

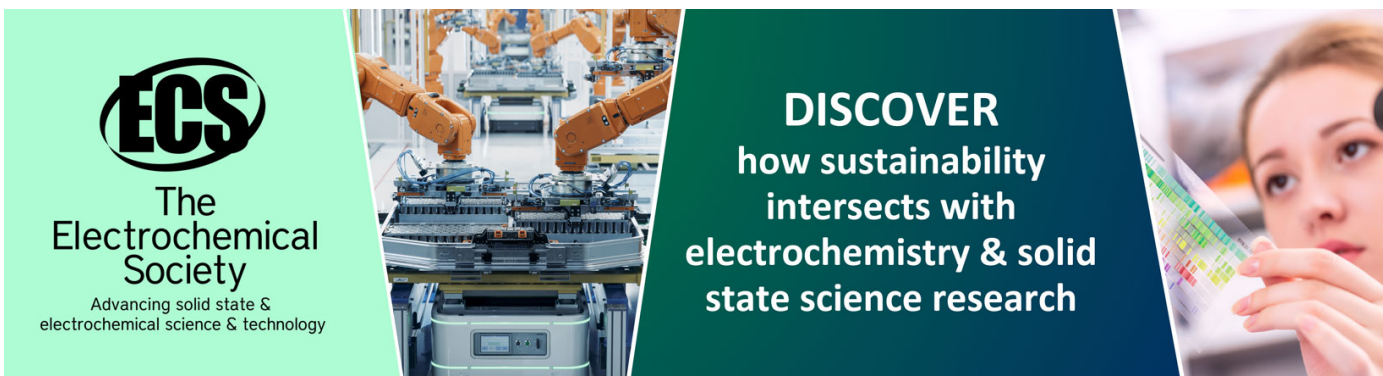
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Photoluminescent properties of copper-doped zinc oxide nanowires

C X Xu¹, X W Sun^{1,3}, X H Zhang², L Ke² and S J Chua²

¹ School of Electric and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, 639798, Singapore

² Institute of Materials Research Engineering, 3 Research link, 117602, Singapore

E-mail: exwsun@ntu.edu.sg

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Abstract

Copper-doped zinc oxide nanowires were fabricated on copper-coated silicon substrate by sintering a mixture of zinc oxide and graphite powders at high temperature. Copper functioned as a catalyst in the zinc oxide nanowire growth and was incorporated during the growth as a dopant. The size of copper-doped zinc oxide nanowires ranges from 30 to 100 nm in diameter and tens to hundreds of microns in length. The photoluminescent excitation spectra showed multiple absorption peaks in the ultraviolet and blue/green region. Correspondingly, broad and continuous photoluminescence spectra were observed extending from the ultraviolet to the red region with shoulder peaks at room temperature, which is different from that of the bulk. The x-ray photoelectron spectroscopy and low temperature photoluminescence were employed to analyse the luminescent mechanism.

1. Introduction

Zinc oxide (ZnO) is an interesting semiconductor with a direct wide bandgap (3.3 eV) and strong excitonic binding energy (60 meV). The remarkable luminescence and photoconduction properties have attracted a lot of interest since the 1960s [1, 2]. It has been widely studied as a thin film transparent conductor [3], low voltage phosphor [4], piezoelectric material [5], gas sensor [6], and buffer layer for gallium nitride [7] and indium tin oxide [8]. Recently, ZnO has shown tremendous progress, especially in p-type doping of ZnO [9, 10], ultraviolet (UV) lasing [11, 12] and nanostructures [13, 14]. For nano-ZnO, the investigation is focused on the fabrication and characterization of the various nanostructures of intrinsic ZnO. Up to now, ZnO nanodots, nanowires, nanoribbons, nanotubes and whiskers have been prepared through various approaches such as catalyst-assisted vapour-phase transport [13], metal–organic vapour-phase epitaxy [15], aqueous thermal decomposition [16], and the porous template method [17]. Some attractive properties and nanodevices have also been reported, such as the lasing action [18] of a ZnO nanowire, the field emission

property [19] of a ZnO nanowire array and a field emission microscopy (FEM) probe [20] of a single ZnO nanorod.

Doping is a widely used method to improve the electrical and optical properties of semiconductors. Various group III metals such as Al [21] and Ga [22], transition metals such as Mn [23] and Fe [24], and rare earth elements such as Eu [25] and Er [26] have been doped into ZnO phosphor and thin film for different applications. The role of Cu as a luminescence activator and as a compensator of n-type materials is of considerable significance for II–VI compound semiconductors in general. Cu-doped ZnO (ZnO:Cu) has been previously used as phosphor [27], and the active material in varistor [28] and surface acoustic wave devices [29]. The emission spectra of ZnO:Cu extend from the ultraviolet to the infrared region depending on the concentration of copper, defects in ZnO, and excitation conditions [30–32]. So far the research on the doping of ZnO, however, has been concentrated on thin film or powder forms. Reports on doped one-dimensional nanostructural ZnO remain rare. In this paper, we shall present the doping effect on the distinct photoluminescence of ZnO:Cu nanowires fabricated by sintering ZnO and carbon powder mixtures.

³ Author to whom any correspondence should be addressed.

2. Experimental details

ZnO nanowires were prepared by heating a mixture of high purity ZnO (99.999%) and graphite powders (99.999%) in air. The mixture was placed at the end of a slender one-end-sealed quartz tube. A copper-coated silicon strip was placed into the quartz tube as a collector. Then the quartz tube was pushed into a tube furnace that was maintained at a temperature of 1150 °C. The mixture was sintered for 30 min. The temperature of the substrate area was about 850 °C due to the temperature gradient. After 30 min sintering, the samples were taken out from the furnace into air for rapid cooling. It was observed that the substrate was covered with a dense white layer product. The nanowires were also fabricated on bare Si wafer under the same conditions for comparison.

The morphology of the product was examined by scanning electron microscopy (SEM) at medium and high magnification, respectively. The crystal structure of the sample was characterized by x-ray diffraction (XRD) using the copper $K\alpha$ line under an accelerating voltage of 40 kV. The photoluminescence (PL) was measured at room temperature (RT) and the low temperature (LT) of 4 K excited by a xenon lamp and a UV laser at 325 nm, respectively. The photoluminescent excitation (PLE) spectra were also measured using a xenon lamp as light source at room temperature. The Raman spectra of the samples were measured with an excitation wavelength of 514.5 nm from an argon laser. X-ray photoelectron spectroscopy (XPS) was applied to study the copper doping concentration and chemical composition in the product using an aluminium $K\alpha$ line with kinetic energy of 1486.6 eV.

3. Results and discussion

Figures 1(a) and (b) show the SEM images of the as-deposited samples with moderate and high magnifications, respectively. It can be seen that the substrate is covered with tangled ZnO nanowires of about 30–100 nm in diameter and tens to hundreds of microns in length. Figure 2 shows the XRD pattern of the ZnO nanowires. As labelled in figure 2, all peaks match the hexagonal ZnO structure with lattice constants of $a = 3.250 \text{ \AA}$ and $c = 5.207 \text{ \AA}$. There is no diffraction signal originated from copper and its compounds in the XRD data. This indicates that the nanowires are composed of wurtzite structural ZnO.

The room temperature PL spectrum (with 350 nm excitation) of the ZnO nanowires grown on copper-coated silicon (solid curve) is shown in figure 3; that of the ZnO nanowires grown on bare silicon (dashed curve) is also shown for comparison. It is interesting to note that the PL spectrum of ZnO:Cu nanowires in figure 3 shows distinct features from pure ZnO nanostructures. As shown in figure 3, the PL of pure ZnO nanowires, in general, shows two distinct peaks: one narrow peak in the UV region and one broad green band in the visible region. The UV emission peaking at about 386 nm originates from excitonic recombination corresponding to the band-edge emission of ZnO. The broad green band is related to the defects [13–18]. It can be seen from figure 3 that the PL spectrum of ZnO:Cu nanowires is so broad (extending from 370 to 650 nm) that the band-edge emission and green band are indistinguishable. It is also interesting to note that

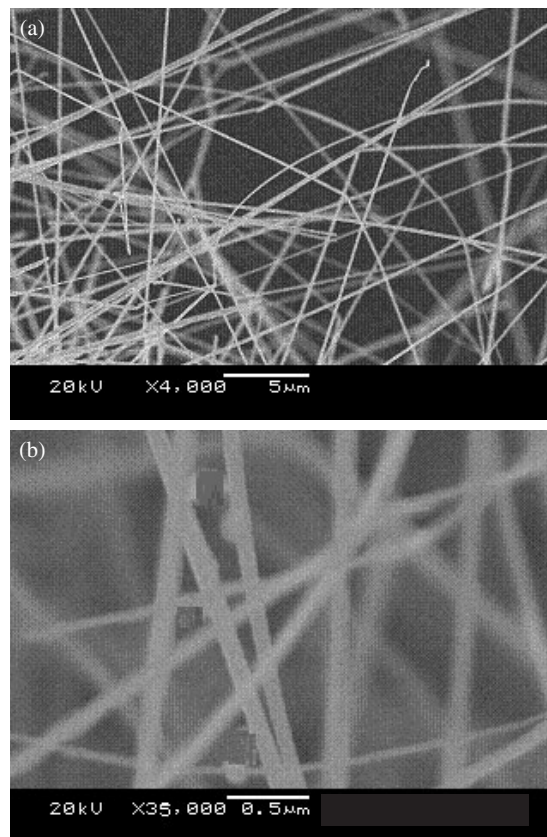


Figure 1. SEM images of ZnO:Cu nanowires with moderate (a) and high (b) magnifications.

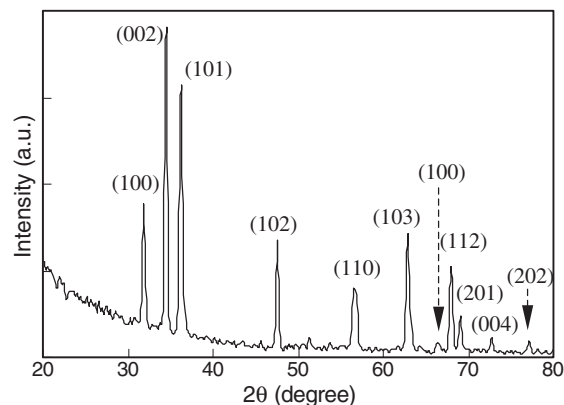


Figure 2. XRD pattern of ZnO:Cu nanowires.

several shoulder peaks are overlapping each other on the broad PL spectrum. It is quite unlikely that these shoulder peaks originate from the fine structure of the excitonic emission because the fine structures, if any, could only be detected at cryogenic temperatures and appear in narrow spacings [27, 33]. It is also unlikely that the peaks originate from interference because the rough morphology of the nanowires (figure 1). The peak at 524 nm with a narrow width is more likely from the transitions between impurity bands.

As copper has been employed as a catalyst for the ZnO nanowire growth, it is possible that the distinct PL spectrum might be due to the doping of copper. To understand the copper doping and the defect state in ZnO nanowires, Raman

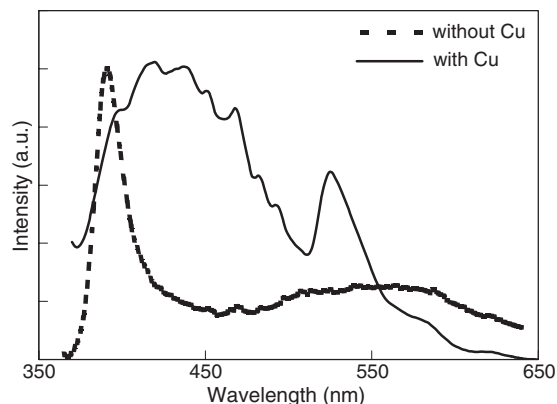


Figure 3. RT-PL spectra of ZnO nanowire fabricated with and without copper as catalyst. The spectra were obtained by 350 nm excitation.

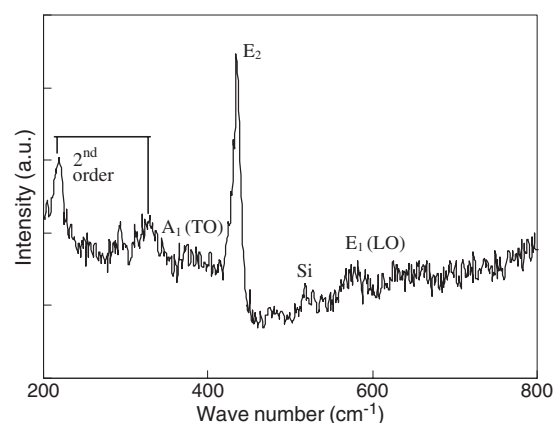


Figure 4. Raman spectrum of ZnO:Cu nanowires.

spectroscopy and XPS were employed. According to group theory, the following fundamental optical modes should exist in a wurtzite ZnO [34–36]: E_2 (low) at 101 cm^{-1} , E_2 (high) at 437 cm^{-1} , A_1 (TO) at 380 cm^{-1} , A_1 (LO) at 574 cm^{-1} , E_1 (TO) at 407 cm^{-1} and E_1 (LO) at 583 cm^{-1} . The low frequency E_2 mode is associated with the vibration of the heavy Zn sublattice, while the high frequency E_2 mode involves only the oxygen atoms [35, 36]. The second order vibrations are at 208 , 334 and $1050\text{--}1200\text{ cm}^{-1}$. From the Raman spectrum of the as-grown ZnO nanowires shown in figure 4, a strong Raman shift signal appears at 437 cm^{-1} due to the E_2 mode of ZnO. Very weak peaks at 584 and 378 cm^{-1} , which correspond to E_1 (LO) and A_1 (TO) modes of ZnO respectively, have also been observed in the Raman spectrum. The other peaks appearing in the low frequency region correspond to the second order vibration modes of ZnO and a weak peak at 520 cm^{-1} originates from the Si substrate. The result further confirms that the nanowires are composed of hexagonal ZnO with few defects. Consistent with the results of XRD, there is no signal corresponding to copper oxide or other copper compounds in the Raman spectrum.

Figure 5 shows the XPS spectrum of the nanowires. All peaks are indexed in the survey spectrum shown in figure 5(a). The peaks at 530.5 eV (figure 5(a)) and 1021.6 eV (figure 5(c)) can be assigned to the binding energy of O $1s$ and Zn $2p^3$ core levels respectively in ZnO [37]. The shoulder in figure 5(b)

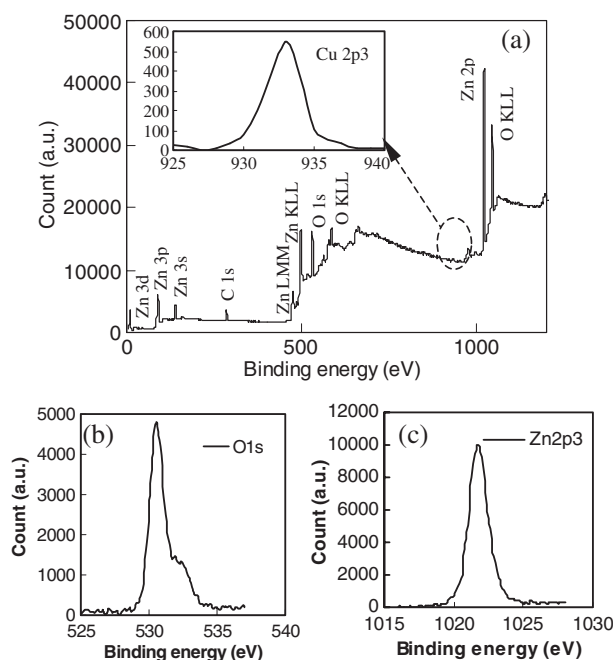


Figure 5. (a) The XPS survey spectrum of ZnO:Cu nanowires with inset Cu $2p^3$ core level spectrum, (b) the XPS spectrum of O $1s$, and (c) the XPS spectrum of Zn $2p^3$.

is caused by adsorbed oxygen [38]. By curve fitting, the calculated ratio of O to Zn is about 0.93 with the adsorbed oxygen deducted. This stoichiometric mismatch indicates that the nanowires are zinc rich and oxygen deficient, though it cannot be detected by the Raman measurement. Consequently, the nanowire must contain oxygen vacancies. A very weak peak is detected at 933.5 eV , which is shown as the inset in figure 5(a). This peak originates from copper doping, which shows a shift of about 1.1 eV relative to the binding energy (932.4 eV) of the Cu $2p^3$ core level in pure copper [37]. It is worthwhile to mention that the peak at 933.5 eV is missing for nanowires grown without the copper catalyst. The quantitative analysis showed that the Cu concentration in the ZnO:Cu nanowire is less than $0.1\text{ at.}\%$. Though the concentration is low, copper plays an important role in the PL spectrum of the ZnO:Cu nanowire. The existence of Cu^{2+} is consistent with the electron paramagnetic resonance (EPR) result reported by Garces *et al* [39]. They obtained the ZnO:Cu sample by annealing a ZnO crystal containing trace amounts of Cu for 1 h at 900°C . Under similar experimental conditions, the ZnO:Cu nanowires in the present paper were grown for 45 min at 850°C . Metal Cu atoms should have been incorporated into ZnO nanowires.

To understand the excitation process, the PLE spectra were measured by monitoring each emission peak in figure 3. Figure 6 shows the PLE spectra of ZnO:Cu nanowires when shoulder peaks of 389 , 418 , 436 , 452 , 468 , 481 , 492 and 524 nm were monitored. When the UV emission peak of 389 nm was monitored, a strong PLE peak appeared at 382 nm that corresponds to the band-edge absorption of ZnO. When the blue and green emission peaks were monitored, the PLE spectra showed two absorption bands: one in the UV region at less than 350 nm and the other one in the violet/blue region between 380 and 480 nm . The peak of the UV absorption band

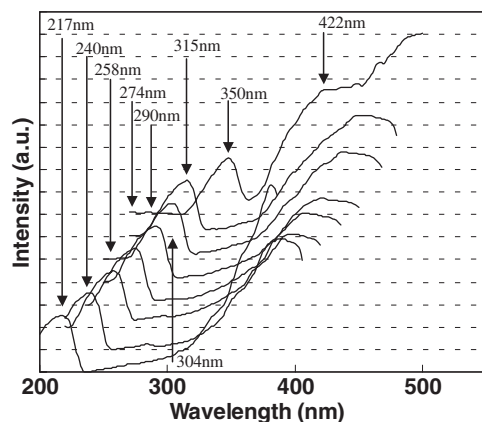


Figure 6. RT-PLE spectra of ZnO:Cu nanowires. The arrows indicate the excitation peaks. From top to bottom, the monitored wavelengths are 524, 492, 481, 468, 452, 436, 418 and 389 nm, respectively. The curves have been relatively shifted in the vertical direction for clarity.

is red-shifted with increase of the monitored wavelength. The violet/blue PLE spectra show broad bands with some shoulder peaks with 524 nm wavelength monitored (the topmost curve in figure 6). The PLE results indicate that the shoulder peaks (figure 3) are related to the energy levels distributed in the bandgap of ZnO.

From figure 6, various absorption peaks at 217, 240, 258, 274, 290, 304, 315, 350 and 422 nm are identified. When the nanowires were excited at these absorption peak wavelengths, various emission spectra were observed. Figure 7 shows the RT-PL spectra of ZnO:Cu nanowire excited at 217, 240, 258, 274, 290, 304, 315, 350 and 422 nm wavelengths respectively. Under the excitation of 217 nm, an emission at 389 nm was clearly observed, which was associated with the band-edge excitonic recombination. Corresponding to different excitation wavelengths, strong blue or green emission peaks were observed on the PL spectra. The shoulder peaks are clearly shown on almost every curve. Though the relative intensity of the shoulder peak varies from curve to curve, the position of the peak is fixed. At an excitation wavelength of 422 nm, two peaks in the yellow and red were observed. This indicates that the various radiation centres from the localized levels, which are the origins of the shoulder peaks, were efficiently excited.

The Cu ion is an active luminescent centre and its emission is sensitive to the environment, such as the doping concentration and defects in the host [40, 41]. Different emission spectra of ZnO:Cu from the ultraviolet to the infrared region have been reported in the powder or the thin film form of ZnO [30–32]. A structured green PL spectrum of ZnO:Cu has been observed in powders and single crystals at low temperature by other researchers [30, 39] and has been attributed to a localized excitation of a Cu^{2+} ion. Consistent with the reported results, the structured PL spectra of ZnO:Cu nanowires are also related to the doped copper ions although our spectra are broader than those reported. Some researchers [30, 39] assumed that the spectral structure corresponded to the replica of the LO-phonon mode of ZnO. However, we obtained the structured spectra at room temperature, at which a phonon replica can hardly have been

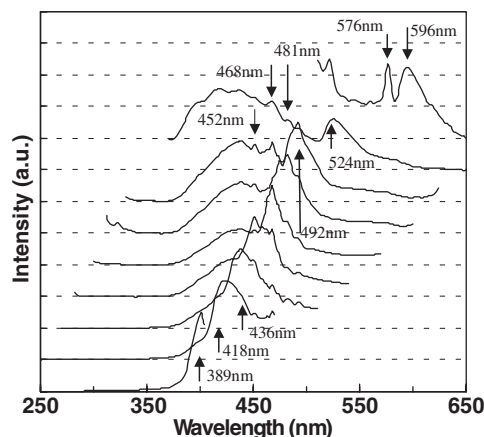


Figure 7. RT-PL spectra of ZnO:Cu nanowires. The arrows indicate the emission peaks. From top to bottom, the excitation wavelengths are 422, 350, 315, 304, 290, 274, 258, 240, and 217 nm, respectively. The curves have been relatively shifted in the vertical direction for clarity.

observed. This indicates a more complicated mechanism of the broad structured spectra we observed than of the reported ones.

It is noted that the RT-PL spectrum of the ZnO:Cu nanowires extends from about 370 to 650 nm. The reported spectra [30, 39] of ZnO:Cu bulk crystals generally show a green band ranging from 430 to 650 nm. In the present case, the properties of the nanowires are affected by the abundant surface states, although the size of nanowires several tens of nanometres in diameter is not significant to generate a strong carrier confinement effect which widens the bandgap. The UV emission from the band-edge excitonic recombination is easy to observe in the one-dimensional nanostructure due to the high surface state density [13]. The expansion in the UV–blue region of the broad RT-PL spectrum is due to the contribution of the UV band as shown in figure 3.

To further understand the spectrum structure and the corresponding energy levels, LT-PL was performed. Figure 8 shows the LT-PL spectrum measured at 4 K. Two discrete peaks at 372 and 438 nm are observed clearly in the UV–blue region. It is obvious that the UV peak at 372 nm originates from the excitonic recombination between the conduction band and the valence band of ZnO. The blue peak at 438 nm is consistent with the location of one shoulder peak (about 436 nm in figure 7) on the RT-PL spectrum. A weak peak at 416 nm can also be observed in the LT-PL spectrum. Other weak peaks are difficult to identify from the noise in this wavelength region. These peaks widen and shift at room temperature due to the phonon scattering, and overlap each other to form a broad spectrum with shoulder structure. A green broad emission band, appearing on the LT-PL spectrum, arises from the oxygen vacancies. The shoulder structure at the leading edge of the broad band is consistent with the reported results by Dingle [30] and Garces *et al* [39], and some of the shoulder peaks are attributed to the replica of the LO-phonon mode at 438 nm which is caused by charge transfer state of the copper ion in ZnO.

The relationship between PL and PLE has demonstrated the existence of multiple energy levels in the forbidden band of the ZnO:Cu nanowire. So the structured PL spectrum

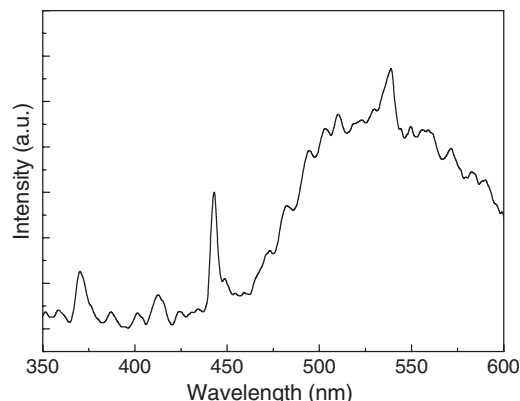


Figure 8. LT-PL spectrum of ZnO:Cu nanowires excited by a UV laser of 325 nm at 4 K.

of the ZnO:Cu nanowire must come from the transitions between the rich energy levels, for example, the energy levels corresponding to the oxygen vacancies, interstitial zinc and copper ions, in the forbidden band. With multiple energy levels in the forbidden band, the excitation and emission processes are very complicated. To identify electron transitions for all the peaks of the PL spectra, the exact energy levels of various defects are required. However, the reported energy levels of various defects differ greatly (see below); furthermore, not all transitions are allowed. So we can only analyse qualitatively the origin of the emission.

The neutral impurities such as interstitial zinc (Zn_i^0) and oxygen vacancy (V_O^0) compose shallow delocalized donor states that are located 0.05 eV below the conduction band [42]. Divalent zinc vacancy (V_Zn^{2-}) and monovalent interstitial zinc (Zn_i^+) provide donor states, which lie below the conduction band from 0.4 to 0.7 eV [42, 43]. The monovalent vacancies of zinc (V_Zn^-) and oxygen (V_O^+) act as acceptors with an energy level of 0.3–0.7 eV and 1.2–1.5 eV respectively above the valence band [42, 43]. A 3d state of Cu^{2+} ($^2\text{T}_2$) composes an electron donor 0.1–0.19 eV below the conduction band [30, 44]. A corresponding acceptor (Cu^+ , h) at about 0.45 eV above the valence band [30, 31] is formed after a Cu^{2+} level is excited due to charge transfer [27–29]. The rich energy levels within the forbidden band of ZnO:Cu are illustrated in figure 9 for better visualization. Because some of the reported energy levels differ greatly, the energy levels shown in figure 9 just illustrate the relative positions. The emission bands with distinct shoulder peaks (figure 7) are associated with electron transfer from the defect state in the forbidden band to the valence band or between the different levels in the forbidden band. As shown in figure 9, the electron transfer from a shallow donor state to a shallow acceptor state or to the valence band is responsible for blue emission; the green peak is related to the deeper states such as transition from a shallow donor state and a deep acceptor state or from a deep donor state to a shallow acceptor state, and the red emission must originate from the recombination between a deep donor level and a deep acceptor level. For example, a blue peak at 436 nm is due to the transfer from the Cu^{2+} ($^2\text{T}_2$) state to the shallow acceptor level (Cu^+ , h) [31] and its replica causes some shoulder structure; a bluish-green peak at 492 nm is due to the recombination of a donor–acceptor pair at the states of

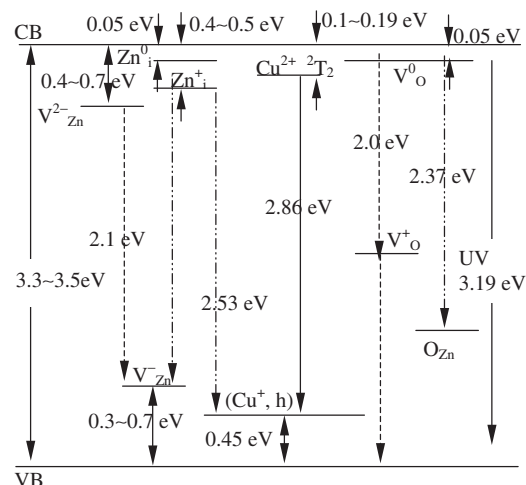


Figure 9. Electron energy level diagram of the defects in ZnO:Cu nanowires. The parameters are collected from [30, 31] and [42–44]. The solid arrows indicate possible blue emission; the dashed arrows indicate possible red emission; and the dot–dash arrows indicate possible green emission.

Zn_i^+ and (Cu^+ , h) [39]; the broad green band peaked at 524 nm results from the recombination of an electron at the bottom of the conduction band or a shallow donor state such as V_O^0 and a hole at an antisite defect O_Zn [43]; and a red peak at 594 nm is attributed to the transfer of $\text{V}_\text{Zn}^{2-} \rightarrow \text{V}_\text{Zn}^-$ [42].

4. Conclusion

Copper-doped ZnO nanowires with wurtzite crystal structure were prepared by copper-catalyst assisted vapour phase transport. Doping of copper was confirmed by XPS. The concentration of copper in ZnO nanowire is less than 0.1 at.%. The defect states of ZnO:Cu nanowires were studied by PL and PLE measurements at room temperature and cryogenic temperature. The defects include vacancies and interstitial atoms of Zn and O, and substitute copper in the zinc lattice. These defects generate rich delocalized and localized donor and acceptor states in the forbidden band of ZnO. The visible emission band with shoulder peaks is related to the transfer from the impurity levels in the forbidden band to the valence band or between the different levels in the forbidden band. Cu^{2+} and its charge transfer state Cu^+ play an important role in the photoluminescent excitation and emission processes. The observed PL spectrum of ZnO:Cu nanowires showed a distinct continuous spectrum from UV to red, which is different from the previously reported ZnO:Cu bulk material.

Acknowledgments

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