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Preparation of antimony sulfide semiconductor nanoparticles by pulsed laser ablation in liquid

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ABSTRACT

In this paper, we report on the synthesis of antimony sulfide (Sb_2S_3) semiconductor nanoparticles by pulsed laser ablation in liquid without using any surfactants or capping agents. Different results were obtained in water and organic solvents. In the case of water, Sb_2S_3 nanoparticles with chemical compositions of stoichiometry were successfully prepared when laser irradiation was performed under the condition with the dissolved oxygen removed by argon gas bubbling. It was shown that thus-obtained Sb_2S_3 nanoparticles exhibit features of not only low-temperature crystallization but also low-temperature melting at a temperature as low as 200 °C. Nanoparticle-coated Sb_2S_3 thin films were found to show good visible light absorption and satisfying semiconductor properties (i.e., carrier mobility and density), which are essential for photovoltaic application. On the other hand, in the case of organic solvents (e.g., acetone, ethanol), such unexpected byproducts as CS_2, CO and CH_4 were detected from the reaction system by GC-MS analysis, which suggests that both Sb_2S_3 and organic solvents were partially decomposed during laser irradiation. The possible mechanism will be discussed.

1. Introduction

Antimony sulfide (Sb_2S_3) has been one of the most studied binary chalogenide materials in recent years, because of its versatile potential applications, such as in photovoltaic conversion [1,2], optoelectronics [3], tribology [4], visible light-response photocatalysis [5], etc. Among these applications, photovoltaic material is the most attractive one, because Sb_2S_3 has a high absorption coefficient (1.8×10^5 cm^{-1} at 450 nm), and a relatively narrow optical bandgap of 1.6–1.8 eV, which is well suited for capturing visible light photons [6,7].

For photovoltaic application, organic-inorganic hybrid thin film solar cells (HSCs) are the often studied targets, in which inorganic nanoparticles are generally used as n-type semiconductors (instead of the conventional C60 derivatives) to blend with the p-type organic semiconductors [8,9]. In the blended active layer, phase separation occurs between the organic semiconductors and inorganic nanoparticles. The photo-generated holes are transported to anode through the organic phase, and electrons are transported to the cathode through the inorganic phase. Since the performance of the solar cell is greatly dependent on the charge transportation efficiency in the active layer, it is thus important to ensure a good electrical contact between the inorganic nanoparticles [10]. However, since inorganic nanoparticles are usually prepared in the existence of surfactants or long-chain ligands (capping agents), the electrical contact is generally poor because such surfactants or capping agents tend to act as an electrically insulating layer that impedes efficient charge transfer between the nanoparticles. To improve this issue, thermally removable ligands (generally short-chain organic molecules) have also been studied by some researchers [11–13]. Nevertheless, the improving effect is still not satisfactory.

From the viewpoint of electrical contact, employment of inorganic nanoparticles with a clean surface (i.e., without any surfactants or capping agents) is ideal, because a clean surface would make it relatively easy to sinter for the nanoparticles due to their larger free surface energies, which thus improve the electrical contact between them. To prepare clean nanoparticles, however, it is necessary to develop a surfactant-free synthesis process, which has always been a challenge for researchers. For Sb_2S_3, although there have been various studies on preparation of nanoparticles (especially, nanorods, nanowires) [14–16], surfactant-free synthesis has been seldom reported so far.

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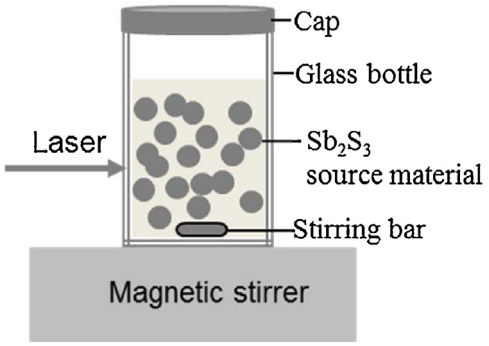

Fig. 1. Schematic diagram of experimental setup.

On the other hand, laser ablation in liquid (LAL), as a promising novel fabrication method of nanoparticles, has attracted much attention in recent years due to its simple procedure and low environmental load [17]. Up to now, various kinds of nanoparticles (e.g., metal, metal oxide, organic substance) have been successfully fabricated by using this method [18–21]. Importantly, several studies have reported that LAL has the potential as a surfactant-free synthesis approach [22,23].

In this work, we attempt to apply LAL to prepare Sb_2S_3 nanoparticles and to confirm whether LAL can be used as a surfactants-free synthesis method for Sb_2S_3. Emphasis was particularly put on the effect of solvents (water and organic solvents) and the dissolved oxygen in the case of water. To our knowledge, although there have been several studies on preparing metal sulfide semiconductor nanoparticles (e.g., MoS_2, CdS, PbS) by LAL [24,25,26], studies on preparing Sb_2S_3 nanoparticles have been limited so far [27,28].

2. Experiment

The experimental setup is schematically shown in Fig. 1. Sb_2S_3 powder with an average diameter of ~20 μm was used as the source material. It was suspended in 20 ml water or organic solvents with magnetic stirring, and the concentration of Sb_2S_3 is 0.1 wt%, unless otherwise specified. In this work, no surfactants or capping agents were used. Laser ablation was carried out from the side wall of the glass bottle with a non-focused beam. In the case of argon gas bubbling, crimp glass vials (closed with a rubber stopper and an aluminum cap) were used, and argon gas bubbling was conducted before the laser irradiation. Nd:YAG pulsed laser with a pulse duration of 8 ns and a frequency of 10 Hz was used as the light source (GCR-100, Spectra-Physics), and three wavelengths (1064 nm, 532 nm, and 355 nm) with various laser fluence were tested. The particle size and chemical composition of the obtained nanoparticles were analyzed by a transmission electron microscopy (TEM, JEOL JEM-ARM200F) coupled with an energy dispersion X-ray analyzer (EDX). The gas products generated during laser ablation were analyzed using a GC-MS analyzing system (JEOL, JMS K-9). The absorption spectra and semiconductor properties (carrier mobility and density) of the Sb_2S_3 thin films were measured with a UV–visible spectrometer (JASCO V-670) and Hall effect measurement system (ResiTest8400, Toyo Corporation), respectively. X-ray diffraction (XRD) measurements were performed on a X-ray Diffractometer (SmartLab Multipurpose, Rigaku Corporation).

Table 1
Chemical compositions of Sb_2S_3 nanoparticles generated from water with and without argon gas bubbling.

Atmosphere during laser irradiation	Chemical composition (atom%)			
	S	Sb	O	S/Sb ratio
Without argon gas bubbling (open system)	41.9	38.1	20.0	1.10
With argon gas bubbling (closed system)	58.0	40.0	2.0	1.45

3. Results and discussion

3.1. Laser ablation in water

3.1.1. The effect of dissolved oxygen in water

Fig. 2 shows the typical images exhibiting changes in the solution color and particle size before and after laser irradiation for 15 min in water at a wavelength of 1064 nm (fluence: 1520 mJ/cm^2). Before laser irradiation, Sb_2S_3 powders subsided at the bottom of the glass vessel due to their large particle sizes (Fig. 2(b)), and thus the solution looks like colorless. After laser irradiation, the color of the solution turned to transparently brown (Fig. 2(c)). TEM images demonstrated that colloid particles with sizes less than 20 nm were formed in the brown solution (Fig. 2(d)), and the dispersion was found to be stable (no precipitation being observed) within about 1 day. The stability of the dispersion was found to be dependent on the Sb_2S_3 concentration, and a higher concentration tends to facilitate the precipitation. However, it was found that the precipitation can be re-dispersed temporarily when ultrasonication was applied, and a better re-dispersion effect was observed at a diluted solution. These results indicate that nanoparticle dispersion can be easily formed by a short period of laser irradiation in water even without addition of any surfactants or capping agents. The LAL-generated nanoparticles were found to have a relatively high minus zeta potential (−20 mV), which may devote to its dispersion in water.

In addition, it was found that the solution color and particle size change little no matter whether laser irradiation was carried out at an open system of atmosphere or at a closed system with the dissolved oxygen removed, which suggests that the dissolved oxygen has little effect on the ablation efficiency.

Table 1 shows the chemical compositions of the Sb_2S_3 nanoparticles generated from water with and without argon gas bubbling. It can be seen that when laser irradiation was performed at an open system of atmosphere, the obtained particle contains a high content of oxygen (~20 atom%), indicating that the nanoparticle might be partially oxidized during laser irradiation. As the result, the elemental ratio of S/Sb deviated greatly from the stoichiometric value (1.5). On the other hand, when laser irradiation was carried out at a closed system with dissolved oxygen removed by argon gas bubbling, the oxygen content of the Sb_2S_3 nanoparticles decreased to 2.0 atom%. This value of oxygen is actually close to that of detected on the Sb_2S_3 source material (1.8 atom%), which may be originated from contaminants adsorbed on the particle surface. This result indicates that the issue of partial oxidation of Sb_2S_3 nanoparticles can be solved by removing the dissolved oxygen in water. As the result, the elemental ratio of S/Sb was improved from 1.10 to 1.45. Taking into account of the experimental error (~ 0.1%) of the EDX measurement, it should be reasonable to consider that Sb_2S_3 nanoparticles with stoichiometric compositions are generated in the later condition.

It is known that water tends to serve as an oxidant when laser ablation was performed in water in many cases [29–31]. For example, it has been reported that ablation of Cu [29], Sn [30], and Co as well as CoO [31] in water lead to formation of CuO, SnO_{n-2}, and Co_3O_4, respectively. These composition changes were explained in

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