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Crystalline α-Sm_2S_3 nanowires: Structure and optical properties of an unusual intrinsically degenerate semiconductor

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ABSTRACT

The lanthanide sulfides have long been a promising class of semiconductors because of their infrared-to-visible range band gaps and excellent thermoelectric properties. However, their applications have been limited due to their time consuming conventional synthetic processes and the lack of sufficient understanding of their electronic properties. To address these shortcomings, here we report a rapid, chemical vapor deposition route which results in thin films of crystalline α-phase samarium sesquisulfide (α-Sm_2S_3) nanowires within a few hours, rather than the typical 4–7 days required in previous synthetic processes. In addition, density functional theory was, for the first time, utilized to calculate the electronic band structure of α-Sm_2S_3 in order to shed insight into the interpretation of their UV–Vis absorption spectrum. We found that the theoretical direct gap in the band states of α-Sm_2S_3 is 1.7 eV. Computation results suggest that this gap can be tuned to a solar optimal ~1.3 eV via systematic sulfur vacancy sites engineered into the crystal structure. Most significantly, the degenerate semiconductor-like behavior long observed in lanthanide sulfide samples have been shown to be present even in the ideal α-Sm_2S_3 structure, suggesting that the observed heavily *p*-type behavior is an unusual intrinsic property of the material resulting from the Fermi level being located significantly below the optically active 1.7 eV band edge.

1. Introduction

The lanthanide sulfides are an intriguing class of semiconducting materials that are of considerable interest for their potential as high temperature thermoelectric materials [1], solar energy conversion materials [2], pigments [3], infrared window materials [4], and phosphor host media [5]. These applications largely stem from their visible light range absorption edges which provide the lanthanide series with their wide range of vibrant colors, from bright yellow (Yb_2S_3), to maroon (Ce_2S_3), to deep brown (Nd_2S_3) [6–8]. Despite their promise in displacing the use of toxic [9] cadmium chalcogenides in pigment applications [3], the lanthanide sulfides have not been utilized in many of the other cadmium chalcogenides' applications such as photovoltaics [10,11] and quantum dots [12,13]. This can be attributed to the time- and energy-intensive conventional synthetic methods and, in part, to the unresolved nature of their optical absorption bands.

The lanthanide sulfides are typically synthesized by sulfurizing the corresponding lanthanide oxides [6–8,14,15] using the highly toxic sulfurization agent hydrogen sulfide (H_2S). Their reaction temperatures range from 1000 °C to 1200 °C with the actual process temperature depending on the lanthanide involved and the resulting crystal structure desired [7]. The major problem associated with this synthetic strategy is the long reaction time required to fully displace the oxygen from the starting oxide reactants: 4–7 days at the peak reaction temperature [6]. Recently, carbon disulfide (CS_2) had been applied as the sulfurization agent in place of H_2S [8]. CS_2 was found to be a more rapid sulfurization agent, bringing the sulfurization time down to around 3 h and the required sulfurization temperatures down to 800–1200 °C [8]. However, this superior sulfurization performance of CS_2 comes at the cost of a 1–5 at.% carbon incorporation into the resulting lanthanide sulfides [16].

In general, the lanthanides prefer to have +3 oxidation states, meaning that a sesquisulfide form (Ln_2S_3) is the preferred stoichiometry. Notably, Yb [6] and Sm [17] may also attain the +2 state,

Abbreviations: CVD, chemical vapor deposition; DFT, density functional theory; PDOSs, projected density of states; SAED, selected area electron diffraction; HRTEM, high resolution transmission electron microscopy; EDX, energy dispersive X-ray spectroscopy.

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but the +3 state is generally favored. The crystal structures of Ln_2S_3 generally can take one of four polymorphs: α, γ, δ, or ε. Originally, a β-phase had also been reported, but it has since been discarded because a slight amount of oxygen was later found to be required for its formation [18]. Between the fifteen lanthanide elements and four polymorphs, the resulting lanthanide sesquisulfide's absorption band edges can range from 1.56 eV (for γ phase Gd_2S_3) to 2.73 eV (for α phase La_2S_3) [7].

Beyond the rough absorption edges, little is known about the nature of the semiconducting band gaps involved with the lanthanide sulfides. This is largely due to the dramatic tailing edge (weak absorption occurring before the main absorption onset) observed in the experimental absorption spectra as noted by Glurdzhidze et al. as far back as 1979 [19]. Typically, this band tailing is considered indicative of a small concentration of impurities in the sample [20]. While Tauc plot analyses of various lanthanide sulfides were attempted as early as 1983 [6], the optical spectra of these semiconductors routinely failed to fit well with direct, indirect, or even direct and indirect forbidden models. Indeed, in a more recent study on single crystalline Gd_2S_3 and Ce_2S_3 samples, Witz et al. [21] could only postulate that some extrinsic sample effects were obfuscating their reflectivity and absorption data. Consequently, they recommended reliable band structure calculations in order to aid with interpreting these compounds' complex optical spectra.

Of the lanthanide sulfides, the samarium sulfide systems are of particular interest for their semiconductor applications. Since samarium exhibits a propensity for taking on both +2 and +3 oxidation states, the reported band gaps for the samarium sulfides range from 0.15 eV for SmS [22], to 2.18 eV for the γ-phase of Sm_2S_3 [7]. Among the different phases of samarium sulfides, α-phase Sm_2S_3 attracts an increasing amount of attention [23] due to its reported band gap in the infrared-to-red range, which are comparable to the industrially important cadmium selenide [12,24]. Nonetheless, challenges in understanding the electronic structures of α-Sm_2S_3 have severely limited its industrial applications. Specifically, failures in applying the semiconductor models, used for simple *p*- and *d*-block compounds, to explain the reported absorption and reflectance spectra of Ln_2S_3 and their band tailing have led to speculations of impure samples in the reported literature and doubts as to the nature of its band gap. Moreover, the wide range of reported α-Sm_2S_3's absorption band edge values, from 1.69 eV [7] to 1.88 eV [8] and to even as high as 4.02 eV [23], has of yet been unresolved. The study of α-Sm_2S_3 has further been exacerbated by the lack of reliable band structure calculations for the electron-dense *f*-block lanthanide sulfides.

Here we report a rapid synthesis of crystalline α-phase Sm_2S_3 by chemical vapor deposition and the characterization of its electronic structure via a combined approach of absorption spectroscopy and first principles calculations. Interestingly, these materials were found to have a high inherent tendency to crystallize as high aspect ratio nanowires with morphologies similar to naturally occurring amphiboles. Absorption spectroscopy of the resulting nanostructured films was taken both to characterize the rough band edge and band gap characteristics. In order to better understand the unexplained band tailing present in the absorption spectra of these materials, first principles density functional theory (DFT) calculations of ideal, Sm-deficient and S-deficient α-Sm_2S_3 models were applied to compute possible electronic structures of α-Sm_2S_3. Remarkably, our DFT study reveals that even in an ideal crystalline state, α-Sm_2S_3 behaves as a heavily degenerate semiconductor (i.e. this material is intrinsically degenerate). This finding matches well with the peculiar experimentally observed behavior of these materials, providing explanation, for the first time, for the prominent tailing edges in their optical absorption spectra which have long been reported for these lanthanide sulfide systems.

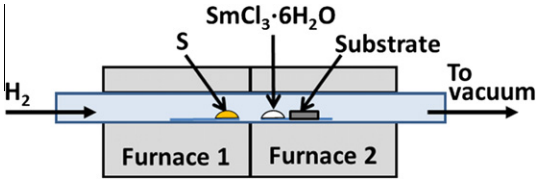

Fig. 1. Schematic of the experimental setup for the synthesis of α-Sm_2S_3 nanowire films.

2. Materials and methods

The α-Sm_2S_3 nanowire samples were synthesized by a CVD process in a 1-in. diameter quartz tube, inside a dual-furnace reactor. Samarium (III) chloride hexahydrate ($SmCl_3{\cdot}6H_2O$), elemental sulfur (S), and hydrogen (H_2) were used as the chemical precursors (Fig. 1). The overall empirical reaction equation is proposed as: $2SmCl_3{\cdot}6H_2O(g) + 3S(g) + 3H_2(g) \rightarrow \alpha\text{-}Sm_2S_3(s) + 6HCl(g) + 6H_2O(g)$. $1 \times 1\text{-cm}^2$ (100) silicon wafers coated with 200-nm thick silicon nitride (University Wafers, South Boston, MA) and $1 \times 1\text{-cm}^2$ quartz slides were used as the substrates to collect products deposited during the reaction. The silicon nitride coating acted as a diffusion barrier to minimize the formation of silicides on the silicon chips during the reaction. Each substrate was pre-rinsed with ethanol and 18-MΩ de-ionized water, followed by drying with nitrogen before use. The silicon nitride coated substrate was located at 12 cm to the left of the center of the dual furnace. If a quartz substrate was to be coated to collect reaction products for their optical characterization, it was placed adjacent to the silicon nitride coated silicon chip.

In a typical reaction run, 0.1 g of elemental sulfur and 0.3 g of samarium (III) chloride hexahydrate (Sigma–Aldrich, Milwaukee, WI) were loaded on two separate quartz boats at 14 cm to the right of the center of Furnace 1 and at 13.5 cm to the left of the center of Furnace 2, respectively (Fig. 1). After the reactor system was pumped down to a base pressure below 9 m Torr, 100 standard cubic centimeters per minute (SCCM) of hydrogen (H_2) was applied to purge the quartz tube in the reactor system. Furnace 1 was then heated to 100 °C over a period of 20 min to vaporize the sulfur and to start the diffusion of sulfur throughout the system. Simultaneously, Furnace 2 was heated to 400 °C to remove the water from the samarium precursor. The flow of the H_2 carrier gas was stopped before Furnace 1 reached 35 °C. After Furnace 1 reached 100 °C and Furnace 2 reached 400 °C, their temperatures were held constant for 10 min until the reactor pressure re-stabilized. This was then followed by increasing the temperature of Furnace 2 to 875 °C and that of Furnace 1 to 200 °C over a period of 10 min. Afterwards, H_2 was re-added to the reaction at 100 SCCM for another 10 min. The typical reaction pressure was at *ca.* 0.6 Torr. At the end of the reaction, the flow of H_2 was stopped. Furnace 1 was opened fully to cool while Furnace 2 was cooled at a rate of over 5 °C/s down to 400 °C before being opened fully for cooling to room temperature.

The morphology and atomic lattice structures of the as-synthesized samples were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4700, Pleasanton, CA), X-ray powder diffraction (XRD) using a Rigaku D/Max-B Diffractometer (2 kW Cu Kα X-ray beam with an average wavelength of 1.544 Å, Rigaku Americas, Woodlands, TX), and transmission electron microscopy (Tecnai F-20, FEI, Hillsboro, OR) with energy dispersive X-ray spectroscopy (EDX). TEM samples were prepared by sonicating the sulfide coated substrates in ethanol for 1–10 s until the ethanol became slightly cloudy, and then drop-casting this solution onto holey carbon TEM grids. UV–Vis-mid-IR absorption spectroscopy was performed on the sulfide coated quartz substrate and evaluated in comparison to a reference quartz standard using a Cary 5000 grating spectrophotometer (Agilent Technologies, Santa Clara, CA). Note that the use of absorption spectroscopy was necessary because the as-synthesized films were determined to be too thin for meaningful diffuse reflectance measurements.

3. Theory and calculations

Absorption spectrum analysis was performed using the standard Tauc method [25–29]. The model behind this method assumes that band-to-band transitions occur between a concave up and a concave down parabolic band in which the lower band is fully occupied and curved concave down. In such a case, it can be shown [20] that:

$$\alpha \cdot h\nu \propto (h\nu - E_g)^n \tag{1}$$

where α is the coefficient of absorption of the material, $h\nu$ is the energy of the incident photon, and E_g is the energy of the band gap being investigated. Additionally, the value of the exponential n provides insights into the relative positions of the two parabolic bands, where a value of $n = 1/2$ corresponds to a direct peak to valley