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Original

Influence of HCl on the NPs-CdSe synthesis prepared by the colloidal method

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Abstract

Cadmium selenide nanoparticles (NPs-CdSe) were synthesized by colloidal route at room temperature and atmospheric pressure using cadmium chloride ($\text{CdCl}_2 \cdot 2.5$ hydrate) and elemental selenium (Se) as precursors. Sodium borohydride (NaBH_4) was used as reducing agent to obtain Se^{2-} ions and an aqueous solution with a NaOH and Penta sodium tripolyphosphate (STPP) was used to protect Cd^{2+} ions. To remove the by-products generated during the chemical reaction and to promote the precipitation of NPs-CdSe, a cleaning process with an aqueous solution of HCl was performed. The HCl volume was varied from 0.2 to 1.2 ml during the cleaning process to study its effects on CdSe synthesis. The crystalline structure was analyzed by inspection of the high-resolution transmission electron microscope (HR-TEM) and X-ray diffraction (XRD). This analysis showed that crystals of CdSe exhibit a face-centered cubic structure (FCC). The calculated crystallite size is 3.5 nm and increases to 4.5 nm as the HCl volume increases. The morphologies of the products were observed by SEM and TEM techniques. HRTEM images showed that NPs-CdSe synthesized to 0.8 ml are composed of a great number of homogeneous and smooth nanospheres which are not appreciable in SEM but are observable in TEM. By contrast, 0.2 and 1.2 ml HCl samples are comprised of a great deal of rods of compounds of Se mixed with CdSe spheres nanostructures. This work, which did not require the use of surfactants complexes or special environment, is considered to have advantages over other works.

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Keywords: CdSe; Semiconductor; Colloidal method

1. Introduction

Over recent decades, the development of the synthesis of low-dimensional semiconductor structures has been established by Brus (1984). Actually, alterations in nanostructures due to the size and morphology have a direct influence on the energy band distribution of the material; therefore, it is necessary to

study the effects related to the nanometric scale. Structures of the type MX (M = Cd, Pb, Hg and X = S, Se, Te) have been characterized (Mansur & Mansur, 2011). However, in these works, the nanoparticles are synthesized using surfactants complexes like carboxylic-functionalized PVA (PVA-COOH), making the process expensive and a lot of times slow because it requires special environments. Other research had used chemical techniques such as sol-gel, chemical bath deposition, spray pyrolysis, colloidal route, among others (Cheng et al., 2003; Onwudiwe & Strydom, 2013) based on the coating of the precursor ions with a hydrophobic surfactant in order to ensure water solubility and long term stability of the nanostructures. In this way, colloidal

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Effect of nitrogen gas in the agglomeration and photoluminescence of Zn-ZnO nanowires after high-temperature annealing

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The effect of anti-agglomeration and enhanced photoluminescence after high-temperature annealing of Zn-ZnO nanowires in nitrogen atmosphere is reported. The Zn-ZnO nanowires were deposited by the hot filament chemical vapor deposition technique and subsequently annealed at 1100°C in oxygen or nitrogen atmospheres. It was found that under both annealing atmospheres, the structure of the nanowires was completely oxidized. Morphological studies suggest that annealing under oxygen-rich atmosphere, grain growth occurs, resulting in a continuous surface with a micrograin-shaped structure. However, it seems that nitrogen-rich annealing partially prevents complete agglomeration and longitudinal structures composed by nanometric grains were observed. Although photoluminescence properties of the annealed nanowires are improved in both annealing atmospheres, it was observed that the PL spectrum of nanowires annealed in nitrogen showed a stronger UV emission than that of the oxygen annealed nanowires.

Keywords: Nanowires; HFCVD; nitrogen annealing; ZnO.

PACS: 81.07.-b; 81.40.-z; 78.55.-m

1. Introduction

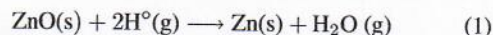
Nanostructured ZnO is a functional material with interesting physical properties for several applications such as dye-sensitized solar cells, excitonic lasing, biosensors, among others [1,2]. The availability of a variety of growth methods results in a large number of different ZnO morphologies and a wide range of nanostructure properties.

Thermal annealing is a process commonly used to reduce intrinsic defects, enlarging grain sizes, releasing accumulated strain energy, and thus improves crystallinity [3]. Additionally, optical properties of the thermal treated material are sensitive to the annealing atmosphere. For example, it has been reported that UV light emission is enhanced by annealing ZnO films in H₂ atmosphere [4], and that the optical properties of ZnO nanorods are improved by post-annealing treatment at 800°C [5]. Despite the benefits of thermal treatment process, the main disadvantage of annealing nanostructures is that grain-growth and agglomeration occurs, which results in formation of bigger particles or continuous structures that exhibit bulk properties [6]. Recently, some efforts have been made with the aim of prevent agglomeration of nanoparticles, subjecting them to smooth thermal annealing and using inert atmospheres [7,8]. In this sense, nitrogen gas is commonly employed in post-annealing treatments since it is fairly inert, in contrast with their oxygen and hydrogen counterparts. It has been also found that nitrogen influences the size of carbon nanotubes [9]. In the present work, the effect of anti-agglomeration in Zn-ZnO nanowires after annealing in nitrogen at 1100°C is studied. The nanowires were also

annealed in oxygen ambient to compare the effect of the gas atmosphere in the structural, morphological and photoluminescence properties.

2. Experimental details

Zn-ZnO nanowires were deposited on crystalline silicon wafers by the hot chemical vapor deposition (HFCVD) technique. ZnO pellets (0.23 g) were placed in a source holder, 2 mm under a tungsten filament. Hydrogen gas was flowed through a quartz tube at a rate of 100 standard cubic centimeters per minute (sccm). The process time and the substrate temperature were 100 s and 350°C, respectively. The main steps for formation of gas precursors are described as follows: first, the tungsten filament is heated up to about 2000°C by applying an AC voltage of 83.4 V. This temperature allows partial dissociation of molecular hydrogen into hydrogen atoms (H^o), which are highly reactive and promote formation of a reducing gas atmosphere. The chemical reaction for decomposition of the ZnO pellet is proposed as follows:



After that, solid Zn is vaporized at 1200°C in the source holder. Thermal annealing was performed in a horizontal quartz tube at 1100°C for 2.5 hours at atmospheric pressure. During annealing, 99.998% purity oxygen or 99.998% purity nitrogen gases were introduced into the tube at a flow rate of 100 sccm. X-ray diffraction (XRD) patterns were measured