A simple and templet-free method to fabricate nickel nanowire arrays with the assistance of magnetic field

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Vertically aligned nickel nanowire arrays were successfully fabricated on silicon wafers by a chemical deposition process with the assistance of an extra magnetic field. The nanowire arrays are composed of polycrystal nickel nanowire typically about 300nm in diameter and a few of micrometer in length. The metal nickel was deposited and synchronously self-assembled into wires in the redox process. The nickel nanowires were aligned with their magnetic easy axes along the external magnetic line of force. A possible growth mechanism is also discussed. This method provides a simple and templet-free method to fabricate nanostructure and opens a new channel for building vertically aligned heterojunction device arrays.

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1. Introduction

Nanostructures have been receiving increasing attention for their excellent performance [1-5]. The potential application including magnetic sensors, lithium-ion batteries, electro-optical sensing devices and the miniaturization of devices are making it more attractive [6-9]. It is very important to control the formation of nanostructures in nanoscience and technology. This is one of the greatest challenges for researchers. As the basic building block of a nanostructure, the nanowire arrays are becoming the focus of intense research efforts. Efficiently precise formation and manipulation of nanowire arrays at desired locations are becoming a key challenge to many researchers [10]. Various fabrication techniques have been developed for the synthesis of nanowire arrays, including templet synthesis, the vapor-liquid-solid growth mechanism, sub-micrometer lithography and electrochemical means [11-14]. However, the sophistication, high cost and low yield of those methods limit their wide application in the microelectronical industry.

In this paper, we successfully fabricated the vertically aligned nickel nanowire arrays on silicon substrate. We present a very simple and economical method to produce vertical aligned nickel nanowire arrays by chemical deposition and manipulate the formation of nanowire arrays at desired location. So it may be applied in the microelectronical industry in the near future. Besides, we are studying the catalytic property and special wettability of the nanowire arrays.

2. Experimental

All chemicals were of analytical reagent grade purity and purchased from approved qualified suppliers. All chemicals were used without further purification. Distilled and deionized water was used throughout the experiments.

Firstly, a silicon wafer was immersed in toluene, acetone and ethanol with ultrasonic for 5min respectively to remove the original organic layer on the surface. Then the silicon wafer was soaked in a freshly prepared piranha solution of 70:30 (v/v) 98% H_2SO_4 and 30% H_2O_2 at 80℃ for 10min; then the silicon wafer was treated with a solution of 4:1 (v/v) 49%HF and 40% NH_4F for 90s. The silicon wafer was rinsed copiously with deionized water and absolute ethanol sequentially, and dried under a stream of nitrogen [15]. Next, a self-assembled monolayer (SAM) was patterned on the silicon wafer by immersing the silicon wafer in an ethanol solution containing 1×10^{-5} mol/L 3-mercapto propyl trimethoxy silane [$(CH_3O-)_3Si-(CH_2)_3-SH$] for 12 h at room temperature. The -O-Si-$(CH_2)_3$-SH- film was formed by methoxy groups (CH_3O-) spontaneously adsorbing on the silicon surface with Si-O-Si covalent bonding. The pendant -SH groups provided the active sites to absorb the catalyst in the following process. Then, the silicon wafer was immersed in the solution. PD(II) was prepared according to Xu's work [16]. The second SAM was formed with the becoming of Pd-SH bonding. The Pd catalyst induced the redox reaction. Finally, the chemical deposition was carried out at 80℃ for 10min under a 0.3T external magnetic field (0-120A/m, designed by Nanjing University, Nanjing, China). The chemical solution plating contains 7.8g/L nickel sulfate, 5.0g/L sodium hydroxide and a given amount of hydrazine. Based on solution reduction reaction, metallic nickel was deposited and synchronously self-assembled into wire under magnetic field.

The structural properties of the as-obtained samples were characterized by an X-ray diffractometer (XRD) with Cu K_α radiation (λ=1.54056 nm). Field-emission scanning

electron microscope (SEM, LEO 1530 FEG, at 10 kV) and energy-dispersive X-ray spectroscopy (EDS, Genesis Spectrum, USA) attached to the SEM instruments were used to examine the morphology and composition of the samples.

3. Results and discussion

Shown in Fig. 1 are the images of vertically aligned nanowire arrays grown on silicon substrate fabricated by this technique. Clearly the figure shows that the wires were growing from the substrate to outside along the direction of magnetic force. The arrays are vertical to the substrate. The nanowires have diameters ranging from 200 to 400 nm and heights exceeding 10 um. The nanowire arrays have a very high aspect ratio. An EDS spectrum of the nanowire arrays were measured. Only Ni signal was detected in the sample, which confirmed that the nanowire arrays were mainly composed of primarily nickel. In order to obtain the nanowire arrays' formation process, the silicon wafer was taken out after the reaction starts 5 minutes, rapidly rinsed with deionized water, and immediately dried with a flow of pure nitrogen. The image was shown in figure1(c). As can be seen from the figure, there are many active sites on the silicon substrate. It is obviously that the nanowires were coming into existence.

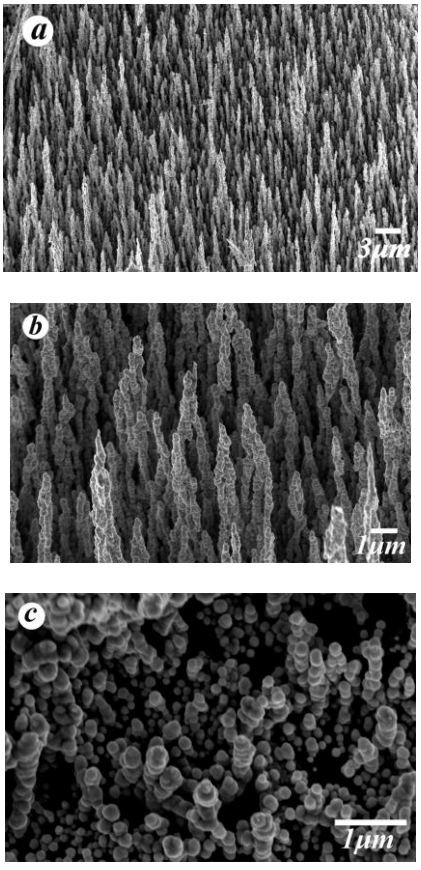

Fig. 1. a. SEM image of the sample. b. magnified image of the sample. C. SEM image of the nanowire arrays after the reaction starts 5 minutes.

The typical XRD pattern of the product is shown in Fig. 2. It shows sharp peaks corresponding to the (111), (200) and (220) diffraction peaks of the metallic Ni crystal. All peaks can be indexed with the reflections of face-centered cubic Ni. We calculated by the Scherrer's equation that the crystalline size is about 11nm. The ratio among the intensity of (111), (200) and (220) diffraction peaks is 100:39:20. It is highly consistent with the conventional value. As we know, (111) is the magnetic easy axis of a cubic nickel crystal [17] which aligned along the long axis of the polycrystalline wires.

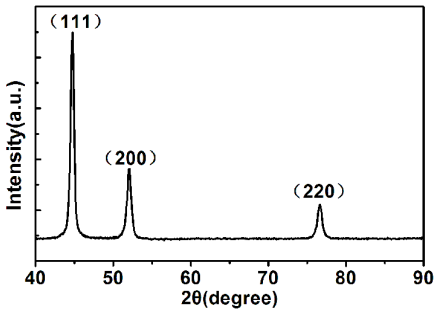

Fig. 2. XRD image of the sample.

Based on the above results, we can deduce that the growth orientation of nanowire arrays was controlled by the size and dispersion of the nickel nanoparticle and the direction of the exteral magnetic field. On the nucleation and growth stage, a number of single nickel particles formed at the active sites. They would self-assemble into a bigger one. Then the big particle would be magnetized in the magnetic field. They would be aggregated on the tip of nanowires under the influence of external magnetic dipoles interaction. These particles would array along the magnetic gradient. At the same time, the head of each nanowires have a much larger surface area, low surface energy associated with the morphology and a higher nucleation density for the effect of the magnetic field. So the nanowires were growing along the magnetic force at predefined positions. During this process, the growth rate perpendicular to the nanowires axis was limited. So the vertically aligned nickel nanowire arrays were successfully fabricated.

4. Conclusions

In summary, a new method to fabricate nanowire arrays was developed. The nanowire arrays vertically aligned on silicon and were localized in desired place by chemical deposition in magnetic field. The results showed that this method would be an effective and tunable way to fabricate the nanowire arrays. The magnetic field provided the attraction force among nickel crystallites to cause them to grow into wires. In addition, the external magnetic field made the nanowires' magnetic easy axes aligned along magnetic line force.

This method represents a direction with the advantages of low-cost, ease of control and flexible to form the nanostructures.

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