Preparation of Thermoelectric Materials from Melts

The most common methods to prepare semiconductors are based on use of melts or vapor phase. A strong tendency to use thin film structures in modern semiconducting devices brought a variety of technologies based on vapor phase deposition. However, in case of thermoelectric materials the bulk ingots are used almost always and the stage of melting the materials is nearly inevitable. Manufacturing of the most common thermoelectric materials (bismuth-antimony tellurides, silicon-germanium alloys) is based on cold- or hot-pressing of the powders but the powders are prepared from the ingots of melted down and crystallized elements. Thus, the methods of preparation of materials from melts remain vital especially in technology of thermoelectrics.

Synthesis/Alloying

Modern thermoelectric materials, from a technological point of view, can be roughly divided into three categories: low-temperature materials (e.g., group V chalcogenides based on Bi₂Te₃), middle-temperature materials (e.g., group IV chalcogenides based on PbTe), and high-temperature materials (e.g., Si-Ge solid solutions). The melting points and approximate total pressures of volatile elements over the melts of the major phases arc shown in Table 1.

<table>
<thead>
<tr>
<th>Temp. Range</th>
<th>Low Temperature Materials</th>
<th>Middle Temperature Materials</th>
<th>High Temperature Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Bi₂Te₃</td>
<td>Sb₂Te₃</td>
<td>Sb₂Se₃</td>
</tr>
<tr>
<td>Tₚ, °C</td>
<td>585</td>
<td>621</td>
<td>612</td>
</tr>
<tr>
<td>P&lt;sub&gt;tot&lt;/sub&gt;, torr</td>
<td>at</td>
<td>Tₚ</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 1. Melting Temperatures and Total Vapor Pressures of Major Thermoelectric Materials
The preparation of chemical compounds and solid solutions from a melt begins with melting the elemental constituents together, a process that can be called synthesis or alloying. It is essential to use high-grade elements of guaranteed purity and to take all necessary precautions to prevent contamination during handling, synthesis, and crystal growth. A common way to perform a synthesis of the chalcogenides is to use scaled clear quartz ampoules of up to 25-mm bore. The preweighed materials are placed into the tube, followed by a quartz plug. The tube is then pumped down to between 10⁻⁵ and 10⁻⁶ torr and scaled circumferentially with a hydrogen torch.

Most of the high-purity commercially available elements are oxidized on the surface, and it is essential to remove the oxides from the ingredients before synthesis. This can be done by etching or by reduction of the element. For example, lead placed in an alumina or graphite boat can be reduced at 700°C in a stream of pure hydrogen. The presence of oxygen causes the solidifying ingot to stick to the quartz walls due to a chemical reaction between PbO and silica. This introduces stresses into the material and can even break the ampoule and expose the hot ingot to the air. In addition, any oxygen in the chalcogenides changes the electrical properties of the final product. To prevent sticking alone, quartz containers can be coated with carbon by pyrolytically cracking acetone or toluene.

The synthesis (alloying) of Si-Ge alloys is a more complicated procedure. The most efficient thermoelectrics in this system, both n- and p-types, contain about 800/Oat of Si and 200/Oat of Ge(Si₈₀Ge₂₀). The high liquidus point of this composition, 1350°C, does not allow the use of vacuum-scaled silica tubes for processing. The quartz glass softens at 1250°C to 1300°C, resulting in collapse of the ampoule. Also, due to the very large gap between the liquidus and solidus points of this composition (1350-1280=70°C) and very low diffusion rates in the solid alloys, a heavy segregation occurs during crystallization, resulting in separation of the solid Si-rich and Ge-rich grains. The usual metallurgical homogenization by annealing cannot be performed in a reasonable period of time. Additionally, the extremely high affinity of silicon for oxygen makes unreasonable a preliminary etching of the Si. As soon as Si is exposed to air or water after etching, a thin film of oxide forms on the surface immediately. Therefore the use of large pieces of Si (and Ge) to minimize the surface area is recommended.

Alloying of Si₈₀Ge₂₀ is done in an RF furnace. The large pieces (10 to 20 mm) of Si and Ge, together with dopant, B for p-type and P for n-type materials, are placed into an open quartz crucible. Improved n-type alloy can also be doped with GaP. The crucible is inserted into a graphite susceptor in the furnace chamber, and the chamber is vacuum pumped. After purging of the chamber by Ar, a slight overpressure of Ar is established (1.1 atm), and the temperature is raised to between 1370°C and 1400°C within 2 to 3 hours. I’ddy currents develop an intensive stirring motion so that the homogenization of the melt can be done in 40 to 50 minutes at maximum temperature. After this, the melt is cast inside the chamber into the water-cooled copper mold, resulting in 12.5-mtn-diameter by 10()-mm-high ingots with fine grains. The bulk wet chemical analysis of the ingots shows reasonable agreement with nominal composition. An example is shown in Table 2.
Table 2

Comparison of nominal and actual SiGe bulk precursor composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>Element</th>
<th>Si</th>
<th>Ge</th>
<th>Ga</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal, at.%</td>
<td></td>
<td>77.5</td>
<td>18.5</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Actual, at.%</td>
<td></td>
<td>77.5</td>
<td>19.0</td>
<td>1.75</td>
<td>1.75</td>
</tr>
</tbody>
</table>

This material, with still segregated microstructure but fine grains, serves as a precursor for the homogeneous ingot preparation.

Crystal Growth

To allow good characterization of the material, the specimens need to be as free of defects as possible. One of the major obstacles to achieving that goal is grain boundaries. The only way to eliminate these defects is to grow single crystals. The alternative is to minimize them by growing polycrystalline ingots with very large grains.

Crystal growth, which is the next step in material preparation from the melt, can be performed in many different ways. The same material can be grown by different methods with different levels of success. Bearing in mind preparation from melts, we divide all possible processes into two large categories for convenience of consideration, with the understanding that this categorization is not absolute.

Category 1: Growth from stoichiometric melts, i.e., from melts with the composition of certain stoichiometric compounds, resulting in a crystal of the same (or nearly the same) composition.

Methods of growth to be considered for this category are:

- Bridgman method (Br)
- Gradient Freeze (GF)*
- Czochralski method (Cz)
- Zone Melting (ZM)

Category 2: Growth from nonstoichiometric melts, i.e., from melts with composition that does not correspond to the grown material. This process may equally result in either stoichiometric (e.g., chemical compound) or nonstoichiometric (e.g., solid solution) crystal growth.

Methods of growth to be considered for this category are:
All methods listed above are well known and we are not going to describe their principles here. Many of them (marked with asterisk) were intensively used at JPL in the past years for different thermoelectric materials preparation. We are going to concentrate on JPL results because they were published in different journals or conference and meeting proceedings and are not easily available for scientific community everywhere.

*Gradient Freeze (GF)*

The gradient freeze process eliminates any moving parts in the apparatus, ampoule, or furnace. Instead of lowering the crucible through the temperature gradient (Fig. 2), the frozen temperature gradient extended over the whole ampoule length, is moved electronically, rather than physically, in contrast to the typical Bridgman apparatus. Correspondingly, the liquid-solid interface is translated up and crystal growth occurs. Such a system can be used not only vertically, but horizontally as well, and is sometimes called horizontal Bridgman (11B).

The GF vertical arrangement has been recently used for growth of promising new high-temperature materials. A refractory compound, Ru$_2$Si$_3$, congruently melting at 1700°C (Fig. 3), has been grown. High-purity Ru and Si, in stoichiometric ratio, were placed in pyrolytic boron nitride crucible with pointed bottom. Heron nitride was found to be the most appropriate container material for ruthenium silicide, in spite of some dissociation and consequent contamination of the melt and crystal by boron. After synthesis of the compound at a minimum of 1765°C, the temperature gradient of 30° to 320/cm was stabilized and growth occurred at rates of 0.8 to 3 cm/day. Single crystalline ingots of the compound with typical dimensions of 12 mm in diameter by 20 mmn high were obtained and their thermoelectric properties measured.

The electron analogue of ruthenium silicide, ruthenium sesquigermanide Ru$_2$Ge$_3$, has been similarly grown in the same furnace. The germanide is a non-congruently melting compound and decomposes peritectically at 1470°C (Fig. 4) but the crystal growth can be achieved from off-stoichiometric Ge-rich solutions. Single crystals of this compound were grown in 12 mm inside diameter graphite or glassy carbon cylindrical crucibles with a conical bottom. The preferential direction of growth was found to be [110] and crystals exhibited a reversible gradual diffusionless phase transformation within 400-600°C (tetragonal at high and orthorhombic at low temperatures). Both of the phases were p-type semiconductors with bandgaps of 0.58 and 0.71 eV, respectively. Maximum ZT value for this material was found to be about 0.4 at 500°C (Fig. 5).

Similar furnace configuration was used to grow single crystals of some thermoelectric compounds with skutterudite structure, CoSb$_3$ and RhSb$_3$. Related phase diagrams (fig.
suggest that growth can be performed from Sb-rich solutions. The single crystals were obtained by slow crystallization of solutions of Co and Rh in Sb (3-9 and 3-14 at\%, respectively) in scaled carbon-coated quartz ampoules. A temperature gradient of about 40-50°C/cm was maintained at the growth interface and the growth rate was about 0.7°C/hr (Fig. 7).

All as-grown samples were p-type with Hall carrier concentration in the $10^{16}$ to $10^{19}$ cm$^{-3}$ range for CoSb$_3$ and between 2 and 7 x $10^{18}$ cm$^{-3}$ for RhSb$_3$. It was found that, for the CoSb$_3$ ingots, the Hall carrier concentration of the samples decreases from the tip to the top of the ingots. Because the ingots were grown from non-stoichiometric melts, during the growth the melt became richer in Sb and the stoichiometry of the samples could gradually change along the ingot, resulting in carrier concentration variations. These stoichiometric deviations might be very small and were not detected by microprobe. The addition of Tc (between 0.1 and 0.2 at\%) into the original melts resulted in n-type electrical conductivity.

Exceptionally high p-type Hall mobilities were obtained on RhSb$_3$ and CoSb$_3$ samples. The Hall mobilities of the two skutterudite compounds are significantly higher than those of Si, Ge and GaAs in the $10^{17}$ to $10^{19}$ cm$^{-3}$ carrier concentration range. A maximum Hall mobility of about 8000 cm$^2$/V·s was obtained for RhSb$_3$ at a carrier concentration of 3.5 x $10^{18}$ cm$^{-3}$.

From the variations of the resistivity with temperature in the intrinsic regime, the band gap of CoSb$_3$ and RhSb$_3$ was estimated at 0.56 and 0.80 eV, respectively. The high hole mobilities measured on the skutterudite compounds CoSb$_3$ and RhSb$_3$ even at high temperatures make these materials interesting new semiconductors and we are planning further studies to investigate their thermoelectric and electronic properties.

**Zone Leveling (ZL)**

ZL is one of the versions of Zone Leveling well described in the literature. As opposed to several reciprocating zone passes, this version is performed using only one zone pass and is based on the phase relationship shown in Figure 8. We consider this process as a crystallization of metal solution because "dilute" liquid solution a crystallizes, resulting in "concentrated" solid solution $x$. It is obvious that if the liquid $a$ composition, which loses component $B$ during crystallization, is constantly replenished by $B$, the crystallizing composition $x$ is the only product of the process.

ZL, of a very difficult and most important high-temperature material, Si$_{80}$Ge$_{20}$ solid solution, is a perfect example of the use of this technique. It was described in 19578, investigated in more detail and applied later, and more recently applied again with some changes. Figure 8 represents the principle of the process. Two precursors of SiGe are prepared: $a$(Si$_{52}$Ge$_{47.5}$) for zone melt, and $x$(Si$_{80}$Ge$_{20}$) for homogenization, e.g., composition leveling. They are loaded into the processing boat (graphite, glassy carbon, carbon-coated quartz), scaled under vacuum in a quartz tube, and zone melted (Fig. 9) at a constant temperature. One pass of the zone was usually employed. Two processes take place simultaneously during the zone passing on both liquid-solid interfaces: melting of
inhomogeneous precursor $x$, on the right interface, and crystallization of homogeneous composition $x$, on the left interface. At each given time the quantity of crystallized material is equal to the quantity of melted precursor. Therefore a constant composition of the melt is maintained, and a perfectly homogeneous Si$_{80}$Ge$_{20}$ solid-solution ingot is yielded. It was found that an RF coil used as a zone heater, instead of the conventional resistance furnace, helps to avoid deterioration of the quartz ampoule (Fig. 10). In this case the graphite boat (crucible) also played the role of an RF susceptor. Two resistance furnaces mounted on both sides of the RF coil maintained sufficiently high pressure in the ampoule, when P (or GaP) was a dopant, and suppressed phosphorus deposition on the tube wall during the process. In this case the whole heating assembly was stationary and the ampoule was translated. The travel rate was about 2 mm/hr, which was slow enough to provide homogeneous recrystallization of the charge. Thus, intercrystalline liquation was avoided.

One more advantage of this version of ZL should be noted: The process is performed at a much lower temperature than $T^{\text{iq}}$ of Si$_{80}$Ge$_{20}$. The processing temperature corresponds to $T^\text{sol}$ of the alloy ($1280^\circ\text{C}$) versus $T^\text{iq}=1350^\circ\text{C}$, and the sealed quartz container can easily survive even when a conventional heater is used.

**Liquid phase epitaxy (LPE)**

Liquid phase epitaxy (LPE) is the growth of a material epitaxially on an oriented, single-crystalline substrate seed from the solution of the material in an appropriate solvent. Usually the material is grown in the form of a thin (10 μm to 100 mm) layer over the polished and etched wafer. The layers reproduce the structure of the substrate (epitaxy) as in any other seeded crystal growth. The basics of the process are illustrated by Figure 11. A mixture of solvent and soluble is heated to a certain temperature. At this temperature, melt is brought into contact with substrate. According to the phase diagram, melt and substrate are in thermodynamic equilibrium, and no changes are expected at this temperature. By lowering the temperature, dissolved material precipitates from the melt and grows epitaxially on the substrate until the substrate is withdrawn from the melt. By introducing a dopant into the melt, the doped layer can be grown on an undoped substrate.

The major advantages of LPE are: (1) LPE can be performed at substantially lower temperatures than bulk growth of the same material from a stoichiometric composition; (2) consequently, the vapor pressures over the melts can be much lower during LPE, thus eliminating a big loss of volatile elements and simplifying the process; (3) solid solutions of certain composition can be grown. LPE has been so widely used in research and manufacturing of semiconductors that a huge number of apparatus designs have been developed. A horizontal configuration of LPE apparatus is shown in Figure 12.

The use of LPE in thermoelectric research can be illustrated by developing of improved SiGe material. It has been found that Si-Ge solid solutions can be more
heavily doped when crystallized from metallic liquid solutions, at lower temperatures than \( T_{\text{liq}} \) (Fig. 13). In this case the use of a solvent, which is also a dopant, is beneficial because the solvent-dopant atoms are incorporated in the SiGe alloy, according to their solid volubility at the temperatures of growth. Si\(_{80}\)Ge\(_{20}\) layers 10 to 100 mm thick were grown from solution in Ga with GaP addition on (III) oriented Si substrates. Temperatures of growth ranged from 750° to 900°C with cooling rates of 30° to 40°C/hr (compared to Si\(_{80}\)Ge\(_{20}\) \( T_{\text{liq}} = 1350°C \)). These low growth temperatures were used because of the selected melt composition of Si\(_{7.7}\)Ge\(_{24.8}\)Ga\(_{67.5}\), which produced a Si\(_{79.9}\)Ge\(_{19.9}\)Ga\(_{0.2}\) crystalline layer at 900°C (Fig. 14). LPE experiments proved the feasibility of enhancing the P-dopant solid volubility in SiGe material in the in-csence of is. This multiple doping had improved the thermoelectric energy conversion efficiency of Si\(_{80}\)Ge\(_{20}\), which is widely employed in radioisotope thermoelectric generators (RTGs).

**Traveling Solution Method (TSM)**

The traveling solution method (called sometimes traveling heater method, T\(T\)HM) is one of the Zone Melting techniques, and the process can be described in almost the same words as Zone Leveling. It is the recrystallization of a concentrated solution through a dilute solution and is usually carried out vertically with one pass of the molten solution zone. The vertical configuration of the apparatus (Fig. 15) provides a more symmetrical thermal field applied to the charge and better uniformity of composition and properties in grown ingot cross sections. TSM has been successfully employed for crystal growth of several well established thermoelectric materials, resulting in high-quality samples. In this case, as in Zone Leveling, the processing temperature can substantially be brought down. At JPL, solvents such as Ga and Sn were used for growth of bulk ingots of Si\(_{80}\)Ge\(_{20}\), with growth temperatures between 800° and 900°C (compared to \( T_{\text{liq}} = 1350°C \) for Si\(_{80}\)Ge\(_{20}\)).

**Concluding Remarks**

A brief review has been given of the preparation of thermoelectric materials from melts. The emphasis was given to works performed at JPL, within the past 8 years. The results were published in different Journals, Conference and Meeting Proceedings and it was our intention to put them together to illustrate the JPL achievements.

**Acknowledgments**

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Vacuum Furnace for Si-Ge Precursors Preparation (schematic)

Figure 1
Two-zone Furnace for Gradient Freeze Process

Figure 2
Figure 3
Figure 4
Calculated ZT values versus temperature for In-doped Ru$_2$Ge$_3$ samples. Results for directions \( \text{II} \) and \( \text{J} \) to the [110] direction of crystal growth are plotted.

Figure 5
Figure 6
Zone Leveling

Figure 8
Zone Leveling
(temperature profile)

Figure 9
Zone Leveling Apparatus

. Figure 10
JPL LIQUID PHASE EPITAXY (LPE)

1. BEFORE GROWTH

2. GROWTH

3. AFTER GROWTH

Figure 11
LPE System

Figure 12
Calculated Ga solid solubility curves as a function of temperature for various Si–Ge alloy compositions in at%: (1) Si; (2) 80% Si; (3) 60% Si; (4) 40% Si; (5) 20% Si; (6) Ge.

Figure 13
LPE-GROWN $\text{Si}_{82}\text{Ge}_{18}$ ON (111) Si
MAGNIFICATION ON 35 nm FILM

INITIAL STAGES OF GROWTH

$\times 62.5$ TERRACED MORPHOLOGY OF COMPLETED LAYER

Figure 14
TRAVELING SOLVENT METHOD (TSM)
APPARATUS SCHEMATIC

Figure 15