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Colour electroluminescence with end light-emitting from ZnO nanowire/polymer film

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Abstract. The ZnO nanowires with polymer film were self-assembly grown on n-type (111) plane of the silicon substrate using polymer assisted complexing soft-template process through a simple polymer complexation and low-temperature oxidizing-sintering, which have smooth top and fine hexagonal columnar structure with average length of about 6 μm and the diameter of about 40 nm. These columnar structured ZnO nanowires had strong near-band ultraviolet emission at ~383 nm and blue electrically driven emission at ~ 400 nm with a relatively low turn-on voltage, as well as a typical diode characteristic property at room temperature. In particular, these structures, being of high aspect ratio and small tip radius of curvature, may possess a good amplified stimulated emission and lasing property. These results suggested a potential application of ZnO nanowire/polymer film as electroluminescence flat panel displays or illuminations in the future.

1. Introduction
One-dimensional (1D) zinc oxide which is an n-type wide band-gap semiconductor nanomaterial with an energy gap of 3.37 eV and high exciton binding energy of ~ 60 meV, has attracted much attention for their unique optical, electronic, and mechanical properties as well as their potential applications in nanodevices. Nanocolumns are structures particularly well suited to lasing and directed luminescence because they can form individual Fabry-Pérot cavities and combine lateral confinement with an appreciable grain length. In particular, it is expected that they would possess a good electron field emission property due to their high aspect ratio and small tip radius of curvature. Therefore, ZnO-based 1D nanostructure could be an appropriate alternative to carbon nanotube (CNT) for field emission displays or electroluminescence flat panel displays. The field-emission properties of ZnO nanowire arrays, and light-emitting diode based on ZnO have been attempted recently, and those pioneer works demonstrated that the micro/nano-structure determines the properties of a given nanomaterial with respect to its specific application. The peculiar geometrical morphologies of ZnO ordered nanostructures may yield emission are achieved. Furthermore, measurements of electroluminescence can reflect the native band structure of the sample, contributing significantly to fundamental research.
The realization of the controlled oriented growth of ZnO nanowires always must be taken into account before the real large-scale ZnO nanowires-device fabrication. Self-assembly of 1D ZnO nanostructures offers an available approach for the problem. In this paper, based on the polar growth behavior of ZnO and polymer grid backbone localization model that we reported before, we prepared single crystalline ZnO nanowires with polymer film on silicon (111) substrate and the luminescence properties have been evaluated.

2. Experimental section

The ZnO nanowires were fabricated on Si (111) wafer by a simple polymer-assisted complexing nucleation method as we reported before. The grown material was characterized by FE-SEM, and high-resolution transmission electron microscopy (HR-TEM). Photoluminescence (PL) measurement was performed at room temperature under the 325 nm UV fluorescent light excitation using a Hitachi F-4500 fluorescence spectrophotometer with a Xe lamp. Electroluminescence (EL) measurements were performed with diode structure in the atmosphere at room temperature. The electroluminescent device structure was ITO/(ZnO/polymer)/Si(111)/Cu.

3. Results and discussion

3.1. Morphology and crystal structure of the nanowires

The morphology of the samples grown on a Si (111) wafer is shown in figure 1a. These ZnO nanowires nearly vertically grew on the substrate, with a straight shape and a uniform diameter. The average length of the nanowires is about 6 µm and diameter of about 40 nm. The further details of morphology and atomic structure of the nanowires stripped from silicon substrate were obtained by using high resolution TEM (HRTEM). It can be seen from figure 1b that a single ZnO nanowire exhibits continuous lattice fringes, which demonstrated that the nanowire is of single crystal with wurtzite structure and its growth direction is along [0001] c-axis.

Figure 1. (a) A FE-SEM image of a well-aligned ZnO NW array; (b) HRTEM micrograph and corresponding selected-area electron diffraction pattern of a single ZnO nanowire.

Figure 2 shows an energy dispersive X-ray (EDX) spectrum of the nanowires on a silicon substrate. It reveals the presence of the Zn, O and Si. Apparently, these nanowires are composed of ZnO and rich in oxygen atoms. These results exhibit that our technique has the advantages over the other reported methods, because it solved the problem of the prevalent defect configuration which is a deficiency in O at the surface of ZnO nanowires.
3.2. Polymer-assisted self-assembling model

The above obtained results can be explained by the polymer-assisted self-assembling preparation of ZnO nanowires via a novel process based on polymer grid backbone localization model\(^\text{17}\). The polymer soft-template controlled the nucleation of ZnO as and further growth into the nanowires along the [0001] direction. By using clingy polymeric membrane as self-assembling complex medium and the polar polymer (such as PVA and PAM) as suspending agent and surfactant, the surface tension of the polymer solution reduced and consequently the wettability to the substrate increased. This makes the ZnO nanowires well attached on the surface of silicon substrate. Besides, the adhesive strength between the ZnO nanowires and the substrate surface increased more efficiently by the later sintering. Therefore, the ZnO nanowires can’t peel from the substrate, ensuring their photoelectricity application well and stable. This technique has solved the lattice mismatch problem of the ZnO to silicon and is more economically feasible. Further more, the ZnO nanowires are rich in oxygen atoms, which obviously resolved the problem of a deficiency in oxygen at the surface of nanowires ever reported. This makes the practical real application of the 1D ZnO nanomaterials as emission nanodevices capable break through in the future.

3.3. Photoluminescence and electroluminescence

The room-temperature photoluminescence spectrum from the ZnO nanowires excited with a wavelength of 325 nm, exhibit a sharp strong UV emission of about ~ 383 nm related to the band to band transition, and a weak blue emission of around 445 nm (shown in figure 3a). The near band-edge UV emission might be attributed to a well-known recombination of free excitons, and the blue emission might result from the oxygen vacancies and zinc interstitial defects in the ZnO nanomaterials. However, different from the PL spectrum, strong peak appears at 400 nm (corresponding to the energy of 3.11 eV) in the electroluminescence (EL) spectrum of the ZnO nanowires on silicon substrate as shown in figure 3b. With increasing alternating current, the intense blue emission was observed indeed by naked eye and the whole surface emission are highly homogeneous according to the photograph inserted in figure 3b. The luminescence mechanism is probably due to the recombination of the localized exciton emission. It could be deduced that the facets of regularly arrayed hexagonal nanowires form natural micro-cavities and these nanowire-crystallites confine the centre-of-mass motion of excitons. As a result of the quantum size effect, the oscillation strength of the excitons, which is favored to the radiation recombination of exciton at room temperature, is largely enhanced. The electronic transport for electrons and holes must occur with only a very small reduction in carrier energy over the transport path length, which corresponds to the nanowire height, that is, ~6 µm.
**Figure 3.** The PL spectrum (a) and EL spectrum (b) of the ZnO nanowires/polymer film on silicon substrate (the transparent anode image of the electroluminescence is shown in the inset picture).

Figure 4a shows the characteristics of emission current density versus applied electric voltage for the several times bias voltage sweeps. Almost identical $J-E$ curves were obtained, which indicates a better stability and repetitiveness of the emission process from our samples. The current-voltage measurements and corresponding oscillograph image in figure 4b at room temperature showed a typical diode characteristic. Electroluminescence band of the ZnO nanowires device is located at the blue–violet region. The better emission homogeneity of the sample comes from a large number of ZnO nanowires as emitters on the surface of the nanowire end. The turn-on field, defined as the electric field which is required to produce a current density of $10 \mu A/cm^2$, is estimated to be about 0.9 V/\mu m. Obviously, the turn-on field and threshold field are much lower than those of the aligned ZnO nanowires. Low turn-on field of the sample is attributed to the sharp geometry morphology of the corners of the nanowire ends. These peculiar geometrical morphologies of ZnO nanostructures yield a large enhanced emission. It follows from these results that columnar structures of ZnO nanowires are well suited to lasing and directed luminescence due to their individual Fabry-Pérot cavities and the combined lateral confinement at an appreciable grain length. In particular, these structures, being of high aspect ratio and small tip radius of curvature, possess a good amplified stimulated emission and lasing property. As the exciton binding energy in ZnO is of 60 meV, this makes exciton stable and provides opportunities for making highly efficient lasers operable at room-temperature.

**Figure 4.** The current-voltage characteristics of the vertically ZnO nanowire/polymer film: (a) emission current density versus applied electric voltage and (b) corresponding temporal oscillograph image.

It is found that colour emission is achieved with low voltage, and change into yellow, violet/blue or even white emission with higher voltage. The reason may be that with increase of voltage, the blue
emission is absorbed by the white’s, or the blue emission stimulated the longer wavelength light such as yellow and white light. Anyhow, it is clear that the colour of the electroluminescence can be controlled by the applied voltage. These results also exhibit the potential application of ZnO nanowires as solid-state electroluminescence flat panel displays or illuminations in the future.

4. Conclusions
In conclusion, the ZnO nanowires have been fabricated vertically on silicon substrate by a polymer-assisted complexing soft-template method. The intense room-temperature blue-electroluminescence of the ITO/(ZnO/polymer)/Si(111)/Cu LED was observed indeed by naked eye. In the hybrid system, the polymer is used not only as binder in the device of LED, but also a dispersion medium in the luminescence layer, which stabilize the ZnO nanowires and passivate the surface of ZnO nanocrystals and therefore prevent them from aggregating and quenching of luminescence. By controlling the content and dimension of the ZnO nanowires in the polymer matrix, the emission strength and the emission wavelength could be adjusted. These results also indicated that the ZnO nanowires might be a promising candidate as electroluminescence flat panel displays or illuminations in the future.

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