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RCA Laboratories, Princeton, N. J.

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Contract No. NObs 88595

Title: Thermoelectric Materials for Power Conversion

Project Serial Number SR007 12 01, Task 802

Progress:

A. Materials Research

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A series of extremely homogeneous Si-Ge solid solution alloys were prepared by the horizontal zone-melting technique. The materials of various compositions were used to make accurate determinations of density, lattice parameter, phase equilibria, and band gap as functions of composition. The densities of about 100 samples were determined to an accuracy of  $\pm 0.1\%$  by the method of Archimedes. The solidus temperatures were determined at intervals of 5-10%Si by the DTA method, and the results confirm the original (1939) phase diagram of Stohr and Klemm.

The nature of the solid-liquid interface that occurs during zone melting of Si-Ge alloy has been observed directly by the technique of decanting the liquid zone during growth. At a slow growth rate, the interface was essentially planar with a cellular morphology which suggested a small amount of constitutional supercooling. At a faster growth rate the interface contained pyramids which projected about 1 mm into the melt, but no branching or dendritic structure could be observed. However, metallographic examination revealed that the interface was very irregular and this leads to trapping of Ge rich regions within Si rich material. The relative smoothness of the decanted interface probably arises from the adherence of zone liquid to the irregular solid surface due to surface tension

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A comparison of the measured carrier concentration of Si-Ge alloys with their impurity concentrations has been made. It was found that two of the impurities used give one carrier per atom when all the impurity was present in solid solution. In contrast another impurity showed a spectrographically determined concentration which was about 50% larger than the carrier concentration, even though the samples had carrier concentrations that were below the maximum solid solubility for that particular alloy composition. It is suspected that the extra impurity is present in some electrically inactive form, perhaps as a compound with oxygen.

Alloys of 70%InAs-30%GaAs have been prepared using the growth technique developed for Si-Ge alloys. Recently grown ingots have a uniform composition along their length, and provide suitable specimens for thermal diffusivity measurements. Optical absorption edge and X-ray fluorescence analysis have been used to determine compositional variations.

#### B. Physical Measurements

High temperature measurements of the specific heats of many III-V compounds are not available. However, this information is needed to convert the measured diffusivity,  $\kappa/c$ , into the thermal conductivity,  $\kappa$ . A plot was made of the measured specific heats,  $c$ , divided by the Dulong-Petit values, versus the temperatures divided by the Debye temperatures for Si, Ge, and all III-V compounds available; the Debye temperatures used were computed from measured and interpolated elastic constants. In this plot, all the materials fall upon one curve with some spread. Curves parallel to this curve and passing through the measured room temperature values are believed to be a good approximation to  $c$  at elevated temperatures.

The thermal conductivity of two samples of GaAs was determined between 300° and 950°K from the measured diffusivity and the assumed specific heat described above. One specimen, having a carrier concentration of  $5 \times 10^{16} \text{ cm}^{-3}$  showed a photon effect between 600° and 950°K. On reheating this specimen, the resistivity and the photon effect increased. Samples of the initial and final conditions were prepared. The measured absorption coefficients of these samples were found to be different which explained the increase in the photon effect. A specimen having  $5 \times 10^{17}$  carriers  $\text{cm}^{-3}$  did not exhibit any photon effect as a result of the higher carrier concentration. The thermal conductivities of both samples agree at room temperature.

The data on GaAs are interpreted in terms of the theory of Liebfried and Schloemann. The anharmonicity parameter,  $\gamma$ , of the III-V compounds, obtained by comparing the experimental thermal conductivities with the theoretical values of Liebfried and Schloemann, are found to be temperature and mass ratio dependent. The temperature dependence is believed to be caused by higher order processes. The correlation of  $\gamma$  values and the mass ratio of the constituent elements of the compounds is ascribed to an effect of optical mode scattering on the lattice thermal resistivity.

The investigation of InAs-GaAs alloys was continued. A sample of 70%InAs, n-type, with a carrier concentration of  $1.3 \times 10^{18} \text{ cm}^{-3}$  exhibited a figure of merit of  $0.9 \times 10^{-3} \text{ deg}^{-1}$  at 750°K which is 30% higher than for Si-Ge alloys at this temperature. The photon effect was studied on an undoped InAs-GaAs sample having a carrier concentration of  $3.9 \times 10^{16} \text{ cm}^{-3}$ . The measured thermal conductivity was strongly frequency dependent in the range 3 and 5 cycles per minute, but seemed to be frequency independent at 12 c.p.m. and above.

C. Feasibility Studies

Aside from the primary requisite of effective thermoelectric materials, the efficiency of a thermoelectric device depends greatly upon the elimination of stray heat losses. The centrally located heat source completely surrounded by the thermocouple elements is the general solution to this requirement. The general principle lends itself to a wide variety of choices ranging from spherical to planar module configurations. When further engineering problems are taken into account the freedom of choice becomes more limited. One of the determining factors is the heat source. Except in the case of electrical heating or possibly gaseous heat transport, the application of the planar module is limited by the difficulty of providing uniform heat distribution.

A thermoelectric generator using toroid shaped couples stacked to form a hollow cylinder offers many thermal as well as mechanical advantages, and leads to a very compact design. The stray heat can be reduced to a minimum. A generator consisting of twenty toroid shaped thermocouples is now under construction. The silicon-germanium material should provide, depending upon the temperature, an output of over 15 watts with 4 volts open circuit voltage. For the bonding of the couples and for the assembly of the stack it has been necessary to set up a high temperature vacuum furnace. Initial experiments show promising results.

Future Work

1. Investigate the preparation of single crystal Si-Ge alloy specimens by growth from the melt.
2. Complete the accurate determinations of physical properties as a function of composition in the system Si-Ge.
3. Prepare further examples of InAs-GaAs alloys.
4. Make measurements of specific heat as a function of temperature for Si-Ge alloys.
5. Make thermal diffusivity measurements on Si-Ge alloys and InAs-GaAs alloys.
6. Continue the fabrication of the cylindrical thermoelectric generator.