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Ultraviolet electroluminescence from Au-ZnO nanowire Schottky type light-emitting diodes

Fan Gao,[1,2,3] Dakuan Zhang,[2] Jianyu Wang,[2] Huabin Sun,[2] Yao Yin,[2] Yun Sheng,[2] Shancheng Yan,[4] Bo Yan,[1] Chenghua Sui,[1] Youdou Zheng,[2] Yi Shi,[2,a)] and Jianlin Liu[3,a)]
[1]*College of Science, Zhejiang University of Technology, Hangzhou 310023, China*
[2]*Key Laboratory of Advanced Photonic and Electronic Materials and School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, China*
[3]*Quantum Structures Laboratory, Department of Electrical and Computer Engineering, University of California at Riverside, Riverside, California 92521, USA*
[4]*School of Geography and Biological Information, Nanjing University of Posts and Telecommunications, Nanjing 210046, China*

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Ultraviolet electroluminescence from Schottky type LED device is demonstrated. The device prototype is based on Schottky junctions formed between Au and the top ends of ZnO nanowire arrays. Rectifying current-voltage characteristics are observed, and three different charge transport mechanisms are discussed in detail. Excitonic electroluminescence at around 380 nm is detected at high forward bias and the linear relationship between intensity and current suggests a LED device performance. The observation of LED signals from the simple Schottky structure provides a potential supplement to the category of ultraviolet LED devices. *Published by AIP Publishing.*
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Ultraviolet light-emitting diodes (UV LEDs) have been explored intensively for their applications in solid-state lighting,[1–3] information storage,[4] UV photolithography,[5,6] medical diagnostics,[7,8] and so on. As one of the most promising light emitting materials in UV wavelength, ZnO has been highlighted for its high crystalline quality and large exciton binding energy of 60 meV at room temperature (RT).[9–12] Although significant accomplishments have been attained in group III-nitride-based UV LEDs in the past decades,[13,14] the pursuit of high-efficiency and cost-saving excitonic LEDs based on ZnO material never ceases. UV LEDs have been realized in ZnO p-n junction structures,[15–17] in which p type and n type segments provide hole and electron injections, separately. However, problems such as p type doping difficulty in ZnO and large lattice mismatch in heterostructures degrade device performances, which obstruct the development and application of ZnO-based UV LEDs. Alternative metal-insulator-semiconductor (MIS) structure has been demonstrated in an Au-MgO-ZnO LED.[18] In this device, the insulator layer of MgO, which is essential for the carrier accumulation at the interface and UV light emission, requires deliberate fabrication procedures. Further exploration of new strategy is necessary for the development of high-performance ZnO UV LEDs from economic and application standpoints. Here, we propose a Schottky LED device prototype based on Au-ZnO bundle nanowires. Different from the MIS structure, the metal-semiconductor (MS) composite avoids deliberate fabrication of the insulator layer, which provides potential and cost-effective solution with simplistic material and fabrication requirements. Also, the unique optoelectronic properties of ZnO, especially its large exciton binding energy at RT, greatly benefit the excitonic light emission from the Schottky type LED devices.

The schematic and fabrication procedure of the device prototype are presented in Figure 1. First, it is the growth of ZnO nanowires. As shown in Figure 1(a), an n type ZnO thin film was grown on Si (100) substrate by plasma-assisted molecular-beam epitaxy (MBE), which was used as a seed film substrate. Then, the substrate was transferred to a chemical vapor deposition (CVD) furnace for ZnO nanowire growth, as shown in Figure 1(b). Undoped ZnO bundle nanowires were grown on top of the substrate by vapor-solid (VS) mode. During growth, the seed layer substrate was placed in the center of the tube and zinc powder (99.999% Sigma Aldrich) source was put in a silica bottle 1 cm away at the upstream side. The furnace was flown continuously by 600-sccm nitrogen and a flow of 300-sccm argon diluted oxygen (0.5%) was introduced as reaction gas. The temperature and

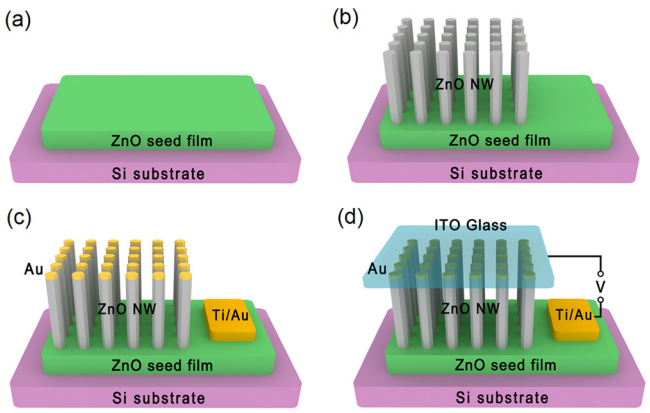

FIG. 1. Sketch of the fabrication process of Au-ZnO nanowire Schottky LED prototype. (a) Deposition of ZnO seed layer on Si (100) substrate by plasma-assisted MBE. (b) CVD growth of ZnO nanowire arrays on top of the seed layer by VS mode. (c) Deposition of Au of 10 nm on the top ends of ZnO nanowires, forming Schottky contact at the interface. Ti/Au (10 nm/100 nm) is deposited as the bottom contact. (d) Application of a piece of ITO glass as the top contact of the device.

a)Authors to whom correspondence should be addressed. Electronic addresses: yshi@nju.edu.cn and jianlin@ece.ucr.edu

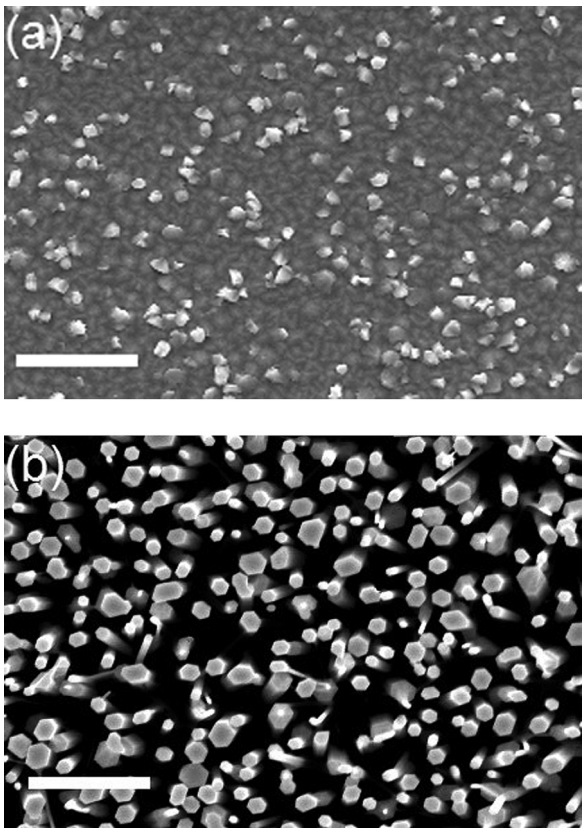

FIG. 2. SEM images of (a) ZnO seed layer substrate and (b) undoped ZnO nanowires grown on top. Hexagonal cross sections are obvious. The scale bars of Figures 2(a) and 2(b) are 2 μm.

time was 515 °C and 40 min for the nanowire growth, respectively. Then, it is the LED device fabrication based on the nanowires and substrate. As shown in Figure 1(c), Au of 10 nm was first deposited on the top ends of ZnO nanowires to form Schottky type metal-semiconductor contact. Subsequently, Ti/Au (10 nm/100 nm) layer was deposited on the ZnO thin film by e-beam evaporation as the bottom contact of the device. The nanowire region was covered by an aluminum foil during this process. At last, a piece of ITO glass was clamped as top contact in Figure 1(d) and the bias was applied to operate the LED device.

Figures 2(a) and 2(b) show scanning electron microscopy (SEM) images of the ZnO seed layer and undoped ZnO nanowires grown on top, respectively. As seen from Figure 2(a), nano-columnar grains are observed on the seed layer surface, which is due to the oriented nucleation process during growth as a result of the large lattice mismatch between ZnO and Si substrates.[19] The top view of as-grown ZnO nanowire arrays in Figure 2(b) shows that the top ends are hexagonal. The nanowires are vertical with respect to the substrate, following the *c*-axis preferential growth direction of the underneath seed film.[20] The diameter and length of the nanowires are on average 300 nm and 3 μm, respectively. The nonuniformity of the nanowires is observed, which originates from the size diversity of ZnO grains on the seed film.

Optical properties of as-grown ZnO nanowires are studied by performing the low-temperature photoluminescence (LTPL) measurement, and the result is shown in Figure 3. The experiment was conducted at 16 K, and a 325-nm He-Cd laser was used as the excitation source. In the spectrum, a

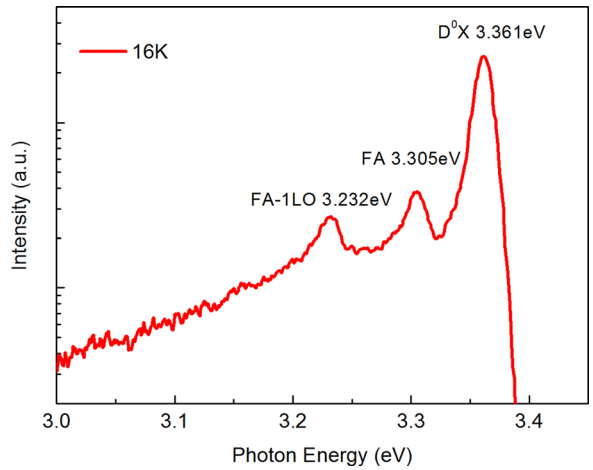

FIG. 3. Low-temperature photoluminescence (LTPL) spectrum of as-grown ZnO nanowires measured at 16 K. Three peaks at 3.361 eV, 3.305 eV, and 3.232 eV are observed.

dominant donor bound exciton (D^0X) peak at 3.361 eV is observed, which is the signature of ZnO with n type behavior and commonly assigned to the I_8 transition in ZnO material.[21,22] The other two peaks at 3.305 eV and 3.232 eV were reported previously, which are attributed to the free electron to acceptor (FA) emission and its first phonon replica of FA (FA-1LO), respectively.[23–25] These acceptor-related emission peaks originate from unintentional incorporation of nitrogen species in the nanowires during the growth. The presence of the phonon replica peak is a proof of good optical quality of the ZnO nanowires since these emissions would have been too weak to be observed if the material contains a great deal of nonradiative recombination centers that reduce the radiative recombination efficiency.

Figure 4 shows current-voltage (I-V) characteristics of the LED device prototype. The I-V curves in semilogarithmic and linear scales are shown in Figure 4(a), which were measured from reverse to forward bias without illumination. The curves exhibit rectifying characteristics, suggesting the formation of Schottky contact[22,26] at the interface of Au and ZnO nanowires. To further study the charge transport mechanisms, the logarithmic plot of the I-V data under forward bias is shown in Figure 4(b). Three distinct regions with different conduction mechanisms are evident. At low voltages in region I, the I-V relation follows a linear dependence ($I \sim V$), indicating that tunneling is the dominant charge transport mechanism. The carrier injection from the electrodes into the semiconductor is quite limited under low biases. Region II shows that the current increases exponentially with the increase in voltage ($I \sim \exp(cV)$) and the ideality factor is derived to be 2.3; thus, the transport mechanism is dominated by recombination tunneling.[27,28] At high voltages in region III, a power law relation is followed ($I \sim V^2$), which reveals a space-charge limited current (SCLC) transport mechanism. The SCLC transport shall be associated with the charge traps distributed in both ZnO nanowires and thin film regions.[29,30]

The LED device was then operated under DC forward bias, and the electroluminescence (EL) spectra are presented in Figure 5. The measurement was conducted by using a homebuilt setup including an Oriel monochromator and a

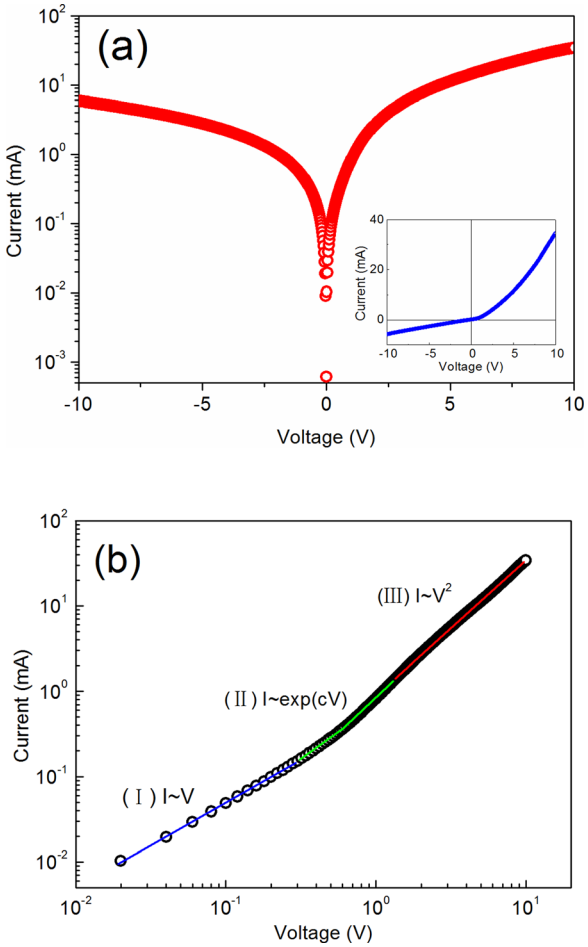

FIG. 4. Current-voltage (I-V) characterization of the Schottky junction based LED device. (a) I-V curve in semilogarithmic scale measured without illumination. Typical rectifying behavior is evident. The inset is the I-V result in linear scale. (b) Log-log plot of the I-V data under forward bias. Three distinct regions, representing three different conduction mechanisms are illustrated.

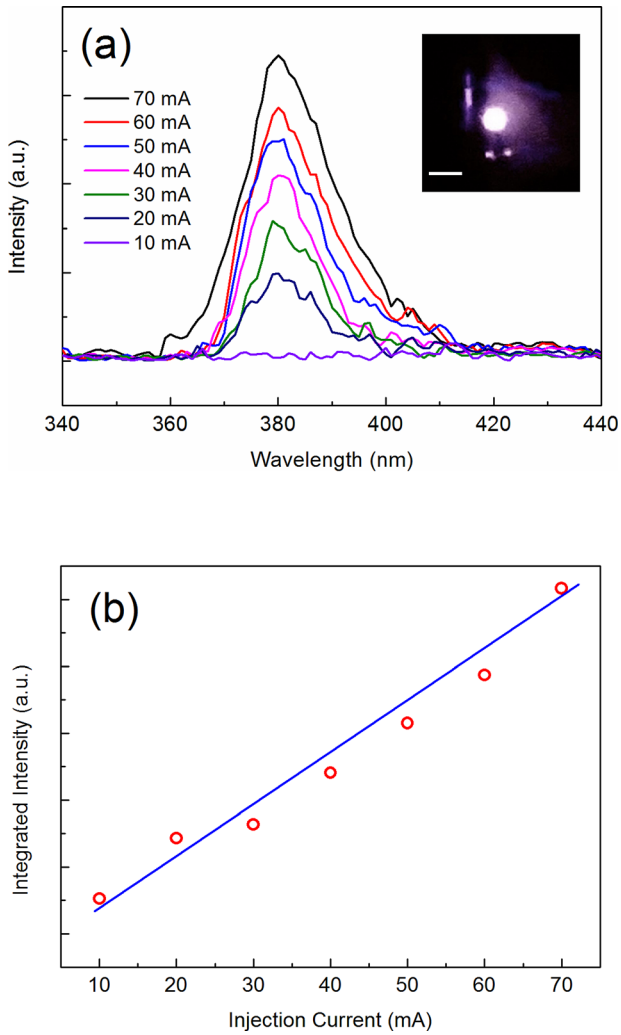

FIG. 5. (a) EL spectra of the Schottky LED device operated with injection currents from 10 mA to 70 mA. UV emission peaks centered at 380 nm are observed, which are from the excitonic luminescence of ZnO. The inset is the light emission photo of the device operated at 70 mA and the scale bar is 1 cm. (b) Integrated intensity of the spectrum as a function of injection current. The relation follows a linear dependence, indicating a LED device performance.

lock-in amplifier with a chopper. Figure 5(a) exhibits the EL spectra of the device operated from 10 mA to 70 mA. At an injection current of 10 mA, there is only background noise shown in the spectrum. Broad UV emission peak centered at 380 nm starts to appear at 20 mA, corresponding to the excitonic luminescence of ZnO.[31,32] Afterwards, the emission intensity increases monotonically as the injection current increases from 20 mA to 70 mA. Figure 5(b) shows a linear relationship between integrated output intensity and injection current, suggesting a typical LED device performance.[18] The red hollows represent calculation data from the spectra, and the blue line is plotted to guide eyes. The inset in Figure 5(a) is the luminescence image of the LED device operated at 70 mA, which exhibits the light emission process in the Au-ZnO nanowire Schottky device.

Finally, we briefly discuss the mechanism of light emission from Au/ZnO nanowire Schottky diode. As sufficiently high forward bias is applied on the Au metal, the Fermi level of Au metal is pushed downwards and the energy band of ZnO nanowire bends upwards sharply, creating a narrow triangular energy barrier for hole tunneling near the Au-ZnO interface. While majority carriers are electrons, some holes can directly tunnel to the valence band of ZnO from the positive pole. These holes interact with electrons in the ZnO nanowires by forming excitons and emitting light readily through excitonic EL.

In conclusion, a Schottky type LED prototype based on Au-ZnO nanowires is demonstrated. The MS device structure is based on vertical ZnO nanowires and Au of 10 nm deposited on the top ends, forming Schottky junction at the interface. Electrical properties of the device are studied by the I-V characterization and a Schottky type rectifying behavior is observed. Light emission from the Schottky device is dominated by free exciton emission at around 380 nm, which is confirmed by the EL measurements. This study provides a Schottky type LED structure with simple material and fabrication requirement, which has potential to be an economical alternative to the p-n and MIS structure UV-LEDs.

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