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HIGH TEMPERATURE ELECTRICAL TRANSPORT PROPERTIES OF LIGHTLY DOPED SILICON-GERMANIUM SOLID SOLUTIONS

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Abstract

Electrical conductivity, differential thermopower, Hall coefficient and Hall mobility were determined on lightly doped, Czochralski-grown $Si_{1-x}Ge_x$ single crystals in the Si-rich regime as well as on pure Ge. The temperature range of measurements was 300 to 1200 K.

The results complement those carried out on highly doped Si-Ge material used in thermoelectric applications.

1 INTRODUCTION

The interest in the silicon-germanium (Si-Ge) solid solution primarily stems from its applicability in high temperature thermoelectric generators. Thermoelements with legs fabricated from highly doped *p*- and *n*-materials, respectively, are used to convert heat into electricity with an overall efficiency of 5 to 6% [1]. The requirements on crystallinity in these applications are low — the occurence of grain boundaries in the materials is even advantageous to reduce the thermal conductivity. Thus, most investigations have been performed on highly doped polycrystals.

Today, there is an interest in single-crystalline, intrinsic Si-Ge, which has the potential to serve as substrate material for strained Si-Ge heterostructures, GaAs, or ZnS. Growth of the Si Ge bulk crystals is preferably performed by Czochralski or float-zone techniques [2].

Such produced Si-Ge single crystals are investigated in this work. We present for the first time high temperature electronic transport data on moderately boron doped, silicon-rich Czochralski-grown Si-Ge single crystals, as well as data on similarly grown Ge. The results are discussed in comparison to data derived earlier on highly doped materials.

2 SAMPLES AND EXPERIMENTAL DETAILS

The investigated $Si_{1-x}Ge_x$ single crystals were grown by the Czochralski technique from quartz crucibles. Material with x = 0.04, 0.1, and 0.2, as well as pure Ge (x=1) has been prepared [3]. The crystals are lightly boron-doped [4]. Origin of the impurity is the quartz crucible, from which the boron is dissolved during the long growth procedure. Table 1, where sample characteristics are listed, shows a clear correlation between the carrier concentration at room temperature and the crystals growth velocity.

The electrical conductivity, Hall coefficient and Hall mobility were determined from 300 to 1200 K using conventional van der Pauw's method [5]. The Seebeck coefficient (differential thermopower) was measured by applying a defined temperature difference across the material and recording the plot ΔV vs. ΔT [6]. The precision of the conductivity and Hall coefficient results are thought to be 10% and about ± 10 μV/K for the Seebeck measurements.

3 EXPERIMENTAL RESULTS

Fig. 1 shows the high temperature Seebeck coefficient, S, of the materials investigated in this study. Literature results for a single crystal of Si [8] are shown for comparison. Above 600 K, S for each sample is negative, as expected in the intrinsic regime for Si-Ge. At lower temperatures, the positive S-values of the Ge-Si and Ge samples are due to the p-type boron impurities. The Si sample is obviously n-type doped.

In the high temperature limit, the absolute values of the Seebeck coefficient of the mixed crystals fall with increasing Ge content. In this temperature range S is only dependent on the intrinsic carrier concentration, which in turn is a function of the band gap. By adding Ge, the band gap decreases which leads to an increase in intrinsic carrier concentration. This is reflected by a reduction of the S-value. It is expectable that the results for the sample of Ge do not fit into this scheme since Ge has a different band structure than the Si-rich Si-Ge.

Fig 2 shows a plot of $1/|R_H|e$ vs. reciprocal temperature with R_H the Hall coefficient and e the electronic charge. Around the extrinsic-intrinsic transition sign changes occur. Except in the vicinity of this region, the plotted values are close to the real carrier concentration, n or p (assuming a Hall factor of unity and neglecting minority carrier effects). In spite of the low carrier concentration of about $2 \cdot 10^{15}$cm^{-3} the temperature where the Hall coefficient changes sign is surprisingly high, which already denotes a very small mobility ratio μ_n/μ_p. The observed increase of the net carrier concentration with increasing Ge content is due to the band gap change in the intrinsic regime and due to the higher dopant content in the extrinsic range.

In spite of the different intrinsic carrier concentration, the high temperature conductivity values of the four Si-rich samples are quite similar. This can be seen from Fig. 3, where the literature values for high purity silicon are added for comparison [8]. The spurious bump in the conductivity curve around 670 K is probably due to the fact that some of the recorded data in this temperature range appeared to be disturbed by noise.

Indeed, the carrier mobility decreases with the alloying of Ge, as shown in Fig. 4. Mobility values are calculated from the Hall coefficient and the electrical conductivity. Above about 700 K the mobility for each sample follows the expected power law behaviour, $\mu_H \propto T^{-a}$, but with exponents significantly larger than the simple $T^{-1.5}$ for acoustic scattering. The mobilities

of the SiGe samples decrease quite rapidly in the intrinsic region with power law exponents of 3.5 – 3.8, as summarized in Table 1.

4 DISCUSSION

4.1 Conductivity

The intrinsic conductivities of our single crystalline Si Ge samples compare with earlier results on polycrystalline material by Levitas [9] and Busch and Vogt [10]. The materials match each other in carrier concentration and type. Samples by Busch and Vogt are similarly boron doped but consist of fine grains. There is virtually no difference in the intrinsic conductivity between the materials of different crystallinity, an effect already been mentioned in [10] for Ge-rich materials of various qualities in cristallinity. This finding supports the assumption that physical properties of polycrystalline Si-Ge really reflect material properties and are not very much influenced by structural characteristics, i.e. grain boundaries.

The maximum in resistivity at a given temperature is reached when $p/n = \mu_n/\mu_p$. If the hole mobility is much lower than the electron mobility, conductivity curves of p-type material of different dopant concentration show cross-overs. As this effect does not occur in the present case, it can again be concluded that the mobility ratio is not very large.

4.2 Mobility

A value of the mobility ratio $b = \mu_n/\mu_p$ which is valid around the extrinsic-intrinsic transition can be calculated from the relation $(b-1)^2/4b = R_{H,max}/R_{H,const}$ [10] with $R_{H,max}$ the maximum value of $|R_H|$ in the mixed conduction regime and $R_{H,const}$ the value in the exhaustion range. Values for the samples measured are listed in Table 1. Compared to those reported in [10] for n-type Si-Ge they are up to 30% higher, but well in the range of the errors.

As mentioned above, the power law exponents a of the mobility-vs.-temperature relations in the high temperature limit are extremely large (cf. Table 1). Around room temperature, exponents a for Si-rich Si-Ge between 2.1 and 2.5, i.e. values exceeding that for ordinary thermal scattering were already reported in [9]. We explain this as a consequence of optical phonon scattering which – as calculated for silicon [11] – leads to a proportionality $\mu \propto T^{-2.2}$. This exponent is also applicable to fit our extrinsic mobility data, but it is obvious that at higher temperatures an additional scattering process takes place. Here, the additional intervalley scattering between the equivalent conduction band minima which – dependent on the relative coupling – leads to power law exponents around 3 [12] may play an important role. An additional alloy scattering, which has $a = -0.5$ and should show up in a reduction of the power law exponent with increasing Ge content, cannot be conclusively stated for the concentration region covered here.

Fig. 5 lines the room temperature mobility of the investigated lightly doped Si-Ge samples into those data measured in heavily doped material from Dismukes et al [13]. Though there is a large gap between the two sets of measurement, all data lie on the same curve. The decrease in mobility on carrier concentration is obviously due to the increasing influence of impurity scattering, which still contributes at room temperature.

4.3 Thermopower

If only one type of carriers is present, the Seebeck coefficient S is proportional to $\ln \sigma$ with σ the electrical conductivity. This relation is usually fulfilled at high dopant concentrations, where the influence of minority carriers can be neglected. This can be seen from Fig. 6 where room temperature literature data of heavily doped Si-Ge is plotted. Data for p-type Si-Ge ($x = 0.15$, 0.2, 0.3) is from Dismukes et al. [13] and for n-type Si-Ge ($x = 0.2$) from Heller et al. [14]. Taking only the $x = 0.2$ values into account, the two data sets can be fitted by

$$S_p = S_{p,0} - a_p \ln(\sigma_p), \text{ with } S_{p,0} = 536 \quad \mu\text{V/K}, \qquad a_p = 59 \quad \mu\text{V/K} \tag{1}$$

for p-type $Si_{0.8}Ge_{0.2}$ and

$$S_n = -S_{n,0} + a_n \ln(\sigma_n), \text{ with } S_{n,0} = 799 \quad \mu\text{V/K}, \qquad a_p = 98 \quad \mu\text{V/K} \tag{2}$$

for n-type $Si_{0.8}Ge_{0.2}$.

The Seebeck coefficients derived in this work do not fit into this linear relation because the comparably low dopant concentration makes the influence of the minority electrons already apparent (cf. Fig. 6.) The deviation can be described by the relation for the ambipolar Seebeck coefficient

$$S = \frac{S_p \sigma_p + S_n \sigma_n}{\sigma_p + \sigma_n}. \tag{3}$$

With the experimental room temperature values for S and $\sigma = \sigma_p + \sigma_n$ (Table 1) and the relations 1 and 2, values for the individual contributions σ_p and σ_n can be calculated. In the present case we get $\sigma_p = 0.1016$ 1/(Ωcm) and $\sigma_n = 0.0164$ 1/(Ωcm) and are now able to derive separate transport values for the holes and the electrons.

For example, one can calculate the hole and electron mobilities, μ_p and μ_n, respectively, via

$$R_H = \frac{\sigma_p \mu_p - \sigma_n \mu_n}{\sigma^2}, \tag{4}$$

with R_H the measured Hall-coefficient. Using the above derived mobility ratio of 2.2 one gets the values listed in Table 2.

5 CONCLUSIONS

Acknowledgment

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References

[1] C.B. Vining, J.-P. Fleurial, Proc. of the 10th Symp. on Space Nuclear Power and Propulsion, Albuquerque New Mexico (Jan. 1993).

[2] J. Schilz, V.N. Romanenko, *Review: Bulk growth of silicon-germanium solid solutions*, J. Mat. Science: Mat. in Electronics **6** (1995) 265.

[3] M. Kürten, J. Schilz, *Czochralski growth of Si_xGe_{1-x} single crystals*, J. Crystal Growth **139** (1994) 1.

[4] X.H. Shi, P.L. Liu, Z.H. Chen, S.C. Shen, J. Schilz, *Photoconductivity spectra for boron acceptors in $Si_{1-x}Ge_x$ alloys*, Appl. Phys. Lett. **68** (1996) 211.

[5] J.A. McCormack, J.-P. Fleurial, *Electrical characterization of SiGe thin films*, Mat. Res. Soc. Symp. 234, ed. D.D. Allred, C.B. Vining, G.A. Slack (1991) 135.

[6] C. Wood, L.D. Zoltan, G. Stapfer, Rev. Sci. Instrum. **56** (1985) 719.

[7] T.H. Geballe, G.W. Hull, *Seebeck effect in silicon*, Phys. Rev. **B98** (1955) 940.

[8] W. Fulkerson, J.P. Moore, R.S. Graves, D.L. McElroy, *Heat transport in silicon from 100 to 1800 K*, Proc. of the Sixth Conf. on Thermal Cond., ed. M.L. Minges, G.L. Denman, Air Force Materials Lab. (1966) 429.

[9] A. Levitas, *Electrical properties of germanium-silicon alloys*, Phys. Rev. **99** (1955) 1810.

[10] G. Busch, O. Vogt, *Elektrische Leitfähigkeit und Halleffekt von Ge-Si Legierungen*, Helv. Phys. Acta **33** (1960) 437.

[11] Bestellt

[12] D.L. Rode, *Semiconductors and Semimetals*, vol. 10, ed: R.K. Willardson, A.C. Beer, Academic Press, New York (1975).

[13] J.P. Dismukes, L. Ekstrom, E.F. Steigmeier, I. Kudman, D.S. Beers, *Thermal and electrical properties of heavilly doped Ge-Si alloys up to 1300 K*, J. Appl. Phys. **35** (1964) 2899.

[14] M.W. Heller, R.D. Nashby, R.T. Johnson, Jr. *Electrical transport properties of SiGe thermoelectric alloys doped with As, P, and As+P*, J. Appl. Phys. **47** (1976) 4113.

Tables

Table 1: Characteristic data of investigated samples.

$Si_{1-x}Ge_x$	growth veloc. mm/h	$1/R_He$(300 K) cm^{-3}	S(300 K) $\mu V/K$	σ(300 K) $\Omega^{-1}cm^{-1}$	$\mu_H \propto T^{-a}$	μ_n/μ_p
$x = 0.04$	2	$1.2 \cdot 10^{15}$	600	0.118	$a = 3.8$	3.8
$x = 0.1$	0.7	$2.0 \cdot 10^{15}$	500	0.083	$a = 3.5$	2.8
$x = 0.2$	0.4	$2.9 \cdot 10^{15}$	410	0.056	$a = 3.5$	2.2
$x = 1$	3	$8.2 \cdot 10^{14}$		0.246	$a = 2.4$	1.9

Figures

Table 2: Monopolar transport values of investigated $Si_{0.8}Ge_{0.2}$ at room temperature.

	mobility cm^2/Vs	carrier conc. cm^{-3}	intrinsic carrier conc. cm^{-3}
holes	455	$1.4 \cdot 10^{15}$	$1.0 \cdot 10^{14}$
electrons	1000	$1.0 \cdot 10^{14}$	$1.0 \cdot 10^{14}$

Figure 1: IIigh temperature Seebeck coefficient for Si-Gc alloys and pure Ge. Data for Si is from Fulkerson (66FMGE).

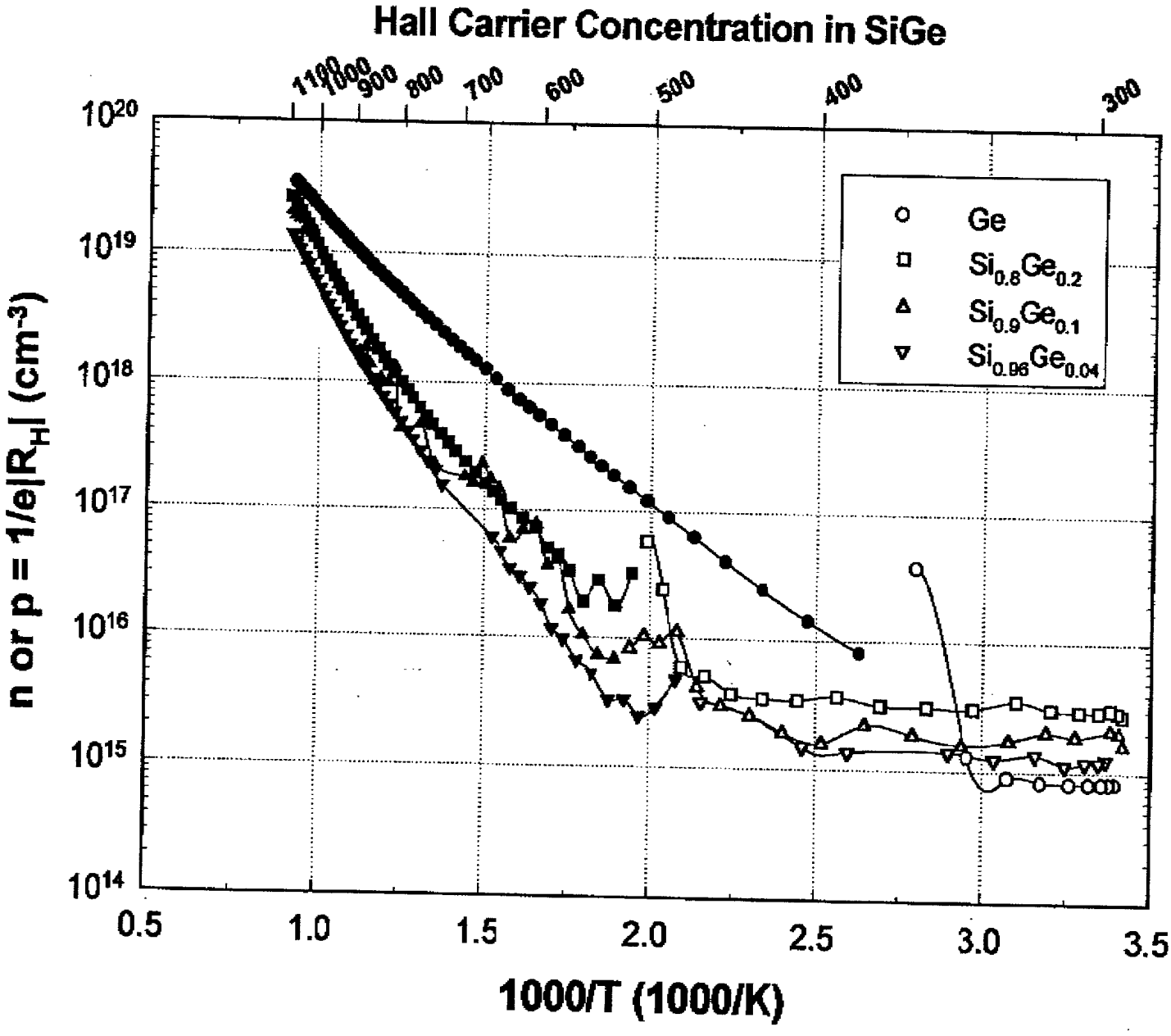
Figure 2: Hall carrier concentration vs. reciprocal temperature for lightly doped Si-Ge alloys. Open symbols indicate the Hall coefficient is p-type and closed symbold indicate n-type.

Figure 3: Electrical conductivity vs. reciprocal temperature for lightly doped Si-Ge alloys. Data for Si is from Fulkerson [8].

Figure 4: High temperature Hall mobility for lightly doped Si-Ge alloys. Open symbols indicate the Hall coefficient is p-type and closed symbols indicate n-type. The dashed lines represent power law fits to the data above about 700 K.

Figure 5: Room temperature Hall mobility of p-type Si-Ge as a function of carrier concentration. Open symbols from (64DESKB); closed symbols this work.

Figure 6: Seebeck coefficient vs. natural logarithm of electrical conductivity. The data at high conductivities are from Dismukes et al. [13] (p-type) and Heller et al. [14] (n-type).



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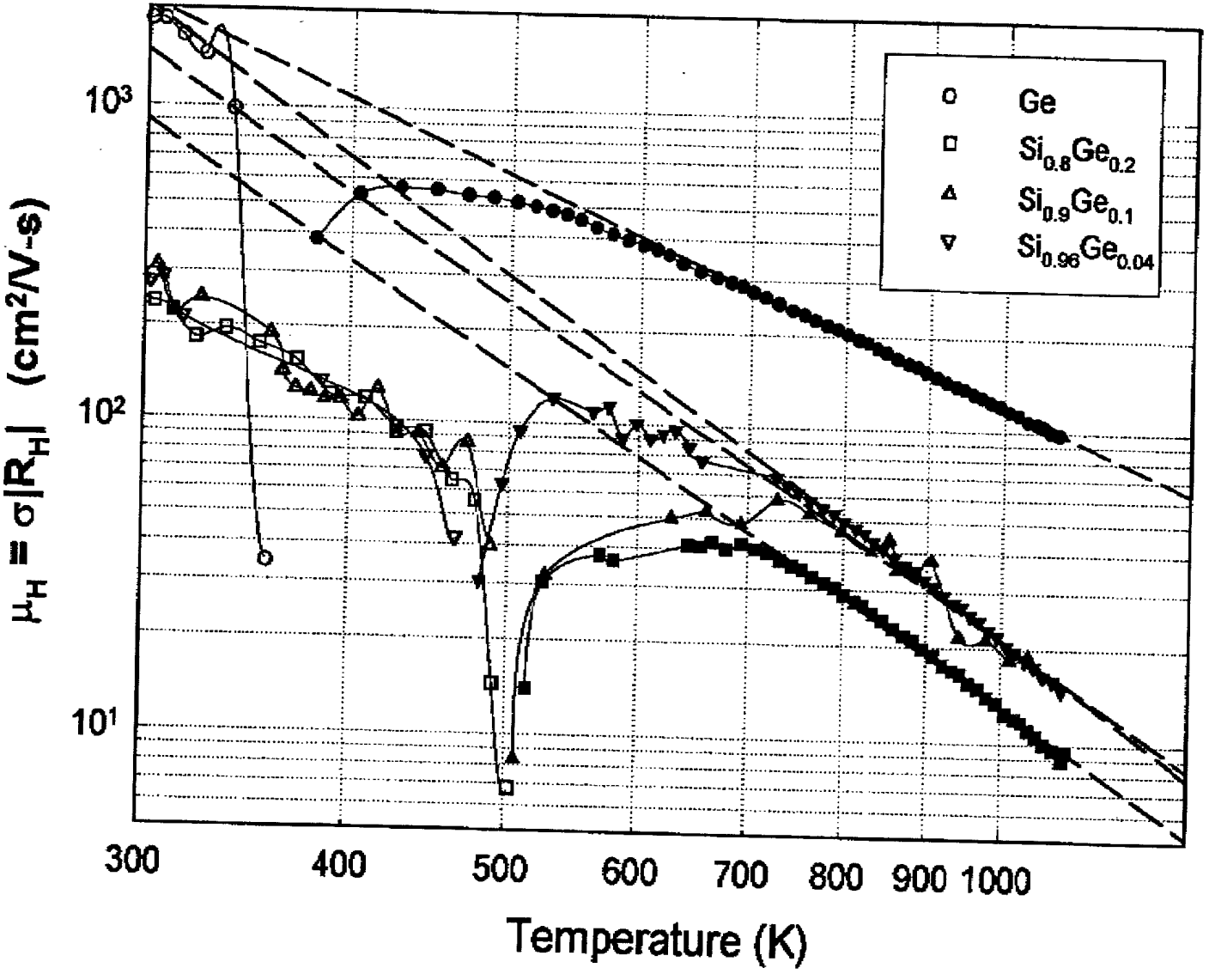
Hall Mobility in SiGe



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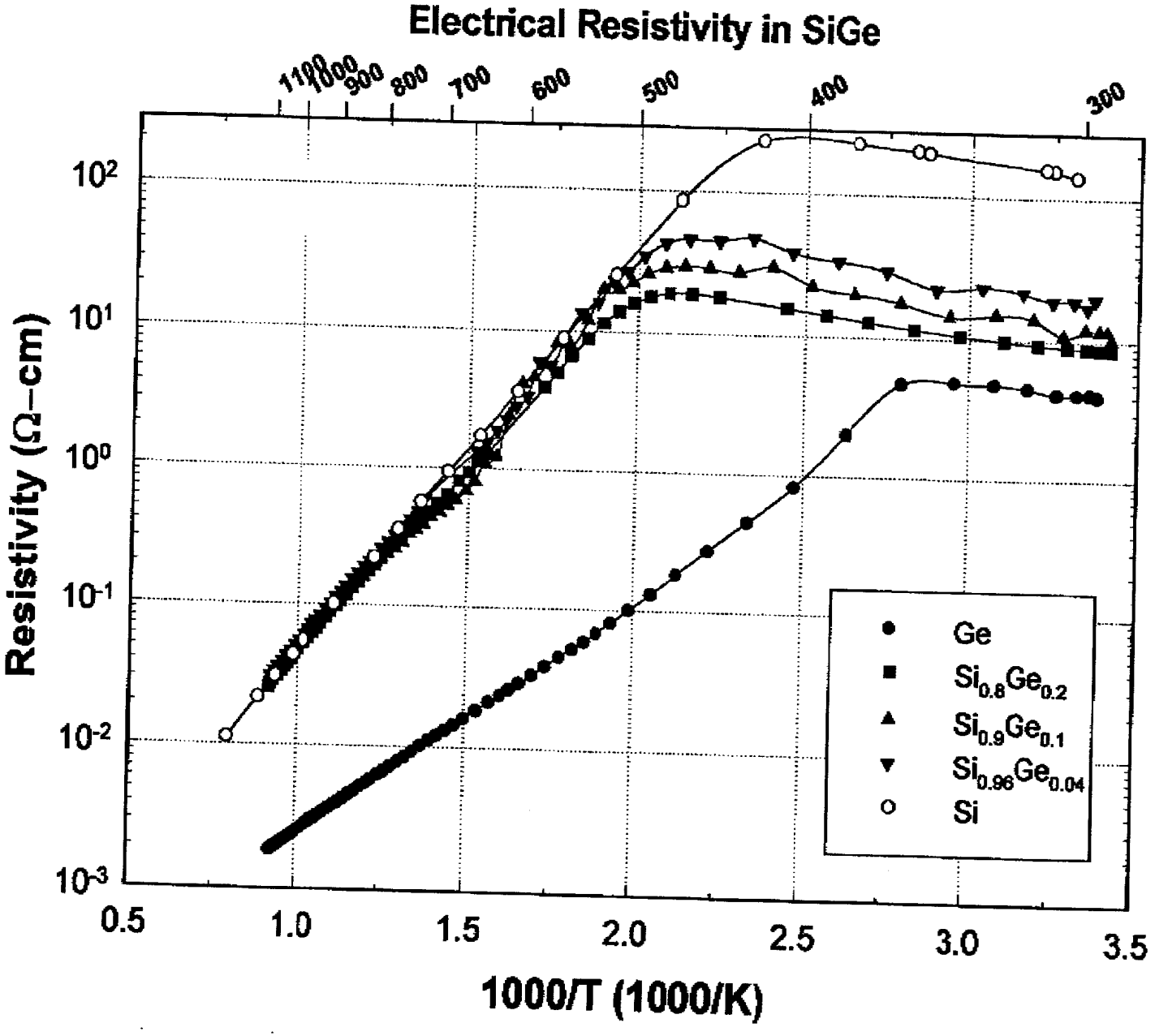
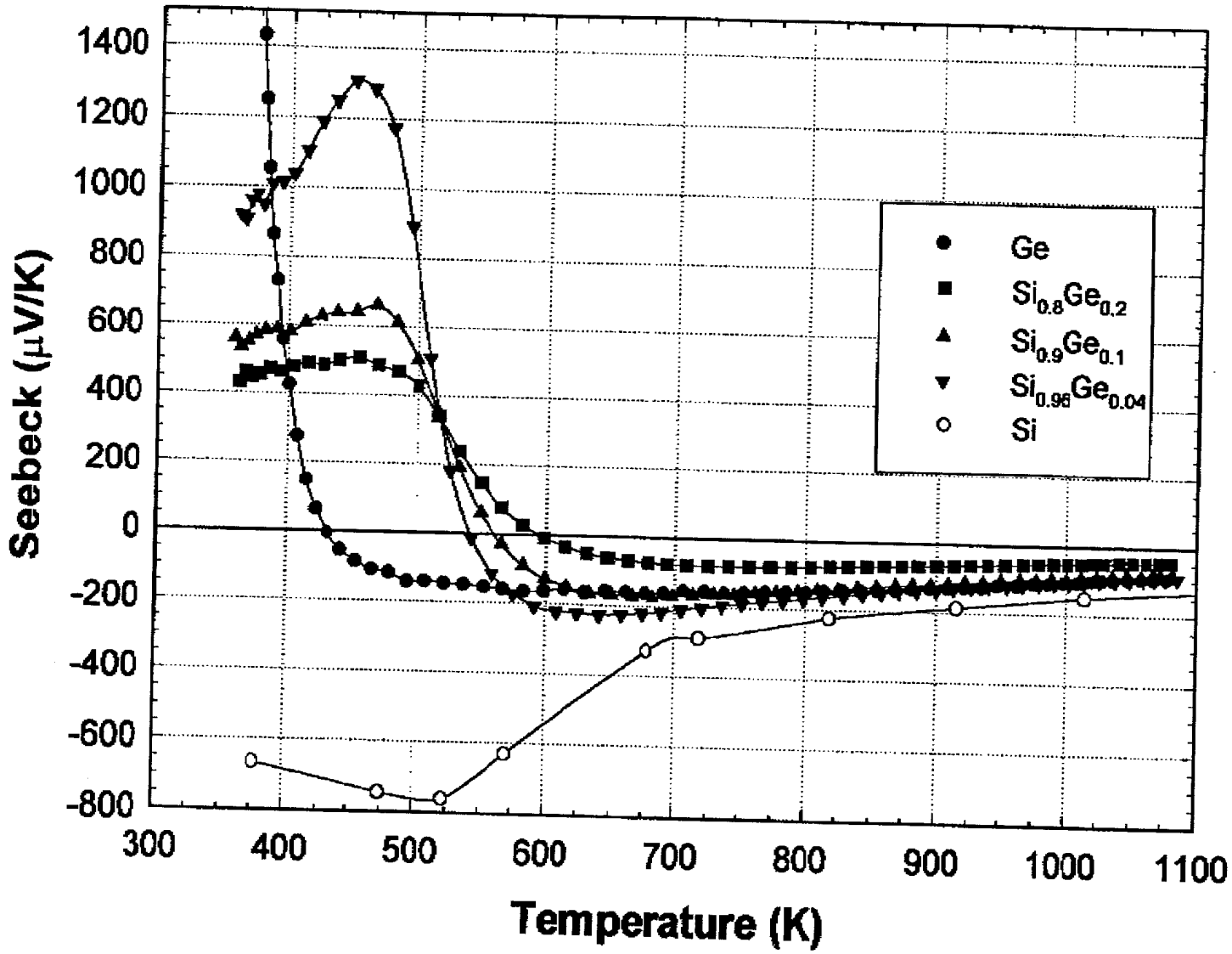

Electrical Resistivity in SiGe
1100
1000
900
800
700
600
500
400
300
Resistivity (Ω–cm)
10²
10¹
10⁰
10⁻¹
10⁻²
10⁻³
0.5
1.0
1.5
2.0
2.5
3.0
3.5
1000/T (1000/K)
Ge
Si0.8Ge0.2
Si0.9Ge0.1
Si0.96Ge0.04
Si
1/3/95
File:SiGe-res.spw (C. Vining)

Seebeck Coefficient in SiGe



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