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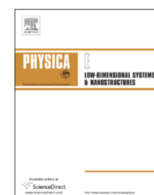

Effects of silver and gold catalytic activities on the structural and optical properties of silicon nanowires

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HIGHLIGHTS

- The optimum catalysts layer thickness and formation of different silicon nanostructure.
- The effect of catalyst type and thickness on the structural properties of SiNWs.
- The effect of catalyst type on the optical properties of SiNWs.
- The origin of PL spectrum of Au and Ag etched SiNWs.

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ABSTRACT

The metal-assisted chemical etching of silicon in an aqueous solution of hydrofluoric acid and hydrogen peroxide is established for the fabrication of large area, uniform silicon nanowire (SiNW) arrays. In this study, silver (Ag) and gold (Au) are considered as catalysts and the effect of different catalysts with various thicknesses on the structural and optical properties of the fabricated SiNWs is investigated. The morphology of deposited catalysts on the silicon wafer is characterized by atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM). It is shown that the morphology of the fabricated silicon nanostructures remarkably depends upon the catalyst layer thickness, and the catalyst etching time directly affects the structural and optical properties of the synthesized SiNWs. FESEM images show a linear increment of the nanowire length versus time, whereas the etching rate for the Au-etched SiNWs was lower than the Ag-etched ones. Strong light scattering in SiNWs caused the total reflection to decrease in the range of visible light, and this decrement was higher for the Ag-etched SiNW sample, with a longer length than the Au-etched one. A broadband visible photoluminescence (PL) with different peak positions is observed for the Au- and Ag-etched samples. The synthesized optically active SiNWs can be considered as a promising candidate for a new generation of nano-scale opto-electronic devices.

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1. Introduction

Semiconductor nanowires have accumulated considerable attention in the past decade due to their unique structural, optical, electronic, mechanical, and thermal properties [1,2]. Since silicon has found widespread applications as an abundant and non-toxic semiconducting material, 1D-silicon nanowires (SiNWs) seem to be a promising candidate for the development of the semiconductor technology. The applicable use of SiNWs in opto-electronics, biomedical, and energy industries has remarkably been highlighted in the recent reports [3–7]. There are many methods for the synthesis of SiNWs including laser ablation, metal-catalytic vapor–liquid–solid, metal-assisted solid–liquid–solid, and oxide-assisted growth [8]. However, some of these methods are expensive, and require energy-consuming processes.

In the recent years, the metal-assisted chemical etching (MACE) method has attracted substantial attention due to its remarkable advantages such as low cost and simplicity in fabricating large surface areas [9]. Moreover, through the MACE method, it is possible to obtain SiNWs with very high and controllable aspect ratios. MACE is a solution-based technique that involves two steps. Firstly, a noble metal such as Au, Ag, or Pt is deposited on a silicon surface either in the form of nanoparticles or as a thin film; the metal catalysts can be deposited by evaporation or sputtering [10,11] or formed in a solution composed of hydrofluoric acid (HF)

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and certain metal salts [12,13]. Secondly, metal-coated silicon samples are immersed in an etchant solution composed of HF and an oxidizing agent, mainly hydrogen peroxide (H_2O_2). During the etching process, the silicon beneath the noble metal is etched much faster than the silicon without the noble metal coverage. As a result, the noble metal sinks the substrate, and pores or wires are generated. Many factors have been identified affecting the morphologies of SiNW arrays by chemical etching such as the intrinsic properties of the silicon substrate, etchant concentration, and etching temperature and time [9]. The geometric details of the silicon structures formed depend mostly on the initial morphology of the noble metal coverage and the distance between metal catalyst. It has been shown that the well-separated Ag nanoparticles created isolated pores, while isolated wire structures were obtained with sufficient high-density Ag particles [14]. The nominal thickness of metal films, deposited by physical methods in vacuum, influences the morphology of the etched structures. Silicon porous structures have been formed using a 3-nm thick Au film as a catalyst, while a 7-nm Au film created the columnar structure [15]. The Ag film with a thickness of 5 nm formed the porous structures, while SiNWs with 20-nm Ag films were fabricated [10]. Recently, Chiou et al. [16] have investigated the use of an optimum thickness layer of an Ag catalyst in the fabrication of a silicon nanowire array through the two-step Ag-assisted chemical etching method. To the best of our knowledge, few studies have considered the thickness, type, and morphology of the noble metal involved in the fabricating process of SiNWs.

In this work, gold (Au) and silver (Ag), with different thicknesses, were used to fabricate SiNWs through the MACE method. Effect of the metal thickness on the formation of a porous or wired silicon structure was investigated. Also systematic studies were performed on the effects of Au and Ag, as noble metal catalysts with different etching times, on the morphology, structure, and photoluminescence (PL) properties of SiNWs.

2. Experimental method

SiNWs were prepared by the Ag- and Au-assisted chemical etchings of the (100)-oriented p-type silicon wafers with resistivity of 1–10 Ω cm. This synthetic process includes four steps, as follow. (1) Silicon wafers were ultrasonically vibrated in acetone and ethanol at room temperature for 10 and 5 min, respectively to remove the organic grease, and then the wafers were washed with deionized water for several times. The wafers were heated in boiling Piranha solution (H_2SO_4 97%:H_2O_2 30%=3:1; v/v) for 20 min to remove the organic residues and heavy metals. The substrates were rinsed thoroughly with deionized water for 15 min, and then immersed in diluted HF for 3 min. (2) Ultra-thin layers of Ag or Au were deposited through the sputtering method in a vacuum of 10^{-7} Torr and a deposition rate of 0.7 A s^{-1} on the silicon wafer. Three different layer thicknesses of Au and Ag (6, 10, and 15 nm) were considered in the experiment. (3) Silicon wafers covered with Ag and Au metals were immersed into the etching solution of 4.6 M HF (40%) and 0.44 M H_2O_2 (30%) at room temperature for different etching times including 20, 40, 60, and 80 min in a sealed Teflon vessel. (4) The wafers were washed repeatedly with water, and immersed in suitable etchants to dissolve the catalysts. The suitable etchant for dissolving Ag and Au are DI-H_2O:HNO_3 63% (1:1; v/v) and HCl 37%:HNO_3 63% (3:1; v/v), respectively. The wafers were cleaned with water for several times, and dried under the N_2 flow.

The surface roughness of the Ag and Au catalyst films was investigated using an atomic force microscopy (DME, Dual scope DS 95). Characterization of the SiNW structure was performed using field emission scanning electron microscopy (FESEM). Optical characterization was carried out through photoluminescence (PL) measurements using Nd:YAG laser with wavelength of 532 nm. The reflectance spectra of the samples were measured using a UV–visible–NIR spectrophotometer (Cary 5000, Varian).

3. Results and discussion

3.1. Structural characterization of ultra-thin Au and Ag layers

Fig. 1 shows the AFM images (left) and surface roughness (right) of the Ag (a)–(c) and Au (d)–(f) films. These measurements show that the surface roughness decreases for the thicker layer, likely to be due to the improvement in the interconnections between the clusters, and formation of a homogeneous and uniform layer. The maximum surface roughness for the Ag and Au layers of 6-nm thickness were about 8.93 and 1.56 nm, respectively. These values decreased to 2.5 nm and 393 pm for layers with 15-nm thickness. Also there was a distinct change in the surface morphology of the Ag-coated films, and the surface morphology of the Au-coated films showed a little thickness dependence.

Fig. 2 shows the FESEM images for the Ag and Au layers with different thicknesses. As one can see in Fig. 2(a)–(c), the size of Ag nanoparticles varies from 20 to 80 nm for the 6-nm layer thickness, while a broad size distribution ranging from 40 to 200 nm is formed for the 10-nm layer thickness. Moreover, by increasing the Ag layer thickness to 15 nm (Fig. 2c), a continuous layer is formed. Fig. 2(d)–(f) show a remarkable change in the FESEM images for the Au nanoparticles with respect to the others. Au nanoparticles with a uniform size distribution of about 30 nm are formed with a 6-nm layer thickness, and by increasing the thicknesses to 10 and 15 nm, a uniform surfaces with different morphologies are formed. As the size of the nanoparticles is uniform and small, continuous films with very low roughnesses are formed in Fig. 2(e).

3.2. Structural properties of silicon nanostructures

In the following discussion and to carry out an explanation of how the catalysts thickness will affect on the morphology of the etched silicon structure, we firstly analyze the metal assisted chemical etching mechanism and representative model in the literature. In the metal-assisted chemical etching (MACE) process, as depicted in Fig. 3, the overall etching process is governed by the interplay between the following two processes: (a) injection of positive holes (h+) into the bulk silicon through a metal–silicon interface, and (b) removal of the oxidized silicon by HF from just underneath the catalyst metal. In fact, in the first step, a noble metal catalytically promotes etching of the silicon substrate in the presence of H_2O_2 solution, and once the oxidant is reduced at the interface between the bulk electrolyte and metal catalyst, the holes, which are the main sources for the oxidation of silicon, are generated. In the second step, generation of the holes leads to the oxidation and dissolution of the silicon underneath the metal, and a direct contact with the electrolyte (HF/H_2O_2) is necessary for etching the oxidized silicon surface.

Several MACE models in which isolated particles or thin metal films are used as catalysts have been developed to describe the mechanism of SiNW formation [9,17]. The reagent and by-product diffusion model used in the silicon etching process has been described by Geyer et al. [17]. Based upon this model, the reagents and by-products diffuse along the interface between the metal film and silicon, and this signifies that the etching rate decreases with increase in the lateral size of the metal catalyst because of the long lateral diffusion distance. Therefore, a suitable diffusion length can facilitate the rapid mass transfer of the reagents and by-products. This process leads to the formation of SiNWs.

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