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Room-Temperature MOCVD of Sb_2Te_3 Films and Solution Precipitation of M_2Te_3 (M = Sb, Bi) Powders via a Novel (*N,N*-Dimethylamino)trimethylsilane Elimination Reaction

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Introduction

Group V chalcogenide materials have potential applications in solar cell[1] and reversible optical storage technology.[2] In addition, Sb_2Te_3 and Bi_2Te_3 have been extensively studied since the 1950s for thermoelectric applications.[3] Bi_2Te_3 and its alloys with Sb_2Te_3 and Sb_2Se_3 are the most efficient compound semiconductor materials currently available for thermoelectric cooling at room temperature. Previous studies on these compound semiconductors have been conducted on bulk materials prepared by high-temperature solid-state synthetic techniques. Thin films of these V/VI semiconductor materials have been less studied, although electrical properties of thin films prepared by sputtering or reactive evaporation have been recently reported.[4] We now report the growth of Sb_2Te_3 thin films by a novel Me_3SiNMe_2 elimination reaction at room temperature using $Sb(NMe_2)_3$ and $(Me_3Si)_2Te$ in a reduced pressure metal–organic chemical vapor deposition (MOCVD) reactor. Conventional MOCVD processes for growing thin semiconductor films require pyrolysis or photolysis of organometallic precursors to break metal–ligand bonds and form the semiconductor material.[5] To our knowledge, this is the first report of a room-temperature MOCVD process for preparing thin binary semiconductor films relying on the chemical reaction of the precursors, not pyrolysis or photolysis of the precursors, to grow thin films of a semiconductor material.

Powders of V/VI semiconductors can be processed by metallurgical methods in order to fabricate thermoelectric materials with greater mechanical strength than melt-grown materials which are easily cleaved. The V/VI semiconductor powders have been prepared by grinding and sifting the melt-grown materials into various particle sizes (50–250 μm).[6] The powders were then processed by hot- or cold-pressed sintering methods. We now report the precipitation of submicron polycrystalline powders of Sb_2Te_3 and Bi_2Te_3 from solutions at unusually low temperatures from the reactions of $Sb(NMe_2)_3$ or $Bi(NMe_2)_3$ with $(Me_3Si)_2Te$, respectively.

Results and Discussion

Solution precipitation methods using elimination reactions to produce semiconductor powders have been previously reported. For example, alkane elimination reactions have been used to prepare bulk metal sulfide materials and chlorotrimethylsilane elimination reactions have been used to prepare nanometer-size particles of GaAs in solution.[7,8] We have prepared submicron polycrystalline powders of Sb_2Te_3 and Bi_2Te_3 at temperatures as low as −30 °C by solution precipitation using 2 equiv of the precursors $Sb(NMe_2)_3$[9] and $Bi(NMe_2)_3$,[10] respectively, with 3 equiv of $(Me_3Si)_2Te$[11] (eq 1). The new Me_3SiNMe_2 elimination reaction efficiently leads to the formation of group V/VI bonds and results in the direct synthesis of Sb_2Te_3 and Bi_2Te_3 at unusually low temperatures (eq 1).[12] The reaction appears to go completion and no intermediate organometallic reaction products have been observed in solution. Furthermore, these reactions appear to be self limiting with respect to the V/VI precursor stoichiometry, thus excess unreacted group V or VI precursor can be recovered. NMR characterization of the reaction byproducts reveals only Me_3SiNMe_2 and any excess starting reagents in solution. Elemental analyses of these powders verify the 2/3 ratio of the V/VI elements and indicate that significant incorporation of the Me_3Si or NMe_2 groups into the solid material does not occur.

$$\underset{\mathrm{M = Sb, Bi}}{2\mathrm{M(NMe_2)_3}} + 3\mathrm{(Me_3Si)_2Te} \xrightarrow[-30\ ^\circ\mathrm{C}]{\text{hexanes}} \mathrm{M_2Te_3} + 6\mathrm{Me_3SiNMe_2} \tag{1}$$

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[1] Bhattacharyz, R. N.; Pramanik, P. *J. Electrochem. Soc.* **1982,** *129,* 332.

[2] Fujimori, S.; Yagi, S.; Yamazaki, H.; Funakoshi, N. *J. Appl. Phys.* **1988,** *64,* 1000.

[3] Yim, W. M.; Rosi, F. D. *Solid State Electron.* **1972,** *15,* 1121.

[4] (a) Patel, N. G.; Patel, P. G. *Cryst. Res. Technol.* **1993,** *3,* 407. (b) John, K. J.; Pradeep, B.; Mathai, E. *Solid State Commun.* **1993,** *85,* 879. (c) Rahman, S.; Muralidhar, K. V.; Sastry, G. S. *Phys. Chem. Glasses* **1993,** *34,* 176. (d) George, J.; Pradeep, B. *Solid State Commun.* **1985,** *56,* 117. (e) Patel, N. G.; Patel, P. G. *Mater. Lett.* **1984,** *3,* 46.

[5] Stringfellow, G. B. *Organometallic Vapor Phase Epitaxy: Theory and Practice;* Academic Press: Boston, 1989.

[6] Wada, H.; Sato, T.; Takahashi, K.; Nakastukasa, N. *J. Mater. Res.* **1990,** *5,* 1052.

[7] (a) Bauch, C. G.; Johnson, C. E. *Inorg. Chim. Acta* **1989,** *164,* 165. (b) Johnson, C. E.; Harris, D. C.; Willingham, C. B. *Chem. Mater.* **1990,** *2,* 141.

[8] (a) Olshavsky, M. A.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1990,** *112,* 9438. (b) Berry, A. D.; Purdy, A. P.; Wells, R. L.; Pasterczyk, J. W.; Johansen, J. D.; Pitt, C. G. *Mater. Res. Soc. Symp. Proc.* **1991,** *204,* 107.

[9] Moedritzer, K. *Inorg. Chem.* **1964,** *3,* 609.

[10] Ando, F.; Hayashi, T.; Ohashi, K.; Koketsu, J. *J. Inorg. Nucl. Chem.* **1975,** *37,* 2011.

[11] Contrary to reports in the literature, we found $(Me_3Si)_2Te$ to be very stable at room temperature when stored in the absence of light. However, $(Me_3Si)_2Te$ is air and water sensitive: Detty, M. R.; Seider, M. D. *J. Org. Chem.* **1982,** 1354.

[12] Organic solvents were distilled under Ar from sodium/benzophenone. Since $Sb(NMe_2)_3$, $Bi(NMe_2)_3$, and $(Me_3Si)_2Te$ are air, water, and light sensitive, all manipulations of these precursors was done under Ar using inert atmosphere techniques. Reaction flasks containing the precursors were wrapped in Al foil to minimize exposure to light during storage. **Bi_2Te_3 Powders:** To a stirring solution of 1.279 g (4.669 mmol) of $(Me_3Si)_2Te$ in 10 mL of hexanes at −30 °C (CCl_4 dry ice bath) was added dropwise (drop time = 20 min) in the dark a solution of 1.118 g (3.276 mmol) of $Bi(NMe_2)_3$ in 10 mL of hexane. After the addition was complete, 10 mL of hexane was used to wash down any trace of $Bi(NMe_2)_3$ in the dropping funnel, and the black slurry was warmed to room temperature slowly and stirred at room temperature overnight. The slurry was filtered and washed with two 10-mL portions of hexane. The black Bi_2Te_3 powder (1.123 g, 90% yield based on $(Me_3Si)_2Te$) was dried under vacuum for 4 h. Anal. Calcd for Bi_2Te_3: Bi, 52.20; Te, 47.80. Found: Bi, 51.40; Te, 47.67; C, 1.18; H, 0.11. **Sb_2Te_3 Powders:** Sb_2Te_3 powders were prepared in an analogous manner using $Sb(NMe_2)_3$. During the reaction a silver mirror deposited from the solution onto the glass walls of the flask. The silver Sb_2Te_3 material (0.260 g, 52% yield based on $(Me_3Si)_2Te$) was scraped off the flask, filtered, washed with hexanes, and dried under vacuum. Anal. Calcd for Sb_2Te_3: Sb, 38.88; Te, 61.12. Found: Sb, 38.69; Te, 60.66; C, 1.54; H, 0.23.

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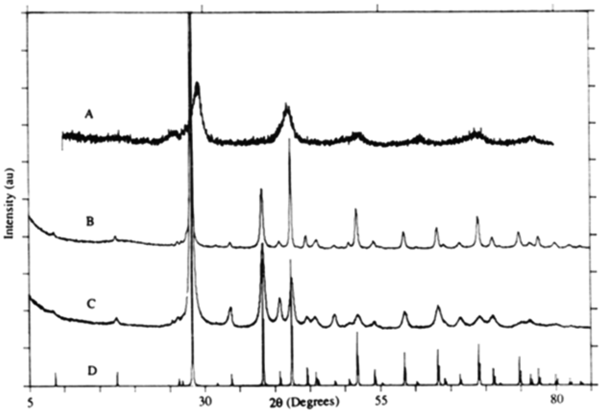

Figure 1. X-ray powder diffraction (Cu Kα) scans of (A) Sb_2Te_3 powder prepared at −30 °C, (B) Sb_2Te_3 powder prepared at −30 °C then annealed at 160 °C for 4 h, (C) Sb_2Te_3 film grown on Si(111) at room temperature, and (D) calculated XRPD pattern for randomly oriented crystallites of rhombohedral Sb_2Te_3.[14]

X-ray powder diffraction (XRPD) data were obtained for the powders and films produced by reaction 1.[13] The XRPD pattern of the fine, silver Sb_2Te_3 powder prepared at −30 °C exhibited very broad peaks that are equivocally assigned to a low-temperature phase of Sb_2Te_3 or (Sb,Te) of poor crystallinity/ordering (Figure 1A). However, annealing of the powder at 160 °C under argon improved the crystallinity and ordering of the material (Figure 1B), and the resulting XRPD pattern was found to match reference and calculated powder patterns for rhombohedral Sb_2Te_3 under ambient conditions (Figure 1D).[14a–c] The crystallite sizes for the annealed Sb_2Te_3 powder are approximately 278–425 Å for general *hkl* and ~685 Å for the (110) reflection, assuming that the observed line broadening is due solely to particle size effects.[14d] Scanning electron microscopy (SEM) of the annealed Sb_2Te_3 powder verifies the submicron particle size (Figure 2). The XRPD pattern for the fine, black Bi_2Te_3 powder prepared at −30 °C (Figure 3A) is unmistakably rhombohedral Bi_2Te_3 (Figure 3C).[14a] Furthermore, the XRPD pattern exhibits additional broadening at *d* spacings of ~3.14, 2.22, and 1.78 Å, which might be attributable to a low-temperature phase of Bi_2Te_3 or (Bi,Te). However, annealing of the Bi_2Te_3 powder at 160 °C results in the disappearance of the additional broad peaks and an improvement in the crystallinity/ordering (Figure 3B). The crystallite sizes for the annealed Bi_2Te_3 powder are approximately 321–484 Å for general *hkl* and ~647 Å for the (110) reflection.[14d] SEM of the annealed Bi_2Te_3 powder verifies the submicron particle size (Figure 4).

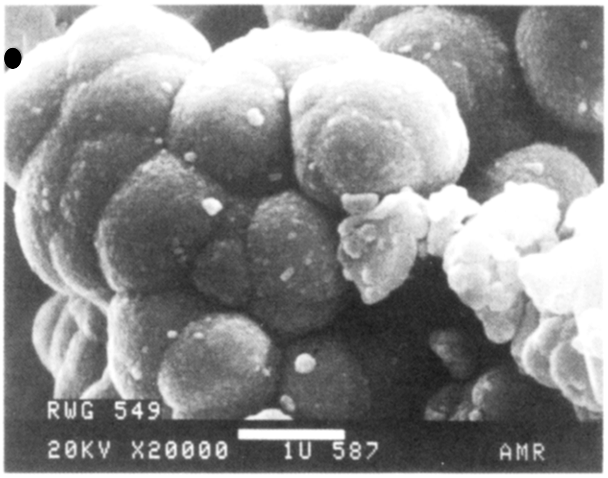

Figure 2. SEM of Sb_2Te_3 powders precipitated out of solution at −30 °C and annealed under argon at 160 °C.

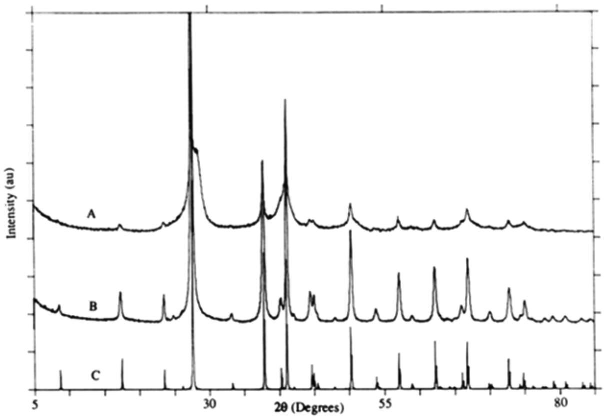

Figure 3. X-ray powder diffraction (Cu Kα) scans of (A) Bi_2Te_3 powder prepared at −30 °C, (B) Bi_2Te_3 powder prepared at −30 °C then annealed at 160 °C for 4 h, and (C) calculated XRPD pattern for randomly oriented crystallites of rhombohedral Bi_2Te_3.[14]

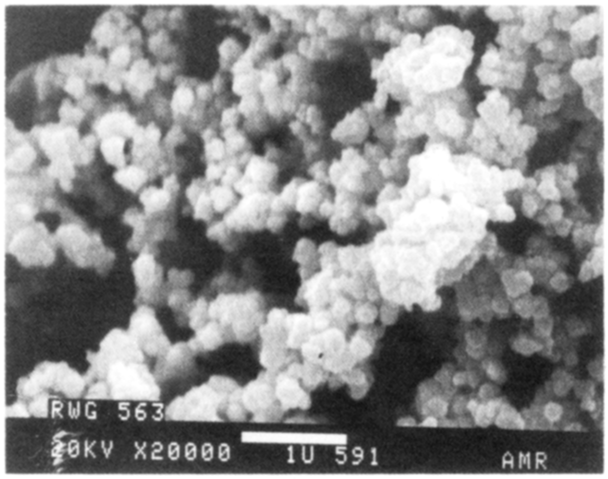

Figure 4. SEM of Bi_2Te_3 powders precipitated out of solution at −30 °C and annealed under argon at 160 °C.

Polycrystalline Sb_2Te_3 films were grown on Si(111) at room temperature in reduced pressure (~0.25 Torr) horizontal and vertical MOCVD reactors using $Sb(NMe_2)_3$ and $(Me_3Si)_2Te$ in the gas phase.[15] The films were grown under Sb-rich conditions with V/VI ratios varying from 1.2 to 1.8. The only volatile byproduct identified by NMR (collected in a −78 °C trap) and the residual gas analyzer (in situ monitoring of reactor exhaust) was Me_3SiNMe_2.[16]

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(13) X-ray diffraction data were obtained using a Scintag PAD V (2θ:θ) diffractometer (220 mm radius) equipped with a N_2(l) cooled solid-state Ge detector and Cu-target X-ray tube. Scans were recorded over the range 5–85° (2θ). Powders were mounted on off-axis "zero-background" quartz substrates using Vaseline. Thin films grown on off-axis-cut Si substrates were mounted directly into the diffractometer.

(14) (a) International Centre for Diffraction Data (1991), Swarthmore, Pa. Entry 15-874 for Sb_2Te_3 and Entry 15-863 for Bi_2Te_3. (b) Anderson, T. L.; Krause, H. B. *Acta Crystallogr.* **1974**, *B30*, 1307 (structural reference for Sb_2Te_3). Feutelais, Y.; Legendre, B.; Rodier, N.; Agafonov, V. *Mater. Res. Bull.* **1993**, *28*, 591 (structural reference for Bi_2Te_3). (c) Smith, D. K., Nichols, M. C., Zolinsky, M. E. *Powd 10, A Fortran IV Program for Calculating X-ray Powder Diffraction Patterns-Version 10* (Pennsylvania State University, University Park, PA, 1982), adapted by Scintag Inc., for use with Scintag software/graphics. (d) After background corrections and α_2 stripping of the sample data, the intrinsic line breadths for the sample peaks were obtained by assuming Cauchy-shaped profiles and subtracting the instrument function from the observed widths obtained from deconvolution. By assuming that the resulting line broadening was due entirely to particle-size effects, apparent crystallite sizes were calculated using the Scherrer equation, $L = 0.9\lambda/\beta \cos \theta$.

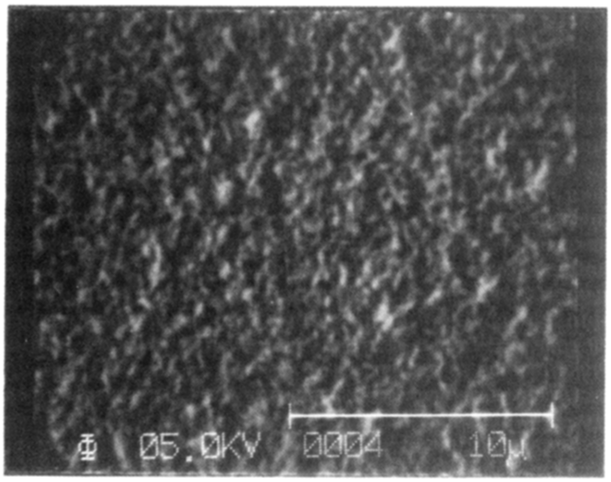

Figure 5. SEM of Sb_2Te_3 film grown on Si(111) in a vertical MOCVD reactor at room temperature.

The surface morphologies of the films vary from smooth, highly reflective surfaces to dull gray with many surface defects depending on the growth rate and reactor conditions. Smooth specular films (Figure 5) were grown at $\sim$0.25 Torr, with V/VI ratios greater than 1, and growth rates at about 1 μm/h. Thin films that were $\sim$0.5 μm thick where highly reflective, where as films grown at atmospheric pressure using Ar as a carrier gas were dull gray with a sooty morphology. The XRPD patterns of the Sb_2Te_3 films grown at reduced pressure at room temperature (Figure 1C) indicate that the films are unmistakably polycrystalline Sb_2Te_3. The films exhibit some preferred orientation in the [015] direction by comparison to the calculated powder pattern for randomly oriented crystallites (Figure 1D). Annealing of the Sb_2Te_3 film at 160 °C under Ar results in delamination of parts of the film from the substrate and only a slight improvement in the film crystallinity. Auger depth profile analyses[17] of the films establishes the 2/3 atomic ratio of Sb/Te throughout the film with carbon and oxygen detected in 3 and 2 atomic %, respectively. No Si was detected in the films within the limits of Auger.

Conditions for optimum Sb_2Te_3 film growth are currently being explored. Although Bi_2Te_3 films have been grown by MOCVD at room temperature using $Bi(NMe_2)_3$ and $(Me_3Si)_2Te$, problems associated with consistent vapor-phase transport due to condensation of the solid $Bi(NMe_2)_3$ in the inlet line and reactor walls are still being resolved. Similar preparation of group V chalcogenide systems have also been preliminarily explored. $P(NMe_2)_3$ and $As(NMe_2)_3$ readily react with $(Me_3Si)_2Te$ at room temperature to give an as-yet uncharacterized precipitate and Me_3SiNMe_2. Furthermore, although $Sb(NMe_2)_3$ does not react with $(Me_3Si)_2S$ in solution even when heated to 55 °C, $Bi(NMe_2)_3$ reacts immediately with $(Me_3Si)_2S$ at room temperature to give a black precipitate of an uncharacterized bismuth sulfide and Me_3SiNMe_2. We have also observed a reaction between $As(NMe_2)_3$ and $As(SiMe_3)_3$ to give As and Me_3SiNMe_2.

The new Me_3SiNMe_2 elimination reaction represents a new methodology for preparing V/VI semiconductor films and powders. Preliminary experiments indicate its potential general usefulness for preparing thin films and bulk powders of other semiconductors or coating materials. This type of reaction also provides a novel synthetic route to forming metal–metal bonds at low temperatures in organometallic molecules.

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(15) (a) Lee, K. E.; Lowe-Ma, C. K.; Higa, K. T. *Mater. Res. Soc. Symp. Proc.* **1993**, *282*, 87. (b) Sb_2Te_3 films were grown in a cylindrical horizontal and vertical Pyrex MOCVD reactor using a coaxial inlet for introduction of the precursors. An UTI 100C residual gas mass spectrometer was used to monitor the depositions and the gaseous byproducts. All the mass spectral data were collected at a 70-eV electron impact energy. Si[111] 4°-off-axis substrates were first degreased then etched with a 10% HF solution. The substrates were blown dry with N_2 and evacuated in the reactors for 1–2 h prior to deposition.

(16) ^1H NMR of Me_3SiNMe_2 (bona fide sample; C_6D_6): 2.38 (s, 6H, Me–N), 0.04 ppm (s, 9H, Me–Si). ^{13}C NMR (C_6D_6): 37.85 (Me–N), –1.31 ppm (Me–Si).

(17) A Perkin-Elmer PHI 600 scanning Auger microprobe was used to determine the elemental composition of the as deposited Sb_2Te_3 films.