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Flow assisted synthesis of highly ordered silica nanowire arrays

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Abstract Silica nanowires were synthesized through a self-supplied vapor–liquid–solid (VLS) mechanism. Unlike randomly entangled nanowires on the substrate, highly ordered nanowire arrays have been successfully fabricated using a sandwich-like configuration to define and enhance the local gas-flow. As-synthesized nanowires were characterized to be amorphous silicon dioxide with Au as catalysts. The role of the sandwich-like structure and the effect of gas-flow on the alignment of silica nanowires are demonstrated.

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1 Introduction

Nanoscale one-dimensional structures have been extensively investigated for their potential applications in various fields [1–3]. Vapor–liquid–solid growth, an effective route to fabricate nanowires of different materials, has been widely used since it was first proposed by Wagner and Ellis [4]. Metal catalysts are used to define the diameter of the nanowire and direct the growth. In addition, many other mechanisms, such as vapor–solid–solid (VSS), solution–liquid–solid (SLS) and oxide-assisted growth (OAG), have also been employed for nanowire synthesis [5–7].

During vapor transport and deposition process, the growth orientation of nanowires or nanotubes was found to be influenced by the carrier gas flow direction [8, 9]. Novel and facile fabrication technology have been established for growth of silicon oxide nanowires. Lai et al. [10] reported the growth of SiO_x nanowires catalyzed by Pt via a facile rapid thermal annealing method. Yang et al. [11] demonstrated the synthesis of ultra-long silica nanowires in acidic environment. Lee et al. [12] reported the synthesis of silica nanowires by direct solid state diffusion from the silica film. The growth of ordered silica nanowire arrays, however, has rarely been demonstrated to our knowledge. In this report, we present the synthesis of silica nanowire arrays through a self-supplied process, with their alignment direction being determined by local gas-flow direction. The importance of the enhanced gas-flow by a simple sandwich-like structure is discussed.

2 Experimental

A cleaned p-type Si (100) wafer was coated with 15 nm Au film and placed in the center of a horizontal quartz tube furnace. For controlled nanowire array growth, a sandwich-like structure was employed; that is, another Si wafer was put on top of the coated substrate and this wafer was either bare or coated with Au film. The Au coated surface was always kept in between. Central temperature of the furnace was increased to 900°C at a rate of 20°C min^{-1} under a constant argon flow of 90 sccm (standard cubic centimeter per minute). Ambient pressure inside the tube was around 1 torr during the entire process. Subsequently, the furnace was cooled down to room temperature.

Morphology and microstructure of the product was characterized by field emission scanning electron microscopy (FESEM, JEOL 6340F) and transmission electron microscopy (TEM, JEOL 2010). The chemical compositions were analyzed using energy dispersive spectroscopy (EDS) attached to the TEM.

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3 Results and discussion

A schematic illustration of the experimental setup (sandwich-like structure) is shown in Fig. 1. Another Si wafer (either bare or coated with Au film) was put on top of the coated substrate to enhance the Ar gas-flow between the two substrates. A representative scanning electron microscopy (SEM) image of the products synthesized without cover wafer is shown in Fig. 2. Dense and entangled nanowires grew on the Si substrate without any preferential alignment direction. The diameters of the nanowires are in the range of 20–100 nm.

Unlike randomly entangled nanowires, well aligned nanowire arrays were successfully synthesized when a sandwich-like structure was used to control the local gas-flow direction [13]. Figure 3 shows the nanowire arrays grown in different configurations. Figure 3a is a SEM image of multilayer nanowire arrays grown on the substrate coated with Au film in a sandwich-like structure. The morphologies are essentially the same on the two wafers when both of them were coated. When a bare Si wafer was used as cover wafer for nanowire array synthesis, ordered nanowires along a single direction were observed on the bare wafer after growth as shown in Fig. 3b. Although no catalyst was deposited before growth, Au nanoparticles were found to attach to the surface of the bare wafer due to contact, therefore resulting in the oriented nanowire growth. The inset in Fig. 3b is a high magnification SEM image of the nanowire arrays.

The structure and chemical composition of the nanowires were studied using TEM and EDS. A typical low magnification TEM image is shown in Fig. 4a. Magnified TEM image of a single nanowire with a diameter of 23 nm is shown in Fig. 4b; a catalyst particle can be observed at the front. The highly diffusive selected area electron diffraction (SAED) pattern taken from the nanowire reveals that the nanowire is amorphous (Fig. 4b inset). Chemical composition was determined with EDS. The catalyst is composed of Au and an atomic ratio of $Si : O = 1 : 2.03$ is obtained from the nanowire (Fig. 4c). Copper peaks are from the copper grid used for TEM characterization.

In order to further demonstrate the effect of gas-flow on the alignment of silica nanowires, the arrays grown at different locations of the wafer were examined. Figure 5a is a depiction of two different locations (b and c) on the wafer; and the corresponding SEM images of the nanowire array morphologies are shown in Fig. 5b and Fig. 5c, respectively. It can be seen that the alignment orientation of the nanowire arrays are determined by the local gas-flow direction (indicated by arrows in Fig. 5a). The alignment orien-

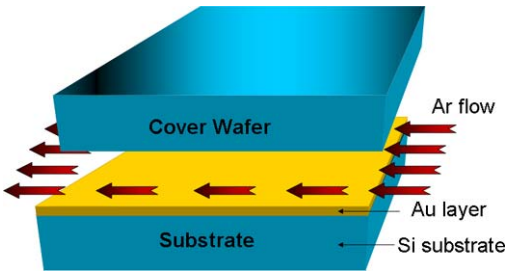

Fig. 1 A schematic illustration of the sandwich-like structures used for nanowire array synthesis

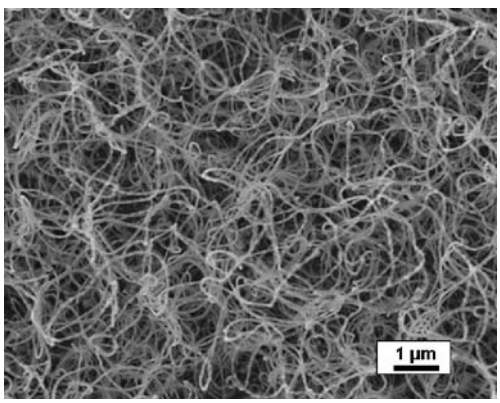

Fig. 2 SEM image of entangled nanowires synthesized without cover wafer

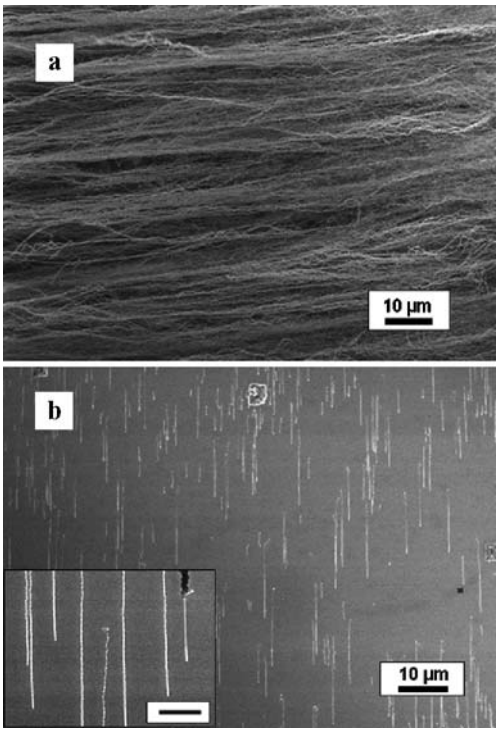

Fig. 3 SEM images of silica nanowire arrays synthesized using a sandwich-like structure: **a** dense and multilayer nanowire arrays grown on the substrate coated with Au film; **b** nanowire arrays grown on the surface of bare substrate used as cover wafer. The *inset* is a high magnification SEM image. Scale bar is 1 μm

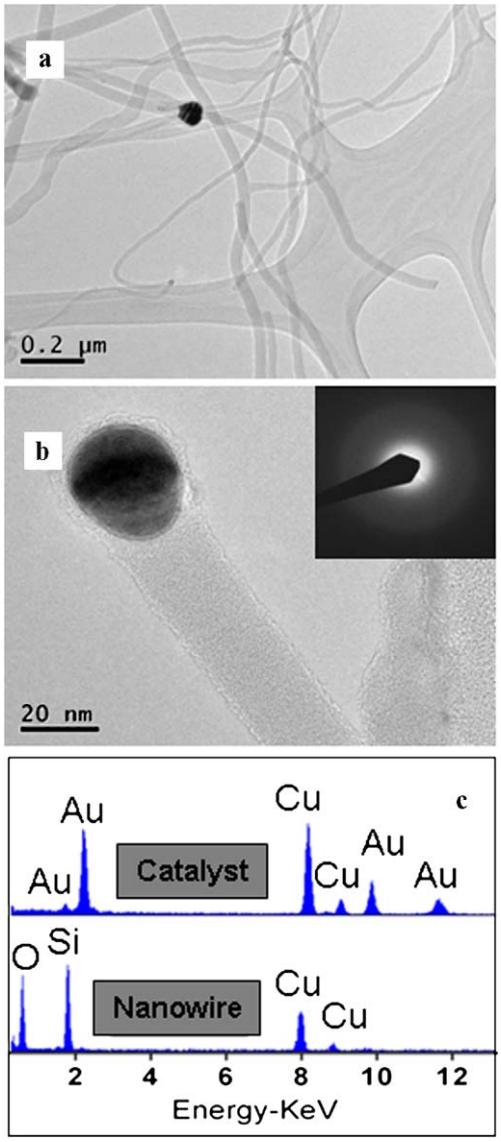

Fig. 4 **a** Low magnification TEM image of the silica nanowires; **b** high magnification TEM image of a single nanowire. The *inset* is SAED pattern taken from the nanowire; **c** EDS spectra of the catalyst particle and the nanowire

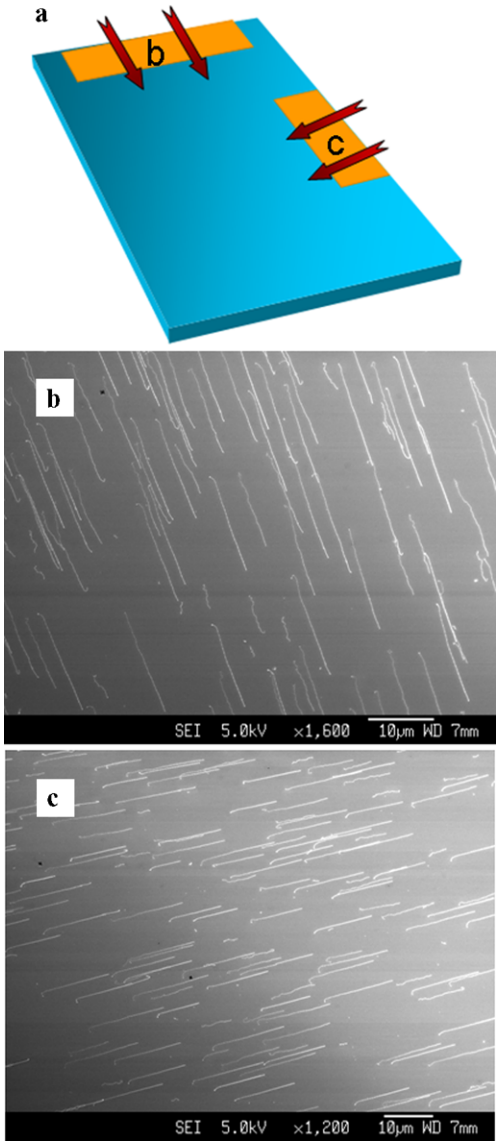

Fig. 5 **a** Depictions of the two regions where the corresponding nanowire morphologies were examined; **b–c** SEM images of the nanowire arrays grew along two different directions

tations of regions b and c are almost perpendicular to each other.

Since metal catalyst particles were always found at the front, the growth of the nanowires can be explained by vapor–liquid–solid (VLS) mechanism [4]. Gas-flow has been demonstrated to affect the growth direction of nanowires or nanotubes due to buoyancy effect and shear flow interaction [8, 9]. Here we show that silica nanowire arrays (Fig. 3) can be readily synthesized through a self-supplied growth process. And the key step is using a sandwich-like configuration [13] to define and enhance the local gas flow, while the nanowires synthesized without cover wafer were randomly distributed on the substrate (Fig. 2).

4 Conclusions

Silica nanowire arrays have been successfully synthesized through a self-supplied growth process. As-synthesized nanowires are found to be amorphous silicon dioxide nanowires. The growth process can be explained by the VLS mechanism. Unlike randomly entangled nanowires, well aligned nanowire arrays were grown using a simple sandwich-like configuration, with their growth direction determined by the local gas-flow.

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