Ultrafast blue light emission from SiC nanowires

Fuli Zhao (赵福利), Hongxin Chen (陈洪新), Shaozhi Deng (邓少芝), Ningsheng Xu (许宁生), Tianqing Jia (贾天卿), and Zhizhan Xu (徐至展)

State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-Sen University, Guangzhou 510275

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Cubic silicon carbide (SiC) nanowires are synthesized in a catalyst-assisted process. The nanowires with diameter of ~ 40 nm exhibit strong blue light emission at room temperature under ultraviolet (UV) femtosecond laser excitation. The photon energy of peak emission is higher than the energy bandgap of cubic SiC which shows involvement of quantum confinement effect. The ultrafast fluorescence is deconvoluted by Monte-Carlo method. The results show two ultrafast decay processes whose lifetimes are about 26 and 567 ps respectively. The mechanisms of such ultrafast processes are discussed.

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Silicon carbide (SiC) has many potential applications in high-performance devices involving high temperature, high frequency, high speed, and high power, such as SiC light-emitting diode (LED)[1,2]. However, due to its indirect bandgap, the quantum efficiency of SiC is very low[3]. Just as the strong photoluminescence (PL) from porous silicon at room temperature[4], intensive light emission from low-dimensional SiC structures has also been reported[5−14]. Still the dynamics of low-dimensional SiC structure needs further investigation[5,8]. Recently, we have synthesized SiC nanowires in a catalyst-assisted process, and have shown that they have very good field electron emission properties[15−17]. In this letter, we detect the time-resolved PL of SiC nanowires and discuss the dynamics of ultrafast blue light emission.

The nanowires were grown by thermal heating at the temperature of 1700 °C under flowing Ar (195 sccm)[15,16]. Figure 1 is a typical scanning electron microscopic (SEM) image of the SiC nanowires and the inset is a diffraction pattern showing the 3C structure of the SiC nanowires. The as-grown nanowires have high purity and the typical diameter is about 40 nm.

The experimental setup for optical emission measurement has been reported before[18,19]. The excitation pulse (160 fs, 320 nm) was produced by an optical parameter amplifier (OPA) (Spectra-Physics, OPA-800C) with a repetition of 1 kHz. By a fused silica lens (75.6-mm focal length), the excitation pulse was focused onto the sample surface at an angle of about 45° to the normal of the surface. The average power of the excitation on the sample was about 400 μW (corresponding to a power density of about 10 GW/cm^2). The PL from SiC nanowires was collected at a direction normal to the sample surface and put into the spectroscope connected with a streak camera (Hamamatsu C1587) with a time resolution of 2 ps. The temporal full-width at half-maximum (FWHM) of our instrument response function (IRF) was less than 10 ps. For comparison, we have measured the PL spectra from both SiC nanowires and SiC powder.

Figure 2 shows the normalized PL spectra of both samples. A large shift of about 29 nm in spectrum of SiC nanowires can be seen compared with that of SiC powder. The PL of SiC powder exhibits a wide band and cannot be all included in screen of the spectroscope. This

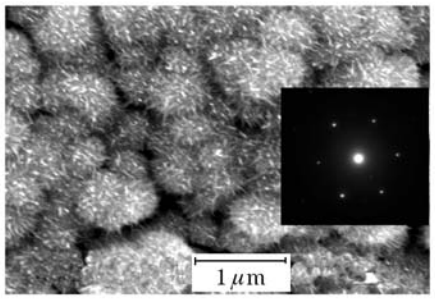

Fig. 1. SEM of SiC nanowires prepared by thermal heating in flowing Ar gas at the temperature of 1700 °C. The inset is a diffraction pattern to show the 3C structure of the SiC nanowires.

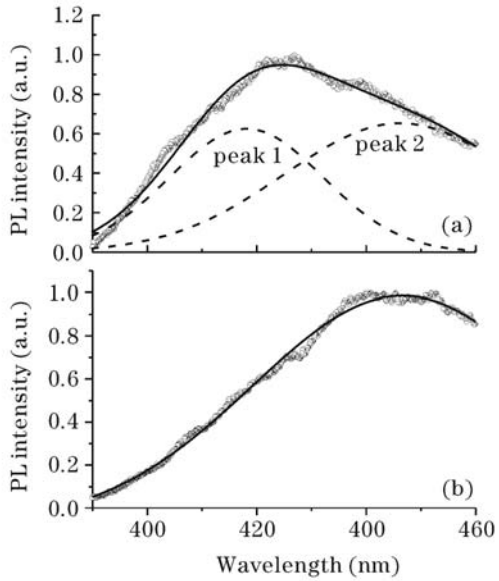

Fig. 2. PL spectra (circles) and the corresponding fitting results (solid lines) of (a) the nanowire sample and (b) the powder sample. The time-resolved PL measurements are performed at room temperature.

spectrum can be well fitted by single Gaussian line with its peak at 447 nm. The spectrum of SiC nanowires is also very broad and indicates multiple peaks. Therefore, we have performed a multi-Gaussian fitting process, which shows two peaks located at 418 and 446 nm, respectively. Compared with the PL spectrum of the SiC powder, we can confirm that the peak at 446 nm comes from emission of SiC powder in the substrate, while the peak at 418 nm emerges from SiC nanowires. Because the diameter of the nanowires has a distribution around a few ten nanometers and the curvature of the apex of the nanowires can be down to a few nanometers, there should be much diversity both in degree of quantum confinement and surface-to-volume ratio of nanowires. This leads to the wide band emission and the slight shift of two PL peaks. Since the bandgap of the bulk 3C SiC is 2.3 eV, corresponding to the wavelength of 539 nm at room temperature, the PL spectrum of nanowires shows a blue-shift. Similar results have been got from other low-dimensional SiC[9−14]. The blue-shift can be explained by the energy bandgap widening due to quantum confinement effect in these nanowires. Such intense blue light emission of as-grown SiC nanowires suggests potential application in optoelectronic devices, especially in harsh environment.

The time-resolved PL measurements are performed at room temperature in order to elucidate the relaxation dynamics of carriers in the nanowires. This is of crucial importance to both fundamental physics and applications because it is useful to understanding the mechanism responsible for the blue-shifted PL.

The fluorescence spectrum detected by the streak camera was transferred into a computer for deconvolution analysis. It is assumed that the detected fluorescence intensity $F_{\rm exp}$ be expressed as[19]

$$F_{\rm exp}(t) = \int f_{\rm pump}(t) F_{\rm theo}(t - t') {\rm d}t', \tag{1}$$

where $f_{\rm pump}$ represents the time-dependent intensity function of the pump laser pulse, t and t' are the corresponding time coordinates of the fluorescence intensity and pump pulse intensity, respectively. The integral covers the whole scale of the pumping pulse. Here we consider the theoretical fluorescence intensity $F_{\rm theo}$ as a sum of multi-exponential form:

$$F_{\rm theo}(t) = \sum \varepsilon_i \exp(-\frac{t}{\tau_i}). \tag{2}$$

We applied a deconvolution procedure based on Monte-Carlo algorithm to search for the optimal fitting results[18,19].

As the new peak at 418 nm is the dominant emission of the SiC nanowires, we will focus on its dynamic analysis. The solid line in Fig. 3 shows the bi-exponential fitting result to the experimental data. The deconvolution result shows that the two decay constants of SiC nanowires are 26 and 567 ps, respectively. It implies the co-existence of two different recombination paths. It should be noted that the decay time of 567 ps is in the same order of magnitude of that of the 3C SiC nanocrystalline films[8] which is at least two orders of magnitude faster than that of the bound-exciton transitions of bulk 3C SiC at low temperature[20]. To our knowledge, the faster process,

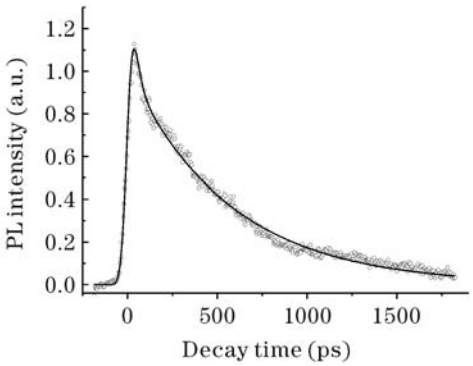

Fig. 3. Room temperature PL decay curves of the dominating emission peak (418 nm) of nanowires sample. The circles represent the experimental data while the solid line represents the fitting result. The ultrafast decay processes are with the lifetimes of 26 and 567 ps, the weights of the corresponding lifetimes in the fluorescence intensity are 47.37% and 52.63%, respectively.

which has an ultrafast decay time of 26 ps, has not been found before. Such ultrafast emission of SiC nanowires might have potential applications in ultrafast optoelectronic devices, such as ultrafast optical switch, especially for environment of high temperature and high radiation.

It is expected that quantum confinement effects occur in low-dimensional SiC[9−14]. Geometrical restriction of the electron-hole pairs should lead to a strong enhancement effect of oscillation strength of the confined levels, resulting in direct transitions in the nanowires and the faster decay process. Similar explanation has been already proposed for low-dimensional Si to account for the fast decay process[21−24]. It is interesting to note that Si nanowires at room temperature were reported to have PL decay time of 20 ps, which attributed to the luminescence due to the quantum confinement effect[24]. We in the similar reasoning attribute the faster decay process of the SiC nanowires to the recombination of the quantum-confined carriers. On the other hand, surface states play an important role in the carriers recombination process with large surface-to-volume ratio in low-dimentional Si[25]. Theoretical study demonstrated the stability of the self-trapped exciton localized at the surface[26]. Furthermore, similar lifetime has been found in low-dimentional Si[21−24] and SiC[5,8] experimentally, which has been attributed to the recombination of the excitons localized at the surface states. Thus, the slower decay process in SiC nanowires could be due to the surface states recombination process. According to the analysis above, we adopt the model previously developed to explore the similar bi-exponential decay behavior in nanosized Si[21−24]. The two decay processes are assigned to a faster recombination of the confined carriers with recombination time in the 100-ps range and a slower one of excitons localized at the surface state with recombination time of the order of nanoseconds, respectively. Our experimental result agrees quite well with the reports on similar nanosized systems[21−24], which strongly suggests the validity of our explanation.

In summary, intensive blue light emission peaked at 418 nm is detected from the as-grown SiC nanowires under ultraviolet (UV) femtosecond laser excitation at room temperature. Time resolved PL analysis result shows a bi-

exponential decay behavior with a faster time constant of 26 ps and a slower one of 567 ps, respectively. The faster decay component is attributed to the direct recombination of the quantum-confined carriers, while the slower one to the recombination of excitons localized at surface states. Such ultrafast emission may have potential application in ultrafast optoelctronic devices, especially those working in harsh environment.

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