

Blue-red electroluminescence from hybrid Eu:Phosphors/ZnO-nanowires/*p*-GaN LED

B. Viana^a, T. Pauporté^a, O. Lupan^{a,b}, L. Devis^c, T. Gacoin^c

^a Institut de Recherche Chimie-Paris, Chimie ParisTech - UMR CNRS,
11 rue P. et M. Curie, 75231 Paris cedex 05, France.

^b † Technical University of Moldova,
168 Stefan cel Mare Blvd., Chisinau, Moldova.

^c Laboratoire de Physique de la Matière Condensée,
Ecole Polytechnique – CNRS, 91128 Palaiseau, France

bruno.viana@chimie-paristech.fr,

ABSTRACT

Nanowire (NW) based light emitting diodes (LEDs) have drawn great research interest due to many advantages compared to thin film based devices. Marked improved performances are expected from nanostructured active layers for light emission. Semiconducting oxide nanowires can act as direct waveguides and favor emitted light extraction without use of lens and reflectors in LEDs. Moreover, the use of ZnO wires avoids the presence of grain boundaries and then the emission efficiency is boosted by the absence of non-radiative recombinations at the joint defects.

In this context, europium (Eu):Chelate/ZnO:Mg-nanowires/*p*-GaN light-emitting-diode (LED) structures have been fabricated showing near-UV/violet electroluminescence and red emission from trivalent europium. Fabricated LED structures exhibit UV-blue light at about 380 nm coming from the *n*-(ZnO:Mg)/*p*-GaN and a sharp red emission at ~611 nm related to the intra-4f transition of Eu ions. It is found that in the case of the ZnO:Mg, the emission wavelength is slightly shifted to smaller wavelength to be well adapted to the trivalent europium excitation band. Radiative energy transfer is achieved through strong overlap between the emission wavelength from *n*-(ZnO:Mg)/*p*-GaN heterojunction and chelate ligand intensive absorption band. Indeed the Eu:chelate/(ZnO:Mg)-nanowires/*p*-GaN structure appears well adapted to UV/blue and red dual emission. Our results shows that the design of LEDs based on the chelate ligands are important issue to enhance the performance of electroluminescence devices based on ZnO nanowire arrays/*p*-GaN heterojunction and rare-earth metal complexes.

Keywords: Hybrid ZnO/GaN structure, Eu:chelate, toward white LED, Electroluminescence,

I. INTRODUCTION

Light emitting diodes (LEDs) are of great interest for energy saving acting as efficient lighting sources for displays and general lighting [1-3]. The research interest increased owing to lower energy consumption and longer lifetime of LEDs compared to the incandescent bulbs and halogen lamps. In this context, we have focused our interest and attention in lighting systems based on emission from different hybrid structures [4, 5] and in particular in europium lanthanides [6] and nano-ZnO for LED applications [3, 7-9]. The europium complexes have attracted scientists' attention due to its line-like emission spectra in the red and its suitability for manufacturing pure red and full-color electroluminescence (EL) devices [10-13]. In the current reports, in order to use the Eu:chelate in the LED system, ZnO/Eu³⁺ transfer are required to obtain strong red EL. The effective overlap between the ZnO emission broad band and the absorption of the europium or host phosphor enables ultrafast energy transfer (ET) through a resonant radiative energy transfer process, which is crucial for good efficiency. Direct energy transfer from ZnO to Eu³⁺ has so far still

been quite low or even not observed [14-18]. In these works defect states were involved in the energy transfer process [16-18] because of the poor energy level overlap and of the very short ZnO excitonic lifetime. This leads to poor energy transfers from ZnO to Eu^{3+} ions [17]. It was reported that while Cu permits the emission to be shifted in the blue range, in the case of the ZnO:Mg, the emission wavelength is slightly shifted to smaller wavelength to be well fitted to the trivalent europium excitation band [3, 7-9]. This tuning of emission wavelengths may allow controlling electroluminescence from LED with different phosphors.

In this work, a new type of phosphor were deposited as Eu-chelate film on top of $n\text{-(ZnO:Mg)/}p\text{-GaN}$ leading to the Chelate: $\text{Eu}^{3+}/\text{ZnO}/p\text{-GaN}$ heterostructures. Such device structure is characterized by the red emission centered at ~ 612 nm when the samples were radiatively excited by a 385 nm ZnO:Mg nanowire/ $p\text{-GaN}$ -based LED. The directional guidance of emitted light from $n\text{-(ZnO:Mg)/}p\text{-GaN}$ structure could be favorable to enhance the phosphor absorption.

II. MATERIAL PREPARATION.

The magnesium-doped ZnO nanowire arrays were grown by electrodeposition according to a technology described in details elsewhere [3,8,9,19]. The substrate was a commercial magnesium-doped GaN (0001)-oriented layer grown on sapphire with the c -axis perpendicular to the substrate. The p-type GaN layer was 3 μm thick and the dopant concentration was $3 \times 10^{18} \text{ cm}^{-3}$. The crystal miscut was 0.59° . Magnesium chloride MgCl_2 has been used as dopant for ZnO in the present work.

A molecular phosphor $\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_3$ (TTA stands for thenoyltrifluoroacetone) was used to synthesize europium chelate following the protocol reported in [20]. The Eu:complex has a quantum yield of 25% measured by comparison with calibrated standards with a strong absorption cross section in the UV in the range 350-400 nm as seen later in this paper.

Considering that europium chelate is highly soluble in ethanol, it does not show significant extinction effect at high concentration or in the solid state. In this way, it is not compulsory to incorporate it into a matrix. Therefore, in our experiments, the molecules were simply dissolved in ethanol at 50 mg/mL. The deposition was made on the glass side of a manufactured microscope slide covered by indium-tin oxide (ITO). Heating the substrates at a temperature close to the evaporation temperature of the solvent, appears to be the optimal deposition temperature to grow spatially homogeneous films and avoid uncontrolled spreading of the solution. Therefore ITO substrate was heated at 60°C during the spray deposition. 1 mL of the solution was deposited using a Paasche Talon gravity airbrush feed with a 0.38 mm nozzle. In our experiments, the air pressure was about 1.5 atm, the air flow was about 100 mL/s, and the solution flow was $\sim 0.1 \text{ mL/min}$. The choice for the compound was governed by the considerations, such as simple synthesis, good solubility, large absorption cross section and good quantum yield, large stoke shift between absorption and emission, absorption in the UV range compatible with LEDs and, as compared to dye molecules, good emission properties even in the bulk state. The Eu-chelate on the ITO is presented in Figure 1.

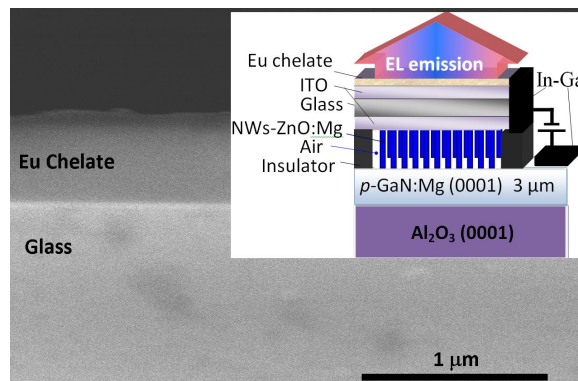


Figure 1. SEM image of the Eu:Chelate/Glass/ITO structure in cross-sectional view. Inset shows the schematic configuration (side view) of the Eu:Chelate /ZnO:Mg-nanowires/ $p\text{-GaN}$ LED structures.