Wavelength-Tunable Electroluminescent Light Sources from Individual Ga-Doped ZnO Microwires

Mingming Jiang, Gaohang He, Hongyu Chen, Zhenzhong Zhang, Lingxia Zheng, Chongxin Shan,* Dezhen Shen,* and Xiaosheng Fang*

Electrically driven wavelength-tunable light emission from biased individual Ga-doped ZnO microwires (ZnO:Ga MWs) is demonstrated. Single crystalline ZnO:Ga MWs with different Ga-doping concentrations have been synthesized using a one-step chemical vapor deposition method. Strong electrically driven light emission from individual ZnO:Ga MW based devices is realized with tunable colors, and the emission region is localized toward the center of the wires. Increasing Ga-doping concentration in the MWs can lead to the redshift of electroluminescent emissions in the visible range. Interestingly, owing to the lack of rectification characteristics, relevant electrical measurement results show that the alternating current-driven light emission functions excellently on the ZnO:Ga MWs. Consequently, individual ZnO:Ga MWs, which can be analogous to incandescent sources, offer unique possibilities for future electroluminescence light sources. This typical multicolor emitter can be used to rival and complement other conventional semiconductor devices in displays and lighting.

1. Introduction

With the development of highly integrated optoelectronic circuits, the feature size of the functional devices such as light-emitting devices, laser, and photodetectors has continued to shrink.^[1-3] Therefore, it is crucial to explore novel

Dr. M. M. Jiang, G. H. He, Prof. Z. Z. Zhang, Prof. C. X. Shan, Prof. D. Z. Shen State Key Laboratory of Luminescence and Applications **Changchun Institute of Optics** Fine Mechanics and Physics **Chinese Academy of Sciences** No. 3888 Dongnanhu Road Changchun 130033, P. R. China E-mail: shancx@ciomp.ac.cn; shendz@ciomp.ac.cn G. H. He Graduate University of the Chinese Academy of Sciences Beijing 100049, P. R. China Dr. H. Y. Chen, Dr. L. X. Zheng, Prof. X. S. Fang **Department of Materials Science Fudan University** Shanghai 200433, P. R. China E-mail: xshfang@fudan.edu.cn DOI: 10.1002/smll.201604034

materials with readily controlled size, shape, and composition as well as application compatibility in order to lay a solid foundation for the practical applications of the aforementioned devices.^[4,5] For example, the performance of lightemitting devices are predetermined by the active material properties such as band gap energy, exciton binding energy, doping level, metal-semiconductor interfaces, and so on.^[6-9] As for the conventional light-emitting diodes based on the semiconductor films, their performances have been dominated by the rectification characteristics, as an example, the built-in potential and threshold voltage of the devices are determined by the intrinsic doping levels across the junction. Hence, it is difficult to modulate junction properties easily by changing doping concentration and doping profile, because they are mainly limited by the strong screening effect and the increasing 3D density-of-states with increasing energy.^[1,4,6,7] Meanwhile, such diodes cannot work under the alternating voltage due to its rectification effect. In addition, the emission wavelengths of the traditional light-emitting diodes are also difficult to adjust due to the band gap of the semiconductor. Albeit recent works have demonstrated the predictability and controllability of emission wavelengths of diodes prepared by chemical or electrochemical doping methods,^[7–9] they usually operate in a liquid environment, which greatly

DVANCED www.advancedsciencenews.com

limits the scope of their applications. Therefore, all-solid-state multicolor visible luminescent devices fabricated by a simple method is still lacking.

Owing to a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, ZnO has received considerable attention as a promising material for optoelectronic devices.^[10-22] In particular, ZnO nano/microstructures are ideal material candidates for many novel applications, such as nanoscale multiplexing biosensors, ultraviolet detectors, and electrically driven lasers.^[23–26] To realize highly efficient optoelectronic devices, enormous efforts have been dedicated to fabricate doped ZnO semiconductor nanostructures with reproducible optical and electronic properties, including the controlled incorporation of n-type and p-type dopants, such as Al, Ga, N, Li, P, and so on.^[27-39] To date, the doped ZnO nano/ microstructures are found to have more potential applications, such as microelectronics, chemical and biological sensor and diagnosis, light-emitting displays, catalysis, optical storage, and so on.^[28,33,44,48,49] Of all elements, Ga is the most effective n-type dopant in ZnO since the covalent bond length of Ga-O (1.92 Å) is nearly equal to that of Zn–O (1.97 Å). Meanwhile, different growth temperature of ZnO (950 °C) and Ga₂O₃ (1100 °C) in a vapor-solid progress is conducive to regulating the Ga-doping component.^[33,40-46] Accordingly, Ga-doped ZnO micro/nanostructures have attracted significant attention due to their notable abilities to give resistance modulation when employed as channel layers of electronic devices.^[44,47–49] Unfortunately, the tuning range of emission wavelengths is limited for a single micro/nanostructure, which is insufficient for many applications: meanwhile, active tuning of individual tunable electronics devices remains extremely challenging.

In this work, Ga-doped ZnO:Gamicrowires (ZnO:GaMWs) are synthesized by a catalyst-free, vapor-solid process. The effects of Ga doping on the morphologies, optical properties, and the electrical properties of the ZnO microwires are investigated. Electrically driven visible emissions based on individual ZnO:Ga MWs is achieved. Corresponding wavelength tunable electroluminescence (EL) emissions could be certified as a function of the Ga-component in ZnO:Ga MWs. Therefore, to explore the intrinsic physical mechanism of EL emission, electrical breakdown measurement and metal quasiparticle films decorated microwires are carried out. It is found that Joule heating effect plays a key role in the EL emissions. Meanwhile, the temperature-dependent photoluminescence (PL) is also investigated, which indicates that a redshift of the visible emission is achieved upon increasing Ga doping concentration. Therefore, the emitters based on individual ZnO:Ga MWs offer huge advantages over conventional light sources on account of rectification characteristics, consisting of semiconductor nano- and microwires. Furthermore, this type of wavelength-tunable micro/nanoscale emitters are particularly attractive as an indispensible building block for various ultracompact photonic devices.

2. Results and Discussion

In the synthesis process, upon temperature increasing, ZnO starts to grow with the consumption of Zn, following by the growth of Ga₂O₃. The Zn concentration decreases while the relative Ga concentration increases in the vapor phase. As a result, more amounts of Ga begin to incorporate into the formed ZnO nucleation sites. The mixed vapor of Zn vapor and Ga vapor grows together with cross infiltration and integration occurring around the ZnO nucleation sites to form the Ga-doped ZnO microwires. Therefore, increasing the ratio weight of Ga₂O₃ precursor and the reaction temperature can increase the Ga-doping concentration in ZnO:Ga MWs. To explore the effect of Ga-dopant in ZnO:Ga MWs. four different weight ratio of the reactive sources ZnO: Ga₂O₃:C, such as 10:1:11 (Sample-1), 9:1:10 (Sample-2), 8:1:9 (Sample-3), and 5:1:6 (Sample-4) have been carried out. Detailed information of the synthesis of Ga-doped ZnO microwires can be referred to the Experimental Section and the Supporting Information. Scanning electron microscope (SEM) images for Sample-1, Sample-2, Sample-3, and Sample-4 have displayed in Figure S1 (Supporting Information). Owing to carbothermal reduction without catalyst, Ga-dopant has little impact on the morphology characterization of ZnO:Ga MWs.^[33,43,44] Therefore, a straightforward identification of the distinction still remains elusive at this stage. Sample-2 and Sample-4 were selected as a representative to nominate in the manuscript. Typical SEM images of ZnO:Ga MWs were shown in Figure 1a,b, respectively. Owing to the insets, the ZnO:Ga MWs possess a perfect hexagonal cross-section under higher temperature. In order to obtain high-quality ZnO:Ga MWs with smooth surfaces and perfect hexagonal cross sections, reaction temperature and the growth time can be increased and extended accordingly (Figure S2, Supporting Information). It implies that ZnO:Ga MWs with perfect hexagonal cross section being collected on the Si substrate and on the inside of ceramic boat without catalyst, indicating the vapor-solid growth mechanism.

In order to determine the internal structure and composition of ZnO:Ga MWs, elemental mapping using energydispersive X-ray spectroscopy (EDX) were performed. The quantification of Ga-doping concentration in ZnO:Ga MWs is not accurate when the actual value of the Ga in ZnO is less than 1% by means of EDX, as well as the overlap between Ga K and Zn L in the EDX spectra.^[30,37,43,44] Therefore, a straightforward identification of the distinction still remains elusive at this stage. Sample-2 was selected as a representative to nominate in the manuscript. Figure 1c presents the EDX elemental mappings of Zn, O, and Ga, respectively. Within the spatial resolution of EDX, the distribution of Ga dopants is uniform throughout the microwires. Transmission electron microscopy (TEM) measurements were carried out to further reveal atomically resolved wurtzite ZnO single crystals. The growth axis is along the [0001] direction, as confirmed by the selected-area electron diffraction (SAED) analysis (Figure 1d inset). The interspacing between ZnO and Ga planes is determined to be 0.271 nm, which is slightly larger than that in intrinsic ZnO microwire (0.260 nm), but much smaller than that in intrinsic Ga₂O₃ microbelt (0.470 nm).^[30,33,44] It indicates the lattice expansion due to the substitution of Ga for Zn.^[30,33,44] The X-ray diffraction (XRD) (Figure S3, Supporting Information) and X-ray photoelectron spectra (XPS) (Figure S4, Supporting Information) ADVANCED SCIENCE NEWS



Figure 1. ZnO:Ga MWs: SEM images of ZnO:Ga MWs for a) Sample-2 and b) for Sample-4, the inset demonstrates the corresponding hexagonal cross section of ZnO:Ga MWs. c) Elemental analysis demonstrated that the distribution of the different elements of Zn, O, and Ga detected by EDS mapping according to the Sample-2, with the bar 1 μ m. d) TEM image of ZnO:Ga MWs, the inset illustrates a lattice spacing of 0.271 nm, as well as the SAED pattern demonstrates the single-crystal structure of ZnO:Ga MWs for Sample-2.

measurements were performed on both undoped and Ga-doped ZnO MWs to further verify the successful incorporation of Ga dopants into the ZnO crystalline host lattices.

To characterize the optical properties of the ZnO:Ga MWs, room temperature and temperature-dependent PL measurements have been carried out using a He-Cd laser with an excitation wavelength of 325 nm. As shown in Figure 2a, the strong near band emission located around 375 nm can be attributed to the exciton recombination of ZnO through exciton-exciton collision processes for both undoped and Ga-doped ZnO MWs. No defect emission can be observed for undoped ZnO, indicating the good crystallinity and purity, which is consistent with XRD results. Interestingly, a weak visible emission (≈500 nm) can be observed for the four ZnO:Ga MWs samples (Sample-1-Sample-4), which may originate from the intrinsic defects, such as zinc interstitials (Zn_i), zinc antisite (Zn_O), and/or oxygen vacancies (V_{Ω}) .^[34–36] With increasing Ga-doping amounts, the weak visible emissions change from green (Sample-1) to yellow (Sample-2), orange (Sample-3), and even red (Sample-4). Furthermore, the temperature-dependent PL spectra in the visible range for Sample-2 and Sample-4 are displayed in Figure 2b,c, respectively. For Sample-2, the visible emission peak around 500 nm is attributed to the defect states such as surface defects and oxygen vacancies (V_0) .^[36,37,43,44] And the emission band obviously redshifted as Ga atoms substitute for Zn sites in ZnO crystalline host lattice, which suggests that the V_O-related defect modes decrease due to Ga-doped effects. For Sample-4, the redshift of the visible emission bands can be obtained as well.^[36,37,43,44] As the Ga content increases, the incorporated Ga ions exert a stronger effect on

the optical properties of ZnO:Ga MWs in combination with the surface defect modes changing from V_O-related donor levels to complex V_O-Ga_{Zn} related impurity levels, and finally turning into Ga_{Zn} related impurity bands. Thus, the donor density of states can evolved from the discrete level to impurity band. Both the room temperature and temperature-dependent PL results reveal that the visible emission bands of ZnO:Ga MWs shift toward longer wavelengths when increasing Gaimpurities due to the longer bond strength of Ga–O than that of Zn–O.^[27,30,36,37,44]

An EL device based on an individual ZnO:Ga MW was constructed with two In electrodes fixed at both ends of microwires. **Figure 3**a displays schematic illustration of the electrically driven light emission phenomenon from a biased individual ZnO:Ga MW EL device, with light-emitting region toward the center of microwires. In order to examine the Ga-dopant influence on the EL emissions, electrically driven light-emitting devices based on four different ZnO:Ga MWs (Sample-1–Sample-4) were constructed, and the results are presented in Figure 3b. The EL peaks are located

around 500 nm for Sample-1, 525 nm for Sample-2, 600 nm for Sample-3, and 638 nm for Sample-4, which suggests that the EL emission of ZnO:Ga MWs can be readily tailored by the Gadoping amounts. Figure 3c–f displays the digital photographs of Sample-1 (green), Sample-2 (yellow), Sample-3 (orange), and Sample-4 (red), respectively. The light emission is so intense that it is visible by naked eyes (Movie S7 in the Supporting Information).

Electrical measurements of a individual ZnO:Ga MW device were carried out to explore the physical mechanism of EL emission. In order to highlight the EL emission transition from green lighting to red lighting, only the EL characteristics based on Sample-2 and Sample-4 were selected. Current-voltage (I-V) characteristics of Sample-2 and Sample-4 are demonstrated in Figure 4a (electrically driven light emission for Sample-1 and Sample-3 can be referred to Figures S6 and S7 in the Supporting Information, respectively). The linear I-V curves indicate the formation of Ohmic contacts between the In electrodes and ZnO:Ga MWs. The electrical conductivity is even comparable to tungsten lamps. Essentially, the Ga-doping in ZnO is responsible for the excellent conductive capabilities. In addition, the I-V characteristics is independent of the electrode materials (e.g., Au, In) and the injected charged particles. Interestingly, our devices can also work well under alternating current. The EL spectra under different injected direct currents for Sample-2 and Sample-4 are illustrated in Figure 4b,c, respectively. The EL emission wavelengths are red-shifted with the increasing incident current and finally centered at 525 nm by applying a current of 25.6 mA for Sample-2. Similarly, the EL peaks are also redshifted and finally centered at 638 nm by applying



Figure 2. a) Room temperature PL spectra for undoped ZnO MWs and ZnO:Ga MWs for Sample-1, Sample-2, Sample-3, and Sample-4. Temperature-dependent PL spectra from 55 to 300 K b) for Sample-2 and c) for Sample-4, respectively.

a current of 97 mA for Sample-4. Bright, stable, and localized light emission toward the center of microwires can be observed for both samples as shown in the optical graphs in Figure 4d,e. It is found that the EL emission changes from green to red for Sample-4 when increasing Ga content, which is typically associated with increasing Ga_2O_3 weight ratio in the source materials.

In addition, a single ZnO:Ga MW with a length ≈2 cm was selected to investigate the relationship between In electrodes and electrical resistances of microwires. A series tandem circuits are formed by dividing the single ZnO:Ga MW



Figure 3. a) Schematic illustration of electrically injected ZnO:Ga MW showing light-emitting regions toward the center of the MWs. b) Normalized EL intensities for Sample-1, Sample-2, Sample-3, and Sample-4; c–f) Emission photos taken by a digital camera for Sample-1, Sample-2, Sample-3, and Sample-4, respectively, which indicate that the corresponding light-emitting areas are located along the microwire length direction.



into several segments using In electrodes (marked as A, B, C, and D in Figure 5a). The resistances of the segments defined as AB, BC, and CD are calculated to be $R_{\rm AB} \approx 23$ MΩ, $R_{\rm BC} \approx 19$ MΩ, and $R_{\rm CD}$ \approx 9 MΩ. The corresponding EL sequence of light emission is: AB segment \rightarrow BC segment \rightarrow CD segment, as demonstrated in Figure 5b (the detailed EL emissions can be referred to Movie S7 in the Supporting Information). Consequently, the segments AB, BC, and CD can be formed to design tandem EL devices. Moreover, electronic resistivity values of ZnO:Ga MWs play a critical role in electrically driven light emission. In order to validate EL emission regions toward the center of the ZnO:Ga MWs, the length of EL devices based on the same MW becomes shorter and shorter by means of In electrodes fixed from one end to the other, as shown in Figure 5c. The EL region shrinks with

the shortened wire length, but remains toward the middle site of the active segments (Figure 5d). For the same wire, the longer the length of ZnO:Ga MW, the lower the threshold current for light-emitting, but with little shift the EL emission wavelengths.

To estimate the robustness of ZnO:Ga MWs, instantaneous electrical breakdown measurements were performed.^[7,8] **Figure 6**a displays SEM image of light-emitting device structure with two In electrodes before injecting current. The distinctive ellipse spot along with the length direction of the MW indicates the emission region (Figure 6b). By care-

> fully increasing the incident current that reaches the broken point, instantaneous electrical breakdown of ZnO:Ga MW happens,^[7,8,34,35] which leads to the failure of single crystalline ZnO:Ga MW toward the EL emission regions (Figure 6c). ZnO:Ga MW recrystal-Then the lized from single crystalline to polycrystalline pearl-like structures in the failure process as shown in Figure 6d,e. The discontinuity point (Figure 6f) because of thermionic emission is defined as the broken point and the corresponding current is the broken current. Thus, current heating can be considered as the major factor for failure in the microstructures.^[7,8] The electrical breakdown behavior of ZnO:Ga MWs in metalsemiconductor-metal (MSM) structure is related to the Joule Heating effect. If we keep the injected currents, which below the broken current, unchanged for a period, the applied voltage is constant. Stable and reproducible bright visible light emission from ZnO:Ga MWs devices can be acquired. Therefore, electrically driven

www.small-journal.com

ADVANCED SCIENCE NEWS www.advancedsciencenews.com





Figure 4. a) *I–V* characteristics of single ZnO:Ga MWs based EL devices. b) EL spectra for Sample-2 with injected currents changed from 24.6 to 25.6 mA with EL peaks at 525 nm. c) EL spectra for Sample-4 with injected currents changed from 93 to 97 mA with EL peaks at 638 nm. d) Digital photographs showing the EL patterns along the microwire length direction, with injected currents ranging from 23.0 to 26.0 mA for Sample-2, respectively (scale bar, 250 μ m). e) Digital photographs showing the EL patterns along the EL patterns along the microwire length direction, with injected currents ranging from 88.0 to 96.0 mA for Sample-4, respectively (scale bar, 300 μ m).

light-emitting devices based on individual ZnO:Ga MW is proved to be an effective electrooptical conversion light sources.

Based on the above results, it can be found out that the EL emissions from individual ZnO:Ga MW is associated with Ga-doping concentration and Joule heating effect. To get more insight into the EL mechanism, electrical transport properties of ZnO:Ga MWs in MSM structures were numerically simulated by the thermionic-field-emission model. A single ZnO:Ga MW with diameter $D = 8 \mu m$ and length L = 5 mm was selected for analysis and modeling. The simulation and analysis of electric potential fields and temperature field distributions have been demonstrated in Figure 7a,b, respectively. The potential field distributes along the length of the microwire from the anode to the cathode under the applied voltage. The temperature field distribution profile illustrates that the hottest spot is always located at the center of the wire, coinciding with the location of the maximum temperature.^[7,8,17] For comparative analysis, silver (Ag) quasiparticle nanofilms were evaporated on the ZnO:Ga MWs to figure out the temperature distribution along the wire. Since the emission regions are toward the center of wire (Figure 7c), three regions defined as I, II, and III are selected and their corresponding SEM images are shown in Figure 7d. It is obvious that the Ag quasiparticles nanofilm can be converted into isolated large Ag nanospheres ($D \approx 50$ nm) in the EL emission region (III) due to self-heating effect. By

contrast, Ag quasiparticle film was also evaporated on the sapphire substrate, and then subsequently annealed in a N₂ atmosphere at 400 °C. It is found that the Ag quasiparicles grow into isolated big Ag nanospheres similarly due to the high temperature annealing as shown in Figure 7e. Therefore, current heating effect instead of thermoluminescence plays a key role in EL emissions. The brightest spot of the emission is always located toward the center of the ZnO:Ga MWs, coinciding with the location of the maximum temperature, which is consistent with the simulation analysis. In such a low current regime, ZnO:Ga MWs used as resistance wires, are largely protect from such undesirable vertical heat dissipation due to Joule heating effect. The thermal conductivity of ZnO:Ga MWs at high lattice temperatures is greatly reduced, which also suppresses lateral heat dissipation, so hot carriers localized spatially toward the center of the ZnO:Ga MWs will greatly increase the efficiency and brightness of the light emission. In other words, EL from individual ZnO:Ga MW works in a mode similarly to a thermodynamic heat engine operating with charged carriers injected into the active region by a combination of electrical work and Joule heating (phonons) drawn from the lattice.

The annealing effects of Ag nanoparticles decorated ZnO:Ga MWs emphasize that the recombination of localized electric field can be appeared toward the center of the wires. Therefore, electrons transported in the wire can be accelerated and become energetic electrons. Then the electrons can



Figure 5. a) EL devices based on the same individual ZnO:Ga MW (Sample-2) with different electrode configurations and b) their corresponding EL images (A, B, C, and D represent In electrodes, which form a series tandem circuits among the segments AB, BC, and CD, while the red and blue circles represent the electrode contact regions). c) EL devices with decreased distances between two In electrodes and d) their corresponding EL images showing that the EL regions are located toward the center of the wire.



be efficiently excited from the valence band (VB) to the conduction band (CB) above the Fermi-level, leaving holes in the VB by means of inelastic collision between ZnO:Ga crystalline host lattices and energetic electrons. Thus, electrons injected into the CB are accelerated by the large potential difference. The accelerated electrons may produce excitons by impact excitation, which can decay radiatively. Owing to the localized electric field rearrangement, EL spectra can be recorded as a function of injected currents. The combination of recombinated localized electric field in ZnO:Ga MWs provides a channel to study the interaction of hot electrons being accelerated by localized electric field and electrons situated at crystalline host lattices.[37,43]

Schematic diagram of electrically injected luminescence dynamics process by means of the inelastic collision between ZnO:Ga crystalline host lattices and electrons is presented in Figure 8a, which indicates high kinetic energy derived from the rearrangement of the localized electric field acceleration. The brilliant fireballs are defined as hot electrons being accelerated by localized electric field, and they collide with ZnO:Ga crystalline host lattices by steady inelastic collision. The inelastic scattering of the primary electrons in the crystal leads to the emission of secondary electrons, Auger electrons, and X-rays, which in turn can scatter as well.^[7,16] Electrons can be motivated and transited



Figure 6. SEM image of ZnO:Ga MWs-based device with a MSM structure (Sample-2) a) before injecting current and b) after injected currents. The distinctive ellipse spot indicates the emission region. c) SEM images of the broken ZnO:Ga MW. d,e) SEM images demonstrate the recrystallization process from single crystalline to polycrystalline pearl-like structures. f) SEM image of the fracture site of the broken microwire.

ADVANCED SCIENCE NEWS www.advancedsciencenews.com



Figure 7. Theoretical simulation and analysis of a) electric potential field and b) thermal field distributions based on individual ZnO:Ga MW. c) Images of the strong emission from a Ag-decorated ZnO:Ga MW based EL device (I, II, and III correspond to the electrode contact region, critical region between light emission or not, and light-emitting region, respectively). d) SEM images of the three marked positions in (c): (I) continuous film, (II) quasiparticle film, and (III) isolated Ag nanospheres ($D \approx 50$ nm), which indicates that the Ag particles gradually form into a spherical shape and continue to grow after self-heating in the light-emitting region. SEM images of 50 nm thin Ag film evaporated on the sapphire substrate e) before and f) after 400 °C annealing.

to CB, thereby forming electron-hole (e-h) pairs. Then, nonequilibrium electrons in the CB energy levels after relaxation and transition to impurity bands, therefore, radiative recombination can occur between electrons occupied at impurity band and holes at VB. To confirm the electrically driven lightemitting physical mechanism, the resistances and the biased voltages were taken into account. Take Sample-2 for example (Figure 8b), once the biased voltage exceeds 5 V, the changes are incompatible with the undoped ZnO MWs due to Joule heating effect. The thermal conductivity of ZnO:Ga MWs at high lattice temperatures (heated due to Joule heating effect) is greatly reduced, which also suppresses lateral heat dissipation. In consequence, recombination of localized electric field toward the center of the wire is formed, that is also why hot electrons become spatially localized at the center of the wire, causing greatly increase of the efficiency and brightness of the light emission. In addition, defect spectroscopy of single ZnO MWs has been indicated that there is a characteristic deep defect levels inside the gap at 0.88 eV from the top of the VB, and a defect level next to the bottom of the CB at 0.11 eV (Figure S5, Supporting Information). The presence of these defect levels attribute to Zn_i^{+2} and V_{Zn}^{-2} , respectively.^[35,36] Moreover, it has been verified that the oxygen vacancies are the dominant acceptor defects in as-grown ZnO MWs. In the typical synthesis process with a hypoxia environment, lattice expansion exists due to the substitution of Ga for Zn. Therefore, the EL peak around 500 nm under

low current injection can be attributed to the recombination of electrons located in the Vo related defect level (the green band) and holes located in the $V_{Zn}^{\ -2}$ related defect level (light blue band) (Figure S5, Supporting Information). When increasing the Ga-content in ZnO:Ga MWs, oxygen vacancy related defect modes will become important. Instead, Ga_{Zn} related defect modes will gradually form a new donor level, or even GaZn related impurity band. The process changing from Vo related defect modes to GaZn related impurity band is a pathophysiological course, accompanied by the donor density of states evolving from the discrete level to impurity band and eventually to band tail. In consequence, increasing doping concentration, the wavefunctions of the donors will overlap and result in the formation of an impurity band as shown in Figure 8c. The band broadens with further increase of the doping and eventually merges with the CB, forming a band tail. In this case, the PL and EL occur from the band tail to the VB or acceptor-like states.

According to the literature, the electrically driven light emission from a single semiconductor component (micro/ nanostructure) can be explained by several different scenarios:^[10] a bipolar EL mechanism where the electrons and holes are injected simultaneously into the structures, such as EL emissions from p–n, p–i–n junction;^[1,2] a unipolar impact excitation process by hot carriers (e.g., metalsemiconductor based Schottky junction);^[9,10] and thermal light emission due to Joule heating effect (e.g., graphene).^[20]





Figure 8. a) Schematic diagram of electrically injected light-emitting dynamics process. b) The resistances of ZnO:Ga MW under biased voltages ranging from -15 to 15 V for Sample-2 and -10 to 10 V for Sample-4, respectively. c) Scheme of the light-emitting processes as a result of an impinging energetic electron stream onto host lattices of ZnO:Ga MWs (yellow solid line encircled electrons is defined as impurity band).

For Ga-doped MWs that are treated as metallic wires, once the biased voltage reaches a certain value, the resistances increase exponentially, which helps to explain the change in electron movements during the transport process. The EL spot and electrically injected breakdown behavior a can be well explained by Joule heating mechanism. Nevertheless, thermal heating can also be ruled out as a source by the experimental observations, such as increasing the injected current brings redshift of the EL, increasing Ga-doping concentration in ZnO MWs brings redshift of the EL in the visible bands, together with the enhanced EL under lowtemperature environment.^[6,17,28,36] Therefore, the electrically injected light-emitting mechanism of ZnO:Ga MWs may provide another electrically driven light emission as following: (1) Rearrangement of localized electric field can be formed toward to the center of ZnO:Ga MWs, so accelerated electrons become spatially localized toward the center and inelastic collision with ZnO host lattices; (2) An impact excitation process under electrical transport can generate an abrupt potential drop and a strong electric field due to Joule heating, and the carriers are accelerated to scatter inelastically and produce electron-hole pairs, then the EL emission can occur through the radiative electron-hole recombination; and (3) Different complex defect levels due to the Ga-impurity content in ZnO:Ga MWs can be used to adjust the EL emission wavelengths.

It can be found that Ga dopant acted as electrical dopants can be used to increase n-type electron concentration of ZnO MWs, as well as improving corresponding electric conductivity. Under an external electrical field, collision ionization interactions between injected carriers and crystal host lattice of ZnO:Ga MWs can occur. Due to the single-crystallinity, heat transport induced by Joule heating effect is greatly reduced. Then hot carriers can be formed

by means of the Joule heating effect, therefore become spatially localized toward the middle segment of ZnO:Ga MWs. Meanwhile, this kind of high-energy particles can motivate the transition of electrons from the VB to the CB, thereby forming the nonequilibrium states of hot electrons. Therefore, the light emission can be attributed to the radiative recombination between the electrons situated at impurity bands and the holes situated at the valence band, respectively.

3. Conclusion

In summary, ZnO:Ga MWs with good single-crystalline structures have been successfully synthesized via a one-step CVD process. The Ga-impurity doping is found to improve electrical conductivities of the ZnO microwires, which could be treated as metallic wires. Owing to the fantastic electronic transport properties and the tunable PL wavelengths in the visible range, individual ZnO:Ga MWs based EL devices can serve as electrically driven light-emitting sources with different colors, which is analogous to the incandescent light. In particular, increasing the Ga-doping concentration leads to redshift of the EL emission peaks in the visible range. The EL emission region is localized toward the center of MWs, no matter how the electrode configurations and the distance between two In electrodes change. Electrical breakdown measurement results indicate that Joule heating effects play crucial roles in the lighting phenomenon. Interestingly, the individual ZnO:Ga MW-based EL devices can also function well under alternating current. The EL emitters prepared in this study provide a versatile route to combine the active functionality of the incandescent sources for future optoelectronic devices.



4. Experimental Section

Preparation of ZnO:Ga MWs: The ZnO:Ga MWs were synthesized on a silicon substrate via a traditional chemical vapor deposition method in a horizontal tube furnace. In a typical process, a mixture of ZnO, Ga₂O₃, and graphite powders with a definite weight ratio of 9:1:10 was served as the reactive sources. Cleaned Si (100) substrates (without any catalyst coating) were placed on the ceramic boat to collect the products. The growth temperature was kept at 1120 °C for 45 min.^[27,30,43] During the synthesis process, a constant flow of argon (99.99%) (120 standard cubic centimeters per minute) was introduced into the tube furnace. In addition, to investigate different Ga content in ZnO:Ga MWs, four different weight ratio of the reactive sources of ZnO: Ga₂O₃. graphite powders, such as 10:1:11 (Sample-1), 9:1:10 (Sample-2), 8:1:9 (Sample-3), and 5:1:6 (Sample-4) were prepared.

Device Fabrication: Quartz substrates were cut into pieces of 3 cm \times 2 cm, and ultrasonically cleaned successively in acetone, ethanol, and deionized water for 15 min. Subsequently, a single ZnO:Ga microwire was selected to transfer onto the quartz substrate. Two indium (In) particles were fixed on the both ends of the ZnO:Ga MW as the electrodes. After annealing for 2 min at 200 °C, the ZnO:Ga MW was fixed on the substrate to give a MSM structure-based EL device.

Analysis Instruments: SEM images were recorded using a Hitachi SEM S-3000N/S-4800. XRD 2 θ scans were carried out by employing a Rigaku X-ray diffractometer. XPS were taken for the high-resolution scan of Zn, Ga, and O atoms. The binding energies were calibrated with respect to the C 1s peak at 284.8 eV. The *I–V* characteristics of the devices were measured using a Keithley 2611 system. The PL measurements were performed using a He–Cd laser line of excitation wavelength at 325 nm, and a micro-Raman spectrometer in a backscattering geometry configuration was used to obtain the emission spectra (model: LABRAM-UV Jobin Yvon). The EL spectra of the device were obtained using a Hitachi F4500 spectrometer. The EL phenomena were observed using an optical microscope.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Grant Nos. 11404328, 11574307, 61505033, 11134009, 51471051, 11374296, and 61376054), National Postdoctoral Science Foundation of China (Grant Nos. 2015M580294, 2016T90336), National Science Fund for Distinguished Young Scholars (Grant Nos. 61425021 and 61525404), and 100 Talents Program of the Chinese Academy of Sciences.



- [2] H. Y. Chen, H. Liu, Z. M. Zhang, K. Hu, X. S. Fang, Adv. Mater. 2016, 28, 403.
- [3] X. Liu, L. L. Gu, Q. P. Zhang, J. Y. Wu, Y. Z. Long, Z. Y. Fan, Nat. Commun. 2014, 5, 4007.
- [4] K. Hu, H. Y. Chen, M. M. Jiang, F. Teng, L. X. Zheng, X. S. Fang, Adv. Funct. Mater. 2016, 26, 6641.
- [5] W. Bao, A. D. Pickel, Q. Zhang, Y. Chen, Y. Yao, J. Wan, K. Fu, Y. Wang, J. Dai, H. Zhu, D. Drew, M. Fuhrer, C. Dames, L. Hu, *Adv. Mater.* **2016**, *28*, 4684.
- [6] J. Xue, Y. Zhao, S.-H. Oh, W. F. Herrington, J. S. Speck, S. P. DenBaars, S. Nakamura, R. J. Ram, *App. Phys. Lett.* **2015**, *107*, 121109.
- [7] Z. Y. Yang, D. L. Wang, C. Meng, Z. M. Wu, Y. Wang, Y. G. Ma, L. Dai,
 X. W. Liu, T. Hasan, X. Liu, Q. Yang, *Nano Lett.* **2014**, *14*, 3153.
- [8] C. H. Liu, C. C. Wu, Z. H. Zhong, Nano Lett. 2011, 11, 1782.
- [9] L. J. Yang, S. Wang, Q. S. Zeng, Z. Y. Zhang, T. Pei, Y. Li, L. M. Peng, *Nat. Photonics* **2011**, *5*, 672.
- [10] J. Zhao, H. Sun, S. Dai, Y. Wang, J. Zhu, Nano Lett. 2011, 11, 4647.
- [11] Q. Zhang, J. Qi, Y. Yang, Y. Huang, X. Li, Y. Zhang, App. Phys. Lett. 2010, 96, 253112.
- [12] Q. H. Cui, Y. S. Zhao, J. N. Yao, Adv. Mater. 2014, 26, 6852.
- [13] O. Ilic, P. Bermel, G. Chen, J. D. Joannopoulos, I. Celanovic, M. Soljačić, Nat. Nanotechnol. 2016, 11, 320.
- [14] D. Mann, Y. Kato, A. Kinkhabwala, E. Pop, J. Cao, X. Wang, L. Zhang, Q. Wang, J. Guo, H. Dai, *Nat. Nanotechnol.* 2007, 2, 33.
- [15] J. Misewich, R. Martel, P. Avouris, J. Tsang, S. Heinze, J. Tersoff, Science 2003, 300, 783.
- [16] W. Strek, B. Cichy, L. Radosinski, P. Gluchowski, L. Marciniak, M. Lukaszewicz, D. Hreniak, *Light: Sci. Appl.* 2015, 4, e237.
- [17] X. Wang, L. Zhang, Y. Lu, H. Dai, Y. Kato, E. Pop, *App. Phys. Lett.* 2007, *91*, 261102.
- [18] X. Zhang, L. Song, L. Cai, X. Tian, Q. Zhang, X. Qi, W. Zhou, N. Zhang, F. Yang, Q. Fan, *Light: Sci. Appl.* **2015**, *4*, e318.
- [19] S. E. Han, A. Stein, D. Norris, Phys. Rev. Lett. 2007, 99, 053906.
- [20] Y. D. Kim, H. Kim, Y. Cho, J. H. Ryoo, C.-H. Park, P. Kim, Y. S. Kim, S. Lee, Y. Li, S. N. Park, *Nat. Nanotechnol.* **2015**, *10*, 676.
- [21] F. Pyatkov, V. Fütterling, S. Khasminskaya, B. S. Flavel, F. Hennrich, M. M. Kappes, R. Krupke, W. H. Pernice, *Nat. Photonics* **2016**, *10*, 420.
- [22] V. E. Dorgan, A. Behnam, H. J. Conley, K. I. Bolotin, E. Pop, Nano Lett. 2013, 13, 4581.
- [23] J.-J. Greffet, R. Carminati, K. Joulain, J.-P. Mulet, S. Mainguy, Y. Chen, *Nature* **2002**, *416*, 61.
- [24] J. Bao, M. A. Zimmler, F. Capasso, X. Wang, Z. Ren, *Nano Lett.* **2006**, *6*, 1719.
- [25] M. Ding, D. Zhao, B. Yao, B. Li, Z. Zhang, C. Shan, D. Shen, J. Phys. D: Appl. Phys. 2011, 44, 075104.
- [26] B. Zhao, M.-M. Jiang, D.-X. Zhao, Y. Li, F. Wang, D. Z. Shen, Nanoscale 2015, 7, 1081.
- [27] G. C. Park, S. M. Hwang, J. H. Choi, Y. H. Kwon, H. K. Cho, S.-W. Kim, J. H. Lim, J. Joo, *Phys. Status Solidi A* 2013, 210, 1552.
- [28] J. Kim, G. V. Naik, A. V. Gavrilenko, K. Dondapati, V. I. Gavrilenko, S. Prokes, O. J. Glembocki, V. M. Shalaev, A. Boltasseva, *Phys. Rev. X* 2013, *3*, 041037.
- [29] B. Cao, M. Lorenz, M. Brandt, H. von Wenckstern, J. Lenzner, G. Biehne, M. Grundmann, *Phys. Status Solidi RRL* 2008, 2, 37.
- [30] W. Liu, F. Xiu, K. Sun, Y.-H. Xie, K. L. Wang, Y. Wang, J. Zou, Z. Yang, J. Liu, J. Am. Chem. Soc. 2010, 132, 2498.
- [31] Y.-J. Doh, K. N. Maher, L. Ouyang, C. L. Yu, H. Park, J. Park, Nano Lett. 2008, 8, 4552.
- [32] M. L. Brongersma, N. J. Halas, P. Nordlander, Nat Nanotechnol. 2015, 10, 25.
- [33] B. Zhao, F. Wang, H. Chen, Y. Wang, M. Jiang, X. S. Fang, D. X. Zhao, *Nano Lett.* **2015**, *15*, 3988.
- [34] M. C. Jun, S. U. Park, J. H. Koh, Nano Res. Lett. 2012, 7, 789.

Y. J. Li, X. Xiong, C. L. Zou, X. F. Ren, Y. S. Zhao, Small 2015, 11, 3728.



- [35] M. Villafuerte, J. Ferreyra, C. Zapata, J. Barzola-Quiquia, F. likawa,
 P. Esquinazi, S. Heluani, M. de Lima Jr., A. Cantarero, J. Appl. Phys.
 2014, 115, 133101.
- [36] W. Ruane, K. Johansen, K. Leedy, D. C. Look, H. von Wenckstern, M. Grundmann, G. C. Farlow, L. J. Brillson, *Nanoscale* 2016, *8*, 7631.
- [37] S. J. Young, C. C. Yang, L. T. Laia, J. Electrochem. Soc. 2017, 164, B3013.
- [38] L. C. Yang, R. X. Wang, S. J. Xu, Z. Xing, Y. M. Fan, X. S. Shi, K. Fu, B. S. Zhang, J. Appl. Phys. 2013, 113, 084501.
- [39] S. S. Shinde, K. Y. Rajpure, Mater. Res. Bull. 2011, 46, 1734.
- [40] Y. Wei, P. Liu, K. Jiang, L. Liu, S. Fan, App. Phys. Lett. 2008, 93,
- 023118. [41] T. Westover, R. Jones, J. Huang, G. Wang, E. Lai, A. A. Talin, *Nano Lett.* **2008**, *9*, 257.
- [42] S. Deshpande, J. Heo, A. Das, P. Bhattacharya, *Nat. Commun.* **2012**, *4*, 216.

- [43] C. L. Hsu, S. J. Chang, Small 2014, 10, 4562.
- [44] G.-D. Yuan, W.-J. Zhang, J.-S. Jie, X. Fan, J.-X. Tang, I. Shafiq, Z.-Z. Ye, C.-S. Lee, S.-T. Lee, *Adv. Mater.* **2008**, *20*, 168.
- [45] C. Xu, M. Kim, J. Chun, D. Kim, Appl. Phys. Lett. 2005, 86, 133107.
- [46] M. J. Zhou, H. J. Zhu, Y. Jiao, Y. Y. Rao, S. K. Hark, Y. Liu, L. M. Peng, Q. Li, J. Phys. Chem. C 2009, 113, 8945.
- [47] C. H. Liu, C. C. Wu, Z. H. Zhong, Nano Lett. 2011, 11, 1782.
- [48] P. C. Yeh, W. C. Jin, N. Zaki, J. Kunstmann, D. Chenet, G. Arefe, J. T. Sadowski, J. Dadap, P. Sutter, J. Hone, R. M. Osgood Jr., *Nano Lett.* 2016, 16, 953.
- [49] Y. B. Zhao, H. Hu, X. X. Yang, D. P. Yan, Q. Dai, *Small* **2016**, *12*, 4471.

Received: December 4, 2016 Revised: January 17, 2017 Published online: March 7, 2017