Low-Temperature Growth of ZnO Nanowire Arrays on p-Silicon (111) for Visible-Light-Emitting Diode Fabrication

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We report on the successful growth of homogeneous and well-covering ZnO nanowire arrays at a low temperature (90 °C) directly on a p-type Si(111) wafer by an electrochemical method. The wires were self-standing and vertically oriented. Room-temperature micro-Raman and photoluminescence emission analyses showed the high global structural and optical quality of the material with a low density of deep defects. The ZnO nanowires of the heterostructure were contacted with a transparent ITO electrode, and a light-emitting diode was fabricated. The device current−voltage curve had a rectification magnitude of about 20 at 2.5 V. The threshold forward voltage was low at 1.4 V. The device emitted a broad visible band centered at 590 nm at room temperature under forward bias. According to the energy band diagram of the junction, the emission has been assigned possibly to Si hole injection to near-interfacial ZnO deep levels, followed by the radiative recombination with electrons of the ZnO conduction band.

1. Introduction

Zinc oxide is a n-type semiconductor with a large band gap of 3.37 eV, a large exciton binding energy of 60 meV, and a wurtzite hexagonal crystallographic structure. ZnO can be grown as individual or arrays of one-dimensional nanostructures that exhibit superior and additional properties compared with bulk and thin films due to a large surface-to-volume ratio, an inherent anisotropy, and quantum confinement of charge carriers.[1−3] These nanostructures have attracted much attention owing to their potentiality for many applications, such as solar cells,[3−5] superhydrophilic−superhydrophobic surfaces,[6,7] nanosensors,[8] field-emission[9] and electroluminescent devices,[10,11] and nanolasers.[12]

The use of nanowire (NW) arrays as emitting layers in light-emitting diodes has been shown to be of special interest compared to thin-film-based devices.[11,13] A marked performance improvement is expected from the nanostructure because the nanowires can act as direct waveguides and favor light extraction without the use of lens and reflectors. Moreover, the use of nanowires avoids the presence of grain boundaries, and then the emission efficiency can be boosted by the absence of nonradiative recombinations at the joint defects. The fabrication of NW LEDs based on ZnO p−n homojunctions is very difficult to achieve due to self-compensation by native donor defects. The synthesis of stable, well-conducting, and reproducible p-ZnO still requires a lot of research. However, interesting alternatives are heterostructures in which ZnO nanowires are the n-type emitter contacted to another semiconductor with a different band gap as the p-type material.[11,13−21] Following this scheme, the growth of ZnO nanostructured layers on a p-Si wafer is especially attractive for the well-known advantages of this single-crystalline substrate and its potential applications in Si-based optoelectronic integrated circuits (OEICs).[14−24]

We report on the use for the first time of electrodeposition (ECD) for ZnO NWs/p-Si heterojunction fabrication. ECD has been chosen as a low-temperature growth method of ZnO nanowires that can be implemented for large-scale production.[25] The technique is of utmost interest for the fabrication of optoelectronic devices notably because the grow process involves the exchange of electrons from the substrate and this insures a very good electrical contact between the ZnO nanowires and the substrate (here, the p-type Si). The growth of homogeneous n-ZnO NW arrays has been achieved directly on p-Si(111). By developing a procedure to impede the oxidation of the silicon wafer substrate after the etching steps, we have successfully grown dense arrays of ZnO nanowires of high structural quality characterized by a strong photoluminescence in the UV due to exciton recombination and a very weak emission in the visible wavelength region due to intrinsic deep structural defects. The prepared heterojunctions were integrated in an LED heterostructure. The p−n diodes had a typical rectifying behavior, and visible electroemission could be observed at room temperature under forward bias polarization.

2. Experimental Section

The ZnO NW arrays were grown on highly boron-doped p-type Si(111) substrates with an electrical resistivity of 0.03 Ω·cm (purchased from ACM, Applications Couches Minces, France). The silicon substrates were platelets cut from a 300 μm thick Si wafer with an initial diameter of 3 in. Before electrodeposition, the Si substrates were sequentially cleaned by using three steps: first, a solvent cleaning was done in a warm acetone bath (50−53 °C) for 10 min and in methanol at room temperature, then Si was treated by the RCA-1 cleaning procedure,[26] and, finally, it was dipped in HF (2%) during 120 s just before starting the growth. The Si substrate was mounted

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