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Full Length Article

Investigation of the growth and in situ heating transmission electron microscopy analysis of Ag_2S-catalyzed ZnS nanowires

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ABSTRACT

We investigated the semiconductor-catalyzed formation of semiconductor nanowires (NWs) – silver sulfide (Ag_2S)-catalyzed zinc sulfide (ZnS) NWs – based on a vapor-liquid-solid (VLS) growth mechanism through metal-organic chemical vapor deposition (MOCVD) with a Ag thin film. The Ag_2S-catalyzed ZnS NWs were confirmed to have a wurtzite structure with a width and length in the range of ∼30 nm to ∼80 nm and ∼1 μm, respectively. Using extensive transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) analyses from plane and cross-sectional viewpoints, the ZnS NWs were determined to have a c-axis, [0001] growth direction. In addition, the catalyst at the top of the ZnS NWs was determined to consist of a Ag_2S phase. To support the Ag_2S-catalyzed growth of the ZnS NWs by a VLS reaction, an in situ heating TEM experiment was conducted from room temperature to 840 °C. During the experiment, the melting of the Ag_2S catalyst in the direction of the ZnS NWs was first observed at approximately 480 °C along with the formation of a carbon (C) shell. Subsequently, the Ag_2S catalyst melted completely into the ZnS NWs at approximately 825 °C. As the temperature further increased, the Ag_2S and ZnS NWs continuously melted and vaporized up to 840 °C, leaving only the C shell behind. Finally, a possible growth mechanism was proposed based on the structural and chemical investigations.

1. Introduction

Over the past few decades, one-dimensional (1D) semiconductor nanowires (NWs) with unique electrical, chemical, and optical properties have been studied as important building blocks for the realization of various nano-electronic devices [1–3]. This research has created potential for various applications [4–6], and research on a global scale has been actively pursued. Among the various semiconductor nanomaterials available, zinc sulfide (ZnS), with a wide band gap of 3.7 eV, has garnered significantly increasing attention as a promising electronic material [7–10]. ZnS has been recognized as a suitable material for the fabrication of flat-panel displays [11], light-emitting diodes [12], infrared windows sensors [13], electroluminescent devices [14] and lasers [15] due to its structural and synthetic diversity and excellent chemical and thermal stability. Vapor-liquid-solid (VLS), solution-liquid-solid (SLS), solution-solid-solid (SSS), vapor-solid-solid (VSS), and supercritical fluid-solid-solid (SFSS) methods have been used to synthesize ZnS NWs [16–19]. Among these methods, the VLS growth method based on the formation of a supersaturated solid after the formation of a liquid metal-semiconductor droplet with an absorbed vapor precursor and a metal catalyst has been widely used to synthesize 1D semiconductor nanostructures, producing NWs with the desired size and location of the metal catalyst. Additionally, many efforts to realize NW fabrication of various semiconducting materials and catalysts have been undertaken with the VLS technique. However, the metal catalysts in the semiconductor NWs synthesized by the VLS method can act as impurities that affect the band gap during operation of the resulting electronic devices. Several reports have described the disadvantages of metal catalysts in semiconductor NWs that must be overcome for the future application of these materials in devices [20–23].

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The fabrication of semiconductor NWs using semiconductor catalysts has been studied as a method for overcoming the disadvantages of metal catalysts and developing new semiconductor materials. In the case of ZnS, although several research groups have recently reported the application potential of photocatalysts prepared using methods such as SLS and SSS to synthesize nanoparticles, NWs and nanorods, including silver sulfide (Ag_2S)-ZnS, Ag_2S-CdS, and Ag_2S-$AgInS_2$ using a Ag_2S semiconductor catalyst [24–27], no studies have reported the fabrication of ZnS NWs through a VLS synthetic method using a Ag_2S catalyst. Ag_2S, used as a catalyst, is an important semiconductor from the II—VI group with a high absorption coefficient and a band gap of ~1 eV. Because of its relatively small band gap, chemical stability, and mixed conducting properties, Ag_2S is an interesting material that can be applied in electrical devices. Recently, Ag_2S has been used in studies of nonvolatile memory devices that function at low operating voltages [28–31]. The nanostructures of Ag_2S and ZnS semiconductors make these materials highly suitable for application in areas such as photoluminescence emitting/quenching, band gap engineering, photocatalysis, solar energy, electrical circuitry, and optical and/or optoelectronic devices [25,26,32–35]. Here, we report the synthesis of ZnS NWs using a Ag_2S semiconductor catalyst and a simple VLS method with a Ag film and ZnS precursor. The properties of the synthesized ZnS NWs, such as the crystallinity, composition, and structure, were analyzed by X-ray diffraction (XRD, Bruker D8 Advance), field-emission scanning electron microscopy (FE-SEM, Hitachi-8230), energy-dispersive X-ray spectroscopy (EDS, Oxford Aztec 80T), and transmission electron microscopy (TEM, JEM-ARM200F). Additionally, the VLS growth mechanism of the Ag_2S semiconductor-catalyzed ZnS NW synthesis was investigated by in situ heating TEM. Through real-time observation of the ZnS NWs, the transitions of the ZnS NWs and Ag_2S semiconductor catalyst were observed, and the results provided valuable insight into the VLS growth mechanism of the ZnS NWs using Ag_2S.

2. Experimental

ZnS NWs were synthesized by metal-organic chemical vapor deposition (MOCVD) using a $Zn(S_2CNEt_2)_2$ single-molecule precursor [36]. The MOCVD equipment was composed of a furnace, a 25 mm diameter quartz tube and a gas pressure control system. A Si (100) wafer was cleaned in an acetone solution and sonicated for 10 min, followed by sonication in deionized water for 5 min, after which the wafer was dried using nitrogen gas. The Ag film (~10 nm) to be used as the catalyst was then deposited on the clean Si wafer for 10 s via ion sputtering. $Zn(S_2CNEt_2)_2$ powder (Sigma Aldrich) was poured into an alumina boat, and Ag-coated Si wafers were placed upstream and downstream of the quartz tube. After reducing the pressure of the furnace tube to 0.1 Torr, a mass flow controller was used to allow for a 100 sccm (sccm denotes one cubic centimeter per minute at standard temperature and pressure) flow of Ar carrier gas, and the pressure within the quartz tube was maintained at 5 Torr using the pressure control system as the temperature of the furnace was increased at a rate of 1 °C per second to 800 °C. When the furnace temperature reached 800 °C, the alumina boat prepared upstream was moved inside the furnace, and the temperature was maintained for 1 h to achieve ZnS NW synthesis. After 1 h, the Ar gas flow was blocked, and the furnace was cooled to room temperature. A nontransparent, gray membrane was observed to have formed over the silicon specimen after cooling to room temperature. The crystalline characteristics of the synthesized ZnS NWs were investigated by XRD, and their morphology was observed by SEM and TEM. A focused ion beam (FIB, FEI NOVA200) was used to observe a cross-section of the ZnS NWs. Chemical composition analysis of the Ag_2S-catalyzed ZnS NWs was conducted by EDS. To investigate the growth mechanism, an in situ heating TEM experiment (Aduro 500, Protochips) was performed on the Ag_2S-catalyzed ZnS NWs.

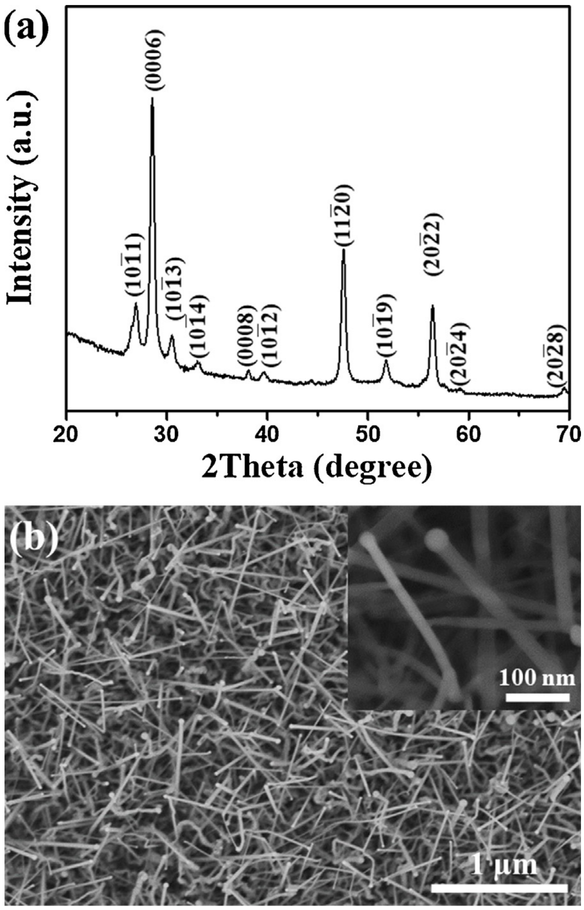

Fig. 1. (a) XRD pattern of ZnS with a wurtzite structure. (b) Low-magnification SEM image of the Ag_2S-catalyzed ZnS NWs (inset: high-magnification SEM image).

3. Results and discussion

XRD was used to analyze the structure of the ZnS NWs synthesized using the Ag_2S catalyst. The XRD peaks corresponded to the hexagonal wurtzite phase of ZnS with lattice constants of $a = b = 3.823$ Å and $c = 18.743$ Å, which match the JCPDS (Joint Committee on Powder Diffraction Standards, card no. 89-2191) well. No other phases were observed, and the absence of a Ag_2S peak was due to the very small amount of the material relative to that of ZnS (Fig. 1a). Fig. 1b shows an SEM image of the ZnS NWs synthesized after deposition of an ~10 nm-thick layer of Ag on the Si wafer, where Ag was used as the catalyst for ZnS NW growth. The low-magnification SEM image indicates the successful synthesis of ZnS NWs over a large area. The width and length of the ZnS NWs grown on the Si wafer were in the range of ~30 nm to ~80 nm and ~1 μm, respectively. The right inset (Fig. 1b) shows a high-magnification SEM image of the ZnS NWs. The spherical structures on the ends of the ZnS NWs provide strong evidence for a VLS mechanism.

A detailed morphological analysis of the ZnS NWs was conducted using TEM. To perform the TEM analysis, the ZnS NWs were directly scattered on a lacey carbon Cu TEM grid. Fig. 2a shows a low-magnification TEM image of typical ZnS NWs, with the Ag_2S catalyst shown as dark spherical structures on the ends of the ZnS NWs. Moreover, high-resolution (HR) annular dark field (ADF)-scanning TEM (STEM) was used to analyze the structure of the ZnS