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Sonochemical Preparation of GaSb Nanoparticles

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A room temperature sonochemical method for the preparation of GaSb nanoparticles using less hazardous Ga and antimony chloride ($SbCl_3$) as the precursors has been described. The formation of GaSb has been confirmed by means of XRD, EDAX, and XPS characterization. TEM and SAED results show that the as-prepared solid consists of nanosized GaSb crystals with sizes in the range 20–30 nm. The photoacoustic spectrum result reveals that the GaSb nanoparticles have a direct band gap of about 1.21 eV. On the basis of the control experiments and the extreme conditions produced by ultrasound, an ultrasound-assisted in-situ reduction/combination mechanism has been proposed to explain the reaction.

The III−V (13−15) compounds are well-known electronic and optical materials.[1] Their technological importance has stimulated the study of their preparation and properties.[2,3] Conventional routes to the synthesis of III−V semiconductors include solid state reaction,[4−6] metalorganic chemical vapor deposition (MOCVD),[7,8] molecular beam epitaxy (MBE),[9,10] and the liquid phase epitaxy (LPE) method.[11] Recently, some new methods such as solid state metathesis (SSM),[12] the pyrolysis of single-source precursors,[13,14] the solution−liquid−solid (SLS) process,[15] a benzene-thermal method[16,17] and a solvothermal coreduction route[18] have been reported. However, most of the new methods developed for the preparation of III−V compounds during the past few years have focused on metallic nitrogen, phosphorus, and arsenic compounds, and some processes use very toxic PH_3 and AsH_3 as precursors. Few extensions of these new methods to the synthesis of gallium antimonide (GaSb) have been reported.[19] Crystalline gallium antimonide (GaSb)[20] is a direct band gap material of interest for the production of various semiconductor devices[21,22] and IR optical devices.[23] A literature review finds that various researchers have prepared gallium antimonide (GaSb) in the solid and vapor phases at high temperatures.[24,25] What makes the preparation of metallic antimonides more difficult than that of the corresponding nitrides, phosphides, and arsenides is that antimony precursors such as SbH_3 and $Sb(R)_3$ (R = Me or Et) are extremely toxic and unstable or unavailable at all. Although a solution phase silyl halide elimination method has been studied for the preparation of GaSb,[25] the precursor, tris(trimethylsilyl)-stibine, is very expensive and a high-temperature posttreatment is require to obtain a crystalline product.

Sonochemistry has proven to be a useful technique for the preparation of nanoparticles and novel materials with unusual properties.[26,27] Up to now, no report on the preparation of GaSb using this technique has been published.

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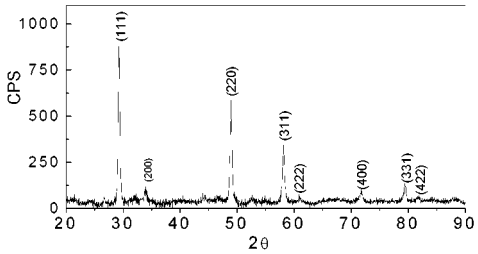

Figure 1. XRD pattern of the as-prepared sample.

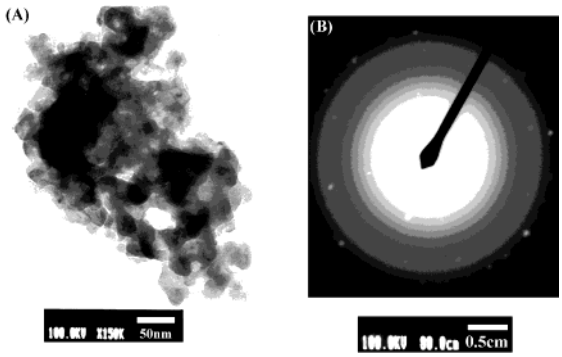

Figure 2. TEM image (A) and SAED (B) of the as-prepared sample.

Herein, we report on a room temperature sonochemical method for the preparation of GaSb nanoparticles using less hazardous Ga and antimony chloride ($SbCl_3$) as the precursors.

In a typical procedure, an appropriate amount of liquid Ga was put into a glass flask and then dispersed at the bottom. $SbCl_3$ was weighed in a glovebox and then mixed with Ga. After that, the flask was filled with toluene to up to 80% of its total volume. The mixture was irradiated with ultrasound for 3 h at room temperature under a H_2/Ar (5/95, v/v) atmosphere, by employing a direct immersion titanium horn (20 kHz, 100 W·cm^{-1}). During the irradiation, a black-gray precipitate appeared and the temperature of the suspension rose to 80 °C. After the irradiation, the solution was cooled to room temperature. The precipitate was then separated from the solution by centrifugation and washed twice with both toluene and absolute ethanol. The resulting black solid was dried in a vacuum at room temperature for 6 h, yielding 90% GaSb by weight.

Figure 1 shows an X-ray diffraction (XRD) pattern of the as-prepared solid recorded using a Rigaku X-ray diffractometer (model 2028, Co Kα λ = 1.78892 Å). All the peak positions are consistent with the standard data of cubic crystalline GaSb, and the same is true for the intensities of the peaks (JCPDS file No.7-215). EDAX analysis gives the atomic ratio Ga:Sb of 47.2:51.8, which is close to the 1:1 stoichiometry. The very weak impurity peaks in the XRD pattern can be attributed to the surface oxides of the nanoparticles.

The sizes of the particles were determined by transmission electron microscopy (JEOL-JEM 100SX microscope). Although the particles are aggregated, it can be seen that the sizes of the individual particles are between 20 and 30 nm (Figure 2). Their selected area electron diffraction shows a spotty crystalline pattern.

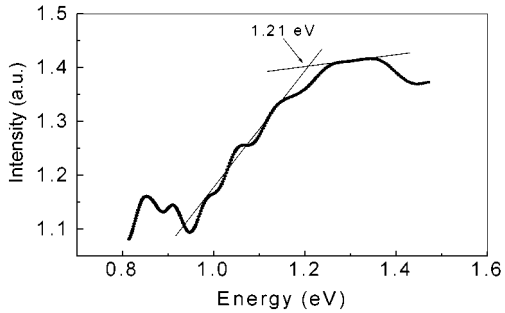

Figure 3. Photoacoustic spectrum of the as-prepared sample.

High-resolution X-ray photoelectron spectroscopy (XPS) data (accumulated on an AXIS HS electron spectrometer system with a monochromatized Al Kα X-ray source) also confirmed the product as GaSb.[28]

GaSb is known as a semiconductor with a direct band gap of 0.7−0.8 eV. In order to understand the interband properties of the GaSb nanoparticles, photoacoustic measurements were conducted employing a homemade instrument which has been described elsewhere.[29] In the present study, the PAS method was used for the measurements of the band gap of nanoparticulated GaSb (Figure 3).

The band gap value was calculated using the "knee method". The measured band gap was blue-shifted relative to the bulk value and was equal to 1.21 eV, which is probably due to the quantum size effect.

On the basis of the slope, it was possible to conclude that this is a direct band gap. The angle of the slope relative to the background is equal to 75°. In the monodispersive single crystal, this angle must be close to 90°. The difference can be explained as a result of some polydispersity of the prepared particles. The reason for the presence of the shoulders at 0.98, 1.05, and 1.14 eV is unclear, but they may be Wannier states leading to the bottom of the band gap or may result from some impurity states in the current compound.

A two-step mechanism of the formation of GaSb is proposed: first, the $SbCl_3$ was reduced by H_2 or H at the high-temperature interface layer of the bubble induced by ultrasound[30] (eq 1):

$$SbCl_3 + {}^3/_2H_2/Ar_{5/95,V/V} \xrightarrow[\text{toluene}]{\text{ultrasound}(((\cdots} Sb + 3HCl \qquad (1)$$

Second, the Sb reacted with the melted Ga in situ, also in the interface layer, forming the GaSb (eq 2).

$$Ga(\text{liquid}) + Sb \xrightarrow{\text{Ultrasound}(((\cdots} GaSb \qquad (2)$$

A control reaction of the direct reduction of $SbCl_3$ by H_2, assisted by ultrasound irradiation, reveals that the pure element Sb is indeed obtained. In fact, pure elemental Sb can be prepared by reducing Sb_2O_5 with H_2 gas at high temperature.[31] However, the reactivity of pure $SbCl_3$ is much slower than that in the Ga/$SbCl_3$ mixture. This difference

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can be explained as follows: According to the phase diagram of gallium antimonide, a mixture of gallium and antimony is not thermodynamically stable and should convert to gallium antimonide.[32] Therefore, if a trace of Sb is formed in the interface layer, it will react with gallium in situ due to the negative Gibbs free energy of formation of GaSb, which will accelerate the reduction reaction of Sb^{3+} by reducing the amount of Sb.[33] A control experiment shows that no GaSb would be formed without the presence of H_2 gas. It is impossible to reduce Ga with H_2, and, therefore, it will be reasonable to reduce Sb^{3+} in our experiment.

In a similar fashion, we can prepare other Ga or Sb related compounds if we choose the suitable solvent and precursors. We also have extended this method to prepare II−VI compounds such as CdSe and so on, with safe precursors.

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In summary, we have developed a sonochemical method for the preparation of GaSb nanoparticles. It is the lowest temperature synthesis of GaSb reported to date. The as-prepared solids are well-crystallized nanoparticles with a direct band gap of about 1.21 eV. The high-temperature and high-pressure region around the bubble induced by the ultrasound promote the reduction of $SbCl_3$ and also provide the site for the reaction between Sb and Ga. This approach overcomes the difficulty of the reaction between bulk Ga and Sb at low temperature or in solution, by using ultrasound-assisted reduction of a soluble $SbCl_3$. It has also been shown that it is a common method to a lot of semiconductor compounds with nanometer scale size.

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