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A New Route to Antimony Telluride Nanoplates from a Single-Source Precursor

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The V−VI class of materials are of special importance because of their thermoelectric properties.[1] They have been suggested as having potential in room-temperature thermoelectric applications. At present, efforts are being made to increase their figure-of-merit (ZT) in order to realize such applications. In this context, antimony telluride (Sb_2Te_3), a narrow band gap, layered semiconductor widely used in thermoelectric generators and coolers, has received much attention.[1−5] The material intrinsically possesses a high ZT due to its large Seebeck coefficient. Seebeck coefficients as high as 185 μVK^{-1} have been reported by Zou et al.[3] At a ZT of about 3, thermoelectric refrigerators or power generators can become competitive with conventional ones.[6] Doped antimony telluride derivatives have the potential for room temperature thermoelectric applications.[7] Ternary alloys of antimony and bismuth such as $Bi_{0.5}Sb_{1.5}Te_3$ and $Bi_2Te_{2.85}Se_{0.15}$ have also been used in thermoelectric coolers.[8]

Preparation of single-crystalline nanomaterials is essential for efficient thermoelectric applications. The growth of antimony and/or bismuth telluride thin films using methods such as metal−organic chemical vapor deposition (MOCVD),[9] flash evaporation,[10] sputtering,[11] and hot wall epitaxy[12] have been reported by various workers. More recently, Wang and co-workers have described a solvothermal approach to hexagonal-shaped Sb_2Te_3 nanoplates.[1] Such nanostructured materials are of particular interest for use in thermoelectric applications as they can give rise to a high figure-of-merit. Previously, we have reported the preparation of one-dimensional In_2S_3 nanorods using a liquid organometallic single-source precursor (SSP), $[Et_2In(S_2CNMe^nBu)]$, by aerosol-assisted chemical vapor deposition (AACVD).[13] It was also determined that the molecular architecture of the precursor plays a significant role by yielding different morphologies. Herein, we report the first example of the generation of pure Sb_2Te_3 thin films from a SSP, $Sb[(TeP^iPr_2)_2N]_3$, using the AACVD process, resulting in hexagonal nanoplates in the temperature range 375−475 °C.

The precursor $Sb[(TeP^iPr_2)_2N]_3$ used in the deposition studies was synthesized according to the reported method.[14] A typical film deposition utilized a solution of 0.100 g of the precursor dissolved in 10 mL of toluene which was converted into aerosols using an ultrasonic humidifier. The glass substrates were placed in an AACVD reactor[15] (5−6 substrates of approximately 1 cm × 3 cm dimensions) and heated at the desired temperature for 10 min before any deposition studies. After initial deposition for 1 h, the reactor was cooled under argon at room temperature to avoid in situ oxidation.

Thermogravimetric analysis (TGA) of $Sb[(TeP^iPr_2)_2N]_3$ showed two decomposition steps. The first weight-loss step corresponds to loss of one ligand moiety, $[(TeP^iPr_2)_2N]$, at ~280 °C (wt % left: 75, calcd 70) followed by further fragmentation at 325 °C, resulting in Sb_2Te_3 (wt % residue 43%, calcd 39%).

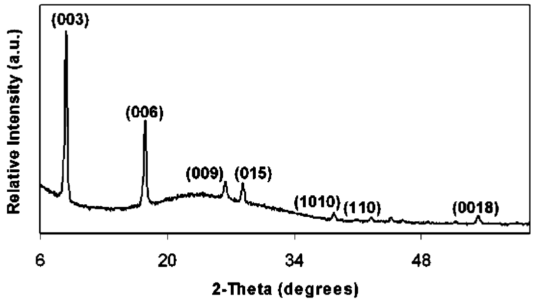

Figure 1. X-ray diffraction pattern of rhombohedral Sb_2Te_3 thin films deposited at 475 °C using a dynamic argon flow rate of 240 sccm.

Deposition studies were attempted between 325 and 475 °C. However, 325 °C was too low a temperature to initiate deposition. When the growth temperature was increased to 375 and 475 °C, good quality black, reflective films were obtained on the glass substrates. The X-ray powder diffraction (XRD, Cu Kα radiation, Bruker AXS) studies of as-deposited films exclusively showed the growth of rhombohedral Sb_2Te_3 (JCPDS: 15-0874) with a preferred orientation along the (003) plane in the temperature range 375−475 °C (Figure 1). XRD studies of hexagonal Sb_2Te_3 nanoplates obtained by the solvothermal method showed a mixture of Te and Sb_2Te_3, which was further elaborated in TEM studies.[1] The cell parameters for a rhombohedral unit cell were calculated and compared with the literature values (JCPDS: 15-0874). The calculated lattice values ($a = 4.257$ Å, $c = 30.373$ Å) are in good agreement with the reported values ($a = 4.264$ Å, $c = 30.458$ Å).

The morphologies of the films were studied by field emission gun scanning electron microscopy (FEG-SEM, Philips XL 30). The images provided in the Supporting Information clearly show the formation of randomly orientated plates. Thus, the deposition temperatures do not have profound effects on the film morphologies. The composition of the films was determined by energy-dispersive X-ray analysis (EDAX) from which the Sb:Te stoichiometry of films was found to be 2:3. No phosphorus peak from a decomposition product of the precursor was detected in the films.

Samples for transmission electron microscopy (TEM, Phillips Technai F30 300 kV FEG TEM) were prepared as suspensions by briefly sonicating the films in ethanol, and then a drop of the suspension was placed on a TEM grid and allowed to dry. Images of the films grown at 475 °C are shown in Figure 2. The presence of hexagonal nanoplatelets can be seen from the TEM images, potentially making such films useful for thermoelectric applications. There is also evidence of some truncated hexagonal-shaped nanoplates (Figure 2b). A HR-TEM image of the same film shown in Figure 2d indicates well-resolved lattice planes of a highly

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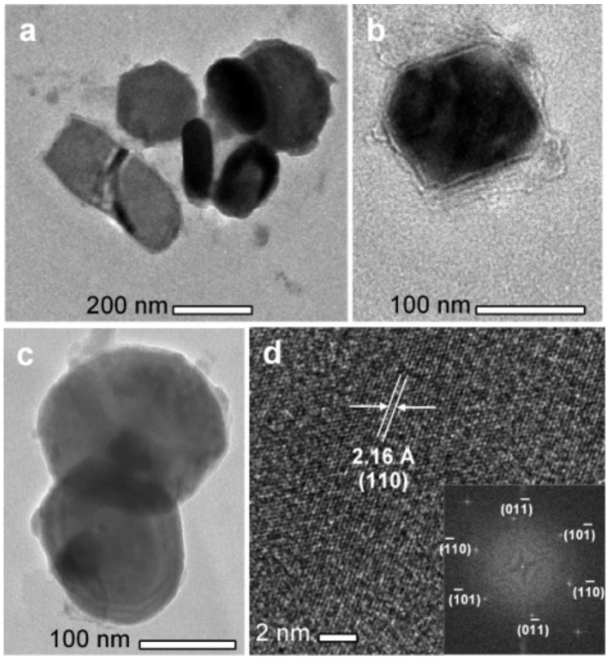

Figure 2. (a) and (c) TEM pictures of Sb_2Te_3 nanoplates showing that their planar dimension varies between 100 and 200 nm; (b) a truncated nanoplate and (d) HRTEM and FFT (inset) of the films grown at 475 °C indicate single crystallinity of the nanoplates.

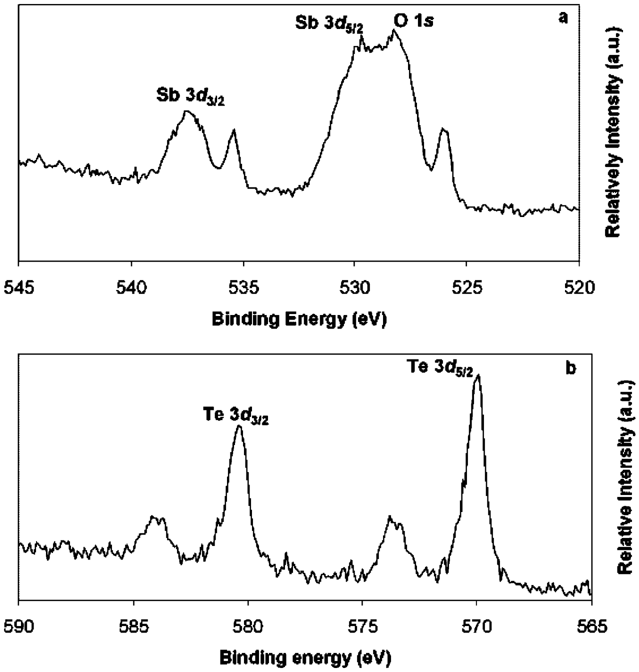

Figure 3. Survey XPS scan for (a) Sb and (b) Te from the films grown at 475 °C.

crystalline material. The calculated lattice spacing of 0.216 nm matches closely with the accepted value of 0.212 nm (JCPDS: 15-0874) for the (110) spacing in Sb_2Te_3. The diffraction spots in the Fast Fourier Transform (FFT) of the same lattice image matches with that of rhombohedral Sb_2Te_3. The presence of hexagonal symmetric spots further confirmed the single crystalline nature of the nanoplates. The planar dimensions of the hexagonal nanoplates vary between 100 and 200 nm with a width of ca. 20 nm. In contrast, the Sb_2Te_3 plates prepared by Wang et al. from $SbCl_3$ and Te powder by a solvothermal method are micrometers in size.[1]

Surface analysis of the films was carried out using X-ray photoelectron spectroscopy (XPS, Kratos Axis) (Figure 3). The Sb $3d_{5/2}$ and $3d_{3/2}$ peaks are observed at 529.7 and 537.3 eV, respectively. Additional peaks (525.9 and 535.4 eV) for Sb 3d indicate different chemical environments i.e., Sb−O and Sb−Te. The values of 539.6 eV ($3d_{3/2}$) and 530.3 eV ($3d_{5/2}$) are reported for antimony oxide in the literature.[16] A broad peak for Sb $3d_{3/2}$ is obtained due to overlapping with the O 1s (529.6 eV) peak. The two Te 3d signals, corresponding to Te−Sb and Te−O, are also seen. The values for Te−O, i.e., 584 eV ($3d_{3/2}$) and 574 eV ($3d_{5/2}$), are comparable to literature values of 586 ($3d_{3/2}$) and 576 eV ($3d_{5/2}$).[17] The presence of the O1s peak indicates that oxidation of the film takes place after exposure to the atmosphere. A minor P $2p_3$ peak at 130.5 eV represents a possible decomposition product, which is present as a contaminant in the deposited films.

Four-point probe resistivity measurements (Jandel voltmeter, model RM3) of the films grown at 475 °C gave conductivity values between 159 and 180 Ω^{-1} cm^{-1} (depending on film thickness), which are comparable to the literature value (320 Ω^{-1} cm^{-1}).[3]

In conclusion, we have demonstrated that $Sb[(TeP^iPr_2)_2N]_3$ can be used as a well-defined precursor to rhombohedral Sb_2Te_3 thin films by CVD. Surface analysis of such films confirmed that the growth temperature does not have a profound effect on the morphologies of the deposited film, which are composed of hexagonal nanoplates. We believe that this growth technique could also be applied to the synthesis of other semiconductor materials with a range of interesting nanostructures.

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Supporting Information Available: Figure showing SEM images of Sb_2Te_3 films deposited on glass at (a) 375 °C, (b) 425 °C, and (c) 475 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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