

SUBJECT: The case against chemistry in SiGe/GaP
FROM: Cronin B. Vining *CBV* ✓
TO: J. Vandersande
J. Suito
J-P. Fleurial
A. Borshchevsky
C. Wood
T. Ohta
DATE: 5/11/90

At our CSTI meeting this morning we had a discussion about the relative roles of chemistry and kinetics in determining the various results observed in n-type SiGe/GaP, particularly as regards the "high" carrier concentrations observed. While the discussion is fresh in my mind, I wanted to make some notes which perhaps some of you may be interested in. This memo contains those notes.

First: Let me again point out the futility of putting too much emphasis on fine-tuning the optimum doping level. Figure 1 shows my calculation for ZT as a function of doping level¹. ZT is really quite flat in the region of optimum doping, which is a rather universal feature of thermoelectrics. Indeed, a 20% change in the doping level, above or below the optimum doping level, only reduces ZT from its optimum value by about 2%. We wouldn't even know if we are 20% off the optimum doping level.

So, quibbling over a 20% change in carrier concentration is really pointless.

Second: Zone levelled samples have been made with high temperature carrier concentrations indistinguishable from T-373. Perhaps we haven't done it lately, but it has been done. This can be seen most easily by looking at the resistivity at 1000 °C for an 80-20 zone-levelled sample (Table I and Figure 2) reported in an RCA Topical Report in 1969². This data (both in the 'as grown' condition and in the 'stabilized' condition) is redrawn in Figure 4, which also shows (solid circle) the resistivity of T373 at 1000 °C³.

Many samples (hot pressed, zone-levelled, annealed, with Ga, without Ga, you name it) have similar resistivity values at 1000 °C. None have remarkably lower values, so I take this value as indicative of the maximum carrier concentration possible. Since this can be achieved with or without Ga, I conclude that Ga has no observable effect on the solubility of electrically active P at

least at 1000 °C.

Recently, a few samples have surfaced with slightly lower resistivity values. This drop may be evidence of some small effect of Ga. Or perhaps it is due to one of the other dozen or so important processing parameters. As noted above, however, a drop from 1.3 mΩ-cm to 1.1 mΩ-cm is virtually irrelevant in regard to ZT.

So, I still think Ga plays no important role at 1000 °C

Third: There cannot be much electrically active Ga in the best samples near room temperature, either. Jean-Pierre included a curve (Figure 5) which shows that the mobility of T373, for example, is essentially the same as zone-leveled materials⁴. My calculations, which in fact find that all of the transport properties of T373 are the same as P-only doped SiGe, also confirm this¹.

If there were a significant amount of electrically active Ga in T373, the properties would be quite different from P-only doped materials. Figure 6 shows the mobility of SiGe calculated by my model (lower, solid curve)⁵. The upper solid curve represents what the mobility would be, if there were no ionized impurity scattering. This means that if (by magic) you could achieve a carrier density of 10^{20} cm⁻³ without any ionized phosphorus in the sample, the mobility would go up by a factor of almost 3. (ZT would actually go up very little because the Seebeck is smaller for acoustic scattering than it is for ionized impurity scattering).

Now, ionized Ga should reduce the mobility by about the same amount as ionized P does, so if the ionized Ga concentration is even 10% of the ionized P concentration the mobility will come down about as indicated by the dashed line in Figure 6. This calculation shows that the amount of Ga in solution at 300 K can't be much more than about 10% of the phosphorus concentration, or we wouldn't be getting the mobility values that we do.

So, I don't think there is much Ga in solution at 300 K.

Fourth: All room temperature carrier concentration values are dominated by kinetic effects. We know from high temperature Hall effect measurements, for example, that the high temperature carrier concentrations are, in saturated samples, in the 4 to 5×10^{20} cm⁻³ range. But, only a few samples, and only relatively recently, have shown such high values after quenching. Often, room temperature values are in the range of 1.5 to 2×10^{20} cm⁻³, again regardless of whether the sample contains Ga or not.

If samples are cooled very slowly, carrier concentrations probably less than 10^{18} cm^{-3} are to be expected, since phosphorus is not very soluble at room temperature. That higher values are observed at room temperature at all is because of kinetics, which prevents the super-saturated solutions from immediately precipitating.

If one concentrates on getting the room temperature carrier concentration up, using heroic and carefully timed annealing and quenching procedures, it is hardly surprising that higher levels of super-saturation can be achieved. The kinetics of precipitation is strongly influenced by the number, distribution, size and kind of nucleation sites in the sample. It would not surprise me to discover that the equilibrium carrier concentration at room temperature is no different with, or with out Ga. But we do not get equilibrium values at all.

So, I do not think anyone has adequately separated the obvious kinetic effects from the theoretically possible chemistry effects to know if the 300 K equilibrium solubilities have been changed at all.

To summarize, I am hard pressed to believe that Ga plays any significant role at the highest temperatures. At lower temperatures, from mobility data as well as direct chemical analysis, we are fairly sure there is very little Ga in solution. It seems to me much more likely that small amounts of Ga and extensive variations in microstructure are much more likely to alter the kinetics of precipitation (which we know is affected) than to alter the equilibrium carrier concentrations (which we only know may be affected). Further, since kinetics dominates the determination of room temperature carrier concentration values in any case, I am reluctant to jump on the chemistry band-wagon without compelling evidence.

If your interested in getting compelling evidence, I suggest emphasizing kinetic studies like the kind performed at RCA⁶ (and others). Jean-Pierre and Alex are already collecting some of this kind of data. If enough data are collected, you can determine the solubility values and the kinetic parameters from analysis of the data. It is also important to reproduce part of what has already been done (say, on zone levelled samples), in order to be sure the new data is valid. If you can't do this, or something like it, due to lack of resources, which may well be the case, then you will never really know what is going on.

1. C. B. Vining, "A Model for the High Temperature Transport Properties of n-Type Silicon Germanium Alloys," submitted to J. Applied Physics, 1990.
2. "Silicon Germanium Thermoelectric Materials and Module Development Program," RCA Topical Report, 1969, cover page attached (Figure 3).

3. Originally presented in-house at JPL 10/11/87 and also presented at a SiGe Integration Meeting in Waltham, MA 10/19/88.
4. J-P. Fleurial, CSTI Meeting handout, 5/11/90.
5. Recent calculation, but the qualitative results are rather obvious.
6. L. Ekstrom and J. P. Dismukes, J. Phys. Chem. Solids, 27, 857-863 (1966).

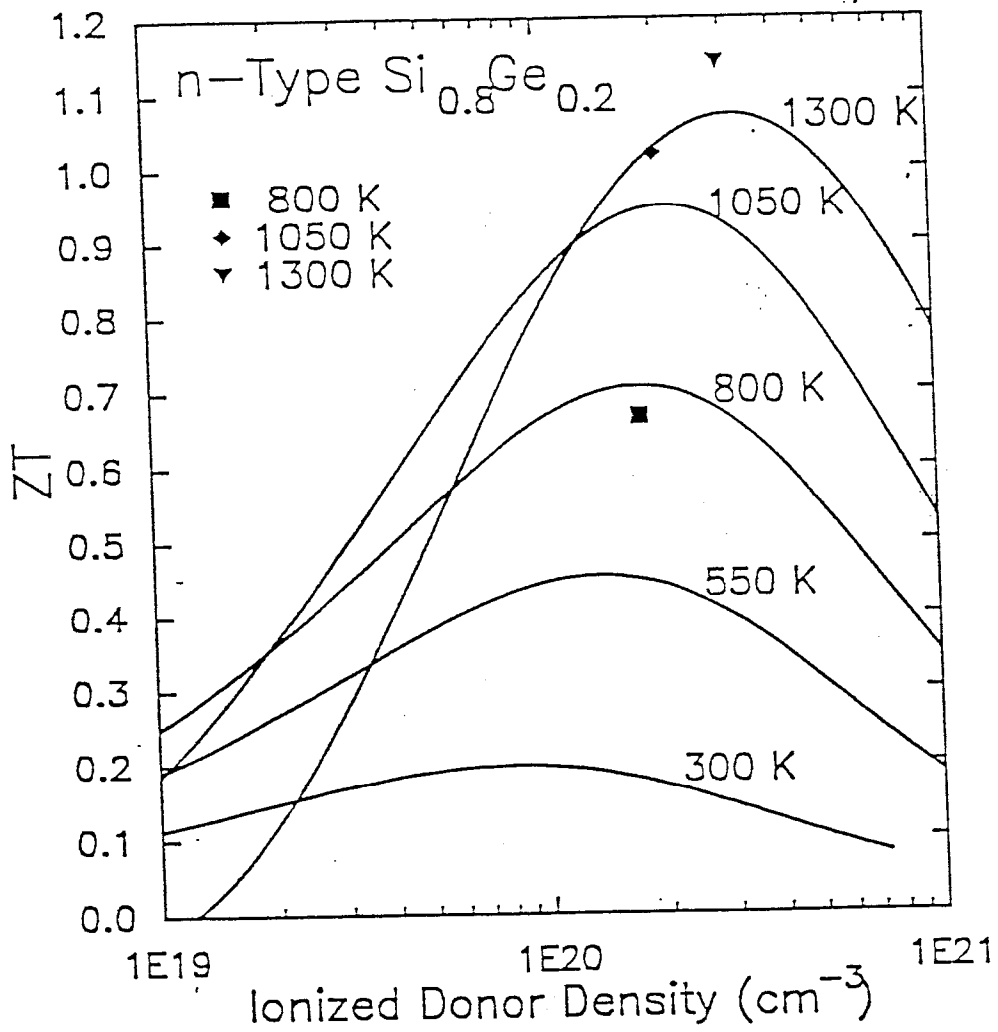


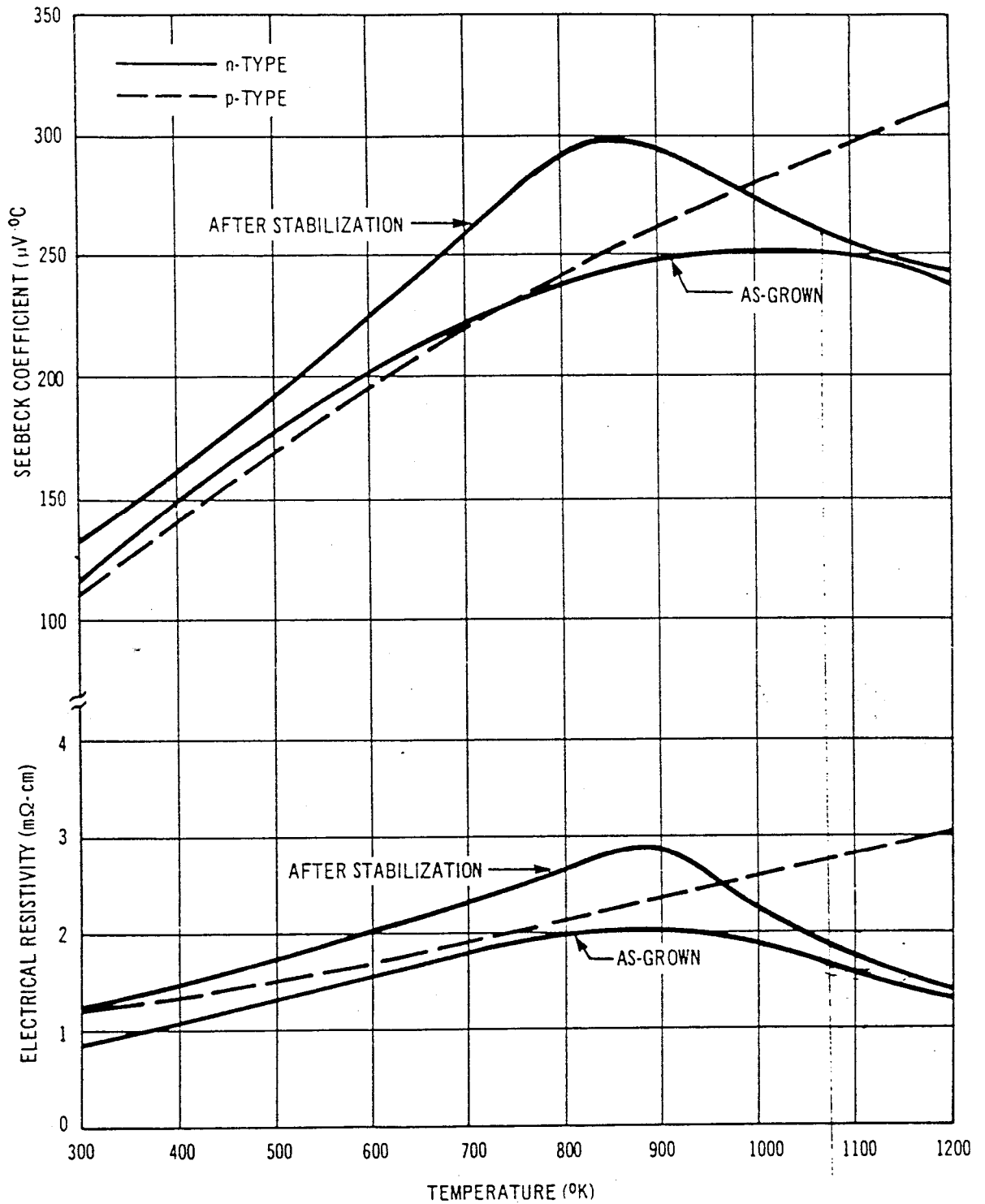
Figure 1

Figure 8: The dimensionless thermoelectric figure of merit of n-type SiGe alloys as a function of ionized donor density. The three points represent experimental results on T373, a heavily annealed sample of SiGe/GaP.

Table I

TABLE II. 80.0 at.% SiGe, STABILIZED THERMOELECTRIC PROPERTIES

Temp. (°C)	n-Type			p-Type		
	Seebeck ($\mu\text{V}/^\circ\text{C}$)	Electrical Resistivity ($\Omega\text{-cm} \times 10^{-3}$)	Thermal Conductivity ($\text{W}/^\circ\text{C-cm}$)	Seebeck ($\mu\text{V}/^\circ\text{C}$)	Electrical Resistivity ($\Omega\text{-cm} \times 10^{-3}$)	Thermal Conductivity ($\text{W}/^\circ\text{C-cm}$)
20	128	1.29	0.0510	106	1.26	0.0547
60	142	1.36	0.0501	125	1.30	0.0525
100	156	1.43	0.0493	142 ¹⁵⁶	1.35 ^{1.32}	0.0517
140	169	1.52	0.0485	156	1.40	0.0508
180	182	1.61	0.0478	168	1.46	0.0500
220	195	1.71	0.0470	179	1.52	0.0492
260	207	1.82	0.0464	188	1.59	0.0485
300	219	1.93	0.0456	198 ²⁰⁰	1.67 ^{1.66}	0.0478
340	231	2.05	0.0449	206	1.75	0.0471
380	243	2.17	0.0443	214	1.83	0.0465
420	255	2.30	0.0437	222	1.91	0.0459
460	266	2.43	0.0431	230	1.99	0.0454
500	276	2.56	0.0426	237 ²³⁸	2.08 ^{2.06}	0.0449
540	285	2.72	0.0421	244	2.16	0.0444
580	291	2.92	0.0417	251	2.25	0.0440
620	294	2.98	0.0413	258	2.34	0.0437
660	289	2.71	0.0408	265	2.42	0.0432
700	276	2.42	0.0411	272 ²⁷¹	2.51 ^{2.50}	0.0432
740	266	2.16	0.0415	279	2.60	0.0431
780	257	1.94	0.0423	286	2.69	0.0431
820	251	1.77	0.0437	293	2.78 ^{2.77}	0.0431
860	246	1.63	0.0446	300 ²⁹⁸	2.87 ^{2.85}	0.0434 ^{4.34}
900	243	1.50	0.0467	307 ³⁰⁶	2.95 ^{2.97}	0.0438 ^{0.44}
940	239	1.39	0.0490	314 ³¹¹	3.04 ^{3.07}	0.0434 ^{0.0445}
980	236	1.29	0.0520	320 ³¹⁸	3.14 ^{3.15}	0.0450 ^{0.0445}
1000	234	1.24	0.0530	324 ³²¹	3.19 ^{3.19}	0.0454 ^{4.63}



A. SEEBECK COEFFICIENT AND ELECTRICAL RESISTIVITY VS. TEMPERATURE

03681L

Figure 6. 80.0 At. % SiGe, Thermoelectric Properties (Sheet 1 of 2)

RCA Topical Report for 1/68 to 11/69
 Figure 2

TOPICAL REPORT

**SILICON GERMANIUM THERMOELECTRIC MATERIALS
AND MODULE DEVELOPMENT PROGRAM (U)**

BY

THERMOELECTRIC PRODUCTS ENGINEERING
SPECIAL COMPONENTS OPERATIONS
ELECTRONIC COMPONENTS
RCA
415 SOUTH FIFTH STREET
HARRISON, NEW JERSEY 07029

PREPARED UNDER
CONTRACT AT(29-2)-2510
FOR THE
ALBUQUERQUE OPERATIONS OFFICE
U.S. ATOMIC ENERGY COMMISSION

FOR THE PERIOD: 1 JANUARY 1968 TO 1 NOVEMBER 1969

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

Figure 3

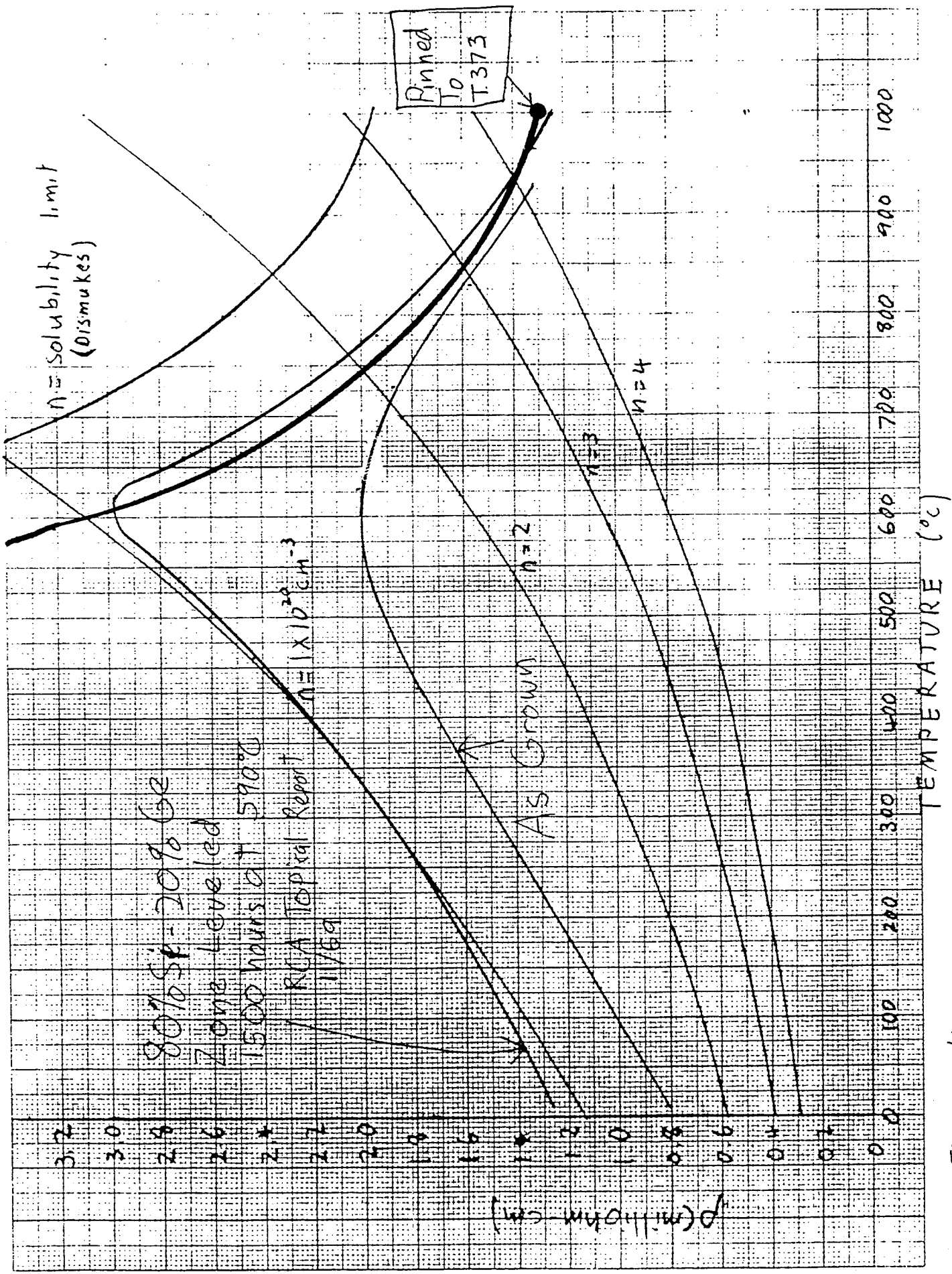


Figure 4

ITM-234 annealing experiments

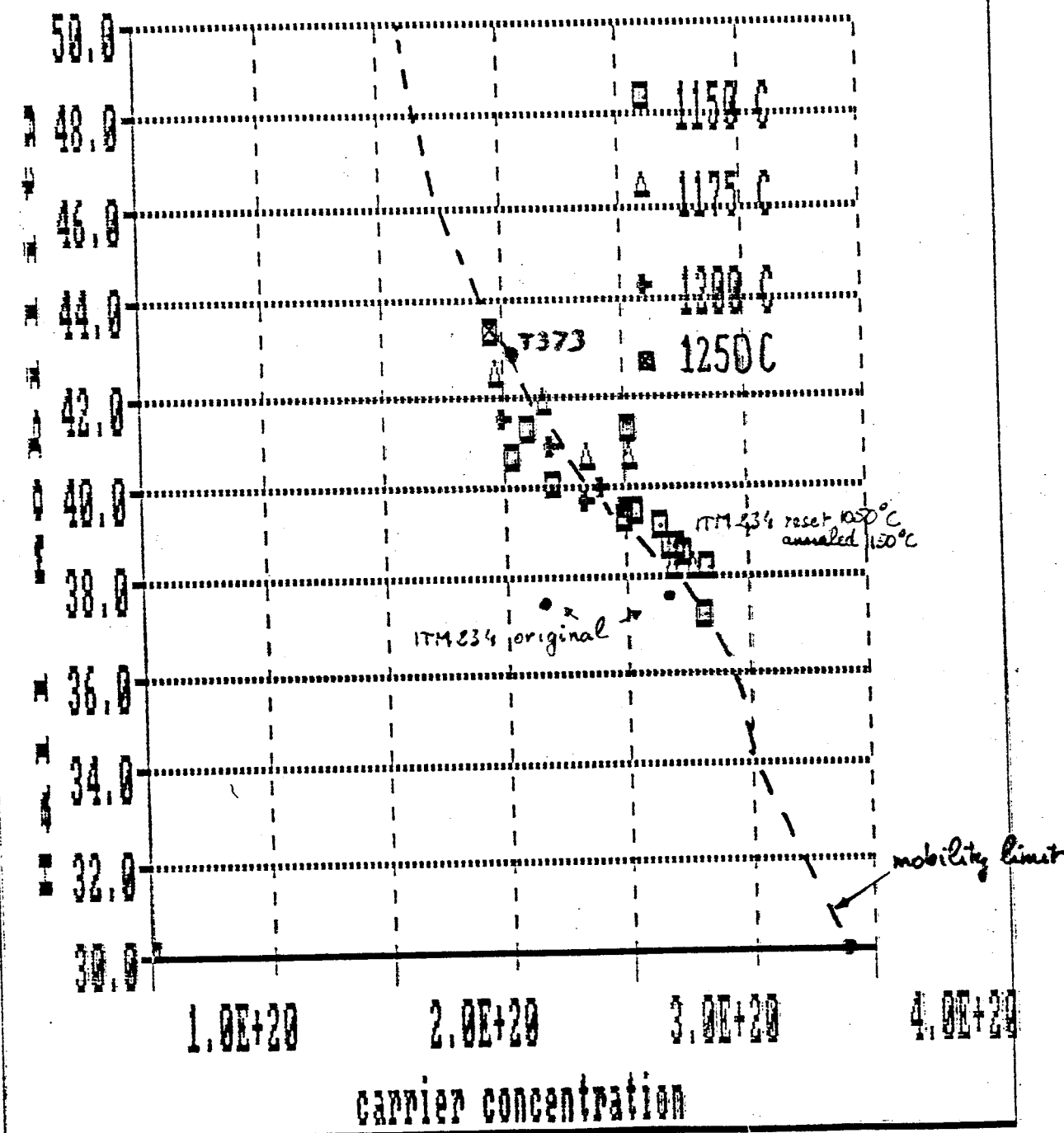


Figure 5.

Calculated Hall Mobility for $\text{Si}_{0.8}\text{Ge}_{0.2}$

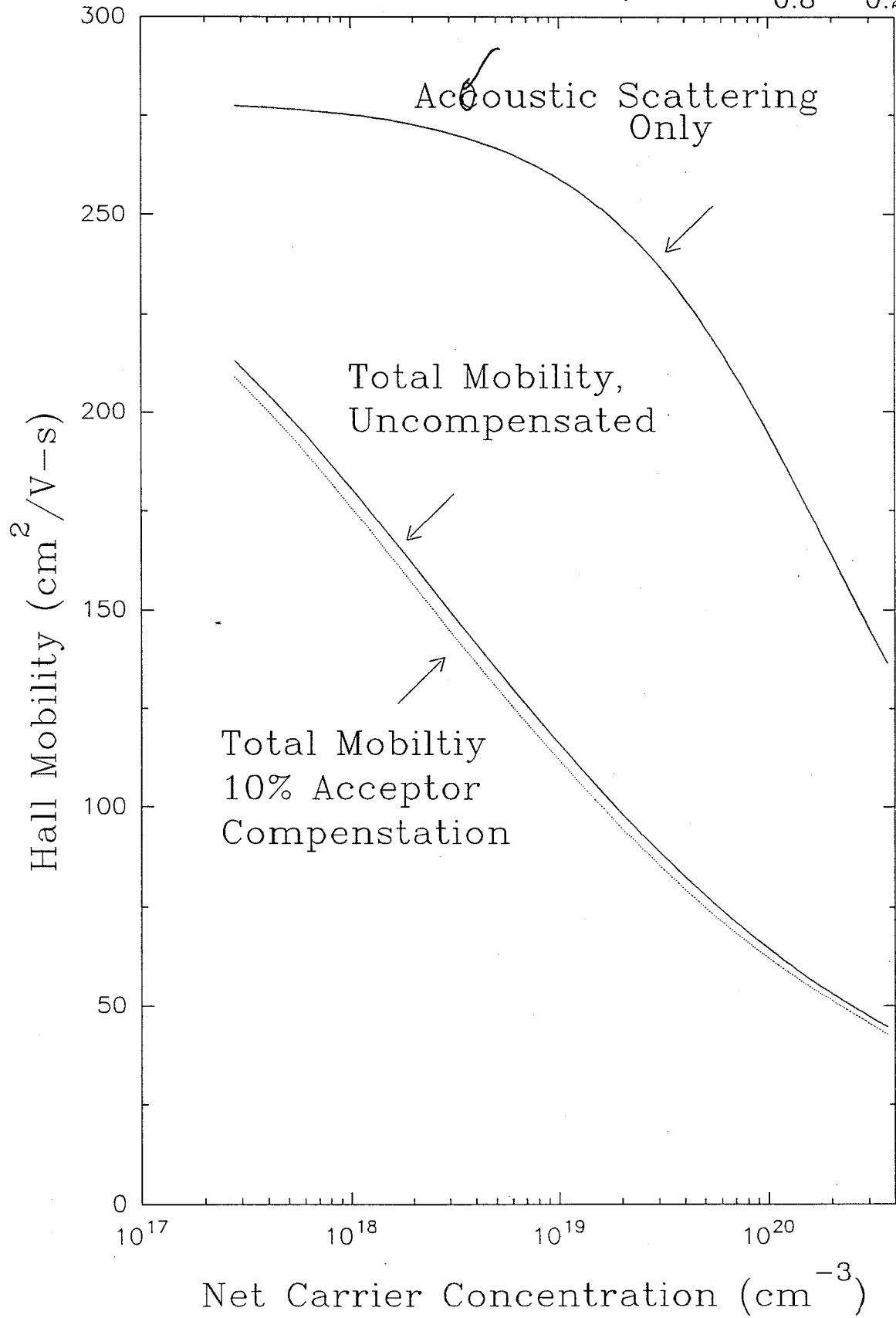


Figure 6.