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Enhancement of multi-photon Raman scattering and photoluminescence emission from Li-doped ZnO nanowires

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Abstract
Uniform Li-doped ZnO nanowires have been fabricated by thermal evaporation method. The ZnO formation and the Li incorporation have been discussed and the formation path of preparation products has also been explained in terms of the stability of Zn and Li vapor in an aerobic atmosphere. The strongest vibration mode at 437.2 cm$^{-1}$ in the multi-photon Raman scattering of the as-prepared products at room temperature indicates that the Li-doped ZnO nanowires still keep the hexagonal (wurtzite) structure. Raman spectra of Li-doped ZnO with different doping concentrations confirm that the variation of Raman peaks in the range of 550 cm$^{-1}$ $\sim$ 650 cm$^{-1}$ is caused by the doping of lithium. The photoluminescence property at room temperature shows a blue-shift compared with undoped ZnO in the ultraviolet region. The Gauss fitting analyzed results indicate that the broad-band is composed of one green luminescence (GL) band, one yellow luminescence (YL) band, and one red luminescence (RL) band, respectively. The GL (2.447 eV) could be attributed to the singly ionized oxygen vacancies. The origin of the YL (2.245 eV) could be assigned to the transition of an electron from the conduction band (or a shallow donor) to the Li acceptor level. The RL (1.977 eV) could be assigned to the transitions between a shallow donor (at low temperature) or the conduction band (at higher temperature). Furthermore, the luminescence spectra at low temperature confirm the increase of defect levels like oxygen vacancies.

1. Introduction

As an II–VI compound semiconductor, ZnO has been studied over the past few years due to its direct and wide band-gap (3.37 eV at room temperature) and large exciton binding energy (60 meV) [1]. These attractive properties open up a wide range of applications for ZnO materials, such as white light-emitting devices, ultraviolet laser diodes, and so on [2–4]. At present, there is a rapidly growing research effort with various doping elements using different methods aimed at exploring doped-ZnO nanomaterials [5, 6], paralleling the domestic and international interest in pure ZnO. Theoretically and experimentally, the doping of ZnO with selective elements alters its shape, impurities, phase and then affects its structures, electrical, optical and so on [7]. However, a significant challenge that needs to be resolved is the fabrication of efficient and reproducible p-type ZnO for practical device applications. One reason for that is ZnO naturally exhibits n-type conduction due to its intrinsic donor defects such as zinc interstitials and oxygen vacancies. In addition to, the high self-compensation of ZnO and low solubility of the dopant are also regard as the difficulties [8]. Substituting group-I elements for Zn atoms and introducing group-V elements into oxygen vacancies is an effective way to achieve p-type ZnO nanostructures [9, 10]. On the basis of the literature surveys, the selected element from group-I elements showed better properties as dopants materials than group-V elements in the light of the shallowness of the acceptor level [11, 12]. Therefore, lithium ion is selected as a dopant in ZnO. Due to its small ionic radius, lithium ion can easily occupy interstitial position (Li$^+$) and can acts as a donor. Furthermore, Lithium ion has the smallest ionic radius (0.76 Å) in group-I elements, which is very close to that of Zn (0.74 Å) [13, 14]. Up to now, p-type Li-doped ZnO...
nanostructures have been synthesized in several groups with different methods. Bin Xiao et al prepared p-type ZnO thin films via doping Li as acceptor by using pulsed laser deposition (PLD). They realized that all the Li-doped films showed high transmittance (about 90%) in the visible region [15]. Nanda Shakti et al reported the growth and ZnO:Li nanorods by a low temperature (300 °C) thermal decomposition method. Depending on the Li concentration, they find that Li-doped ZnO nanorods with strong visible region luminescence have potential applications in optoelectronic devices [16]. Compared with other synthetic methods like hydrothermal method, chemical vapor deposition method [17, 18] and pulse laser deposition, thermal evaporation used in this work was a pure-crystalline, low-coast, facile, and high-yielding method in synthesizing various morphologies [19] just by reasonably controlling the heating rate and deposition time.

In this paper, Li-doped ZnO nanowires were fabricated by a simple and high-yield thermal evaporation method. The surface morphology of the as-prepared products was measured by scanning electron microscopy. The multi-photon Raman scattering properties of Li-doped ZnO nanowires were investigated by Raman spectroscopy. The photoluminescence of Li-doped ZnO nanowires was also investigated.

2. Experimental

Undoped and Li-doped ZnO nanowires were fabricated by a simple thermal evaporation in oxygen atmosphere with the presence of Au as a catalyst. A mixture of pure zinc oxide powder (Zn 99.9%) and lithium hydroxide powder (LiOH · H₂O 99.9%) in a 20:1 weight ratio was used as the precursor material to grow the doped ZnO nanostructures. Theoretically, the specific weight of lithium in the as-prepared production is about 7% which is the molar mass ratio of lithium atom to zinc atom. The experimental system consists of horizontal tube furnace, quartz tube, ceramic boat and control system. The source material was placed in one side of the alumina ceramic boat, with two gold-plated silicon chips fixed on the other side of the ceramic boat as substrates from the mixtures about 2 to 3 cm. The boat was then placed in a quartz tube. One end of the quartz tube communicates with the atmosphere, which ensures the oxygen-enriched reaction environment in the quartz tube. The other end of the quartz tube is connected to an argon gas bottle, and the trace argon gas introduced can play a role in transporting the generated sample material. This mixture was heated up to 800 °C and the temperature of the substrates were maintained at about 750 °C for 90 min during the deposition of the nanostructures. Then the furnace cooled to room temperature gradually. According to these conditions, undoped ZnO and samples with Li doping of 10% and 15% by weight were prepared as comparison. The mass ratios of oxide powder (Zn 99.9%) to lithium hydroxide powder (LiOH · H₂O 99.9%) were 100:7 and 100:10, respectively.

The as-prepared products were characterized and analyzed using scanning electron microscopy (SEM) (JEOL, JSM-5610LV). The Raman spectra (inVia-Reflex, Renishaw) were excited by a 532 nm Nd:YAG laser at room temperature. A room temperature photoluminescence was employed to study the optical properties of the Li-doped ZnO nanowires. PL measurements of the as-prepared products were performed using 325 nm He–Cd laser as the excitation source on a SP2557 (ARS Instrument) fluorescence spectrometer. The luminescence was resolved with a monochromator at HUV and detected by a high sensitivity photomultiplier tube.

3. Result and discussion

The SEM images of the undoped and Li-doped ZnO nanowires have been shown in figure 1. Li-doped ZnO nanostructures with 7% doping concentration were mainly studied, as shown in figures 1(a) and (b). The morphology of the sample taken from the substrate is shown in figure 1(a). The top ending spherical structure stimulated and guided by the catalyst is a sign of VLS growth. However, the samples from the wall of the boat revealed in figure 1(b) is a sequence of homogeneous nanowires growing by the VS method, which is not affected by the catalyst. The length of them usually ranges from several micrometers to several tens of micrometers. The appearance of these two different morphological samples can be attributed to the existence of the catalyst. The substrate used in this experiment is a gold plated silicon wafer. The gold coatings are plated on the silicon wafer by magnetron sputtering. When the temperature is higher than 175 °C, the coating layering occurs in the form of gold particles. Then the gold particles act as a catalyst. Therefore, the sample near the substrate may grow by the VLS method. However, the source material is further away from the substrate, so the VS method growth is not excluded. In addition, the SEM images of undoped ZnO nanostructures are shown in figure 1(c). The samples with different morphology growing by the VS method are white floccules in ceramic boat. In addition to the wire-shaped ZnO shown in figure 1(c) I, tubular and nanoflower-like ZnO are also present under the influence of temperature gradient and gas pressure in high temperature tubular furnace (750 °C ~ 800 °C). Therefore, we can draw the following conclusions through the comparison of undoped and Li-doped ZnO. For the thermal evaporation method, the slight difference in the experimental environment can result in different sample.
morphology, such as catalyst, growth temperature zone, heating pressure and so on. Furthermore, the doping of lithium has hardly impact on the size of ZnO.

Then the Li-doped ZnO formation discussed as follows. At beginning, the mixtures of pure zinc powder and lithium hydroxide powder were heated. The zinc powers were heated to generate Zn vapors and reacted with O$_2$ in the aerobic atmosphere. The reaction equation is as follows:

$$2 \text{Zn}(g) + \text{O}_2(g) \rightarrow 2 \text{ZnO}(g)$$

(1)

Owing to the doping of ZnO, lithium doping might replace zinc sites or form lithium gap or replace zinc gap. The process is as follows:

$$2\text{LiOH} \cdot \text{H}_2\text{O}(s) \rightarrow \text{Li}_2\text{O}(g) + 3\text{H}_2\text{O}(g)$$

(2)

In the high temperature doping process of ZnO, the lattice changes of Li$_2$O can be expressed as follows:

$$\text{Li}_2\text{O} \rightarrow 2\text{Li}^{2+} + \text{V}^{\text{X}} + \text{O}^{\text{X}}$$

(3)

$$\text{Li}_2\text{O} \rightarrow 2\text{Li}^+ + \text{O}^{2-}$$

(4)

where \(\text{Li}^{2+}\) represents lithium on Zn lattice, \(\text{Li}^+\) is lithium in interstitial position and \(\text{O}^\text{X}\) is oxygen or lattice site. And as time goes by, a part of the interstitial lithium atom would take place of the lattice position of the zinc atom, such as the equations

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**Figure 1.** (a) SEM images of the products from the gold-plated silicon substrate. (b) SEM images of the woollike products from the wall of the boat. (c) SEM images of undoped ZnO.
where $\text{ZnZn}^+$ represents zinc in zinc site and $V_O^+$ is oxygen vacancy on lattice site [20]. And then those resultants in succession condensed on the low temperature Si substrate and walls of the ceramic boat.

Multi-photon Raman scattering property is deemed to be a rapid method in investigating the crystal degree, crystal defects, crystal lattice distortion and phase transition of materials [21]. Figure 2(a) shows the Multi-photon Raman scattering property of Li-doped ZnO nanowires at room temperature. The spectrum is normalized to the same intensity of the $E_{2}^{\text{high}}$ mode. (b) Multi-photon Raman scattering property of the undoped ZnO nanowires at room temperature. The spectrum is normalized to the same intensity of the $E_{2}^{\text{high}}$ mode. (c) Multi-photon Raman scattering spectra of Li-doped ZnO nanowires at different doping concentrations (0%, 7%, 10%, 15%). The spectra are normalized to the same intensity of the $E_{2}^{\text{high}}$ mode.

$$\text{Li}^+_i + \text{ZnZn} + e^- \rightarrow \text{Li}^+_i \text{Zn} + \text{Zn}^+_i$$

$$\text{Li}^+_i + e^- \rightarrow \text{Li}^+_i \text{Zn} + V_O^+$$

Figure 2. (a) Multi-photon Raman scattering property of the Li-doped ZnO nanowires at room temperature. The spectrum is normalized to the same intensity of the $E_{2}^{\text{high}}$ mode. (b) Multi-photon Raman scattering property of the undoped ZnO nanowires at room temperature. The spectrum is normalized to the same intensity of the $E_{2}^{\text{high}}$ mode. (c) Multi-photon Raman scattering spectra of Li-doped ZnO nanowires at different doping concentrations (0%, 7%, 10%, 15%). The spectra are normalized to the same intensity of the $E_{2}^{\text{high}}$ mode.

Multi-photon Raman scattering property is deemed to be a rapid method in investigating the crystal degree, crystal defects, crystal lattice distortion and phase transition of materials [21]. Figure 2(a) shows the Multi-photon Raman scattering property of Li-doped ZnO nanowires (7% of Li doping concentration). A comparison with the Multi-photon Raman scattering property of the undoped ZnO nanowires from the same experimental condition is shown in figure 2(b). Note that the spectra had been normalized to the intensity of the $E_{2}^{\text{high}}$ mode, respectively. The peak at 437.2 cm$^{-1}$ belongs to vibrational mode, which is the $E_{2}^{\text{high}}$ mode corresponding to the vibrations among the oxygen atoms in the non-polar face. This sharp, strong, and dominant mode indicates that the Li-doped ZnO nanowires still keep the hexagonal (wurtzite) structure as undoped ZnO [22]. It demonstrates that the introduced Li or the point defects do not cause a large amount of strain in the material. The peak at 332.6 cm$^{-1}$ can be assigned to the second-order vibration mode with $E_{2}^{\text{high}} - E_{2}^{\text{low}}$ (2E$_2$). The peaks at 380.3 cm$^{-1}$ and 410.3 cm$^{-1}$ can be also assigned to the transverse-optical mode with A$_1$(TO) and the first-order transverse-optical mode with E$_1$(TO), respectively. The spectral peak at 583.9 cm$^{-1}$ belongs to the longitudinal
optical mode (LO), like $A_1$(LO) or the $E_1$(LO) mode. It is reported that the $E_1$(LO) mode can occur at 584 cm$^{-1}$ as this mode is related to the defects such as oxygen vacancies, zinc interstitials or their complexes [22, 23]. Well, the $A_1$(LO) mode located at 574 cm$^{-1}$ is not observed. Obviously, the intensity of $E_1$(LO) mode in Li-doped ZnO is much higher than that of undoped ZnO. In addition, the Multi-photon Raman scattering property of Li-doped ZnO shows a new peak at 613.3 cm$^{-1}$. It can be assumed the doping of the lithium element causes the distortion of ZnO lattice. These differences in peaks between Li-doped and undoped ZnO can be attributed to the surface phonon mode and the Raman scattering peaks would be originated by Li doping to form defects in ZnO [24]. In order to further confirm that the variation of Raman peaks in the range of 550 cm$^{-1} \sim 650$ cm$^{-1}$ is caused by the doping of lithium, we studied the multiphoton Raman scattering spectra of Li-doped ZnO at different doping concentrations (0%, 7%, 10%, 15%). The spectra are shown in figure 2(c). Apparently, the $E_1$(LO) mode of Li-doped ZnO with different doping concentrations is broadened and enhanced compared with pure ZnO. It is possible that the defect level such as oxygen vacancies has been increased after annealing. The comparison curves show that the Li-doped ZnO with 10% doping concentration has the widest and strongest $E_1$(LO) mode. Hence the difference between Li-doped ZnO and unalloyed ZnO can indicates that lithium ion is successfully doped into ZnO.

The photoluminescence (PL) spectra of the wool-like products at room temperature were investigated. Figure 3(a) shows the PL spectrum of Li-doped ZnO nanowires with different doping concentration. 7% Li-doped ZnO nanostructures were mainly studied, as shown in black solid line. A weak ultraviolet (UV) emission peak at 383.6 nm and an intensive broad-band emission at 517.8 nm are observed. A comparison with the PL spectrum of the undoped ZnO nanowires from the same experimental condition also has been shown in figure 3(a) (red solid line). The intensive UV emission peak at 385.1 nm and an emission band at 507.4 nm from the undoped ZnO nanowires are also observed. The UV emission at 385.1 nm is near band edge (NBE) emission. The green band emission at 507.4 nm is a deep-level-emission (DLE) and is attributed to singly ionized oxygen vacancy in ZnO [25]. In this work, one end of the quartz tube communicates with the atmosphere and the other one is connected to an argon cylinder. Then the oxygen content in the quartz tube is less than the external atmosphere. So during high-temperature annealing, the oxygen pressure inside the nanowires is higher than the outside environment. Oxygen usually frees out of the lattice to form oxygen vacancies [26, 27]. When the
electrons belonging to the oxygen vacancies recombine with holes from the valence band, or oxygen vacancies complex with zinc vacancies, green light is emitted [28]. Hence the presence and increase of oxygen vacancies is considered to be the cause of green light. Compared with the PL spectrum of the undoped ZnO nanowires in the UV region as shown in figure 3(b), the PL spectrum of the 7% Li-doped ZnO nanowires has 1.5 nm blue-shift (shifts from 385.1 nm to 383.6 nm). However, the emission intensity of the undoped ZnO nanowires is stronger than that of the 7% Li-doped ZnO nanowires. The UV emission of the 7% Li-doped ZnO is a negligible. The UV/DLE ratio of the doped ZnO is a signification factor for comparing the optical properties of the ZnO [29]. The UV/DLE ratio of the Li-doped ZnO nanowires is smaller than the UV/DLE ratio of the undoped ZnO nanowires. The spectral lines of Li-doped ZnO at 10% and 15% doping concentrations are shown in the blue and purple solid lines of figure 3(a), respectively. Obviously, almost neither of them has UV emission. So the results indicate that the doping of Li reduces the crystalline quality of ZnO in this work.

In the visible region, the PL spectrum of Li-doped ZnO nanowires shifts from 507.4 nm to 517.8 nm.

In order to study the luminescence of the samples at low temperature, the samples with 7% and 10% lithium doping concentration were selected for research. Figure 4 shows the PL spectrum at 10 K for the Li-doped ZnO samples. Distinctly, the intrinsic luminescence peaks of ZnO doped with 7% lithium show obvious characteristics, while the intrinsic luminescence peaks of ZnO doped with 10% lithium can be neglected. However, in the defect region, the emission peak of Li-doped ZnO with 10% doping concentration is obviously wider and stronger than that of 7% sample. This indicates that under the influence of 10% doping concentration, the sample is quenched to produce more defects such as oxygen vacancies or interstitial lithium, and the defects cause new luminescence peaks to appear. Figure 3 shows that the doping concentration of Li in the ZnO sample is 10% and 15%.

![Figure 4. PL spectra of Li-doped ZnO samples with 7% and 10% doping concentration at 10 K.](image-url)
which is manifested as broadening and enhancement of defect luminescence. Well, this is consistent with the study of the peak position of $E_2$(LO) mode in Raman spectra.

4. Conclusion

Li-doped ZnO nanowires were fabricated by thermal evaporating. SEM images show that samples have diverse morphologies due to the existence of catalyst. The new Raman mode at 601.1 cm$^{-1}$ indicates that lithium ion is successfully doped into ZnO and causes the distortion of ZnO lattice. The PL spectrum of the Li-doped ZnO nanowires shows a week UV emission peak and an intensive broad-band emission peak at 517.8 nm. The analyzed results of the broad-band emission show that the broad-band is composed of one green luminescence (GL) band, one yellow luminescence (YL) band, and one red luminescence (RL) band. In addition, Raman spectra and low luminescence spectra of samples with different doping concentrations confirm the increase of oxygen vacancies in the materials. The homogeneous Li-doped ZnO nanowires prepared by the thermal evaporation method are excellent novel functional materials and will have very broad application prospects.

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References

[1] Boudjouan F, Chelouche A, Touam T, Djouroudi D, Mahiou R, Chadefayn G, Fischer A and Boudrioua A 2016 J. Mater. Sci., Mater. Electron. 27 8040
[2] Taerzourit M, Chelouche A, Touam T, Djouroudi D, Boudjouan F, Khodja S, Oubenia S, Fischer A and Boudrioua A 2014 Eur. Phys. J. Appl. Phys. 67 10502
[3] Ozgur U, Alivov Y I, Liu C, Teke A, Reschikov M A, Dogan S, Avrutin V, Cho J S and Morkoç H 2005 J. Appl. Phys. 98 041301
[4] Feng Q, Liu J, Liu J, Mei Y, Song Z, Tao P, Pan D, Yang Y and Li M 2015 Mater. Sci. Semicond. Proc. 40 436
[5] Yousefi R, Khorsand Z and Jamali-Sheini F 2013 Ceram. Int. 39 1371
[6] Liu W, Xiu F, Sun K, Xie Y H, Wang K L, Wang Y, Zou J, Yang Z and Liu J 2010 J. Am. Chem. Soc. 132 2498
[7] Hyun J-W, Kim G B and Lee J H 2017 J. Korean Phys. Soc. 71 697
[8] Chand P, Gaur A, Kumar A and Gaur U K 2014 Ceram. Int. 40 11915
[9] McCluskey M D and Jokela S J 2009 J. Appl. Phys. 106 071101
[10] Bagheri N, Majles Ara M H and Ghazyani N 2016 J. Mater. Sci., Mater. Electron. 27 1293
[11] Sa aedi A, Yousefi R, Jamali-Sheini F, Cheraghizade M, Zak A K and Huang N M 2014 Ceram. Int. 40 4327
[12] Zeng Y, Ye Z Z, Lu J G, Xu W Z, Zhu L P and Zhao B H 2006 Appl. Phys. Lett. 89 042106
[13] Duan X, Yao R H and Zhao Y J 2008 Appl. Phys. A Mater. Sci. 91 467
[14] Wardle M G, Goss J P and Briddon P R 2005 Phys. Rev. B 71 155205
[15] Xiao B, Ye Z, Zhang Y, Zeng Y, Zhu L and Zhao B 2006 Appl. Surf. Sci. 253 895
[16] Shakti N, Devi C, Patra A K, Gupta P S and Kumar S 2018 AIP Adv. 8 015306
[17] Feng L B, Liu A H, Liu M, Ma Y H, Wei J and Man B Y 2010 Mater. Charact. 61 128
[18] Ohara S, Mousavan T, Sasaki T, Umetsu M, Naka T and Adachi H 2008 J. Mater. Sci. 43 2393
[19] Senthil Kumar M, Chikara D and Srivatsa K M K 2011 Cryst. Res. Technol. 46 991
[20] Kritiha R, Sankar S and Subbhashree G 2014 J. Mater. Sci. Mater Electron 25 5201
[21] Huang Y Q, Liu M D, Li Z, Zeng Y K and Liu S B 2003 Materials Science and Engineering B 97 111
[22] Jothilakshmi R, Ramakrishnan V, Thangavel R, Kumar J, Saruua A and Kuball M 2009 J. Raman Spectrosc. 40 556
[23] Youn C J, Jeong T S, Han M S and Kim J H 2004 J. Crystal Growth 261 526
[24] Wang Q E and Zhang J 2018 J. Luminescence 195 371
[25] Lin B X, Fu Z X and Jia Y B 2001 Appl. Phys. Lett. 79 943
[26] Studenikin S A, Golego N and Cocivera M 2004 J. Appl. Phys. 95 1246
[27] Kang H S, Kang J S, Kim J W and Lee S Y 2004 J. Appl. Phys. 95 1246
[28] Arjamand Y and Eshghi H 2016 Modern Physics Letters B 30 1450081
[29] Saeedi A, Yousefi R, Jamali-Sheini F, Cheraghizade M, Zak A K and Huang N M 2013 Superlattices Microstruct. 61 91
[30] Kroger F A and Vink J H 1954 J. Chem. Phys. 22 250
[31] Bylander E G 1978 J. Appl. Phys. 49 1188
[32] Van Dijken A, Meulenkamp E, Vanmaekelbergh D and Meijerink A 2000 J. Appl. Phys. 79 7983
[33] Van Dijken A, Meulenkamp E, Vanmaekelbergh D and Meijerink A 2000 J. Phys. Chem. B 104 1715
[34] Umar A and Hahn T B 2006 Appl. Phys. Lett. 88 173120
[35] Wang X J, Vlasenko L S, Pearton S J, Chen W M and Buyanova I A 2009 J. Phys. D: Appl. Phys. 42 175411
[36] McCluskey M D, Coroeliowski C D, Lj V P, Tarun M C, Teklemichael S T, Walter E D, Nortom M G, Harrison K W and Ha S 2015 J. Appl. Phys. 117 112302
[37] McNamara J D, Albarakati N M and Reschikov M A 2016 *J. Luminescence* **178** 301