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Fabrication of nanostructured silicon carbide from rice husks and its photoluminescence properties

Jin LI, Takashi SHIRAI and Masayoshi FUJI†

Advanced Ceramics Research Center, Nagoya Institute of Technology, Crystal Plaza 4th Floor, 3–101–1 Hommachi, Tajimi, Gifu 507–0033, Japan

Nanostructured silicon carbide (SiC) particles and whiskers have been fabricated by pyrolysis of rice husks (RHs) in argon atmosphere. The results revealed that a complete carbothermal reduction of silica was achieved at 1600°C for 2 h and the final product was β-SiC. The β-SiC obtained on the bodies of pyrolyzed rice husks (PRHs) was mainly particles having diameters of 100–200 nm and the wool-like product formed on the inner walls of the graphite crucible was β-SiC whiskers with diameter of around 170 nm and tens of micrometers in length. Compared to bulk β-SiC, down-shifts and asymmetric broadening were observed on both transverse optical (TO) and longitudinal optical (LO) phonon peak in Raman scattering spectra of the nanostructured SiC. The photoluminescence (PL) spectra revealed that the nanostructured β-SiC, especially the β-SiC whiskers, showed excellent blue light emission property. The PL emission peak was considerable blue-shifted relative to that for the bulk β-SiC.

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Recently, the photoluminescence properties of SiC have received considerable attention. Compared with bulk crystal SiC, SiC nanostructures show more excellent optical performance because of their low dimensionality, quantum confinement and shape effects.[1)–3)] Up to now, much effort has been devoted to fabricate various kinds of SiC nanostructures with special optical properties. For example, Xi et al. synthesized β-SiC nanorods, nanoneedles by a magnesium-catalyzed co-reduction route, displaying excellent and shape-dependent optical properties.[4)] Wu et al. synthesized twinned zigzag SiC nanoneedles with SiC nanoparticles aggregates as byproducts via silicon evaporation onto multiwall carbon nanotubes and this kind of nanostructured SiC showed considerable blue shifts of multi-PL peaks relative to the bulk β-SiC.[5)] Niu et al. employed thermal evaporation of ZnS and carbon on silicon wafer to produce β-SiC nanowires arrays and show a blue emission luminescence at 430 nm.[6)] Li et al. synthesized β-SiC nanospheres and nanowires by a metal coreduction method, showing a wide blue emission luminescence centered at 443 nm.[7)] Even though they were basically successful, most of them involve complex procedures, extra metal catalyst or expensive precursors.

As we known, huge amounts of rice husks (RHs) are produced annually in the world as an agricultural byproduct of rice threshing. RHs have been proved to be an economical and promising raw material for producing SiC, due to high surface area and intimate contact available for carbon and silica.[8)–12)] However, few literatures are accessible about optical properties of SiC that fabricated by pyrolysis of RHs. In this study, nanostructured β-SiC particles and whiskers were prepared by using RHs as precursors. The microstructure and optical properties of the β-SiC were studied.

RHs were collected from a local rice mill factory of Japan. The RHs are composed of about 75 mass % organic constituents (hemicelluloses, cellulose and lignin), 5 mass % water, 18 mass % SiO_2 and 2 mass % other impurities (0.88 mass % K_2O, 0.46 mass % SO_3, 0.31 mass % Al_2O_3, 0.23 mass % CaO, 0.07 mass % P_2O_5, 0.04 mass % MnO and 0.01 mass % Fe_2O_3). High-purity argon (>99.999%) gas was used as the shielding gas in this work. In a typical experimental procedure, 6g of RHs placed in an airtight graphite crucible (80 × 80 × 10 mm) were put into an electric furnace. After evacuating to ~5 Pa, high-purity argon gas was introduced to the furnace at constant flow rate of 2 L/min and maintained at a positive pressure of ~50 kPa throughout the whole following experiment. The furnace was firstly heated to 1000°C at a rate of 15°C/min, then up to 1500 and 1600°C respectively at a rate of 10°C/min. After maintained at target temperature for 2 h, the furnace was cooled down to room temperature naturally and pyrolyzed rice husks (PRHs) were received. Then the PRHs were calcined in air at 600°C for 3 h to remove the residual carbon and leached by dilute HF solution to remove the impurities. The final product was denoted as SiC-PRHs. On the other hand, wool-like products with light green color formed on the inner walls of graphite crucible, which were also collected without any further treatment and denoted as SiC-crucible. The crystal structures of the samples were characterized by X-ray diffraction patterns (XRD, Rigaku, UltimaIV). Morphology observation and microstructure analysis were performed by scanning electron microscopy (SEM, JEOL, JSM-7600F) and Transmission electron microscopy (TEM, JEOL, JEM2010). Raman scattering spectra was produced by a micro-Raman spectrometer (JASCO, NRS-3100) using 532 nm excitation wavelength at room temperature. The photoluminescence (PL) spectra were performed in a spectrofluorometer (JASCO, P-6500) with a Xe lamp at room temperature.

Figure 1 shows the XRD patterns of the products. Major diffraction peaks at $2\theta = 35.6$, 41.4, 60.0, 71.8 and 75.5° can be indexed as (111), (200), (220), (311) and (222) reflections of β-SiC, respectively (JCPDS Card No. 29-1129). The small peak

† Corresponding author: M. Fuji; E-mail: fuji@nitech.ac.jp

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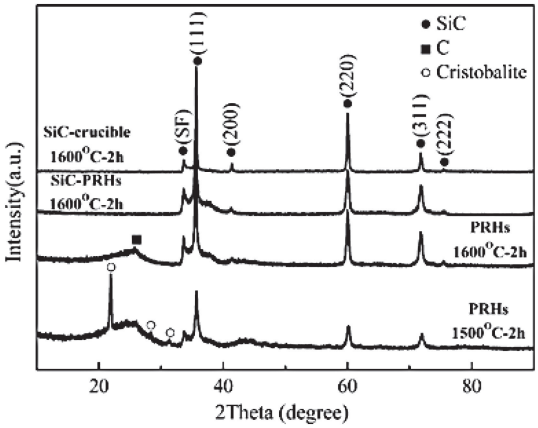

Fig. 1. XRD patterns of the products.

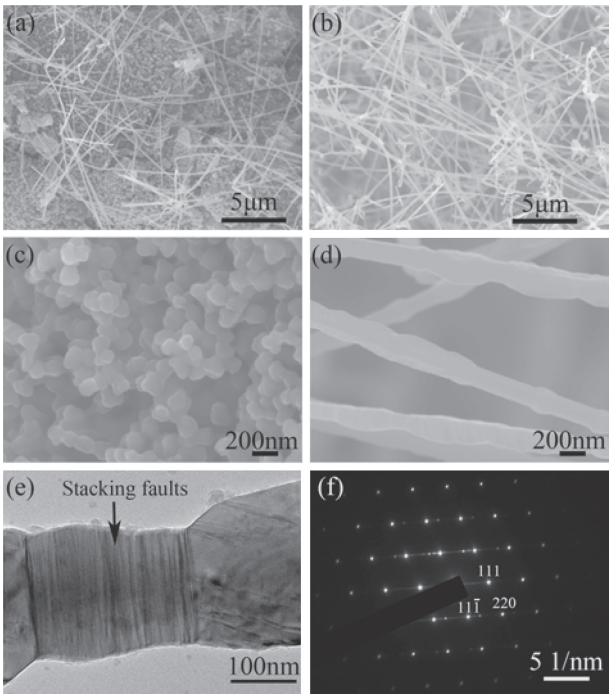

Fig. 2. SEM images of the products obtained at 1600°C for 2 h: (a) SiC-PRHs (b) SiC-crucible (c) β-SiC particles (d) β-SiC whiskers. (e) TEM image of a typical β-SiC whisker and (f) its corresponding SAED pattern.

ahead of the most intensive peak (111) marked with SF is attributed to the stacking faults of β-SiC.[13] Characteristic peaks of cristobalite are found in the XRD pattern of the PRHs obtained at 1500°C for 2 h, revealing that the reaction was not completed and unreacted SiO_2 crystallized to cristobalite. The diffraction peak at around 26° in the XRD pattern of the PRHs obtained at 1600°C for 2 h confirms the existence of residual carbon and no noticeable peaks of SiO_2 can be detected, indicating a complete carbothermal reduction. Thus, the products obtained at 1600°C for 2 h were selected for further study. Only characteristic peaks of β-SiC are observed in the XRD patterns of SiC-PRHs and SiC-crucible, revealing that pure β-SiC was obtained.

As can be seen in **Figs. 2**(a) and 2(b), the SiC-PRHs is mainly composed of particles with small amount of whiskers dispersing on surface, whereas the SiC-crucible is composed of β-SiC whiskers having several to tens of micrometers in length.

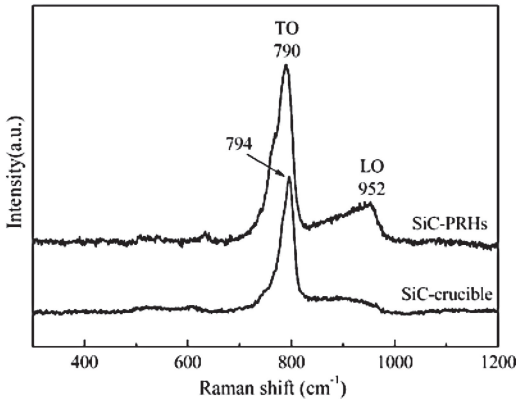

Fig. 3. Raman spectra of the β-SiC obtained at 1600°C for 2 h.

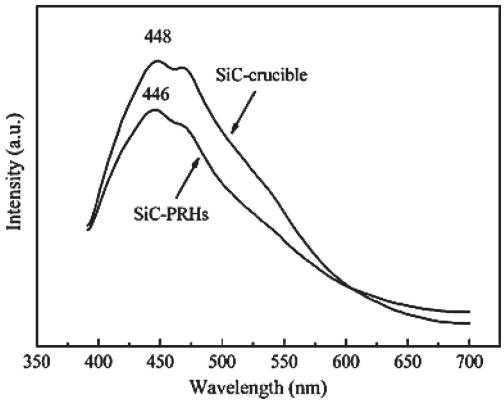

Fig. 4. Photoluminescence (PL) spectra of the β-SiC obtained at 1600°C for 2 h.

Figures 2(c) and 2(d) exhibit the morphology of the β-SiC particles and whiskers. The β-SiC particles have diameters of 100–200 nm and the whiskers show diameter of around 170 nm. Figure 2(e) shows the TEM image of a typical whisker. The stacking faults are valid on the whisker, which is consistent with the result of the XRD pattern. From the SAED pattern of the β-SiC whisker [Fig. 2(f)], it can be concluded that the β-SiC whisker has a single crystal structure and grow along the [111] orientation.

Figure 3 displays the typical Raman spectra taken from the SiC-PRHs and SiC-crucible. As can be seen in the Raman spectrum of the SiC-PRHs, the characteristic peaks at around 790 and 952 cm^{-1} are attributed to transverse optical (TO) phonon mode and longitudinal optical (LO) phonon mode at Γ point of β-SiC, respectively. Relative to that for bulk β-SiC,[14] the characteristic peak centers are down-shifted by 6 and 20 cm^{-1}, respectively. Furthermore, obvious asymmetric broadening was observed on both of the peaks, especially on peak of LO phonon mode. From the Raman spectrum of SiC-crucible, an intense peak of TO phonon mode was detected at 794 cm^{-1}. However, no obvious peak of LO phonon mode was detected. The unique optical properties exhibited in Raman spectra can be ascribed to the size confinement effects and defects of nanostructured β-SiC.[15),16)]

The photoluminescence (PL) properties of the products were investigated at room temperature under excitation wavelength at 367 nm. The PL spectra of the as-obtained β-SiC are shown in **Fig. 4**. It can be found that the SiC-PRHs and SiC-crucible display strong blue light emission at 446 and 448 nm, respectively. Compared with that of bulk β-SiC (519 nm),[17] the PL

peak position is considerable blue-shifted, which is attributed to the quantum confinement effect of nanomaterials and involved defects.[18] Furthermore, the SiC-crucible shows higher peak intensity, indicating that the β-SiC whiskers have a better light emission performance than the β-SiC particles. It is believed that the more excellent light emission property of the β-SiC whiskers is ascribed to the high length/diameter aspect ratio and large amounts of stacking faults of one-dimensional structure.

In summary, nanosized β-SiC particles and whiskers have been fabricated by pyrolysis of RHs in this study. The β-SiC particles have diameters of 100–200 nm and the β-SiC whiskers show diameters of around 170 nm and several to tens of micrometers in length. The nanostructured β-SiC, especially the β-SiC whiskers, show excellent blue light emission property.

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