Selective growth of silica nanowires on nickel nanostructures created by atomic force microscopy nanomachining

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Abstract

We report the selective growth of amorphous silica nanowires on nickel nanostructures created by an atomic force microscopy nanomachining and lift-off process. Successful growth of patterned nanowire bunches or single nanowires on Si substrates has been realized by thermal annealing. The growth mechanism is found to be a combination of vapour–liquid–solid and solid–liquid–solid modes. In addition, the relationship between the nanowire length and the growth time has a nonlinear dependence.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One-dimensional nanomaterials have been the focus of extensive research activities in recent years due to their novel properties and applications in nanodevices [1]. In particular, silica nanowires have been found to emit strong blue light [2] and they can be potentially used as emitters or interconnects [3] in nanophotonic devices. For the synthesis, catalytic growth is commonly employed, and several methods, including laser ablation [2], thermal evaporation [4, 5], thermal annealing [6–8], and chemical vapour deposition [9, 10], have been reported in the literature. Two types of growth mechanism, namely vapour–liquid–solid (VLS) [1, 2, 7] and solid–liquid–solid (SLS) [6, 8, 11], have been used to explain the catalytic growth. Additionally, size control has also been realized by sol–gel methods with the use of anodic alumina membranes [12, 13].

In many applications, selective area growth of nanowires is of great importance for device construction. Taking carbon nanotubes for example, various techniques have already been utilized, such as photolithography, e-beam lithography, microcontact printing, and shadow masking [14, 15]. Among these techniques, e-beam lithography is frequently applied to generate nanoscale catalytic templates for patterned growth of individual nanowires. On the other hand, scanning probe lithography is well known for the effective creation of nanostructures [16], and naturally can be utilized for the selective growth of nanowires.

Since reports on the selective growth of silica nanowires have been absent in the literature to our knowledge, it would be of great interest to realize such a goal. In this paper, we report the selective growth of amorphous silica nanowires on nickel catalytic templates that are created by an atomic force microscopy (AFM) nanomachining and lift-off process [17]. Successful growth of patterned nanowire bunches or single nanowires on Si substrates has been realized by thermal annealing. In addition, the growth mechanism has also been explored.

2. Experiment

A schematic diagram of the experimental procedure is shown in figure 1. A solution of 1.25 wt% poly(methylmethacrylate) (PMMA) in chlorobenzene was spin-coated on a silicon substrate. After a 30 min soft baking at 150 °C, a PMMA film with a thickness of around 30 nm was produced. A commercial AFM (Smena-B, NT-MDT, Russia) and rectangular silicon probes (NSC15, MikroMasch, Russia) were employed for the experiment. By scratching or indenting the PMMA film at
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PMMA
substrate

Ni nanostructures

Ni coating
substrate

silica nanowire growth
substrate

Figure 1. Schematic diagram of the experimental procedure. (a) A PMMA film was spin-coated on the substrate. (b) The PMMA film was scratched or indented by an AFM tip. (c) A nickel film was coated. (d) Nickel nanostructures were created after lift-off. (e) Selective growth of silica nanowires was realized by thermal annealing.

Figure 2. (a) SEM and (b) TEM images of silica nanowires grown at 1100 °C for 20 min on a nickel film. The inset in (b) is the electron beam diffraction pattern.

Figure 3. SEM images of (a) a 3 × 3 array of nickel squares created by scratching, (b) the corresponding silica nanowires after a growth time of 390 s, (c) a zoomed view of the marked region in (b), and (d) a zoomed view of the scattered white spots in (b).

3. Results and discussion

To verify if silica nanowires were grown successfully, a nickel film was first used as the catalyst. An SEM image of the result after a growth time of 20 min is shown in figure 2(a) and it clearly exhibits the generation of nanowires. A TEM image of the nanowires is shown in figure 2(b) and indicates that the diameters range roughly between 15 and 30 nm. From the electron beam diffraction pattern shown in the inset, the amorphous nature of the nanowires is ascertained. In addition, an average composition of SiO$_1.6$ is determined from energy dispersive x-ray (EDX) spectrometry analysis on several nanowires. Also, the catalysts at the nanowire ends are found to be nickel silicide, as expected in consideration of the high growth temperature. The photoluminescence spectrum obtained with excitation from a 325 nm He–Cd laser manifests two emission peaks at 420 and 470 nm, which are in agreement with those reported in the literature [2]. All the above results confirm the successful growth of amorphous silica nanowires.

For the selective growth of silica nanowires, nickel nanostructures were created and used for subsequent catalytic growth. The SEM images of a 3 × 3 array of squares created by scratching and the corresponding nanowire bunches after a growth time of 390 s are shown in figures 3(a) and (b), respectively. A zoomed image of a nanowire bunch is also shown in figure 3(c). It is interesting that there are scattered white spots outside of the original squares, as can be seen in figure 3(b). A zoomed image of the spots is provided in figure 3(d) and it reveals that there are no nanowires on these spots. An EDX analysis indicates that the major composition is nickel. It is obvious that the spots originate from the diffusion of nickel into the substrate and the subsequent transformation into nickel silicide at the high growth temperature. The spots have the shape of an inverted pyramid due to the (001) substrate plane and appear as rectangles, as in figure 3(d).

In addition to large patterns, nanodot arrays were also created by tip indenting. The AFM image of a 10 × 10
Figure 4. (a) AFM image of a 10 × 10 nanohole array on a PMMA film created by indenting, and (b) the corresponding SEM image of the created nickel nanodots after lift-off. Zoomed SEM images of the nanodots (c) before and (d) after thermal annealing at 1000 °C for 20 min.

Figure 5. (a)–(d) SEM images of single silica nanowires grown at 1100 °C for periods of 300, 360, 390 and 420 s, respectively, and (e)–(h) the corresponding zoomed images of the nanowires.
is still of value. An investigation of the growth kinetics detail is currently under way.

4. Conclusion

The selective growth of amorphous silica nanowires on nickel nanostructures by thermally annealing silicon substrates has been successfully performed. The nickel nanostructures, including squares and nanodots, are created by an AFM nanomachining and lift-off process. With the use of nickel nanodots as catalysts, single silica nanowires with a uniform diameter of 20 nm have been grown successfully. Furthermore, it is found that each nanodot catalyst splits into two nanodots and they are present at both ends of a nanowire. Consequently, the growth mechanism is considered a combination of VLS and SLS modes in contrast to reports in the literature. In addition, the nanowire length can be controlled by the growth time, and a nonlinear dependence has been observed.

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