University of Glasgow | School of Chemistry

Nanostructured Thermoelectric Materials for Renewable Energy Generation

Jamie B. Gallagher[a], Yimin Zhao[a], Douglas Paul[b] Duncan H Gregory[a]

a WestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow, G12 8QQ. Email: Duncan.Gregory@glasgow.ac.uk
B School of engineering, University of Glasgow, G12 8QQ. Email Douglas.paul@glasgow.ac.uk

Chemical Vapour Growth of Bismuth Telluride

Introduction: Thermoelectronic materials are substances capable of converting heat directly into electricity using the Seebeck effect. These materials are also capable of working in reverse and will produce a temperature gradient when connected to an electrical power source. These materials are of great interest in today's energy frugal environment. They are capable of taking existing systems and increasing the efficiency by reclaiming the heat created as a by-product of an inefficient system. The results described below are experiments aimed at producing nanoscale thermoelectronic materials.
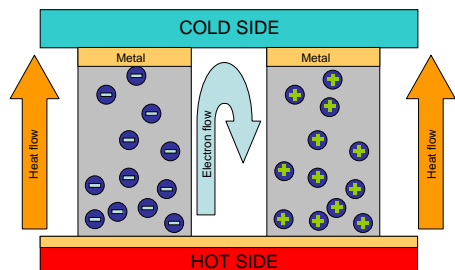
Theory

Figure 1: Simplified schematic of a thermoelectric module.

A simplified schematic of a thermoelectric device can be seen above in Fig: 1. The two main constituent parts are an n and p type semiconductor. These are positioned to be electrically in series but thermally in parallel. When a temperature gradient is applied there is a movement of the charge carriers away from the heat source. Comparing the flow of positive holes to a electrical flow in the opposite direction it can be seen how the circuit is formed[1].
An ideal thermoelectric material has a very good electrical conductivity and a very poor thermal conductivity. It is imperative that the gradient be maintained over the device.
In current thermoelectric generators many of these small n-p pairings of millimetre dimensions are connected; approximately 40 per square centimetre.

Optimising Efficiency:

One of the current leading methods that is proving successful both theoretically and experimentally is that of decreased dimensions. Dresselhaus et al. proved theoretically that by reducing thermoelectronic materials to the nanoscale the efficiency of these devices can be multiplied many times. This is represented in Fig: 2. This is due to the combination of many effects such as phonon scattering at the boundaries leading to poor thermal conductivity and quantum confinement effects.
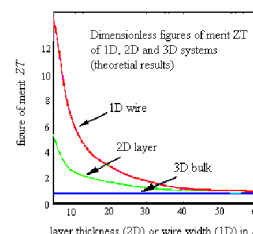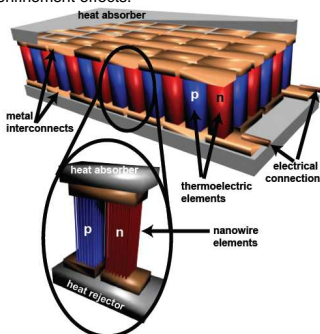

Figure 2: Increased ZT with decrease in dimensions[2].

Figure 3: Theoretical nanowire device

The ultimate goal of the Gregory groups study of thermoelectronic materials is to build working devices made of nanowires arrays. Using a speciality in chemical vapour deposition techniques. The leading materials for near room temperature applications[3] - Bismuth and Antimony Telluride are studied. Figure 3 shows a theoretical projection of what such a nanoscale device may look like. Wires are substituted in place of the bulk ingots currently used.

Experimental setup

The experiments described below were achieved through chemical vapour deposition. Chemical vapour deposition has proven an extremely useful way of growing new morphologies of materials. This method allows for an extremely natural growth formation on the surface of substrates, leading to regular growth of low dimensional structures on surfaces.

The reactants of bismuth and tellurium are ground together in a nitrogen environment and transferred into a silica quartz tube. A kink is made in the tube and a silicon substrate suspended by this above the reactants, keeping the metals and silicon wafer 4-5cm apart. The whole tube is then sealed under 4mbar vacuum to create a single use reaction ampoule. The entire vessel is heated at either constant temperature above 450ºC in a box furnace or a temperature gradient is applied in a tube furnace to keep the substrate cooler than the reactants

Experimental set up is altered to achieve desired conditions such as stoichiometry of reactants, surface coating on Si (such as nickel or gold coating) and temperature.
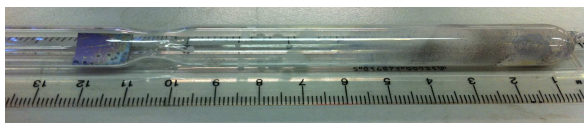

Figure 4: Sealed reaction ampoule

Material analysis

For confirmation of the materials produced the first step of all sample is X-ray diffraction. Below is one such pattern (fig 5) produced by an Panalytical X'pert powder diffractometer.
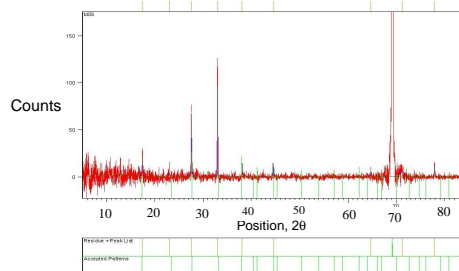

Figure 5: Typical XRD pattern

The pattern shown results from a standard CVD reaction (red/blue) and is compared to a standard accepted pattern for Bi_2Te_3 (green). Main peaks match confirming structure. Missing peaks are attributed to preferential growth direction along the c-axis. Composition also confirmed by EDX and TEM electron diffraction.
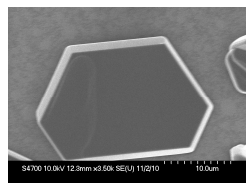
Low dimensional growth
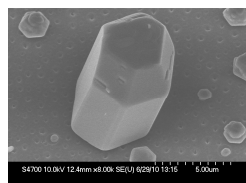

Figure 6: hexagonal single crystal plate

Figure 7: Vertically grown plate

Within the group there have been many successful low dimensional structures achieved. Bismuth telluride has a hexagonal crystal structure and this is often reflected in the growth obtained. With hexagonal platelets of 10-40 µm common and easy to achieve (fig: 6). There has also been success in encouraging these platelets to obtain a vertical growth perpendicular to the surface of the substrate (fig:7).
Of particular interest are the nanosheets and nanowires obtained. The structure of bismuth telluride naturally forms layers with van der Waals forces holding these sheets together in the bulk material, it is therefore easy for the material to have a fixed termination point. Fig: 11 shows a sheet approx 5-10nm thick, highlighted by the electron transparent nature. Also newly discovered are the nanowires seeded from the surface of larger particles (fig 9/10). These are not fully analysed but result from reaction involving a slightly increased bismuth concentration to combat the difference in vapour pressure between the materials.
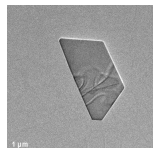

Figure 11: Nanosheet of Bi2Te3

Figure 8/9 (left): TEM image and electron diffraction pattern.

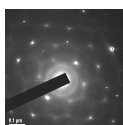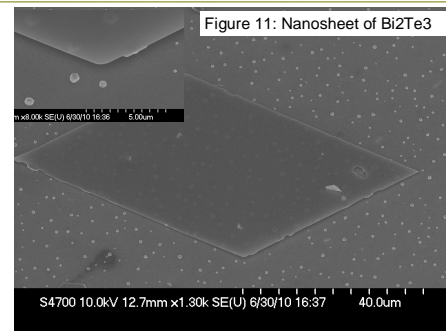Figure 9/10 (right): Nanowires in non-stoichiometric sample.

References
1. CRC Handbook of Thermoelectrics, edited by D.M. Rowe, CRC Press, 2006
2. G. Snyder and E. Toberer, *Nature Mater.*, 2008, **7**, 105
3. X. Sun, Z. Zhang and M. S. Dresselhaus, *App. Phy. Let.* 1999, **74**,4005