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Synthesis, Structural and Photoluminescence Properties of Mg_2Si/Si Nanosheet Bundle Composites

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Abstract

Mg_2Si/Si nanosheet bundle composites were synthesized by Ca atom extraction from $CaSi_2$ powders by thermal treatment under $MgCl_2$ vapor. The structural and photoluminescence properties of the composites were examined. The Mg_2Si deposits were formed and distributed inhomogeneously on the Si nanosheets. The Mg_2Si/Si nanosheet bundle composites were also synthesized on Si substrates for photoluminescence measurements. It was found that the structural modification of the Si nanosheet bundles to form the composites with Mg_2Si deposits affected the emission property of the Si nanosheets.

1. Introduction

Low-dimensional materials have attracted much interest due to their enhanced or modified optical, electronic and mechanical properties compared to those of bulk materials. A nanosheet bundle is also one of the potential structures for technological applications. The Si-based nanosheet bundles have been successfully synthesized by extraction of Ca atoms from $CaSi_2$ crystals. The structural and photoluminescence (PL) properties of the bundles were characterized in the past [1,2]. The structural and surface modifications of the nanosheet bundles are further required to improve materials properties and enhance new functions.

In this study, the nanosheet bundles were structurally modified to synthesize the Mg_2Si/Si nanosheet bundle composites, and structural and photoluminescence properties of the composites were characterized.

2. Experimental procedure

The Mg_2Si/Si nanosheet bundle composites have been synthesized by Ca atom extraction from the $CaSi_2$ powders or $CaSi_2$ micro-walls on Si substrates by thermal treatment under $MgCl_2$ vapor. The $CaSi_2$ micro-walls were grown on Si substrates and the growth conditions of the $CaSi_2$ are described elsewhere [3]. The $CaSi_2$ powders or the Si substrates with the $CaSi_2$ micro-walls and the $MgCl_2$ powder were placed on opposite sides of each other inside a sealed stainless-steel cell in an Ar atmosphere with detected oxygen of less than 0.1 %. The $MgCl_2$ was carefully stored to avoid its deliquescence. The cell was heated to the highest thermal treatment temperature of 500 to 650 °C and the temperature was maintained for 10 h. The heaters were then turned off, and the cell was naturally cooled. After the thermal treatment process, the treated composites were washed in ethanol a few times for a few minutes to remove the residual chloride compounds. The resulting powders were further washed by an HCl solution (35–37w/w%) for 1 h to remove the MgO formed as a by-product. The morphological and structural properties of the composites were characterized.

PL measurements of the composites synthesized from $CsSi_2$ micro-walls on the Si substrate were performed at temperatures between 19 and 300 K within a closed cycle helium cryostat. The signals were detected using a high sensitive CCD sensor with a cw 532 nm second harmonic generation (SHG) Nd:YVO_4 laser as the excitation source. The excitation intensity was 80 mW.

3. Results and discussion

Figures 1(a) and 1(b) show an SEM image and its enlarged image of the Mg_2Si/Si nanosheet bundle composites synthesized from $CaSi_2$ powders by thermal treatment at 600 °C under $MgCl_2$ vapor, respectively. The nanosheets bundles with a thickness of about one micro-meter are formed with a small void space. The bundles were divided into thinner nanosheets, namely nanosheets were easily exfoliated from the bundles.

Figure 2 shows XRD spectra of the $MgCl_2$ treated powders at 500, 600 and 650 °C. It is shown that $CaSi_2$ phase still remain in the powders treated at 500 °C, and as the treatment temperature increases, $CaSi_2$ phase disappear and the formation of Mg_2Si phase is confirmed, which results are different from that of the use of deliquescent $MgCl_2$ as a source material [4].

Figure 3 shows STEM image and EDS mappings of a piece of the nanosheet synthesized by the thermal treatment at 600 °C. Mg is inhomogeneously distributed around the Si nanosheet. In addition, Ca is also distributed imhomogeneously and the distribution of Ca is consistent with that of Cl. It is considered that $CaCl_2$ remains around the nanosheest by insufficient washing after the thermal treatment.

Figure 4 shows that TEM and HRTEM images with an FFT pattern of the nanosheet synthesized by the thermal treatment at 600 °C. The HRTEM image in Fig.4(b) was taken at the square part shown in Fig.4(a). According to the plane spacing of about 0.32 nm, the diffraction spots could be indexed as the so-called $1/3\{422\}_{Si}$, which are observed only

for very thin and atomically smooth flat two dimensional Si sheets. Additional spots or periodic structures marked as A and B are resulted by double diffractions of Si and Mg_2Si crystals and superposition of the lattice images of Si and Mg_2Si. The epitaxial relationship between the Mg_2Si deposits and the Si nanosheet is given by (211), $[\bar{1}11]$ Mg_2Si // (111), $[0\bar{1}1]$Si.

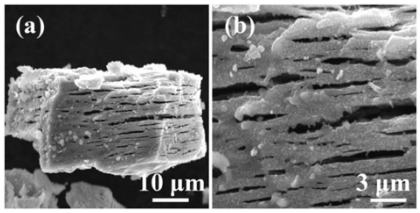

Fig. 1 SEM images of the Mg_2Si/Si nanosheet bundle composites synthesized from $CaSi_2$ powders by the thermal treatment at 600 °C.

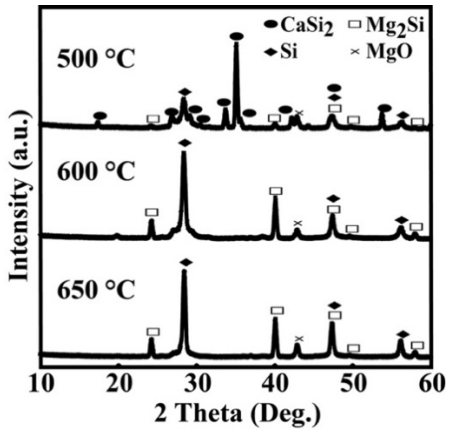

Fig. 2 XRD spectra of the $MgCl_2$ treated powders at 500, 600 and 650 °C, obtained with a Cu Kα1 source.

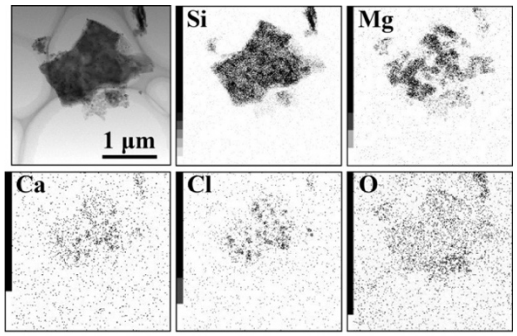

Fig. 3 STEM image and EDS mappings of a piece of the nanosheet synthesized by the thermal treatment at 600 °C.

Figure 5 shows normalized PL spectra of the composites synthesized by the thermal treatment at 600 °C in the temperature range between 19 and 300 K. The PL property of the Si nanosheets was explained by the superlattice-like layered structural model, and the PL peaks are observed around 2.03 eV, which peaks are also observed slightly at low temperatures, as shown by an arrow in Fig.5 [2]. According to the almost no or small temperature dependence of the peak energy, it is possible that the emission peaks of the bundles are originated from defect related sites in the band gap of the nanosized Si [5].

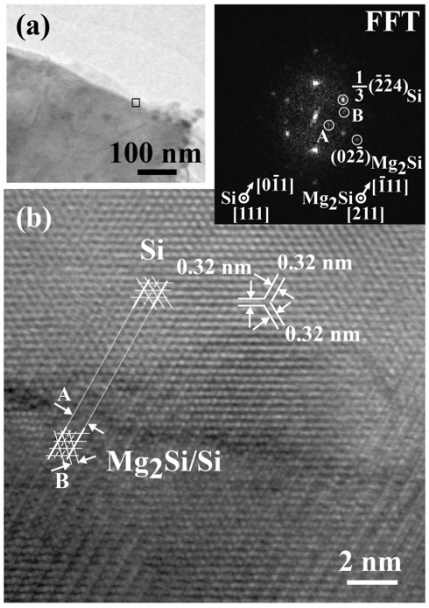

Fig. 4 TEM and HRTEM images with an FFT pattern of the nanosheet synthesized by the thermal treatment at 600 °C.

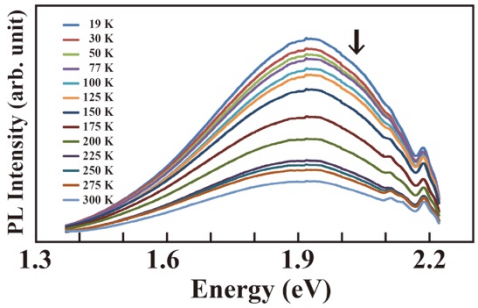

Fig. 5 PL spectra of the composites synthesized by the thermal treatment at 600 °C in the temperature range between 19 and 300 K.

4. Conclusions

Mg_2Si/Si nanosheet bundle composites were synthesized by Ca atom extraction from $CaSi_2$ powders by thermal treatment under $MgCl_2$ vapor. The Mg_2Si deposits were formed and distributed inhomogeneously on the Si nanosheets. It was found that the structural modification of the Si nanosheet bundles to form the composites with Mg_2Si deposits affected the emission property of the Si nanosheets. It is possible that the emission peaks of the bundles are originated from defect related sites in the band gap of the nanosized Si.

Acknowledgements

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