical etching, which leads to the formation of large-area, well-separated, vertically aligned SiNW arrays. The structure and optical

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properties of such arrays were compared with those of the arrays obtained by natural drying. The structure of the a-Si:H coated SiNW array was also investigated.

2. Experimental details

SiNW arrays were fabricated by combining the AAO template and Au-assisted chemical etching, as described previously [23]. Briefly, an ~300 nm thick aluminum (Al) film was deposited on a SiO_2-covered Si (100) substrate by thermal evaporation. The Al film anodizing and pore widening were then conducted using diluted phosphoric acid solution for an appropriate duration. Thereafter, inductively coupled plasma (ICP) etching was performed to excavate the barrier layer at the bottom of the AAO pores and the SiO_2 layer as well as to pattern the surface of the Si substrate under a Cl_2/BCl_3 plasma, followed by removal of the AAO mask and SiO_2 layer. An ~15 nm thick Au film was then deposited onto the patterned Si substrate using an ion sputter coater, which formed a mesh-like Au film on the Si substrate. Finally, Au-assisted chemical etching was conducted by immersing the Au mesh-covered Si substrate into an etching solution of hydrofluoric acid (HF 4.4 M)/hydrogen peroxide (H_2O_2 0.4 M), and an ordered array of vertically aligned SiNWs was obtained. The basic fabrication procedure is schematically presented in Fig. 1.

The resulting SiNW array samples were rinsed with deionized water and then dried naturally in air or through supercritical drying in a supercritical fluid system (Spe-ed SFE-helix). To conduct the supercritical drying, the deionized water was first replaced with ethanol as an intermediate fluid. The a-Si:H layer was deposited on the SiNW arrays at 250 °C using silane (20 sccm 20% diluted in H_2) as source gas. Plasma was produced using an excitation frequency of 27.12 MHz and a power density of 55 mW/cm^2. The chamber pressure during the deposition was set constant at 750 mTorr. The morphology of the arrays was characterized by scanning electron microscopy (SEM, Hitachi S-4800). Ultraviolet-visible spectra were measured using a UV–vis spectrometer (Shimadzu UV-3600) with an integrating sphere setup.

3. Results and discussion

Fig. 2 shows the typical three stages of the SiNW growth. First, prior to SiNW formation, the silicon wall surrounding the hole formed by the ICP etching must be etched away. The SiNWs are not formed at this stage (Fig. 2a); the duration is determined by the depth of the hole. Subsequently, the SiNWs start to peep through the Au mesh as the mesh layer sinks because of the erosion of the silicon under the Au layer, as shown in Fig. 2b. The SiNWs then continuously increase in height as the etching proceeds (Fig. 2c). Au was clearly observed at the interfacial region between the SiNWs and substrates, whereas no Au particle was found on top of each SiNW, which is consistent with the observation that Au was not deposited on the bottom of the holes [23]. The etching rate obtained from Fig. 2d is approximately 250 nm/min in the present conditions, supposed a linear relationship between the SiNW height and the etching time [12,14]. Fig. 3a shows a large-area separated vertical SiNW array obtained by etching for 13 min and natural drying. The cross-section SEM image shown in Fig. 3b indicates that the SiNWs exhibit uniform diameter along the height direction, unlike the tapered SiNWs fabricated by Ag-assisted chemical etching because of the gradual dissolution of Ag in etching solution [24]. The height of the SiNWs is approximately 1.6 μm, whereas the areal density is about 43 μm^{-2}, and the average diameter is 70 nm, in accordance with the hole distribution of the Au mesh.

Extending the etching time leads to the formation of higher nanowires with significantly high aspect ratio. Through etching for 30 min, followed by natural drying, a sheaf-like structural array with an average SiNW height of 6.7 μm was observed, as shown in Fig. 4a and b. The nanowires bend to agglomerate tightly at their tips, forming microsized conical-frustum structures. The top of the frustum is highly bushy, with many nanowires sticking together, whereas the base is sparse, with separated nanowires rooted in the silicon substrate (shown in the inset of Fig. 4a). It has been

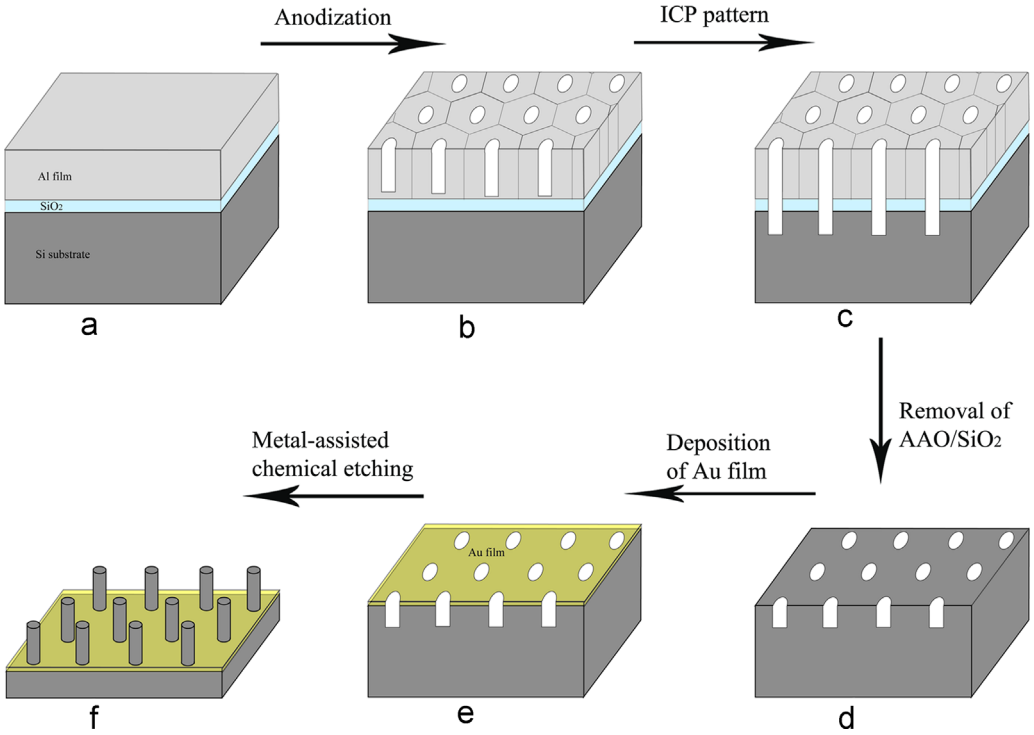

Fig. 1. Schematic of the SiNW fabrication process.