Applied Surface Science 456 (2018) 515–525

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Solid-phase diffusion controlled growth of nickel silicide nanowires for supercapacitor electrode

Mohammad Mukhlis Ramly[a,*], Fatin Saiha Omar[b], Aliff Rohaizad[a], Zarina Aspanut[a], Saadah Abdul Rahman[a], Boon Tong Goh[a,*]

[a] Low Dimensional Materials Research Centre, Department of Physics, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia
[b] Center for Ionics University of Malaya, Department of Physics, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia

ARTICLE INFO

Keywords:
NiSi
Nanowires
Solid-phase diffusion control
FESEM
Supercapacitor

ABSTRACT

This work reports on the influence of nickel (Ni) thickness on the growth of nickel silicide nanowires (NiSi NWs) using a solid-phase diffusion controlled growth treatment. The NiSi NWs were grown on two different substrates (i.e. crystal silicon (c-Si) and Ni foil) which were coated with Ni film with different thicknesses; 110 ± 5 and 220 ± 5 nm. FESEM images revealed that the shape, the size and the density of NiSi on both substrates were strongly dependent on the thickness of Ni film. These NWs exhibited morphology of straight NWs with diameter and length of between 16 to 23 nm and 2.9 to 3.9 μm, respectively. The NWs showed a single-crystalline Ni_3Si_2 phase with a preferred orientation in the (1 0 0) plane. XRD diffractogram proved that the formation of Ni-rich NiSi NWs is strongly dependent on the Ni film's thickness rather than on the types of substrates. NiSi NF220 demonstrated the highest specific capacity with a maximum value of 313.3 C/g. This is attributed from the high density of NWs which endows more redox reaction and the high conductivity of Ni foil substrate that facilitated the high charge transfer kinetics. The fabricated NiSi NWs//activated carbon-based asymmetric supercapacitor exhibited the maximum energy density of 13.37 W h/kg at 200 W/kg and good cyclic stability with 79% capacity retention after 3000 cycles.

1. Introduction

Electrical energy storage systems have become one of the key issues studied in addressing the current energy challenges such the rapid depletion of fossil fuels, environmental pollution and global warming [1,2]. Rechargeable energy storage devices including conventional capacitors, electrochemical capacitors (ECs), batteries, and fuel cells are widely used in various applications such as consumable electronics, transportations, and renewable energy [3]. Generally, batteries are unable to support technologies which require sufficient and quick power due to their several disadvantages, i.e. limited cycle life, abrupt failures, poor low-temperature kinetics, and safety concerns [4]. ECs are one of the best candidates for alternative energy sources as they able to provide long lifespan ($> 10^6$ cycles) and high power densities ($> 10\,kW\,kg^{-1}$)[5]. Extensive studies have been carried out to explore the properties of different types of electrode materials to obtain high performance of ECs including carbon-based materials [6–9], metal oxides [10,11] and conducting polymers [9,12]. However, those materials have their own disadvantages which limit the utilization of the materials for commercialization. For instance, ECs based on carbon-based materials (such as graphenes and activated carbons) which store energy through electrostatic ion adsorption have low energy densities despite a high rate capability. While ECs based on metal oxides and conducting polymers which store energy via faradaic reaction exhibit poor power densities even though can store higher energy. For EC's to be commercially viable, their energy-storing capacity and rapid charging need to be significantly enhanced but producing such devices remains a challenge [13–16].

Currently, the use of Si-based nanowires (NWs) such as Si NWs [17] and SiC NWs as electrode materials [18–20] has been extensively investigated in ECs. Cui et al. reported that the use of porous Si NWs electrodes in EC exhibited a relatively larger specific capacitance at high current densities compared to EC based activated carbon electrodes [21]. However, the longer and tortuous pore structure of porous Si NWs were inefficient for ion diffusion. Metal silicides have recently been reported have several advantages compared to the other electrode materials such as good mechanical stress, high electrical conductivity, and high electrochemical capability [22–26]. Moreover, the metal silicides have excellent interfacial properties with Si and possess low internal resistance as they are produced as binder-free electrodes (the

* Corresponding authors.
E-mail address: gohbt@um.edu.my (B.T. Goh).

https://doi.org/10.1016/j.apsusc.2018.06.140
Received 4 October 2017; Received in revised form 14 May 2018; Accepted 15 June 2018
Available online 19 June 2018
0169-4332/

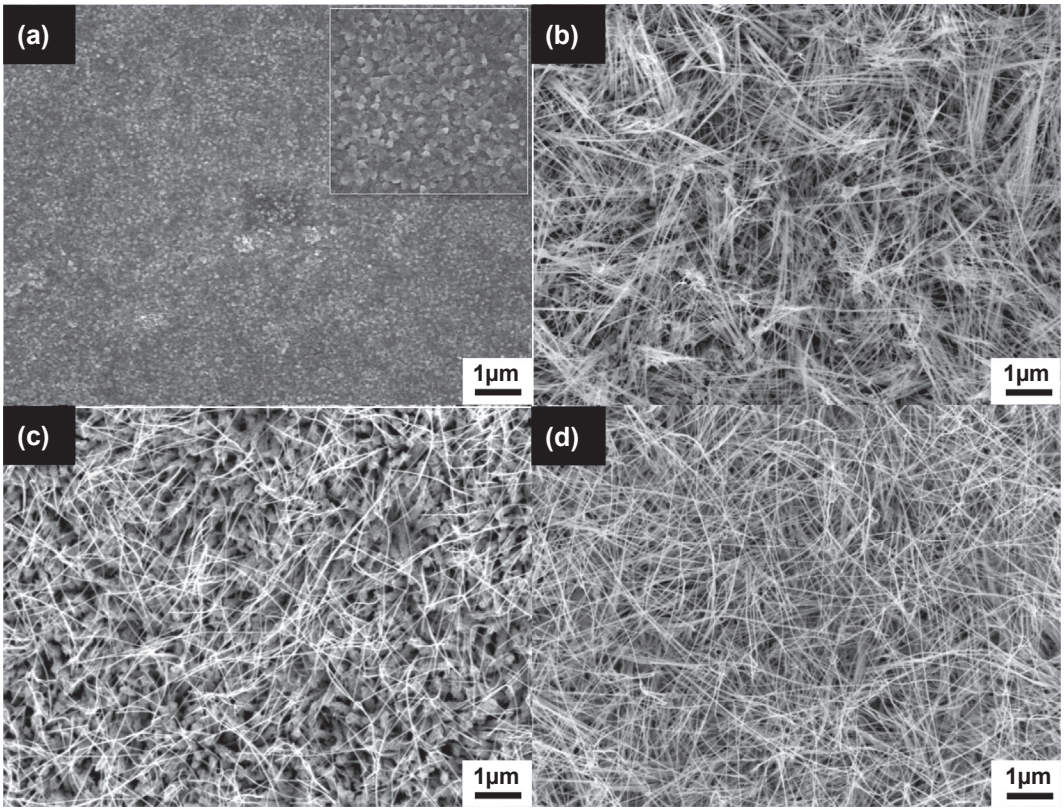

Fig. 1. FESEM images of (a) NiSi CS110, (b) NiSi CS220, (c) NiSi NF110, and (d) NiSi NF220.

materials can be grown directly on conductive substrates). Ni silicides, cobalt silicides ($CoSi_2$) and titanium silicides ($TiSi_2$) are among the few metal silicide materials are considered promising candidates as electrode materials for supercapacitors. However, $CoSi_2$ and $TiSi_2$ have some limitations in terms of high resistivity and high Si consumption which is the main concern in commercial integrated circuits [27–29]. The low resistivity, high metallic properties, low formation temperatures, low Si consumption and fast diffusion of Ni in Si at temperature below 350 °C of Ni silicides are beneficial to be used as good electrode materials [30–33]. Moreover, NiSi with nanowire morphology can supply extremely large surface area which is another plus point that can address the limitations of other metal silicides for EC applications.

In this work, NiSi NWs were grown using the conventional chemical vapor deposition (CVD) system followed by the solid-phase diffusion controlled growth. There are a variety of growth techniques for NiSi nanowires, most of which can be divided into three categories [34]: delivery of Si to Ni film [28,31,35,36], delivery of Ni to Si NWs [30], and simultaneous delivery of Si and Ni [37,38]. Due to its simplicity and low cost, CVD has been chosen in this studied. The solid-phase diffusion controlled growth has demonstrated the capability to grow high density, long, and thin NiSi NWs (the estimated length and diameter are approximately 5 μm and 20–30 nm respectively) [36]. The objectives of this work are to study the effects of Ni film thickness on the growth of NiSi nanostructures on c-Si and Ni foil substrates in terms of the morphological and structural properties. Moreover, the capacitive behaviors of the NiSi nanostructure electrodes in three-electrode configuration and asymmetry EC were investigated by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS).

2. Experimental methods

2.1. Electrode fabrications

NiSi NWs were grown on Ni-coated crystal silicon (c-Si) and Ni foil substrates in a home-built CVD system [39]. Ni thin films with the thicknesses of 110 ± 5 and 220 ± 5 nm were coated on both the substrates by thermal evaporation prior to the growth of the NiSi NWs. During the evaporation process, the base pressure, substrate temperature, filament temperature, and hydrogen flow rate were maintained at 0.6 mbar, 150 °C, 1600 °C, and 100 sccm, respectively, while the substrate-to-filament distance was fixed at 2.5 cm. The filament temperature was measured using a Reytek, Raynger 3i pyrometer. The thickness of the evaporated Ni thin films was determined using a KLA-TENCOR mechanical surface profilometer. The Ni thin films on the c-Si and Ni foil substrates were then annealed at the temperature of 480 °C followed by H_2 plasma treatment for 10 min at the same temperature prior to the growth of the NiSi NWs. This one-step process of annealing followed by H_2 plasma treatment was done to allow Ni nanoparticles to form for the solid-phase diffusion controlled growth of NiSi NWs. For the H_2 plasma treatment process, the rf power and the hydrogen flow-rate were fixed at 6 W (210 mW/cm^{-2}) and 100 sccm, respectively. The deposition pressure, substrate temperature, H_2 flow-rate, and SiH_4 flow-rate were fixed at 3 mbar, 480 °C, 100 sccm, and 3.5 sccm, respectively, during the growth process. NiSi NWs grown on Ni-coated crystal silicon (c-Si) with the Ni thicknesses of 110 ± 5 and 220 ± 5 nm were labeled as NiSi CS110 and NiSi CS220, respectively. NiSi NWs grown on Ni foil substrates with the Ni thicknesses of 110 ± 5 and 220 ± 5 nm were labeled as NiSi NF110 and NiSi NF220, respectively.