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GO-SI SUPERSONIC FLIR WINDOW

MORGAN SEMICONDUCTOR, INC
2625 NATIONAL CIRCLE
GARLAND, TEXAS 75041

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Final Report for period 1 July 1978 through 31 March 1979

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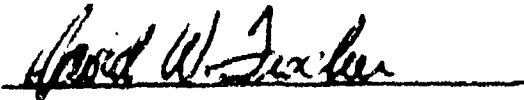
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David W. Fischer
Project Engineer

FOR THE COMMANDER



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20 ABSTRACT (Continue on reverse side if necessary and identify by block number) The purpose of the program was to evaluate the infrared optical properties and related physical properties of melt formed Germanium-Silicon alloys as potential supersonic FLIR window materials. The approach was to combine the infrared transparency of germanium with the excellent physical properties of silicon to produce a window material capable of withstanding the temperature		

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excursions and rain drop impact occurring during supersonic flight. Attention was confined to alloys with silicon content below 50 atom percent⁵⁰ to avoid the intrinsic lattice absorption that occurs at 9 μ m^{micrometers} in the infrared for silicon or silicon rich alloys. A zone levelling technique was selected and modified in a manner expected to yield materials free of oxide absorption. A melt form method was selected rather than vapor phase because of the potential problems in scaling up to produce large FLIR windows.

Unfortunately, the growth of alloy compositions with silicon content above 5% proved to be impossible to do at least under the operating conditions and with the equipment used. Major problems were long term temperature stability, zoning rates and reactivity of the molten alloys with quartz boats and ampoules. Although the concentration range up to 50 atom percent⁵⁰ silicon was covered, infrared transmission was not obtained for any compositions with silicon content above 5 atom percent⁵. Rain erosion samples were submitted for evaluation covering five compositions. Physical and optical evaluation data are presented. Discussions related to the best Ge-Si alloy composition for FLIR applications are presented along with a projection of the related physical-optical parameters expected for that composition. The experimental conditions required to produce such an alloy are discussed. ↗

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FOREWARD

The report was prepared by Morgan Semiconductor, Garland, Texas under contract F33615-78-C-5105. The work was administered under the direction of the Air Force Materials Laboratory, Laser and Optical Materials Branch, Wright-Patterson Air Force Base, Ohio. Dr. David Fischer was the contract monitor.

The work performed at Morgan Semiconductor was under the direction of Dr. A. R. Hilton of Amorphous Materials, Inc., Garland, Texas. Dr. Hilton served as a special consultant to Morgan Semiconductor. The results reported cover the period 1 July 1978 through 31 March, 1979. The report was submitted for approval in May, 1979.

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INTRODUCTION AND SUMMARY

The optics of Airborne Forward Looking (FLIR) reconnaissance systems are protected from air stream damage by an external window. Present windows fabricated from current optical materials have sufficient optical and physical properties to meet the requirements of FLIRS used in subsonic aircraft. However, in the future, FLIRS must be designed for continuous use at speeds of Mach 1.5. Temperatures of 200°C will be generated as the window producing decreases in transmission and optical distortion in present windows. The impact of supersonic rain drops will damage conventional materials producing transmission loss or even catastrophic failure. Clearly, a new supersonic infrared optical material is needed.

Germanium, the industry standard, has been extensively used for years in FLIRS because of its optical quality and transparency in the operational band of 8-12 μ m. However, germanium is not useful above about 100°C and its physical properties are such that it will not withstand supersonic rain drop impact without damage. Silicon on the other hand, has the required physical properties to withstand rain erosion and an upper use temperature of 300°C but suffers from intrinsic absorption at 9 μ m in the middle of the 8-12 μ m spectral band. Ideally, a better optical material would result if the attributes of these two materials could be combined. That is, combine the excellent physical properties of silicon with the transparency of germanium to produce a supersonic window material.

Results published in the literature indicate the combination is possible. Germanium-Silicon alloys (Ge-Si) have been prepared and evaluated from an electronic device stand point. Optical results obtained during evaluation of the materials

show that the silicon intrinsic absorption at $9\mu\text{m}$ is not present in the alloy until the silicon content is 50 atom percent or greater. Furthermore, the addition of silicon to germanium affects the properties in a nonlinear manner. That is, about 80-90% of the physical property improvement in the alloy occurs before the silicon content reaches 50 atom percent. The purpose of this program was to prepare and evaluate germanium rich alloys as possible supersonic window materials.

Attention was confined to alloys with silicon content of 50 atom percent or less. The method selected for preparing evaluation samples was a modified zone levelling technique. The plan was to use evaluation results and rain erosion results to select the best composition for the FLIR supersonic window application. The overall program goal was to provide 85% transmission at $8-12\mu\text{m}$ while at 200°C and survive Mach 1.5 rainfield tests without significant damage. The best composition would then be prepared in large plates for further evaluation and testing.

Unfortunately, the growth of any alloy compositions with silicon content above 5% proved to be impossible to do at least under the operating conditions of the equipment at hand. Major problems were temperature stability, zoning rates and reactivity with the quartz boats and ampoules. Although the concentration range up to 50 atom percent silicon was covered, infrared transmission was not obtained for any composition with silicon content above 5%. Rain erosion samples were submitted covering five compositions.

Physical and optical evaluation data are presented. Discussions related to the best silicon-germanium alloy composition for FLIR applications are presented along with a projection of physical-optical parameters. A discussion of the experimental conditions required to prepare the alloy is given.

II TECHNICAL DISCUSSION

A. BACKGROUND, FLIR WINDOW PROBLEM

Infrared optical materials transparent in the "passive" 8-12 μ m FLIR window generally do not have good physical properties relative to optical materials used in the visible region of the spectrum. However, over the years windows made from germanium (Ge), gallium arsenide (GaAs), polycrystalline zinc selenide (Zn Se) and polycrystalline zinc sulfide (ZnS) have been used for subsonic speeds with good success. However, for supersonic speeds of mach 1.5 or more, none is satisfactory for one reason or another.

Germanium is the most extensively used infrared optical material in FLIR systems. The transparency of Ge at 8-12 μ m, the optical homogeneity and the availability at a moderate cost relative to other materials have been factors contributing to its general use for refractive lens elements. For external window use however, Ge has disadvantages. First of all, the low band gap of Ge leads to a rather low (100 $^{\circ}$ C) temperature limit before the intrinsic carriers become of sufficient concentration to make the material absorbing. Another surprising fact is that germanium (and GaAs as well) are somewhat susceptible to rain impact fracture. The hardness (around 700 Knoop) and strength of both Ge and GaAs appears great enough to resist rain erosion. However, both materials have similar crystal structures which have cleavage planes. For best optical quality, Ge and GaAs are prepared in large grain (cm's in size) or single crystal form. With grain orientation relative to the surface a random process, some cleavage planes are exposed to rain drop impact allowing pieces of the window to be broken from the front surface. The result is a severe loss in trans-

mission due to rain erosion.

The first infrared optical material used extensively in military hardware was silicon (Si). Domes made from Si were used on heat seeking missiles operating in the 3-5 μ m atmospheric window. Silicon is an excellent optical material from the standpoint of hardness (1150 Knoop), optical quality and upper use temperature (around 300 $^{\circ}$ C). Unfortunately, Si has a lattice type intrinsic absorption that occurs at 9 μ m. Silicon has not been used for FLIRS, even though it is less costly than other materials.

The external window material for supersonic FLIRS must have physical properties comparable to silicon and an upper use temperature of 200 $^{\circ}$ C. The window is rather large so that a melt formed material would be advantageous from a cost and ease of production viewpoint. A very desirable solution would be to combine the excellent optical properties of Ge with physical properties of Si in the form of a Ge-Si alloy.

B. GERMANIUM-SILICON ALLOYS

The investigations of Ge-Si alloys reported in the literature ⁽¹⁾ have concentrated on the growth of single crystal materials for electronic device applications. Nevertheless, enough evaluation results exist to guide our selection of compositions most suitable for optical applications.

(1) Optical Properties - The matters of most importance are the existence of the Si-Si intrinsic absorption at $9\mu\text{m}$ and the change in band gap for the alloy as silicon is added to germanium. Raman studies of germanium-silicon (Ge-Si) alloys ⁽²⁾ have shown that considerable silicon can be added to germanium before there is any trace of the silicon lattice absorption at $9\mu\text{m}$ in the resultant alloy. For an alloy of 22 atom % silicon, no silicon lattice frequency is observed. The spectrum is completely dominated by the germanium lattice frequencies. Conversely, for 76 atom % silicon, the germanium lattice frequencies are practically undetected with silicon completely dominating. For 54 atom % silicon, the frequencies due to Si-Si atoms, Ge-Ge atoms, and another species, Ge-Si are observed.

The same change in lattice vibration frequencies has been studied by infrared absorption ⁽³⁾. The lattice absorption in Ge-Si alloys is not observed until the silicon content exceeds 50%.

The majority of the change in the band gap in germanium occurs with only a small addition of silicon in germanium ⁽⁴⁾. Addition of 25 atom % silicon to germanium raises the band gap from 0.64 ev to 0.87 ev, approximately fifty % of the difference between the two pure materials (silicon is 1.1 ev).

In short, the band gap changes in a nonlinear manner making it possible to dramatically improve the properties of germanium with the addition of only a small amount of silicon. In this way, the infrared transparency of germanium can be preserved while its physical properties are improved dramatically. The result should be an improved optical material with a band gap large enough to allow operation at 200°C without excessive free carrier absorption. The absorption edge occurs at about 1.4 μ m compared to 2 μ m for germanium.

(2) Physical Properties - Properties of prime importance for window applications are hardness, volume expansion coefficient, strength, and thermal conductivity. A few general statements can be made concerning these properties.

The hardness of silicon is 1150 Knoop while germanium is 850. A 50-50 alloy would have a hardness of about 1000 if you assume a direct linearity. The expansion coefficients would be about $4-5 \times 10^{-6}/^{\circ}\text{C}$, an average between 6 for Ge and 3 for Si. Thermal conductivity will be high relative to most materials but probably no better than that of Ge, about 0.1-0.2 cal/cm sec⁰K. Alloys generally do not have improved thermal conductivity. Resistance to rupture is hard to predict because of the sensitivity to surface flaws. Germanium is generally considered to have a rupture modulus above 8,500 psi. Silicon is considered to be higher, of the order of 15-20,000 psi. The alloy, especially if it is fine grain, should have a rupture modulus much better than Ge, of the order of 15-20,000 psi. All of these parameters are important from a window stand point because of resistance to thermal shock. Generally, a material with a high rupture modulus, low volume expansion coefficient and high thermal conductivity is resistant to thermal shock. Such a property is important for external windows which may undergo dramatic temperature variations due to changes in altitudes or speeds.

C. GROWTH OF GE-SI ALLOYS

(1) Method, Normal Zone Levelling Technique

Small single phase polycrystalline alloys have been grown ⁽¹⁾ in horizontal boats. The emphasis was in all cases directed towards device applications where single crystal, single phase material was important. As illustrated in figure 1 the phase diagram for Ge-Si ⁽¹⁾⁽⁵⁾ consists of a complete series of solid solutions. Single phase materials can be grown as illustrated in the drawing by the zone levelling procedure. For materials 50% or less in silicon, the temperature involved will be 1100°C or less, well within the range of wire resistive heated furnaces.

The procedure followed is to weigh out Ge-Si mixtures corresponding to the Cs and Cl (where l is for liquid phase and s is for solid) and melt in separate containers. The solids are then powdered and the procedure repeated several times until the resultant powders are uniform in composition. The two separate powders are then packed into a tube in separate portions as indicated in the diagram and zoned at the indicated temperature using a slow rate of zoning (less than 1"/hr) and with repeated passes. The normal process was not adopted for one main reason. Powdering a crystalline material of this type tends to increase dramatically the oxygen concentration due to surface absorption. It is well known that the silicon-oxygen bond absorbs infrared radiation very strongly at 9 μ m, the precise wavelength lattice absorption that prevents silicon from being used as a FLIR material. Therefore, it was decided to work only with melt formed crystals which would be low in oxygen concentration.

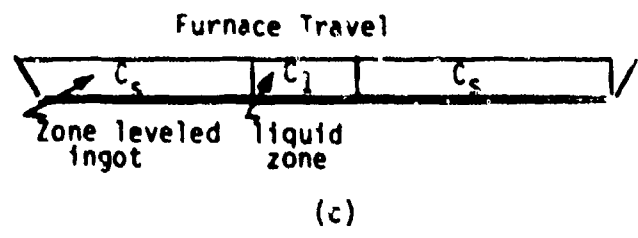
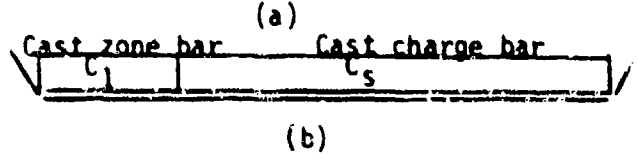
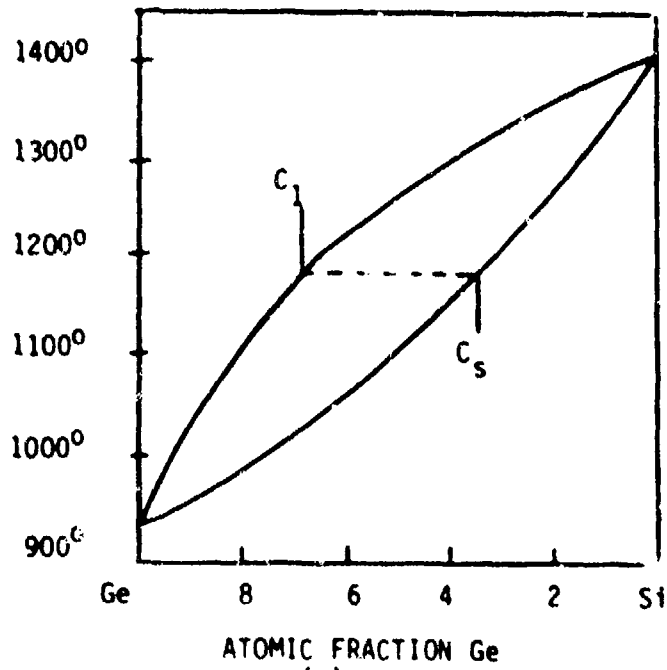
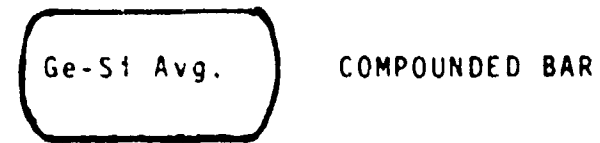
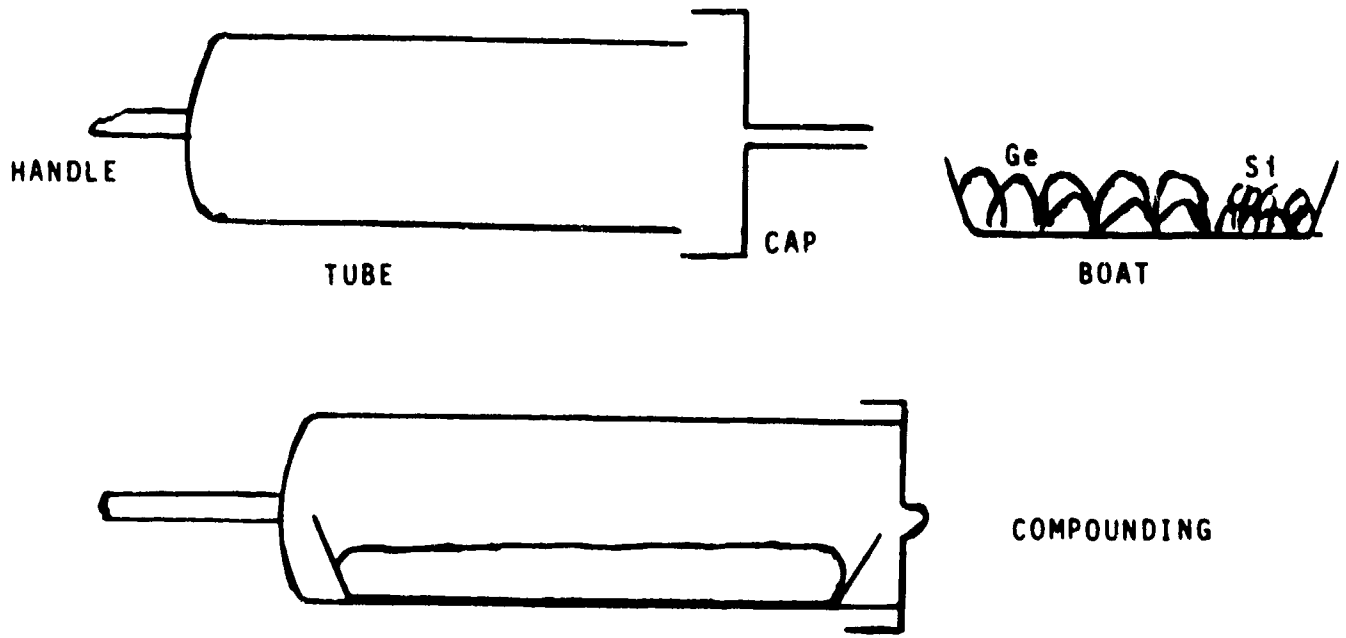


Figure 1 The zone-leveling procedure for Ge-Si alloy showing (a) the phase diagram, (b) the initial arrangement of the materials, & (c) the situation during zoning.

(2) Modified Zone Levelling Technique

An understanding of the procedure followed to grow an alloy of specific ratios can be gained from figure 1. If one desires a composition of Cs (S is for solid), a composition is weighed out corresponding to the average between Cs and Cl (l is for liquid in equilibrium with Cs). The reactants are sealed in a high purity evacuated quartz tube and heated to a temperature well above the top liquidus curve. The material is rocked to mix and then rapidly quenched to a temperature below the solidus curve, say about 1000°C. The temperature is maintained to prevent thermal shock fractures. Then a zone is passed through the mixture with the temperature maintained at the melting point of Cs. The liquid zone corresponding to Cl is allowed to travel through the crystal horizontally leaving behind an alloy of composition Cs. The size of crystals in Cs will be determined by the width of the zone, the gradient at the traveling zone edge and the horizontal velocity of the zone. Growth following this procedure for optical applications should be easier than for device applications where homogeneous single crystal material is mandatory. The equipment required for the zone levelling technique is similar to that used in the horizontal Bridgman growth of single crystals of GaAs as used at Morgan Semiconductor, Inc.

A diagram depicting the procedure is shown in figure 2. Reactants are weighed out precisely and sealed in a large open mouth tube. The reactants are not broken to avoid exposure to oxygen. After bake out and seal off, the reactants are placed in a Bridgman furnace and compounded above the liquidus temperature. A list of average compositions, compounding temperatures and required zoning temperatures as a function



(DOTTED LINES INDICATE REGION WHICH SHOULD YIELD SILICON RICH PLATES)

FIGURE 2

MODIFIED ZONE LEVELLING TECHNIQUE

of compositions are listed in table 1. As depicted in figure 2, zoning tends to concentrate the excess germanium rich liquid at the bottom and outside of the bar due to differences in gravity. The portion of the bar from which the desired solid can be removed is indicated.

An enlarged drawing of the Ge-Si phase diagram (5) is shown in figure 3. The desired alloy compositions are indicated in the figure along with the liquid phase in equilibrium with the solid at the growth temperature. The diagram was used to compile the list of compositions and growth conditions listed in table 1. The conditions were used in the "modified" zone levelling procedure followed in this program.

(3) Alloy Evaluation

Physical and optical properties related to the use of the Ge-Si alloys were used as criteria to evaluate the usefulness of each composition. The specific parameters measured and used in the evaluation are: infrared transmission, resistivity, number of carriers, mobility of carriers, thermal conductivity, hardness and crystallinity. The change in these parameters with composition once established may be used to establish the best composition for the FLIR window application. Of course, rain erosion results would be used to judge the final suitability. The methods used to establish all parameters are discussed under the results section.

TABLE 1

PARAMETERS USED TO GROW Ge-Si ALLOYS
BY THE MODIFIED ZONE LEVELLING TECHNIQUE

Desired Solid Phase Composition	Liquid Phase Composition	Melt Composition	Liquidus Temp. °C	Growth Temp. °C
Ge ₈₅ Si ₁₅	Ge _{97.7} Si _{2.3}	Ge _{91.3} Si _{8.7}	1092	970
Ge ₇₅ Si ₂₅	Ge _{94.3} Si _{5.7}	Ge _{84.6} Si _{15.4}	1160	1007
Ge ₆₅ Si ₃₅	Ge _{90.2} Si _{9.8}	Ge _{77.6} Si _{22.4}	1208	1040
Ge ₅₅ Si ₄₅	Ge _{84.8} Si _{15.2}	Ge _{69.9} Si _{30.1}	1253	1092
Ge ₅₀ Si ₅₀	Ge _{81.5} Si _{18.5}	Ge _{65.7} Si _{34.3}	1270	1118

GERMANIUM SILICON BINARY
DIAGRAM

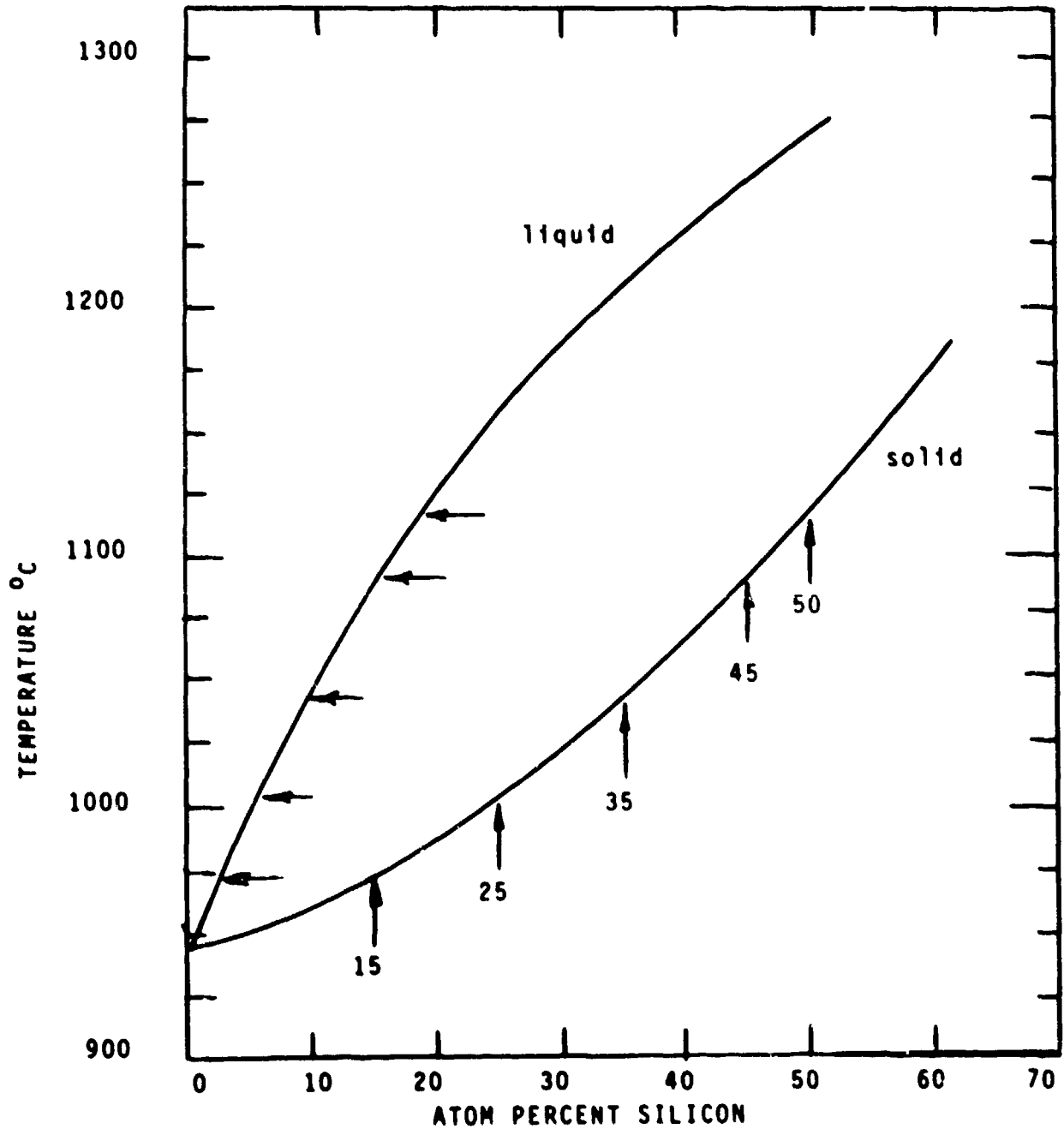


Figure 3. Germanium-Silicon Binary Diagram

III RESULTS

A. GENERAL DISCUSSION

Evaluation of the temperature profile in the Horizontal Bridgman furnace showed that producing a sharp thermal gradient would be very difficult. The heating elements are much too long and modification would be virtually impossible. Consequently, a standard Honeywell controlled germanium zone refiner was purchased and rebuilt to use for preparing the small (200gms) survey samples of Ge-Si alloys. However, the temperature limitation for the unit was 1050-1100°C making the unit unfit for compositions with silicon content 40 atom percent or above. The Bridgman was used in these cases. Also, The Bridgman was used for compounding the average mixtures. the germanium zoner was then used to form the solid. Both units had zone speeds which could be operated as low as 0.25"/Hr. The evaluation of the temperature gradient in the germanium zone refiner yielded a number of 70°C/in or about 30°C/cm.

A number of difficulties were encountered in the preparation of the crystals. First of all, the Ge-Si material tended to wet the quartz boat. As a consequence, the compounded mixture often times fractured the quartz boat and the crystal when it was quenched in the Bridgman furnace. It was then necessary to open the tube and place the crystal in a new boat before the zone-growth process. Thus, the material was exposed to more contamination by the air and through sealing the quartz tube. The problem was never completely solved. More care was exercised in the compounding-quenching process but fracture of the quartz and crystal continued as a persistent problem.

A second problem involved separating the germanium rich liquid from the zoned solid. The zoner was changed from a horizontal to an inclined position to increase the tendency for separation using gravity. Some improvement was noticed. A second approach used in the latter stages of the program was to abandon the average composition approach. Compositions were selected which were only slightly more rich in germanium than the desired solid. Some improvement was noted but not substantial. A third approach was to use the "normal" zone levelling technique in our equipment. Compositions representing the solid and liquid phases were compounded, powdered and packed in a tube as depicted in figure 1. Results were not substantially different from those obtained using the modified approach.

Different zone rates were used with some changes in results. Comparisons are available in later sections. The equipment used was of standard Semiconductor design. Growth rates or zone rates of 0.5-1"/Hr. represent the bottom limit for the equipment. A search in the literature reveals⁽¹⁾ that zone rates of less than 1mm/Hr are recommended for alloys with silicon contents above 10 atom percent. The required zone rate is 5-10 times slower than the capability of the equipment used.

Generally, poor results were obtained in trying to prepare the Ge-Si alloys in sufficient quality to evaluate optically. The main reason the quality is poor is due to the wide separation of the liquidus-solidus curves for the binary (as shown in figure 1) and (figure 3) which leads to extreme experimental conditions required to produce single phase good quality crystals. This fact will become more apparent in the evaluation results discussions which follow.

B. CRYSTALLINITY

Most investigators agree that good crystallinity can be obtained using standard semiconductor crystal growth techniques for Ge-Si alloys provided the concentration of silicon is 5 atom percent or less. This fact is illustrated in figure 4 which shows microphotographs of etched $\text{Ge}_{95}\text{Si}_5$ alloys at about 100X magnification. Note the large grain, single phase structure. According to the literature ⁽¹⁾, zone rates of 4mm/Hr. produce good results which is consistent with the operational conditions of this program.

Closer examination, even at the low silicon content, reveals that all is not well as far as crystallinity is concerned. Figure 5 shows the same large crystals at 600x magnification. Some of the large grains are decorated with what is referred to in the literature ⁽¹⁾ as "poxlike" structures. These small crystallites are considered to be retained liquid films due to constitutional super cooling. An alternate explanation when these structures are observed in germanium growth or gallium arsenide growth is that they represent small cellular structures at the boundaries between twins due to super cooling. Regardless of their nature or structure, they would serve to scatter light and decrease infrared transmission.

The other structural extreme realized in the preparation of the Ge-Si alloys is depicted in the photographs shown in figure 6 for $\text{Ge}_{55}\text{Si}_{45}$ alloys. The magnification is 100x. Dendritic growth and two phase separation is very apparent in both photographs. The poor crystalline structure for the high silicon content crystals to a large part must be attributed to the high zoning rate and the low thermal gradient. For the higher silicon content materials, gradients of 40-60°C/cm have been reported ⁽¹⁾ to produce good results.

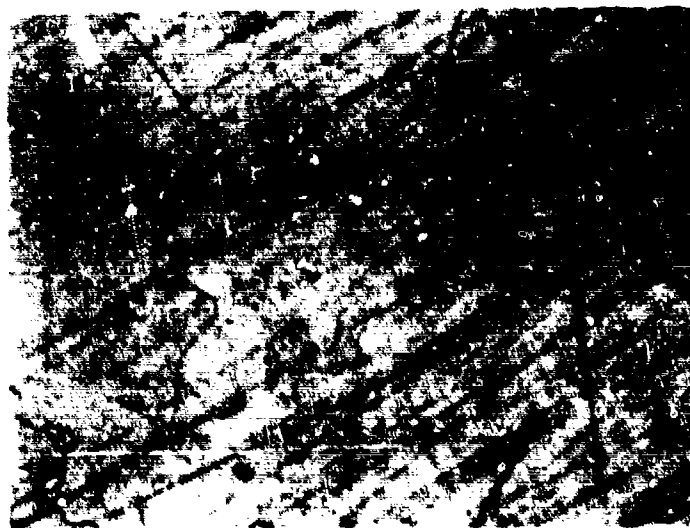
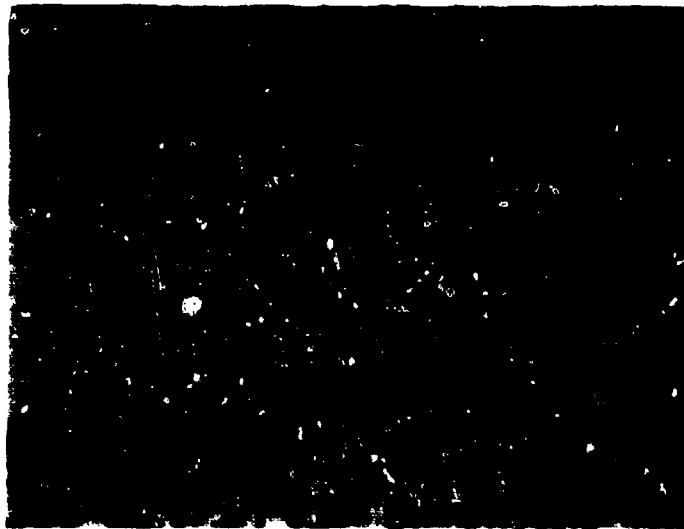
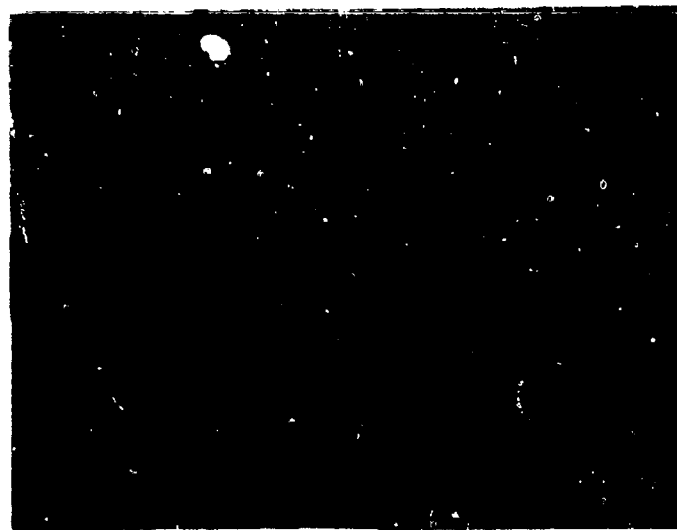


Figure 4. Crystallinity of $\text{Ge}_{95}\text{Si}_5$ Alloy. Magnification 100X, View Taken Perpendicular to Growth Axis. Large Grains are Single Phase.



(A)



(B)

Figure 5. Crystallinity of Ge-i Alloys. Magnification 600x "Poxlike" Structure Revealed for (A) $\text{Ge}_{95}\text{Si}_5$ & (B) $\text{Ge}_{55}\text{Si}_{45}$



Figure 6. Crystallinity of $\text{Ge}_{55}\text{Si}_{45}$ Alloy.
Magnification 100X. View Perpendicular to Growth
Axis. Dendritic growth & Two Phase Separation are
Apparent.

C. OPTICAL EVALUATION

No appreciable transmission was found for any Ge-Si alloys with silicon content believed to be above 5 atom percent. The phrase "believed to be" is used because of the results shown in figure 7. The transmission and absorption edge along with calculated absorption from a sample meant to be $\text{Ge}_{95}\text{Si}_5$. The transmission units for the absorption edge are in arbitrary units while the transmission measurements for 0.2cm samples are in absolute values. Samples were cut from the front and tail of the crystal. Note the transmission for the front of the crystal is quite high, about 45%, the same you would expect for a solid of index 4. Calculated absorption coefficients are shown in the dash curve. They were obtained by reducing the thickness of the 2mm sample and re-measuring. Note the strong wavelength dependence indicating scattering by grains or the existence of a small particulate second phase.

Measured absorption edge transmission easily demonstrates there is a difference in compositions for front and back portions of the curves. All the absorption edge values are summarized in table 2. The band gap values are plotted in figure 8 showing the measured literature values ⁽⁴⁾. From both figures it becomes apparent that the true value of the composition in the front of the bar was $\text{Ge}_{97.5}\text{Si}_{2.5}$ which changed to $\text{Ge}_{95}\text{Si}_5$ at the end of growth. Once more the evidence is strong that good optical quality is not obtained once the silicon content reaches 5 atom percent, at least under the growth conditions used in this program.

Attention should be called to the fact that the method used in this program did not result in $9\mu\text{m}$ absorption due to

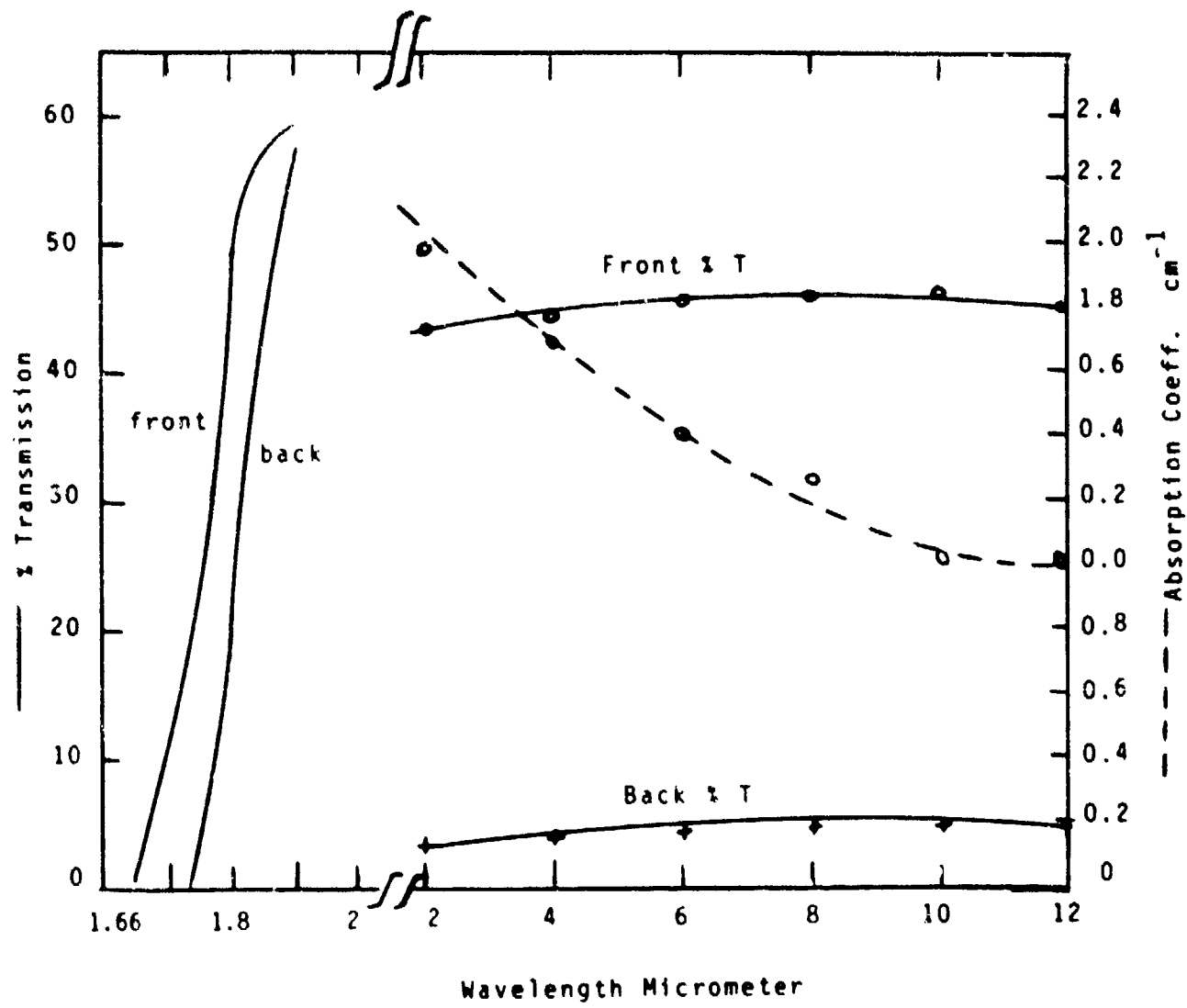


Figure 7 Transmission, absorption edge & absorption Coefficient for Ge-Si Alloys.

TABLE 2

BAND GAP OF GERMANIUM-SILICON ALLOYS
DETERMINED BY ABSORPTION EDGE

SAMPLE	COMPOSITION	ABSORPTION EDGE um	BAND GAP ev
1 (front)	$\text{Ge}_{97.5}\text{Si}_{2.5}$	1.76um	0.70
(back)	$\text{Ge}_{97.5}\text{Si}_{2.5}$	1.66um	0.75
2	$\text{Ge}_{95}\text{Si}_5$	1.66um	0.75
3 (front)	$\text{Ge}_{95}\text{Si}_5$	1.76um	0.70

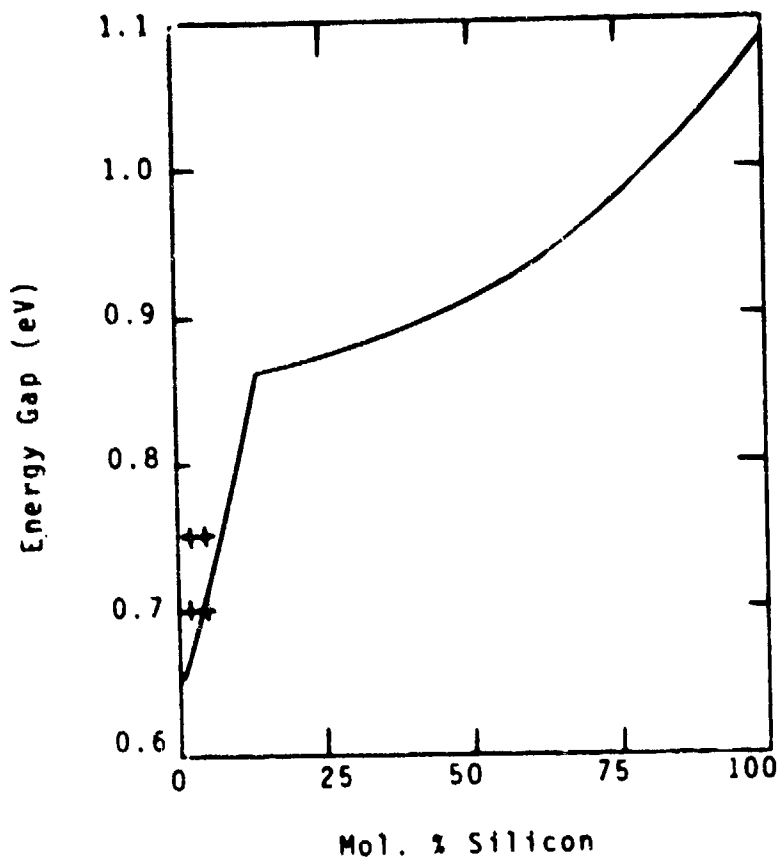


Figure 8 Band Gap of Ge-Si Alloys (4)

oxide contamination. No silicon lattice absorption was observed either but none was expected at such low concentrations.

D. DENSITY

The density variation for Ge-Si alloys is reported in the literature ⁽⁶⁾ to be an almost linear function of composition. The linearity is demonstrated in figure 9. The experimental points plotted on the line are due to the measured densities of the samples prepared for rain erosion tests. The values were obtained by simply measuring the dimensions and weighing on an analytical balance. The method, although not entirely accurate, was used as an indicator of the quality and a check on the presumed composition. From the plot, it is apparent that only three of the five are close to the values expected.

The discussion of density is inserted at this point because it is an important parameter in predicting the refractive index of solids. The prediction can then be used to evaluate the seriousness of compositional variation along the length of a crystal in regards to its use as a refractive infrared optical material.

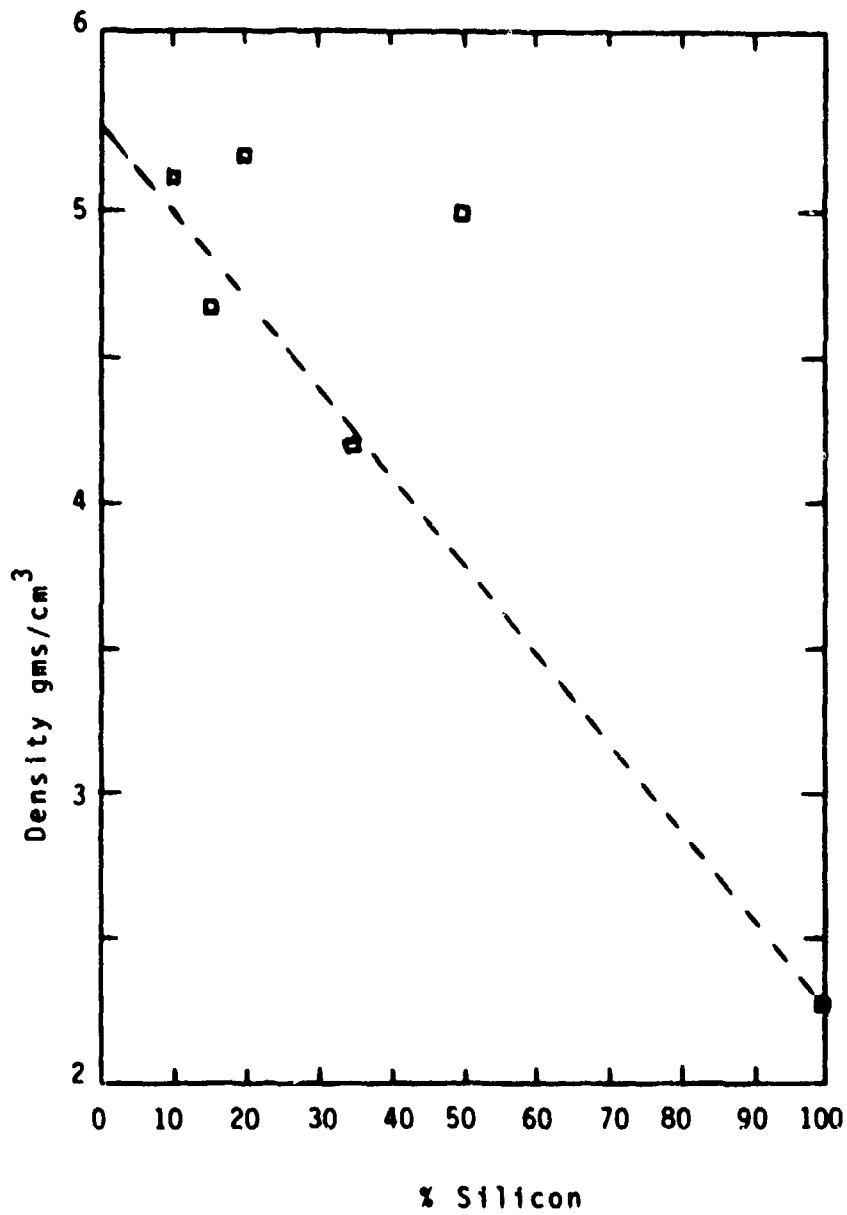


Figure 9. Density of Ge-Si Alloys.

E. REFRACTIVE INDEX

The expression for Molar Refraction, attributed to Lorentz and Lorenz, has been used to qualitatively predict the refractive index for chalcogenide glasses ⁽⁷⁾⁽⁸⁾. The Molar Refraction R for a solid can be calculated from atomic refraction values. That is for an A-B solid, the refraction can be calculated from

$$R_{AB} = X_A R_A + X_B R_B$$

Where X_A, X_B are atomic fractions of A, B
 R_A, R_B are atomic refraction values for elements A & B

$$\text{Also } R_{AB} = \frac{N^2 - 1}{N^2 + 2} \times \frac{\text{Mol. Wt}}{d}$$

Where N is the nondispersive refractive index of solid AB

Mol wt is the calculated weight for the solid AB

d is the density

Assuming the nondispersive index for germanium is 4.00 and that of silicon is 3.42, atomic refraction values for the two elements are:

$$R_{Si} = 9.4$$

$$R_{Ge} = 11.4$$

Accepting these values and the density variation for Ge-Si

alloys, the refractive index was calculated for silicon contents up to 50 atom percent. The results are shown in table 3. From the values in the table a surprising fact emerges: the refractive index does not change much until a silicon content of 20 atom percent is reached. For the previous results presented for variation along the crystal of 2.5-5.0 atom percent, the index change would be very small, less than 0.003.

F. HARDNESS

The microhardness was measured using a Leitz Miniload Hardness Tester and a KNOOP diamond. The Knoop hardness is given by the relation

$$H = 14.23 \times 10^3 P/d^2$$

where: P is the applied load in grams

d is the length of the indentation in micrometers

The measured values for pure germanium and eight Ge-Si alloys are given in table 4. Each value represents the average of three readings. The results are presented graphically in figure 10. The point for $Ge_{65}Si_{35}$ appears very high (890), much higher than obtained for the other compositions. The point appears spurious. From the curve a hardness of greater than 750 may be expected for 25 atom percent silicon.

G. THERMAL PROPERTIES

Thermal conductivity was measured on 8 Ge-Si alloys containing from 5-50 atom percent silicon. A Thermal Comparator was used for the measurement. The instrument which measures

TABLE 3
CALCULATED REFRACTIVE INDEX
Ge-Si ALLOYS

COMPOSITION	REFRACTIVE INDEX
Ge	4.00
Ge ₉₀ Si ₁₀	4.00
Ge ₈₀ Si ₂₀	3.97
Ge ₇₀ Si ₃₀	3.90
Ge ₆₀ Si ₄₀	3.85
Ge ₅₀ Si ₅₀	3.76
Si	3.42

TABLE 4
HARDNESS VALUE
Ge-Si ALLOYS

ATOMIC % Ge	HARDNESS (Kgms/mm ²)
100	675
99	645
92.5	654
95	667
90	730
80	750
65	890
55	740
50	790

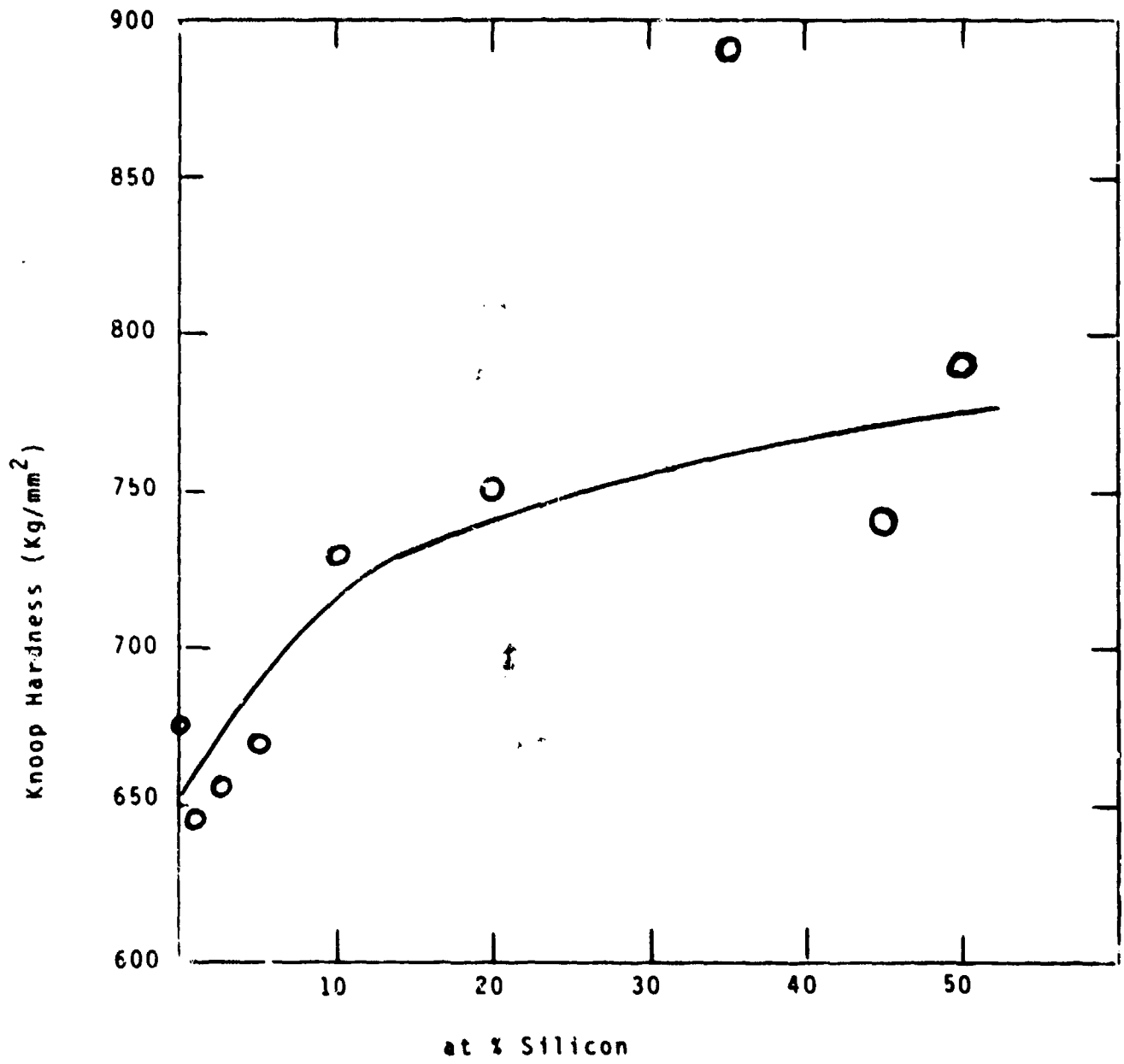


Figure 10 Hardness vs composition for Ge-Si Alloys

the rate of cooling experienced by the tip of a heated probe placed in contact with the surface of the sample was calibrated using a set of standard samples of known value. The standards used were pure germanium and silicon. The surfaces of all samples were prepared in the same manner, ground but not polished. The measured values are plotted in figure 11. The error bars shown do not represent absolute error but rather the variation obtained from several readings on the same sample. Wide variation was found for some samples measured along the direction of growth. Porosity and micro cracks also affected reproducibility on individual samples.

The literature value for pure germanium is $0.58 \text{w/cm}^{\circ}\text{C}$. The value was too large to be shown in figure 11. The disorder caused by the addition of 5 atom percent Si drops the thermal conduction to 25% of the value of pure germanium. The change going from 5-50% is rather small. The results obtained for Ge-Si alloys agrees well with theory and results published in the literature ⁽⁹⁾. Perhaps a better way to present the data and compare to previous results is to plot the reciprocal of thermal conductivity, thermal resistivity. The plot is shown in figure 12. Literature values are shown in the solid line. Again, good agreement is obtained for compositions up to about 10 atom percent silicon indicating the useful range of the method used in this study.

H. ELECTRICAL EVALUATION

The importance of electrical evaluation of each sample was recognized from the beginning of the program because of the known "free carrier" absorption effects in silicon and germanium. Polished samples were prepared from each useful

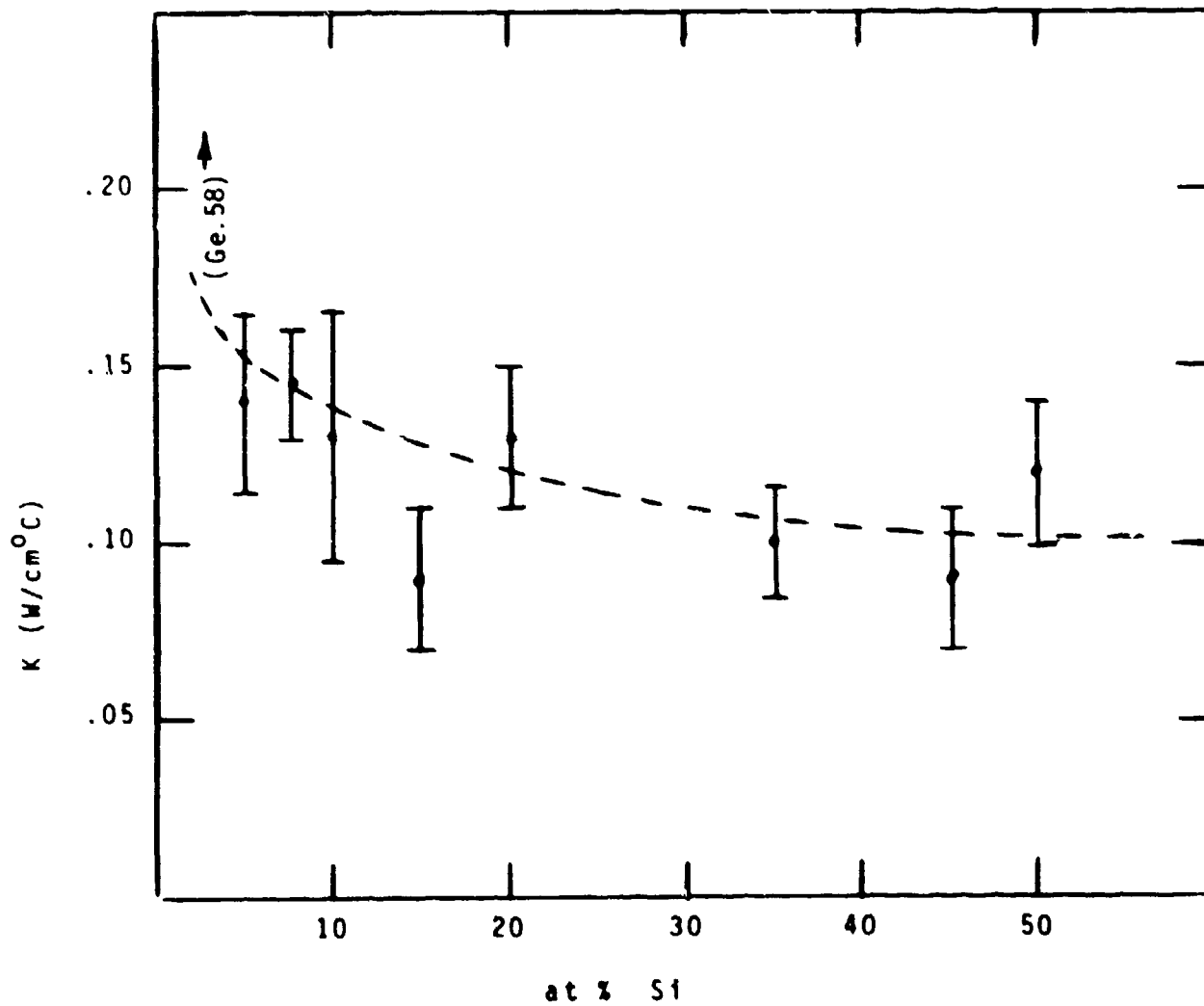


Figure 11. Thermal Conductivity vs. composition
For Ge-Si Alloys

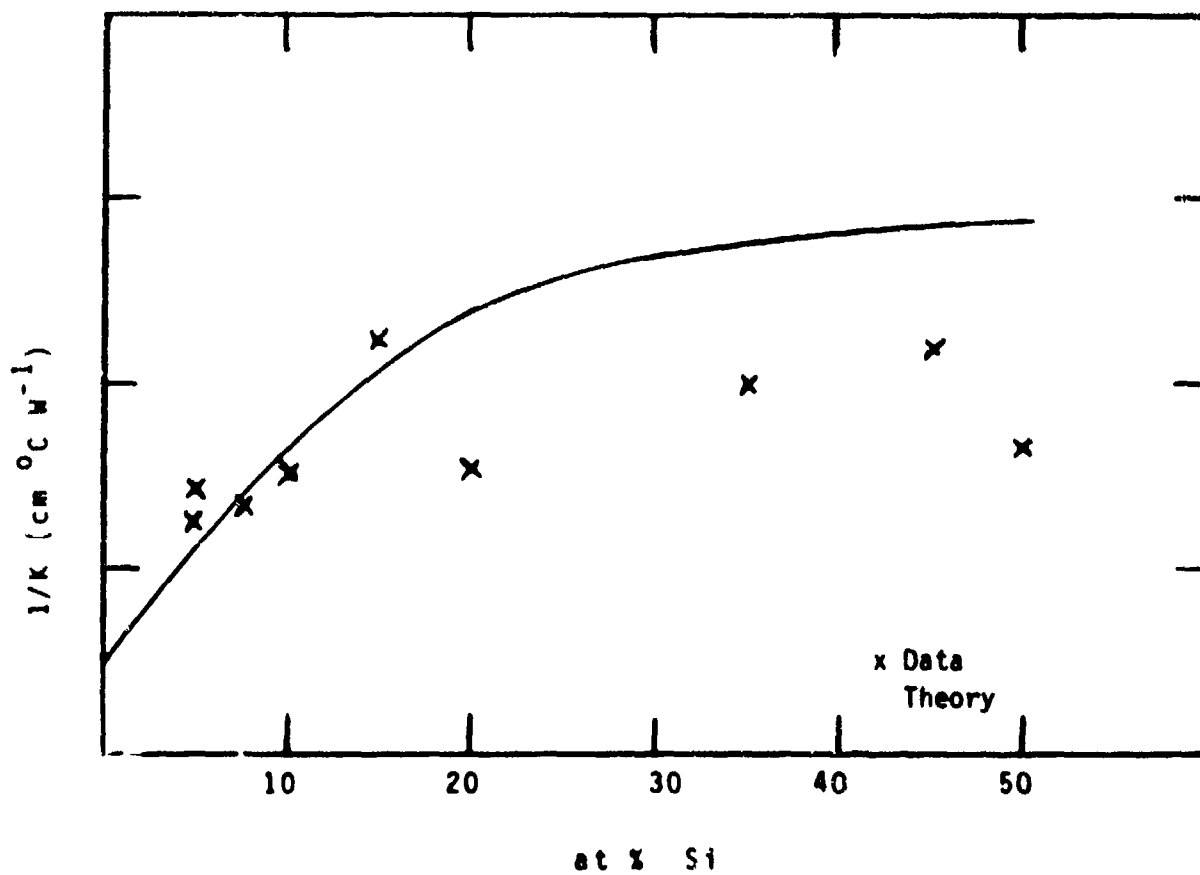


Figure 12. Thermal resistivity vs. Composition for Ge-Si Alloys

crystal and Hall bars prepared for measurements. A summary of the results are shown in table 5. The indicated compositions are given along with resistivity, carrier concentration (with type indicated), mobility of the carrier, zone temperature used in preparation and the zoning rate. For those rates not listed, 0.5-1 in/hr was used. The resistivity as a function of composition is plotted in figure 13. Variation for various compositions is indicated. Note that the resistivity decreases dramatically with the addition of 5-10 atom percent silicon. The decrease is 2-3 orders of magnitude. The resistivity then begins to increase as more silicon is added and the crystallinity becomes poor. A plot of the mobility for the alloys illustrates this point further. In figure 14, the measured mobility is plotted as a function of composition. The n type samples are indicated by (-) and the p type as (+). A general trend is that mobility decreases with increasing silicon content. Also, after the silicon content becomes larger than 10 atom percent, the sign of the carrier becomes predominately p type. Generally, highly disordered solids demonstrate p type conduction which is attributed to hole "hopping" mechanism. Again, the poor crystalline perfection is indicated.

I. RAIN EROSION RESULTS

The samples prepared for rain erosion evaluation were prepared too late in the program to make results available for this report. In all, five samples were submitted. As mentioned earlier, these samples were used to prepare the density plot. Judging by where they fell on the plot, only three of the five may produce results indicative of Ge-Si alloys.

TABLE 5

ELECTRICAL EVALUATION OF Ge-SI ALLOYS

<u>COMPOSITION</u>	<u>RESISTIVITY</u>	<u>CARRIER</u>	<u>MOBILITY</u>	<u>ZONE</u>	<u>ZONE</u>
	<u>ohm cm</u>	<u>Conc.</u> N	<u>Cm²</u> <u>Volt Sec</u>	<u>Temp.</u> <u>°C</u>	<u>Rate</u> <u>in/hr.</u>
Ge	0.01	(-) 6×10^{17}	873		-
Si _{2.5} Ge _{97.5} (F)	3.3	(-) 7×10^{15}	254	947	-
Si _{2.5} Ge _{97.5} (B)	11	(-) 5×10^{16}	123	947	-
Si ₅ Ge ₉₅	0.05	(-) 3×10^{17}	462	950	-
Si ₅ Ge ₉₅ (N)	0.08	(-) 3×10^{17}	298	950	-
Si _{7.5} Ge _{92.5}	0.04	(-) 4×10^{17}	425	955	-
Si ₁₀ Ge ₉₀	0.3	(+) 3×10^{16}	62	962	-
Si ₁₅ Ge ₈₅	0.05	(+) 1×10^{17}	127	970	1
Si ₂₀ Ge ₈₀	3.5	(+) 6×10^{15}	29	987	-
Si ₂₅ Ge ₇₅	0.08	(+) 2×10^{18}	479	1007	1
Si ₂₅ Ge ₇₅	0.19	(+) 2×10^{17}	156	1007	2
Si ₂₅ Ge ₇₅	0.18	(+) 2×10^{17}	155	1007	4
Si ₃₅ Ge ₆₅	2	4×10^{16}	-	1040	0.25
Si ₃₅ Ge ₆₅	14	2×10^{16}	-	"	0.5
Si ₃₅ Ge ₆₅	0.4	(+) 2×10^{16}	97	"	1
Si ₃₅ Ge ₆₅	11	(-) 2×10^{16}	-	"	2.5
Si ₃₅ Ge ₆₅	15	(+) 3×10^{15}	118	"	-
Si ₃₅ Ge ₆₅	2	(+) 4×10^{16}	90	"	-
Si ₃₅ Ge ₆₅	1	(+) 4×10^{16}	117	"	-
Si ₄₅ Ge ₅₅	0.2	(+) 1×10^{16}	322	1092	1
Si ₅₀ Ge ₅₀	1	(+) 5×10^{16}	122	1118	0.25

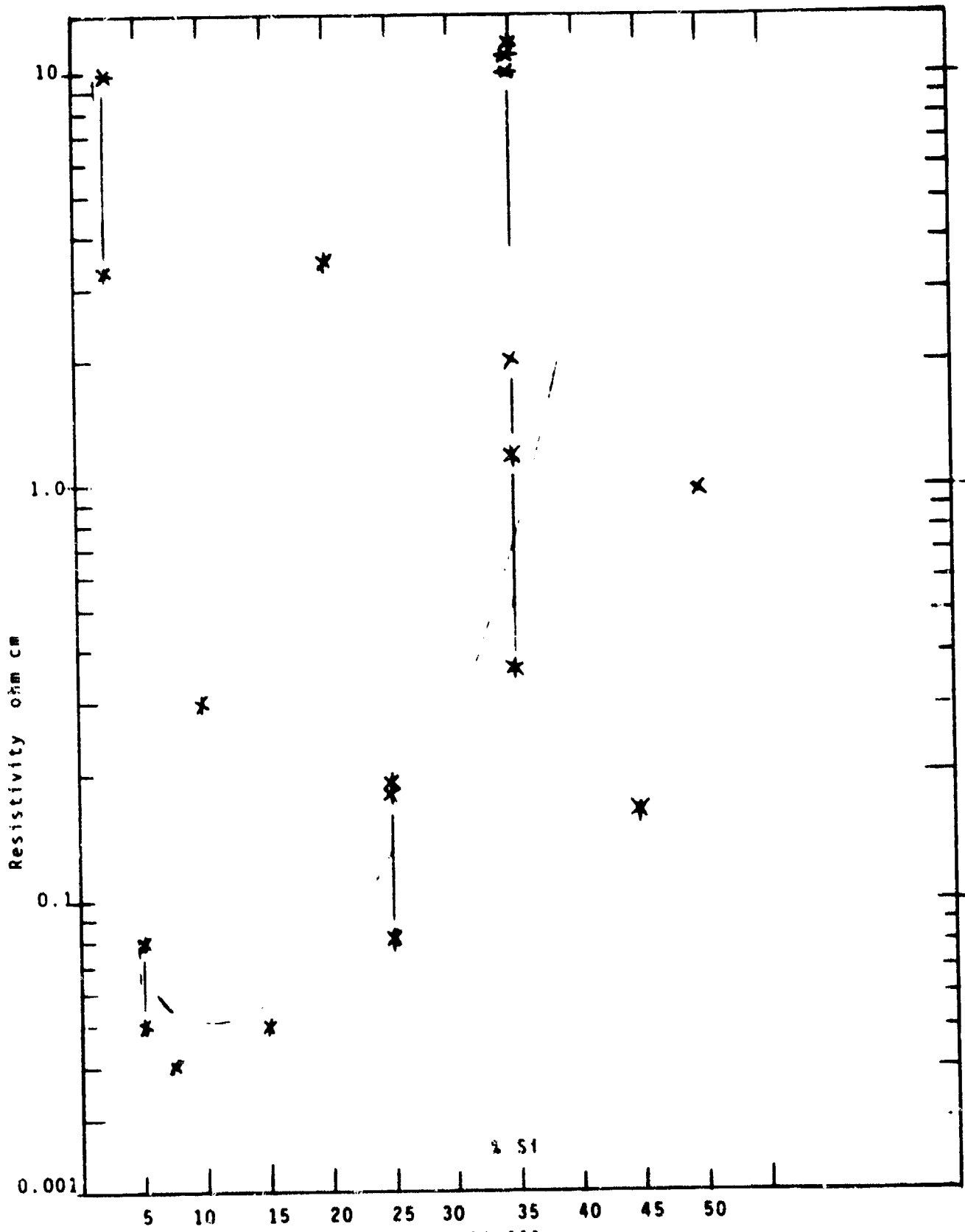


Figure 13 Resistivity of Ge-Si Alloys 36

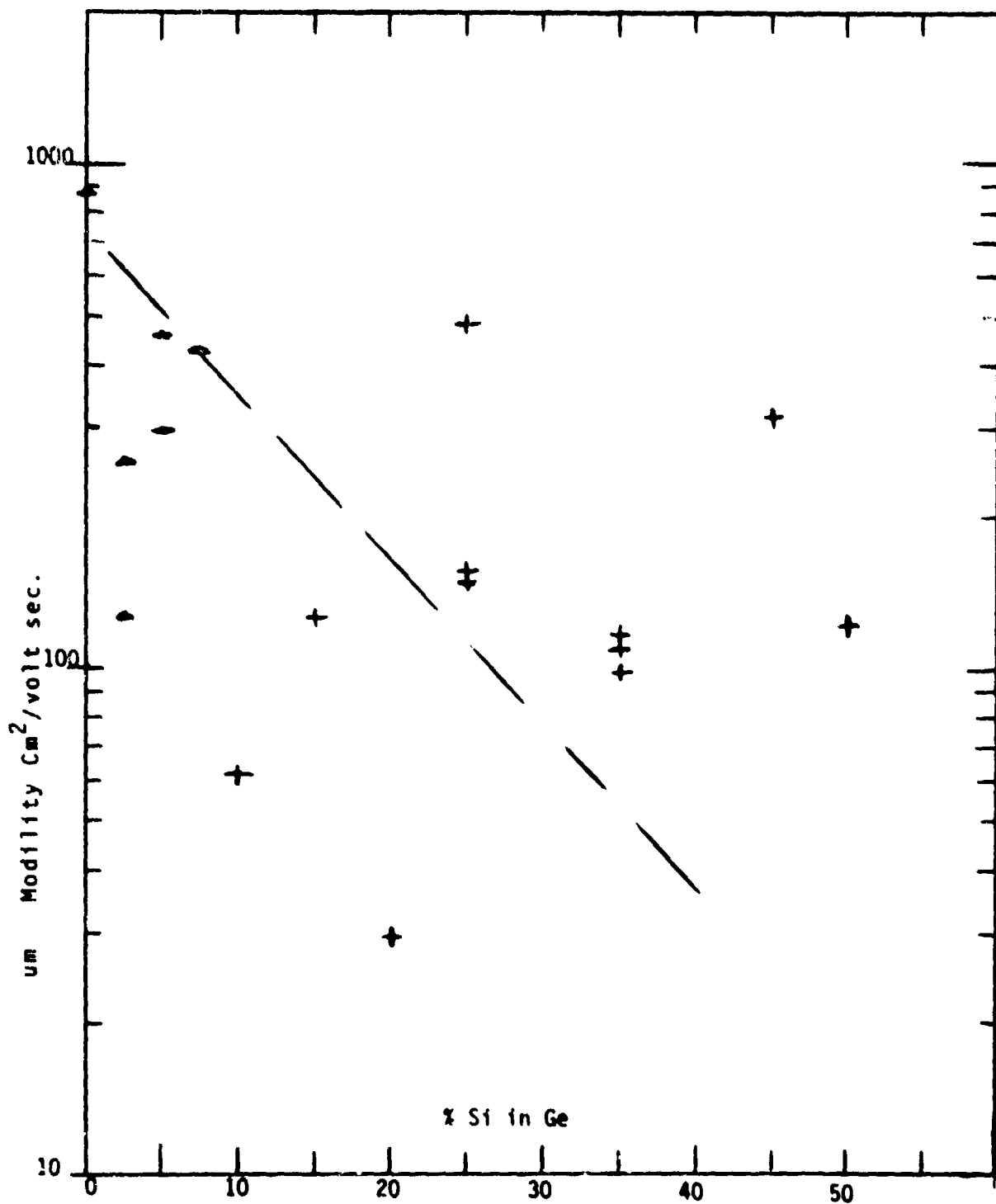


Figure 14. Mobility of Ge-Si Alloys
 + p type conductors, - n Type Conductors

IV. CONCLUSIONS AND DISCUSSION OF RESULTS

The melt growth of Ge-Si alloys containing 5 atom percent or more silicon becomes experimentally very difficult. All results of this program and results reported in the literature support this statement. The critical growth conditions become zone rate, zone gradient and temperature control. Because of the higher temperatures involved and the longer zoning times required for high silicon content material, one may say that the probability of success decreases with increasing silicon content. It is instructive to predict the properties of a material which one might hope to prepare, the conditions required to produce and decide if the effort required would be worth the expected end results. The composition selected is $\text{Ge}_{75}\text{Si}_{25}$, considerably above what was achieved here.

Judging from the results reported, the expected properties are listed below along with those of germanium for comparison.

<u>PROPERTY</u>	<u>$\text{Ge}_{75}\text{Si}_{25}$</u>	<u>Ge</u>
Band Gap	0.87 ev (1.4 μm)	0.64ev (1.94 μm)
Refractive Index	3.94	4.00
Knoop Hardness	750	675
Thermal Conductivity w/cm ⁰ C	0.11	0.58
Rain Erosion Resistance	?	Fair
Lattice Absorption 9 μm	None	None
Resistivity ohm cm	0.1-10	5-50

The band gap improvement would help provide an upper use temperature above germanium but probably of the order of only 50-100°C depending upon carrier mobility and beginning resistivity (which may be lower than germanium).

The refractive index change is minimal and of no consequence. The hardness is improved by 10-15% but the help relative to rain erosion is not known. The thermal conductivity of all mixed alloys is lowered substantially as indicated. The conclusion is that the properties would be improved over germanium but in the 10-20% range everything considered. Attempts to raise the silicon content to say 35% would improve the physical properties further. However, the improvements would be minimal in comparison to the 25 atom % level because of the nonlinearity of the important parameters band gap and hardness. Considering the increase in compounding temperatures and zoning temperatures, the increase would not be justified. Prolonged use of quartz at temperatures above 1100°C leads to increase contamination and eventual quartz failure under vacuum.

The required process changes can be evaluated. The refractive index in the 25 atom % range is found to change approximately 0.007/atomic percent. A good quality requirement on an infrared window material would be 0.001 for a 1cm thick plate (π phase shift at 10 μ m). The corresponding change would be about 0.1 atomic percent. From figure 3, evaluated at 25 atom %, the temperature change required to produce 0.1 atom percentage in silicon content is 0.3°C. The required temperature control to insure a refractive index number good to 0.001 would be about $\pm 0.1^\circ\text{C}$ over a long term. If the plate is 12 inches long and the required zoning rate 1"/day(1mm/Hr),

The temperature in the growth zone (1-2" wide) would have to be $\pm 0.1^{\circ}\text{C}$ absolute over a 10-12 day period. Such control would be difficult indeed.

CONCLUSIONS

1. Growth of Ge-Si alloys with enough silicon content to substantially improve the physical properties of germanium becomes very difficult to achieve with the quality required for a good infrared window.

2. Growth of good quality Ge-Si Alloys would require careful temperature control ($\pm 0.1^{\circ}\text{C}$) over long periods of time (10-12 days) at growth rates difficult to maintain (1"/24hours).

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