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Citation: *Appl. Phys. Lett.* **89**, 143101 (2006); doi: 10.1063/1.2358313

View online: <http://dx.doi.org/10.1063/1.2358313>

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# Ultraviolet photoluminescence from 3C-SiC nanorods

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(Received 18 March 2006; accepted 14 August 2006; published online 2 October 2006)

An intensive sharp photoluminescence at 3.3 eV is observed from single-crystal 3C-SiC nanorods. Structural characterization reveals that the nanorods contain a fairly large amount of threefold stacking faults. We tentatively attribute the emission to these stacking faults, which structurally resemble 6H-SiC nano-layers of 1.5 nm embedded in a 3C-SiC matrix. The emission mechanism is discussed in terms of spontaneous polarization at the stacking faults. © 2006 American Institute of Physics. [DOI: 10.1063/1.2358313]

SiC is known for its wide-band-gap electronic structure as well as excellent thermal and mechanical properties, thus is potentially useful for applications in high-temperature electronics and short-wavelength optics.<sup>1</sup> SiC has been the leading material for high-temperature, high-power and high-frequency electronic devices due to advances in the crystal growth and doping ability for both *n* and *p* types.<sup>2</sup> However, applications of SiC in optical devices are limited by its indirect band gap nature, which results in very low light emission efficiency.<sup>3</sup> Increasing the light-emission efficiency for SiC has received considerable interest in the last two decades. Significant improvements have been made by using either porous or nano-sized systems.<sup>4–7</sup> In these systems, the enhancements in light emission are mainly attributed to either surface defects or quantum confinement effects.

Improved luminescence has also been observed from SiC quantum well (QW) structures.<sup>8,9</sup> The polytypism of SiC leads to a unique type of structure-only QW structures involving thin layers of cubic 3C-SiC (which has the smallest energy gap, ~2.4 eV) embedded in higher energy gap SiC polytypes, such as 4H- (energy gap=3.3 eV) and 6H-SiC (energy gap=3.0 eV).<sup>10</sup> Because of the spontaneous polarization difference between cubic and hexagonal SiC, internal electric fields are expected in the QW structures, which leads to the redshift of the luminescence peaks.

In this letter we report an intensive ultraviolet (UV) photoluminescence (PL) from threefold stacking faults in single-crystal 3C-SiC nanorods, which structurally resemble 6H-SiC layers of 1.5 nm thickness embedded in a 3C-SiC matrix. In contrast to the aforementioned QW structures, quantum barrier structures should be formed in the current case

since 6H-SiC has a higher energy gap than 3C-SiC.

The SiC nanorods used in this study were synthesized via catalyst-assistant crystallization of amorphous silicon carbonitride (*a*-SiCN).<sup>11</sup> In brief, a polysilazane precursor was first decomposed to *a*-SiCN powder at 1000 °C. The *a*-SiCN powder was then reacted with a catalyst (FeCl<sub>2</sub> in this study) to form Si-C-Fe liquid alloy droplets at temperatures higher than the tertiary eutectic point of the system. The nanorods were precipitated and grew from the liquid droplets at 1700 °C via a solid-liquid-solid mechanism.<sup>11</sup> All heat treatments were performed in an ultrapure N<sub>2</sub> atmosphere. The obtained nanorods are 80–200 nm in diameter and up to a few micrometers in length, and grown along [111] direction (Fig. 1).

The room-temperature steady-state PL spectrum of the nanorods was measured using a UV lamb micro-Raman

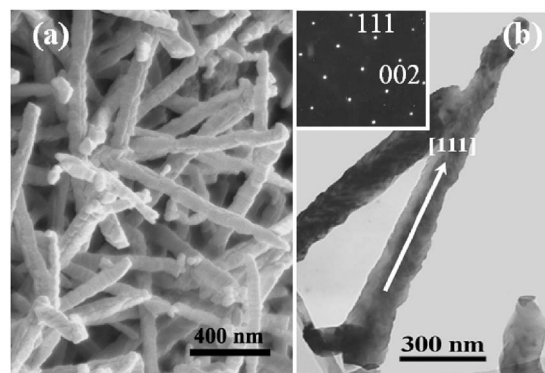


FIG. 1. (a) Scanning electron microscopy image showing the morphology of the SiC nanorods. (b) TEM image of an individual nanorod. The inset is the corresponding electron diffraction pattern, showing that the nanorod grows along [111] direction.

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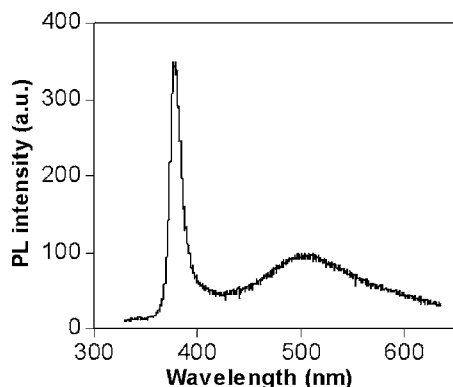


FIG. 2. Room-temperature steady-state PL spectrum of the SiC nanorods.

spectrometer with a He–Cd laser of 325 nm wavelength and 5 mW output power as the excitation light source. The spectrum (Fig. 2) reveals two emission peaks: a strong, sharp UV emission at 378 nm (3.3 eV) and a broad, green emission ranging from 450 to 600 nm. The intensity of the UV emission is more than five times higher than that of the green emission. While the broad emission between 450 and 600 nm might be attributed to 3C-SiC,<sup>7,12</sup> the strong emission at 3.3 eV, which is significantly higher than the band gap of crystalline 3C-SiC, is difficult to explain and has never been observed in 3C-SiC previously. The UV emission cannot be attributed to structural defects in SiC, such as dislocations, carbon di-interstitial, di-vacancies or isolated vacancies at the Si site, because the PL signals resulting from these defects are in the unique range of 1.9–2.3 eV.<sup>13,14</sup> The UV emission is also different from that observed in porous or nano-sized 3C-SiC, where PL signals associated with either quantum confinement or surface defects are generally below 2.8 eV.<sup>4–6</sup> In addition, the dimensions of the nanorods are too large to have significant quantum confinement effects. A 3.26 eV PL peak has been frequently observed in crystalline silicon dioxide films and was attributed to oxygen vacancies.<sup>15–17</sup> However, this cannot explain the current results since no such oxide films were observed on the surface of the nanorods. The absence of an oxide film is due to the fact that the nanorods were synthesized in an ultrapure N<sub>2</sub> environment.

In order to understand the origin of the UV emission, the structure of the SiC nanorods was characterized using high-resolution transmission electron microscopy (HRTEM). Figure 3(a) is a typical HRTEM image of the nanorods, showing that the nanorods contain a fairly high concentration of stacking faults, which are perpendicular to [111], growth direction [Fig. 1(b)]. This result is consistent with x-ray diffraction (XRD) pattern that revealed a large amount of stacking faults in the SiC nanorods [Fig. 3(b)]. Detailed observation at higher magnification [inset in Fig. 3(a)] reveals that the stacking faults are threefold in nature (three immediately adjacent single stacking faults). It should be noted that the region around the threefold stacking faults resembles the structure of 6H-SiC [Fig. 3(c)]. Therefore, the structure of the nanorods can be viewed as a 3C-SiC matrix containing 6H-SiC-like nano-scaled layers. According to this model, the thickness of these 6H-SiC-like layers should be about the length of the *c* axis of 6H-SiC unit cell, which is ~1.5 nm. Such thin layers cannot be detected by XRD since the formation of XRD peaks requires at least several unit

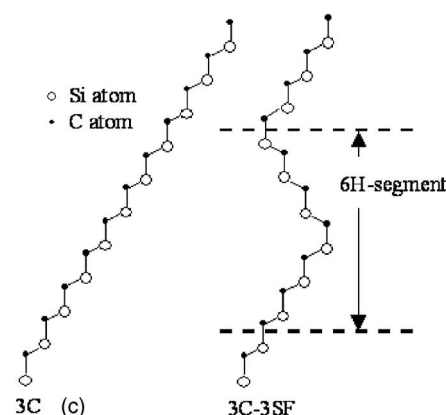
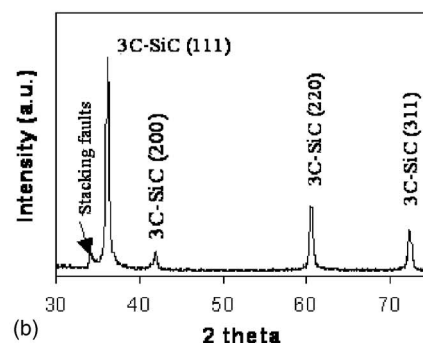
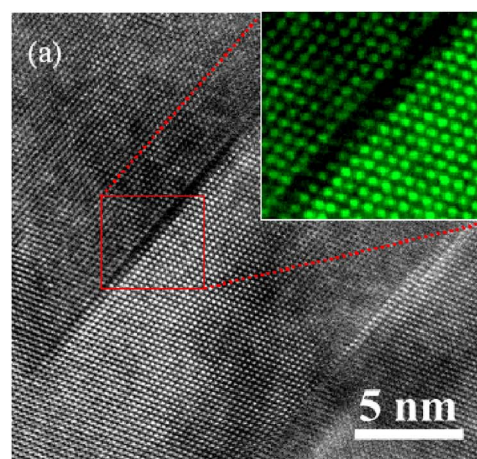


FIG. 3. (a) Raman spectrum of the nanorods. The red line is the experimental result and the blue line is the curve fit by addition of the pink lines. (b) XRD pattern showing that the nanorods are pure 3C-SiC containing stacking faults. (c) HRTEM image showing the stacking faults in the nanorods. The inset is the enlargement of the selected area revealing the threefold stacking fault nature. (d) Schematic model of perfect 3C-SiC and 3C-SiC containing a threefold stacking fault; the region around the stacking fault (between two dash lines) shows the structure resembling that of 6H-SiC.

cells. Thus XRD pattern showed only 3C-SiC peaks [Fig. 3(b)].

Based on the above discussion, we tentatively attribute the intensive light emission at 3.3 eV to the unique structure of the SiC nanorods. According to Qteish, Heine, and Needs, in SiC a spontaneous polarization takes place around each hexagonal turn,<sup>18</sup> which is quite strongly localized at the turn. Such spontaneous polarization leads to electric dipole moments being built in throughout the 6H-SiC nano-layers. These electric dipoles can cause opposite charges on both sides of the nano-layers.<sup>19</sup> These localized charges can lead to potential barriers in the conduction band at the boundaries of the 6H-SiC nano-layers.<sup>18</sup> The barriers will constrict elec-

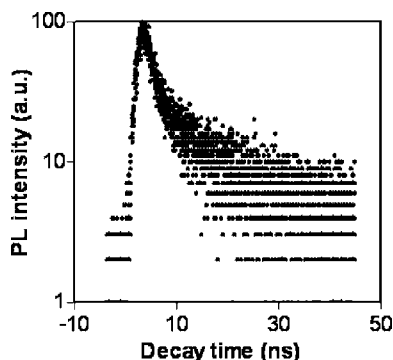


FIG. 4. Room-temperature time evolution of the luminescence intensity of the emission at 3.3 eV.

trons within 6H-SiC layer and thus electronically isolate the layers from the 3C-SiC matrix. Consequently, the 6H-SiC layers may act as free-standing nano-sized sheets of 1.5 nm in thickness, which should lead to strong blueshifted light emission (3.3 eV is higher than the band gap of bulk 6H-SiC) due to a quantum confinement effect. It is instructive to note that the position and shape of the 3.3 eV emission observed from the nanorods closely resembles that of the PL peak theoretically predicted for 1.5 nm 6H-SiC clusters.<sup>20</sup>

Further characterization of the PL behavior of the nanorods was carried out by measuring their room-temperature time-resolved PL spectrum using a fluorescence lifetime spectrometer with a resolution of 100 ps. Figure 4 shows the time evolution of the luminescence intensity of the emission at 3.3 eV. The best fit to the curve was obtained using a biexponential decay process. The biexponential decay implies that multi levels may be involved in the radiative recombination. Two decay time constants of 1.0 and 6.5 ns were obtained. It should be noted that the decay times of around 1 ns are at least two orders of magnitude shorter than that for bulk SiC.<sup>21</sup> Such short decay times were typically observed for the emission from nano-structured indirect-band-gap materials.<sup>22,23</sup>

In summary, we report an intensive sharp UV emission from single-crystal 3C-SiC nanorods grown via catalyst-assisted pyrolysis of a polymeric precursor. We attribute this

unique emission to the threefold stacking faults in the 3C-SiC matrix. The nanorods, which could possibly be assembled into nanostructures capable of emitting strong ultra-violet light, would be useful for short wavelength nanode-vices.

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