Temperature and excitation power dependence of photoluminescence of ZnO nanorods synthesized by pattern assisted hydrothermal method

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Abstract

Pattern assisted ZnO nanorods (NRs) growth are performed using electron beam lithography (EBL) and hydrothermal method. The patterns of lines, circles and squares are prepared on polycrystalline ZnO seed layer using PMMA as photoresist. It is found that the ZnO NRs can only grow on the area with ZnO seed layer, not on the PMMA surface. The TEM results show that the ZnO NRs have single crystal structures with good orientation along the c-axis. The excitation power dependence of photoluminescence (PL) spectra of ZnO NRs shows that with excitation power increasing, the near band edge emission increases rapidly than the defects related visible emissions. The temperature dependence of PL spectra was measured in the temperature range of 13-300 K. The dependence of peak position and peak energy of exciton bound (D^0X) emission of ZnO NRs on temperature were analyzed. Two non-radiative recombination channels for the D^0X emission are discussed in detail.

Keywords: ZnO NRs, Pattern assisted growth, Photoluminescence

1. Introduction

ZnO as a promising compound semiconductor has attracted a lot of research interests due to its direct wide bandgap (3.37 eV at room temperature) and large exciton binding energy of 60 meV [1]. In particular, ZnO NRs have received much attentions in the past decades owing to their unique structural, physical and chemical properties. All of these unique properties make ZnO to be a promising candidate for the applications in optoelectronic devices, such as short wavelength lasers [2], light emitting diodes [3], ultraviolet photodetectors [4], field emission devices [5], nanogenerators [6], gas sensors [7], solar cells [8] and nonlinear optical applications [9]. To realize high stability and high optoelectronic device performance, it is very important to not only grow ZnO NRs with high quality and high uniformity, but also control their diameter, length and the accurate growth positions.

Various methods have been carried out to control the density, sizes and distributions of ZnO NRs including vapor-liquid-solid (VLS), metal organic chemical vapor deposition (MOCVD), hydrothermal method and so on. Qi et al. [10] synthesized ZnO NRs arrays by MOCVD using GaN quantum dot as template. They found that ZnO NRs with uniform shape and length were grown align vertically on the template, the density could be easily tuned by adjusting the density of GaN quantum dot. In our previous work, ZnO NRs were synthesized by hydrothermal method using sol-gel derived ZnO seed layer. It was found that the diameters of ZnO NRs could be

adjusted by annealing the seed layers under various temperature [11]. Nevertheless, the growth area and position can be achieved via VLS process using metal (gold or tin) as catalysts or pattern assisted hydrothermal method. The VLS growth process usually introduce catalyst residual atoms into ZnO NRs, which is incompatible for the future optoelectronic devices application. Compared with VLS method, pattern assisted hydrothermal method is desirable due to its low growth temperature, low cost and potential applications for large scale devices. Tsangarides et al. synthesized ZnO nanowires (NWs) on controlled patterns by hydrothermal method [12]. The patterns were prepared by inkjet-printing zinc acetate on silicon substrate. It was found that the ZnO NWs could be fabricated in accordance with the desired pattern under low temperature and mild conditions. Jung et al. [13] synthesized patterned ZnO NRs via hydrothermal method combined with nanoimprint lithography technique. The ZnO seed layer was selectively coated only on the hydrophilic silicon oxide surface. It was found that the nucleation and initial growth of ZnO NRs were proceeded only on the ZnO seed layer, not on the silicon oxide surface. The photoluminescence study indicated that the seed layer treated with oxygen plasma had more oxygen vacancy than untreated ones. To meet the requirement of various devices, a good understanding of the defects and impurity in ZnO NRs is necessary. Temperature dependence of PL measurement is a good way providing the information related to the band gap, defect and impurity in ZnO. Song et al. [14] synthesized ZnO nano/micro-rods on Zn foil and investigated their temperature dependence of PL properties. They found that at low temperature the main non-radiative process was thermal effect while at high temperature was thermal escape from the structural defects assisted by LO photon scattering.

In this article, patterned and aligned ZnO NRs are synthesized by combined EBL and low temperature hydrothermal method. The effect of pattern sharps (circles, squares and lines) and sizes on the structures and morphologies of ZnO NRs are studied. Furthermore, the temperature and the excitation laser power dependence of PL properties of ZnO NRs are also investigated in detail.

2. Experiments

Schematic diagram of the experimental process for pattern assisted ZnO NRs growth is shown in Fig. 1. Si substrates were cleaned in ultrasonic baths for 10 minutes in acetone, ethanol and deionized (DI) water, respectively. ZnO seed layers were deposited on pre-cleaned Si substrates by atomic layer deposition (ALD) method (CambridgeNanoTech Savannah 100) at a deposition temperature of 250 °C and a working pressure of 30 mTorr. Diethylzinc (DEZ) and deionized (DI) water were used as precursors for ZnO deposition. The precursors were kept at room temperature during ZnO growth process and nitrogen (N₂) was used as carrier gas to carrier DEZ and DI water into the chamber with a gas flow of 20 sccm (standard cubic centimeter per minute). One ALD cycle consisted of DEZ pulsing of 0.015 s, N₂ purge 5 s, DI water pulsing 0.015 s, and N₂ purge 5 s, respectively. 300 ALD cycles were carried out to reach a ZnO film thickness of about 50 nm. For the pattern preparation, 70 nm photoresist layer of PMMA (495 PMMA 2) was spin-coated on ZnO seed layer at a rotation speed of 3000 rpm and then baked on a hotplate at 180 °C for 3 minutes. The

patterns (arrays of circles, squares and lines) were performed using EBL system (Raith 150) with a beam voltage of 10 kV and a dose ranged from 150 to 300 $\mu\text{C}/\text{cm}^2$. After electron beam exposure, the samples were developed in a mixed solution of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) with a volume ratio of 1:3 for 1 minute and in pure IPA solution for 30 s, respectively.

ZnO NRs were grown on the prepared patterns via hydrothermal method. The solution for ZnO NRs growth was obtained by mixing the chemical precursors of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, HMTA) in a equimolar ratio of 3 mmol/L in DI water. The substrates with patterned ZnO seed layers were placed facing down immersing in the aqueous solution in a hydrothermal reactor. The reactor was put in an oven and maintained at 90 °C for 8 hours. Then the reactor was cooled down to room temperature, the substrate was taken out and rinsed in DI water several times to remove the absorbed chemicals. Finally, the samples were dried using a nitrogen gun in air.

The morphologies and crystalline structures of ZnO seed layer and ZnO NRs were measured by field emission scanning electron microscope (FE-SEM, Zeiss), X-ray diffraction (XRD, Bruker, D8, Advance.) and high resolution transmission electron microscope (HR-TEM, FEI, Tecnai, F20). The temperature and excitation power dependence of PL of ZnO NRs were measured by a luminescence spectrometer excited by a He-Cd laser (325 nm, 30 mW).

3. Results and discussion

SEM image and XRD pattern of ZnO seed layer deposited on Si substrate by ALD are shown in Fig. 2(a) and Fig. 2(b), respectively. It can be observed from Fig. 2(a) that the ZnO seed layer possess a smooth surface morphology with uniform particle distribution. The average grain size is about 30 nm. The similar morphologies of ZnO thin films were reported by Napari et al. [15] and Laube et al. [16] via ALD method. The XRD pattern in Fig. 2(b) indicates a polycrystalline structure of ZnO seed layer with multiple diffraction peaks. All diffraction peaks match the hexagonal wurtzite crystal structure of ZnO [17]. In addition, the dominated peak is ZnO (101), indicating that the ZnO seed layer can't form the preferential of c-axis of ZnO (002) orientation, which can be ascribed to the film thickness is only 50 nm and the low growth temperature of 250 °C.

The SEM images of PMMA patterns on ZnO seed layer prepared by EBL method are shown in Fig. 3. Fig. 3(a) and (b) illustrate the circle and square patterns with a diameter or side length of 10 μm . Fig. 3(c) shows line pattern with a width of 5 μm and length of 50 μm . Fig. 3(d) shows circle dots with an area of 200×200 nm and a dot to dot distance of 600 nm. The SEM images of ZnO NRs grown on the patterned ZnO seed layer via hydrothermal method are shown in Fig. 4. The results indicate that the ZnO NRs are successfully grew confined to the patterns with ZnO seed area. The ZnO NRs grow on big patterns (circles, squares and lines) in Fig. 4(a)-(e) show well orientation perpendicular to the substrates while the NRs at the edge of the patterns have a tendency to grow outward. The average diameter and length of ZnO NRs are about 300 nm and 4 μm , respectively. A hexagonal surface of ZnO NRs grew on different patterns are obtained. For the big patterns, the changes of the pattern shape

have little effect on the diameter, length and surface morphology of ZnO NRs. When the pattern decrease to small circle dots (as shown in Fig. 4(f)), the surface morphology of ZnO NRs is still hexagonal but the average diameter decreases to about 250 nm. The length of ZnO NRs grew on the marginal area is longer than others, which can be attributed to that the marginal area of the patterns are often the preferred nucleation sites for materials growth, the catalytic atoms preferred to diffuse to these areas to form ZnO nucleus [13]. When the pattern area decrease to 200×200 nm dots, the pattern growth of ZnO NRs is not clear, which can be ascribed to the long growth time (8 hour), small seed area and dot to dot distance. The similar results were reported by Wang et al [18]. Furthermore, one dot area with one ZnO NRs growth is not obtained, which can be attributed to the polycrystalline structure of ZnO seed layer.

Additional microstructural characterization is carried out by TEM. Fig. 5(a) shows a high resolution TEM images of ZnO NRs, depicting that the ZnO NRs is single crystal structure. The lattice spacing of ZnO NRs is 0.26 nm, which is consistent with the (002) plane of hexagonal ZnO [19]. Fig. 5(b) illustrates a typical TEM image of a single ZnO NR with a diameter of 300 nm, which is in good agree with SEM results. The selected area electron diffraction (SAED) pattern in Fig. 5(c) suggests that ZnO NRs possess a good crystalline quality with growth orientation along the c-axis [20, 21].

Fig. 6(a) shows the excitation power dependence of PL spectra of ZnO NRs. It can be observed that all PL spectra of ZnO NRs under various excitation power have similar features including a sharp UV emission band, two broaden visible emission bands and a red emission band with peaks centered at 375.8 nm, 486.8 nm, 647.8 nm and 754.6 nm, respectively. The sharp UV emission band is related to the near band edge emission from the direct band gap of ZnO. The two broaden visible emission bands can be attributed to the deep level emissions related to the intrinsic defects, such as zinc and oxygen vacancies, zinc interstitials and oxygen interstitials, etc. [22-24]. The origination of the red emission band is still in controversial. Some researchers attributed it to the defects in ZnO as the two broaden visible emission band. Some others believed that it is a second order feature of the UV emission band [24, 25]. With the excitation power increasing, the intensity of all emission peaks increases gradually and there is no peak shifts observed. Fig. 6(b) shows the dependence of the PL intensity of four peaks on the excitation power. It can be seen that the intensity of UV emission increases more rapidly than other peaks, which is in good agree with Silver/ZnO and Gold/ZnO core-shell nanoparticles [24]. The various changes in the PL intensity with excitation power can be understood by considering the emissions are related to different types of defects in ZnO NRs, and they give different response to the excitation power.

Fig. 7(a) shows the temperature dependence of PL spectra of ZnO NRs measured in the temperature range of 13-300 K. It can be seen that with temperature increasing, the intensity of dominated peak decreases gradually and the peak position shifts to long wavelength (red shift). This is a common temperature dependence PL feature of ZnO and has been observed in ZnO thin films and nanostructures [26, 27]. The PL

spectra of ZnO NRs at 13 K is shown in Fig. 7(b). It can be observed that at a temperature of 13 K, the dominated peak is located at 3.369 eV, which is typically attributed to the exciton bound shallow neutral donor (D^0X) [28]. On the high energy side of the D^0X emission at 13 K, there are two weak shoulders located at about 3.390 eV and 3.417 eV. By carefully evaluation, these two peaks are in good agree with the reported values of A-free exciton emissions (FX) of the ground state of A excitons ($FX_A^{n=1}$) and first state of A excitons ($FX_A^{n=2}$) [29, 30], respectively. The peak at 3.356 eV can be attributed to the donor to bound excitons (D^0X) emissions [31, 32]. It is known that the longitudinal optical (LO) phonon replicas occur with a separation of $\hbar\omega_{LO} = 72$ meV, which corresponding to the LO-phonon energy in- ZnO [33]. As a result, the peak at 3.347 eV can be identified to the $FX_A^{n=2}$ -1LO transition. The peak at 3.333 eV is likely a two-electron satellite (TES) of the donor-bond exciton emission and the peak at 3.324 eV can be attributed to the transition between free electrons in the conduction band to the acceptor level (eA^0) [34]. Fig. 7(c) shows the relation of the peak positions of D^0X emission with temperature (triangle dots). The relation of temperature and peak position of ZnO can be modeled by the Varshni relation [35]:

$$E_g(T) = E_g(0) - \alpha \frac{T^2}{(T+\beta)} \quad (1)$$

Where $E_g(T)$ and $E_g(0)$ represent the band gap energy at a certain temperature and 0 K, respectively. α and β are the Varshni thermal coefficient. The red solid line in Fig. 7(c) represents the best fitting results. It can be seen that the fitting curve is in good agree with the experimental data. The best parameters obtained from the fitting process are $E_g(0) = 3.37$ eV, $\alpha = 1.54$ meV/K and $\beta = 1757.6$ K. These obtained parameters for ZnO NRs are comparable to the previous reported values of ZnO thin films, nanowires and quantum dots [36-38]. The full width and half maximum (FWHM) of D^0X increases gradually with temperature increasing, which is in good agree with previous reported ZnO epitaxial layers, N-In codoped ZnO thin films and Cu incorporated ZnO NRs [39-41].

The temperature dependence PL intensity of ZnO NRs are shown in Fig. 7(d). It can be observed that the PL intensity increases rapidly first and then smoothly with temperature increasing. The dependence of PL intensity on temperature can be described by the well-known Arrhenius expression [42]:

$$I(T) = \frac{I(0)}{1 + A_1 \exp(-E_{a1}/k_B T) + A_2 \exp(-E_{a2}/k_B T)} \quad (2)$$

Where $I(T)$ and $I(0)$ are the PL intensity at a temperature T and 0 K, respectively. A_1 and A_2 are constants and k_B is Boltzmann constant, E_{a1} and E_{a2} are activation energies. The best fitting gives rise to two activation energies of 1.04 and 42.58 meV, indicating that there are two non-radiative recombination channels for the D^0X emission. Commonly, the activation of E_{a1} describes the non-radiative recombination at low temperature while E_{a2} describes the non-radiative recombination at high temperature. The trend of fitted values E_{a1} and E_{a2} are similar with previous reported ZnO nanowires [42]. Fang et al. [28] reported the temperature dependence PL of Al-coated ZnO nanostructures and their result showed that the fitting parameters of E_{a1} and E_{a2} were 4.1 and 26.5 meV, respectively. The

activation energy E_{a1} is much lower than the exciton binding energy of bulk ZnO (60 meV) [43], indicating that at low temperature the excitons are capped and the dominated non-radiative process is thermal effect. At high temperature, the activation energy E_{a2} is still much lower than the exciton binding energy of bulk ZnO, which also confirms that the dominated peak comes from the D^0X emission.

4. Conclusions

ZnO NRs were selected area grew on ZnO seed layer/Si substrate by combined ALD, EBL and hydrothermal method. The results show that ZnO NRs can only grow on the area with ZnO seed layer, not on the PMMA surface. The TEM results show that the ZnO NRs have a single crystal structure with a diameter of about 300 nm. The power dependence PL spectra indicate that the ZnO NRs have a sharp near band edge UV emission at 375.8 nm, two broaden defects related visible emission bands and a red emission band centered at 486.8 nm, 647.8 nm and 754.6 nm, respectively. With excitation power increasing, the near band edge emission increases rapidly than the defects related visible emission. The temperature dependence PL spectra were measured in the temperature range of 13-300 K. The PL spectra at 13 K shows a dominated peak of D^0X emission at 3.369 eV, two FX emission at 3.390 eV and 3.417 eV, two weak D^0X peak at 3.356 and 3.347 eV, a TES emission of the donor-bond exciton peak at 3.333 eV and eA^0 emission peak at 3.324 eV. The dependence of peak position, peak energy of D^0X emission of ZnO NRs on temperature were theoretical analyzed. Two non-radiative recombination channels for the D^0X emission are obtained.

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Figure captions

Fig. 1 Schematic diagram depiction of pattern assisted ZnO NRs growth process

Fig. 2 (a) SEM image and (b) XRD pattern of ZnO seed layer.

Fig. 3 SEM images of patterns on ZnO seed layer: (a) circles, (b) squares, (c) lines and (d) circle dots.

Fig. 4 SEM images of ZnO NRs grew on different patterns: (a) and (b) circles, (c) and (d) lines, (e) squares and (f) circle dots.

Fig. 5 (a) HR-TEM images and (b) TEM images of ZnO NRs, (c) SAED pattern of ZnO NRs.

Fig. 6(a) Power dependence PL spectra of ZnO NRs, (b) the relation of peak intensity with excitation power.

Fig. 7(a) Temperature dependence PL spectra of ZnO NRs, (b) PL spectra of ZnO NRs at 13K, (c) the relation of peak position and (d) peak intensity with temperature, the solid red lines are the fitting curves.

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Fig. 5(a) HR-TEM images and (b) TEM images of ZnO NRs, (c) SAED pattern of ZnO NRs.

Fig. 6(a) Power dependence PL spectra of ZnO NRs, (b) the relation of peak intensity with excitation power.

Fig. 7(a) Temperature dependence PL spectra of ZnO NRs, (b) PL spectra of ZnO NRs at 13K, (c) the relation of peak position and (d) peak intensity with temperature, the solid red lines are the fitting curves.