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Controllable growth of silicon nanowire arrays fabricated by two-step silver catalyzed chemical etching

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ABSTRACT

Silicon nanowire arrays (SiNWs) were prepared by the two-step silver catalyzed chemical etching process. The influence of various factors such as deposition time of silver nanoparticles, etching process and post-treatment conditions on the morphology and structure of SiNWs were systematically investigated. Scanning electron microscopy (SEM), X-ray diffraction (XRD), Ultraviolet–Visible spectroscopy (UV–Vis) and Fourier-transform infrared spectroscopy (FTIR) were used to characterize the SiNWs. The results revealed the existence of a positive linear relationship between length and etching time, which could be used to control the length of the SiNWs. The length and diameter of the nanowires both gradually decreased as the duration of the post-treatment process increased. SiNWs can be obtained with better uniformity by optimizing the post-treatment duration. In addition, four different lengths of SiNWs with regular and uniform morphology were fabricated using the above controllable growth process. The results showed that the silver catalyst was completely removed after the as-obtained SiNWs were immersed into HNO_3. All the as-prepared SiNWs showed a good light reflection performance, which was enhanced with increasing lengths of the arrays. The reflectance of the as-obtained SiNWs was found to be less than 1% within the range of the visible spectrum (300–800 nm). These results confirm that this simple fabrication method can help achieve controllable growth of SiNWs of desired sizes.

1. Introduction

Silicon nanowires array (SiNWs) have received considerable interest as potential building blocks for devices in the fields of nanoelectronics [1], energy storage [2], biosensing [2–4], and solar cells [5,6]. Their popularity is due to their many unique characteristics such as high surface area, small size and quantum effects. A wide variety of growth techniques have been used to fabricate SiNWs, including chemical vapor deposition (CVD) [7], laser ablation [8], thermal evaporation [9], reactive ion etching (RIE) [10], and metal-catalyzed chemical etching [11,12]. Among all these synthesis methods, the metal-catalyzed chemical etching process is the most promising for fabricating high densities of single crystalline SiNWs.

Silver (Ag) has been the most frequently used catalyst for the growth of SiNWs. Various methods have been reported for the preparation of silver nanoparticles, such as masking preparation [13], annealing treatment [14], silver mirror reaction [15]

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and pretreatment for the surface of the silicon wafer [16]. However, most of these methods are expensive and/or involve complex process control. In recent years, a simple and inexpensive two-step silver catalyzed chemical etching method for the synthesis of SiNWs has received considerable attention. In this process, the first step is the preparation of silver nanoparticles by electrode-less chemical deposition using the mixed solution of $AgNO_3$ and HF, and; the second step is the synthesis of SiNWs using the silver nanoparticles as an etched mask, in the mixed oxidizing solution of H_2O_2 and HF. This method has been used successfully by many studies [17,18]. However, to date, there have been no systematic investigations of morphological and structural control of the silicon nanowire arrays prepared by this method. Since the structure of the device determines its performance, it is important to be able to control the length, distribution density, and morphology of SiNWs, so that they can meet different requirements in practical applications.

In this paper, silicon nanowire arrays were obtained by two-step silver assisted chemical etching method. The morphology changes of the SiNWs were systematically investigated by adjusting key experimental parameters including the deposition time of silver nanoparticles, etching process and post-treatment conditions. SEM, XRD, UV and FTIR were used to characterize the as-obtained SiNWs.

2. Experimental

The silicon nanowire arrays were prepared by silver catalyzed chemical etching of n-Si (100) oriented wafers (1 cm × 1 cm) with resistivity of about 2.8 Ω cm. The Si wafers were firstly cleaned with acetone (20 min), ethanol (20 min) and deionized water (4 times), and subsequently immersed in H_2SO_4 and H_2O_2 mixed solution for 30 min to remove the organic contaminants on the surface. The samples were then immersed into 5% HF solution to dissolve the thin oxide layer formed on the surface. Secondly, this cleaned wafer was transferred into an Ag deposition solution containing 0.005 M $AgNO_3$ and 4.8 M HF, and maintained for a certain time at room temperature. Thirdly, the silicon wafers covered with Ag nanoparticles were immersed into the mixed etching solution of HF (4.8 M) and H_2O_2 (0.4 M) for a certain time at room temperature. When the etching processes were accomplished, the samples were dipped into the aqueous solution of HNO_3 and then rinsed with deionized water to remove the residual silver. Lastly, the samples were subjected to two different post-treatment methods to further investigate structural regulation of SiNWs. One method was to use KOH solution (0.1 M) to etch the as-obtained samples for a certain time at room temperature. Another post-treatment method was thermal oxidation in a tube furnace at 800 °C with the O_2 flow rate of 50 sccm for different times, followed by HF (10% solution) etching to remove the surface oxidation layer.

In addition, based on the above methods of regulation and adjustment of the structure of the SiNWs, a series of silicon nanowire arrays with different lengths were prepared. In the first step, a solution of 4.8 M HF and 0.005 M $AgNO_3$ was used for depositing silver particles. In the second step, the Si wafer was etched in the oxidizing solution with 4.8 M HF and 0.4 M H_2O_2. The silver particles were then removed by immersing in dilute HNO_3. The structural and optical properties of all the as-prepared samples were studied by the below techniques.

The surface and side-view morphologies of the samples were characterized by scanning electron microscopy (SEM) using a HITACHI-4700 instrument. The structural properties of the grown SiNWs were examined using X-ray diffraction (XRD: Ricoh Company D/max 25000 PC) using Cu Ka radiation ($\lambda = 0.1546$ nm). The optical reflectance spectra and absorbance spectra were examined by a UV spectrophotometer (SHIMADZU-2600), and the IR absorption spectra were obtained using a Nicolet380 FTIR instrument.

3. Results and discussion

In order to sustain the robust catalytic activity of the deposited Ag nanoparticles and to obtain ideal SiNWs structure, proper thickness of the silver layer is vital. SEM images in Fig. 1 show the different morphologies of the deposited Ag nanoparticles with various deposition times on the Si substrate, and the corresponding results. The etching time of 10 min was kept constant. When the deposition time is 40 s, the nanoparticles are dispersed on the surface with considerable separation between the particles and limited interconnection between them. As the deposition time increases, the deposited Ag nanoparticles tend to form interconnected networks with shrinkage of the interspaces. When the deposition time reaches about 120 s or more, the surface of Si wafer is almost completely overlaid by multilayered Ag nanoparticles with few gaps left. Thus, a short deposition time causes the deposited Ag layer to have too many gaps between the metal nanoparticles, which in turn leads to random and disordered etching of Si, as shown in Fig. 1 (a2) and (a3). In the case of long deposition times, the paucity of gaps in the deposited Ag layer prevents the etching solution from coming into contact with the Si covered by Ag nanoparticles, which makes for non-uniformity of the SiNWs in Fig. 1 (f2) and (f3). In general, an obvious trend is that the surface coverage of Ag nanoparticles gradually increases with the increasing deposition times, and then begins to overlap and eventually form multilayer silver particles. This leads to the decreased surface density of the as-obtained SiNWs. The top portion of the SiNWs has a tendency to cluster and is not characterized by the uniform dispersed state. This, may be caused by two reasons: (1) uneven of chemical etching, and; (2) non-uniform morphology of the deposited Ag nanoparticles [19]. It is seen that the density of SiNWs clusters increases as the Ag deposition time increases. Furthermore, the length of SiNWs firstly increases and then decreases with the increasing of silver deposition time. The length reaches its maximum when the deposition time is 80 s, as seen in Fig. 1 (g). The reason for this could be the existence of an optimum point at which there is a balance between the formation of nanowires and the destruction of as-formed nanowires in the process of etching [19], and

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