THIN FILM TECHNOLOGY

Thermoelectric Energy Conversion 2: Thin Film Materials

By Dr. Peter M. Martin, *Senior Technologist and Thin Film Editor*

I am usually not one for editorial commentary, but I am compelled to comment on how our irresponsible congress is holding back progress in science and technology. With the continuing resolution no new projects can be funded and continuing projects at the national and government laboratories limp along with an 8% per month budget. Many of the National Laboratories will be laying off staff. The United States is falling behind in many areas of technology, particularly in alternate forms of energy conversion, and I feel that we will soon pay the price. New initiatives such as the Solar America Initiative cannot be funded until we have spending bills. Partisan bickering, pork barrel spending and earmarks are degrading the technological base of this country. The 110th congress appears to be no different. The house of representatives took a day off to watch the national championship football game. Soon European and Asian countries will be far ahead of the United States in technology development.

Quoting from the Capitol Observer: "The failure of the 109th Congress to pass most fiscal year 2007 bills "has produced a crisis in science financing" that could result in the closure of large research facilities, delay studies and leave thousands of scientists without jobs, according to federal and private sector officials, the New York Times reports. Last year, Congress approved two of 11 FY 2007 appropriations bills and passed a continuing resolution to fund most federal agencies at FY 2006 levels until February. According to the Times, with inflation, the "budgets translate into reductions of about 3% to 4% for most fields of science and engineering." Democrats last month said that they would seek a CR to fund most federal agencies at FY 2006 levels until the fall, rather than pass the FY 2007 appropriations bills. Scientists maintain that the delay in passage of the FY 2007 appropriations bills could affect a number of important studies. Raymond Orbach, undersecretary for science at the Department of Energy, in a recent statement said, "A yearlong continuing resolution takes away many of the opportunities for advancing science. We urge Congress to continue critical investments in America's scientific leadership." Michael Lubell, a senior official at the American Physical Society, said, "The message to young scientists and industry leaders, alike, will be, 'Look outside the U.S. if you want to succeed'" (Broad, New York Times, 1/7)."

Last month I introduced you to the basics of thermoelectric materials and bulk materials in particular. This month I will focus on recent developments in thin films, low dimensional materials and nanocomposites. **Figure 1** shows the historical timeline of TE materials and **Figure 2** shows the projected increase in the dimensionless figure of merit (ZT)

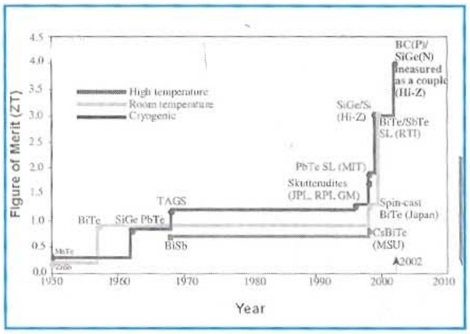


Figure 1. Timeline of thermoelectric materials [1].

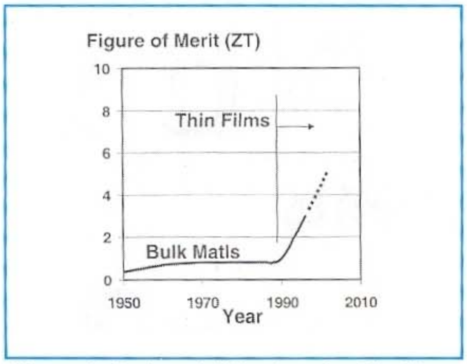
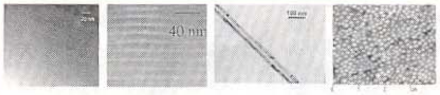


Figure 2. Projected ZT values for thin films.



Bulk

Superlattice 2D

Nanowire 1D

Quantum Dots 0D

Figure 3. Progression of 3D – 0D low dimensional structures.

with time. **Figure 3** shows the progression from bulk (3D) materials to zero-dimensional quantum dots. Until the mid 1990's, the dimensionless figure of merit ZT (= $\sigma S^2/\kappa$) was stalled at ~ 1 with Bi_2Te_3 and PbTe being the most important bulk materials. Development of thin film and low dimensional TE materials began in the early 1990's, spearheaded by Hick's and Dresselhaus' paper [2]. Since then, quantum well structures, nanowires, nanotubes and quantum dots have been the objects of development with varying degrees of success. Let's begin with thin films and 2D (quantum well) structures. Thin films have several disadvantages compared to bulk materials, but as we shall see, they also offer several advantages. The disadvantages are

- More expensive to synthesize
- Large surface areas needed to generate sufficient power or cooling
- Correct crystal phase compositions hard to synthesize
- Substrate required
- Doping often difficult

They, however, offer the following advantages:

- A large range of compositions possible
- Compositions not possible with bulk materials can be synthesized
- Quantum structures and effects can be exploited
- Composition can be varied relatively easily
- Possible to isolate electrical properties from thermal properties

Let's briefly review the concept of low dimensional structures. Quantum wells, quantum wires and quantum dots employ modulations of band gaps and the density of states to confine charge movement in two, one and zero dimensions, which significantly enhances electronic, thermoelectric and galvanomagnetic properties. These materials are usually semiconductors. Quantum wires take advantage of anisotropy in the Fermi surface to focus electrons in specific directions. MIT has grown Bi quantum wires in alumina temples, which were grown to take advantage of this anisotropy [3]. Carbon nanotubes based on C_{60} (fullerines) have been extensively studied and developed. Quantum dots have applications for high efficiency cascade lasers [4]. **Figure 4** shows how density of states (g_{3D}, g_{2D}, g_{1D}, g_{0D}) varies in the lattice for low dimensional structures [4].

Quantum well films consist of hundreds to thousands of nano-scale layers (1 – 20 nm) with alternating band gaps, one with a small band gap and one with a larger band gap. A band gap difference of ~ 0.3 eV is generally needed to realize quantum effects. The layer with the larger band gap is used to confine charge carriers in the small band gap layer. If the energy of the incident electrons is just right, they can tunnel through the potential barriers without attenuation. The electrical properties of these films can be engineered by varying layer thickness and period, and can be separated from those related to phonon propagation (thermal conductivity).

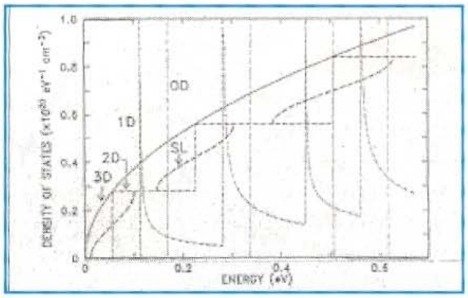


Figure 4. Density of states for 3D – 0D structures [4].

Thermoelectric properties of thin films and nanostructured materials can be enhanced by quantum confinement. Hicks and Dresselhaus wrote the pioneering paper describing this enhancement in low 2D structures (quantum wells and superlattices)[2]. Quantum wells confine charge carriers in two dimensions, quantum wires confine them in one dimension and quantum dots confine them in 0 dimensions. As shown in **Figure 4** charge carrier confinement narrows down as we progress from superlattice (2D), quantum wire (1D) and quantum dot (0D) structures. The enhancement in electrical conductivity can be related to the width of the quantum well by the relation

$$\sigma_{2D}/\sigma_{3D} = (\pi/a)(F_{0,2D}/F_{1/2,3D})(?/(2m_z kT)^{1/2}),$$

where a is the width of the quantum well (usually < 30 Å), $F_{0,2D}$ is the 2D Fermi function, $F_{1/2,3D}$ is the 3D Fermi function, and m_z is the charge carrier mass in the z direction (perpendicular to the superlattice interface). The Fermi function is defined as

$$F_i = \int_0^\infty x^i dx/(e^{(x-\xi^*)} + 1) \text{ and}$$

$$\xi^* = (\xi\ ?^2\pi^2/2m_z a^2)/kT,$$

Table 1. Power factors of Si and $Si_{0.2}Ge_{0.}$ films and $Si/Si_{0.2}Ge_{0.8}$ quantum well structures.

Material	Seebeck Coefficient (μV/K)	Conductivity (S/cm)	Power Factor
Si	600	60	.0065
$Si_{0.8}Ge_{0.2}$	800	35	.0067
Si/ $Si_{.0.8}Ge_{0.2}$ Quantum Well Structure	750	300	.051

where ξ is the potential energy relative to the conduction band edge. The critical QW dimension for enhancement is

$$a \le \pi(F_{0.2D}/F_{1/2,3D})(\ ?/(2m_z kT)^{1/2}).$$

Using these relations, the enhancement in the electrical conductivity alone can be an order of magnitude.

Table 1 shows the enhancement in power factor for a Si/$Si_{0.2}Ge_{0.8}$ quantum well structure with 1000 layers, each 100 Å thick, deposited by magnetron sputtering. Note that the power factor increase for the quantum well structure is at least an order of magnitude compared to the single layer Si or Si/$Si_{0.2}Ge_{0.8}$ film. An exact measurement of the thermal conductivity of this film is needed to obtain ZT, but is estimated to be in the range 0.01 – 0.1 W/cmK.

Other promising thin film thermoelectric materials are Bi_2Te_3, PbTe, $(AgSbTe)_x(GeTe)_{100-x}$, AgPbTe, SnTe, Sb_2Te_3, SiC, B_4C, B_9C, and conductive oxides. Bulk and nanocomposites include skutterudites ($CoSb_3$), clathrates ($Sr_8Ga_{16}Ge_{30}$), conductive oxides (ITO, ZnO), doped oxides (TiO_2), bismuth and lead tellurides, and other tellurides ($AgPb_mSbTe_{2+m}$).

The substrate presents one of the biggest problems with thin film and low dimensional structures. It is impossible to deposite a thin film without a substrate, and because it is much thicker, the substrate is a usually a thermal (and often electrical) shunt for the thin film. The substrate will have the thermal conductivity in the range 0.1 – 0.01 W/cmK. As a result, most of the heat flows through the substrate instead of the thin film. **Figure 5** demonstrates how the substrate degrades ZT of a thin film. ZT of the film/substrate system is plotted against substrate thickness, with the intrinsic (no substrate) ZT of the thin film as 3.2. However, this value is never achieved because the thermal conductance of the substrate dominates for all realistic substrate thicknesses. The ZT of film/substrate system will never approach the intrinsic ZT of the film for Si substrates, and not much better for SiO_2 substrates. The only hope for success is to use a substrate with very low thermal conductivity, such as a polymer (κ ~ 0.001 W/cmK), and this presents its own problems. The optimum situation is to release the thin film from the substrate but again this presents other problems. Thin films are mechanically weak and stress can easily fracture them. The release process may also degrade or destroy the film.

There has been some success with a few low dimensional structures. At PNNL we have deposited thin films with promising thermoelectric properties (I cannot identify materials due to IP considerations) on low thermal conductivity polyimide substrates. High quality PbTe/PbSeTe superlattices have been deposited by RTI by molecular beam epitaxy (MBE)[8]. The thermoelectric and electric properties were found to depend critically on layer thickness. Thicknesses ~ 20 - 50 nm worked the best. The films were deposited onto expensive GaAs substrates and released using a chemical process. ZT ~ 2 has been achieved for these superlattices at 550 K. Thermoelectric devices (next month's topic) developed with these superlattices demonstrated very promising cooling performance. Cooling devices were able to pump heat fluxes up to 700 W/cm² with localized cooling and heating rates 23,000 faster than bulk devices with bulk materials.

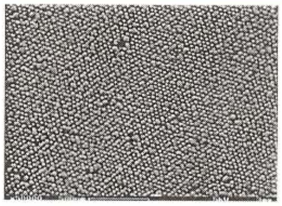


Figure 6. PbTe/PbSeTe quantum dot structure [9].

PbTe/PbSeTe quantum dot structures have demonstrated ZT~2 at 550 K [9]. **Figure 6** shows the quantum dot array.

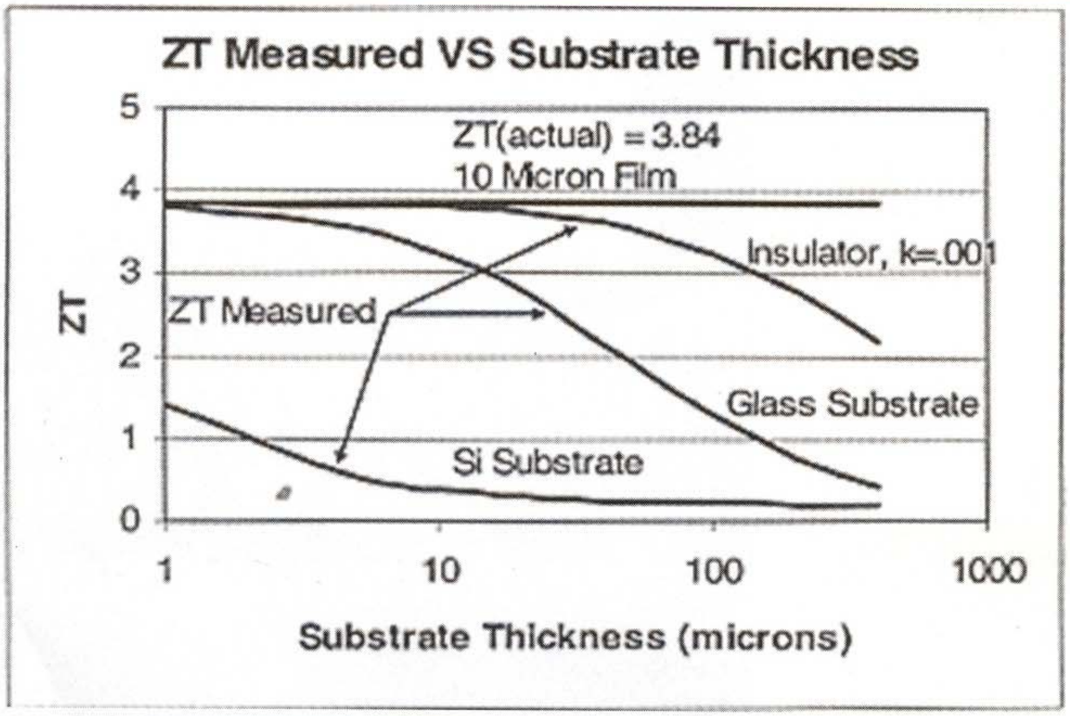
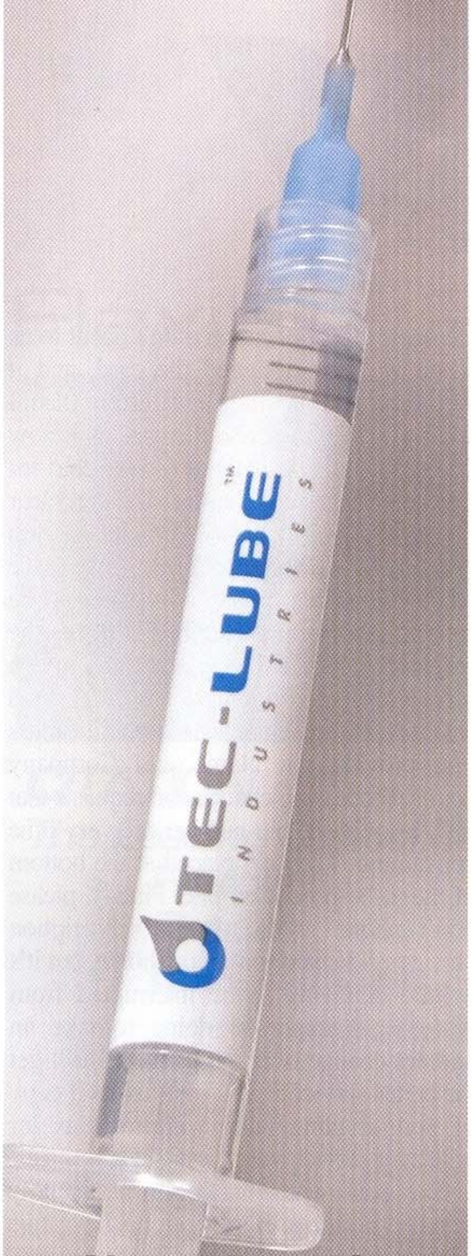


Figure 5. ZT of a thin film/substrate system plotted against substrate thicknesses for Si and SiO_2 substrates.



Layers of PbTe and PbSeTe are deposited by molecular beam epitaxy and PbSeTe quantum dots spontaneously form due to stress at the interfaces. ZT of the quantum dot arrays ranges from 0.6 at 300 K to 2.1 at 550 K. It must be emphasized that both these low dimensional structures are deposited by MBE, which is slow and expensive. PECVD processes are now being explored for deposition of the superlattices.

To date, thin film and quantum well structures have not yet lived up to expectations, probably because we do not understand all the nuances involved in deposition and issues involved in achieving these complex structures. Cost is also one of the big questions for extensive development of these materials, thin films in particular. The materials and process equipment aren't cheap. Costs can be projected to be less than $0.10/W in ten years, but the way the price of oil keeps skyrocketing, thermoelectric power generation and waste heat recovery may look very attractive by then.

I will complete our discussion on thermoelectric energy conversion next month with a description of thermoelectric power generating and cooling devices and systems.

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