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Tin catalyzed silicon nanowires prepared by magnetron sputtering



materials letters

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ABSTRACT

Tin (Sn) catalyzed silicon nanowires (Si NWs) were grown by the method of magnetron sputtering at temperatures ranging from 250 to 400 °C. As the growth temperature increases from 250 to 400 °C, the length and density of Si NWs first increases and then decreases. A mixed phase of amorphous and nanocrystalline silicon exists in the synthesized Si NWs, and the crystallization degree of Si NWs increases rapidly with further increase in growth temperature. Sn nanoparticles on the top of Si NWs can be observed, which indicates that the vapor–liquid–solid (VLS) growth mechanism is responsible for Si NWs growth.

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1. Introduction

In the last few years, silicon nanowires (Si NWs) as onedimensional (1D) structure materials have attracted much attention due to their unique optical, thermoelectric and magnetic properties [1–3]. The potential applications for Si NWs have included lithium-ion battery anodes [4], and photovoltaic solar cells [5-7]. The synthesis of Si NWs has been reported using various metal catalysts, such as Au, Al, Cu, Ag, etc. [8-11]. Particularly, Si NWs using Au metal catalyst have been intensively attracted due to several advantages such as good thermal stability, and chemical inertness, and can be deposited easily. Some problems have been recently presented from metal (Au) contamination in Si NWs that degrades the optical and electronic properties. Compared with the Au catalyzed NWs growth, nanowires growth with alternate catalyst can be carried out at low temperatures, and the low temperature growth is useful in microelectronic device fabrication. Therefore, it is a meaningful issue that new materials are examined for the growth of Si NWs at low temperature. Among the catalysts for the growth of Si NWs, tin (Sn) appears to be a favorable catalyst due to the relatively low Sn–Si eutectic temperature (232 °C) [11] and low solubility in Si [12]. The low eutectic temperature provides an opportunity to low-temperature growth of Si NWs using magnetron sputtering deposition (MSD).

Synthesis of Si NWs using Sn as a catalyst has been recently reported by plasma enhanced chemical vapor deposition (PECVD) [1,12–14], hydrogen radical assisted methods [15], and electron beam evaporation [16]. MSD is a safe process with rich resource usability, high deposition rate, low growth temperature, and is suitable for large-scale production for the synthesis of Si NWs

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http://dx.doi.org/10.1016/j.matlet.2015.03.065 0167-577X/© 2015 Elsevier B.V. All rights reserved. compared with other methods such as PECVD, hydrogen radical assisted method, electron beam evaporation.

In this paper, a magnetron sputtering method has been employed to grow Si NWs using Sn as a catalyst at the temperatures of 250–400 °C. For the first time, Si NWs using Sn as catalyst by MSD have been successfully synthesized. The morphology, element composition and structure of as-prepared Si NWs were characterized by a scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDX) and Raman spectroscopy respectively. Finally, the growth mechanism of Sn catalyzed Si NWs was investigated.

2. Experimental details

Sn catalyzed Si NWs were synthesized by MSD using an undoped crystalline silicon (c-Si) 3-inch diameter target. First, Sn thin films with thickness of 20 nm were deposited on glass substrates by DCmagnetron sputtering at a pressure of 5×10^{-4} Pa. Before the deposition of the Sn film, the glass substrates were cleaned sequentially with ultrasonic agitation for 20 min in a bath containing acetone, ethanol and deionized water. Without breaking the pressure, the Sn coated substrates were heated for 0.5 h at temperatures ranging from 250 to 400 °C. Subsequently, argon (Ar) was introduced to the sputtering chamber for Si NWs growth. The DC-power, working pressure and growth time were set to 40 W, 1 Pa and 90 min, respectively. After the growth, a layer of black products was found to be deposited on the substrate. The morphology and element composition of as-prepared Si NWs were characterized by SEM (Hitachi S-4800) and energy-dispersive X-ray spectroscopy (EDX) attached to SEM. The crystalline structure of as-prepared Si NWs was investigated by the Raman spectrometer (Renishaw 2000) using a 633 nm laser line as an excitation source.



3. Results and discussion

The effects of growth temperature on the morphology of asprepared Si NWs were discussed. Fig. 1(a)–(d) shows the SEM images of Sn-catalyzed Si NWs grown at 250–400 °C. When the growth temperature is 250 °C, there is little Si NWs, as shown in Fig. 1(a). When the temperature increases to 300 °C, random alignment of Si NWs with bent morphology can be observed. It can be found that the density of as-synthesized Si NWs increases with increase of the growth temperature. As the growth temperature increases from 250 to 350 °C, the average length of the obtained Si NWs approximately increases from 10 μ m to 40 μ m. But when the growth temperature rises to 400 °C, the average length of the obtained Si NWs becomes shorter. Therefore, if the density and length of Si NWs are only taken into account, the optimum growth temperature for Si NWs is $350 \,^{\circ}$ C. At higher growth temperature, the Sn thin film tends to condense and form larger Sn–Si alloy droplet at the tip of Si NWs, as shown in the insets of Fig. 1(a)–(d).

The detailed chemical compositions of as-prepared Si NWs were studied by EDX measurement. The inset in Fig. 2 shows the highmagnification SEM images of a single Si NWs capped a spherical catalyst droplet on its tip. The corresponding EDX analysis carried out on the stem and tip of the Si NWs were shown in Fig. 2(a) and (b), respectively. The EDX spectrum obtained from catalyst droplet of Si NWs (Fig. 2(a)) indicates that the catalyst droplet mainly comprises Si and Sn elements. The presence of Sn catalyst droplet locating on the tip



Fig. 1. SEM images of Sn-catalyzed Si NWs grown at different temperatures: (a) 250 °C, (b) 300 °C, (c) 350 °C and (d) 400 °C. Insets are the high-magnification SEM images of Si NWs capped a spherical catalyst droplet.



Fig. 2. The corresponding EDX spectra of Fig. 1(c) obtained from the (a) tip and (b) stem of Si NWs grown at 350 °C. The inset in the EDX spectrum is a high-magnification SEM image of a single SiNW.



Fig. 3. Room temperature Raman spectra of Sn-catalyzed Si NWs grown at different temperatures.

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