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# On the origin of green emission in zinc sulfide nanowires prepared by a thermal evaporation method

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## ABSTRACT

The optical properties and morphological features of ZnS nanowires fabricated by a thermal evaporation process have been systematically studied. We have observed both ZnS nanowires and ZnO structures in one fabrication batch. One common green emission peak in the photoluminescence spectra centered at 516–520 nm appears and is independent of the donor parts of the source materials and the catalytic metals. This peak is attributed to the contribution of ZnO structures by means of X-ray diffraction and Raman spectroscopic analysis. The exponential degradation of the photoluminescence intensity of ZnS and ZnO in air under UV laser irradiation not only indicates the significant role of oxygen diffusing into ZnO structures but also provides additional confirmation regarding the degradation that occurs inside ZnS nanowires. The emission model related to defects and ligand fields that occurs in both ZnS and ZnO as a result of this fabrication approach is discussed.

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## 1. Introduction

Research on ZnS nanowires has attracted much attention in the last few years, not only from the application point of view but also in fundamental research [1,2]. ZnS nanowires, together with the other II–VI semiconductor materials, have emerged as one of the most promising new classes of electronic devices because we are now able to produce nano-LEDs [3], FEDs [4], and lasers [5,6] based on a single nanowire working at room temperature. Furthermore, their optical properties exhibit the occurrence of quantum effects in low-dimensional systems.

The optical mechanism underlying the emission wavelength remains controversial, hampering the full exploitation of the optical features of these promising wires. The optical emission of ZnS nanowires seems to be dependent on the fabrication approach. Lieber et al. [7] introduced the chemical vapor deposition method of fabricating ZnS:Mn single nanowires. These wires revealed two emission bands at 330 nm and 590 nm, which were related to band-to-band excitation and Mn impurities, respectively. Meanwhile, by using thermal evaporation techniques, it is observed that the products displayed an additional emission band at approximately 510–520 nm. Zhang et al. [8] assigned this band

to the presence of Au catalytic ions. Lu et al. [9] suggested that it was attributable to the energy transfer between sulfur and zinc vacancies. Fang et al. [10] indicated that this strong emission should be ascribed to Au<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, and Cd<sup>2+</sup> impurities that may appear in the source materials during preparation of ZnS nanocrystals. Recently, Schrier et al. [11] used theoretical calculations to determine the optical properties of ZnO/ZnS heterostructures and proposed a theoretical model for the ZnS/ZnO heterostructures. It was demonstrated that the formation of ZnO/ZnS nanoheterostructures can substantially reduce the optical band gap in comparison with the natural band energies for both ZnS and ZnO. Therefore, the green emission may be interpreted as a result of lattice mismatch defects between ZnS and ZnO at the interface region [12] or as a result of the defect emissions of ZnS and ZnO [13].

In this report, we resolve the issue of the green emission through systematic research on ZnS nanostructures fabricated from nanopowders using a thermal evaporation approach that involves a temperature-controlled catalytic growth process with and without doping materials. We show the simultaneous appearance of ZnS nanowires and ZnO structures on the silicon substrate as well as a surrounding layer of ZnS wires. The origin of the green peak at 516–520 nm is ascribed as a contribution of ZnO structures. It is a common emission from all of our samples independent of ZnS doping or the use of catalytic metals. For further understanding, a UV laser has been employed to investigate the degradation of PL intensity in the air, which provides additional

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proof of oxygen diffusion into our structures and is observed in both ZnS and ZnO.

## 2. Experimental details

Undoped and doped ZnS nanowires with Cu, Ag and Mn impurities have been prepared using a thermal evaporation technique involving a horizontal tube furnace system, as shown in Fig. 1. The details of the procedure can be found elsewhere [14]. Briefly, our ZnS nanopowders with an average diameter in the range 2–5 nm, with and without dopants, were placed in the central position of the horizontal tube whose temperature was set to 1150 °C. Several Pt- and Au-coated silicon strips were placed at the downstream end of the tube furnace to deposit onto incoming materials from the aluminum crucible. Prior to execution of the experiment, the tube was purged for 30–60 min with high-purity Ar gas to eliminate the residual water and oxygen (Ar was chosen as carrying gas because of its non-reactivity). Subsequently, the furnace was heated to 950 °C at a rate of 10 °C/min with an Ar flow of 30 sccm (standard cubic centimeters per minute). Later, the temperature was increased to 1150 °C and held at that value for 1 h with an Ar flow of 80 sccm, followed by a slow cooling to room temperature.

The morphologies, compositions and microstructures of the products were examined using field emission scanning electron microscopy (FE-SEM 4800 Hitachi) combined with energy dispersive X-ray spectroscopy (EDX). The structure and crystallinity were characterized and analyzed by means of X-ray diffraction (XRD) with Cu  $K_{\alpha}$  radiation, which has  $\lambda=1.54056 \text{ \AA}$  (Siemens D5000). PL spectra were acquired by using a UV excitation source at 325 nm (He–Cd laser) with a Peltier-cooled CCD camera (Acton, Winspec). Filters at 340 and 370 nm were used together with a neutral filter. We were also equipped with a He closed-cycle cryostat with a temperature controller to measure the PL at low temperatures. To investigate the optical properties of nanowires alone, we eliminate the influence of the silicon substrate by dispersing the nanowires mechanically into a pure ethanol solution and subsequently depositing them onto a quartz substrate.

## 3. Results and discussion

### 3.1. Structural and morphological features

One of the most fascinating aspects of ZnS structures fabricated using a thermal evaporation method is the possibility of forming different types of structures in just one experiment batch.

Typically, we obtained one-dimensional ZnS crystallites in the highest temperature region where the formation of nanowires is dominant. This temperature range is approximately 1000 to 1100 °C, which we term zone 1 and depict in Fig. 2a. The diameter of these nanowires is approximately 50–200 nm, while their length can be up to a few tens of microns or even several hundred microns. In a lower temperature region, from 800 to 1000 °C, which is labelled as zone 2 in Fig. 2b, we obtained a lower density of nanowires grown on a substrate. The average length of the nanowires in this area is rather short and on the order of a few micrometers, as shown in the inset of Fig. 2b. For the remainder of

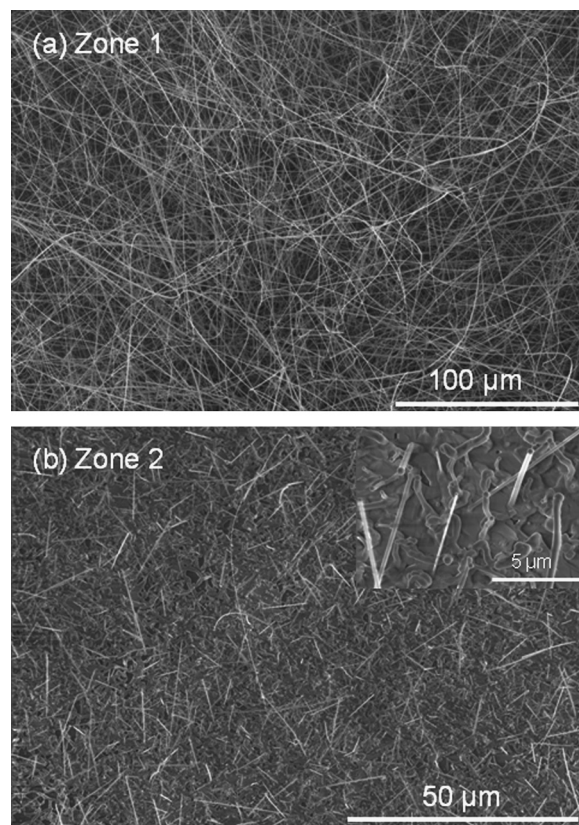


Fig. 2. Typical FE-SEM images of the Mn-doped ZnS nanowires grown on a silicon substrate coated with a 20 nm film of Au acting as a catalytic metal. (a) Represents the highest density area, with mass production of predominantly one-dimensional nanowires. (b) Displays a minority of wires growing on a substrate. The small bead located on the tip serves as a catalytic metal (Au in this case) in a vapor–liquid–solid mechanism for the growth of wires (inset).

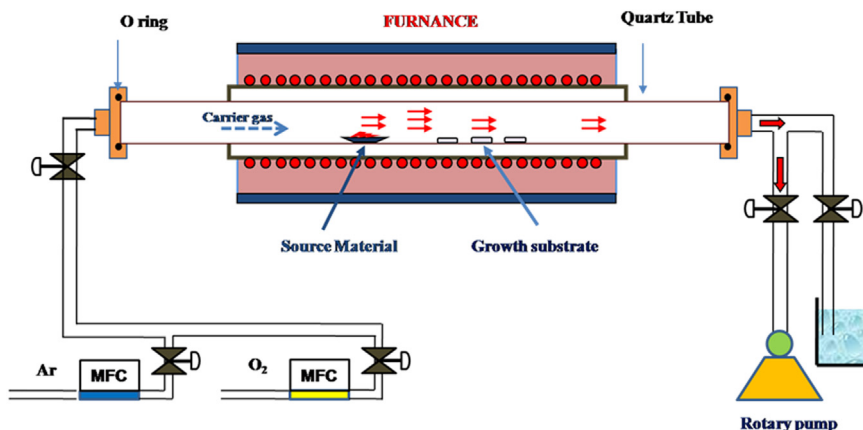


Fig. 1. Schematic diagram of the experimental apparatus used to grow 1D ZnS nanostructures.

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