Low operation voltage in AC type inorganic electroluminescence devices using ZnO nanorods layer

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Abstract: *Inorganic AC-EL device including ZnO nanorods layer as an intermediate layer for lowering of operation voltage have been newly developed. The device structure is Al/thick $BaTiO_3$/ZnS:Mn/ZnO-nanorods/ SiO_2/ITO/Glass. The ZnO nanorods layer was grown by chemical vapor deposition method (CVD) combined with laser ablation of Mn. The obtained ZnO layer was composed of many well-aligned and hexagon-shaped nanorods with a flat tip vertically to the substrate. The mean diameter and length of ZnO nanorods are 100-300 nm and 2.5 µm, respectively. The EL device using the as-deposied ZnO nanorods layer and the device using the ZnO nanorods layer annealed in atmosphere of O_2 at 600°C for 30 min were investigated. The EL characteristics are measured by 1kHz sinusoidal driving voltage. The threshold voltage of the device using an as-deposited ZnO nanorods layer was considerably lowered to 115 V from 187 V for the device without a ZnO nanorods layer, although the maximum luminance was reduced by about 80 %. On the other hand, the device using an annealed ZnO nanorods layer shows no-improvement in the threshold voltage. Thus, the luminance-voltage characteristics were sensitive to properties of ZnO nanorods.*

Keywords: inorganic; electroluminescence; zinc oxide; nanorod; field enhancement; operation voltage.

Introduction

ZnO is a well-known II-VI compound semiconductor with a wurtzite structure. ZnO has a wide band gap of 3.37 eV, large excitonic binding energy of 60 meV, and strong piezoelectric characteristics. For these properties, this material has been extensively studied for a variety of applications, e.g., UV light emitting lasers and diodes, other light emitting materials, transparent conductive electrodes, and surface acoustic wave devices [1-3]. In addition, it has been known recently that the ZnO nanostructures, such as nanowires, nanorods, nanotubes, nanowalls, nanopropellers and nanocoral reefs, can be grown [4-7]. Therefore, the ZnO nanostructures have attracted much attention in application of nanoscale electronic and photonic devices. Especially, nanowires and nanorods of ZnO have been demonstrated to be applicable to field-emission cathodes [8-9]. In this application, the geometry of 1-D ZnO such as nanowires and nanorods can generate “field enhancement”, that is, local enhancement of electric field at their apexes by the concentration of electric fluxes, resulting in low operation voltage.

In the past years, efficient blue phosphor materials such as $BaAl_2S_4$:Eu for thin film inorganic electroluminescence (TFEL) device show significant progresses[10-11]. Inorganic TFEL devices, which generally have a double insulator structure of electrode / insulator layer / active layer / insulator layer / electrode, have the disadvantage that the operating voltage is AC and too high (~200V). This causes higher cost of an EL display system. To spread inorganic TFEL displays on the flat panel display market, the reduction of the operation voltage has been a very important subject. Given an active material, it is difficult to decrease the required electric field in the active layer to emit light. It, therefore, is necessary to improve the device structure for lowering operation voltage. However, very few studies have been reported on low operation voltage, except for studies on the insulating materials with high-permittivity[12].

In a new attempt to lower the operation voltage of inorganic thin film electroluminescent device, we studied thin film electroluminescent device using ZnO nanorods layer adjacent to an EL active layer as an intermediate layer. From the similarity with the application of ZnO nanorods to a field emission cathode, the ZnO nanorods layer in an EL device is expected to have the field enhancement effect in the EL active layer close to the apexes of nanorods, resulting in the lower operation voltage of EL device.

Previously, we have developed a new synthesizing method of ZnO nanorods on a Si wafer by chemical vapor deposition combined with laser ablation of impurity [13], and reported that this method makes it possible to control the size and the number density of ZnO nanorods by changing a laser-ablated impurity and laser ablation period [14]. As a first EL application of ZnO nanorods, we proposed a DC type TFEL device with a structure of ITO electrode / ZnS:Mn / ZnO nanorods / p-/p++-Si(111) / Au electrode[15-16]. The DC type TFEL device showed stable DC voltage operation. The device, however, had the disadvantages of a high operation voltage and non-uniform luminescence in the area of the ITO electrode.

Because of the difficulty of the growth of ZnO nanorods layer on a polycrystalline film except for a Si wafer, no results has ever been reported on the application of ZnO nanorods to a conventional AC-TFEL device with double insulator layers. In this paper, we report for the first time on the EL characteristics of the AC-TFEL device using ZnO nanorods layer as an intermediate layer to lower the operation voltage.

Experimental

Figure 1 shows a device structure that is a double insulator type AC thin film electroluminescent (ACTFEL) device using ZnO nanorods layer as an intermediate layer. The substrate (54 mm X 37 mm) is a pilex glass coated with the 30 nm thick ITO film. A 300 nm thick SiO_2 layer are prepared by an electron beam deposition at 200°C of substrate temperature. And then, a ZnO nanorods layer was grown by chemical vapor deposition method combined with laser ablation of Mn using the growth equipment shown in Figure 2.

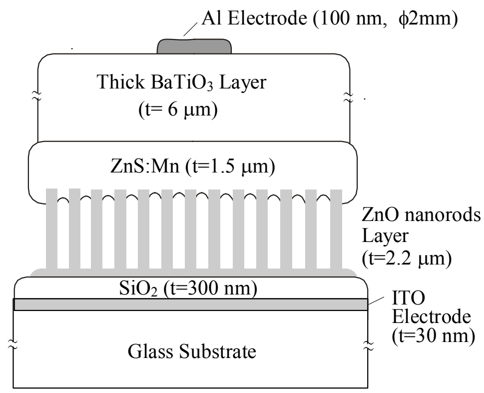

Figure 1. Device Structure

The precursors to synthesize ZnO are metal Zn vapor and O_2. The equipment is composed of a deposition chamber and a Zn evaporation chamber separated by a wall with an orifice of 1mm in diameter. N_2 is used as carrier gas to transport Zn vapor from the Zn evaporation chamber to the deposition chamber. Mn doping by a laser ablation was simultaneously started with CVD growth of nanorods to obtain a rod shape of ZnO [14]. The growth conditions for ZnO nanorods are shown in Table 1. In order to investigate effects of ZnO nanorods properties on EL characteristics, ZnO nanorods with/without post-annealing in O_2 atmosphere for 30 min at 600°C were prepared.

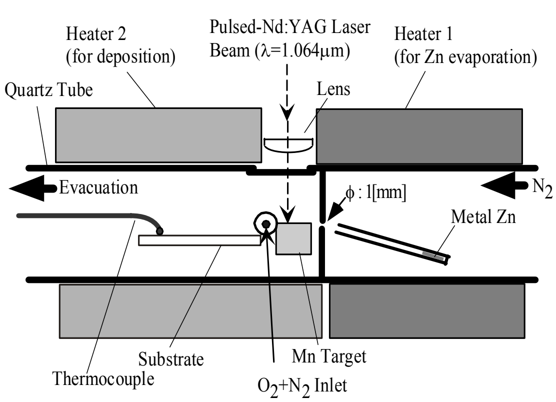

Figure 2. Growth Equipment for ZnO Nanorods

And then ZnS:Mn layer was deposited by an electron beam deposition at 200°C. $BaTiO_3$ thick film as a top insulator layer was spin-coated using a dielectric paste(FUJIKURAKASEI Co., LTD, FEL-615). Finally, Al electrode was deposited by thermal evaporation. A EL device without ZnO nanorods layer is also prepared as a reference. The measurement of EL characteristics of the devices performed using an ac sinusoidal driving voltage. Luminance and transfer charge of the devices were measured using a conventional luminance meter and a Sawyer-Tower circuit, respectively.

Table 1. Growth Conditions for ZnO nanorods

Zn Evaporation Temperature (ºC)	580
Growth Temperature (ºC)	530
Flow Rate of N_2 for Zn (SCCM)	5.0
Flow Rate of O_2 for Zn (SCCM)	1.5
Flow Rate of O_2 (SCCM)	1.5
Growth Pressure (Pa)	26.6
Growth Time (min)	15
Laser Ablation Target	Mn
Laser Irradiated Area (mm^2)	0.13
Laser Energy Density ($J/Shot{\cdot}mm^2$)	0.92
Laser Repetition Frequency (Hz)	10
Laser Ablation Time (min)	3 or 5

Results and discussions

Figure 3 shows the SEM images of as-deposited ZnO nanorods. Following the growth of a continuous layer of ZnO, nanorods with the shape of hexagon prism and with flat tip grow approximately vertically to the substrate. The thickness of the continuous layer of ZnO is about 150nm. The diameter and length of ZnO nanorods are about 100-300 nm and 2.2 μm, respectively.

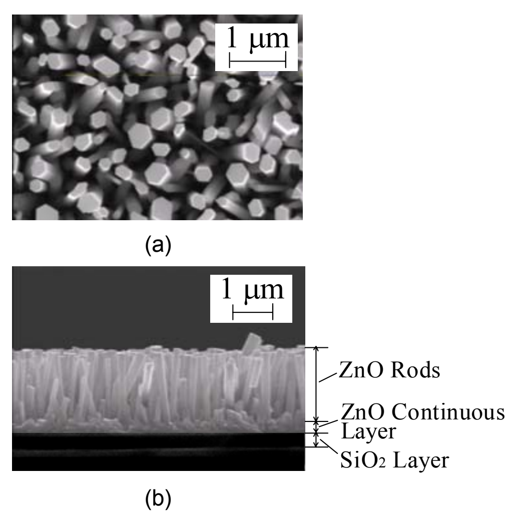

Figure 3. SEM Images of ZnO nanorods.
(a) Top View and (b) Cross-sectional View

The Mn concentration in the continuous layer and in nanorods detected by EDX are about 0.6 at% and less than the value of the detection limit (~0.3 at%), respectively. The surface morphology and Mn concentrations of each part show no change by annealing in atmosphere of O_2 at 600 °C for 30 min.

Figure 4 shows PL spectra of these ZnO nanorods. The UV emission around 380 nm is due to a near band-edge transition of ZnO. The strong broad peak around 650 nm, whose origin is oxygen vacancy[17], is observed in the spectrum of as-deposited ZnO nanorods. This peak disappears by annealing in atmosphere of O_2 at 600 °C for 30 min, although the intensity of UV emission remains unchanged.

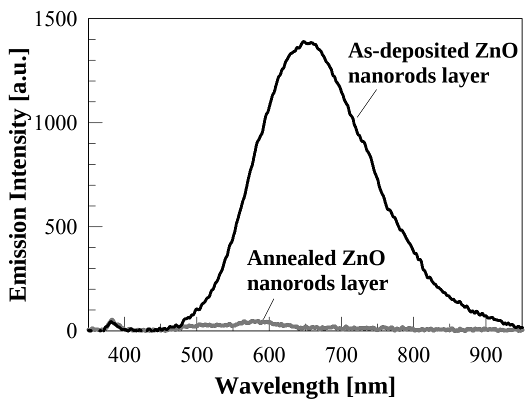

Figure 4. Photoluminecence Spectra of ZnO Nanorods Layers.

Figure 5 shows the SEM images of the cross-sectional view of the sample after the ZnS:Mn layer and thick $BaTiO_3$ Layer is coated on the sample. The thickness of ZnS:Mn layer is about 1.5 µm. Mn concentration was about 0.5 at.% by EDX. It is observed that the upper region between ZnO nanorods top is covered continuously by a ZnS:Mn layer.

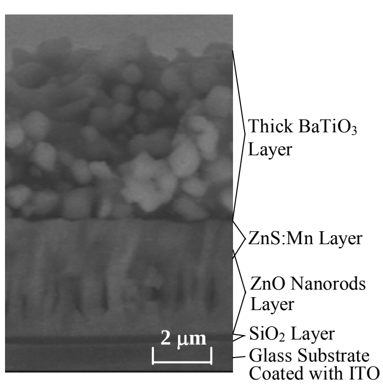

Figure 5. Cross-sectional SEM Image of the Device with ZnS:Mn and Thick $BaTiO_3$ Layer on ZnO Nanorods Layer.

The EL spectra from the EL devices with a ZnO nanorods layer are same as that of the conventional ZnS:Mn film, having a emission peak at 580nm. No electroluminescence from the ZnO nanorods layer is observed. In addition, these ACEL devices show uniform electroluminescence under a top electrode area, which was not obtained in the DC type EL device with a ZnO nanorods layer[16].

Figure 6 shows luminance(L) and luminous efficiency(η) versus applied voltage(V) characteristics of the EL devices with/without a ZnO nanorods layers, just before breakdowns of the devices. The characteristics of the EL device without a ZnO nanorods layer also plotted in this figure as a reference. The qualities of the ZnS:Mn layers of the three EL devices shown in this figure are almost same, because the films were deposited at the same time. The maximum luminance of the EL device without a ZnO nanorods layer is 1198 cd/m^2 at 277 V, and the luminance is almost saturated. On the other hands, the maximum luminance of the EL devices with an as-deposited and annealed ZnO nanorods layers are 175 cd/m^2 at 206 V and 341 cd/m^2 at 328 V, respectively, and the devices break down before the luminance are enough saturated. These maximum luminance values are lower than that of the device without a ZnO nanorods layer. However, it should be noted that below the medium luminance of about 175 cd/m^2, applied voltages of the EL device with an as-deposited ZnO nanorods layer are lower than that of the device without a ZnO nanorod layer. For instance, the applied voltage required to reach 100 cd/m^2 in luminance is 186 V for the device with an as-deposited ZnO nanorods layer, while it is 220 V for the device without a ZnO nanorods layer. In particular, the threshold voltage of the EL device with an as-deposited ZnO nanorods layer is considerably lowered to 115 V from 187 V for the device without a ZnO nanorods layer. On the other hands, applied voltages of the devise with an annealed ZnO nanorods are higher than that of the device without a ZnO nanorods layer over all luminance region. The luminous efficiency at the luminance of 100 cd/m^2 is 0.20 lm/W for the device with an as-deposited ZnO nanorods layer, while it is 0.28 lm/W for the device without a ZnO nanorods layer.

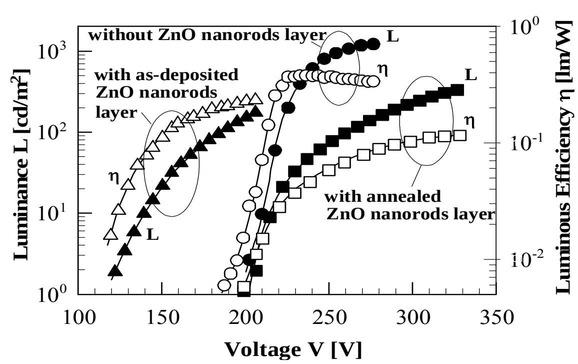

Figure 6. L－V and η –V Characteristics of EL devices Driven at 1kHz Sinusoidal Driving Voltage.

The maximum luminance of the devices with a ZnO nanorods layer is lower than that of the device without a ZnO nanorods layer due. The most likely reason is the local luminescence from only upper region of ZnS:Mn layer between ZnO nanorods. However, it should be noted that the use of an as-deposited ZnO nanorods layer decrease an operation voltage below a medium luminance in spite of the inclusion of an excess voltage drop along the ZnO nanorods layer which is thicker than the ZnS:Mn layer. From this result, we consider that "field enhancement" in the region of ZnS:Mn close to the top of ZnO nanorod provide the reduction of applied voltage. The L-V characteristics considerably depend on annealing of ZnO nanorods layer, although their morphology are the same. This fact indicates that the effect of ZnO nanorods layer on L-V characteristics is very sensitive to properties of ZnO nanorods layer.

Conclusions

The inorganic ACTFEL device using ZnO nanorods layer as an intermediate layer has been newly developed to reduce operation voltage. The luminance-voltage characteristics are very sensitive to properties of a ZnO nanorods layer. With an as-deposited ZnO nanorods layer, the operation voltage is reduced below the luminance region about 15% less than the saturation luminance for the device without a ZnO nanorods layer, although maximum luminance of the devices with a ZnO nanorods layer is lower than that of the device without a ZnO nanorods.

We consider that further reduction of operation voltage is achieved by optimizing not only properties of ZnO nanorods but their morphology, and believe that this device is a promising technology for lowering operation voltage of an inorganic EL device.

Acknowledgments

This work partly supported by the JSPS Grant-in-Aid for Scientific Research (c) (16510091).

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