

## Structural and Photoluminescence Properties of Si-based Nanosheet Bundles Rooted on Si Substrates

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### Abstract

Si nanosheet bundles were synthesized by Ca atom extraction from CaSi<sub>2</sub> micro-walls grown on Si substrates using inositol hexakisphosphate solution treatment or thermal treatment under FeCl<sub>2</sub> vapor. The structural and photoluminescence properties of the Si nanosheet bundles were examined. Quantum confinement effect was observed by the photoluminescence measurements for these Si nanosheet bundles. The observed Si nanosheets consist of thinner Si layers, which affect the photoluminescence property of the Si-based nanosheets. Superlattice-like layered structural model is proposed to describe the Si-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 also one of the potential structures for technological applications. The Si-based nanosheet bundles have been synthesized from CaSi<sub>2</sub> micro-walls grown on Si substrates. The structural properties of the bundles were characterized in the past [1]. In this study, the synthesis of Si nanosheets by extraction of the Ca atoms from CaSi<sub>2</sub> powders using inositol hexakisphosphate (IP6) C<sub>6</sub>H<sub>18</sub>O<sub>24</sub>P<sub>6</sub>, is reported. In addition, the photoluminescence (PL) property of the bundles is characterized, and the results are discussed in terms of quantum confinement effect and surface states of the nanosheets.

### 2. Experimental procedure

First, CaSi<sub>2</sub> micro-walls were grown on Si substrates [2]. Then, Si-based nanosheet bundles have been synthesized by Ca atom extraction from the CaSi<sub>2</sub> micro-walls on Si substrates by IP6 in an aqueous solution or thermal treatment under FeCl<sub>2</sub> vapor. The growth conditions of the micro-walls and nanosheet bundles are described elsewhere [1,2]. The structural property of the nanosheets were characterized by SEM and TEM. PL measurements were performed at temperatures between 18 and 300 K within a closed cycle helium cryostat. The signals were detected using a standard lock-in technique with a cw 532 nm second harmonic generation (SHG) Nd:YVO<sub>4</sub> laser as the excitation source and an InGaAs photodetector. The excitation intensity was 80 mW. In addition,

the PL measurements were also carried out under excitation by a 405 nm laser diode (40 mW). Moreover, a high sensitive CCD sensor was used for visible range PL measurements.

### 3. Results and discussion

Figures 1(a) and (b) show SEM images of the nanosheet bundles synthesized on Si substrates by IP6 solution treatment and thermal treatment under FeCl<sub>2</sub> vapor, respectively. The nanosheets with a thickness of several to tens of nanometers are observed, and the nanosheets are stacked with a small void space to form a bundle. Figures 2(a) and (b) show TEM images of a part of Si nanosheets. It is pointed out that thinner layers are overlapped near the edge and corner of the bundle structure for both cases. The detailed structural analysis of the Si nanosheets was reported elsewhere [2].

Figures 3(a) and (b) show PL spectra of the Si nanosheet bundles synthesized by the IP6 solution treatment and the thermal treatment under FeCl<sub>2</sub> vapor, respectively, under 532 and 405nm excitations at 18 K, detected by an InGaAs photodetector. In the spectra, the main peaks around 1.1 eV are due to the Si substrates. In this case, by the excitation light with a wavelength of 532 nm, optical transition in the nanosheet region occurs as well as in the Si substrates.

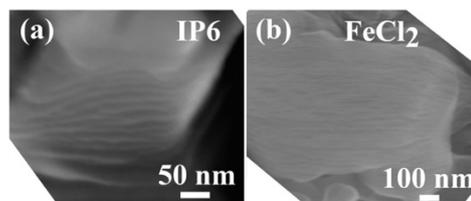


Fig. 1 SEM images of the nanosheet bundles synthesized on Si substrates by (a) IP6 solution treatment and (b) thermal treatment under FeCl<sub>2</sub> vapor.

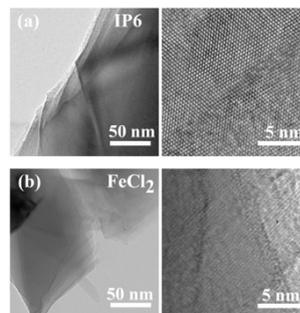


Fig. 2 TEM images of a part of Si nanosheets synthesized by (a) IP6 solution treatment and (b) thermal treatment under FeCl<sub>2</sub> vapor.

On the other hand, by the excitation light with a wavelength of 405 nm optical transition in the nanosheets region mainly occurs with more enhancement at the surface region of the nanosheets. Figures 3(c) and (d) show enlarged PL spectra of above mentioned ones shown in (a) and (b) under 532 nm excitations at 18 K, respectively. In addition to the main peaks at 1.1 eV, small relatively broad emission bands were observed. The broad peak observed in visible region is most likely due to the quantum confinement effect of the Si nanosheets.

To analyze more clearly the PL property observed in the visible region, the spectra were obtained by a high sensitive CCD sensor. Figure 4 shows normalized PL spectra of the Si nanosheet bundles in the temperature range between 19 and 300 K and synthesized by (a) the IP6 solution treatment and (b) the thermal treatment under FeCl<sub>2</sub> vapor. Because of the high sensitivity of the CCD sensor, the peaks are clearly seen, and the difference of the shapes of the spectra compared with those shown in Fig.3 is due to the difference of the wavelength dependence of the detector sensitivity between the InGaAs photodetector and the high sensitive CCD sensor. The sharp PL spectra were obtained for the Si nanosheets synthesized by the IP6 solution treatment. The emission around 2 eV is due to radiative recombination from quantum states in two-dimensional (2D) quantum well. On the other hand, the spectra show broad emission bands, which consist of multiple peaks for the bundles synthesized by the thermal treatment under FeCl<sub>2</sub> vapor.

Figure 5 shows the temperature dependence of integrated PL spectra of the nanosheet bundles. The temperature dependence of PL intensity of the bundles synthesized by the IP6 solution treatment is well described as the following expression [3],

$$I(T) = \frac{I_0}{1 + c \exp\left(-\frac{\Delta E}{k_B T}\right)} \quad (1)$$

where  $\Delta E$  is activation energy of non-radiative recombination channel of  $\Delta E = 45$  meV. On the other hand, for the FeCl<sub>2</sub> treated Si nanosheet bundles, the result suggests the existence of multiple non-radiative recombination channels with shallow activation energy near the surface region considering with the results shown in Fig.3. Considering with previous results, the surface nanosheet is oxidized [1]. In addition, previous SEM and TEM observations showed that the thickness of the nanosheets is several to a few tens nano-meters [1]. On the other hand, according to Ref.4, the PL peak energy suggests that the thicknesses of the Si 2D layers are estimated as around 1 to 2 nm in the Si nanosheet bundles [4]. Thus, to describe the structural and photoluminescence properties of the Si nanosheet bundles, superlattice-like layered structural model is proposed. The optical property of Si/SiO<sub>2</sub> superlattice (SL) has been reported [5-7]. The photoluminescence property of the Si/SiO<sub>2</sub> SL agrees well with the results obtained here.

#### 4. Conclusions

Photoluminescence of the Si nanosheet bundles synthesized by Ca atom extraction from CaSi<sub>2</sub> micro-walls on Si substrates, using IP6 solution treatment or thermal treatment

under FeCl<sub>2</sub> vapor, was investigated. For both cases, the bandgap broadening of the Si nanosheets due to the quantum confinement effect in 2D nanosheet layers is observed. The superlattice-like layered structural model is proposed to describe the Si-nanosheet bundle structures.

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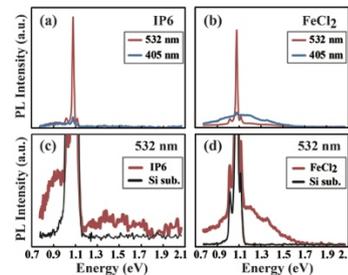


Fig. 3 PL spectra of the Si nanosheet bundles synthesized by (a), (c) the IP6 solution treatment and (b), (d) the thermal treatment under FeCl<sub>2</sub> vapor, respectively, under 532 and 405 nm excitations at 18 K, detected by the InGaAs photodetector.

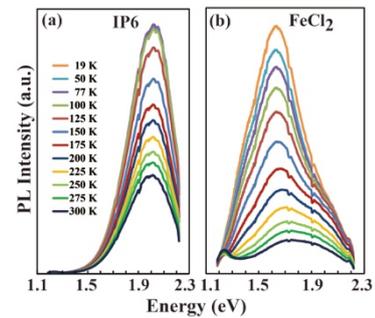


Fig. 4 Normalized PL spectra of the Si nanosheet bundles in the temperature range between 19 and 300 K and synthesized by (a) the IP6 solution treatment and (b) the thermal treatment under FeCl<sub>2</sub> vapor, detected by the high sensitive CCD sensor.

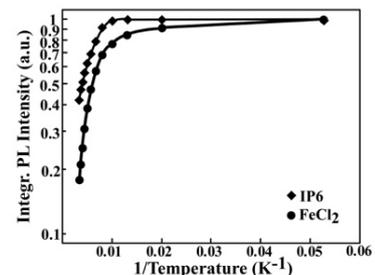


Fig. 5 Temperature dependences of normalized integral intensity of the PL peaks of the Si nanosheet bundles.