COMMUNICATION

Low-Voltage UV-Electroluminescence from ZnO-Nanowire Array/p-GaN Light-Emitting Diodes

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Nanowire (NW)-based light-emitting diodes (LEDs) have drawn great interest because of their many advantages compared to thin-film-based devices. Marked improved performances are expected from nanostructured active layers for light emission. Nanowires can act as direct waveguides and favor light extraction without use of lenses and reflectors. Moreover, the use of wires avoids the presence of grain boundaries and then the emission efficiency is boosted by the absence of nonradiative recombinations at the joint defects. The junctions between the n- and p-type semiconductors can also be of very high quality with low interfacial strain and defect density as a result of a reduced contact area between the two materials in the case of epitaxial heterojunctions. Integration of nanowires is especially promising for the preparation of short-wavelength emitters such as superluminescent UV-light-emitting diodes and laser diodes. GaN is the main wide-bandgap semiconductor (E_g = 3.39 eV) used for the preparation of blue and UV LEDs. However GaN nanowire arrays are difficult to grow.[1,2] Alternative materials for the preparation of nanostructured UV LEDs mainly include ZnO.[3–5] ZnO has a similar wide bandgap of 3.37 eV and a larger exciton binding energy of 60 meV (compared to 29 meV in the case of GaN) that should favor light emission at room temperature.[3,6] ZnO and GaN share the same wurtzite hexagonal structure. A lot of research efforts have focused on the preparation of p-type ZnO to realize LEDs based on homojunctions made of this semiconductor.[7–9] For the moment, however, reproducible and stable p-type ZnO material with sufficient high conductivity and carrier concentration is still at the development phase.

An alternative promising approach is to grow n-type ZnO NWs on p-type GaN.[10–17] ZnO NWs can be grown by various techniques. Most of these efforts for LED applications have been focused on vapor phase growth. Recently, devices have been fabricated by integrating MOCVD (metal organic chemical vapor deposition)[10–14] or MOVPE (metal organic vapor phase epitaxy)[15] grown epitaxial ZnO NWs on p-GaN. However, the LED performance characteristics remain unsatisfactory. Zhang et al.[10] have prepared a device with a rather high emission onset voltage of 12 V and a blue–violet electroluminescence (EL) with a decreasing emission wavelength from 440 to 400 nm by increasing the applied voltage up to 35 V. Jeong et al.[11] have prepared a UV LED with an emission threshold of 6 V and a maximum of EL at 12 V. The performances degraded at higher voltage. The heterojunction had to be annealed in H_2 to activate the emission. Up to now, the integration of ZnO NWs grown from solution in LEDs has not been very successful.[16–19] Classically a two-step approach is used: the GaN single crystal is first covered with a ZnO seed layer (which later creates interface states) and the NWs or nanorods are subsequently grown from a zinc ion precursor solution. Until now, however, only visible light emitting diodes (dominated by a violet emission in the literature)[16,19] have been obtained by this method. Moreover, the application of high voltages in the several tens of volts range was necessary to observe the electro-emission and some authors have pointed out the poor stability of the system and a decrease of light emission with increasing the diode current.[16] However, for consumer electronics it is very important to develop stable LEDs that can work at lower applied voltages.

In the present Communication, electrodeposition has been used as a facile, low-cost, catalyst- and seed-layer-free growth technique of ZnO-NW arrays.[20–27] The method is clean, using only zinc ions and molecular oxygen as the growth precursor dissolved in an aqueous bath.[24] In the literature, epitaxial ZnO has been successfully grown by the technique on n-type GaN(0001) because of the low lattice mismatch between ZnO and GaN (1.9% for the *a* lattice parameter).[20,25,26] The electrodeposition process involves an exchange of electrons between the substrate (the electrode) and the solution and this insures a very good electrical contact between the deposit and the substrate. Moreover, it was demonstrated recently that the method is outstanding for growing high-quality ZnO NWs after optimizing various growth parameters such as the bath temperature, the supporting salt, the precursor concentration, and so on.[23] By this method, high-quality ZnO presenting a unique excitonic photoluminescence (PL) emission in the UV without significant emission in the visible wavelength range due to deep intrinsic defects was demonstrated.[23] Here, we have prepared a high-quality epitaxial heterojunction between electrodeposited ZnO NWs and a p-type GaN(0001) thin film substrate supported on sapphire. The heterostructure has been used to fabricate a light-emitting diode (LED). The device presents a stable emission in the UV at 397 nm combined with a low forward-voltage emission threshold of 4.4 V and a high brightness above 5–6 V.

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