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The growth of silicon nanowires by electroless plating technique of Ni catalysts on silicon substrate

Jung-Fu Hsu [a], Bohr-Ran Huang [b,*]

[a] Graduate School of Engineering Science and Technology, National Yunlin University of Science and Technology, Yunlin 640, Taiwan, ROC
[b] Department of Electronic Engineering, College of Engineering, National Yunlin University of Science and Technology, 123 University Road, Section 3, Touliu, Yunlin, Taiwan 640, ROC

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Abstract

The silicon nanowires (SiNWs) in this research were synthesized on silicon substrates via a catalytic reaction under N_2 atmosphere by the thermal chemical vapor deposition system. Nickel catalyst was deposited on the silicon substrates by electroless nickel plating technique. It was found that the Ni content was increased from 0.31 wt.% (30 s, 75 nm) to 15.52 wt.% (300 s, 370 nm) from the energy dispersive X-ray spectroscopy analysis. It was also shown that the sizes of the Si–Ni alloy droplets and the growth density of SiNWs were both increased as the thickness of the electroless plating layer increased. It was concluded that the diameters, lengths and growth densities of SiNWs could be controlled by the Ni content of the electroless plating layer on the silicon substrate.

Keywords: Silicon nanowires (SiNWs); Electroless nickel plating; Si-Ni alloy droplets

1. Introduction

Since the discovery of silicon nanowires (SiNWs) [1], it has been anticipated that they should exhibit potentially useful electrical, optical, mechanical and chemical properties due to their small dimensions, unique shapes and high surface-to-volume ratio. Many efforts have been made to improve the synthesis of SiNWs by employing different techniques, such as excimer laser ablation [2], chemical vapor deposition (CVD) [3] and other methods [4–6]. In most of these previous studies, the SiNWs were synthesized using metallic catalysts. However, these catalyst materials are usually prepared using expensive facilities, such as sputter coaters or evaporators, causing the cost of silicon nanowires fabrication to increase.

The electroless deposition process experienced numerous modifications to meet the challenges needs of a variety of industrial applications since Brenner and Riddell invented the process in 1946 [7]. The electroless plating technique has many advantages [8,9], such as low temperature processing, simple process with non-expensive deposition facilities and simpler control of the composition of the deposited thin films. Recently, electroless plating technique has become one of the most attractive manufacturing methods in mass-production of nanostructures [10]. Tsai et al. [11] have investigated the catalytic effect of electroless Ni–P alloy on Si wafer for the growth of carbon nanofibers.

In this work, the electroless plating technique was adapted to prepare the metal catalysts on silicon substrates for the synthesis of SiNWs by the solid–liquid–solid (SLS) mechanism method [5,12–14]. The correlation between diameters, lengths, nucleation densities of SiNWs and process of the electroless plating treatment were investigated.

2. Experimental details

The substrates used were n-type (resistivity about 3–5 Ω cm) Si(100) wafers. The silicon substrates were cleaned ultrasonically in acetone and in ethanol in turn for 10 min each, and then leached with in deionized water. In order to help the Ni

* Corresponding author. Tel.: +886 5 5342601x4315; fax: +886 5 5312063.
E-mail address: huangbr@yuntech.edu.tw (B.-R. Huang).

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Table 1
Chemical compositions and operating conditions of bath

Chemicals	Concentration (g/l)
$NiSO_4 \cdot 6H_2O$	87
$NaH_2PO_2 \cdot H_2O$	24
$C_2H_2(COONa)_2 \cdot 6H_2O$	4.1
$C_3H_4(OH)(COOH)_3 \cdot H_2O$	2
$Pb(CH_3COO)_2 \cdot 3H_2O$	1.5×10^{-3}
$CH_3COONa \cdot 3H_2O$	30
Operating conditions: pH: 4.6 (adjusted with H_2SO_4). Bath temperature: 85 °C.	

electroless plated on silicon substrates. Prior to the electroless plating process, the etched silicon substrates were first sensitized by immersion in $SnCl_2$/HCl solution (10 g/l $SnCl_2$ +40 ml/l HCl) for 20 min and then activated by immersion in $PdCl_2$/HCl solution (0.3 g/l $PdCl_2$+2.5 ml/l HCl) for 5 min. For the electroless plating of the nickel, the simple bath consisted of a mixture of $NiSO_4$, NaH_2PO_2, $C_2H_2(COONa)_2$, $C_3H_4(OH)(COOH)_3$, $Pb(CH_3COO)_2$ and CH_3COONa as listed in Table 1. During plating, the bath was maintained at a temperature of 85 °C and the pH of the bath was kept constant at 4.6 adjusted with H_2SO_4 aqueous solution. The deposition times were varied from 30 s to 300 s. Then, for the synthesis of SiNWs, the samples were placed into a thermal CVD system under an N_2 ambient pressure of approximately 2.67×10^4 Pa at 955 °C for 1 h. After the growth of SiNWs process, the samples were cooled down to 25 °C under the same N_2 ambient. An energy dispersive X-ray spectroscopy (EDS) (Oxford Inca Energy 400, operated at 15 keV) was used for elemental analysis of the electroless Ni catalyst layer. A field emission scanning electron microscope (FESEM) (Jeol JSM 6700F, operated at 3–5 kV) was used for the SiNWs examination using secondary electron (SE) imaging and backscattered electron (BSE) imaging.

3. Results

The energy dispersive X-ray (EDS) spectra of the electroless nickel plating on silicon substrates are shown in Fig. 1. Fig. 1(a)–(c) illustrate the EDS spectra of the deposit plating for 30 s, 180 s and 300 s, respectively. Fig. 1(a) is the EDS spectrum of 30-s Ni plating sample, in which the Si, P, S, Ni and O signals were present with a small Ni content of 0.31 wt.%. The P signal in the EDS spectrum reveals that P co-precipitated with Ni in the initial stage of deposition. In addition, the S signal is probably attributable to the $NiSO_4$ or the pH adjusting solution H_2SO_4, which was also responsible for some sample oxidation. As deposition time increased, it was found that the Ni content of 180-s and 300-s Ni plating samples increased to 3.5 wt.% and 15.52 wt.%, as shown in Fig. 1(b) and (c), respectively. The Ni content was clearly increased as the deposition time increased. The thickness of the Ni electroless plating layer on the silicon substrate also were increased from approximately 75 nm to 370 nm. In other words, the Ni content increased as the thickness of the Ni electroless plating layer on the silicon substrate increased.

Fig. 2 shows secondary electron (SE) images of the SiNWs grown on the Si substrate. Fig. 2(a)–(c) illustrate the growth morphologies of the SiNWs with deposit plating for 30 s, 180 s and 300 s, respectively. Fig. 2(a) is the SE image of 30-s Ni plating sample, which shows short length and a low growth density of the SiNWs. The average length and growth density of SiNWs were both increased as the electroless plating time increased, as shown in Fig. 2(b) and (c), for 180-s and 300-s Ni plating samples, respectively. The detailed properties of the SiNWs were summarized in Table 2. 30-s Ni plating sample showed that the SiNWs have average diameter ~8 nm, average length <1 μm and low growth density; 180-s Ni plating sample showed that the SiNWs have average diameter ~14 nm, average length <10 μm and medium growth density; and 300-s Ni plating sample showed that the SiNWs have average diameter ~20 nm, average length >10 μm and the highest growth density.

Backscattered electron (BSE) images do not offer as many morphological details on contrasting domains as the secondary electron (SE) images, but they can provide more explicit information on chemical differences between different domains in a sample. The contrast of a BSE image depends on the backscattered electron generation rate, which increases with the mean atomic number of the specimen [15]. Fig. 3(a) and (b) illustrate SE images with BSE images of 30-s and

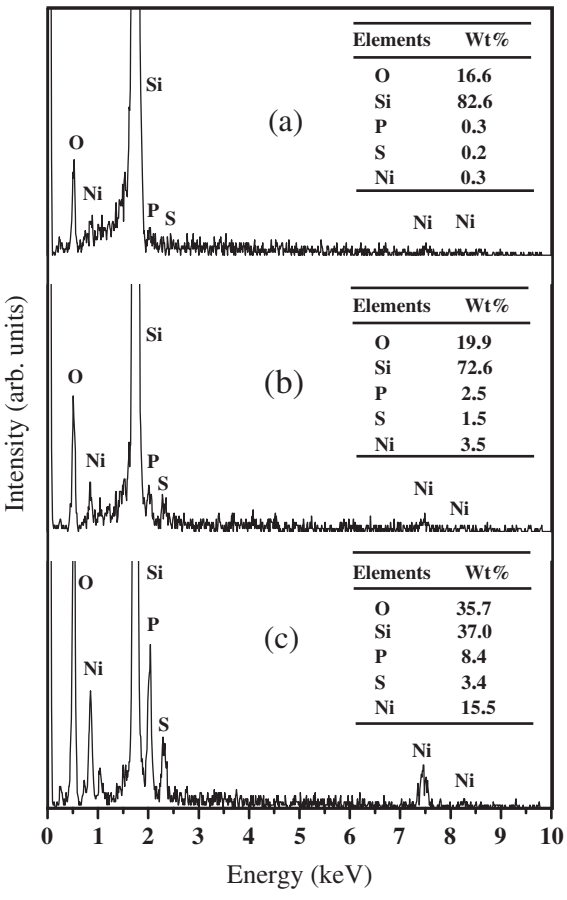

Fig. 1. EDS spectra of the electroless nickel plating on silicon substrates for the deposition time of (a) 30 s, (b) 180 s and (c) 300 s.