

H.W. KIM<sup>✉</sup>  
S.H. SHIM

# Fabrication and structural characterization of Mg<sub>2</sub>SiO<sub>4</sub> nanowires

School of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

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**ABSTRACT** This article demonstrates the first reported successful synthesis of Mg<sub>2</sub>SiO<sub>4</sub> nanowires. We have thermally heated Au-coated Si substrates, using a quartz tube with its inner surface pre-coated with MgO nanostructures. We have characterized the sample morphologies by using scanning electron microscopy and transmission electron microscopy (TEM). X-ray diffraction analysis and high-resolution TEM observation coincidentally revealed that the nanowires were crystalline with an orthorhombic Mg<sub>2</sub>SiO<sub>4</sub> structure. We have discussed the possible growth mechanism of Mg<sub>2</sub>SiO<sub>4</sub> nanowires.

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## 1 Introduction

One-dimensional (1D) nanostructures (nanotubes, nanobelts, nanowires, and nanorods) become the subject of extensive research concerning their peculiar and interesting physical properties and their potential applications in both the investigation of mesoscopic physics and the fabrication of nano-devices [1–4]. Accordingly, considerable efforts have been made to fabricate some important inorganic materials with their 1D nanostructures. Furthermore, with the development of nanotechnology, the demand to synthesize a wide variety of nanowires as well as to develop the novel fabrication method has been increased.

Forsterite (Mg<sub>2</sub>SiO<sub>4</sub>, boiling point = 1890 °C) is a member of the olivine family of crystals, which is an important silicate because it is one of the main constituents of the earth's upper mantle and is thought to be a principal component of interstellar dust particles. Mg<sub>2</sub>SiO<sub>4</sub> can be regarded as an ideal substrate material for electronics due to its low electrical conductivity [5]. Also, this material can be a promising material as an active medium for tunable lasers [6, 7], due to its good properties like refractoriness, low dielectric permittivity, chemical stability, and excellent insulation properties even at high temperatures.

Mg<sub>2</sub>SiO<sub>4</sub> has been grown by various techniques including the conventional solid state reaction of MgO and SiO<sub>2</sub> [8], heating of the mixed powders prepared by alkoxy-method [9], the polymer precursor method [10], and the sol–gel method [11]. Based on a widely accepted requirement of a nanostructure in which at least one dimension is less than 100 nm [12], in spite of their scientific and technological importance, only a limited kind of Mg<sub>2</sub>SiO<sub>4</sub> nanomaterials such as Mg<sub>2</sub>SiO<sub>4</sub> fishbone-like structures has been obtained until now [13], and thus the synthesis of 1D nanostructures of Mg<sub>2</sub>SiO<sub>4</sub> remains challenging to materials scientists, chemists, and physicists. In this paper, for the first time, we report the production of Mg<sub>2</sub>SiO<sub>4</sub> nanowires, by a synthetic route comprising the heating of Au-coated Si substrates with the simultaneous evaporation of MgO in a furnace tube.

## 2 Experimental

The growth process was carried out in a quartz tube (diameter 55 mm). The experimental apparatus has been described elsewhere [14]. As a starting material, we used standard polished *p*-type (100) Si wafers. The Si substrate was cut into small pieces with dimensions of 20 × 20 mm, which was subsequently blow-dried in N<sub>2</sub> gas. In order to fabricate the Au-coated Si substrates, a layer of Au (thickness = 120 nm) was deposited by sputtering. A piece of the Au-coated substrate was placed in the alumina boat, which was put in the middle of the quartz tube. The quartz tube was inserted into a horizontal tube furnace. The inner surface of the quartz tube was pre-coated with a white layer of MgO, which had been unintentionally deposited during the thermal evaporation of MgB<sub>2</sub> powders for preparing MgO nanowires [15]. During the experiment, a total constant pressure and steady air flow (~ 3.1% O<sub>2</sub> in a balance of Ar) was maintained at 2 Torr. The gas flow rates of Ar and O<sub>2</sub> were estimated to be 510.2 and 16.3 standard cm<sup>3</sup>/min, respectively. The substrate temperature was set to 1000 °C. After a typical 2 h heating process, the substrate was cooled down to 25 °C at an average cooling rate of 100 °C/h (measured in the range of 100–1000 °C) and then removed from the furnace for analysis.

As-grown samples were investigated and analyzed using glancing angle (0.5°) X-ray diffraction (XRD, X'pert MPD-

✉ Fax: +82-32-860-7544, E-mail: hwkim@inha.ac.kr

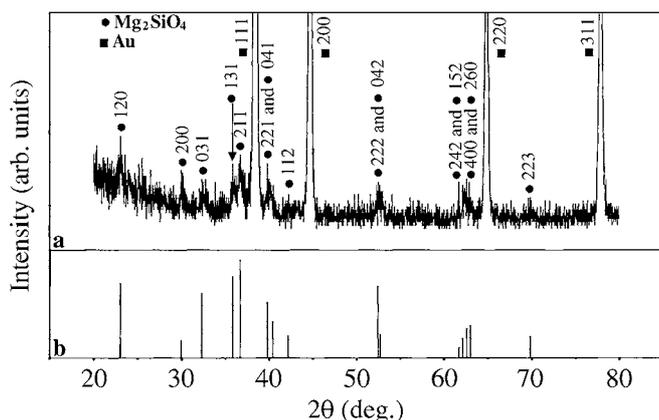
Philips with Cu  $K_{\alpha 1}$  radiation), scanning electron microscopy (SEM, Hitachi S-4200), and transmission electron microscopy (TEM, Philips CM-200) with energy-dispersive X-ray (EDX) spectroscopy attached. TEM samples were prepared by sonicating the substrates in acetone. A drop of the dispersion solution was then placed on a porous carbon film supported on a copper grid.

### 3 Results and discussion

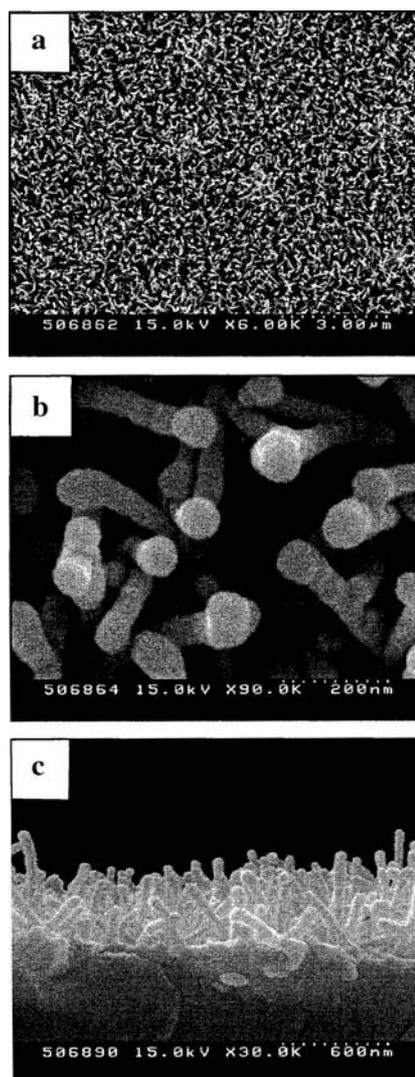
An XRD was used to determine the sample phase. Figure 1a displays the typical XRD spectrum of the product. Apart from the Au-related peaks which are from the underlying substrate, nearly all recognizable reflection peaks can be readily indexed to the orthorhombic  $Mg_2SiO_4$  structure with lattice parameters of  $a = 5.982 \text{ \AA}$ ,  $b = 10.198 \text{ \AA}$  and  $c = 4.755 \text{ \AA}$ , which is consistent with the standard data file (Fig. 1b; JCPDS: 34-0189). Although the XRD pattern reveals that the product is an  $Mg_2SiO_4$  phase, the relative intensity of the diffraction peaks deviates from that of the bulk, suggesting a different oriented growth direction of the nanowires.

We have examined the morphology and size of the resulting product by observing the SEM images. Figure 2a shows the top-view SEM image of the product, indicating the deposition of 1D structures over a large area. Figure 2b represents an enlarged SEM image, revealing that the 1D structures are indeed nanowires with a circular cross section. No metal catalyst particle can be seen at the tips. Figure 2c shows the side-view SEM image of the  $Mg_2SiO_4$  structures, indicating that the growth direction of the nanowires is randomized. Statistical observation of many SEM images indicated that the average diameter of nanowires varied from 10 to 80 nm.

TEM was employed for further structural study of the sample. Figure 3a shows a low-magnification TEM image, revealing that the product consists of an agglomeration of nanowires with wavy or bumpy surfaces. We surmise that this phenomenon is similar to that of periodic instabilities or diameter modulation observed by several research groups in the growth of various nanowires including Si [16–18], GaP [19], and  $Bi_2S_3$  [20]. This phenomenon is known to result from the instability of the diameter of the liquid droplet in terms



**FIGURE 1** (a) XRD pattern of the product and (b) the standard XRD pattern of bulk  $Mg_2SiO_4$  with JCPDS No. 34-0189



**FIGURE 2** (a) Top-view, (b) enlarged, and (c) side-view SEM images of the  $Mg_2SiO_4$  structures

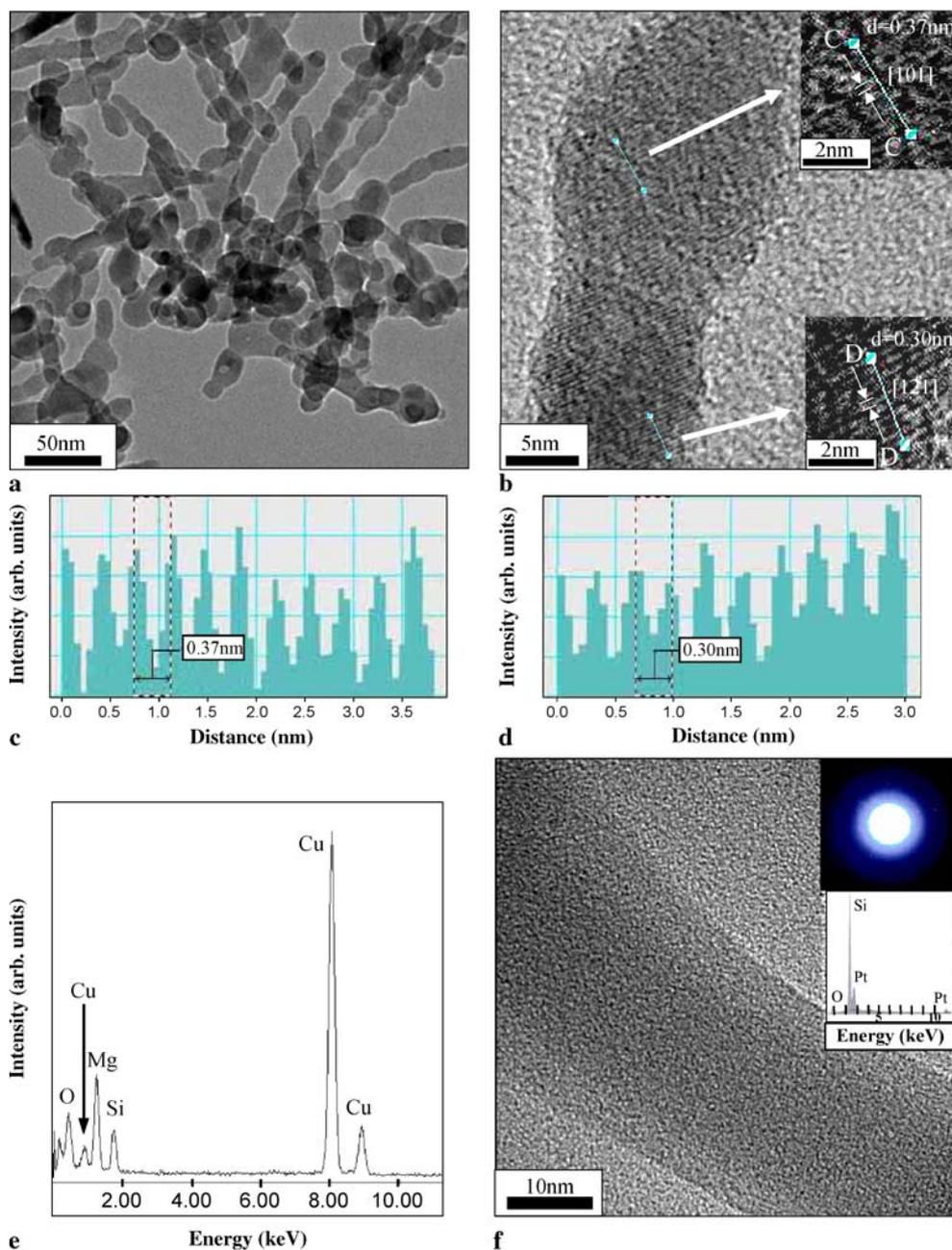
of the vapor liquid solid (VLS) process or from the ledge mechanism, in which the nanowire surface provides the preferential nucleation sites [19]. The diameter of nanowires in the present image is modulated in the range of 10–40 nm. It is noteworthy that no spherical droplet or nanoparticle can be seen at the tips of the nanowires, agreeing with the SEM observation.

Figure 3b exhibits the high resolution TEM (HRTEM) image of a single nanowire, suggesting that this part of the nanowire comprises two crystalline nodes. The lattice resolved images corresponding to each node are shown in the insets. The line profiles, measured across the C and D lines on the insets in Fig. 3b are given in Fig. 3c and d, respectively. It can be clearly observed that the interplanar spacings are approximately 0.37 nm and 0.30 nm, which correspond to the distance of the neighbouring (101) and (121) planes in an orthorhombic  $Mg_2SiO_4$  structure, respectively. EDX microanalysis indicated that not only the stem part but also the tip part of the nanowire contained only Mg, Si and O, as shown in Fig. 3e. The strong signals for Cu came from the TEM copper grid on which these  $Mg_2SiO_4$  nanowires were supported.

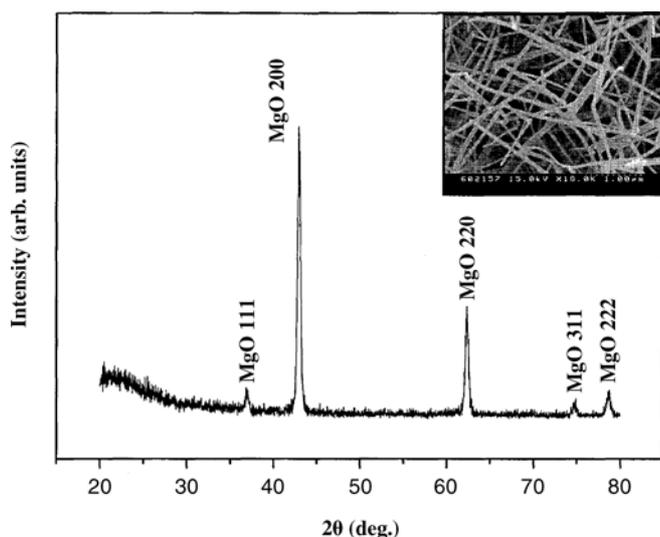
In our preliminary experiments, simple heating of Au-coated Si substrates with a clean quartz tube without MgO pre-coating, generated  $\text{SiO}_x$  nanowires with no Mg element (Fig. 3f), showing that Mg elements came from the MgO-coated quartz tube. Comparison studies of HRTEM images (Fig. 3b and f) reveals that the  $\text{Mg}_2\text{SiO}_4$  nanowires are crystalline, whereas the  $\text{SiO}_x$  nanowires are close to amorphous. It has been reported that temperatures as low as  $850^\circ\text{C}$  were sufficient to produce crystalline  $\text{Mg}_2\text{SiO}_4$  [21], agreeing with the present observation. By analyzing the white product on the inner wall surfaces of the quartz tube after the thermal heating of  $\text{MgB}_2$  powders, we have confirmed that the precoated product corresponded to a large quantity of MgO nanowires (Fig. 4). During the subsequent thermal heating process at  $1000^\circ\text{C}$ , we suppose that the MgO

nanowires can be the source of MgO vapor in spite of their low partial pressures. Therefore, the Mg and O elements in the  $\text{Mg}_2\text{SiO}_4$  nanowires may originate from the vapor which was re-evaporated from the MgO nanowires on the quartz surface, and also from some additional oxygen vapor in the air ambient.

No extra Si source was introduced in the vapor phase of the present study and the bulk Si substrate is the only Si source. When the heating was carried out under the same conditions on bare-Si substrates in the absence of Au layers, we did not obtain any nanostructures, thus revealing that the Au layer played a crucial role in the formation of nanowires. We surmise that during the heating process in the furnace, the deposited Au layer reacts with the underlying Si substrate, forming the liquid alloys and subsequently promoting the pre-



**FIGURE 3** (a) Low-magnification TEM image. (b) TEM image of a bumpy-surfaced single nanowire, showing the lattice fringes (the insets show the enlarged images). The line profile, measured across the C and D lines on the insets in (b) are given in (c) and (d), respectively. (e) Typical EDX spectrum showing the presence of Mg, Si, and O. The Cu signal is from background scattering off the TEM copper grid. (f) TEM image of the  $\text{SiO}_x$  nanowires synthesized without using the MgO-coated quartz tube (the insets show the SAED and SEM-EDX pattern, respectively). The Pt-related peak is due to the preparation of SEM specimens)



**FIGURE 4** XRD pattern of the MgO nanowires predeposited on the quartz surfaces (*inset*: corresponding SEM image)

cipitation and nucleation of nanowires from the liquid alloy surface. In the present work, although Au-coated substrates were employed, the SEM and TEM analysis provided no evidence that the metal catalyst was present at the tips of the nanowires. Hence, the growth mechanism cannot be ascribed to the tip-growth VLS mechanism. In the present base-growth process, the Au-containing liquid alloy may stay at the bottom of the nanowires during the growth process. By a similar mechanism, amorphous Si nanowires were previously grown by heating the Ni-coated Si substrates [22].

Herein, there may be two possibilities. One is that the nucleation of solid Si from the Au-Si liquid alloy is followed by the procedure that Mg- and O-related vapors adsorb on the Si nuclei surface, reacting to form the  $\text{Mg}_2\text{SiO}_4$  nanowires. The other possibility is that the associated vapor diffuses onto the Au/Si liquid alloy, forming a complex Au-Mg-Si-O fluid phase. Subsequently, the solid  $\text{Mg}_2\text{SiO}_4$  starts to grow on the liquid phase surface. In both cases, the vapor phase needs be involved for the incorporation of Mg and O elements. Although further systematic study is underway to reveal the detailed growth mechanism, we tentatively suggest that the growth of  $\text{Mg}_2\text{SiO}_4$  nanowires is a combinational process which comprises solid, liquid, and vapor phases.

## 4 Conclusions

We have synthesized  $\text{Mg}_2\text{SiO}_4$  nanowires by heating Au-coated Si substrates in an MgO-coated quartz tube furnace at 1000 °C. SEM, XRD, EDX, and TEM have been employed to characterize the as-synthesized samples. Structural studies show that the produced nanowires are an orthorhombic  $\text{Mg}_2\text{SiO}_4$  structure with diameters in the sub-100 nm regime. We reveal that the Mg elements in the as-synthesized  $\text{Mg}_2\text{SiO}_4$  nanowires originate from MgO nanowires which were predeposited on the quartz tube surface. This combinational approach may open up a new way to synthesize nanowires of many other alloy compounds.

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