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BARNES ENGINEERING COMPANY

22 July 1966

FINAL REPORT/BEC Project #3752

Thermopile Improvement

ABSTRACT

The following report describes investigations performed at Barnes Engineering Company* for the purpose of improving the performance of thin film thermoelectric infrared detection devices (i.e., thermopiles). This work has disclosed that the thermoelectric properties of vapor deposited films of antimony, bismuth, and tellurium are highly dependent on deposition rate. Significant correlations were also observed between thermoelectric properties, substrate temperature, and chamber pressure. With proper control of deposition parameters, bulk Seebeck coefficients of these elemental materials are easily reproduced, and film resistivities which are less than twice bulk values can be consistantly obtained. Fabrication of thermopiles using techniques developed during these studies has shown that elemental thermopile parameters (i.e., resistance, responsivity, and time constant) can be controlled to far closer tolerances than could be achieved with previously used deposition techniques.

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Thermoelectric alloys of Bi-Te-Se (n-type) and Bi-Te-Sb (p-type) have been fabricated and films of these materials have been deposited and studied. Bulk thermoelectric properties have been obtained in these films. Although consistant reproducibility of film properties has not yet been achieved with these alloys, experiments have indicated the additional techniques and controls necessary to achieve reproducibility.

Very thin (2μ) plastic films of Union Carbide "Parylene N" have been used in place of 1/4 mil (6μ) mylar on thermopile substrates. Thermopiles deposited on 2μ Parylene N substrates show no improvement in responsivity over standard mylar devices.

I. DESCRIPTION OF EXPERIMENTAL APPARATUS

IA. Vacuum System and Associated Apparatus

Depositions were performed in an 18" Cooke vacuum system capable of a practical ultimate pressure of slightly less than 1μ Torr. The source boats were of 0.010" molybdenum (manufactured by the Rembar Corporation) with 2" x 1/2" reservoirs 1/8" deep. Two boats were positioned about 5 cm apart, and about 20 cm from the substrates. The geometry of the apparatus was such that the maximum angle of incidence of the evaporant on the outermost substrates could not exceed 15 degrees. A hinged shutter was designed to permit deposition rate to be stabilized prior to exposing the substrates to the vapor stream. (See Section IB for a description of the quartz cyrstal rate monitor.) In the latter part of the project, rate and thickness control were developed to a point where the shutter was unnecessary.

Twelve (12) 0.005" thick stainless steel masks were held in place with "glass tape" to the 1/8" thick stainless steel mask holder (see Figure 1). The holder was rigidly fastened to four (4) 1/2" diameter steel rods screwed into the base-plate.

The substrate holder was of 1/4" aluminum and could receive up to ten substrates at once. Two (2) 300 watt strip heaters were fastened to the top of the substrate holder, and preliminary measurements showed that the entire substrate holder maintained a temperature to within ±2°C after equilibrium was achieved. The holder was hinged to the mask plate such that the position of each substrate could be shifted to the adjacent mask, which is a mirror image of its adjacent neighbors (see Figure 1) by means of a solenoid actuated mechanism.

In this manner, the complete thermocouple could be fabricated without requiring the exposure of the film to atmospheric pressure prior to deposition of the second material. An iron-constantan thermocouple was fixed to the center of the top of the substrate holder to monitor substrate temperature.

For fabrication of multi-junction thermopiles the mask holder shown in Figure 1 was replaced with one which hold two sets of masks positioned so that thermopile substrates could be moved in vacuo to the proper masks by means of electromagnets attached to a vertical rotary feed-through. This plate also had provision for attachment of the strip heaters described above.

The Sloan crystal changer and its solenoid actuator were attached to one side of the steel mask plate such that the crystal-to-source distance was about 20 cm. The fixtures for water cooling of the changer allowed easy removal of the change for cleaning and re-loading. A crystal edge mask was attached to the changer to prevent shorting of the crystal edges to ground during deposition. The edge mask could accept various Sloan perforated attenuation masks for purposes of easy monitoring of the higher deposition rates.

The substrates were 1.75" x 0.50" x 0.015" stainless steel (see Figure 2), to one side of which a sheet of 1/4 mil mylar had been cemented with Hysol epoxy resin.

During investigations of alloy materials, it was necessary to use glass substrates to permit heat treatments at temperatures as high as 350°C. For this purpose 40 mm x 22 mm x 0.2 mm cover glasses were used.

IB. Sloan DTM-3 Thickness Monitor and Accessories

The Sloan DTM-3 quartz crystal oscillator monitor contains a five range meter calibrated to read monitor crystal frequency change from 1 kc full scale deflection to 100 kc full scale deflection. The manufacturer claims the device to give a frequency change linear with deposited mass for changes up to somewhat over 100 kc, and our calibration measurements verified this. For the first three runs, the mass of each crystal was measured before and after deposition, and the "crystal constant" thus determined was 11.1 μgm/cm^{2}kc ±2.5%, averaged for ten crystal samples.

The DTM-3 provides a recorder output that gives -4.5V dc for a full scale deflection of the meter. With the use of a 4,500 to 1 divider network, we were able to utilize a 1 mv Bristol strip chart recorder for deposition rate monitoring. Since the above crystal constant and the recorder chart speed are known, the mass deposition rate could be controlled by adjusting boat temperature during deposition such that a pre-determined slope was maintained on the recorder. To facilitate monitoring, lines of the desired slope were drawn on the chart paper prior to the deposition run.

Since the chart speed is limited to 1.5 inches per minute, it was felt that the faster rates would more easily be monitored by introducing a perforated deposition attenuation mask in front of the crystal. By measuring the deposited film mass on both the attenuated monitor crystal and an exposed control crystal, we found the actual attenuation of the Sloan "10%" mask to be about 6.5% in our installation.

In general, mass deposition rate can be controlled to within ±20% with this arrangement. Film thickness measurements were made using a "Swedish Gage" accurate to ±0.1μ. Due to irregularities in substrate surfaces, these measurements of film thickness may have been in error by as much as 50% in some cases, but even this accuracy was sufficient to observe significant differences in film density, as will be discussed.

IC. Seebeck Coefficient Measurements

The Seebeck apparatus consisted of two (2) massive copper heat sinks, one of which was immersed in water at room ambient temperature, while the other was heated slightly by a nichrome heating coil surrounding it (see Figure 3). A copper-constantan differential thermocouple was embedded in Hysol epoxy resin with each junction just below the surface of each copper sink. The experimental film thermocouple was screwed in place on the apparatus with a bit of vacuum grease under each junction to improve contact with the copper sinks. Both the copper-constantan output and that of the sample were measured to the nearest 1μv on a Rubicon model #2732 potentiometer when possible. Output voltages of samples having resistances greater than a few hundred ohms were measured on a Hewlett-Packard Model #425A microvoltmeter.

The Seebeck coefficient of copper-constantan is sufficiently linear in the 18°C to 28°C range to permit graphical interpolation of the temperature increment to the nearest 0.02°C. Measurements on the first few samples were taken at various temperature increments (ΔT) in the range from 2°C to 12°C, and it was observed that the Bi-Sb film Seebeck coefficients were not quite linear with ΔT and varied by a few percent over the above range. Thus, for convenience, a range of from 4.5°C to 5.5°C was chosen as our standard increment above room ambient and all Seebeck measurements described below were taken in that range. We have found that Seebeck measurements made with this equipment are reproducible to ±0.5% for low resistance samples, while measurements made on high resistance samples with the microvoltmeter were reproducible to ±3%.

Resistance measurements of the samples were taken on a Simpson "Volt-Ohmist", accurate to ±5%. Early resistance measurements were also checked on a four place Wheatstone bridge. Electrical connections to the samples were made by attaching #38 copper wire to the thermocouple legs with a silver filled conducting epoxy resin which requires curing for 30 minutes at 80°C (see Figure 2) or with a fast drying silver filled paint.

ID. Electron Bombardment Apparatus

A few alloy depositions were performed using an electron gun instead of resistance heated boats. This device, manufactured by the Materials Research Corporation, consists of a circular filament centered a few millimeters above a circular carbon crucible which holds the source material. The crucible is held in a massive water cooled copper heat sink which holds two additional crucibles and can be moved under the filament by means of a push-pull vacuum feed-through. A 5 kv, 500 ma power supply provides the acceleration potential for the device.

II. INVESTIGATIONS OF BISMUTH-ANTIMONY FILMS

IIA. Description of Experimental Procedure

Of primary interest in this project were the effects of deposition rate and substrate temperature on bismuth-antimony (Bi-Sb) thermocouple characteristics. Depositions were performed at nominal rates of $10^2 \mu$gm/cm^{2}min (about 33 Å/sec) and $10^3 \mu$gm/cm^{2}min (about 330 Å/sec). For each of the two rates at least three depositions were performed to determine the effects of substrate temperature. Temperatures of 80°C, 155°C, and 230°C were investigated. The materials used were of 0.99999 purity obtained from the Gallard-Schesinger Corporation.

Other experiments were performed to uncover any effects due to chamber pressure, final film thickness, and order of deposition.

In addition, it was discovered that a variable rate technique produced better films than could be obtained by deposition at constant rates. In this method, the first ~0.1μ or so of the film is deposited at a slow rate ($10^2\mu gm/cm^2 min$) whereafter the remainder of the film is deposited at a rate increased by an order of magnitude.

A total of fifteen (15) vacuum depositions were performed under various conditions to produce Bi-Sb thermocouples. Three of these deposition "runs" utilized the double rate technique just described. Each run yielded ten (10) samples upon which resistivity and Seebeck coefficient measurements were taken. The data from each run was subjected to a simple statistical analysis to determine average values and standard deviations of the significant parameters.

IIB. Results of Bismuth-Antimony Experiments

Table IA summarizes the Bi-Sb experiments performed at constant deposition rates. From the data in Groups I and II at least three conclusions are immediately apparent:

1. The film Seebeck coefficient is directly proportional to the substrate temperature. In the region from 80° to 155°C, bulk Seebeck coefficients (nominally, 100μv/°C for

Bi-Sb) are consistantly obtained at the higher temperature, with a ~10% reduction in this parameter occuring at the lower temperature.

2. At substrate temperatures in excess of 200°C, the "sticking coefficient" of the impinging bismuth atoms is reduced to a negligible value.

3. Resistivities of bismuth films deposited at the slower rate ($10^2 \mu gm/cm^2 min$) are significantly lower (about 50%) than those deposited at the higher rate ($10^3 \mu gm/cm^2 min$).

The depositions in Group III were performed in order to uncover any effects which might be a function of total film mass per area. The films in this group were one-half the mass of those discussed above, but were only one-third as thick, i.e., the thinner films were about 30% more dense than the thicker films (see Table IA). It also appears that resistivities of films of this mass per area ($1.1\ mg/cm^2$) are nearly independant of deposition rate.

However, the thinnest films made in this study, ~1μ, (see Group IV) were deposited at the constant rate of $10^3 \mu gm/cm^2 min$ and gave resistivities as high as any observed in the thicker films. In addition, the standard deviations for resistivities in this particular run were by far the highest observed, especially in the case of the bismuth film wherein the standard deviation of 15% was twice that of the average standard deviation of all other Bi-Sb experiments. Although no positive conclusions can be drawn from the data in Groups III and IV (Table IA), techniques which have become standard practice in thermopile fabrication at Barnes Engineering Company are definitely contraindicated. Specifically, we refer to the practice of deposition at rates in excess of $10^3 \mu gm/cm^2 min$ in conjunction with a monitoring technique which stops the deposition at a pre-determined value of film resistance per area. Clearly, this will result in very poor reproducibility of resistance values of the thermopiles and, in fact, this has been a major problem in thermopile fabrication in the past.

The problem of reproducibility in films as thin as 1μ has been solved by the development of the variable rate technique mentioned briefly in the preceding section. It is well known that preferred orientation of crystallites in elemental films is more likely to occur at minimal deposition rates. Furthermore, it is well known that preferred orientation is more likely to occur in atoms which impinge on an oriented polycrystalline surface than in atoms which are deposited on an amorphous surface. Thus, if a thin oriented layer ($\sim 0.1\mu$) is deposited onto amorphous substrates at a slow rate, it should be possible to increase the rates considerably for the remaining 1μ or so of the elemental film without significantaly degrading the final film properties.

Table IB summarizes three experiments performed to test this hypothesis. Comparison of resistivity data between these samples and those deposited at constant "fast" rates ($\gtrsim 10^3 \mu gm/cm^2 min$) shows a consistant reduction with this technique. Further experiments with thermopiles made with this technique have resulted in far better reproducibility of resistance than previously obtainable, as will be discussed in the next section.

At this point one might question the advantage of the variable rate technique over that of simply depositing the entire film at a constant "slow" rate ($\lesssim 10^2 \mu gm/cm^2 min$). From the standpoint of easily applied production techniques, deposition of a film at a constant slow rate is far more time consuming and requires far more attention (on the part of the production technician) than would be required in the variable technique. Secondly, there is reason to suspect that the proportion of contaminating residual gas molecules trapped in the film is a function of total deposition time alone; thus, the advantages achieved at slower constant rates at these pressures (1µ Torr) may well be degraded by such contamination after a certain period of time. (This hypothesis could explain the lack of rate vs. resistivity correlation observed in Group III.)

Table IC summarizes two experiments performed to determine what effects deposition order and chamber pressure might have on film properties. Both depositions were performed at "fast" rate ($\gtrsim 10^3 \mu gm/cm^2 min$), and in both cases the bismuth was the first material deposited, contrary to the procedure in all the other depositions described. These experiments were felt necessary since previous thermopile production techniques at BEC have used bismuth as the first material deposited. Comparison of the data in Table IC with that discussed previously (see Figure 4) reveals a significant increase in the Sb film resistivity and a small but significant decrease in Seebeck coefficient. The latter phenomenon is especially interesting from the point of view of improving existing thermopile production procedures, and may be explained by considering an observation frequently made during vacuum deposition of Bi; viz., that the paths taken by Bi atoms in the vapor phase are far less "linear" than desirable. In other words, Bi shows a great tendency to diffuse around obstacles which may exist between the Bi boat and any surface in the vacuum chamber. Thus, it is likely that a small amount of Bi condenses on the surface of the Sb during the Bi deposition, in spite of the presence of an optical baffle between the two source boats. In this manner deposition from the Sb boat would result in an ultra-thin film of Bi being condensed on substrates prior to pure Sb deposition. It is clear that this would have no effect on the Seebeck coefficient if the Sb boat is the first used, but would tend to "short out" some of the Seebeck voltage if the Bi boat is the first used.

Figure 4 presents data concerning Seebeck voltage vs. temperature taken from representative experiments. The deposition order phenomenon just discussed is clearly indicated therein.

IIC. Thermopile Fabrication

Four essentially identical deposition runs were performed to fabricate a total of eight (8) Bi-Sb 308 element thermopiles. This particular thermopile configuration was chosen because the vast amount of production data available for it would allow valid comparisons to be made between the old deposition procedures and those discussed in this report. Deposition rates were held to 100μgm/cm^{2}min or less for the first 0.22 mgm/cm^2 (~4000Å), whereafter the rate was increased approximately an order of magnitude until a total film mass of ~0,67mgm/cm^2 was achieved (~1.2μ). This deposition schedule was easily reproduced from run to run. The average total deposition time for all depositions was 5.0 ± 0.5 min, while the average deposition time at the slower initial rate was 3.7 ± 0.4 min.

The resistances and post-blackened responsivities (in air) of the eight thermopiles from these runs were measured. The average resistance values were 2.9kΩ ± 0.6kΩ, while average air responsivity values were 0.18v/w/cm^2 ± 0.03 v/w/cm^2. Standard deviations for each parameter were about 6%. No time constants were measured on these devices. The brief table below compares these eight detectors with (20) devices made using the old deposition techniques characterized by resistance monitoring, deposition rates in excess of 10^{3}μgm/cm^{2}min, and deposition of the Bi film prior to the Sb film.

Deposition Process	Number of Sample	Resistance in k Ω	Air Responsivity in v/w/cm^2
Old	20	3.5 ± 1.0	0.22 ± 0.04
New	8	2.9 ± 0.6	0.18 ± 0.03

It is immediately apparent that the ranges of parameters are significantly less with the new process. This fact is further emphasized when one considers that the average values of the (20) samples made by the old process do not include many (~35%) rejected because they were "out of spec" for the 308 element device. Thus, the true ranges for a random selection of old process devices must be significantly larger than those indicated in the table, very likely by as much as a factor of two.

The reason for the lower responsivity of the new process devices cannot be definitely stated at this time, and this writer suspects that the explanation awaits further investigations of time constant and thermal conductivities.

Three additional thermopile depositions (six thermopiles) were made to determine the correlation between thermopile resistance and total film mass per area. The deposition rate schedule was identical to that described at the beginning of this section, except that the total film mass deposited was 0.55 mgm/cm^2 for two of the runs and 0.44 mgm/cm^2 for the other. Considering the small number of samples for which average values were taken, the excellent linearity of the resistance vs. film mass data in Figure 5 attests to the high degree of control of film properties which can be achieved by quartz crystal film mass monitoring. The responsivities of these additional six devices were essentially the same as the first eight, i.e., 0.18 ± 0.03v/w/cm^2.

IID. Annealing Experiments

Two groups of Bi-Sb thermocouple samples were subjected to a tamperature of 145°C in air for various time intervals until a total of 37 hours annealing had been completed. The samples at room ambient were placed on a flat aluminum hot plate which had been stabilized at 145°C as determined by an iron-constantan thermocouple attached to the plate. After the desired intervals the power to the plate was discontinued and the plate and samples allowed to cool to near room ambient at a rate of slightly less than 2°C min. Seebeck coefficients and resistances were than measured.

Significant resistivity reductions (by as much as 50% for thicker samples) were observed in practically all of the samples within the first two hours of annealing. The same statement holds for the Seebeck coefficients, although the greatest reduction of this parameter was a mere 3%. Table II gives for each sample the resistivities and Seebeck coefficient as a ratio of the parameter after annealing to that before annealing. The table shows that the resistance of the less dense 6μ samples decreased by an average of 20% from the initial values, while the resistance values of the thinner samples ($\lesssim$2μ) decreased negligibly (viz., ~3%).

Seebeck coefficients of all samples decreased slightly, with an average decrease of 3%. As a control, six (6) un-annealed samples chosen from the same runs as the annealed samples were examined for resistance and Seebeck coefficient changes. Resistance values were not measureably different from those originally measured, but Seebeck coefficients had decreased an average of 2%. Since our Seebeck measurements are reproducible to ±0.5%, these small changes are definitely significant, and probably due to metallic diffusion at the junctions over a period of months. Such a phenomenon would be increased at elevated temperatures. Practically this small degrading of Seebeck coefficient is immeasurable, since the responsivity of a thermopile device cannot be measured by usual means to better than ±5%.

III. BISMUTH-TELLURIUM INVESTIGATIONS

IIIA. Bismuth-Tellurium Thermocouples

Three vacuum depositions of bismuth-tellurium (Bi-Te) have been performed and evaluated. Table III summarizes the significant deposition parameters from Runs #016, #017, and #018, and gives average values and standard deviations for Seebeck coefficients and resistivities of the tellurium films. For all depositions the total film mass per area was the same (1.1 mgm/cm^2), as was the nominal film thickness (~2μ).

In a preliminary study made in 1964, we had learned that the best Te films were obtained when depositing on a substrate at ambient temperature (~25°C). This fact was utilized in Run #016, wherein the Te was first deposited onto an ambient substrate. Thereafter the substrate temperature was increased to 155°C, and the Bi film was deposited. For Run #016, both films were deposited at a rate of 100 μgm/cm^{2}min. This run give the best results with an average Seebeck coefficient of 420 μv/°C. Assuming a Seebeck value of -60 μv/°C for Bi alone this implies a Te value of 360 μv/°C for the Te film. This is in excellent agreement with values of ~375 μv/°C quoted for bulk polycrystalline Te. The average resistivity of the Te films from Run #016 was 600 $\mu\Omega$ -m (6 x 10^{-2} Ω-cm). This value is just twice that reported for some forms of bulk polycrystalline Te.*

For Run #017 deposition rate was increased an order of magnitude to 1000 μgm/cm^{2}min, while all other parameters were maintained at the values used in Run #016. Althougn the Bi films from this run appeared quite continuous under microscopic examination, the Te films were cracked and "flaky" and were easily brushed off the substrate.

For Run #018 the substrate temperature was raised to 80°C prior to the deposition of the Te films. All other parameters were maintained at the same values used in Run #016. The Te films from this run were continuous, but very black in color. (The Te films in Run #016 exhibited the expected shiny metallic appearance.) Although this black appearance might be the result of a thinner film due to a lower "sticking coefficient" at the 80°C substrate temperature, our available instruments have not been able to discern any significant difference in thickness between these Te films and those of Run #016. If we assume that no significant thickness difference

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* Smith, Jones, and Chasmar, "The Detection and Measurement of Infrared Radiation", p. 77.

exists, then the resistivity of these films is four times that of our nominal bulk value of 300μΩ-m. The average Seebeck coefficient of these samples was 393 μv/°C. This is about 6% lower than the value from #016, and is probably just significant when one considers standard deviation values (see Table III), and the ±3% reproducibility of the measurement.

It is interesting to note that the values of the standard deviations in Table I are within the region of values achieved in the Bi-Sb experiments (see Table I). Specifically, standard deviation values for the Seebeck coefficient are less than 2% in all 18 runs evaluated to date, regardless of materials; just as all standard deviations values for resistivity are between 4% and 8%. This observation merely lends strength to the obvious hypothesis that the large resistance spreads observed within a given run are not due to mechanisms inherent in the materials, but rather due to some mechanism inherent in the deposition process or in the nature of the substrates and masks.

IIIB. Bismuth-Tellurium Thermopiles

Two vacuum depositions of 308 element Bi-Te thermopiles were performed, one of which was unsuccessful due to poor alignment of both substrates relative to the masks. Deposition parameters for these runs were essentially the same as those of Run #016 (see Table III).

Resistance, responsivity and time constant of the two devices were measured and compared with average values of (20) Bi-Sb thermopiles chosen at random. The brief table below presents the significant data.

Samples	Resistance in KΩ	Air Respons. in $v/w/cm^2$	Air Time Constant in ms
20 Bi-Sb	3.5 ± 1.0	0.22 ± 0.04	15 ± 3
Bi-Te #1	230	1.01	18
Bi-Te #2	260	1.01	17

Thus, the Bi-Te thermopiles have responsivities 4.6 times that of comparable Bi-Sb devices, with resistivities 70 times that of the Bi-Sb devices. Time constants of the Bi-Te thermopiles are comparable to those of the Bi-Sb devices.

IIIC. Bismuth-Tellurium Thermocouples with Gold "Bridge" At Junction

Attempts to accurately measure the resistance of Bi-Te thermocouples revealed that the resistance of these devices is a function of the voltage applied to them. In addition, measurements of the Seebeck coefficient of Bi-Te thermocouples were initially hampered by excessive noise signals which were eliminated only by careful electrostatic shielding of the sample. These phenomenon were attributed to the "diode action" occuring at the n-p junction at the Bi-Te interface.

It had been suggested that these problems could be eliminated by the introduction of vacuum deposited gold "bridges" between the Bi and Te legs at the junction regions. Theoretically, since the entire junction is at a constant temperature, this technique should <u>not</u> affect the Seebeck coefficient of the junction. To insure that this was the case, a group of eight (8) single junction thermocouples were fabricated with gold "bridges" between the Bi leg and the Te leg. The 0.3μ gold film was deposited onto the cover glass substrates using a substrate temperature of 180°C. Thereafter, vacuum was broken to allow a change of masks, and the Te and Bi films were deposited as previously described with no break in vacuum between depositions.

The mean Seebeck coefficient for these eight samples was 413μv/°C (with a standard deviation of 1.4%), which is very close to the value of 420μv/°C previously observed. Resistance values for these samples were on the order of 10k Ω, comparable to the samples previously described. The resistance of these samples did not vary with applied voltage, nor was electrostatic shielding necessary during Seebeck measurements. Thus, the introduction of the gold bridge eliminates the bothersome diode junction without affecting the thermoelectric properties of the device.

IV. FILM THERMOCOUPLES OF Bi-Te-Se AND Bi-Te-Sb ALLOYS

IVA. Formation of the Alloys

The purpose of this phase of the project was to repeat the best results obtained by the Materials Research Corporation as described in the Bureau of Ships Research Report #AD 426725. We worked with the two compositions which gave the best overall results for the investigations at MRC, specifically:

1. An n-type alloy composed of (75% Bi_2Te_3 + 25% Bi_2Se_3) + 0.1% AgI; and

2. A p-type alloy composed of (25% Bi_2Te_3 + 75% Sb_2Te_3) + 2.3% Te.

Three 30 gm batches of each composition were weighed and placed in pre-cleaned quartz tubes for subsequent evacuation, sealing, and melting. The materials used were all of 0.99999 purity obtained from the Semi-Elements Corporation. Measurements of mass of the materials were accurate to at least four significant figures.

As proper facilities were not available at BEC, the tubes and contents were sent to Machlett Laboratories in Stamford for evacuation (to 10^{-5} Torr) and sealing.

The sealed tubes were then heated with a bunsen burner until the molten contents achieved a temperature sufficient to emit a dull red glow. At this temperature the melt was agitated for about ten minutes, whereupon the tube and contents were "water quenched". One tube of each alloy had been improperly sealed and the contents oxidized severely upon heating.

The remaining four ingots, still in their evacuated tubes, were heated at 350°C for 24 hours in order to homogenize the ingots.

One ingot of each alloy was then removed from its tube and cut into convenient slabs or wedges with a clean jeweler's saw blade. It was decided to evaporate from single slabs of material rather than pulverized material in order to facilitate a uniform deposition rate and reduce spattering of the melt.

In order to insure that the starting materials were not limiting our film properties, slabs of each alloy were cut from the same ingots used for the deposition runs. The slab dimensions were approximately 1-1/4" x 1/8" x 1/16". Number 38 copper wires were attached to each end of the slabs with conductive silver paint. The slabs were then placed on the Seebeck apparatus (see Figure 3). A 15°C temperature differential was then impressed between the ends of the slab and the resulting Seebeck voltage measured on the "Rubicon" thermocouple potentiometer. Neglecting the contribution of the copper, these measurements gave a value of -177μv/°C for the n alloy and +135μv/°C for the p alloy. These values are in good agreement with bulk values of -170μv/°C and +170μv/°C reported in the Bureau of Ships Report #AD 426725.

IVB. Alloy Deposition by Resistance Heating

Since the component materials within each alloy differ widely in vapor pressure-temperature characteristics, fractional distillation of the alloy constituents proved to be a major handicap to successful vapor deposition of these materials both in the work done at BEC and that reported by investigators at MRC in the Bureau of Ships Research Report #AD 426725. Although these investigators claimed to have been able to consistantly reproduce near bulk properties in alloy films deposited from resistively heated boats, the variability of their own data sheds doubt on this claim. In the course of following their procedures as closely as possible at BEC we have been unable to verify their claims of reproducibility.

Ten (10) vacuum depositions have been completed here with these materials. In all cases the "n" alloy was the first deposited. Seebeck coefficients for the n-p junctions have been as low as 10μv/°C and as high as 218μv/°C. The addition of a third electrical lead attached to the film thermocouple junction allowed the Seebeck coefficient of <u>each</u> material to be measured, and the highest values obtained have been +168μv/°C for the "p" material and -145μv/°C for the "n" material, although these values did not occur in the same deposition.

Our experiments have tended to verify the observations of the above mentioned investigators' concerning the effects of annealing on the alloy films. We have also observed certain effects which can be correlated with the re-use of the alloy melt after a deposition, a phenomenon observed by investigators at MRC.

We have also frequently approached bulk resistivity values with these alloys (~$10^3 \mu\, \Omega$ cm), but as with Seebeck coefficients reproducibility has not been consistantly achieved.

Table IV summarizes the results of six (6) depositions performed with these alloys. Four other runs were unsuccessful due to film flaking resulting from inadequately cleaned substrates.

Referring to the table, no useful conclusions can be drawn concerning the final Seebeck coefficients of Runs #019, #020, #021, #022, and #031, all of which were performed by deposition from resistively heated boats. The annealing experiments performed on the samples of Run #020 agree qualitatively with the observations at MRC insofar as the Seebeck coefficient of thermocouple passes through a minimum somewhere between ambient and 350°C. However, our value of -145μv/°C for the n-film is much greater than the -90μv/°C reported in #AD 426725 (see Page 72 of that report).

Run #022 shows only that deposition onto a 220°C substrate produces results as unpredictable as those onto an ambient substrate.

We were unable to anneal thermocouples deposited on mylar covered substrates much above 200°C for fear of melting the mylar. Run #031 was, therefore, deposited onto glass substrates to permit vacuum annealing near 350°C immediately after deposition.

IVC. Alloy Deposition by Electron Bombardment

When installed in our vacuum system, the distance from monitor crystal and substrates to the source crucibles in the MRC electron gun (described on Page 8) was about 20 cm, the same source to substrate distance which existed during depositions from resistance boats (see Page 2). Prior to the first deposition experiment, the gun was energized under high vacuum to clean and outgas the carbon crucibles in which the source alloys were to be placed.

For Run #040 (see Table IV), slightly over 1 gm of each alloy was placed into the carbon crucibles. It was necessary to break the alloy ingots into ~1 mm sized particles in order to fill the crucibles. As with the preceding resistance boat run (#031), materials were deposited onto 220°C glass substrates, whereafter the films were annealed in vacuum at ~325°C for about 30 minutes. The results of this run were the most encouraging to date so far as the "p" film was concerned, for a Seebeck coefficient of +168μv/^{o}C was obtained.

Run #041 attempted to repeat these results, but yielded no data due to poor adherence of the films to inadequately cleaned substrates. Thus, for Run #042 the carbon crucibles had been used on two previous occasions. After each use a significant amount of alloy residue remained in the boat. Additional fresh alloy material (~0.5 gm) was added to the appropriate boats for each run.

The data from Run #042 (Table IV) shows the "n" Seebeck coefficient more than twice that of the first electron gun deposition, indicating the same correlation between Seebeck coefficient and melt re-use claimed by investigators at MRC. The p-film Seebeck coefficient has been reduced to one-third of the first value, however.

These observations would indicate that proper re-use of the n-alloy crucibles, combined with the use of fresh crucibles and melts for the p-alloy should permit depositions of films of these materials which consistantly achieve bulk properties.

V. INSULATION FILMS

Table V lists, in addition to mylar, seven "plastic" films which could feasibly be used in place of mylar as the insulation film in thermopile substrates. The data listed in the table is taken from manufacturers' specifications. As seen in the table, all eight materials possess approximately the same thermal conductivity (~2 x 10^{-4} to 5 x 10^{-4} cal/sec·cm·°C). Thus, none of the films offer any significant advantage over mylar in thermal conductivity alone. However, the two Union Carbide "Parylene" films are available in thicknesses as low as 4 x 10^{-6} inches, nearly two orders of magnitude thinner than can be obtained with the other plastics. It was believed that the thermal impedance of a device using a Parylene thin film should be determined entirely by the thermal properties of the metal film deposited thereon.

Four (4) 308 element thermopiles were deposited onto substrates covered with films of 2μ thick "Parylene N". The responsivities of these devices were comparable to devices made with 1/4 mil (6μ) mylar, suggesting that the hypothesis ending the above paragraph is in error. Another thermopile was made on Parylene employing Bi-Sb films only ~0.5μ thick, half that of what has become the "standard" thickness for thermopiles in this program. The 0.5μ device had nearly three times the resistance of typical 1μ samples, with a responsivity about 30% above the average value of standard samples.

Although inconclusive, these observations strongly support the hypothesis that the great majority of heat flow from hot to cold junctions of the thermopile is through the Bi and Sb films, rather than through the plastic insulation film as had been suggested previously. (See "The LPHS Thermopile Detector and the Effect of its Design Parameters on the Sensitivity of the LPHS", 31 December 1964 by J. M. McLauchlan.) A simple analysis of the physics of the device performed at BEC concludes that only 14% of the heat flow is through the 1/4 mil mylar in a thermopile of the 21 element LPHS configuration. Calculations of LPHS thermopile responsivity based on this analysis were in error by less than 10% from measured values.

VI. RECOMMENDATIONS

1. It is strongly recommended that the recently developed deposition technique for bismuth-antimony described

in Section II of this report be incorporated into thermopile production facilties at BEC at the earliest convenience. When comparing the reproducibility achieved with Bi-Sb in this project with that typical of standard resistance monitoring techniques previously in use in thermopile production, it is not unlikely that these newly developed techniques would increase thermopile production yield by as much as a factor of two.

2. In spite of the improvement in reproducibility realized for Bi-Sb in this study, the responsivities of experimental thermopiles fabricated under this project have been about 10% below average values (see Page 17). Since our detailed experiments with Bi-Sb reveal no possible explanation for this reduction relative to Bi-Sb film properties themselves and experiments with Parylene reveal no obvious explanation, an experimental program to investigate and control the thermal paths between hot and cold junctions in thermopile devices is strongly indicated. Such a program would, for example, involve measurements of thermal impedance for hot to cold junctions as a function of substrate geometry, type of insulating film and its adhesive, thermoelectric film pro-

perties, et cetera. Experiments could be designed to quantitatively determine the effects of misalignment between substrate grooves and thermoelectric film junctions. Surely some experiments must be performed to determine the effects of very thin Bi and Sb films ($<0.5\mu$) on thermopile performance.

3. The increased responsivity of bismuth-tellurium (Bi-Te) thermopiles could be extremely useful in many applications despite the inherent high impedance of these devices (see Section III). It is likely that the Te film resistance could be reduced by as much as 50% by simply depositing thicker films at appropriate rates. For this reason, a few more experiments with Bi-Te are in order. We have shown, however, that near bulk Te properties are easily and consistantly obtained, and would anticipate no major obstacles in the production of Bi-Te thermopile. Bi-Te thermopile configurations should be designed to include provisions for gold bridges at the junctions.

4. More work is required to develop techniques which allow the bulk properties of the "n" and "p" alloys to be consistantly reproduced in deposited films. The experiments

described in Section IV have indicated the steps to be taken to achieve this end. Once the proper techniques for deposition of these materials are developed, a new thermopile substrate design would be required to allow annealing at sufficiently high temperatures (viz., 350°C). Here again the Union Carbide "Parylene" plastic films look promising.

PREPARED BY:	APPROVED BY:
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PAW:msh

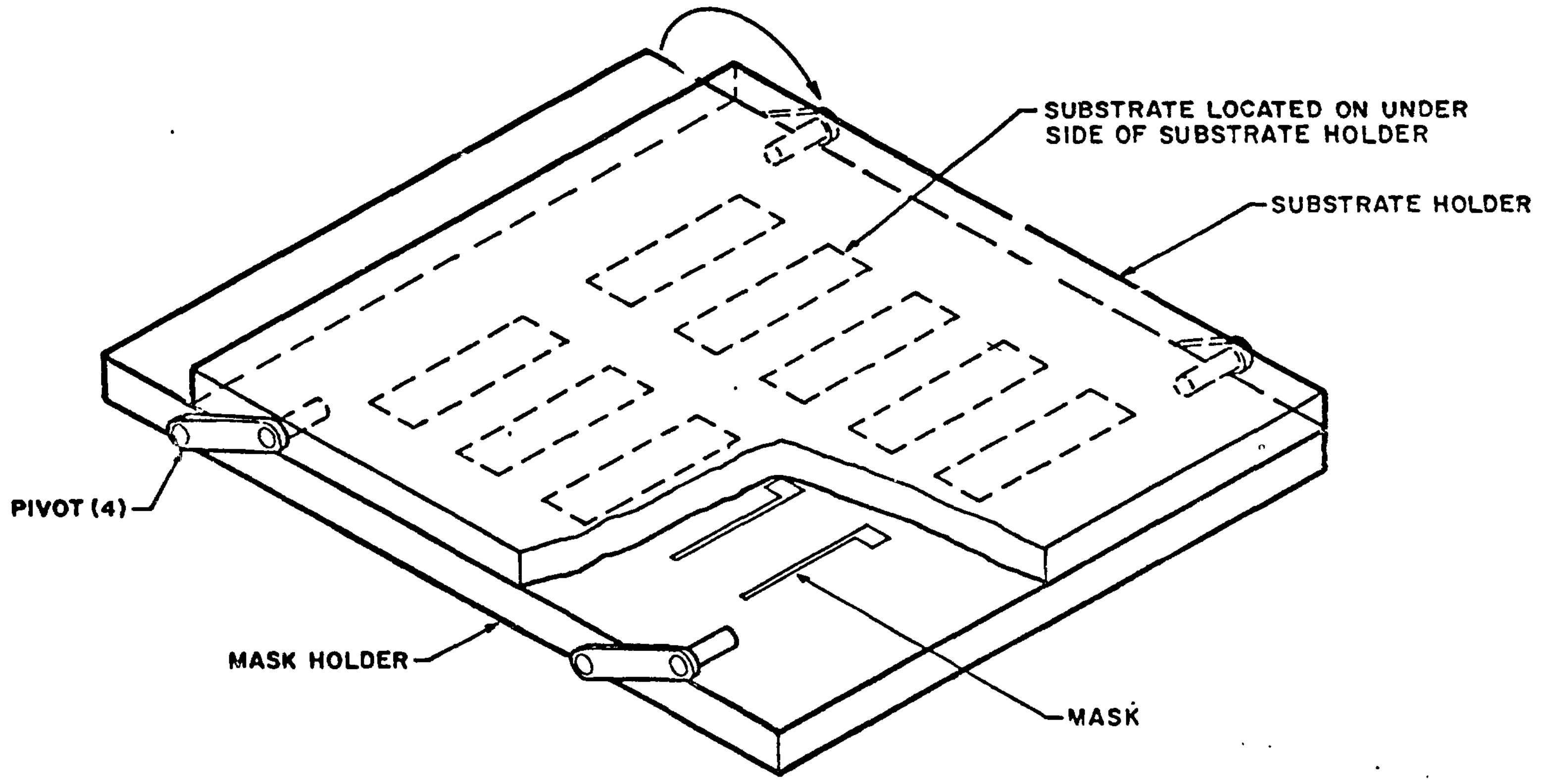
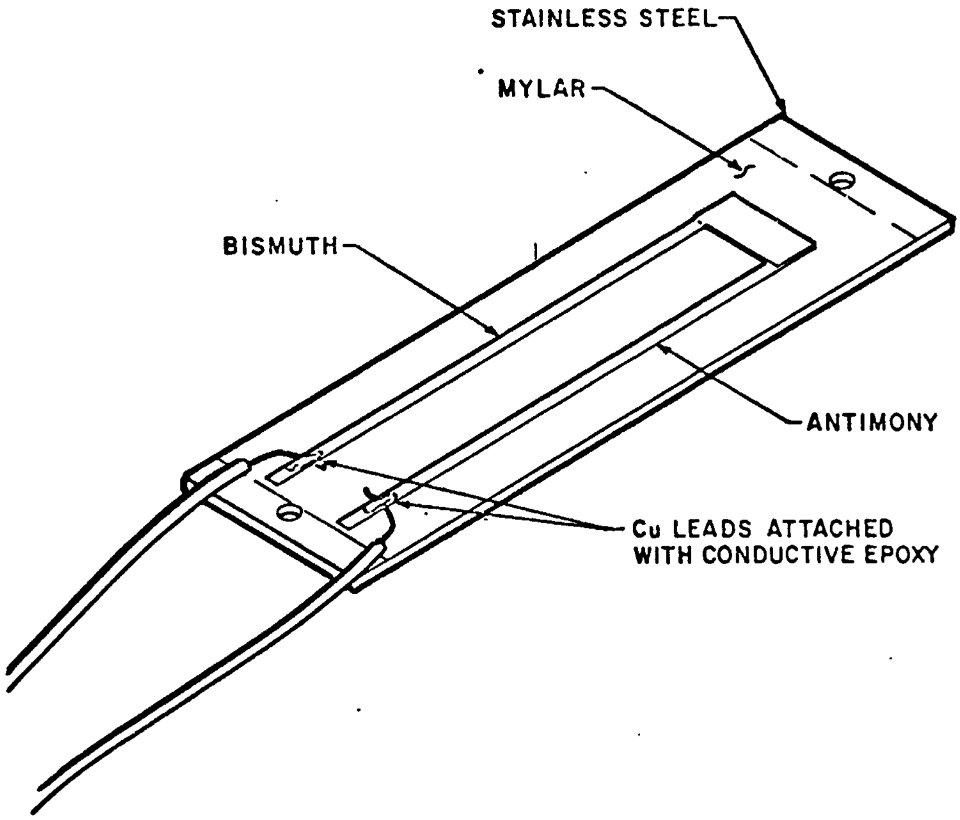


Figure I MASK HOLDER AND SUBSTRATE CHANGER MECHANISM



SCALE: 2-1

Figure 2 DETAIL OF FILM COUPLE AND SUBSTRATE

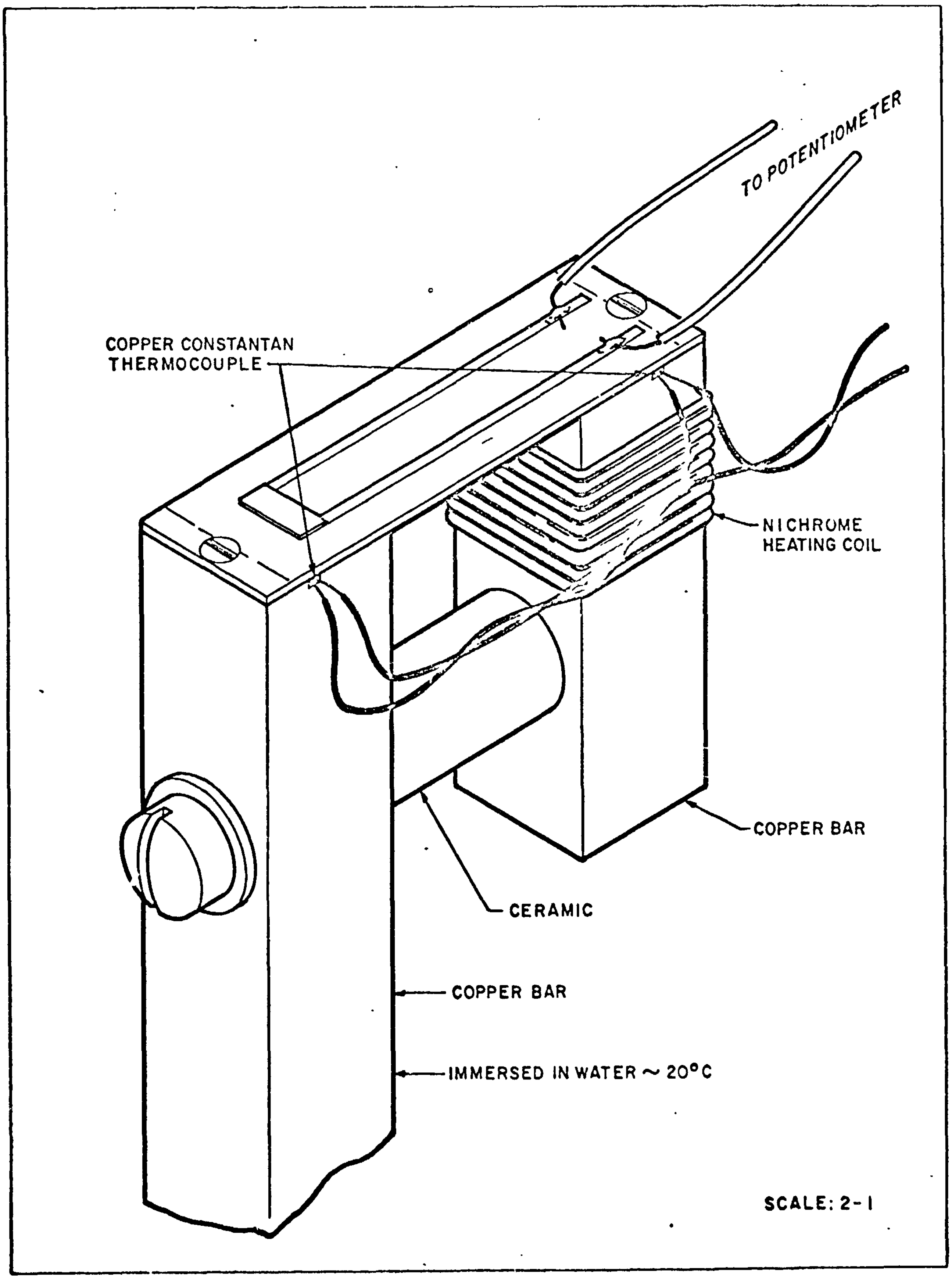
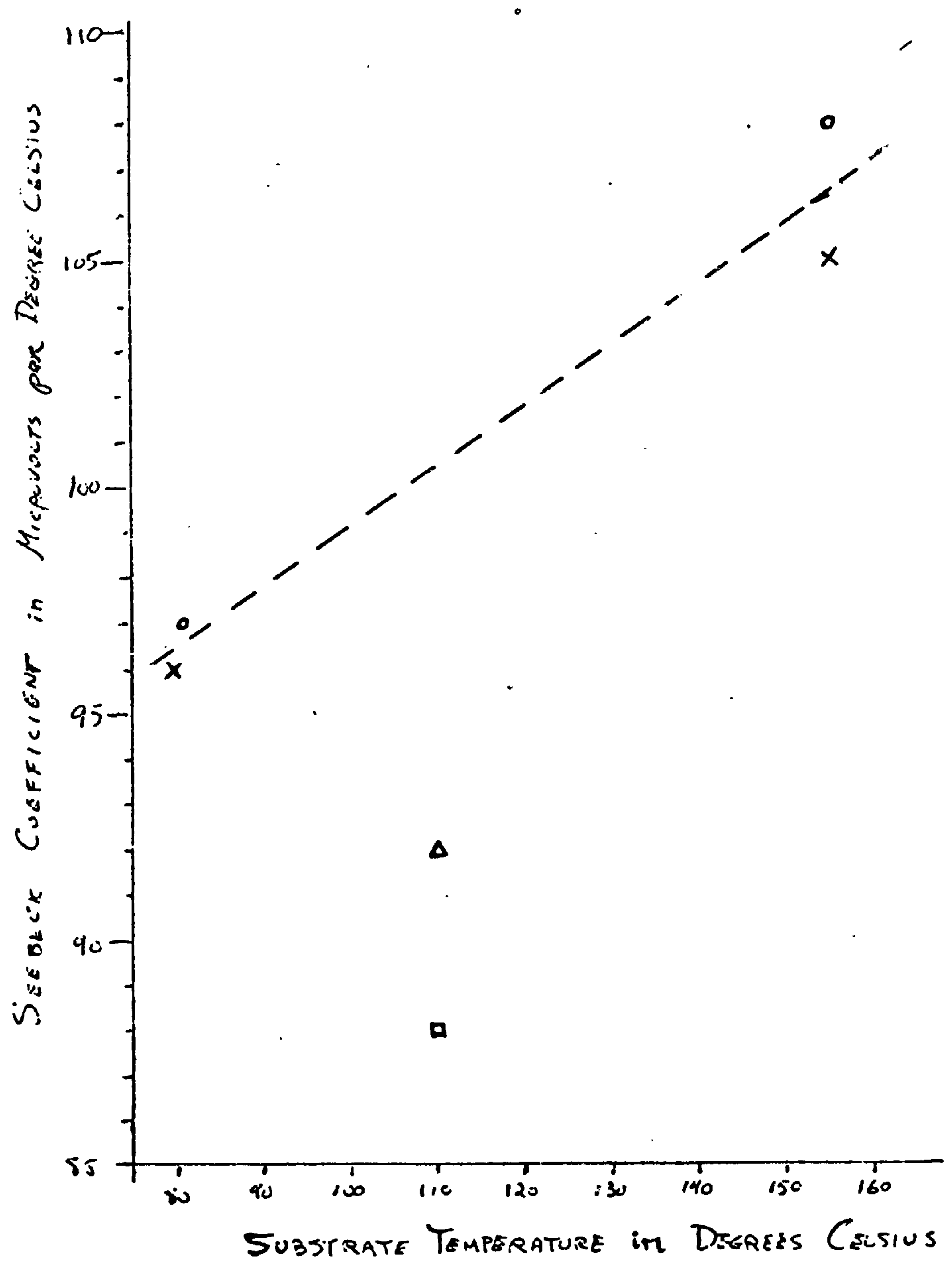


Figure 3 SEEBACK APPARATUS

FIGURE 4

SEEBECK COEFFICIENT vs. SUBSTRATE TEMPERATURE for VACUUM DEPOSITED BISMUTH-ANTIMONY THERMOCOUPLES

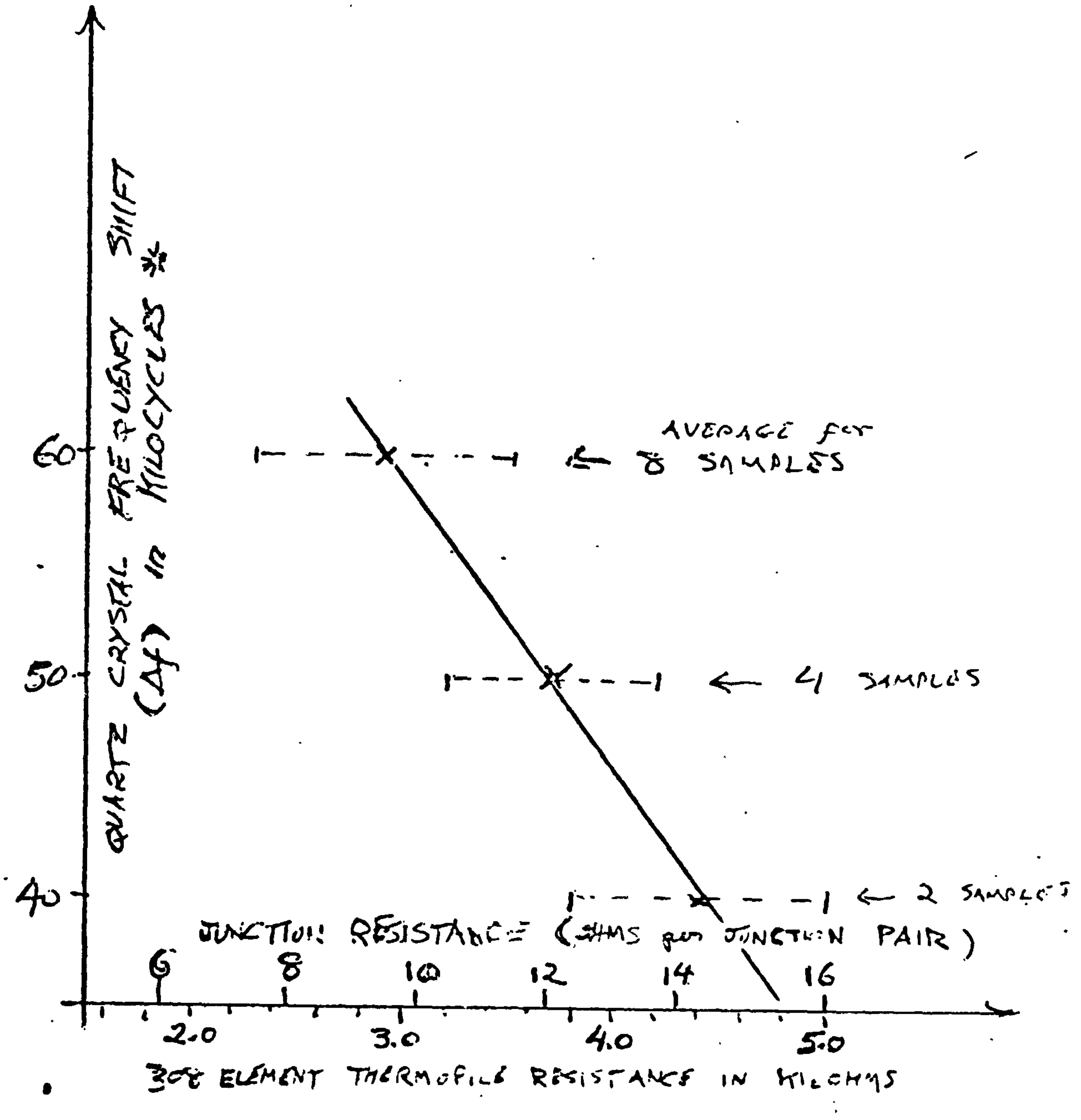
o = Sb DEPOSITED FIRST AT $\sim 10^3$ µgm/cm² min, $\sim 10^{-6}$ TORR
x = Sb DEPOSITED FIRST AT $\sim 10^2$ µgm/cm² min, $\sim 10^{-6}$ TORR
Δ = Bi DEPOSITED FIRST AT $\sim 10^3$ µgm/cm² min, $\sim 10^{-6}$ TORR
□ = Bi DEPOSITED FIRST AT $\sim 10^3$ µgm/cm² min, $\sim 10^{-5}$ TORR



MATERIAL	FINISH	DRAWN BY B.O.W	DATE 12/10/65	
DESCR		DWG. NO.	REV	

FIGURE 5

FILM MASS VS THERMOPILE RESISTANCE for BISMUTH-ANTIMONY



* NOTE: FILM MASS/AREA = $(11.1\,\mu gm/cm^2 kc) \times \Delta f$

MATERIAL	FINISH	DRAWN BY O.A.W.	DATE 5/20/66
DESCR		DWG. NO.	REV

TABLE I - SUMMARY OF BISMUTH-ANTIMONY FILM THERMOCOUPLE EXPERIMENTS

IA - Depositions at Constant Rate (Sb First)

Group #	Run #	Dep. Rate in $\mu gm/cm^2 min$	Total Dep. Time in Min. Sb	Total Dep. Time in Min. Bi	Substrate Temp. in °C	Press. Range in μ Torr	Film Mass Per Area in mgm/cm^2	Nominal Film Thick. in μ	Resist. Rel. to Bulk for Sb	Std. Dev. in %	Resist. Rel. to Bulk for Bi	Std. Dev. in %	Seebeck Coefficient in μv/°C	Std. Dev. in %
I	003	$\sim 10^2$	20	20	80	1 → 2	2.2	~ 6μ	3.6	8	2.2	6	96	0.6
	001	"	"	"	155	2 → 4	"	"	2.9	8	2.2	6	105	1.8
	002	"	"	"	230	3 → 4		"	4.4	9	open	-	Bi open	-
II	008	$\sim 2 \times 10^3$	1.3	0.9	82	0.7 → 2	2.2	~ 6μ	3.7	7	3.6	10	97	0.5
	005	"	1.5	1.0	155	2 → 4	"	"	3.4	7	4.3	7	108	0.6
	010	"	0.8	0.5	202	1 → 4	1.1	2μ	3.5	6	open	-	Bi open	-
III	011	$\sim 3 \times 10^3$	0.5	0.3	155	1 → 4	1.1	2μ	2.1	4	1.7	4	109	-
	012	$\sim 10^2$	11	9	"	0.7 → 1.5	"	"	2.3	7	1.5	8	105	0.9
	013	$\sim 4 \times 10^1$	27	27	"	0.5 → 0.9	"	"	2.8	8	1.6	3	106	0.7
IV	009	$\sim 2 \times 10^3$	0.5	0.2	155	2 → 3	0.55	~ 1μ	3.3	9	4.7	15	111	1.4

IB - Depositions at Variable Rate (Sb First)

Run #	Dep. Rate in $\mu gm/cm^2 min$ Initial*	Dep. Rate in $\mu gm/cm^2 min$ Final	Substrate Temp. In °C	Press. Range in μ Torr	Film Mass Per Area in mgm/cm^2	Nominal Film Thick. in μ	Resist. Rel. to Bulk for Sb	Std. Dev. in %	Resist. Rel. to Bulk for Bi	Std. Dev. in %	Seebeck Coefficient in μv/°C	Std. Dev. in %
004	$\sim 2 \times 10^2$	$\sim 10^2$	155	1 → 2	2.2	~ 6	2.6	6	2.6	3	105	0.7
014	$\sim 10^2$	"	"	0.7 → 2	1.1	~ 2	2.0	6	1.4	7	107	1.3
015	$\sim 10^2$	"	"	0.5 → 1.6	2.2	~ 6	2.7	10	1.9	8	95	-

* Initial rate maintained for first ~0.5μ of film.

TABLE I - SUMMARY OF BISMUTH-ANTIMONY FILM THERMOCOUPLE EXPERIMENTS (cont'd)

IC - Depositions at Different Pressures With Bi First

Run #	Dep. Rate in $\mu gm/cm^2 min$	Substrate Temp. in °C	Press. Range in μ Torr	Film Mass Per Area in mgm/cm^2	Nominal Film Thick. in μ	Resist. Rel. to Bulk for Sb	Std. Dev. in %	Resist. Rel. to Bulk for Bi	Std. Dev. in %	Seebeck Coefficient in μv/°C	Std. Dev. in %
006	$\sim 2 \times 10^3$	110	2 → 4	2.2	~ 6	6.0	5	4.3	8	92	1.6
007	"	110	23 → 45	"	"	4.8	4	3.0	9	88	1.0

TABLE II

ANNEALING OF BISMUTH-ANTIMONY THERMOCOUPLES IN AIR AT 145°C

IIA - Antimony Resistivity

Sample #	Initial ρ (μΩ-cm)	Nominal Thickness (μ)	Ratio Relative to Initial Value After N Hours N = 2	N = 30	N = 37	
1-1	162	~6μ	0.87	0.80	0.82	Average after 37 hrs. ~0.80
1-2	135	~6μ	0.87	0.79	0.78	
5-5	135	~6μ	0.86	0.82	0.80	
5-7	135	~6μ	0.86	0.79	0.81	
9-2	109	~1μ	0.90	0.90	0.90	Average after 37 hrs. ~0.97
9-6	179	~1μ	0.94	0.93	[illegible]	
11-4	97	~2μ	1.08	0.90	0.96	
12-2	72	~2μ	0.97	[illegible]	0.97	
12-6	108	~2μ	0.97	[illegible]	0.99	
13-6	102	~2μ	0.97	1.20	1.00	
14-3	75	~2μ	1.00	1.00	1.00	
14-5	120	~2μ	1.00	0.89	0.95	

Sample #	Initial ρ (μΩ-cm)	Nominal Thickness (μ)	Ratio Relative to Initial Value After N Hours N = 1	N = 4	N = 8	N = 28	
1-3	108	~6μ	1.00	1.00	0.73	0.92	Average after 28 hrs. ~0.66
1-7	101	~6μ	0.89	1.00	1.07	0.71	
5-1	216	~6μ	0.67	0.67	0.67	0.62	
5-5	117	~6μ	0.77	1.07	1.08	0.62	
6-1	322	~6μ	0.78	0.84	0.78	0.79	
6-9	216	~6μ	0.83	0.83	0.83	0.67	
15-1	153	~6μ	0.73	0.73	0.73	0.59	
15-6	182	~6μ	0.54	0.46	0.46	0.35	
13-1	150	~2μ	0.96	1.04	1.08	1.04	
13-2	132	~2μ	0.84	0.91	0.91	0.89	

TABLE II (Cont'd)

ANNEALING OF BISMUTH-ANTIMONY THERMOCOUPLES IN AIR AT 145°C

II3 - Bismuth Resistivity

Sample #	Initial ρ (μΩ-cm)	Nominal Thickness (μ)	Ratio Relative to Initial Value After N Hours			
			N = 2	N = 30	N = 37	
1-1	270	~6μ	0.88	0.82	0.84	Average after 37 hrs. ~ 0.78
1-2	216	~6μ	0.84	0.66	0.72	
5-5	630	~6μ	0.82	0.73	0.77	
5-7	670	~6μ	1.08	0.85	0.80	
9-2	160	~1μ	0.93	0.99	0.97	Average after 37 hrs. ~ 0.97
9-6	700	~1μ	0.97	0.81	0.84	
11-4	234	~2μ	0.93	0.93	0.93	
12-2	90	~2μ	0.96	0.96	0.97	
12-6	210	~2μ	0.97	0.97	0.97	
13-6	216	~2μ	0.97	0.95	0.96	
14-3	134	~2μ	1.00	0.95	0.95	
14-5	210	~2μ	0.97	0.97	0.97	

Sample #	Initial ρ (μ -cm)	Nominal Thickness (μ)	Ratio Relative to Initial Value After N Hours				
			N = 1	N = 4	N = 8	N = 28	
1-3	360	~6μ	0.50	0.50	0.95	0.45	Average after 28 hrs. ~ 0.74
1-7	315	~6μ	0.80	1.14	0.69	0.74	
5-1	396	~6μ	0.91	0.91	0.91	1.00	
5-9	450	~6μ	0.88	0.88	0.76	0.82	
6-1	950	~6μ	0.87	1.00	0.95	0.80	
6-9	540	~6μ	0.77	0.80	0.80	0.73	
15-1	308	~6μ	0.61	0.68	0.68	0.59	
15-6	252	~6μ	1.00	1.00	1.00	0.80	
13-1	186	~2μ	0.97	0.97	0.97	0.97	
13-2	192	~2μ	0.91	0.94	0.91	0.94	

TABLE II (Cont'd)

ANNEALING OF BISMUTH-ANTIMONY THERMOCOUPLES IN AIR AT 145°C

IIC - Seebeck Coefficients

Sample #	Initial Value in μv/°C	Relative Value After 37 hrs. @ 145°C
1-1	106	0.97
1-2	108	0.97
5-5	107	0.98
5-7	107	0.98
9-2	110	0.96
9-6	105	0.96
11-4	109	0.98
12-2	107	0.95
12-6	107	0.98
13-6	107	0.97
14-3	103	0.98
14-5	107	0.97

Average Value after 37 hrs. ~ 0.97

Sample #	Initial S(μv/°C)	Ratio Relative to Initial Value After N Hours			
		N = 1	N = 4	N = 8	N = 28
1-3	103	0.97	0.96	0.98	-
1-7	105	0.99	0.99	0.99	-
5-1	110	0.99	0.99	1.00	0.98
5-9	106	0.98	-	-	-
6-1	102	1.00	1.01	0.99	0.98
6-9	95	0.99	0.99	1.01	1.00
15-1	99	1.00	0.99	1.00	1.00
15-6	96	0.97	0.99	1.00	-
13-1	105	0.98	0.99	0.98	0.98
13-2	108	0.97	0.97	0.99	0.97

TABLE III - Summary of Bismuth-Tellurium Film Thermocouple Experiments

NOTES:
1) For all runs below, Te was the first material deposited.
2) In all cases the total film mass per area was 1.1 mg/cm^2 (~2µ).
3) In all cases pressure range during deposition was from 0.5 to 1.5µ Torr.

Run #	Nominal Dep. Rate in µgm/cm^{2}min	Te Substrate Temperature in °C	Bi Substrate Temperature in °C	Te Resistivity Rel. to Bulk	Std. Dev. in %	Seebeck Coefficient in uv/°C	Std. Dev. in %
016	10^2	25	155	2	6	420	1.8
017	10^3	25	155	-- *	--	-- *	--
018	10^2	80	155	4	5	393	1.7

* Te films from Run #017 were discontinuous and "flaky".

TABLE IV - SUMMARY OF Bi-Te-Se (N-TYPE) AND Bi-Te-Sb (P-TYPE) FILM THERMOCOUPLE EXPERIMENTS

Run #	Dep. Rate in μgm/cm^{2}min	Boat & Melt Re-use	Film Mass Per Area mg/cm^2	Nom. Thick. in μ	Substrate Temp. in $^\circ$C	30 min. Vac. Anneal Temp. in $^\circ$C	N-Film Sheet Resistance in ohms/sq.	P-Film Sheet Resistance in ohms/sq.	N vs. P Seebeck Coef. in μv/$^\circ$C	N vs. Cu Seebeck Coef. in μv/$^\circ$C	P vs. Cu Seebeck Coef in μv/$^\circ$C	
019	100	0	1.1	~2	25	200	$\sim 10^6$	$\sim 10^3$	30	-	-	Deposition from Resistively Heated Boats
020	40	1	1.1	2	25	80 145 200	50 " "	50 " "	158 36 163	- -145	- +15	
021	25	2	0.33	0.7	25	- 215	12 open	6 open	10 open	- -	- -	
022	25	3	0.33	0.7	215	-	100	20	144	-97	+50	
031	25	4	0.33	0.7	220	325	50	5	97	-	-	
040	3 → 30	0	0.33	0.7	220	325	42	46	218	-50	+168	Dep. by electron bombardment
042	3 → 30	2	0.33	0.7	225	325	42	46	160	-110	+50	

TABLE V - Available Insulation Films Compatible With Present Thermopile Substrate Configurations

RADE NAME	Chemical Designation	Mfgr.	Min. Available Thick.- in.	Thermal Cond. cal/sec cm°C	Useful Temp. Range °C	Softening Temp. °C	Melting Temp. °C
MYLAR	Polyester Film	DuPont	0.15×10^{-3}	3.63×10^{-4}	-60 to 150	not listed	250 to 265
KAPTON	Polyimide Film	DuPont	0.5×10^{-3}	3.72×10^{-4}	-269 to 400	None	Chars above 800
TEFLON	Fluorocarbon Film	DuPont	0.5×10^{-3}	4.65×10^{-4}	-85 to 200	not listed	285 to 295
PARYLENE "N"	Poly-Para Xylyene	Union Carbide	0.004×10^{-3}	approx. 3×10^{-4}	not listed	not listed	400
PARYLENE "C"	Mono Chloro -P-Xylylne	Union Carbide	0.004×10^{-3}	approx. 3×10^{-4}	not listed	not listed	280 to 300
KYNAR	Polyvinylidene-Flouride Film	Pennsalt Chemicals	1.0×10^{-3}	3.6×10^{-4}	not listed	not listed	170
STYROFLEX FILM	Polystyrene	Natvar	0.25×10^{-3}	2.4 to 3.3×10^{-4}	not listed	not listed	not listed
TEDLAR	Polyvinyl Flouride	DuPont	0.5×10^{-3}	not listed	-70 to 107	not listed	300 with decomposition

(19)