Synthesis and thermoelectric characterization of nickel/silicon nanowire arrays by electroplating technique

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A new integrate thermoelectric materials based on silicon nanowires (SiNWs) was described. In this structure, the SiNWs was fabricated by chemical etching technique as the backbone, and then a thin layer of Nickel nanoparticles was plated on the sidewall of SiNWs by elelctroplating and thermal rapid annealing technique, which characterized by Energy Dispersive Spectroscopy (EDS), and Scanning Electron Microscopy (SEM) to obtain the information on the structural and morphological properties. The thermoelectric behaviors of Ni/SiNWs have been investigated. It is conclude that the Ni/SiNWs nanocomposite could realize power output. So the Ni/SiNWs nanocomposite is a good alternative for integrate thermoelectric devices.

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1. Introduction

Nanostructured materials have attracted great interest in their novel physical and chemical properties different from those in bulk state and in their potential applications for developing new types of electronic, magnetic, optic, photocatalytic, and energy storage devices. In particular, the fabrication of Ni/SiNWs (silicon nanowires) nanostructure has recently attracted much attention because of their unique magnetic properties, pseudo capacitance characteristics and other potential technological applications. Several techniques have been reported to form materials nanostructure based on silicon, for example, implantation of metal ions into Si followed by thermal annealing [1, 2], metal catalyzed growth using a Si source (SiH_4) in a CVD reactor [3], metal silicide growth from Si nanowire template [4] and metal-induced direct nickel silicide formation on silicon [5], etc. In this paper, we reported a different method to form Ni/Si nanowires on Si nanowires substrate based on electrolplating technology. This method is compatible with the conventional top-down technical approach and has several advantages over the aforementioned synthesis methods, such as low cost and easy to be implemented. For all the nanostructure synthesis standard silicon manufacturing techniques are employed which would enable easy integration of these nanostructures with routine device technology. Scanning electron microscopy (SEM), Energy Dispersive Spectroscopy (EDS), I-V curves and I-△T curves were used to characterize the morphologies, microstructure and thermoelectrical properties of the as-formed nanowires. The variation relationships between thermoelectric current and temperature were reported about the structure reference on the Room Temperature.

2. Experimental details

The nanostructure of silicon nanowires plated nickel were prepared via two steps, namely, the fabrication of silicon nanowires and electroplating Ni on it.

Specimens and solutions

Single-polished P-type silicon-wafers (resistivity about 10-20 Ωcm) were used as the substrates for SiNWs growth. $AgNO_3$ (35mM) and HF 20% (concentration of solution) were used as-received without further purification. For the electroplating of the nickel, the simple bath consisted of a mixture as listed in Table 1. In all preparations absolute ethanol and deionized water were used.

Fabrication of SiNWs

The specimens were degreased first by ultrasonic-cleaning in acetone for 10 min and then by soak-cleaning in solutions of H_2SO_4 (98%): H_2O_2 (30%) (3:1) for 10 min after rinsed with deionized water. These prepared silicon substrates were etched for 30 min with a mixture of solution consisted of $AgNO_3$ (35mM) and HF (20%) at Room Temperature. Silver particles adhered on the etched SiNWs were removed by immersion in HNO_3 (about 50%), and then silicon wafers were then rinsed with deionized water and dried at 30 °C by nitrogen. Later, some high-quality Si nanowire arrays were produced on the Si substrates [6].

Table 1. Materials and conditions used in the electroplating nickel process.

Chemical name	Concentration(M)	Main function
$NiSO_4 \cdot 6H_2O$	3 m	Ni source
Ammonium chloride	0.53	Conductive salt
Ethylene diamine tetraacetic acid	0.36	Complexing agent
Ammonia	X	Adjust pH 8－9

Fabrication of Ni/Si nanostructure

The surface wettability of SiNWs substrate were activated and enhanced by infused into a special buffer solution for 40s.

The Ni naoparticles were produced on the sidewall of the SiNWs by electroplating. The Ni/SiNWs sample was dipped in the electroplating solution and the important instrumental conditions are listed in Table 1. $NiSO_4 \cdot 6H_2O$ was used as the Ni source and EDTA as the complexing agent. In practice, the plating bath was warmed at 65±1℃ with stirring and pH 8–9 adjusted by ammonia, and the current density was 50 mA cm^{-2} [7]. After plating, the Ni/SiNWs was annealed for 400 sec at the temperatures 750°C with a rapid thermal annealing (RTA) system in Ar atmosphere, finally, the top unreacted Ni and other impurities were chemically removed in the solution of H_2SO_4:H_2O_2: H_2O = 1:2:3(volume ratio), leaving NiSi-SiNWs nanostructure in substrate. Adopted annealing process get Ni-Si phase to form ohmic contact. The schematic diagram was shown in Fig. 1.

The elemental composition of thin film was examined using Energy Dispersive Spectroscopy (EDS). The Seebeck coefficient of samples was determined from the thermoelectromotive force (ΔV) and temperature difference (ΔT) by $S=\Delta V/\Delta T$. The time evolution of the thermoelectromotive force was monitored by a digital multimeter while the temperature was measured by a thermocouple.

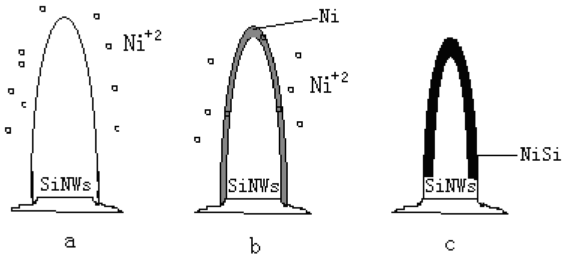

Fig. 1. The schematic diagram of the NiSi-SiNWs nanostructure.

3. Results and discussion

Fig. 2 shows SEM images for the SiNWs growth in the etchant which HF/$AgNO_3$ of aqueous precursor was used. Fig. 2(a) and (b) are the top view and cross-sectional view picture of the as-prepared SiNWs. It was found that it is a bundle-like structure and all SiNWs are vertically aligned to the substrate. The interface between the SiNWs and the bulk silicon was clear and layered. The length of the SiNWs is about 70 µm, the diameters of SiNWs ranged from 60 to 300 nm. The structure has good surface quality and provides more effective surface area than a planar electrode. The total equation Oxidation-reduction was shown in Eq. (1). Two simultaneous processes occur at the silicon surface: electroless silver deposition (EMD) on a silicon surface based on the galvanic displacement reaction and the oxidation of silicon, either an electron-releasing or hole-consuming. SiF_4 created in the reaction could be changed H_2SiF_6 in HF (aq).

$$Si + 4F^- + 4H^+ + 2Ag^+ = SiF_4 + H_2\uparrow + 2Ag + 2H^+ \quad (1)$$

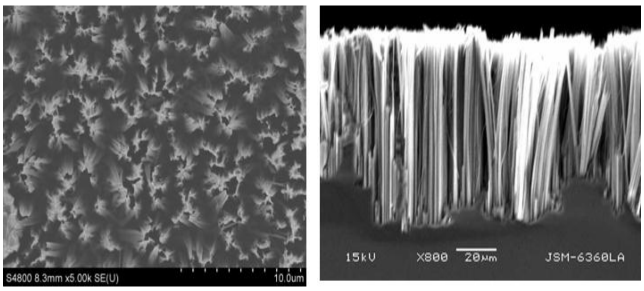

Fig. 2. SEM images of the SiNWs. (a): top view; (b) cross-sectional.

Fig. 3 shows the cross section of the Ni/SiNWs structure. This micrograph corresponds to process stage depicted schematically in Fig. 1. An additional thin layer of Ni nanoparticals can be observed on the inner sidewall of silicon nanowires (SiNWs). The diameter of Ni particles ranges from tens to hundreds of nanometer. And it can be observed that nickel particles were deposited onto the silicon nanowires all over, even including the root section.

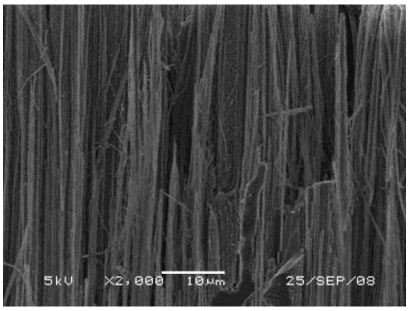

Fig. 3. The cross section of the Ni/SiNWs structure.

Fig. 4 shows the typical EDS patterns of the sample. It was verified that the layer plated onto the SiNWs is Ni. In addition, according to the EDS spectrums of multiple measurements in different parts of Ni/SiNWs, The characteristic peaks of Si were found. It was implied that Ni coating formed is a thin layer.

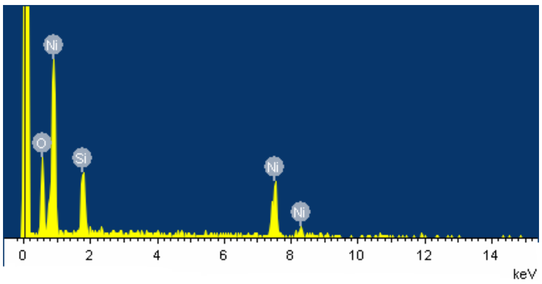

Fig. 4. EDS patterns of the NiSi-SiNWs nanostructure.

The I-V characteristics of the Ni/SiNWs also have been measured at the testing platform shown in Fig. 5 (a), and the corresponding current (I) versus voltage (V) (I–V) curve is plotted in Fig. 5(b). It is found that the structure shows an ohmic contact characteristic.

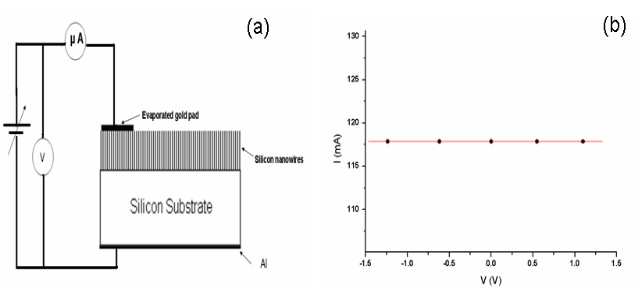

Fig. 5. (a) the testing platform of I-V characteristics; (b) the relationship between I and V.

The thermoelectric properties testing platform is shown in Fig. 6.

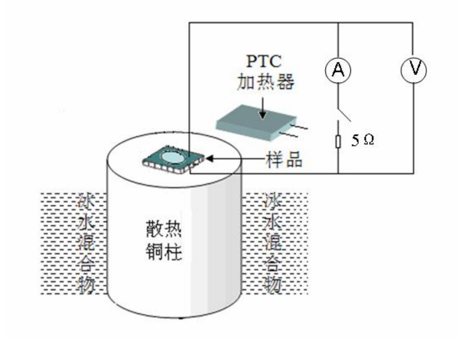

Fig. 6. The thermoelectric properties testing platform.

When the circuit of load resistance in open state, the surface of Ni/SiNWs composite was heated by PTC, the relationships between the temperature difference and thermoelectric voltage of Ni/SiNWs is shown in Fig.7 (a). The data (ΔT, ΔV) of Ni/SiNWs obtained at each temperature point was used to derive the Seebeck coefficient, calculated from the slope of the ΔT-ΔV plot. It can be found that the Seebeck coefficient of Ni/SiNWs is 350 μV/K.

When the circuit of load resistance in close state, given the temperature difference on the Ni/SiNWs composite. The relationship between the temperature difference and thermoelectric voltage of Ni/SiNWs is shown in Fig. 7 (b). It is illuminate that the structure could realize power output. When the temperature difference more than 150 K, the current and voltage all decreased, it may be caused by resistivity higher by temperature increased.

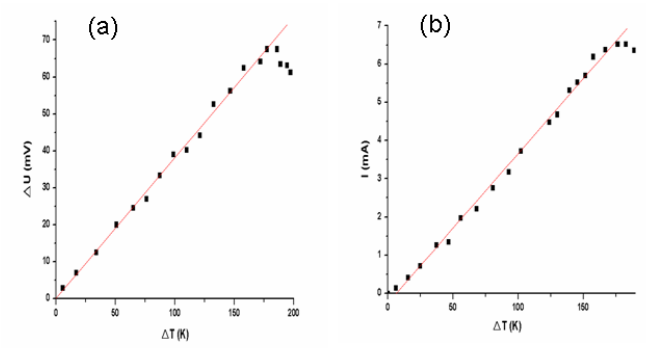

Fig. 7. (a) testing result of ΔT-ΔV, and (b) ΔT-I.

4. Conclusion

In summary, silicon nanowire was fabricated by chemical etching technique, and then electroplated nickel nanoparticles on the sidewall of SiNWs. The Ni/SiNWs naocomposite exhibits favorable thermoelectric properties. Nickle plated is thus a suitable method to enhance the thermoelectric property of silicon nanowires and the mature silicon technology renders Ni/SiNWs attractive to power generation.

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