Sr₂SiO₄ flower-like nanostructures grown by thermal oxidation of SrSi₂ with Ga droplets

Qing Yang⁺, Miyoko Tanaka⁺, Shuhua Liang⁺, Kazuki Ogino⁺, Takahito Yasuda⁺, Hirokazu Tatsuoka⁺,*

⁺Faculty of Material Science and Engineering, Xi'an University of Technology, 5 South Jinhua Road, Xi'an 710048, China
⁺Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-8561, Japan
⁺National Institute for Materials Science, 3-13 Sakura, Tsukuba 305-0003, Japan

Abstract

Sr₂SiO₄ flower-like nanostructures were grown by thermal oxidation of SrSi₂ powders with Ga droplets. The morphology and structure of the Sr₂SiO₄ flower-like nanostructures were investigated using transmission electron microscopy. The leaves of the Sr₂SiO₄ flower-like nanostructures became narrow towards the tips. Sr, Si and O were homogeneously concentrated on each leaf. In addition, the formation mechanism of the Sr₂SiO₄ flower-like nanostructures was discussed.

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Keywords: Sr₂SiO₄; nanostructure; thermal oxidation; Ga; transmission electron microscopy

1. Introduction

Presently, as a promising phosphor, Sr₂SiO₄ has attracted much attention, due to its high luminous efficiency, color rendering index (CRI) and color stability [1-5]. Sr₂SiO₄ provides a broadband absorption in the UV/Blue region due to its low symmetry of crystallographic sites. It is suggested that Sr₂SiO₄ will be a suitable host lattice for a new type of phosphor approach for white light-emitting-diode (LED) applications.

On the other hand, nanostructures made of various kinds of inorganic materials have been intensively investigated, which exhibit unusual optical, electronic or mechanical properties compared with those of the bulk materials [6]. However, to the best of our knowledge, Sr₂SiO₄ nanostructures have seldom been reported to date.

In this study, we report the simple growth of Sr₂SiO₄ flower-like nanostructures through a thermal oxidation process. The morphological and structural properties of the Sr₂SiO₄ flower-like nanostructures are demonstrated, and the formation mechanism is discussed.

* Corresponding author. Tel.: +81-53-478-1099; fax: +81-53-478-1099.
E-mail address: tehtats@ipc.shizuoka.ac.jp.
2. Experiments

The Sr$_2$SiO$_4$ flower-like nanostructures were grown by thermal oxidation of SrSi$_2$ powders with Ga droplets. The Ga metal was melted around 35-40 ºC, then mixed with the SrSi$_2$ powders using a steel or wood stick. As a result, millimeter-sized Ga droplets were adhered to the SrSi$_2$ powders. The SrSi$_2$ powders with Ga droplets were placed in a vacuum chamber, which was then evacuated to a base pressure of $10^{-4}$ Torr. The nanostructure growth was performed by exposure of the SrSi$_2$ powders with Ga droplets to the leaked air for 24 h at 900 ºC.

The as-grown Sr$_2$SiO$_4$ flower-like nanostructures were characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) with selected area electron diffraction (SAED), and scanning transmission electron microscopy (STEM) with energy-dispersive X-ray spectroscopy (EDS).

3. Results and Discussion

Figures 1(a) and (b) show the TEM images and corresponding SAED patterns of Sr$_2$SiO$_4$ flower-like nanostructures with bouquet-like morphology, respectively. As shown in Fig. 1(a), the leaves of the flower-like nanostructures become narrow towards the tips and the length extends to 1~2 μm. As marked in Fig. 1(b), all rings could be indexed to the diffraction peaks of orthorhombic Sr$_2$SiO$_4$ (JCPDS Card No. 76-1494). In addition, it is considered that the bright spots, which are also observed in Fig. 3(b), should be due to the overlapped domains of the leaf, which could be clearly observed in Figs.3 (a) and (c).

![Fig. 1](image1.jpg)

Fig. 1 (a) TEM image of Sr$_2$SiO$_4$ flower-like nanostructures with (b) corresponding SAED pattern.

![Fig. 2](image2.jpg)

Fig. 2 (a) TEM image of Sr$_2$SiO$_4$ flower-like nanostructures. (b) STEM image of the leaves marked by the circle in (a), with corresponding EDS mappings of (c) Sr, (d) Si and (e) O.
Figure 2(a) shows the TEM image of the Sr$_2$SiO$_4$ flower-like nanostructures with radial morphology. Fig. 2(b) shows the STEM image of the leaves as marked by the circle in Fig. 2(a). The corresponding EDS mappings of Sr, Si and O are shown in Fig. 2(c-e). As revealed by the EDS mappings, Sr, Si and O atoms are homogeneously concentrated on each leaf.

Fig. 3 (a,c) HRTEM images of two leaves shown in Fig. 2(b). (d,e) enlarged HRTEM images of the rectangles D and E enclosed areas in (a,c). (b) corresponding SAED pattern from the leaf shown in (a). Figures 3(a) and (c) show the HRTEM images of the two leaves shown in Fig. 2(b), respectively. Figs. 3(d) and (e) show the enlarged HRTEM images of the rectangles D and E enclosed areas in Figs. 3(a) and (c), respectively. As indexed in Figs. 3(d) and (e), the interplanar spacings of 0.256 nm, 0.263 nm, 0.283 nm and 0.354 nm correspond to the (122), (113), (103) and (020) planes in orthorhombic Sr$_2$SiO$_4$, respectively. Fig. 3(b) shows the corresponding SAED pattern from the leaf shown in Fig. 3(a). All rings could be indexed to the diffraction peaks of orthorhombic Sr$_2$SiO$_4$.

It has been identified that three compounds exist in the Sr-Si-O system: Sr$_3$SiO$_5$, Sr$_2$SiO$_4$ and SrSiO$_3$ [7]. Sr$_3$SiO$_5$ is not stable at room temperature but decomposes into Sr$_2$SiO$_4$ and SrO [8]. In addition, the enthalpy of formation of Sr$_2$SiO$_4$ is higher than that of SrSiO$_3$ [9]. Therefore, the formation of Sr$_2$SiO$_4$ is thermodynamically favored compared to that of SrSiO$_3$.

The nanostructure growth is mainly explained by the vapor-liquid-solid (VLS) or vapor solid (VS) mechanisms. In the VS mechanism, nanostructures are grown directly from the vapors of precursors without a liquid state. The VLS mechanism is generally based on a catalytic reaction. Although Ga droplets were involved in the nanostructure growth, no additional droplet was observed on the top or bottom of the as-grown flower-like nanostructures. On the other hand, the vapor pressure of gallium at 900 °C is nearly equal to 10$^{-4}$ Torr [10], and the gallium is easily evaporated during the nanostructure growth process. In addition, the pressure for the decomposition of SrSi$_2$ at 900 °C is also about 10$^{-4}$ Torr [11], which indicates the decomposition of SrSi$_2$ to Sr and Si at the elevated temperatures.

Figures 4(a) and (b-d) show the STEM image and corresponding EDS mappings of the Sr$_2$SiO$_4$ flower-like nanostructures, respectively. The distribution of Sr and Si at the center is a little higher than that at the leaves. It is assumed that SrSi$_2$ powders were covered by Ga droplets during the nanostructure growth process, the distribution of Sr and Si reveals the outward diffusion of Sr and Si from the center. In other words, the SrSi$_2$ powders were consumed gradually and decomposed to Sr and Si, which were then dissolved into the Ga droplets.
It is well accepted that supersaturation plays an important role in the nanostructure growth [12,13]. Gallium can guarantee a suitable supersaturation due to its liquid state at the elevated temperatures [14]. Therefore, it is considered that the diffusion of Sr, Si and O species into Ga droplets contributed to the formation of the Sr$_2$SiO$_4$ nanostructures. Finally, the consumption of SrSi$_2$ and evaporation of gallium resulted in the flower-like morphology.

4. Conclusions

Sr$_2$SiO$_4$ flower-like nanostructures were grown by thermal oxidation of SrSi$_2$ powders with Ga droplets. The leaves of the Sr$_2$SiO$_4$ flower-like nanostructures became narrow towards the tips. In addition, Sr, Si and O were homogeneously concentrated on each leaf. It is expected that the growth of the Sr$_2$SiO$_4$ nanostructures may expand the range of applications for white LEDs.

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