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# Phonon-assisted stimulated emission in Mn-doped ZnO nanowires

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## Abstract

Well-crystallized Mn-doped ZnO nanowires were synthesized by a high-temperature chemical reduction method. The microscopic and macroscopic photoluminescence (PL) spectra of these Mn-doped ZnO nanowires were studied. Both the free-exciton emission band and the second-order longitudinal optical (2LO) phonon-assisted emission band were observed in the microscopic PL spectra. Furthermore, from the power dependent macroscopic PL spectra, the stimulated emission was observed around the 2LO phonon-assisted emission band with an increase in pump fluence, which relates to the strong exciton-phonon couplings along the *c*-axis in these Mn-doped ZnO nanowires. The nonresonant micro-Raman scattering spectrum demonstrates the strong 2LO phonon mode, which is enhanced by Mn doping. Resonant micro-Raman scattering shows multi-LO modes, due to the strong exciton-phonon coupling via a deformation potential induced by the Mn ions in these Mn-doped ZnO nanowires. Moreover, the low-temperature UV PL band is discussed to demonstrate the activity of phonons in the Mn-doped ZnO nanowires.

## 1. Introduction

One-dimensional (1D) semiconductor nanostructures (nanowires and nanobelts) have aroused a great deal of interest due to their unique physical properties and wide potential applications in constructing nanoscale electronic and optoelectronic devices [1–3]. In particular their strong optical confinement in a radial direction suggests that semiconductor nanowires are a good particle transport medium, and can be used as nanolasers and nanowaveguides [4–6]. ZnO

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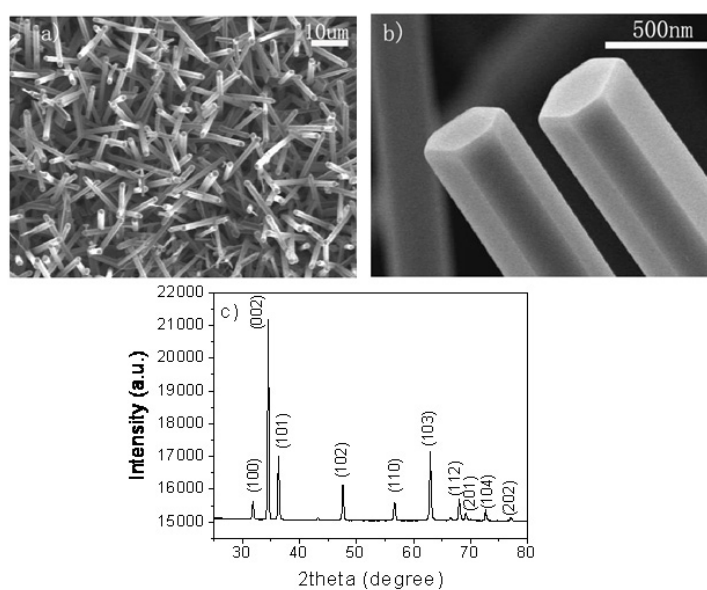
is considered to be a promising material for light-emitting devices in the ultraviolet region since it has a large band gap (3.37 eV) and exciton binding energy ( $\sim 60$  meV) at room temperature. Under high excitation, the ultraviolet stimulated emission and lasing generally occur at the free-exciton emission band in ZnO nanowires [7–11]. Moreover, there exists a strong exciton and longitudinal optical (LO) phonon coupling in ZnO nanowires [12]. For imperfect ZnO nanowires with impurities and defects, the impurity-induced crystal deformation and defects can remarkably change the exciton–phonon coupling; this plays an important role in the emission processes of ZnO nanocrystals, and always induces a phonon replica together with the free-exciton emission band [13–15]. Several groups have reported that spontaneous free-exciton emission and  $n$ LO phonon-assisted emission coexist in imperfect ZnO nanocrystals [16, 17].

Recently, nanoscale Mn-doped dilute magnetic semiconductors have been widely investigated for their potential application in photonics and spintronics. In previous reports on the luminescence of Mn-doped nanocrystal, Chang *et al* [18] and Jung *et al* [19] observed that the band gap of  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  nanocrystal decreases with increasing Mn content. Zheng *et al* [20] observed blue and ultraviolet cathodoluminescence peaks from the  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  thin film, and attributed their emissions to the intra-d-shell transitions of  $\text{Mn}^{2+}$ . Ronning *et al* [21] observed that the point-defect related green emission of Mn-doped ZnO nanobelts was enhanced by Mn implantation. In the above mentioned literature when the Mn content in the ZnO nanocrystals is more than 1% it can be seen that the luminescence of various Mn-doped nanocrystals is very different for varied morphologies and Mn doping contents. There are only a few reported studies on the PL of trace Mn-doped ZnO nanowires, except for a number of reports on their magnetic properties. Up to now there have been no reports on the properties of ZnO nanostructures with minor Mn doping.

We have studied the PL spectra of ZnO nanowires with minor Mn doping, and significant changes in the emission spectra for different doping levels were observed [22]. However, no detailed study on the influence of trace-doped Mn on the exciton emission was reported in Mn-doped ZnO nanowires. In this work, we prepared trace Mn-doped ( $\sim 200$  ppm) ZnO nanowire arrays through a simple high-temperature chemical reduction method, and studied the stimulated emission behaviour under high excitation at room temperature. Through the nonresonant and resonant micro-Raman spectra, the influence of doped Mn on the 2LO phonon-assisted exciton emission was investigated. We found that a definite number of Mn ions in the ZnO nanowire can enhance the exciton–phonon coupling, leading to the 2LO phonon-assisted stimulated emission under high excitation. This work will help us to understand the influence of trace doping on exciton behaviour and related luminescence properties in semiconductor nanostructures.

## 2. Experimental details

Mn-doped ZnO nanowires were synthesized by a high-temperature chemical reduction method in a tube furnace, which can be described as follows. Pure  $\text{Zn}(\text{OH})_2$  and  $\text{Mn}(\text{OH})_2$  nanoscale powders (molar ratio 1:2), which were prepared in advance by co-precipitation chemical methods, were mixed together with graphite and placed onto the centre of a pyramid-like quartz tube. A piece of Au particle deposited silicon wafer was previously placed at the sharp end of the tube to collect the sample. Finally, the pyramidal tube was put in the middle of a long large quartz tube, which was quickly inserted into a furnace with a temperature of  $1200^\circ\text{C}$  for 90 min. After allowing the furnace to cool to room temperature, the silicon wafer in the pyramid-like quartz tube was covered with nanowire arrays. After ultrasonic cleaning with alcohol, the Mn oxides and other dust on the surface of the ZnO nanowires was removed for further optical study.



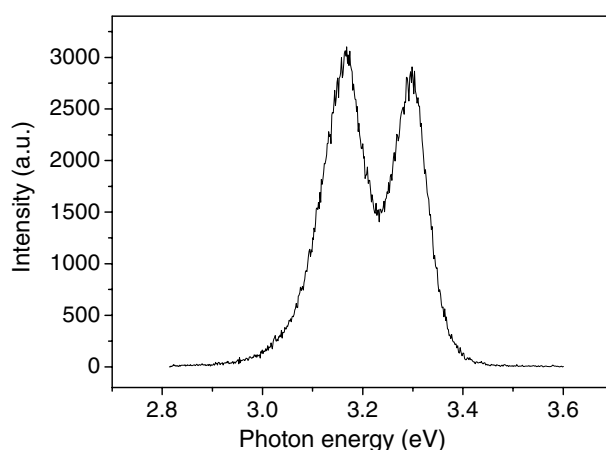
**Figure 1.** (a) SEM of the as-grown Mn-doped ZnO nanowire array. (b) High-resolution SEM of the nanowires. (c) The XRD patterns of as-grown Mn-doped ZnO nanowires.

The morphologies of the nanowires were observed with a scanning electron microscope (SEM, Hitachi S-5200). 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 ( $\lambda = 1.54178 \text{ \AA}$ ). The element analysis was carried out with an inductively coupled plasma-mass spectrometer (Thermo Element X7). Pump fluence dependent macro-PL spectra were measured under femtosecond (fs) laser excitation. The PL was dispersed by a monochromator with a  $150 \text{ grooves mm}^{-1}$  grating, and detected with a liquid-nitrogen cooled charge coupled device (CCD) camera. The spectral resolution of the system was  $0.26 \text{ nm}$ . The nonresonant and resonant micro-Raman spectra were measured by a microscopic confocal spectrometer (WITec alpha 200), using the  $442 \text{ nm}$  line and the  $325 \text{ nm}$  line of a He–Cd laser as the excitation source, respectively. The micro-PL spectrum from a nanowire was also measured with this microscopic confocal spectrometer with the excitation of the  $325 \text{ nm}$  line.

### 3. Results and discussion

The SEM image of the Mn-doped ZnO nanowires in figure 1(a) indicates that the length and average diameter of the nanowires are around  $15\text{--}25 \text{ }\mu\text{m}$  and  $500 \text{ nm}$ , respectively. A local enlargement of this image (see figure 1(b)) indicates that the nanowires are uniform along the  $c$ -axis direction, and terminate with flat hexagonal tips, which is beneficial for working as an optical cavity. Powder x-ray diffraction patterns in figure 1(c) indicate that these nanowires are single phase with a hexagonal wurtzite structure. The strong and sharp refraction peaks show that the nanowires are well crystallized. For the uncleaned sample in figure 1(c) there may be minor impurities related to manganese oxides. For the cleaned sample, no obvious structural changes induced by the dopant are observed, since only about  $200 \text{ ppm}$  of Mn was detected in the nanowires from the results of element analysis.

A solid–gas–solid reaction mechanism was involved during the formation of Mn-doped ZnO nanowire by the high-temperature reduction reaction. The MnO ( $-698 \text{ kcal mol}^{-1}$ ),

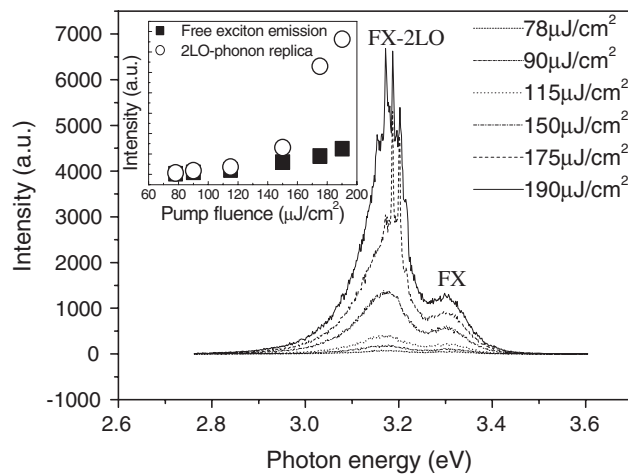


**Figure 2.** Microscopic PL of Mn-doped ZnO nanowires.

decomposed from  $\text{Mn}(\text{OH})_2$ , has a larger heat of formation than that ( $-578 \text{ kcal mol}^{-1}$ ) of ZnO from  $\text{Zn}(\text{OH})_2$ , and the vaporization (boiling) temperature of Mn ( $1962^\circ\text{C}$ ) is much higher than that of Zn ( $907.0^\circ\text{C}$ ). This means that the reduction of MnO and vaporization of Mn have a much lower efficiency than that of the Zn counterpart in the heating tube, hence a low Mn vapour might involve the formation of ZnO. In addition, during the crystallization, high temperatures lead to high activities of phonon vibrations; this would lead to the segregation of Mn to the surface of the ZnO crystal due to the stress. Therefore, only trace amounts of Mn are incorporated into the ZnO nanocrystal through this technique, although the amount of Mn in the powder precursors is in the ratio 1:2. Most manganese was left as Mn oxides. Trace parts of these may adhere to the surface on the ZnO nanowire. To eliminate the influence of the Mn oxides, we performed ultrasonic cleaning with alcohol for a few minutes to remove the Mn oxides and other dusts before measuring their PL spectra. The XRD measurement cannot detect such a small amount of Mn in cleaned ZnO nanowire, because such small amounts cannot modify its wurtzite structure. Moreover, the reported results for high-content Mn-doped ZnO nanostructures reveal that more Mn doping does not change the wurtzite structure of ZnO, and the manganese was doped into the crystal lattice.

Figure 2 shows the micro-PL spectrum from the nanowires under He–Cd laser excitation. It consists of two peaks in the ultraviolet region, one located at 3.3 eV and the other located at 3.17 eV. The peak at 3.3 eV is attributed to recombination of the free exciton at the ZnO band edge (FX). The spacing between the two peaks is 130 meV, which is not consistent with reported spin–orbit splitting levels of the Mn ions [23], but is very close to the energy of 2LO phonons ( $A_1$  mode). Therefore, the peak at 3.17 eV can be attributed to the exciton–2LO phonon band (FX-2LO, polaronic exciton band). It is clear that the PL spectra of the Mn-doped nanowires are different from those of undoped ZnO nanowires prepared by the same method, as the latter only show free exciton emission at room temperature [24].

Figure 3 shows the macroscopic far-field power-dependent PL spectra of the Mn-doped ZnO nanowires. Two emission bands appear in the PL spectra, which are consistent with the above assignments (see figure 2). At low pump fluence, both emission bands (the FX band and the FX-2LO band) are broad, and possess similar emission intensities. With the increase in pump fluence, the FX band retains the broad spontaneous emission while the 2LO phonon replica turns sharper and increases rapidly. When the fluence increases to  $175 \mu\text{J cm}^{-2}$ , two ultra-narrow emission lines each with a linewidth as narrow as 0.4 nm emerge from the FX-

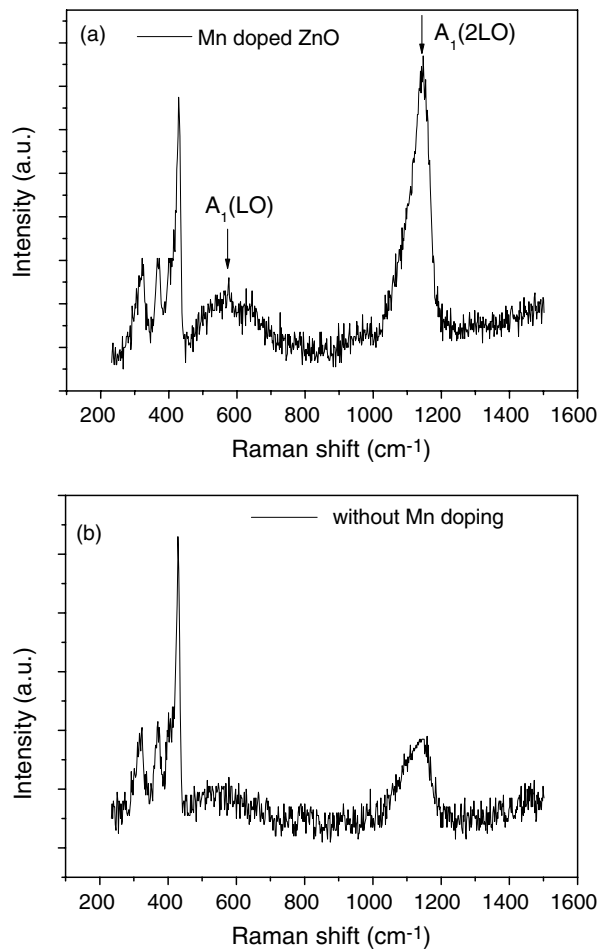


**Figure 3.** The evolution of macro-PL under different pump fluences of Mn-doped ZnO nanowires. The inset shows the 2LO phonon-assisted emissions as a function of the pump fluence compared with the free exciton emission.

2LO broad band. As the pump fluence further increases, more ultra-narrow emission modes at around 392 nm can be detected. Two obvious sharp peaks are at 3.1716 eV (391.72 nm) and 3.1869 eV (389.84 nm), respectively. The wavelength span is 1.88 nm. According to the mode spacing ( $\Delta\lambda$ ) and the Fabry–Perot (F-P) cavity condition,  $\Delta\lambda = \lambda^2/2nL$ , where  $n$  is the refractive index of the nanowire, the length of the nanowire should be 17  $\mu\text{m}$ , which is consistent with the length obtained from the SEM image. This demonstrates that the modes are the lasing modes, which stem from the strong coherent feedback of the F-P cavity formed by the two end faces of the nanowire. However, the FX emission band does not produce similar behaviour. The inset of figure 3 shows the detailed behaviour of the intensity of FX and FX-2LO emission as a function of the pump fluence. The integrated intensity of the FX emission increases almost linearly with the pump fluence (shown as closed squares in the inset of figure 3). However, the integrated intensity of the FX-2LO peak experiences a superlinear dependence on the pump fluence (open circles). The appearance of the lasing mode and the superlinear increase of intensity are clear evidence of stimulated emission. This 2LO phonon-assisted stimulated emission occurs in the Mn-doped ZnO nanowires, and the threshold pump fluence is around  $150 \mu\text{J cm}^{-2}$ .

Under high-intensity excitation, the amplified light emission in the optical confined micro-cavity produces enough gain to compensate the optical losses, leading to the appearance of multimode lasing. The number of lasing modes increases with increasing fluence, as shown in figure 3, which shows that more modes can compensate the optical losses and form the oscillation between the two end facets. The increase in mode number indicates a broadening of amplified light emission at the FX-2LO band. Moreover, the maximum of the PL band shifts to the low-energy side. The broadening and redshift of the 2LO phonon-assisted band is a typical characteristic of the formation of an electron–hole plasma (EHP), which comes from the interaction between carriers [25].

The LO phonon-assisted stimulated emission is related to the strong exciton–2LO phonon coupling in these Mn-doped nanowires. To further understand the phonon characteristics in these nanowires, and the influences of Mn doping on the exciton–phonon coupling, we examined the nonresonant micro-Raman modes of a single nanowire, both with and without



**Figure 4.** (a) Nonresonant micro-Raman modes from the Mn-doped ZnO nanowires. (b) The Raman modes from undoped ZnO nanowires.

Mn doping at room temperature as shown in figure 4 (with 442 nm excitation). In both Raman spectra, the peak at  $326\text{ cm}^{-1}$  is attributed to a second-order phonon process. The bands at  $372$  and  $439\text{ cm}^{-1}$  correspond to the  $A_1(\text{TO})$  mode and the nonpolar optical phonon mode  $E_2^{\text{high}}$ , respectively. The two bands at  $\sim 574$  and  $1147\text{ cm}^{-1}$  are the 1LO and the 2LO ( $A_1$  mode) modes, respectively. There are no apparent impurity-related modes in the Raman spectrum due to the low Mn concentration in the doped nanowires. However, there exists a large difference in the LO phonon modes in the Raman spectra between the two nanowires. For doped nanowires, the 2LO phonon mode is stronger than that without doping, and the 1LO phonon mode also becomes slightly enhanced by doping (see figure 4). Moreover, the intensity of the 2LO phonon mode is much stronger than that of 1LO phonon for Mn-doped nanowires. The intensity ratio between the second- and first-order Raman scattering is closely proportional to the electron-phonon coupling strength and symmetry selection [12]. The relative intensity ratio  $I_{2\text{LO}}/I_{1\text{LO}}$  of these Mn-doped nanowires ( $\sim 4.9$ ) is very much larger than that of the undoped sample ( $\sim 3$ ) and the reported result in [12] ( $\sim 2.6$ ), which reflects the significant enhancement of exciton-phonon interaction in the Mn-doped ZnO nanowires.

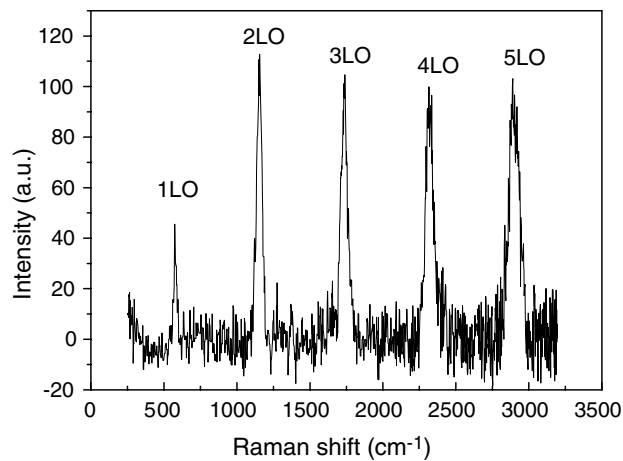
From the above results, a strong exciton-phonon coupling interaction exists in these Mn-doped ZnO nanowires. Moreover, the 1D structure with large aspect ratio enhances

the nonlinear coupling between exciton and phonon [26], which means that the exciton–LO phonon coupling strength in 1D semiconductor nanostructures is much higher than that in the corresponding bulk materials. The stimulated emission occurring at the 2LO phonon-assisted emission band reflects the strong coupling of the 2LO phonon with excitons. Because the 2LO phonon is not forbidden by the symmetry selection in contrast to the 1LO phonon, Permogorov [27] indicated that the highest-intensity line in the Raman scattering spectrum is the second-order line 2LO, which means that the density of the 2LO phonon state is larger than that of 1LO phonon. The large density of the 2LO phonon together with the stronger coupling to excitons in these nanowires, is responsible for the stimulated emission occurring at the 2LO phonon bound states under high excitation.

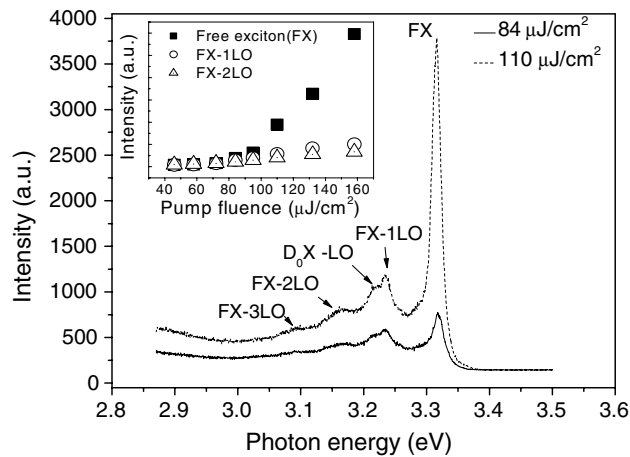
The nonresonant Raman of ZnO nanostructures with high doping levels has been widely studied. Awasthi *et al* reported the nonresonant Raman spectra of ZnO ceramics and thin films with different doping levels, and observed that the LO phonon modes of  $580\text{ cm}^{-1}$  are significantly enhanced with increasing Mn/Fe doping level in ZnO ceramics. Moreover, when the doping concentration increases to around 3%, this LO phonon mode was enhanced to the maximum [28]. Hasuike *et al* also studied the Raman scattering of ZnO doped with Ga and N (codoping), and magnetic impurities. Their results still show that the LO phonon mode gets enhanced to maximum when the doping concentration increases over 0.2% [29]. These results indicate that the doped impurities will drastically enhance the electron–phonon coupling, and change the phonon spectral profile in the Raman spectra. In the Raman spectra of doped samples, in addition to the appearance of impurity-related modes, some phonon modes, especially the LO phonon modes, can be enhanced by the dopant at proper doping levels [30]. Moreover, the Raman modes in nanocrystal and bulk material show a large difference [31]. The different structures show varied doping effects on each Raman mode, especially the LO phonon mode. Due to the selection rules, the 2LO phonon of the nanowire is dominant in the coupling with exciton or carriers at low doping levels [27], while at definite high doping levels, the 1LO phonon may be dominant in Raman scattering, as reported by Hasuike *et al* [29]. However, over-doping will make too many trap-centres within the nanowires. In such a situation, carrier trapping determines the optical processes, which will obstruct the coupling of excitons and phonons. In our ZnO nanowires with Mn doping of 200 ppm, the trace Mn has a minor effect on the 1LO phonon mode, while the 2LO phonon mode is enhanced greatly and leads to the coupling of 2LO phonons and excitons becoming dominant, as shown in figures 4(a) and (b). Therefore, the enhancement of phonon–exciton coupling dominates the emission processes in these Mn-doped ZnO nanowires. This conclusion is consistent with our Raman and PL data.

As a trace impurity, the doped Mn increases the surrounding structural fluctuation in the nanowire, which increases the deformation potential in the lattices. Because the exciton interacts with the LO phonon through both the Fröhlich interaction and the deformation potential [12], this means that the trace Mn increases the interaction between excitons and phonons. To further demonstrate the enhancement of the deformation potential by Mn impurities, the resonant micro-Raman scattering spectrum of the Mn-doped ZnO nanowires is shown in figure 5. The resonant Raman spectrum consists of five sharp lines with equal frequency span between the nearest neighbouring lines. The line at  $574\text{ cm}^{-1}$  is the 1LO Raman mode, and the other lines are the respective multiple modes ( $n$ LO,  $n = 2, 3, 4$  or  $5$ ) of the 1LO mode (see figure 5). It is reported that if the number ( $n$ ) of multiple phonon scattering processes in a semiconductor is in proportion to the polaron coupling coefficient ( $\alpha$ ), then the maximum frequency shift  $n\omega_{\text{LO}}$  will be proportional to the deformation energy ( $\frac{1}{2}\alpha\hbar\omega_{\text{LO}}$ ) [32]. Hence, the large Raman frequency shift of more than 5LO modes ( $5\omega_{\text{LO}}$ ) indicates that a very large deformation potential exists in these Mn-doped ZnO nanowires. For undoped ZnO nanowires, resonant Raman scattering with a 5LO Raman frequency shift has not been reported in the literature so far.





**Figure 5.** Resonant micro-Raman modes from Mn-doped ZnO nanowires.



**Figure 6.** PL spectra at 77 K under two different pump fluences, above the threshold (dash line) and below the threshold (solid line). The inset shows the LO phonon-assisted emissions and free exciton emission as a function of the pump fluence.

Through coupling with 2LO phonons, the high-density thermal excitons could be cooled down and relaxed to the lowest state more quickly than those excited excitons without coupling with phonon. Therefore, the coupling of free excitons with 2LO phonons could lead to the accumulation of a large number of states at high excitation. Before their dissociation, they may produce stimulated emission through exciton interactions. While more density is produced, more carriers are generated due to the dissociation of excitons and doping. The intense production of carriers may lead to Coulomb screening, and then an EHP in these nanowires at high excitation. The appearance of stimulated emission at the 2LO phonon-assisted exciton band indicates a strong exciton–phonon coupling, which coincides with the conclusion of [33]. The strong 2LO phonon–exciton interaction originates from trace Mn doping, and dominates the interactions under high excitation in these ZnO nanowires.

To further study the behaviour of LO phonons, the stimulated emission of these nanowires was measured at 77 K. Figure 6 shows the PL spectra corresponding to the pump fluences

of  $110 \mu\text{J cm}^{-2}$  (above the threshold) and  $84 \mu\text{J cm}^{-2}$  (below the threshold). The 1LO and 2LO and even the 3LO phonon-assisted emissions are shown in the spectra, but no stimulated emission occurred at the phonon replica. Stimulated emission only occurred at the free-exciton emission band, as shown in the inset of figure 6, which shows the LO phonon-assisted emissions and free exciton emission as a function of the pump fluence. This indicates that excitonic emission dominates the low-temperature emission. The emission at 77 K is quite different from that at room temperature. According to the theoretical analysis and experimental results, stimulated emission is attributed to the exciton–exciton scattering mechanism at 77 K [34, 35]. At low temperatures, the population of LO phonons will be much less than that at room temperature due to the reduction of thermal effects, which leads to the coupling of excitons and a decrease in LO phonons. Therefore, LO phonon-assisted emission is not dominant in the recombination at low temperature.

#### 4. Conclusion

In summary, 2LO phonon-assisted stimulated emission was observed in Mn-doped ZnO nanowires at room temperature, which means there is strong exciton–phonon coupling in these nanowires. The nonresonant and resonant Raman data demonstrate that the Mn doping enhances the exciton–phonon interaction. At a Mn doping level of 200 ppm the 2LO phonon-assisted exciton emission dominates the optical process in the 1D nanostructure. The results show that the emission properties in ZnO nanostructures are sensitive to the doping and structural quality of the nanowires. The low-temperature PL in the UV band indicates that the LO phonon is not so active as that at room temperature in the Mn-doped ZnO nanowires.

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