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FACILE PREPARATION OF NANOCRYSTALLINE GALLIUM ANTIMONIDE

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FACILE PREPARATION OF NANOCRYSTALLINE GALLIUM ANTIMONIDE

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Abstract: The 1:1 reaction of $GaCl_3$ with $Sb(SiMe_3)_3$ in pentane solution affords an intermediate material which, upon thermolysis, yields nanocrystalline GaSb with an approximate average particle size of 12 nm. The product was characterized through powder X-ray diffraction, elemental analysis, and HRTEM.

Keywords: A. Nanostructures, A. Semiconductors, B. Chemical Synthesis, C. Electron Microscopy, C. X-Ray Diffraction.

Introduction

Nanocrystalline 13-15 semiconductors have attracted much attention recently due to their interesting electronic and optical properties (1) and, as a result, synthetic pathways to these materials have been investigated extensively over the past few years (2). In 1989, the first use of dehalosilylation reactions to prepare the 13-15 compound semiconductors ME (M = Ga (3a), In (3a), and Al (3b), E = As; M = In (3c, d), E = P) was reported. Since that time, researchers in our laboratory (4) and in others (5) have utilized this methodology to prepare 13-15 materials of nanoscale dimensions. While the use of dehalosilylation to prepare nanocrystalline Group 13-phosphides (4, 5b, d) and -arsenides (5a, c) is well documented, the preparation of Group 13-antimonides by this method has been studied less extensively (*vide infra*). Gallium antimonide-based compound semiconductors, for example, have recently been of interest for their potential in electronic applications (6).

A literature review finds that numerous researchers have prepared gallium antimonide (GaSb) in the solid and vapor phases (6, 7), however, solution phase preparations are limited (2b). In an attempt to remedy this situation, we recently reported the production of GaSb by a solution-phase silyl halide elimination method and examined the purity, crystallinity, and particle size of the resultant product in a detailed manner (8). The utility of this method has also been demonstrated recently by Schulz *et al.* (9). Herein, we detail our results for the 1:1 mole reaction of gallium(III) chloride with tris(trimethylsilyl)stibine in pentane solution to afford an intermediate material which, upon annealing, afforded nanocrystalline GaSb (eq. 1).

$$GaCl_3 + (Me_3Si)_3Sb \xrightarrow[\text{-}Me_3SiCl]{\text{room temp.}} \text{red-brown powder} \xrightarrow[\text{-volatiles}]{\Delta} \text{GaSb (nanocrystalline)} \qquad (1)$$

Experimental

All manipulations of air and moisture sensitive materials were performed in a Vacuum Atmospheres HE-493 Dri-Lab containing an argon atmosphere or by general Schlenk techniques. Pentane was distilled from Sodium/Potassium alloy under dry dinitrogen. $GaCl_3$ was purchased from Strem Chemicals and was used as received without further purification. GaSb was purchased from Alfa AESAR and used as received. Tris(trimethylsilyl)stibine, $(Me_3Si)_3Sb$, was prepared according to literature methods (10) with slight modifications. Elemental analysis was performed by E+R Microanalytical Laboratory, Inc., Corona, NY. X-ray powder diffraction (XRD) data were obtained on a Philips XRG 3000 diffractometer using Cu Kα radiation (λ = 1.5418 Å; graphite monochrometer). Transmission electron microscopy (TEM) data were collected on a TOPCON EM002B instrument utilizing a 200 kV accelerating voltage at the North Carolina State University Analytical Instrumentation Facility.

A 250 mL round-bottomed flask equipped with a Teflon valve and a stir bar was charged with $Sb(SiMe_3)_3$ (0.682 g; 2.00 mmol) dissolved in 30 mL of pentane. To this clear, slightly yellow solution, $GaCl_3$ (0.352 g; 2.00 mmol) dissolved in 25 mL of pentane was added *via* pipet. An immediate orange-red color developed with the formation of a dark precipitate. This mixture was allowed to stir for 12 h at room temperature. The volatiles were removed *in vacuo* to yield a red-brown powder (0.439 g) of empirical formula $C_2H_6Ga_2SbCl$ (based upon C, H, Ga, Sb, Cl analyses) which was isolated as an intermediate material. The volatiles were then hydrolyzed with deionized water and titrated with NaOH (0.0997 M, 17.10 mL, corresponding to the elimination of 1.70 mmol (56.7%) of Me_3SiCl).

The gallium-antimony containing intermediate was thermally decomposed as follows: The red-brown powder was loaded into a sublimator, heated under vacuum at 75 °C for 15 min., and then ramped by 30 °C increments from 75 to 285 °C, 20 °C increments from 285 to 325 °C, and 25 °C increments from 325 to 400 °C. Sustained heating of the sample at 400 °C for 24 h afforded a black powder containing GaSb (0.227 g; 59% yield based on Ga) with only a trace of by-product residue detected on the sublimator coldfinger. Hydrolysis and titration of the decomposition volatiles yielded only 0.1 mmol (3.3%) of detectable Me_3SiCl. Anal. Calcd(found) for GaSb: Sample 1, Ga, 36.41(23.53); Sb, 63.59(59.14); C, 0.00(1.80); H, 0.00(0.37); Cl, 0.00(<0.30); Ga:Sb ratio 1.0:1.4; Sample 2, Ga, 36.41(25.63); Sb, 63.59(49.82); C, 0.00(1.06); H, 0.00(0.28); Cl, 0.00(2.78); Si, 0.00(1.64); Ga:Sb ratio 1.0:1.1.

Results and Discussion

A powder X-ray diffraction (XRD) pattern of the red-brown intermediate material showed it to be amorphous in nature. Annealing this powder at 400 °C for 24 h afforded a black powder containing GaSb, initially confirmed by elemental analysis (EA). From the EA results, *vide infra*, the Ga:Sb ratio was calculated as 1:1.4, indicating that there was excess antimony present in the sample. Thus, the sample composition was calculated as 65% GaSb (Ga and Sb constitute 83% of the sample weight) with minimal contamination from carbon and essentially none from hydrogen or chlorine. Since the initial sample was not analyzed for silicon content, we could not conclude with complete certainty that the remaining impurity was silicon. To resolve this question, we submitted a second sample of the annealed material for full elemental analysis (C, H, Cl, Si, Ga, Sb). For the second sample, the Ga:Sb ratio was calculated as 1:1.1, indicating that excess antimony was still present in the powder. The GaSb composition of this sample was calculated as 70% (Ga and Sb constitute 75% of the sample weight) with minimal contamination from carbon, hydrogen, chlorine, and silicon. To date, we are unable to unambiguously account for the remaining sample percent composition and studies are ongoing to address this issue.

The XRD pattern of the black powder obtained from the reaction (eq. 1) is shown in Figure 1. Comparison of this plot with an XRD pattern of a bona fide sample of 99% pure GaSb confirms the presence of GaSb in the powder. The labeled peaks in Fig. 1 correspond to the (111), (220), and (311) reflections of cubic GaSb, as reported by JCPDS (11). In agreement with the EA results, there are peaks in the XRD pattern which indicate the presence of excess antimony, most notably the peak at 40° 2θ angle, which matches the (104) reflection of hexagonal Sb. The large peak at 29° 2θ matches both the (200) reflection of cubic GaSb and the (012) reflection of hexagonal Sb, however, it is unclear which species is responsible for its presence. Due to the relative intensity of this peak, it is conceivable that it has contributions from both the (200) GaSb and (012) Sb lattice planes; however, no attempt was made to resolve these peaks. Using the XRD data, an approximate average particle size of 12 nm was calculated for the sample by the Scherrer equation (12).

Fig. 1. XRD pattern of annealed GaSb nanocrystals. A 12 nm approximate average particle size was calculated for the specimen from the XRD data. The y-axis shows relative intensity.

Figure 2 shows a section of the high-resolution transmission electron micrograph (HRTEM) obtained on the GaSb containing sample. The majority of the lattice fringes observed correspond to the (111) reflection plane of cubic GaSb, however, lattice fringes corresponding to the (220) reflection plane are also visible. The d-spacings corresponding to these reflections are 3.5 and 2.2 Å, respectively, and by counting the number of planes observed for a particular crystallite, its size may be approximated. The range of crystallite sizes obtained from this procedure is in good agreement with the average size calculated from the XRD data. As further evidence of the sample identity, an electron diffraction ring pattern of the sample was indexed to that of cubic GaSb (11). It is interesting to note that a small number of particles are present in the TEM images (though none are seen in Figure 2) which match the 3.1 Å d-spacing of the (012) reflection of hexagonal Sb. This is not surprising, though, considering that the EA and XRD results have established the presence of excess antimony in the sample.

Fig. 2. Transmission electron micrograph (TEM) of the GaSb quantum particles. The marker represents the scale. Lattice planes of several small crystallites are visible.

The preliminary EA, XRD, and HRTEM data given above suggest that nanocrystalline GaSb has been formed by the silyl elimination route. This result is significant in that it represents, to the best of our knowledge, the first preparation of GaSb under these conditions. Future studies in this area will focus on optimizing the reaction and decomposition conditions to produce higher-quality GaSb, as well as forming other Group 13-antimonides.

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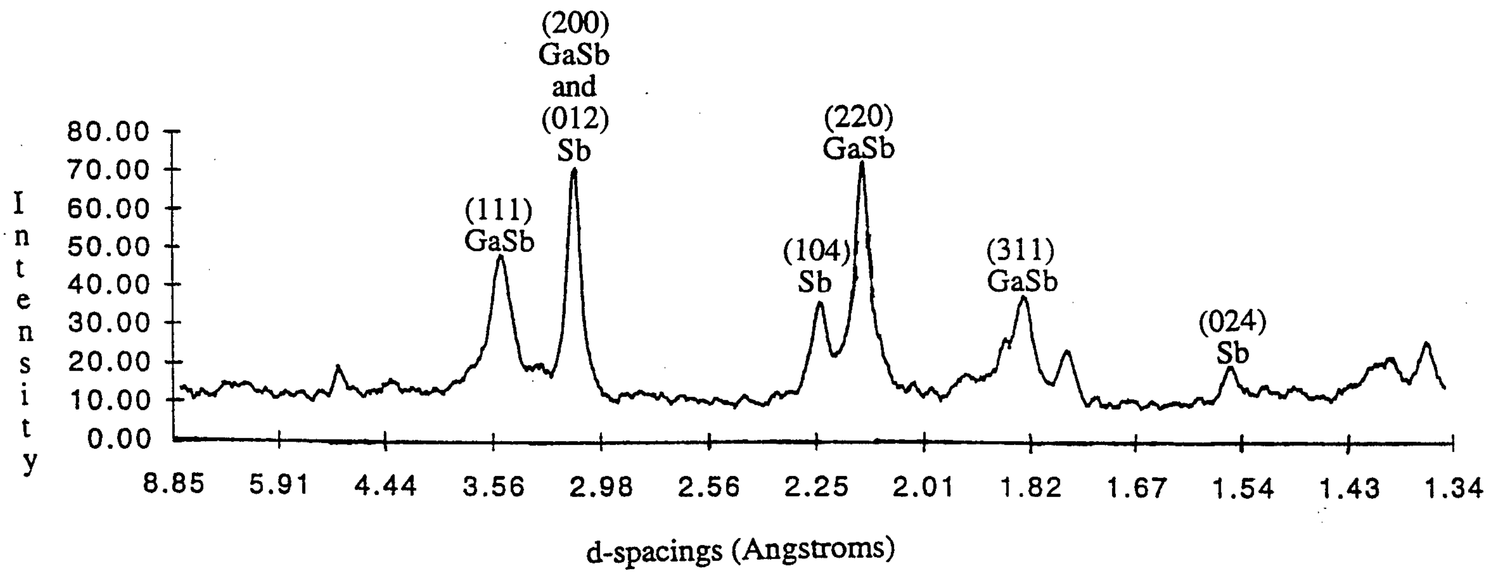
(200)
GaSb
and
(012)
Sb
(220)
GaSb
(111)
GaSb
(104)
Sb
(311)
GaSb
(024)
Sb
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Intensity
8.85
5.91
4.44
3.56
2.98
2.56
2.25
2.01
1.82
1.67
1.54
1.43
1.34
d-spacings (Angstroms)

Figure 1.

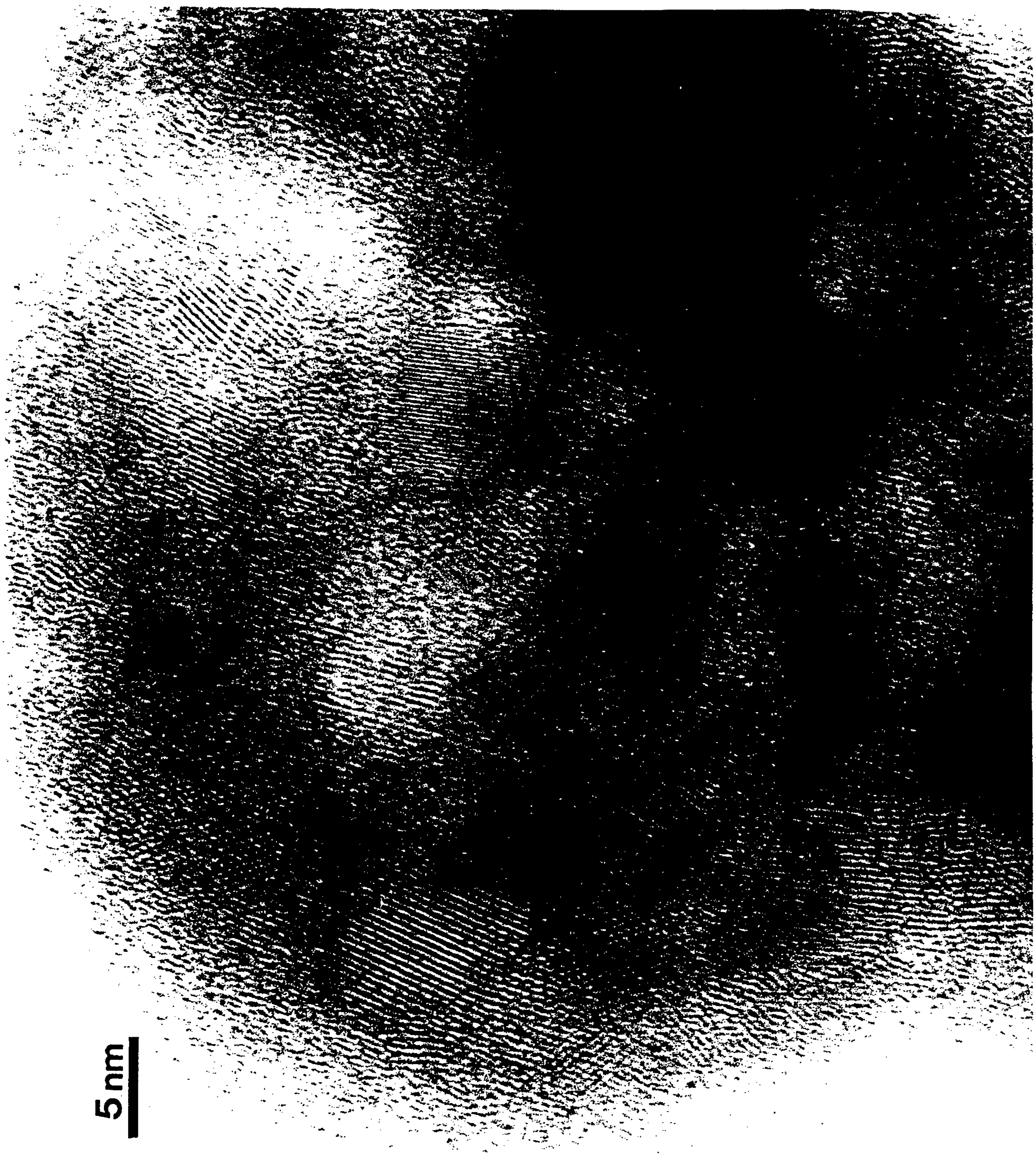

Figure 2.

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