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Fine Structural and Photoluminescence Properties of Mg_2Si Nanosheet Bundles Rooted on Si Substrates

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Abstract

Mg_2Si nanosheet bundles were synthesized by Ca atom extraction from $CaSi_2$ micro-walls grown on Si substrates by thermal annealing under $MgCl_2$/Mg mixed vapors. The fine structural and photoluminescence properties of the Mg_2Si nanosheet bundles were examined. The observed Mg_2Si nanosheets consist of thinner Mg_2Si layers which affect the photoluminescence property of the Mg_2Si nanosheets. A superlattice-like layered structural model is proposed to describe the luminescent property of the Mg_2Si nanosheet bundle structures.

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 one of the potential structures for practical technological applications [1]. The Si-based nanosheet bundles have been synthesized from $CaSi_2$ micro-walls grown on Si substrates. The structural and optical properties of the Mg_2Si/Si composites have been characterized in the past [2]. In this study, the synthesis of Mg_2Si nanosheets by extraction of the Ca atoms from $CaSi_2$ micro-walls grown on Si-substrates by thermal annealing under $MgCl_2$/Mg mixed vapors is reported. In addition, the photoluminescence (PL) property of the bundles is characterized, and the results are discussed in terms of the superlattice-like structures in the nanosheets.

2. Experimental procedure

First, $CaSi_2$ micro-walls were grown on Si(111) substrates [3]. The Si-based nanosheet bundles were then synthesized by Ca atom extraction from the $CaSi_2$ micro-walls by thermal treatment under $MgCl_2$/Mg vapors. The $MgCl_2$/Mg vapors were supplied to the $CaSi_2$ micro-walls by the evaporation of $MgCl_2$ powders and Mg balls at the molar ratio of $CaSi_2$:$MgCl_2$:Mg = 1:2:8. The structural property of the nanosheets was characterized by SEM and TEM. PL measurements were performed at room temperature (RT). The signals were detected using a standard lock-in technique with a cw 532-nm second harmonic generation (SHG) Nd:YVO_4 laser as the excitation source and an InGaAs photodetector (NIR). The excitation power was 80 mW. In addition, the PL measurements were also carried out under excitation by a 405-nm laser diode (38 mW). Moreover, a highly sensitive CCD sensor was used for the visible range PL measurements (VIS).

3. Results and discussion

SEM images of the nanosheet bundles synthesized on Si substrates are shown in Fig. 1. Micrometer-sized walls were observed, and sheets with a thickness on the order of 100 nm were also observed in the wall. The sheets were stacked with a small void space to form a bundle, moreover, the sheets were exfoliated from each other to form much thinner nanosheets.

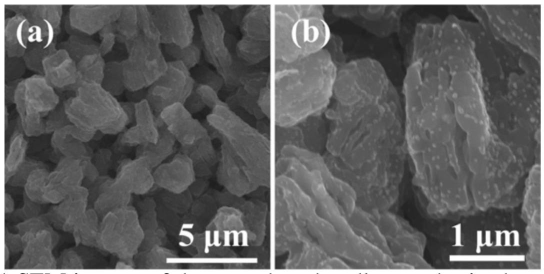

Fig. 1 SEM images of the nanosheet bundles synthesized on the Si substrate.

A TEM, STEM image and corresponding EDS mappings and HRTEM image with an FFT pattern of a piece of the nanosheet scratched off from the substrate are shown in Fig. 2. Mg atoms were homogeneously distributed throughout the nanosheet. In addition, Ca and Cl atoms were rarely distributed. However, it was observed that the nanosheets were partially oxidized.

An HRTEM image with an FFT pattern of the nanosheets observed roughly parallel to the nanosheet surface is shown in Fig.2(c). According to sets of the observed lattice spacings and the FFT spots, the observation direction is perpendicular to the Mg_2Si[211], and the Mg_2Si(211) planes are roughly parallel to the interfaces of ~1 nm-thick periodic multilayers, which would be originated from $CaSi_2$(0003) planes. This is consistent with the crystalline orientation relationship between the Mg_2Si deposits and the Si(111) nanosheet given by (211), $[\bar{1}11]$ Mg_2Si // (111), $[0\bar{1}1]$Si, as reported in Ref.2. Additional spots or lattice planes resulting from the superposition of the diffraction conditions were observed, which suggests the existence of multiple growth variants during the initial stage of the Mg_2Si formation from the $CaSi_2$ templates with the crystalline orientation relationship mentioned above.

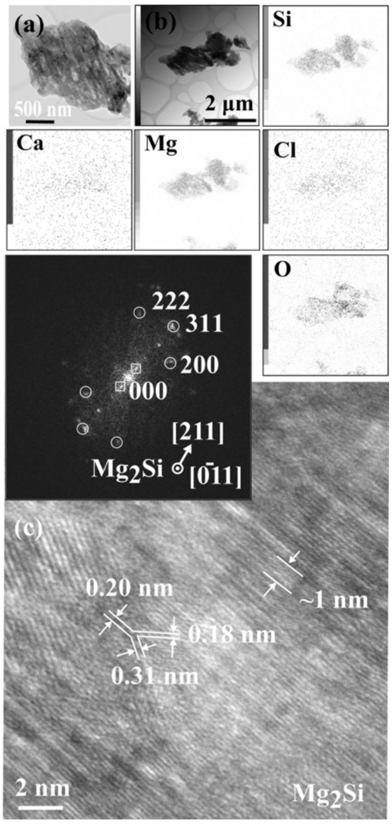

Fig. 2 (a) TEM, (b) STEM image and EDS mappings and (c) HRTEM and corresponding FFT patterns of a piece of the nanosheet scratched off from the substrate.

PL spectra of the Mg_2Si nanosheet bundles on the Si substrates normalized by the number of photons under the 532 and 405nm excitations at RT are shown in Fig. 3. The 405-nm excitation PL spectra show PL peaks around 1.2 (P2) and 2.6 eV (P4). On the other hand, small broad peaks around 1.1 (P1) and 2.0 eV (P3) were observed by the 532-nm excitation. Considering the absorption spectrum of Mg_2Si around the band gap edge, the PL spectra with 405-nm excitation will show the optical transitions of the nanoscale-Mg_2Si near the surface. Thus, it is considered that the bigger peaks, P2 and P4, in the spectra are due to the surface region of the Mg_2Si nanosheet bundles. On the other hand, the P1 and P3 would be due to the optical transition in the deeper region near the substrates.

The energy band gap of Mg_2Si was experimentally obtained as ~0.8 eV [4]. Recently, the experimental result of the optical property showed the estimated band gap of Mg_2Si as 0.61 eV at RT [5], and the photoluminescence peaks from Mg_2Si were observed around ~0.924 eV [6]. Though it would be doubtful that the P1 emission would be caused by the Si substrate, it was found that the P2 emission was observed in the higher energy region compared to the expected energy gap. The blue shift of the emission peak due to radiative recombinations caused by the superlattice-like (~ 1nm) structure that originated from the template $CaSi_2$(0003) layered structure. Migas *et al*. reported that the 2D-Mg_2Si turns out to have a direct band gap of 1.14 eV with the first direct transition in the Γ point [7], which roughly agrees with the P2 emission.

It should be mentioned that the PL emissions were due to Mg_2SiO_4, because of the oxygen distribution suggests the existence of Mg-silicate phases [8]. According to the literature, a series of 1.9~2.3 eV emission peaks were observed [9]. Considering that the equivalent peak of P3 was not observed in the VIS spectra with the 405-nm excitation, the P3 peak is not likely from Mg_2SiO_4. It should be also noted that the emission around 1.9~2.0 eV appeared as a new emission peak of the Mg_2Si composite [2]. Thus, it is considered that the P3 emission is related to Mg_2Si. The P4 emission is unknown at this time.

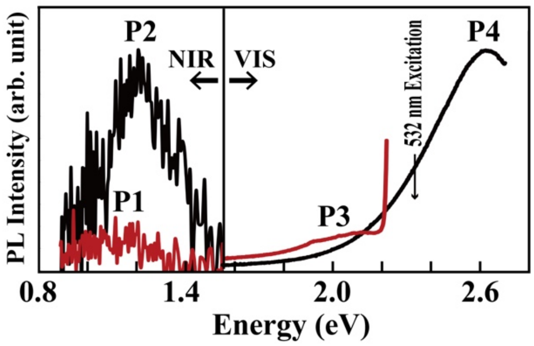

Fig. 3 PL spectra of the Mg_2Si nanosheet bundles under 532 (red) and 405-nm (black) excitations at RT. The NIR and VIS indicate the used detector (the InGaAs photodetector and the CCD sensor, respectively). The intensity in each of the NIR and VIS regions was normalized by the maximum intensity in each region, considering with by the number of photons under the 532 and 405nm excitations.

4. Conclusions

The Mg_2Si nanosheet bundles were synthesized from $CaSi_2$ micro-walls on Si substrates by thermal treatment under $MgCl_2$/Mg vapors. The nanosheet feature of Mg_2Si originated from the source $CaSi_2$ crystals to the Mg_2Si nanosheet bundles affected the emission property. It is possible that the emission peaks of the bundles originated from the bandgap broadening due to the quantum confinement effect in the 2D nanosheet layers by the formation of the superlattice-like structure in the nanosheets.

Acknowledgements

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