Contract Number: TECO-4397-050

SUPPORT FOR IMPROVED SILICON GERMANIUM THERMOELECTRIC MATERIAL DEVELOPMENT

PROGRAM STATUS REPORT

AND

FINANCIAL REPORT

Month Ending November 30, 1986

Prepared For:

Thermo Electron Corporation
Waltham, Massachusetts

Prepared By:

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Thermoelectric Technology Group
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December 1986

SUPPORT FOR

IMPROVED SILICON GERMANIUM

THERMOELECTRIC MATERIAL DEVELOPMENT

PROGRAM STATUS REPORT

Month Ending November 30, 1986

I. SIGNIFICANT EVENTS/ACCOMPLISHMENTS

1000 Program Plan

No Activity.

2000 Thermoelectric Material Evaluation

2100 Thermoelectric Material Preparation

No Activity.

2200 Construction of Data Base

The high temperature thermal diffusivity, electrical resistivity and Seebeck coefficient has been determined on samples from T-257, p-type SiGe/GaP prepared by TECO. The results of these measurements are summarized in Figures 1 through 3 and Table 1.

High temperature properties of T-255, n-type SiGe/GaP were reported last month. The electrical measurements were repeated by reinstrumenting the same piece of T-255 and remeasuring the high temperature electrical properties, as summarized in Table 2. The average resistivity and Seebeck increased by about 8% and 5%, respectively, consistent with dopant precipitation. The electrical power factor from the second run agreed with the first run results to within 1.6%.

A method for determining thermal diffusivity accounting for use of an exponential heat pulse and heat losses has been derived based on analysis of the heat diffusion equation. This is described in detail in the appendix.

2300 Chemical and Physical Analysis

Differential thermal analysis (DTA) is shown in Figure 4 for GE p-type SiGe and TECO n- and p-type SiGe/GaP. The liquidus temperature of GE p-type SiGe is 1364 °C and 1347 °C and 1349 °C for TECO n- and p-type SiGe/GaP. The solidus of GE p-type SiGe is reasonably well defined by the break in the DTA curve at about 1275 °C. The onset of melting in the SiGe/GaP material is much less well defined, but is clearly lower than in SiGe, suggestive of a two phase material.

2400 Thermophysical and Strength

Samples of GE prepared p-type SiGe, TECO prepared n- and p-type SiGe/GaP have been submitted for thermal expansion, compressive strength and high temperature flexure measurements. The thermal expansion of GE p-type SiGe is shown in Figure 5. The thermal expansion coefficient is found to vary linearly with temperature from 3.95 to 4.91 x 10_6/C between 0 and 1000 °C. Table 3 summarizes initial results of mechanical strength measurements.

3000 BOND DEVELOPMENT

Two samples of p-type SiGe bonded to Graphite have been received from TECO and subjected to high temperature specific contact resistivity measurement. Results are shown in Figures 6 and 7. For T-109, the closest electrodes were placed 0.5 cm from the bond line on each side of the bond. The relatively large contact resistance shown in Figure 6 at high temperatures may be a result of measurement error in that most of the measured resistance between the two leads is bulk resistance, which must be accounted for.

In an effort to improve the precision of the measurement, for T-114 electrodes were placed about 0.1 cm on either side of the bond. The resulting high temperature contact resistance, shown in Figure 7, was much lower and possibly consistent with program goals of 30 μohm-cm^2, although the data show considerable scatter.

A measurement of the contact resistivity reduces to

$$R_{contact}=R_{bond}A-r_{SiGe}d_{SiGe}-r_C d_C,$$

where $R_{contact}$ is the specific contact resistivity, R_{bond} is the measurement of the resistance between the two probes spanning the bond, A is the cross-sectional are, $r_{SiGe}d_{SiGe}$ is the bulk contribution from the SiGe and $r_C d_C$ is the bulk contribution from the graphite.

The error in the contact resistance measurement will be given by the accumulation of each of the errors in the terms on the right-hand side above. For example, an error in the estimate of the placement of the probes of 0.002" (which is less than the size of the probe), will contribute about 22 $\mu ohm-cm^2$, using typical values of 3 mohm-cm and 1.3 mohm-cm for the resistivity of SiGe and graphite, respectively. An error in the estimate of the bulk material resistivities of 1% will contribute about the same amount with probes placed 0.5 cm from the bond.

Figure 8 illustrates the problem. Resistance (or voltage) is measured along the length of a sample. The slope determined on each side of the bond is extrapolated to the bond and the difference between the extrapolated values determines the specific contact resistance. High contact resistances can be determined with reasonable accuracy (such as occur here at low temperatures). Low resistance values, however, require very accurate knowledge of the slope and positions of the closest probes. The 1000 C curve in Figure 8, for example, represents 42 $\mu ohm-cm^2$, which is comparable to the measurement error. More work is required to improve the accuracy of these measurements.

4000 PROGRAM MANAGEMENT

A review meeting held a TECO on November 5, 1986 was attended by W. Terrill, L. DeFillipo and C. Vining of GE the primary purpose of which was to discuss bond development work at TECO. C. Vining presented results of analysis of thermal diffusivity measurements incorporating the effects of an exponential heat forcing function.

II. PLANNED ACTIVITIES NEXT MONTH

1000 Program Plan

No activity.

2000 Thermoelectric Material Evaluation

2100 Material Preparation

No activity

2200 Construction of Data Base

No activity.

2300 Chemical and Physical Analysis

No activity.

2400 Thermophysical and Strength Measurements

Strength measurements on GE produced p-type SiGe and TECO produced n- and p-type SiGe/GaP will be completed.

3000 BOND DEVELOPMENT

Specific contact resistivity measurement techniques will be improved and measurements performed on TECO provided bonds.

4000 PROGRAM MANAGEMENT

The next monthly review with the Jet Propulsion Laboratory and Thermo Electron is scheduled for early January at JPL will be attended by Dr. Vining.

III. FINANCIAL MANAGEMENT

See Attached Form: NASA 533M

IV. PROBLEM AREAS AND PLANNED RESOLUTIONS

None

V. ACTION ITEMS

None

VI. KEY PERSONNEL

Program Manager: C. Vining
Thermoelectric Measurements: R. Van Der Beck
Mechanical Strength Measurements: J. Roetling

Table 1: Summary of the high temperature thermoelectric properties of T-257, p-type SiGe/GaP.

SAMPLE: T-257-B Annealed by program 1
DESCRIPTION: p-Type SiGe/GaP
Molecular Weight 35.05

Prepared by: TECO
Measured by: GE

TEMPERATURE		SEEBECK COEFFICIENT	ELECTRICAL RESISTIVITY	THERMAL DIFFUSIVITY	HEAT CAPACITY	DENSITY	THERMAL CONDUCTIVITY	ELECTRICAL POWER FACTOR	FIGURE OF MERIT	DIMENSIONLESS FIGURE OF MERIT
		Seebeck and Resistivity Measured Simultaneously GE-SCO		Laser Flash Diffusivity GE-SCO	Drop Calorimetry Ames Lab. MHPS-077P	Immersion Density Thermal Expansion GE-RSO	Calculated	Calculated	Calculated	Calculated
# Points in Fit		105	106	10	11					
Temp. Range of D		22 C 1000 C	22 C 1000 C	447 K 1352 K	375 K 1375 K					
RMSD (%)		0.79	0.95	1.33	0.93	0.10	2.36	2.52	4.88	4.88
									Z	ZT
A		9.10183E+01	9.57061E-01	2.08023E-02	4.66300E+00	2.949				
B		2.64246E-01	1.46961E-03	2.77925E-05	1.62220E-03	4.300E-06				
C		-3.27179E-04	-6.98358E-07	-4.52231E-08	6.31000E+04					
D		3.86576E-07	2.19977E-09	1.83699E-11	4.184					
E		-2.04644E-10	-1.39479E-12							
F										
G										
H										
Units for Temp: Equation		C A+BT+...HT^7	C A+BT+...HT^7	K A+BT+...ET^4	K D=(A+BT+C/T^2)/MW	C A/(1+B(T-27))^3	a*Cp*d	S^2/r	S^2/rk	K ZT
(K)	(C)	(microV/K)	(milliohm-cm)	(cm2/sec)	(J/g-K)	(g/cm3)	(W/cm-K)	(microW/cm-K2	(1000/K)	
275	2					2.950				
300	27	97.88	0.9961			2.949		9.62		
325	52	103.89	1.0317			2.948		10.46		
350	77	109.56	1.0668			2.947		11.25		
375	102	114.92	1.1017		0.6828	2.946		11.99		
400	127	120.01	1.1364	0.0259	0.6812	2.945	0.0518	12.67		
425	152	124.84	1.1711	0.0258	0.6806	2.944	0.0518	13.31	0.2569	0.1092
450	177	129.46	1.2059	0.0258	0.6810	2.943	0.0517	13.90	0.2685	0.1208
475	202	133.87	1.2410	0.0257	0.6820	2.942	0.0517	14.44	0.2792	0.1326
500	227	138.10	1.2765	0.0256	0.6836	2.941	0.0516	14.94	0.2892	0.1446
525	252	142.17	1.3124	0.0255	0.6856	2.940	0.0515	15.40	0.2985	0.1567
550	277	146.10	1.3489	0.0253	0.6880	2.940	0.0514	15.82	0.3073	0.1690
575	302	149.90	1.3860	0.0252	0.6908	2.939	0.0513	16.21	0.3154	0.1814
600	327	153.60	1.4237	0.0250	0.6937	2.938	0.0512	16.57	0.3231	0.1939
625	352	157.19	1.4621	0.0248	0.6969	2.937	0.0510	16.90	0.3304	0.2065
650	377	160.70	1.5013	0.0246	0.7003	2.936	0.0508	17.20	0.3373	0.2192
675	402	164.12	1.5412	0.0244	0.7039	2.935	0.0506	17.48	0.3438	0.2321
700	427	167.47	1.5819	0.0242	0.7076	2.934	0.0505	17.73	0.3501	0.2450
725	452	170.75	1.6233	0.0240	0.7114	2.933	0.0502	17.96	0.3560	0.2581
750	477	173.96	1.6654	0.0237	0.7153	2.932	0.0500	18.17	0.3617	0.2712
775	502	177.11	1.7083	0.0235	0.7192	2.931	0.0498	18.36	0.3671	0.2845
800	527	180.19	1.7517	0.0233	0.7233	2.930	0.0496	18.53	0.3722	0.2977
825	552	183.19	1.7957	0.0230	0.7275	2.929	0.0493	18.69	0.3770	0.3110
850	577	186.12	1.8402	0.0228	0.7317	2.928	0.0491	18.82	0.3815	0.3242
875	602	188.97	1.8851	0.0226	0.7359	2.927	0.0489	18.94	0.3856	0.3374
900	627	191.72	1.9303	0.0224	0.7402	2.926	0.0487	19.04	0.3894	0.3504
925	652	194.37	1.9757	0.0221	0.7446	2.925	0.0485	19.12	0.3927	0.3633
950	677	196.90	2.0212	0.0219	0.7489	2.924	0.0483	19.18	0.3956	0.3758
975	702	199.31	2.0666	0.0217	0.7534	2.923	0.0482	19.22	0.3979	0.3879
1000	727	201.56	2.1117	0.0216	0.7578	2.923	0.0480	19.24	0.3995	0.3995
1025	752	203.65	2.1564	0.0214	0.7623	2.922	0.0479	19.23	0.4005	0.4106
1050	777	205.55	2.2006	0.0212	0.7668	2.921	0.0478	19.20	0.4008	0.4209
1075	802	207.24	2.2440	0.0211	0.7713	2.920	0.0478	19.14	0.4002	0.4302
1100	827	208.70	2.2863	0.0210	0.7759	2.919	0.0478	19.05	0.3986	0.4385
1125	852	209.90	2.3275	0.0209	0.7804	2.918	0.0478	18.93	0.3960	0.4456
1150	877	210.81	2.3672	0.0208	0.7850	2.917	0.0478	18.77	0.3924	0.4512
1175	902	211.40	2.4053	0.0208	0.7896	2.916	0.0479	18.58	0.3875	0.4554
1200	927	211.65	2.4414	0.0208	0.7942	2.915	0.0481	18.35	0.3815	0.4577
1225	952	211.51	2.4753	0.0208	0.7989	2.914	0.0483	18.07	0.3741	0.4582
1250	977	210.94	2.5067	0.0208	0.8035	2.913	0.0486	17.75	0.3653	0.4566
1275	1002	209.93	2.5353	0.0208	0.8082	2.912	0.0489	17.38	0.3551	0.4528
1300	1027	208.41	2.5608	0.0209	0.8128	2.911	0.0494	16.96	0.3435	0.4466
INTEGRATED AVERAGE 500 C TO 1000 C		200.36	2.146	0.0218	0.7627	2.922	0.0485	18.79	0.3875	0.3970

Table 2: Summary of a second determination of the high temperature thermoelectric properties of T-255, n-type SiGe/GaP.

SAMPLE: T-255-B2 Annealed by program 1 — Prepared by: TECO; Measured by: GE
DESCRIPTION: n-Type SiGe/GaP
Molecular Weight 37.52
This run represents a remeasurement of the electrical properties only of T-255-B1

TEMPERATURE	SEEBECK COEFFICIENT	ELECTRICAL RESISTIVITY	THERMAL DIFFUSIVITY	HEAT CAPACITY	DENSITY	THERMAL CONDUCTIVITY	ELECTRICAL POWER FACTOR	FIGURE OF MERIT	DIMENSIONLESS FIGURE OF MERIT
	Seebeck and Resistivity Measured Simultaneously GE-SCO		Laser Flash Diffusivity GE-SCO	Drop Calorimetry Ames Lab. MHPS-077P	Immersion Density Thermal Expansion GE-RSO	Calculated	Calculated	Calculated	Calculated
# Points in Fit	101	95	10	11					
Temp. Range of D	36 C 1017 C	36 C 1017 C	458 K 1363 K	375 K 1375 K					
RMSD (%)	0.62	0.82	1.33	0.93	0.10	2.36	2.07	4.43	4.43
								Z	ZT
A	-1.25964E+02	1.05682E+00	7.59077E-03	4.66300E+00	2.989				
B	9.15618E-01	-1.95767E-03	6.89831E-05	1.62220E-03	4.300E-06				
C	-1.08301E-02	3.28885E-05	-9.41154E-08	6.31000E+04					
D	3.84301E-05	-1.27465E-07	3.68043E-11	4.184					
E	-6.34712E-08	2.38781E-10							
F	4.95557E-11	-2.05427E-13							
G	-1.47415E-14	6.52031E-17							
H									
Units for Temp:	C	C	K	K	C				K
Equation	A+BT+...HT^7	A+BT+...HT^7	A+BT+...ET^4	D*(A+BT+C/T^2)/MW	A/(1+B(T-27))^3	a*Cp*d	S^2/r	S^2/rk	ZT

(K)	(C)	(microV/K)	(milliohm-cm)	(cm2/sec)	(J/g-K)	(g/cm3)	(W/cm-K)	(microW/cm-K2)	(1000/K)	
275	2				0.6628	2.990				
300	27	-108.48	1.0256		0.6524	2.989		11.47		
325	52	-102.69	1.0276		0.6454	2.988		10.26		
350	77	-104.20	1.0506		0.6407	2.987		10.34		
375	102	-110.75	1.0874		0.6378	2.986		11.28		
400	127	-120.51	1.1329		0.6363	2.985		12.82		
425	152	-132.02	1.1828	0.0227	0.6358	2.984	0.0431	14.74	0.3416	0.1452
450	177	-144.16	1.2342	0.0229	0.6361	2.983	0.0435	16.84	0.3870	0.1741
475	202	-156.11	1.2853	0.0231	0.6371	2.982	0.0438	18.96	0.4326	0.2055
500	227	-167.28	1.3350	0.0232	0.6386	2.981	0.0441	20.96	0.4755	0.2378
525	252	-177.31	1.3828	0.0232	0.6405	2.980	0.0443	22.74	0.5136	0.2696
550	277	-186.01	1.4289	0.0232	0.6427	2.979	0.0444	24.21	0.5454	0.3000
575	302	-193.32	1.4737	0.0231	0.6453	2.978	0.0445	25.36	0.5703	0.3279
600	327	-199.30	1.5180	0.0230	0.6481	2.977	0.0445	26.17	0.5883	0.3530
625	352	-204.11	1.5629	0.0229	0.6510	2.977	0.0444	26.66	0.6000	0.3750
650	377	-207.93	1.6093	0.0228	0.6542	2.976	0.0443	26.87	0.6060	0.3939
675	402	-211.01	1.6582	0.0226	0.6575	2.975	0.0442	26.85	0.6077	0.4102
700	427	-213.61	1.7105	0.0224	0.6610	2.974	0.0440	26.67	0.6063	0.4244
725	452	-215.95	1.7671	0.0222	0.6645	2.973	0.0438	26.39	0.6029	0.4371
750	477	-218.28	1.8285	0.0219	0.6682	2.972	0.0435	26.06	0.5988	0.4491
775	502	-220.79	1.8951	0.0217	0.6719	2.971	0.0432	25.72	0.5951	0.4612
800	527	-223.65	1.9669	0.0214	0.6757	2.970	0.0429	25.43	0.5926	0.4740
825	552	-226.95	2.0437	0.0211	0.6795	2.969	0.0426	25.20	0.5917	0.4882
850	577	-230.76	2.1251	0.0208	0.6835	2.968	0.0423	25.06	0.5930	0.5041
875	602	-235.08	2.2102	0.0205	0.6874	2.967	0.0419	25.00	0.5965	0.5220
900	627	-239.85	2.2980	0.0203	0.6915	2.966	0.0416	25.03	0.6021	0.5419
925	652	-244.96	2.3872	0.0200	0.6955	2.965	0.0412	25.14	0.6094	0.5637
950	677	-250.28	2.4764	0.0197	0.6996	2.964	0.0409	25.29	0.6179	0.5870
975	702	-255.60	2.5640	0.0195	0.7037	2.963	0.0406	25.48	0.6269	0.6112
1000	727	-260.72	2.6482	0.0193	0.7079	2.962	0.0404	25.67	0.6355	0.6355
1025	752	-265.39	2.7275	0.0191	0.7121	2.961	0.0402	25.82	0.6428	0.6589
1050	777	-269.41	2.8001	0.0189	0.7163	2.960	0.0400	25.92	0.6479	0.6803
1075	802	-272.54	2.8647	0.0187	0.7205	2.959	0.0399	25.93	0.6500	0.6988
1100	827	-274.65	2.9202	0.0186	0.7248	2.958	0.0398	25.83	0.6484	0.7133
1125	852	-275.61	2.9658	0.0185	0.7290	2.957	0.0399	25.61	0.6426	0.7230
1150	877	-275.43	3.0014	0.0184	0.7333	2.956	0.0400	25.28	0.6326	0.7275
1175	902	-274.20	3.0275	0.0184	0.7376	2.956	0.0401	24.84	0.6188	0.7271
1200	927	-272.25	3.0456	0.0184	0.7419	2.955	0.0404	24.34	0.6020	0.7224
1225	952	-269.97	3.0579	0.0185	0.7463	2.954	0.0408	23.83	0.5839	0.7153
1250	977	-268.05	3.0680	0.0186	0.7506	2.953	0.0413	23.42	0.5667	0.7083
1275	1002	-267.44	3.0911	0.0188	0.7549	2.952	0.0420	23.21	0.5532	0.7053
1300	1027	-269.38	3.1035	0.0191	0.7593	2.951	0.0427			
INTEGRATED AVERAGE 500 C TO 1000 C		-258.47	2.634	0.0195	0.7125	2.961	0.0410	25.13	0.6138	0.6293

TABLE 3: MECHANICAL STRENGTH OF GE P-TYPE SiGe

Si/Ge (GEP-1)
4 POINT FLEXURE AT ROOM TEMPERATURE
(Spans = 1.25 & 0.625 in.)

NO.	MAX. STRESS (ksi)	MAX STRAIN (%)	MODULUS (Msi)
R-A	29.98	0.152	19.7
-B	30.07	0.152	19.8
-C	27.39	0.138	(19.8)*
Mean	29.15	0.147	19.8
S.D.	1.52	0.008	0.06

* Curve erratic. Modulus taken between start and failure points.
All curves linear.

Si/Ge (GEP-1)
COMPRESSION AT ROOM TEMPERATURE

NO.	MAX. STRESS (ksi)	MAX STRAIN (%)	MODULUS (Msi)
N-1	79.79	0.364	21.9
O-1	94.76	0.418	22.7
P-1	114.30	0.511	22.4
Q-1	89.86	0.402	22.4
Mean	94.68	0.424	22.35
S.D.	14.49	0.062	0.33

Curves are linear.

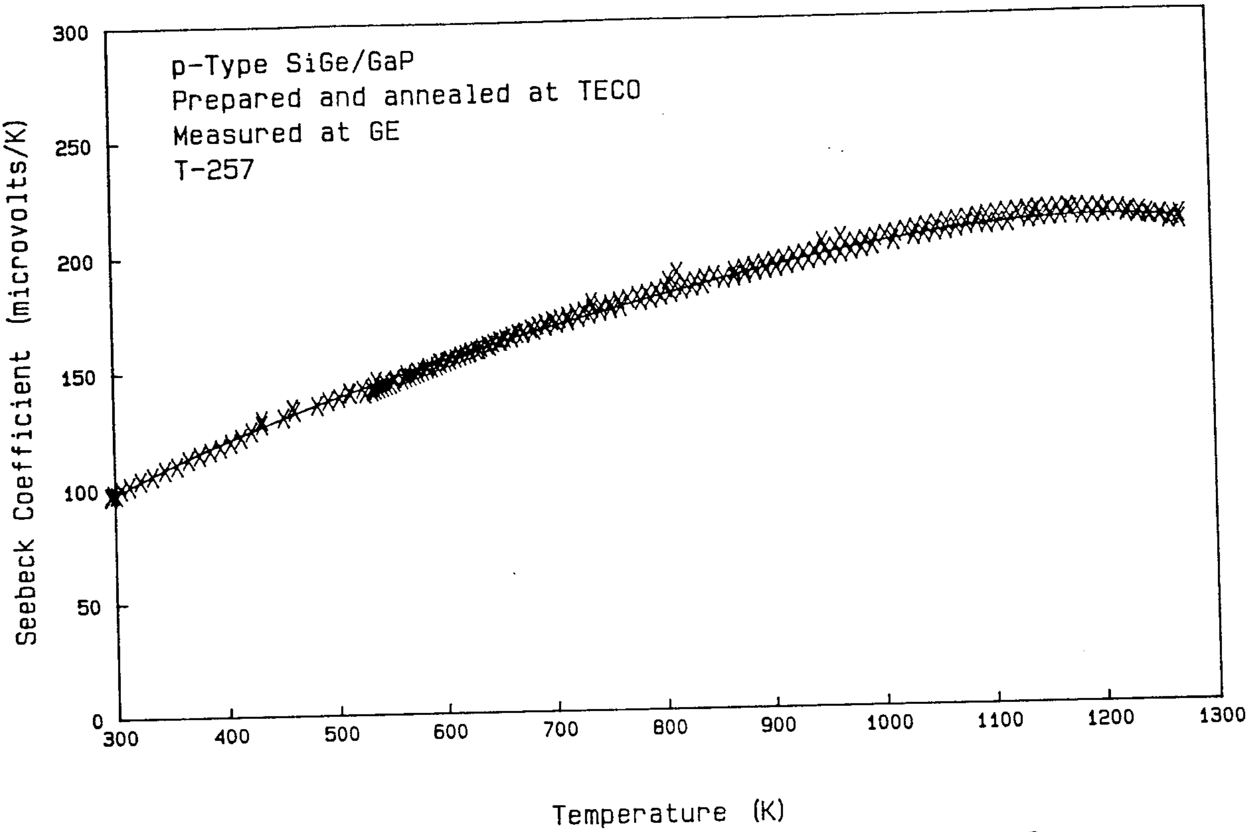

Figure 1: Seebeck coefficient as a function of temperature for T-257, p-type SiGe/GaP. Both warming and cooling data are shown. The solid line represents a fit to the warming data used for figure of merit calculations.

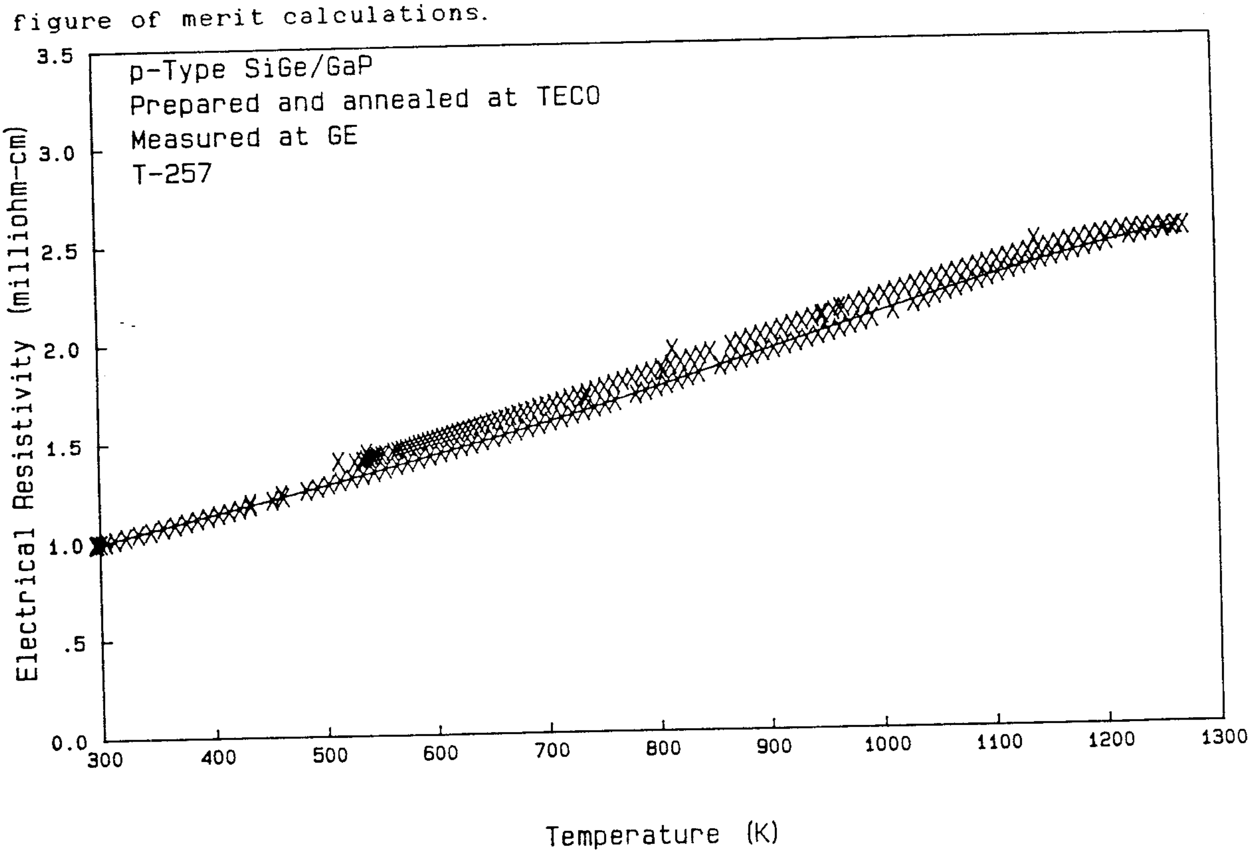

Figure 2: Electrical resistivity as a function of temperature for T-257, p-type SiGe/GaP. Both warming and cooling data are shown. The solid line represents a fit to the warming data used for figure of merit calculations.

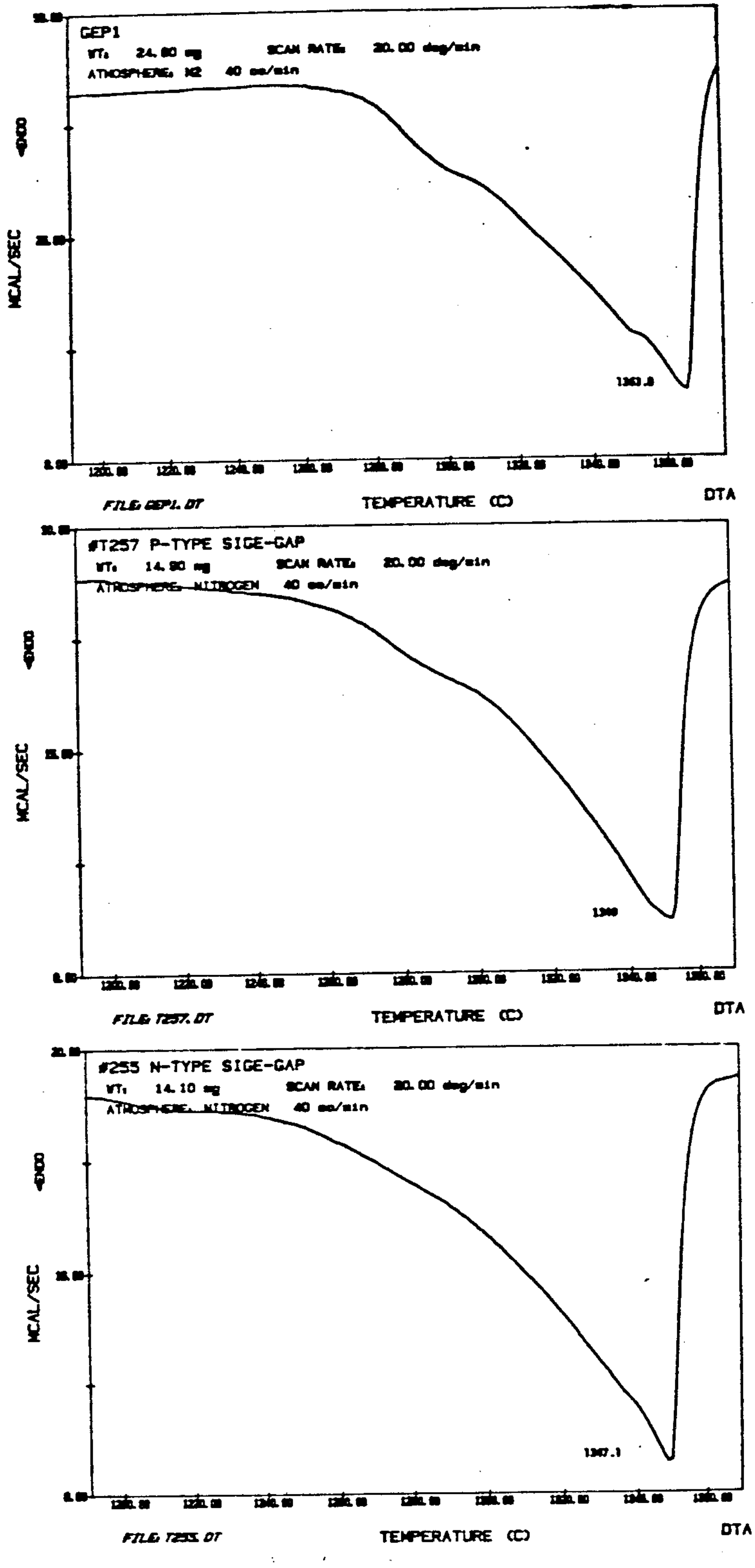

Figure 4: Differential thermal analysis as a function of temperature for p-type SiGe and p- and n-type SiGe/GaP

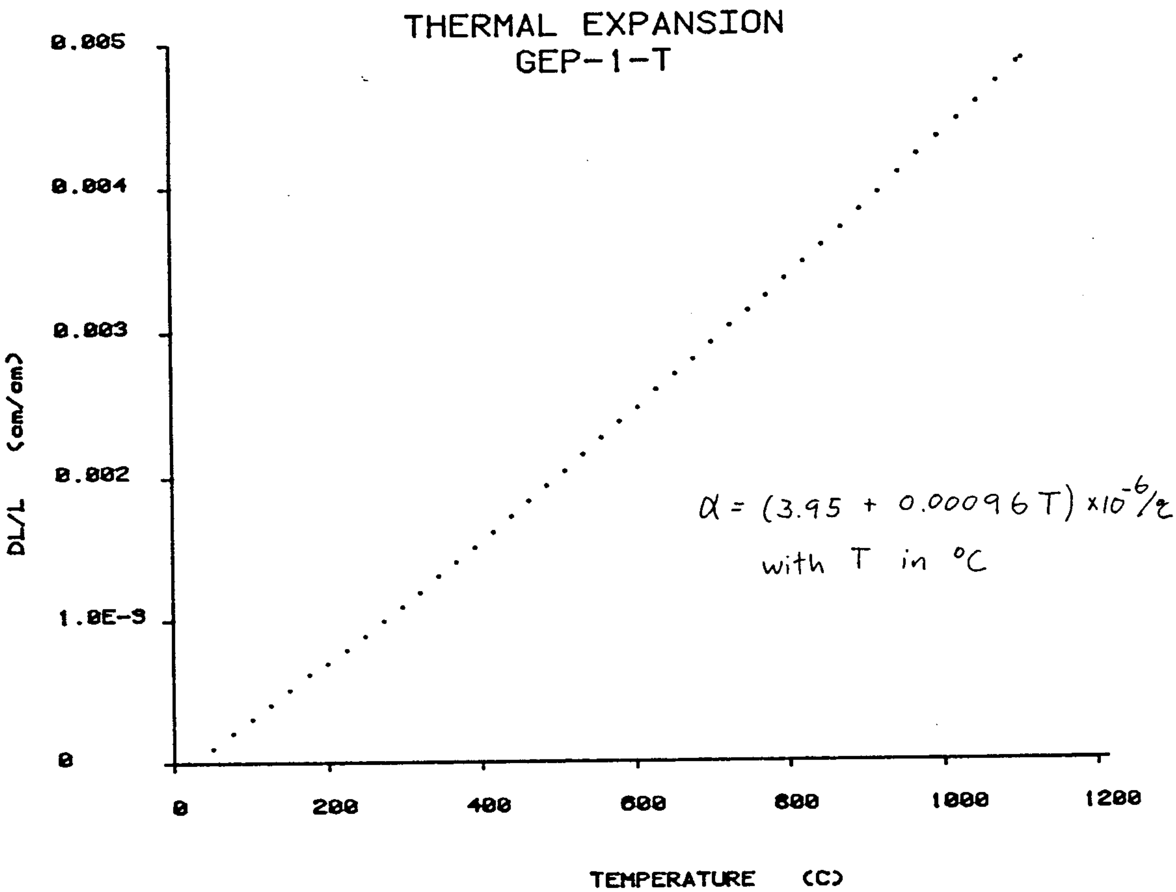

Figure 5: Thermal expansion as a function of temperature of p-type SiGe. The curvature indicates a temperature dependent thermal expansion coefficient.

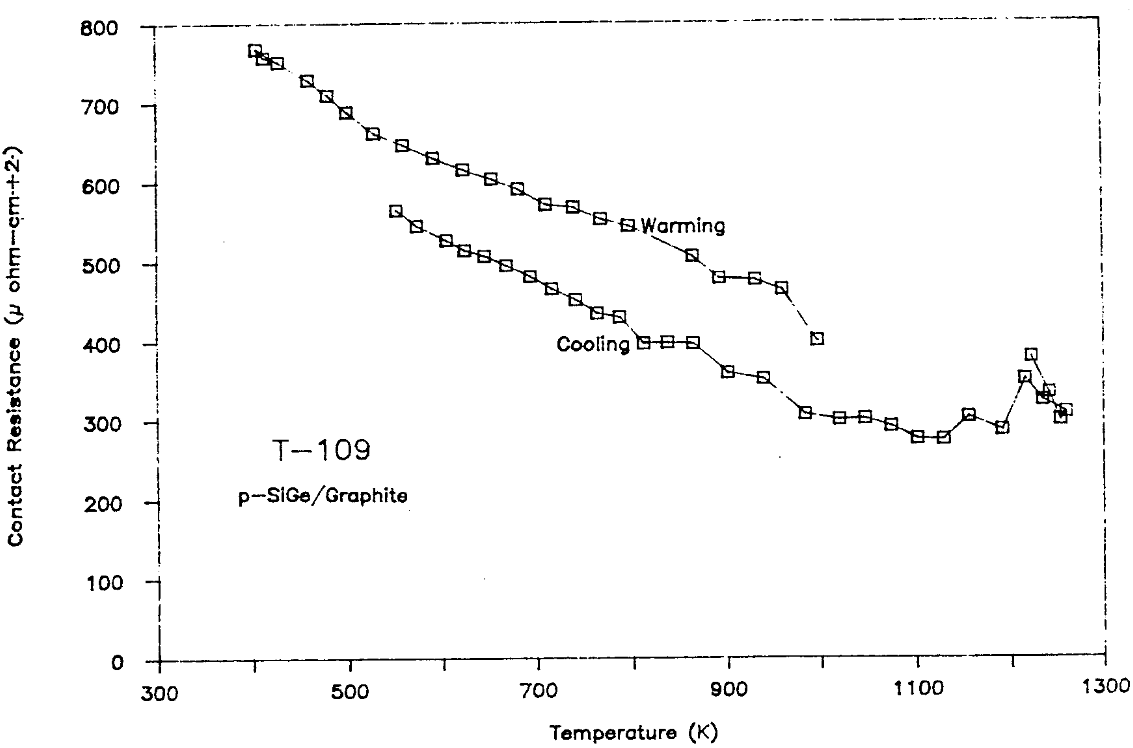

Figure 6: Contact resistance as a fuction of temperature for T-109, p-type SiGe bonded to Graphite.

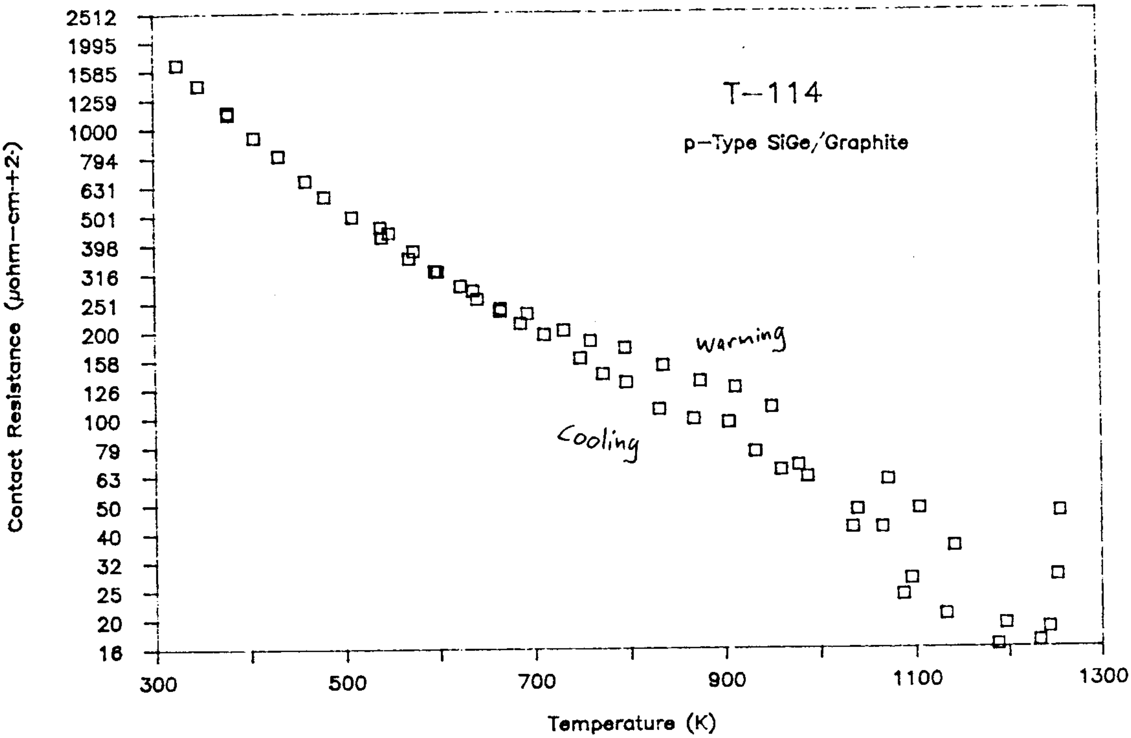

Figure 7: Contact resistance as a fuction of temperature for T-114, p-type SiGe bonded to Graphite.

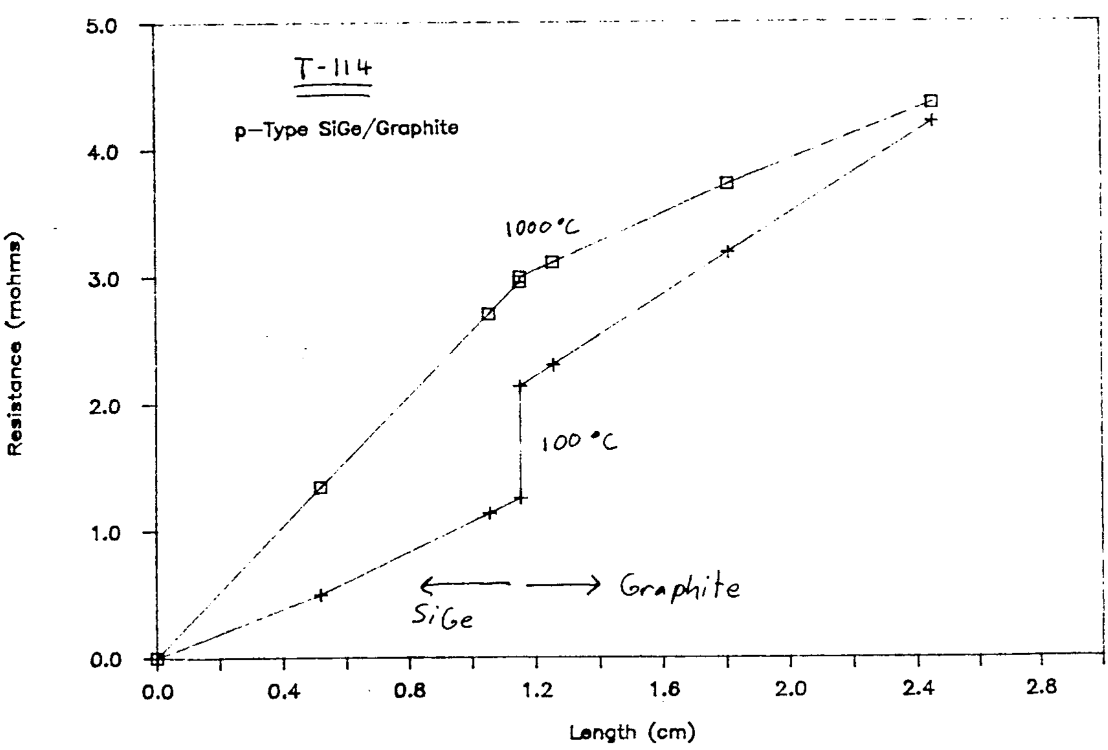

Figure 8: Contact resistance determination technique.