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Optical processes in the formation of stimulated emission from ZnO nanowires*

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This paper studies power dependent photoluminescence spectra, the stimulated emission occurring at ultraviolet (UV) band instead of the green emission band of ZnO nanowires, which are prepared with a chemical reduction method. The dynamics of the UV emission and green emission is given to demonstrate the reason of stimulated emission occurring at UV band but not the green emission band under high excitation, which indicates that the slow decay rate of trap state makes it easy to be fully filled and saturated, while the fast decay rate of near-band-edge exciton state makes the UV emission dominate the radiative recombination under high excitation. The UV emission, as well as the corresponding stimulated emission, occurs in competition with the green deep-trap emission. In addition, when pump fluence further increases, the multiple lasing modes appear. The dependence of these lasing modes on the pump fluence is first discussed. This diagram should be helpful to understand and design the optical nanodevices of ZnO nanowires.

Keywords: ZnO nanowire, stimulated emission, dynamics, lasing mode
PACC: 7135, 7215L, 7230J

1. Introduction

One-dimensional semiconductors have become an important kind of material for their potential applications in microelectronic and micro-photonic devices such as optical waveguide[1−4] and nanowire laser.[5,6] ZnO nanowires are being intensively investigated for their large exciton binding energy (60 meV) and wide band gap (3.37 eV). Especially the large exciton binding energy, which is much greater than the thermal energy (26 meV, 300 K), inhibits thermal depopulation of the lowest, radiative transition, and then results in more efficient excitonic emission at room temperature. These are highly advantageous to realize a nanolaser with a low and temperature-insensitive optical-gain threshold, a narrow emission line, and high-temperature stability. Since Yang *et al* demonstrated the room-temperature ultraviolet (UV) laser in a ZnO nanowire array grown on sapphire substrates,[7] the optically pumped UV stimulated emission and lasing have been widely studied in nanopowder,[8] nanowires,[9,10] nanobelts[11] and thin films[12−14] at room temperature.

Nanostructures have a higher surface to volume ratio than the bulk material. For ZnO nanowire, the deep-trap-type emission (green emission) from surface state and near-band-edge emission (UV emission) always exists simultaneously.[15,16] In quantum-size nanowires, the surface-trap-state recombination may quench the near-band-edge emission entirely.[16] However, the situation in realizing stimulated emission is quite different. In reported results, the dependence of the ratio of the near-band-gap emission to the deep-level emission on the excitation energy from different ZnO samples was discussed.[17] However, no analysis on the stimulated emission at UV band in contrast to the green emission was given.

Furthermore, no dynamic reasons were discussed for these situations. In this paper, we first demonstrate the dynamic causes of the stimulated emission occurring at UV emission instead of the green emission even although the deep-level green emission plays a dominant role in the photoluminescence (PL) spectrum under Xe lamp excitation. Moreover, the dependence of the multiple lasing modes on the pump fluence was discussed.

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2. Experimental

The ZnO nanowires were prepared by a chemical reduction method, which was mentioned in our previous report.[18] The morphologies of the nanowires were observed with scanning electron microscopy (SEM, Hitachi S-5200). The chemical composition was also checked by energy dispersive spectroscopy (EDS) detector equipped on the SEM system. Powder x-ray diffraction (XRD) data were obtained by a Japan Rigaku D/MAX-2400 type diffractometer equipped with graphite-monochromatized Cu$K\alpha$ radiation ($\lambda =$ 1.54178 Å). The PL of ZnO nanowires was excited with an UV light (266 nm) from Xe lamp. The pump fluence dependent PL and the time-resolved PL were obtained under femtosecond (fs) laser excitation (266 nm, ∼120 fs, 0.7 mJ, 1 kHz). The pump fluence dependent PL was measured with a monochromator and a liquid nitrogen-cooled charge coupled device (CCD) camera. The spectral resolution of the system is 0.26 nm. The time-resolved PL was focused into a polychromator and detected by using a photon counting streak camera (Hamamatsu C2909) with a time resolution of 20 ps, and the spectral resolution of polychromator is 0.2 nm.

3. Results and discussion

The morphologies of the nanowires are shown in Fig.1(a) and Fig.1(b). Figure 1(a) shows the random growth of ZnO nanowires with a large aspect ratio. The average length of the nanowire is 20–70 μm and diameters range between 200 nm and 400 nm. The local enlargement of this image shown in Fig.1(b) indicates that the nanowires are uniform along the c axis direction, which is beneficial for using as an optical resonant cavity. The EDS spectrum indicates that the nanowire is composed of Zn and O as shown in Fig.1(c). Powder XRD patterns shown in Fig.1(d) indicate that these nanowires are single phase with a hexagonal wurtzite structure. The strong and sharp diffraction peaks illuminate that the nanowires are well crystallized.

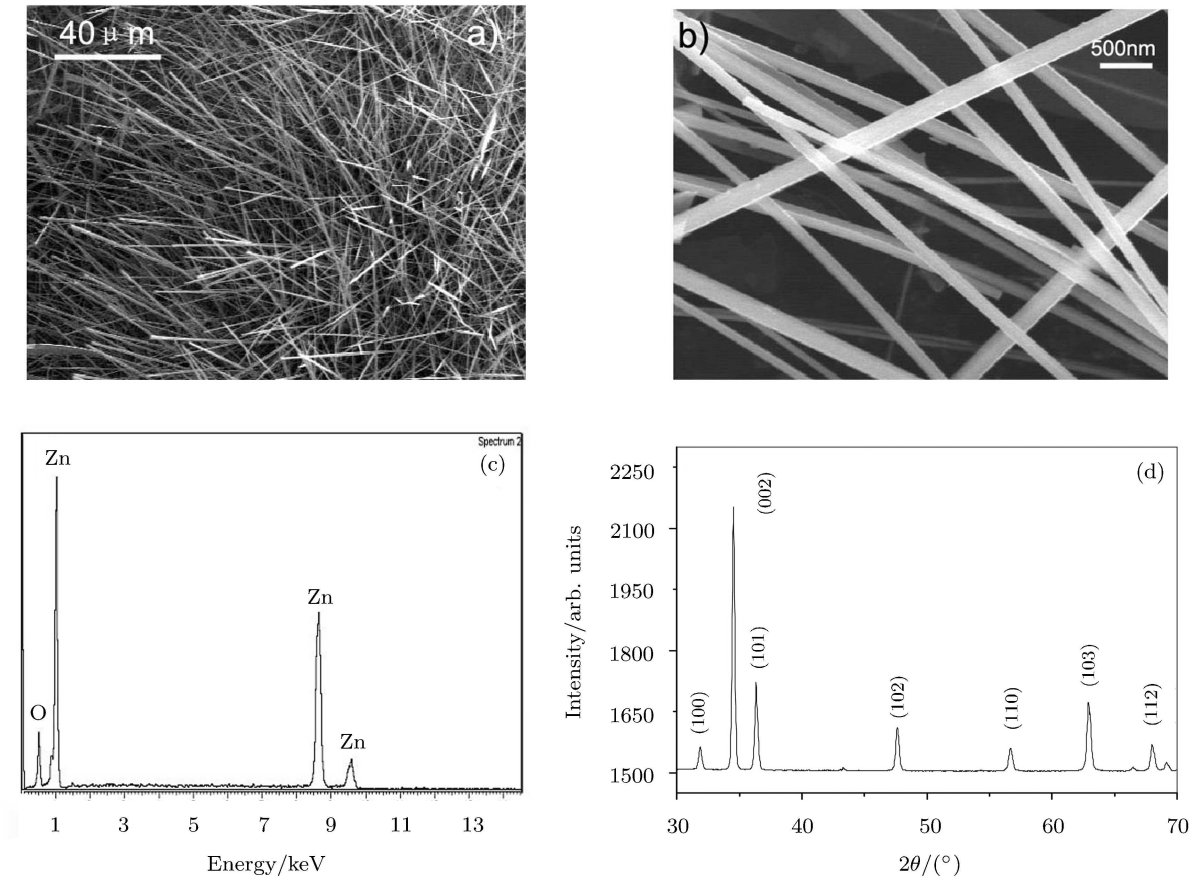


Fig.1. (a) SEM of as-grown nanowire array. (b) Local enlargement SEM of the ZnO nanowires. (c) Energy dispersive spectroscopy (EDS) acquired from one ZnO nanowire. (d) The XRD of ZnO nanowires.

Figure 2 shows the PL of the ZnO nanowires excited with 266 nm line of a Xe lamp at room temperature. The Xe lamp was used as low excitation for comparing with the high excitation by the fs laser. There is only one peak at around 505 nm in the PL spectrum, which corresponds to the green luminescence band from the deep-level defect states,[19] while no near-band-edge emission appears. This indicates that there exist many trapping sites in the nanowires. Figure 3 shows the evolution of PL spectrum under different pump fluences. The dependences of PL intensity and FWHM (full width at half-maximum) of UV emission band on pump fluence are shown in the inset. There are two emission bands in the PL spectra. The peak at 507 nm is consistent with that at low excitation in Fig.2. The UV band at 392 nm is attributed to the near-band-edge exciton emission of ZnO nanowire. At low pump fluence, both bands are very broad, and the intensity of green emission is stronger than that of UV band, which is similar to the situation at low excitation. With the increase of pump fluence, the green emission always keeps the broad spontaneous emission, while the UV band turns sharp and increases rapidly. When the fluence increases to 87 μJ/cm^2, a sharp peak appears on the high energy shoulder of the exciton band, and the intensity of the sharp peak at 390 nm experiences a strong superlinear dependence of the pump fluence, illuminated as open circle in the inset of Fig.2. However, the integrated intensity of the broad green emission band at 507 nm keeps the linear increase with increasing the excitation energy, shown as closed square in the inset of Fig.2. Furthermore, accompanying with the appearing sharp peak, we find that the FWHM of UV band also become drastically narrow, and with the further increase of pump fluence, the FWHM becomes much narrower, shown as open triangle in the inset of Fig.3. The FWHM of the sharp peak is only 3 nm. These results indicate a clear evidence of the stimulated emission. The threshold pump fluence is at around 85 μJ/cm^2, and the stimulated emission is attributed to the exciton–exciton scattering mechanism.[20,21] The blue-shift of UV emission peak after the threshold is due to the band filling effect at high carrier density.[22] When the high-resolution PL spectra at UV band were detected under much higher excitation, more ultra-narrow emission modes at around 392 nm were detected, as shown in the Fig.4. Each emission mode is as narrow as 0.3 nm. According to the mode spacing ($\Delta\lambda$ = 0.77 nm) and the length of nanowire (L, 20 − 70 μm) from the SEM, these emission modes satisfy the F-P cavity condition, $\Delta\lambda = \lambda^2/2nL$, where n is the refractive index of the nanowires. This demonstrates that the modes are the lasing modes, which stem from the strong coherent feedback of F-P cavity formed by the two end faces of nanowire.

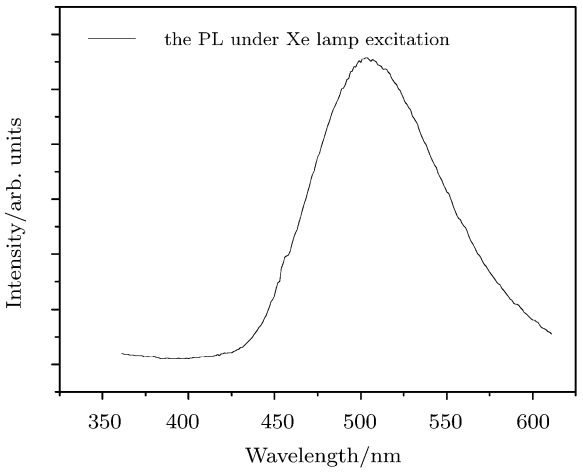


Fig.2. The PL spectrum under a Xe lamp excitation.

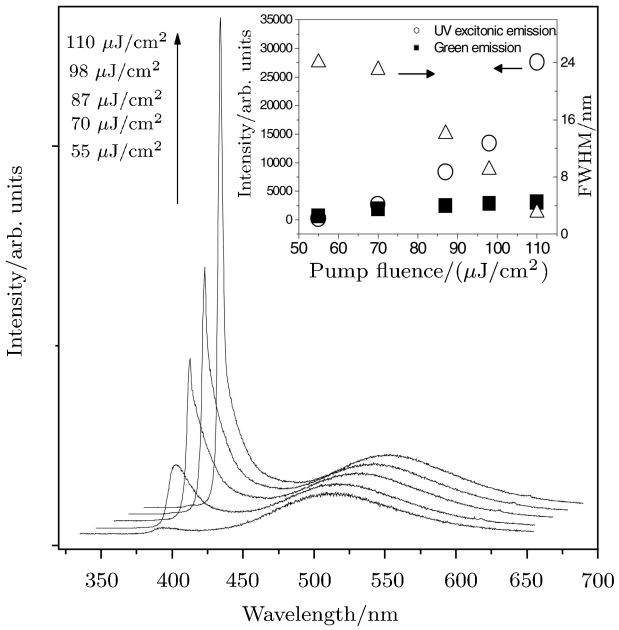


Fig.3. The evolution of room-temperature PL as the pump fluence increased from 55 μJ/cm^2 to 110 μJ/cm^2 in the ZnO nanowires. Inset: The UV emission intensity as a function of the pump fluence compared with the green emission, and the pump fluence dependent FWHM of UV band.

By comparing the situation under low excitation with that under high excitation, it could be found that, although the intensity of the green emission is

dominant in the PL spectrum under Xe lamp excitation, the intensity of the UV emission drastically increases, and even lasing appears with the pump fluence increase under high excitation. There exists a competing relationship between the two emissions under different excitation conditions. The two emissions, excitonic emission and deep-level emission, have their own decay channels and different dependences on the pump fluence. Eventually, the stimulated emission occurs at UV emission band under high excitation.

To understand the different dependence of the exciton emission and the trap-state green emission on the pump fluence, the dynamics of the excitonic emission and the green emission were studied. Figure 5(a) shows the dynamics of the deep-trap state recombination, the inset gives the high-resolution decay process of onset phase and the rise time after being excited is ∼2 ns, as marked by the arrow. The decay time of green emission fits well to a tri-exponential function with the time constants of 37 ns (52%), 296 ns (35%), and 1800 ns (13%). These decay components correspond to the radiative and nonradiative recombination process. The multi-exponential decay kinetics gives a better view of the different relaxation mechanisms, which were observed previously in several semiconductor nanoparticle and can be attributed to the different charge carriers relaxation processes.[23−25] The decay of the charge carriers related to the trap states experiences a complicated relax and recombination process and usually has a slower decay rate than that of the free exciton recombination. Figure 5(b) shows the time-resolved spectra of exciton emission under the pump fluence of 70 μJ/cm^2 and 98 μJ/cm^2 respectively. The decay curves both fit well to the bi-exponential functions with a fast time constant $t_{\rm f}$ and a slow time constant $t_{\rm s}$. For the pump fluence at 70 μJ /cm^2, the fast time constant $t_{\rm f}$ is 84 ps with the amplitude 49%, and the slow decay time $t_{\rm s}$ is 630 ps with the amplitude 51%. According to the reported result of ZnO nanowires and nanoribbons,[11] the slow constant is attributed to the weakly bound exciton spontaneous radiative decay, and the fast one relates to the free exciton decay, which has a significant dependence on the pump fluence. When the pump increases to 98 μJ /cm^2, above the threshold, the fast decay component $t_{\rm f}$ shortens to 28 ps and the amplitude increases to 89%, while the slow decay component is 590 ps with the amplitude 11%. The free exciton decay becomes much faster with the pump fluence above the threshold. It should originate from the exciton-exciton collision. The increase of the amplitude means that most free excitons participate in the collision under high carrier density.

According to the above-mentioned fitted results, there exists a great difference on the rise time and radiative recombination lifetime between the green emission and the UV emission. It is well known that the rise time of the charge carrier decay after excitation is a combined process of carrier relaxation towards the subband edges, and subsequent relaxation from large K state to $K = 0$, then the exciton recombines to light.[26] For the decay process of deep-trap state emission, the rise time is ∼2 ns, as shown in the inset of Fig.5(a), which is much longer than the rise time (∼2 ps) of exciton radiative decay under high carrier density.[27,28] This demonstrates that the deep-level emission involves many processes and a long cooling time in comparison with the UV emission. The recombination radiative time of the trap state ranges from tens of nanosecond to hundreds of nanosecond. However, for the near-band-edge excitonic emission, the radiative recombination time are 84 ps (70 μJ /cm^2) and 28 ps (98 μJ/cm^2), which are much shorter than that of trap state recombination. The difference on decay process of these two emissions determines the intensity evolution with the pump fluence.

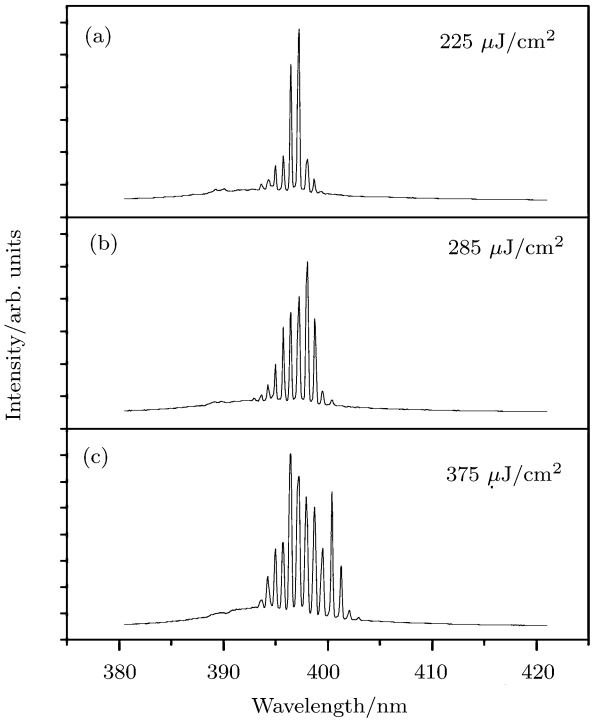


Fig.4. The detailed evolution of multiple lasing modes under higher pump fluence in ZnO nanowires.

For the trap-state related emission, the carriers

are trapped very fast (∼1 ps) at the beginning of non-radiative decay.[29] After being trapped, these trapped carriers will undergo a long relaxation process to the lowest trapped states and subsequently recombine via the radiative pathway with holes. So if the trapping sites are relatively rich enough, then the green emission will be comparable with or even stronger than the UV emission at lower pump fluence. This is consistent with our observation with Xe lamp excitation and fs laser excitation below the threshold energy. However, the cooling and radiative recombination process of the trap state carriers is very slow, which obstructs the trapping sites to be vacated, and then induces the saturation behaviour under high carrier density, thus the UV emission becomes the main decay pathway under high excitation for the short cooling time and radiative recombination time. Moreover, the decay rate will become faster and faster with increasing the pump fluence, while the green emission keeps its slow relaxation and recombination rate with the increase of pump fluence. The great differences on carrier cooling and recombination between the two emissions induce the superlinear increase of the UV emission intensity with the increase of pump fluence in contrast to the linear increase of green emission intensity, as shown in the inset of Fig.3. In addition, the difference between these two emissions is related to the different densities of state. Compared with the high density of the near-band-edge exciton state, the density of trap state is rather low for the limited trapping sites in the ZnO nanowires, which are easily saturated at high excitation.

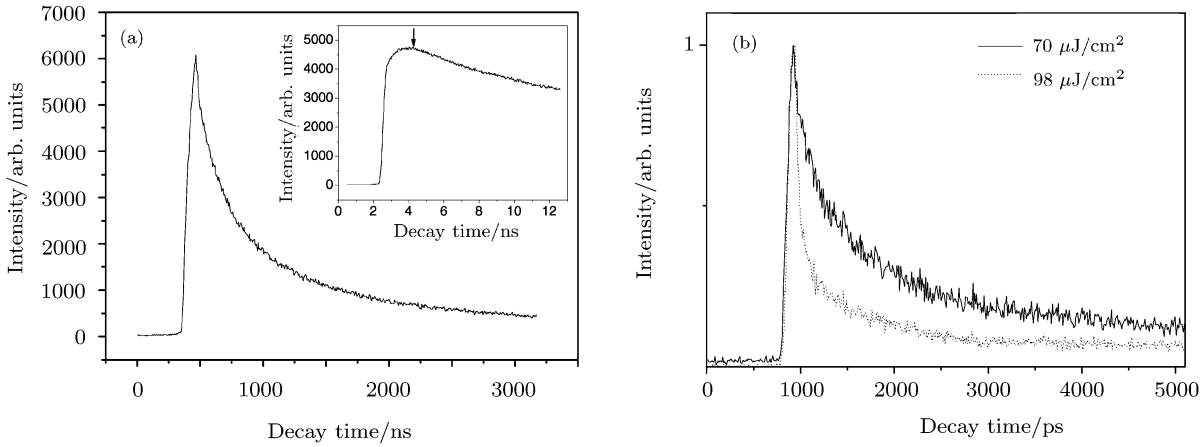


Fig.5. (a) The decay time of the deep-trap state recombination. Inset: The high-resolution decay process of onset phase and the rise time was marked by the arrow. (b) The decay time of near-band-edge exciton recombination from ZnO nanowire at two pump fluences, 70 μJ /cm^2 (solid line) and 98 μJ/cm^2 (dot line), respectively.

Therefore, the longer relaxation and slow radiative recombination rate together with the lower density of the trap/surface states make it easy to be saturated when enough carriers are generated under high excitation. The trap-state recombination will not be the main radiative channel at high pump fluence, which makes a rather less influence on the formation of stimulated emission at excitonic band in such nanostructure, even though the surface-defect-related states are inevitable in these nanostructures.

After the stimulated emission occurring at UV band, further rising the pump fluence, the carrier density increases to a higher extent to form the electron-hole plasma (EHP). The broad EHP recombination will lead to form the multiple lasing modes in the limit ZnO nanowire cavity. In these ZnO nanowires, the orderly multiple lasing modes were observed under higher excitation. Figure 4 shows the high-resolution PL spectra at UV band under the excitation of 225 μJ/cm^2, 285 μJ/cm^2, and 375 μJ/cm^2 respectively. The lasing mode also has a great dependence on the pump fluence. The regularity of the multiple lasing modes exists as follows. Firstly, the strong mode corresponds to the optical gain maximum, which is the peak position of the amplified spontaneous emission (ASE). In this position, the mode firstly overcomes the optical loss during propagation along the c axis of the ZnO nanowire. It is well known that the broadening of emission band and the red-shift of the emission peak are the main characteristics of EHP

recombination.[30] Therefore, accompanying with the broadening of UV ASE band and the enhancement of the emission intensity with the increase of pump fluence, there are more modes which can compensate the optical losses and form the oscillation between the two end facets. There are more modes under the pump fluence of 375 μJ/cm^2 than that at 285 μJ/cm^2, and 225 μJ/cm^2, as shown in the Fig.4(c). In the same way, the red-shift of the ASE wave packet will make the strongest mode shift to the low energy side. As the situation of Fig.4(b) in comparison with that of Fig .4(a), it is consistent with the presumption, while the situation in Fig.4(c) has the diversity. The fluctuation of intensity in Fig.4(c) between the different lasing modes is due to the high sensitivity of the F-P modes to the local surface quality and the cleanliness of the microcavity along the nanowire.[31] The appearance of many lasing modes demonstrates the good quality of the end facet of the nanowires. A good understanding about the rules of multiple lasing modes is also important for the design and optimization of material and devices.

4. Conclusion

In a common concept, the green emission from ZnO nanostructures in air is unavoidable. Here we reported the competing behaviours between green emission and UV emission of ZnO nanowires through the power dependent PL spectra. It can be found that, although the surface defect states extensively exist in these ZnO nanowires, the stimulated emission and lasing occur at the UV band with the increase of pump fluence. Through the time-resolved PL spectra of these two emissions, we found that the deep-level emission, competing with near-band-edge emission, depletes a few carriers at high excitation. Most excited carriers recombine through the UV radiation. Moreover, the pump fluence dependent lasing modes were shown under higher excitation. During the stimulated emission, a nonlinear effect of EHP formation induces emission band shifting and broadening under higher excitation, which leads to the strongest lasing mode redshift and the number of lasing mode increase with the increase of pump fluence. The above-mentioned processes of lasing mode should be helpful to understand and optimize the optical devices of nanowire.

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