Synthesis and photoluminescence properties of the 4H-SiC/SiO_2 nanowires*

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4H-SiC/SiO_2 nanowires are synthesized and the temperature-dependent photoluminescence (PL) properties of the nanowires are studied. Their structure and chemical composition are studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectra. At room temperature, an ultraviolet PL peak and a green PL band are observed. From the PL spectrum measured in the temperature range from 80 K to 300 K, the free excition emission, donor bound excition emission and their multiple-phonon replicas have been observed in ultraviolet region, and their origins have been identified. Moreover, it has been found that the temperature dependence of the free exciton peak position can be described by standard expression, and the thermal activation energy values extracted from the temperature dependence of the free exciton and bound exciton peak integral intensity are about 40 meV and 181 meV, respectively.

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As an important wide band gap semiconductor, silicon carbide (SiC) nano-materials are suitable for fabrication of high frequency and high power electronic devices which can be operated at high temperature and in harsh environment[1,2]. Moreover, field emission properties of SiC one-dimensional nanomaterials have been studied by many research groups and the results show low turn-on and low threshold electric field values, which indicated that they could have potential applications in field-emitting electron devices[3-5]. In particular, SiC nanowires/nanorods or nanocables could have potential applications in light-emitting devices[6,7].

Among various polytype structures, the 3C-SiC nanowires or nanocables have been synthesized by several techniques, such as laser ablation[8], arc-discharge[9], and chemical vapor deposition[10]. However, the related studies of 4H-SiC nanowires synthesis and their optical properties have rarely been reported. In this paper, using catalyst-assistant gas-solid reaction, the 4H-SiC/SiO_2 nanowires are successfully synthesized. At the same time, the room and variable temperature PL properties of these nanowires are investigated in detail.

The SiC nanowires used in this study are synthesized by catalyst-assistant gas-solid reaction. Briefly, 1 g SiO_2 (spectrally pure) and 0.6 g $FeCl_3\cdot 5H_2O$ (analytically pure) powders are mixed with 5 mL deionized water. Then the mixture is spread uniformly over the surface of clean Si (100) substrate. After the drying (in vacuum) and annealing (in hydrogen atmosphere) treatment process, the SiC nanowires are synthesized on Si substrate using methane (purity 99.99%) and hydrogen (purity 99.999%) with a gas flow of 15 mL/min and 50 mL/min, respectively, in an aluminium oxide horizontal tube furnace system. The growth temperature is about 1500 °C and the growth time is 10 min. The pressure of system is kept at about 74648 Pa in the synthesis process.

Fig.1(a) shows a typical SEM image of the sample. The as-grown sample is nanowires with 20—50 nm in diameter and 10 μm in length. Fig.1(b) shows a typical TEM image of the nanowires. It can be seen that the nanowires has a core-shell structure with a core about 20 nm and shell about 15 nm. After several measurements, we estimate the core diameter ranging from 3 nm to 20 nm. Fig.1(c) displays the high-resolution transmission electron microscopy (HRTEM) image of a nanowire. The core has well defined fringe separation of 0.25 nm which is consistent with the d-spacing of (102) plane of 4H-SiC, suggesting that the growth direction is [102][11].

Fig.2(a) shows the XRD pattern of the nanowires. The nanowires possess a SiC singlecrystal hexagonal struc-

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ture with a preferred (102) orientation, which is in good agreement with the HRTEM result. Fig.2(b) shows the Raman spectra of the nanowires. It is well established that there only optical phonon scattering model at 796 cm^{-1} and 972 cm^{-1} for 3C-SiC polytype, whereas, for 4H-SiC polytype, except the optical phonon scattering model, there are transverse and longitudinal acoustic phonon scattering model. A transverse optical (TO) phonon model at 781 cm^{-1} with the E_2 symmetry is observed. Meanwhile, an axial longitudinal acoustic (LA) model with A_1 symmetry near 620 cm^{-1} is also observed, which is the characteristic Raman model of the 4H-SiC structure[12]. Compared with the bulk 4H-SiC, the TO and LA model have some increase, which may be caused by quantum confinement effects[13].

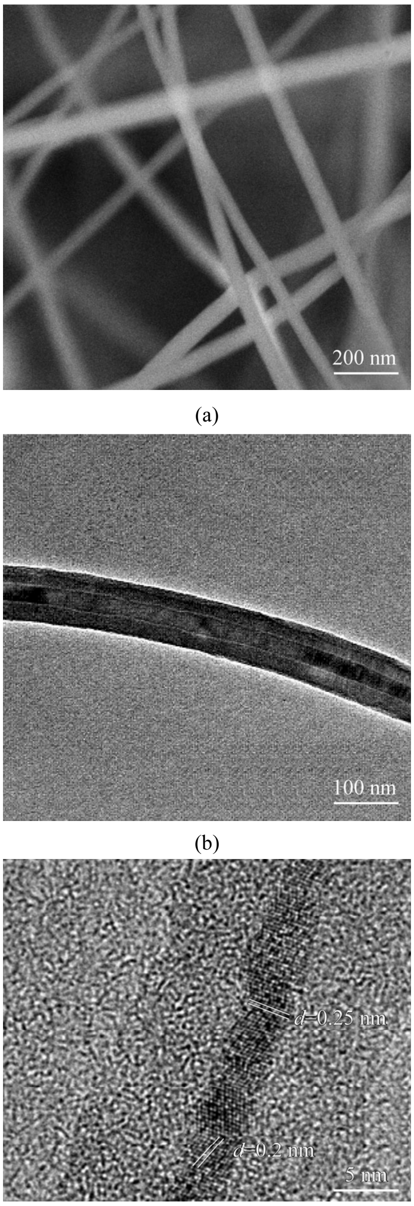

Fig.1 (a) SEM, (b) TEM and (c) HRTEM images of the prepared nanowires

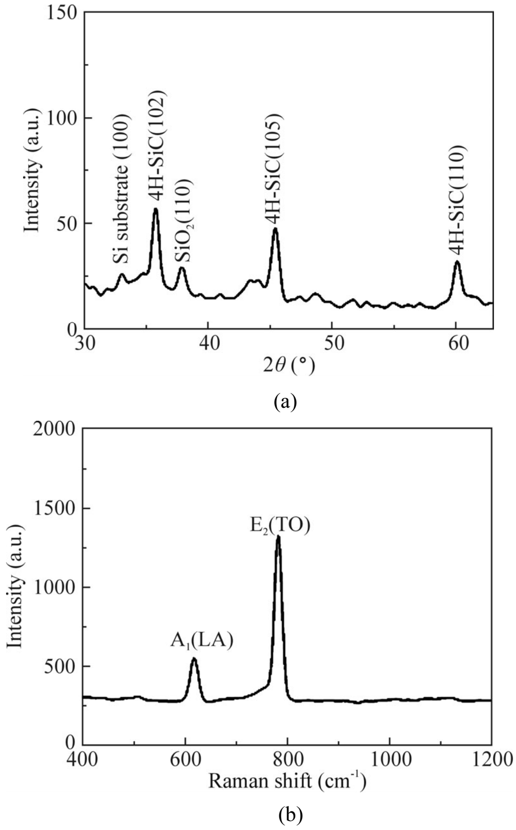

Fig.2 (a) XRD and (b) Raman results of the prepared nanowires

The variable temperature PL measuring technique is an effective tool to study radiative recombination mechanism of the photo-excited carriers, semiconductor band edges, excitons, impurities, and defect levels. The PL spectrum of the nanowires is measured using a UV lamb micro-Raman spectrometer with a He-Cd laser of 325 nm wavelength as the excitation light source. The variable temperature measuring process is carried out in a liquid nitrogen close cycle cryostat system. A series of PL spectra for the nanowires as a function of temperature from 80 K to 300 K are shown in Fig.3. One UV PL peak at 386 nm (3.2 eV) and a broad PL band ranging from 425 nm to 650 nm are observed at room temperature (300 K). The origin of green PL band may be from the radiative recombination of oxygen deficiency of SiO_2 shell[14,15]. As the temperature decreases, the ultra-violet and green band intensity increase and the ultra-violet peak shifts to longer wavelengths.

To clarify the origins of ultra-violet band, the PL spectrum of this band at 80 K is shown in greater detail in Fig.3(b). In this spectrum, four emission peaks in the vicinities of 3.333 eV, 3.294 eV, 3.225 eV and 3.155 eV are observed. The later three peaks have a same energy spacing about 70 meV, which is just the energy of LA phonon associated with bound exciton of 4H-SiC[16]. These peaks may be due to free excitons peak associated with free excition emission, donor bound excition emission and their multiple-phonon replicas, which can be named as FE (A Peak), D_oX (B peak), D_oX-LA (C peak), and D_oX-2LA peak (D peak), respectively.

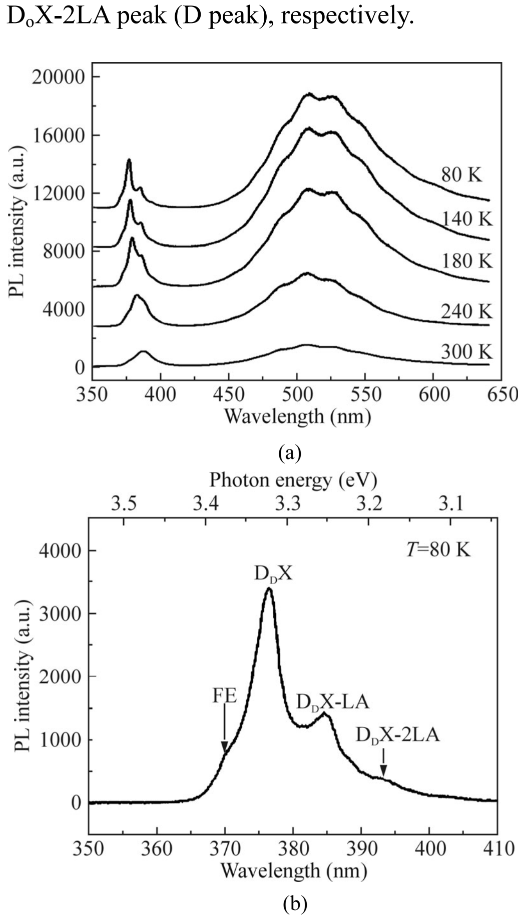

Fig.3 (a) Temperature dependence and (b) 80 K PL spectrum of the prepared nanowires

Fig.4 shows temperature dependences of the A and B peaks PL integrated intensity. In order to observe the activation energies associated with these peaks, the Arrhenius equation is used to fit these data:

$$I(T) = \frac{I_0}{1 + A\exp(-E_V/K_BT)}, \tag{1}$$

where I_0 is the PL maximum integrated intensity, A is constant, K_B is Boltzmann constant, T is temperature and E_V is the thermal quenching activation energy. The activation energy is usually similar to the binding energy of FE. As displayed in Fig.4(a), we find the intensity increase linearly, it is not possible to observe the maxima, and thus the ~40 meV activation energy expected for peak A, which is larger than that of the thermal activation energy of ~26 meV at 300 K. This suggests that the FE could survive at room temperature. From the experimental result, we can observe that the PL from free excition emission is quenching rapidly above 150 K. The activation energies obtained for peak B is ~181 meV, which may be due to excitons bound to stacking faults. The stacking fault related bands around 0.2 eV below E_c in 4H-SiC are reported by theoretical calculation. The PL of the bound exciton quenches at 180 K, as shown in Fig.4(b).

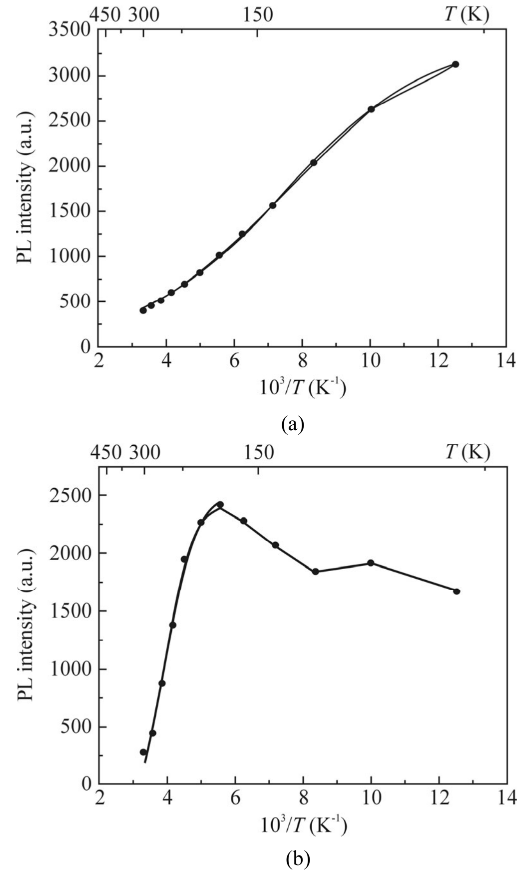

Fig.4 Temperature dependence of the PL peak integral intensities of (a) FE and (b) D_0X

The temperature-dependent of free excition emission energy is shown in Fig.5. Fittings to these data are carried out using the Varshni equation, which suggests the empirical law for $E_g(T)$:

$$E_g(T) = E_0 - \frac{\alpha T^2}{\beta + T}, \tag{2}$$

where E_0 is the band gap at 0 K, T is temperature and α and β are constants. Given the binding energy of the FE in SiC nanowires being nearly independent of temperature, $E_g(0)$, α, β are 3.347 eV, 0.0059 eV/K and 1500 K, respectively. It is significant that the empirical Varshni's expression can give an adequate predication of the positions of the FE peaks as a function of temperature. It is worth to mention that the free exciton band gap at 80 K is about 3.35 eV. The value is 86 meV larger than the 3.264 eV which is taken by Choyke et al[16] at 77 K.

For semiconductor nanomaterials, some theoretical models have been developed dealing with the band gap widening and binding energy of FE. To theoretically identify the band gap and binding energy increase, we first estimate the Bohr radius R of 4H-SiC and then obtain the increase in the band gap and exciton binding energy as the nanowire diameter decrease to 3 nm. For

4H-SiC, the longitudinal and transverse effective masses of electron are m_l(e) =0.42m_0, m_t(e)=0.29m_0, and the effective masses of hole are m_l(h)=0.66m_0, m_t(h)=1.75m_0[17]. As an approximate calculation, we take the effective mass of electron as $m(\mathrm{e})=\left[m_{\mathrm{l}}(\mathrm{e})m_{\mathrm{t}}(\mathrm{e})\right]^{1/2}$=0.349$m_0$ and that of hole as $m(\mathrm{h})=\left[m_{\mathrm{l}}(\mathrm{h})m_{\mathrm{t}}(\mathrm{h})\right]^{1/2}$=1.075$m_0$. The Bohr radius R can be written as $R=\dfrac{\varepsilon_0 m_0}{\mu\alpha_0}$, where $\mu=\dfrac{m(\mathrm{e})m(\mathrm{h})}{m(\mathrm{e})+m(\mathrm{h})}$ is the reduced mass of the exciton, ε_0=10.03 is the high-frequency dielectric constant of 4H-SiC, and α_0=0.053 nm. Under the effective-mass approximation, the size dependence of the band gap can be represented as follows: $E^*=E_{\mathrm{g}}+\dfrac{h^2}{8\mu r^2}-\dfrac{1.8e^2}{4\pi\varepsilon_0\varepsilon_r}$, where E_{g}=3.26 eV is the band gap of bulk material and r=d/2. For the SiC core of nanowires with diameter of d=3 nm, we can estimate E^* to be 3.726 eV. For core with diameter of 20 nm, E^* is equal to ~3.260 eV, just being the band gap of bulk 4H-SiC, indicating that the quantum confinement effect does not exist.

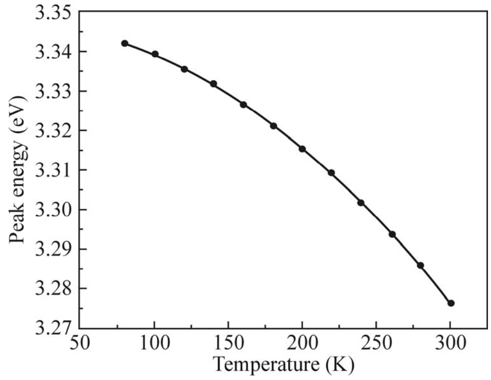

Fig.5 Temperature dependence of the FE PL peak position

We have synthesized the 4H-SiC/SiO_2 nanowires and investigated the room and variable temperature PL of these nanowires. Spectral analyses suggest that the UV PL peaks arise from free excition emission, donor bound excition emission and their multiple-phonon replicas and the green PL band may be from the radiative recombination of oxygen deficiency of SiO_2 shell. The PL from free and donor bound excition emission are observed to quench rapidly above 150 K and 180 K with activation energy of ~40 meV and ~181 meV, respectively. The temperature-dependent PL emission energy of free excitions peak is investigated and it is found that the temperature-dependent band gap is similar to that observed in the bulk.

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