Nanostructure growth

Direct Observation of the Growth Process of MgO Nanoflowers by a Simple Chemical Route

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Novel flowerlike nanostructures consisting of MgO nanofibers were successfully synthesized by a simple chemical route with H₂O at 950°C in an Ar atmosphere. Various durations of heating gave different growth stages that led to varied product morphologies. The synthesized products were systematically studied by X-ray powder diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, and energy-dispersive X-ray analysis. The results show that the nucleation and growth process of the nanoflowers seems to be a vapor–solid mechanism, and that the total heating time during the reaction process is a critical factor for the development of MgO nanoflowers. Initially, Mg particles formed on the Si substrate, followed by the formation of MgO clusters as nucleation centers on the magnesium melt surface and the nucleation of short MgO nanofibers, then growth of the MgO nanofibers occurred, and finally MgO nanoflowers were formed. Besides nanoflowers, novel hierarchical MgO nanostructures were also observed. These nanostructures may be used as three-dimensional composite materials and as supports for other materials.

1. Introduction

One-dimensional nanomaterials, such as nanotubes,[1] nanowires,[2] and nanobelts or nanoribbons[3] have attracted much attention in the past decade because of their novel physical properties and potential applications in constructing nanoscale electric and optoelectronic devices.[4] Up to now, much attention has been given to the preparation of nanostructures of the family of oxides with interesting optical and electrical properties. Several binary oxide nanostructures such as ZnO, SnO₂, Ga₂O₃, SiO₂, In₂O₃, and Al₂O₃ have been successfully synthesized.[5–10]

MgO is a typical wide-bandgap insulator showing high secondary electron emission (SEE) yield, and MgO nanostructures have drawn special attention due to their unique ability to pin the magnetic flux lines within a high-temperature superconductor (HTSC).[11] The use of MgO as a passivation layer in high-electron-mobility transistors, a substrate for carbon nanotube growth, and a thin-film capacitor is also known.[12] Recently, various MgO nanostructures have been synthesized. For example, MgO fibers were prepared using two sol–gel routes.[13] MgO fishbone or fernlike nanostructures were generated by selective Co-catalyzed growth.[14] MgO nanowires were synthesized by oxide-assisted catalytic growth[15] and a vapor-phase precursor method using MgB₂ powders.[16] MgO nanobelts were fabricated by a simple chemical vapor deposition process using infrared irradiation,[17] the evaporation of a Mg₃N₂ precursor,[18] and the heating of Mg in an Ar/O₂ flow.[19] Several MgO mor-
phologies including linear nanobelts and two- and three-di-
mensional entities have been produced by a thermal treat-
ment,[20] and MgO and Ga-filled MgO nanotubes have also
been synthesized.[21] However, no studies have been report-
ed on the synthesis of other MgO nanostructures. Here, we
describe for the first time the direct observation of the nu-
cleation and growth process of MgO nanoflowers, with
aligned distribution on a Si substrate, and novel hierarchical
MgO nanostructures exhibit morphologies comparable to that of radiolarian
and may provide insight into the formation of microbiologi-
ical systems.

2. Results

Figure 1 shows the XRD patterns of the synthesized
products after different total heating times. With increasing
heating time, the synthesized products vary from pure Mg
to a combination of Mg and MgO, and finally to pure MgO,
and the morphologies vary from particles to nanoflowers
and hierarchical nanostructures (shown by scanning electron
microscopy (SEM) observations). The total heating time
during the reaction process was a critical factor for the for-
mation of MgO nanoflowers. Four stages could be clearly
identified.

2.1. Initial Stage: Growth of Mg Particles

In the first five minutes, Mg powder is evaporated and
converted into micrometer-sized particles on the surface of
a Si wafer (Figure 2). However, some of the particles are
not spherical and their diameter is not uniform, which may
be a result of the aggregation of melting Mg (the melt point
of Mg is about 651°C and the temperature of the Si sub-
strate is about 850°C).

2.2. Second and Third Stages: Formation of MgO Clusters

and Nucleation of Short MgO Nanofibers

As the heating process continues, the formation of MgO
clusters as nucleation centers on the magnesium melt sur-
face occurs initially, followed by the nucleation of short
MgO nanofibers. Figure 3a and b shows the high-magnifica-
tion SEM images obtained after 10 minutes of heating,
which indicate that the nucleation seems to initiate random-
ly on the surface of Mg particles. Figure 3c shows a low-
magnification SEM image after 20 minutes of heating,
which reveals that some MgO nanofibers are typically hun-
dreds of nanometers in length. The high-magnification SEM
image after 20 minutes of heating reveals that MgO nano-
fibers essentially nucleate from the surface of Mg particles
(Figure 3d).

2.3. Final Stage: Growth of Nanoflowers

An extended heating time elongates the nanofibers and
finally forms the nanoflowers. Figure 4a reveals that the as-
synthesized products consist of a large quantity of flowerlike
branched nanostructures produced by a 30-minute heating
process. These structures exhibit the so-called nanoflower
morphology, which has been reported for silicon-based one-
dimensional nanostructures and MoS2 nanostructures.[22] Fig-
ure 4b shows a representative high-magnification SEM
image of a nanoflower, which reveals that the nanoflower
consists of nanofibers with lengths up to several microme-
ters and diameters of 20–80 nm; a few small nanoflowers
can be also seen. The morphology, structure, and composi-
tion of the MgO nanoflowers have also been characterized
in detail using TEM, high-resolution (HR)TEM, selected-
area electron diffraction (SAED), and energy-dispersive X-
ray (EDX) analysis. A TEM study verifies nanostructures
consisting of radially attached fibers (Figure 5a). The EDX
analysis shows that all the nanostructures are composed of
Mg and O elements (the corresponding atomic ratio is near
1:1), as illustrated in Figure 5b, where the Cu signal came
from the TEM grid used for supporting the sample. The
SAED pattern and HRTEM image (Figure 5c) reveal that the MgO nanoflowers are structurally uniform and single crystalline. The resolved spacing of about 0.209 nm corresponds to the (200) lattice planes \( (d = 2.1045 \text{ nm}) \) of MgO. The SAED pattern (Figure 5c, inset) recorded perpendicular to the nanofiber long axis could be indexed for the [001] zone axis. The axis direction of the MgO nanofiber could be determined as [100] growth by combining HRTEM and the defocused electron technique. In our HRTEM observations, most of the MgO nanofibers grew along the [100] rather than the [111] direction, which agrees with the deduction from XRD analysis and with the previously synthesized MgO nanostructures.[15–18] It is known that MgO has a rock-salt structure with a surface energy decrease when going from the (111) plane to the (110) and the (100) planes. Kinetic factors determine that the growth rate is the highest for high-energy surfaces along the [111] direction and the lowest for low-energy surfaces along the [100] direction. However, the thermodynamics requires the formation of crystals with well-faceted surface planes with low surface energy, which can be met with growth along the [100] direction and with four equivalent [100] side surface planes. For growth along the [111] direction, the side surface is usually [110] or [112] or both, with higher surface energies that are thermodynamically less favorable. Thus, the growth of MgO nanofibers along the [100] direction is controlled by thermodynamics.

Figure 3. a, b) SEM images taken after 10 min of heating; MgO nanofibers start to grow out from the Mg particles. c) Low-magnification SEM image after 20 min of heating, which shows that the MgO nanofibers are typically hundreds of nanometers in length. d) High-magnification SEM image after 20 min of heating, which reveals that MgO nanofibers essentially nucleate from the surface of Mg particles.

Figure 4. SEM images of MgO nanoflowers after 30 min of heating. a) Typical low-magnification image of the as-synthesized MgO nanoflowers. b) A representative high-magnification image of a nanoflower consisting of MgO nanofibers, which have lengths up to several micrometers and diameters of 20–80 nm; a few small nanoflowers can be also seen.
In the final product, besides MgO nanoflowers we also find a few novel hierarchical MgO nanostructures with fourfold symmetry. The output ratio of MgO nanoflowers to hierarchical nanostructures in the products is about 5:1 based on SEM observations. Figure 6 shows typical SEM images of the hierarchical nanostructures at low and high magnification, respectively. Figure 6a shows a low-magnification image of the hierarchical nanostructures. The high-magnification image in Figure 6b clearly shows that the hierarchical nanostructures have fourfold symmetry, and consist of nanofibers with lengths up to several micrometers and diameters of 80–120 nm. EDX analysis shows that all the secondary nanofibers and the major core nanowires are pure MgO. Similar nanostructures were reported in previous work, such as hierarchical ZnO nanostructures on In₂O₃ core nanowires,[23] aligned junctions and networks of SnO nanostructures and MgO nanobelts,[24] and nanowire–nanoribbon junction arrays of ZnO.[25] For hierarchical oxide nanostructures, Lao and Ren et al. confirmed that the multicompositional hierarchical nanostructures are formed by a two-step mechanism. The primary nanowire or nanobelt develops first, and then the secondary nanorods grow epitaxially on the primary nanostructures at different stages of vapor supply in the system, which is evidenced by the uniform length of the secondary nanorods.[23] In our experiment, the growth mechanism of such hierarchical MgO nanostructures is not completely clear. However, it is possible that some MgO nanowires were formed initially by the vapor–solid process on the Si substrate, followed by the growth of the hierarchical MgO nanostructures, because of the uniform length of the secondary MgO nanofibers. In our experiment, cubic MgO grows along the [100] or [001] direction to form the fourfold symmetry, instead of the [110] or [111] direction to form the sixfold symmetry. These hierarchical nanostructures open a brand new field not only to nanomaterials synthesis, but also to their applications in numerous fields.[23]

Several mechanisms have been proposed to account for the growth of nanowires, which include vapor–liquid–solid (VLS),[26] vapor–solid (VS),[27] and oxide-assisted mechanisms.[28] In our experiment, no transition metal was employed as a catalyst, which is different from previously reported procedures for the formation of other nanostructures.[29] The VLS mechanism could be ruled out because no metal catalyst was used and no alloy particle was observed at the tips of the nanoflower. The growth of MgO nanoflowers through the oxide-assisted mechanism is less likely because the experiments were performed in an Ar atmosphere. The catalyst-free growth appears to be a VS process. Based on the above observations, the growth of the nanoflowers could be divided into four steps. A growth model is proposed for the MgO nanoflowers grown on Si wafers (Figure 7). The first step is the evaporation of Mg powders in a higher temperature zone, and direct deposition on a Si substrate at a lower temperature of about 850°C (Figure 2). The second step is the formation of MgO clusters as nuclea-
tion centers on the magnesium melt surface (Figure 3a and b) through the following reaction:

\[ \text{Mg} + \text{H}_2\text{O} \rightarrow \text{MgO} + \text{H}_2 \] (1)

The third step is the nucleation of short MgO nanofibers and their growth (Figure 3c and d). When MgO on the magnesium melt surface becomes supersaturated, it has to precipitate out of the surface in a certain form. This is the driving force for nanofiber growth. The last step is the formation of the MgO nanoflowers (Figure 4), which will be formed radially through reaction (1). On the basis of growth processes of MgO nanoflowers and experimental observations, the growth of MgO nanoflowers in this work via a VS mechanism is possible.

3. Discussion

The results described in Section 2 show that, by a simple chemical route with H$_2$O at 950°C in an Ar atmosphere, the nucleation and growth process of the nanoflowers can be observed. Our systematic experiments at varied heating time (5–30 min) show that the total heating time is a critical factor for determining the morphologies of the resulting MgO nanoflowers. Products at a specific growth stage can be obtained within a certain total heating time, because this time has a dominant influence on the morphologies of the products. Optimization of the duration of heating is important in nanostructure synthesis.

The relatively low processing temperature is one of the advantages of this method. Previous studies that directly used MgO solid as the source material required an operation temperature higher than 1200°C. Although the synthesis of MgO nanofibers was successfully achieved by a simple chemical route with H$_2$O at 950°C, we found that MgO nanostructures could also be generated in situ at temperatures as low as 600°C. Figure 8 shows the SEM images of MgO nanostructures synthesized in situ at 800 and 600°C for 30 min in a flow of Ar gas (100 sccm). In these cases, no deposition was found on the silicon substrate. However, when the reaction temperature was lower than 600°C, no nanostructures could be found either in the ceramic boat or on the silicon substrate; we only found some MgO particles and blocks, which may be because almost no Mg vapor appeared when the reaction temperature was lower than 600°C.

Herein, we have mainly discussed the effect of total heating time, but other experimental parameters such as the gas flow rate, the heating rate, the distance between the source materials and deposition substrate, and the pressure in the furnace also have an influence on nanostructure development.

4. Conclusions

Novel flowerlike and hierarchical MgO nanostructures consisting of MgO nanofibers have been successfully synthesized by a simple chemical route with H$_2$O at 950°C in an Ar atmosphere. Direct observation of the growth process of MgO nanoflowers indicates that four stages are involved:
the growth of Mg particles, the formation of MgO clusters, the nucleation of short MgO nanofibers, and the formation of MgO nanoflowers consisting of nanofibers which have lengths up to several micrometers and diameters of 20–80 nm, with an average of 50 nm. The hierarchical MgO nanostructures have fourfold symmetry and also consist of nanofibers, which have lengths up to several micrometers and diameters of 80–120 nm. These MgO nanostructures may be useful in reinforcing composite materials or in further modifying other nanostructures.

5. Experimental Section

High-purity (99.9 %) magnesium powders were placed in a ceramic boat, which was inserted at the center of a horizontal alumina tube furnace for heating. A Si wafer (6 cm long and 16 mm wide) was placed downstream in the alumina tube (3 cm away from the source material) to act as the deposition substrate for material growth. Water was introduced into the reaction by placing an alumina crucible with about 50 mL distilled water on the upstream side of the alumina tube. The system was heated to 950 °C in 8 min. High-purity Ar was adopted as a protecting medium and as a carrier gas. During the heating process, the Ar flow rate was kept at 100 sccm (sccm = standard cubic centimeters per minute). A series of growth experiments were performed at different heating times of 5, 10, 20, and 30 min with other parameters essentially the same.

After the system was cooled to room temperature, the Si wafer was removed from the alumina tube. The as-synthesized products were characterized and analyzed by X-ray diffraction (XRD; PW1710 instrument with Cu Kα radiation), scanning electron microscopy (SEM; JEOL JSM 6700F), high-resolution transmission electron microscopy (HRTEM; JEOL 2010, operated at 200 kV), and energy-dispersive X-ray spectroscopy (EDX). For SEM observations, the product was pasted on an Al substrate using conductive carbon paste. Specimens for HRTEM investigations were briefly ultrasonicated in ethanol, and then a drop of the suspension was placed on a carbon-film-coated holey copper grid.

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