

Self Growth of Silica Nanowires on a Si/SiO₂ Substrate

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ABSTRACT

The growth of amorphous silica nanowires by on-site feeding of silicon and oxygen is reported. The nanowires were grown on a nickel-coated oxidized silicon substrate without external silicon or oxygen sources. Transmission electron microscopy observation revealed that the nanowires, which have diameters of less than 50 nm and a length of several micrometers, were grown using a traditional vapor-liquid-solid mechanism. Blue photoluminescence was observed from these nanowires at room temperature. An approach to grow nanowires without external precursors may be useful when integrating nanowires into device structures. This can benefit the fabrication of nanowire-based nanodevices.

Key words : Silica nanowires, VLS mechanism, Photoluminescence

1. Introduction

Nanowires with a one-dimensional structure have great potential as building blocks in the fabrication of electronic, optoelectronic, electromechanic and sensor devices in nanometer scale.¹⁻³⁾ In particular, nanowires have advantages over thin films with respect to the study of the fundamental basis of their range of application. They also offer thermodynamically stable features and are typically single crystalline and free of defects. Moreover, the free standing nature of nanowires makes it possible to exclude the effect of thermal and lattice mismatches between the substrate and nanowires and opens the possibility of determining the intrinsic electrical and optical properties. To exploit this potential, however, the fabrication of nanowires for practical applications requires a controlled and/or in-situ procedure, such as the self-alignment of nanowires with hetero- or homo-interfaces for junction structures and doped nanowires.⁴⁻⁶⁾ Another key feature in the realization of the potential of nanowires is their integration into device architectures. Typically, most nanowires are grown using a vapor-liquid-solid (VLS) mechanism⁷⁾ with a metal catalyst with which the reactant vapor species are supplied externally from various solid, liquid, and gas precursors.⁸⁻¹²⁾ However, these methods are limited in their practical application for several reasons. First, the corrosive and flammable nature of the precursors can induce critical damage to integrated materials (e.g., Si, SiO₂, Al₂O₃, and metal). Second, there is an associated lack of controllability due to vapor species from external sources that are characterized

by a long diffusion length. This paper reports the synthesis of silica nanowires through the “on-site” supplying of reactant vapor without the involvement of external silicon or oxygen sources. The results imply that this approach feasibly integrates nanowires into the device architecture in the fabrication of nanowire-based nano devices.

2. Experimental procedure

Synthesis of silica nanowires was carried out in a hot-wall quartz tube reactor system. The substrates used were non-oxidized and oxidized silicon with a SiO₂ thickness of 500 nm as prepared by wet oxidation. The substrates were deposited on 2 nm of Ni as a catalyst by sputtering and were then placed in an area of uniform temperature in the center of the tube reactor. The system was heated to 800°C under a flow of hydrogen (H₂) at a rate of 1,000 cm³min⁻¹ and these conditions were maintained for 5 min. The nanowires grown on the substrates were characterized by scanning electron microscopy. Further structural and composition analyses of individual nanowires were performed using transmission electron microscopy. The optical properties were measured by photoluminescence (PL) at room temperature with an excitation wavelength of 325 nm (He-Cd laser).

3. Result and discussion

Fig. 1(a) shows SEM images of the substrates after the heat treatment. Nanowires with fairly uniform diameters ranging from 20 to 50 nm and lengths of ten micrometers [inset in Fig. 1 (a)] were grown and were distributed over the entire area of the substrates by simply heating the substrate under a flow of H₂. It was also possible to grow nanowires using different transition metal catalysts such as Co or Fe. Importantly, the nanowires were not grown on

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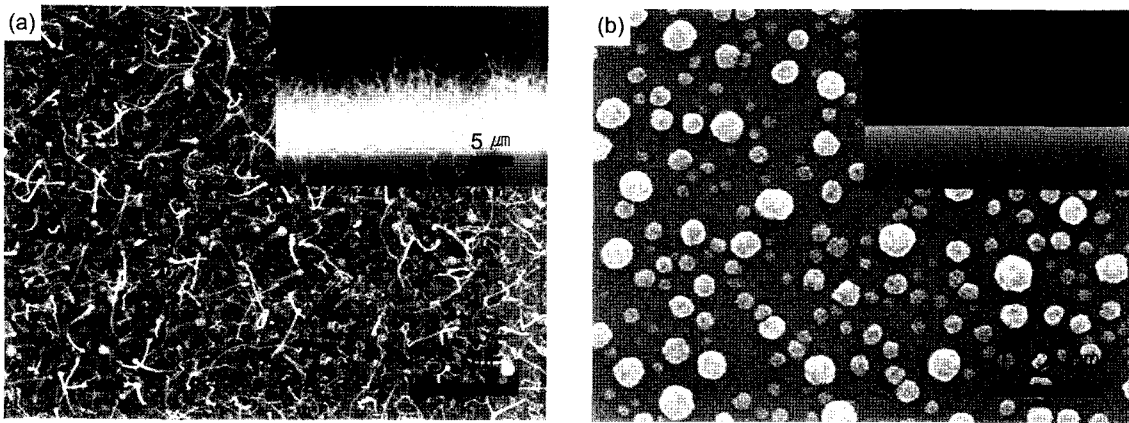


Fig. 1. SEM images of oxidized silicon (a) and a non-oxidized silicon substrate (b) after a heat treatment under a hydrogen atmosphere: The two insets show cross-sectional views of image (a) and (b), respectively.

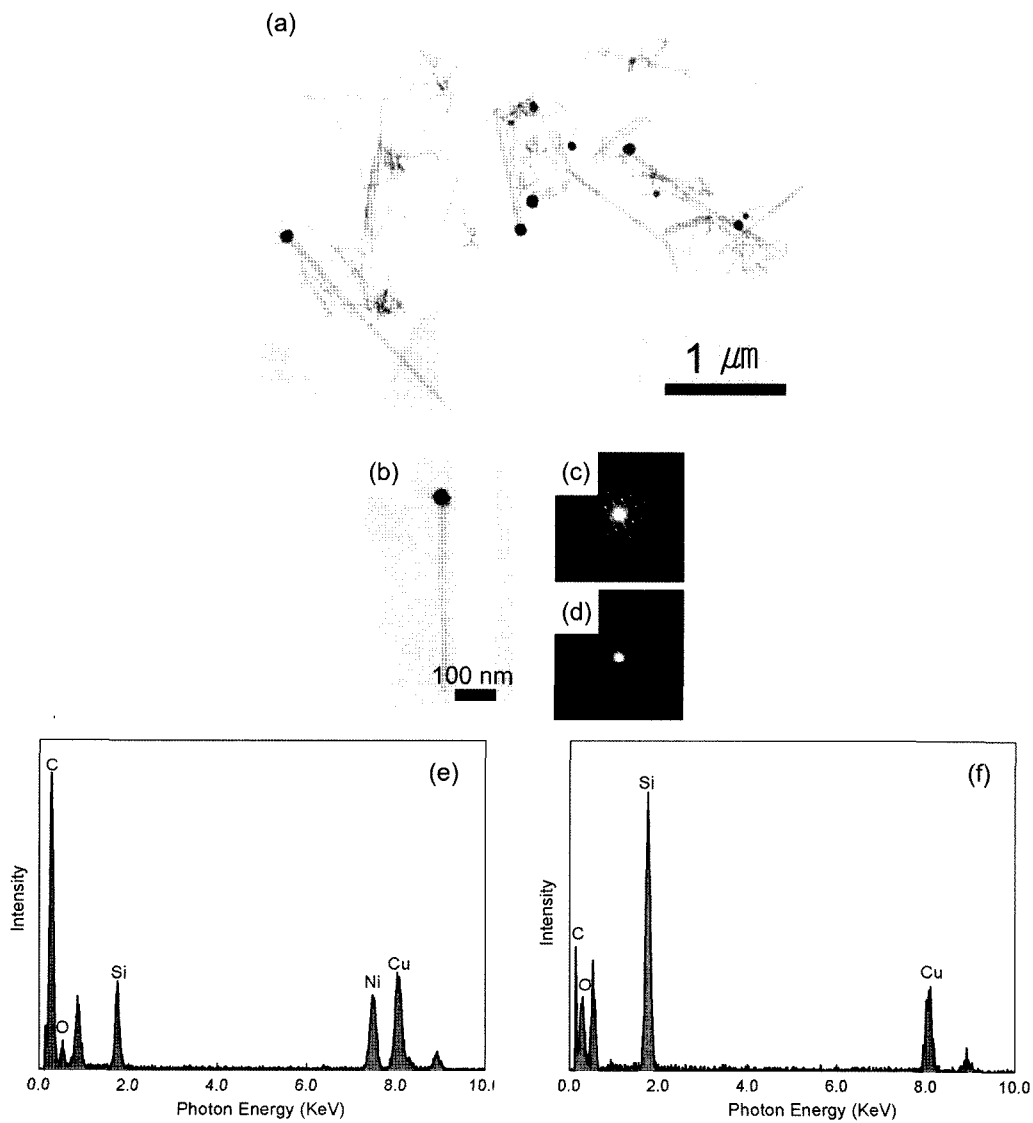


Fig. 2. (a) A low-magnification TEM image of silica NWs grown on oxidized silicon substrates, and (b) image of a typical individual NW. SAED patterns and EDS spectrums for the tip [(c) and (e)] and NW [(d) and (f)] of individual NWs, respectively.

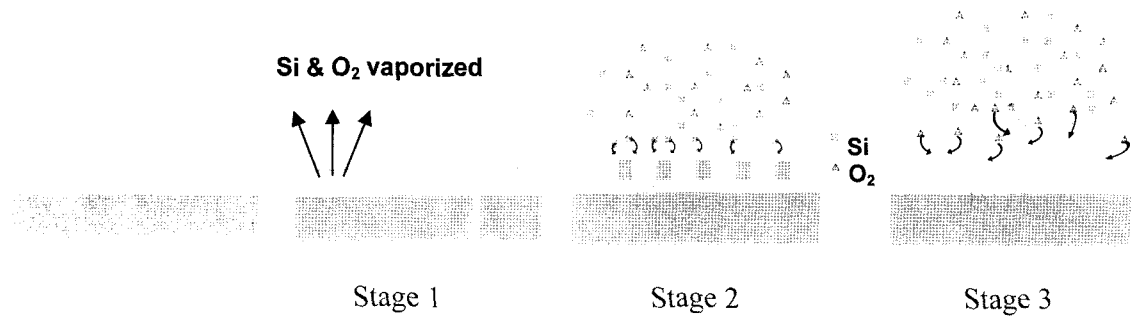


Fig. 3. Schematic description of the VLS growth mechanism of silica nanowires catalyzed by Ni.

non-oxidized silicon substrates [inset in Fig. 1 (b)] and only dot-like catalysts with a diameter of < 50 nm were observed, as shown in Fig. 1 (b). This result implies that the amorphous silica film of the oxidized Si substrate should play an important role in the growth of silica nanowires. This suggests that the silicon and oxygen sources are generated from the amorphous silica film.

The detailed morphology, structure, and composition of the nanowires were characterized by TEM. The low-magnification TEM image shown in Fig. 2 (a) and (b) demonstrates that most nanowires, with uniform diameters ranging from 20 to 50 nm and lengths of several micrometers, have a globule at the end of nanowires. Selected-area electron diffraction (SAED) patterns for the tip and the nanowires [Figs. 2 (c) and (d)] reveal that the globule is crystalline while the nanowire has an amorphous structure. Energy dispersive X-ray spectroscopy (EDS) analysis shows that the globule is mainly composed of Ni and Si elements [Fig. 2 (e)] while the nanowire consists of Si and O [Fig. 2 (f)]. This indicates that alloy globule at the end of nanowires is Ni-Si alloy.

The existence of alloy globules at the ends of the nanowires reflects that the nanowires are grown via a metal-catalyzed vapor-liquid-solid (VLS) mechanism. This VLS mechanism of amorphous silica nanowire growth can be described in three stages, as follows. (Fig. 3).¹³⁻¹⁴

1. Si and oxygen vaporization and formation of a liquid metal droplet stage: As the temperature increases, Si and oxygen are vaporized from the oxidized Si surface. The as-formed liquid Ni droplets provide an active site for the adsorption of vaporized Si. The Si atom diffuses through the liquid Ni and eventually forms a Ni-Si eutectic solution.

2. Precipitation of Si and growth of Si nanowire stage: The vaporized Si continues to diffuse into the Ni-Si liquid, resulting in supersaturation of the Ni-Si liquid and precipitation of Si from the liquid droplets. The precipitation of Si leads to the growth of the Si nanowires.

3. Oxidation of Si nanowire stage: Owing to the vaporized oxygen from the SiO₂ thin film and residual oxygen in the reactor, a sufficiently high temperature (800°C) causes oxidation of Si nanowires which creates the amorphous SiO_x nanowires.

Li *et al.*¹⁵ reported that SiC nanowires were synthesized

from amorphous silica thin film that was deposited onto a substrate as a silicon source with highly ordered pyrolytic graphite as a carbon source at under low pressure at high temperatures. In this study, as SiO₂ is present on the surface of the oxidized silicon substrate, Si and O can be supplied to the catalyst through the reaction of SiO₂ (s) = Si (g) + O₂ (g) and can induce the growth of silica nanowires via the VLS mechanism. Although the partial pressure of Si and oxygen through this reaction at the aforementioned processing temperature (800°C) is relatively low, it may enable the growth of Si nanowires. Therefore, it is suggested that silica nanowires can be self-grown on substrates by supplying reactant vapor from an amorphous silica film throughout this growth process without the involvement of an external source.

Fig. 4 shows the typical photoluminescence spectrum measured from the silica nanowires at room temperature. The excitation wavelength was 325 nm. A broad PL emission peak centered at 478 nm (approximately 2.6 eV in photon energy) was observed in these nanowires. Nishikawa *et al.*¹⁶ observed several luminescence bands in various types of high-purity silica materials. The bands ranged from 1.9 to

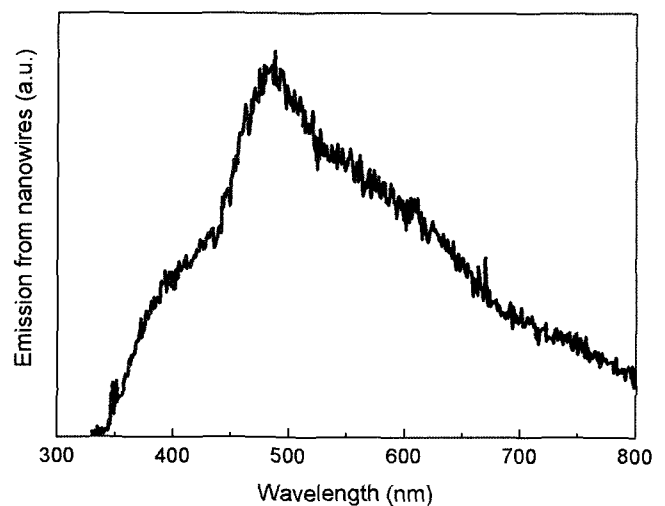


Fig. 4. Photoluminescence spectrum of silica NWs recorded at room temperature under excitation of 325 nm: The PL emission peak of silica nanowires is centered at 487 nm (approximately 2.55 eV in photon energy).

4.3 eV under 7.9 eV of excitation. It was revealed that the 2.7 eV band was ascribed to the neutral oxygen vacancy ($\equiv\text{Si-Si}\equiv$) that resulted from the forbidden transition from the triplet state to the singlet state at the neutral oxygen vacancy. In addition, Yu et al.¹⁷ showed that silica nanowires emitted stable and intensive blue light emission at energies of 2.65 and 3.0 eV due to oxygen deficiencies. Thus, the blue emission from the nanowires may have been caused by an optical transition in the defect centers of the oxygen deficiency. The photoemission as well as the blue shifting of the peak position in the silica nanowires is principally attributed to optical transitions in defect centers of the oxygen deficiency, indicating that with the increase in the number of oxygen vacancies, the band gap of the silica nanowires dramatically.

4. Conclusions

This study shows that silica nanowires can be prepared via on-site feeding of a reactant precursor by simply positioning the precursor in the substrate. The fabricated silica nanowires have diameters of 20~50 nm with lengths of a few micrometers. It was confirmed that silica nanowires can be grown via the VLS mechanism through observations by low-magnification TEM and EDS analyses. In addition, blue emission (478 nm, about 2.6 eV) was observed via PL measurements of the silica nanowires. This is believed to have originated from optical transition of the oxygen vacancy.

The on-site feeding approach may be a feasible way to integrate nanowires into different types of device architecture.

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