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Ultraviolet-Emitting ZnO Nanostructures on Steel Alloy Substrates: Growth and Properties

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ABSTRACT: ZnO nanostructures with a variety of morphologies and sizes, such as urchinlike structures composed of small-head nanonails, vertically aligned nanonails and nanocones, comblike nanostructures, hierarchical nanostructures, etc., have been synthesized via the simple thermal evaporation process onto the steel alloy substrate without the use of any metal catalyst or additives. It was observed from the detailed morphological and structural studies that substrate temperature, distances between source material and substrates, concentration of zinc vapors, zinc partial pressure, concentrations of reactant gases, and choices of substrates have serious impact on the morphologies and structural properties of as-grown products. Therefore, within certain reaction parameters, specific morphologies can be obtained. Detailed structural observations confirmed that the as-grown products are single-crystalline with the wurtzite hexagonal phase and grown along the (0001) directions. Raman-scattering and room-temperature photoluminescence (PL) studies revealed that the as-grown products have good crystallinity with excellent optical properties. The low-temperature PL (LTPL) studies, measured in the temperature range from 11−300 K, of the vertically aligned ZnO nanonails grown at position "B" revealed the presence of excitonic emissions and their multiple-phonon replicas in the ultraviolet region. Additionally, it has also been found that the temperature dependence of free exciton peak position can be successfully described by the standard Varshini's expression.

1. Introduction

Nanostructures of ZnO acquired a special place because of their diversity in properties, such as direct wide band gap (3.37 eV) at room temperature, large saturation velocity (3.2×10^7 cm/s), high breakdown voltage, and large exciton binding energy (60 meV). These versatile properties of ZnO provide an opportunity to recognize itself as one of the most multifunctional materials; therefore, they can be used as ultraviolet (UV) lasers, light emitting diodes, photodetectors, piezoelectric transducers and actuators, hydrogen storage, chemical and biosensors, surface acoustic wave guides, solar cells, photo catalysts, etc.[1−4] Because of its noncentrosymmetric structure, ZnO exhibits a piezoelectric nature and by exploring these properties, Z. L. Wang and co-workers recently fabricated ZnO nanowire-based nanogenerators that were able to convert mechanical energy into electric power.[5]

Hitherto, variety of ZnO nanostructures were synthesized by numerous fabrication techniques and reported in literature.[1−6] However, the controllable synthesis of 1D ZnO nanostructures in terms of size, shape, and composition is very important to realize the grown nanostructures for practical device applications.[1−5] Including different 1D ZnO nanostructures, the synthesis of novel and complicated ZnO nanonails have particular interest in optoelectronics because of their special architecture.[7] There are very few reports on the synthesis and characterization of ZnO nanonails in the literature. Lao and Ren et al. demonstrated the synthesis of ZnO nanonails via vapor transport and condensation process using the ZnO, In_2O_3 and graphite powders at 1000 °C.[8] Shen et al. grew the ZnO nanonails on silicon substrate using Zn and In powders by a two-zone thermal evaporation system at 300−800 °C.[9] Using the mixtures of zinc, indium, and In_2S_3 powders in the two-heating-zone tube furnace, Shen et al. again synthesized ZnO nanonails at 550−900 °C on a silicon substrate.[10] The growth of aligned ZnO nanonails and nanopencils on a silicon substrate by modified thermal evaporation process at 600 and 700 °C, respectively, was recently reported by Shen et al., in which an adiabatic layer was used.[11] In all the reported results discussed above, the obtained products were single-crystalline but exhibiting a strong deep level emission, which is related to the structural defects and impurities of the corresponding structures. Nevertheless, it is important to have good optical properties for the synthesized nanostructures to utilize them for the fabrication of efficient optoelectronic devices. Moreover, in all the reported results, high temperature, modified thermal evaporation process and additives were used to synthesize ZnO nanonails. Therefore, it is still needed to explore a simple, low-temperature, and catalyst-free approach to synthesize high-quality ZnO nanonails.

In this paper, we present detailed structural and optical properties of urchinlike structures composed of small-head nanonails, vertically aligned nanonails, and nanocones grown on a steel alloy substrate via a simple thermal evaporation method by using only metallic zinc powder in the presence of oxygen at modest temperature ranges between 550 and 440 °C, without the use of any metal catalyst or additives. Importantly, our synthesized ZnO nanostructures are exhibiting only a sharp and strong UV emission in the room-temperature and low-temperature photoluminescence (PL) spectra, confirming that the as-grown nanostructures have excellent optical properties with good crystallinity. Moreover, compared to other previously reported results, our approach to fabricate ZnO nanonails and nanocones are quite simple, easy, efficient, and cost-effective; all the grown ZnO nanostructures reported here have good reproducibility under the same experimental setup and conditions employed for this work.

2. Experimental Section

In a typical reaction process, the source material, high-purity metallic zinc powder (99.999%), was put into a quartz boat and placed at the left-hand side of center of quartz tube. Three pieces of steel alloy substrates (1×1.5 cm), mentioned as "A", "B", and "C", were placed

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