1965

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Recommended Citation

Schoenthaler, David, "An analysis of the effects of ultrasonics on diffusion and the diffusion of copper acceptors in germanium" (1965). *Theses and Dissertations*. 3389.
https://preserve.lehigh.edu/etd/3389

AN ANALYSIS OF THE EFFECTS OF ULTRASONICS ON DIFFUSION AND THE DIFFUSION OF COPPER ACCEPTORS IN GERMANIUM

by

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A THESIS

Presented to the Graduate Faculty

of Lehigh University

in Candidacy for the Degree of

Master of Science

Lehigh University

1965

CERTIFICATE OF APPROVAL

This thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

May 20, 1965
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ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. John D. Wood of Lehigh University for his guidance and constructive criticism throughout this investigation. Also due appreciation are the personnel of the Western Electric Company Engineering Research Center of Princeton who have helped in many ways. In particular sincere thanks are offered to Mr. L. J. Peek for the required computer program and to Mr. F. W. Christensen for his general assistance during this study.

Gratitude is also expressed to my wife for her patience and understanding during the period of this thesis investigation.

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ABSTRACT

An attempt is made to determine the mechanism of diffusion enhancement with ultrasonics. Three hypothetical explanations of this phenomenon are offered. First, a cyclical change in lattice geometry of the base material could increase the probability of reducing the activation energy for diffusion. It is expected that such an enhancement would be anisotropic and result from a reduction in the isothermal work required for an atom to jump in a particular direction. Secondly, it is possible for localized temperature increases at points of structural imperfections and high strain to increase the diffusion coefficient from an increase in the atomic kinetic energy. Finally an excess of vacancies could be generated by the movement of dislocations as a result of the high strain rate associated with ultrasonics.

In order to determine which effect is predominant the diffusion of copper acceptors in germanium in the presence of ultrasonics is examined. This diffusion couple was chosen for its high diffusivity, ease of measurement, and extreme structure sensitivity. For the temperature range of 500°C to 700°C ultrasonic energy at a strain maximum of approximately 0.001 at 40 Kcps had no effect on the diffusivity or solubility of copper acceptors. It is postulated that ultrasonics did not introduce point defects and dislocations or alter their mobility to any significant degree. It is deduced that there is no significant temperature increase in the germanium from ultrasonic straining. Finally, it is suggested that ultrasonic energy enhances the interstitial diffusion of copper by altering the geometry of the germanium lattice.

INTRODUCTION

The applications of ultrasonic energy are, in this decade, solving many industrial problems such as material cleaning, nondestructive testing, soldering, and welding. Ultrasonic cleaning results basically from the violent action of cavitation, while nondestructive testing employs the fundamental laws of physics concerning the propagation of mechanical waves through various media. The advantages of ultrasonic energy obtained during soldering result from efficient cleaning and wetting in one step while ultrasonic welding is more complex. In this case surface cleaning and breakup of oxides result in nearly pure material contact; this combined with frictional heating and material seizure will result in a weld usually showing no signs of recrystallization. Hence, a solid state weld is formed with both similar and dissimilar materials.

The field of ultrasonics in general involves the production and use of mechanical vibrations at cyclic frequencies above the audible range. As a compressive force is applied to a crystalline substance, the lattice is strained in the direction of the force. Upon removal of the force the lattice will vibrate in a manner comparative to a compressed spring. The resultant tensile and compressive strains of the lattice are propagated through the material in the direction of the initial force thus providing a traveling wave. When the dimensions of a crystalline body are of a resonant length, a pressure wave is reflected at a surface 180° out of phase with the impinging wave. This results in a standing pressure wave of a sinusoidal nature having nodal points of zero strain and antinodes of maximum strain which alternate between compression and tension. The integral strain of the half wavelength section between stress nodes gives rise to a displacement or excursion of one node when the other is held stationary. Such an excursion occurs at the driving frequency and is used as the tool for soldering and welding.

Objectives of This Study

In view of the success achieved with the application of ultrasonics to the above processes, a greater emphasis is being placed on its effects during solid state metallurgical reactions. The reactions of principle interest are diffusion, precipitation, and age hardening and recrystallization. The effect of ultrasonics on these solid state reactions, as discussed below, is dependent on the high frequency cyclic straining of the structure of the materials involved rather than the net excursion of a resonant length of material. A general objective of this work is to obtain a better understanding of the changes found in these physical mechanisms during the application of ultrasonic straining.

All of the above solid state reactions involve atom transport, which is best examined in a study of diffusion. For this reason the specific objective of this endeavor is to study the effects of ultrasonic energy on diffusion in the solid state. It has been revealed from a review of the literature, cited below, that ultrasonic straining increases case depth during carburization. In view of this, it is implied that diffusion reactions in general are enhanced with ultrasonics; however, no direct analysis for diffusion coefficients was performed. In this study an attempt will be made to analyze proposed mechanisms of ultrasonic diffusivity enhancement, both theoretically and experimentally.

Ultrasonically Enhanced Solid State Reactions

One of the earliest reports of enhanced diffusion during cyclic straining, is the work of Schenck and Schmidtmann (1) who were concerned with the effect of cyclic stressing upon diffusion. In their first experiments, plain carbon steel was carburized under the influence of a cyclic load at 500 cycles per minute (cpm). When comparing the case depth achieved during straining with samples treated identically without the cyclic load, the former depth was increased and the influence was more effective at higher temperatures and greater strain. Static straining before pulsating did not alter the results; while the increase in case depth was also noted when pulsating only during an anneal, after a previous carburization treatment. Thus, it was concluded that cyclic stressing aided diffusion and it was not merely improving contact between the iron and the carburizing medium. They next exposed specimens to carburizing while loaded ultrasonically at 450 kilocycles per second (Kcps). Even though the strain was less in this instance the case depth was greater than at 500 cpm. It was concluded that the total energy, involving both frequency and amplitude, influenced carburization.

Rozanski (2) studied carburization under the influence of ultrasonics as a means of aiding the process without increasing the temperature. His main interest was to determine more about the simultaneous occurrence of graphitization with increased diffusion under ultrasonics as reported by Tanaka, Yoshida and Tagaki (3), where cementite was decomposed by ultrasonic vibrations. Hence, Rozanski excited small diameter, acoustically resonant, one half wavelength bars ultrasonically in a furnace for carburizing. At 28 Kcps, several samples of smallest diameter failed one quarter wavelength from the end. Here at the point of maximum stress and strain graphite was found; the amount decreased near the center and with lower temperature. Case depth in general did increase in the larger diameter specimens which did not fail and no graphitization was found in the unexcited specimens. It was concluded that the graphitization was accelerated by the increased rate of carbon diffusion due to the ultrasonic straining, and a critical value of stress was required before graphite particles were formed.

Pogodin-Alekseev (4) verified an increase in case depth during carburization with ultrasonics, having a direct proportionality with the stress amplitude. It was also possible to accelerate precipitation hardening of nickel based alloys at both elevated and room temperatures. He suggested that changes occur in the lattice parameters which accelerate diffusion, saturation of the matrix, and precipitation of excess solute from it.

In a study of the influence of ultrasonics on precipitation hardening of iron base alloys, a reduction, by a factor of 50, in the time required to obtain a fixed hardness was found. Also aluminum alloys were age hardened 20-25 times faster with ultrasonics, with the final hardness obtained being greater in the aided specimens. The effectiveness of ultrasonics appears to be independent of frequency between 300 cps and 1500 Kcps but dependent on intensity. These findings were those of Gudtsov as reported by Ermakov and Al'ftan (5).

A similar study by Ermakov and Al'ftan (5) involved the aging of half wavelength specimens of an alloy composed of 78.6% Ni, 1.4% Ti, and 20% Cr at temperatures from 700°C to 800°C. At a stress maximum (antinode) of 3.5 Kg/mn^2 at 700°C with 23-26 Kcps a Rockwell B hardness of 98-100 was obtained in 20-25 minutes which would require 16 hours without ultrasonics. It was claimed that stressing of the lattice increases the diffusion coefficient of alloying elements due to a decrease in the activation energy.

Al'ftan (6) attempted to determine which of the two factors, frequency and intensity, is most important in the enhancement of solid state reactions. Diffusion is a function of the kinetic energy of the atoms and their respective positions, with the kinetic energy being proportional to temperature and the position related to deformation. Under ultrasonic compression a unit volume of material will increase in temperature while in tension the temperature will decrease. According to Al'ftan the strain or pressure is proportional to the product of frequency and amplitude and the speed of pressure change is proportional to the product of $(\text{frequency})^2$ and amplitude. In a complete cycle, the change in temperature of a unit volume of material is minimized as a result of the heat transfer between zones of tension and compression. This change in temperature varies directly with the rate of pressure change and inversely with the pressure. Diffusivity is proportional to this change in temperature. In view of this, static elastic deformation will not accelerate diffusion in agreement with the work of Schenck (1), since from this analysis, diffusivity is proportional to frequency.

The influence of ultrasonic high temperature heating on the structure of technical iron was studied by Balalaev (7). An annealed, one half wavelength rod of iron (0.04%C) was subjected to high temperature heating due to internal friction caused by ultrasonic straining. The microstructure parallel to the longitudinal axis was examined before and after the application of ultrasonics. Upon examination, they found that ultrasonic heating introduced points of active structural defects which intensified the dissipation of energy during ultrasonic straining. The increase in temperature at the defects was sufficient to induce localized recrystallization by heating to the 910°C transformation temperature.

HYPOTHETICAL EXPLANATIONS

The fundamental nature of diffusion is expressed by Fick's Laws, the first being a tendency for all single phases to be homogeneous. The mechanism for achieving homogeneity is a flow (flux J) of atoms in a direction to reduce a concentration gradient $(\frac{\delta C}{\delta X})$. This is expressed by the following, Fick's First Law, where D the diffusion coefficient or diffusivity is a proportionality constant and temperature (T) is constant:

$$J = -D\left(\frac{\delta C}{\delta X}\right)_T \quad .$$

His second law considers the principle of conservation of matter during this flow of atoms and specifies the concentration as a function of time (t). Thus, Fick's Second Law is:

$$\frac{\delta C}{\delta t} = -\frac{\delta J}{\delta X} \quad .$$

Under non-steady-state conditions it is found that $\frac{\delta C}{\delta t} = D\left(\frac{\delta^2 C}{\delta x^2}\right)$ providing the diffusivity is not a function of position and concentration.

According to Lazarus (8) these laws are only ideal in that certain conditions are implied but in reality are practically nonexistent. Experimental observations rarely are related to these factors in such a simple manner. For example the diffusivity is usually not a constant but a function of one or more of the parameters of instantaneous time, temperature, position, and composition. Another objection (8) is the implication that the driving force is only the chemical concentration gradient of the diffusing component. In addition to this, the chemical potential gradient affects atom transport, and the chemical potential of each component is not independent but a function of the other components. In view of this, it is found that the fundamental equations are sufficient only for the limiting case of infinitesimally small gradients in the prime parameters.

Geometric and Probability Analysis

Lazarus (8) develops two basic approaches to the problem of determining the characteristic features of diffusion. The first is based on maintaining thermal equilibrium during atom transport between states of different energy. If an atom is considered to pass from one lattice site where it possesses free energy G_1 to another site of energy G_1, it must pass through an unstable position of higher free energy G_2. A relationship between jump frequency (W), and state free energies (G_1) and (G_2) is developed with the following three assumptions. First all atom states are in thermal equilibrium with the lattice. Secondly the energy band of each state is small compared to the difference in energy between states. Finally the time required to change states is long compared to the thermal relaxation times of the lattice. The relationship developed by Lazarus is shown below:

$$W = n\bar{v} \,\text{Exp} - \frac{G_2 - G_1}{kT} \quad .$$

The equilibrium state of each atom was considered to be a simple harmonic oscillator of frequency $\bar{v}$; k = Boltzmann's constant, T is the absolute temperature, and n is the number of independent paths from state 1 to state 2. If the isothermal work, (G_2-G_1), required to move atoms from state 1 to state 2 is reduced, the jump frequency and hence diffusivity would be increased.

The second approach of Lazarus was based on the dynamics of the diffusing atom and the position of its nearest neighbors. The highest probability of an atom jumping lattice sites is composed of the simultaneous occurrence of the following two requirements. The first is that the thermal vibration of the atom be sufficient to carry the atom from one lattice equilibrium site to another. Secondly, the nearest neighbors must move apart sufficiently to allow the passage of the atom to its new position.

The possible effects of ultrasonic straining on the above principles can best be explained with the aid of a simple geometric model. Consider a body centered cubic unit cell with a vacancy in the central atom site. If an atom of radius R_3 were to diffuse to this site it must pass through a constriction of radius R_1 in the (100) plane between the four corner atoms. Swalin (9) considers such a model in his report on an elasticity concept of diffusion. The prime concern here is the calculation of the enthalpy of movement to the constriction in the (100) plane.

The basic Arrhenius equation, below, relates the diffusivity D to the activation energy Q and temperature T:

$$D = D_0 \operatorname{Exp}(-\frac{Q}{kT}) .$$

In this case D_0 and k are constants. Swalin states that $Q = \Delta H_1 + \Delta H_2$ where ΔH_1 is the enthalpy of vacancy formation and ΔH_2 is the enthalpy change of jumping to the saddle point in a reversible manner. This enthalpy of jumping consists of the elastic shear strain energy of passing through the saddle point. This is the sum of the stored energy of constriction enlargement from R_1 to R_2 and the energy of compressing the atoms from radius R_3 to R_2, $(R_3 > R_2 > R_1)$. By assuming that ΔH_2 is independent of temperature, Swalin approximates ΔH_2 by ΔG_2 the free energy change of jumping. This is also the isothermal work of jumping used by Lazarus and is defined by the following:

$$\Delta G_2 = \frac{A(R_3 - R_1)R_3}{\frac{R_1 + BR_3}{R_1}} .$$

In this relationship A and B are constants. When considering (R_1) the constriction diameter to be only slightly less than the atom size (R_3), it is found that the free energy change is reduced with an expansion of R_1. This reduction in ΔG_2 will reduce Q and increase D of the Arrhenius equation.

In consideration of the analysis of Lazarus and the above model of Swalin, a strain in the [100] direction will extend the cell in a manner such that the constriction in the (100) planes parallel to the strain axis is expanded cyclically more than the remaining two planes. Hence, with four passages changing size cyclically at ultrasonic frequencies, it should be evident that at some time during each cycle the isothermal work of changing states (G_2-G_1), as above, should be minimized. This should lead to an increase in diffisivity with the increase being more evident normal to the strained direction, than in any other direction.

Temperature Considerations

It is obvious from the Arrhenius equation, the work of Lazarus (8) and atomic kinetic energy considerations that an increase in temperature will increase the diffusivity. Whenever work is done on a material during ultrasonic straining, heating will occur and every cycle involves one quarter of a period each of the following: applying tension, relaxing tension, applying compression and relaxing compression. During the half periods of relaxing of stress cooling should occur, with the amount of cooling dependent on the heat transfer rate of the material involved. Usually the cooling rate is slower than that of forced heating and net heating is found.

Balalaev (7) heated specimens to temperatures of the order of 1000°C with ultrasonics. However, insufficient information is available concerning his equipment and it is the author's opinion that an unreasonable amount of strain must have been exhibited at 20 Kcps. It is expected, based on past experience of the author, that the degree or percentage of heating by ultrasonics, on a macro scale, is insignificant in comparison to the temperatures involved for most solid state reactions and in consideration of the normal power densities of ultrasonic transmission lines.

The possibility may exist for localized heating at points of structural defects and high strain as observed by Balalaev (7). These effects could be responsible for increased diffisivity. It is expected that these localized high temperature areas could not be measured with thermocouple instrumentation and hence their presence known or controlled.

Strain Rate Effects

The enhancement of diffusion in metals by means of simultaneous plastic deformation has been a subject of much controversy over the past decade. The controversy is due to both contradictory experimental evidence and theory. The mechanism of interest is the possibility of creation of point defects during straining of the base material, with the diffisivity increase being dependent on the amount of strain or strain rate.

The most common diffusion mechanisms involve point defects: primarily vacancies. Substituional diffusion can occur by annihilation of vacancies in a direct interchange with a neighboring atom or by their combination with diffusing interstitial atoms which prefer to come to rest substitutionally. Hence, if point defects can be created during deformation, diffusivities would be higher due to an excess of vacancy sites.

Dislocation theory, in its normal application, explains the concept of slip and plastic flow as resulting from the movement of dislocations. However, limited movement of dislocations and the resultant vacancy creation can occur in the elastic region as suggested by Read (10) and Cottrell (11). Stress fields of dislocations interact and lock dislocations into metastable positions. In order to cause unit slip the externally applied force must be sufficient to break these dislocations apart and promote gliding by overcoming all other obstacles. If the applied stress is not sufficient to overcome all obstacles it is expected that the dislocations may move to new metastable positions. It is also known that stresses lower than the critical slip stress may cause reversible displacement of dislocations; this reversible strain is added to the elastic strain which in effect lowers the apparent elastic moduli. Creep, which normally occurs at high temperatures under stresses within the elastic limit, is nothing more than limited plastic flow which decreases with time as the dislocations come upon obstacles.

Because of these possibilities of dislocation movement within the elastic region, ultrasonic elastic straining could provide the limited dislocation travel required to create point defects. Buffington and Cohen (12) reported the enhancement of the self-diffusion of alpha iron by a uniaxial compressive plastic strain. The ratio of strained to unstrained diffusivity (D_s/D_u) was found to be a linear function of strain rate and independent of the magnitude of the strain. Supersaturation of the iron with vacancies at the high strain rates was postulated as being the mechanism of enhancement. At the lower strain rates the vacancy source and sink actions of the dislocations approach their thermo-equilibrium level.

Forestiere and Girifalco (13) offered a theoretical analysis of the linear relationship of the diffusivity ratio with a strain rate and backed up their theory with diffusion enhancement with silver. In particular their results indicated a greater influence of strain at low temperature and high strain rates. The vacancy supersaturation effect of Buffington and Cohen, above, was applied with the addition of the following concept to explain the temperature dependence of enhancement. At low temperatures vacancies are produced by a geometry mechanism and migrate to fixed sinks while at higher temperature the production is thermally activated and annihilation is by a combining with divacancies to form a stable and immobile trivacancy.

The enhancement of self-diffusion in single crystal silver while undergoing plastic torsional strain was reported by Lee and Maddin (14). A supersaturation effect was claimed to be the reason for their results and in an analysis similar to Forestiere and Girifalco (13), it was determined that the number of excess vacancies (N_x) is proportional to the product of strain rate $(\dot{\epsilon})$, vacancy lifetime (λ), and the mole fraction of vacancies per unit strain (n). This is shown as follows:

$$N_x = \dot{\epsilon}\lambda n \ .$$

Also it was demonstrated that the diffusivity (D_s) is proportional to the production rate (P) of excess vacancies and the number of vacancy lifetime jumps (J). This is related as follows:

$$D_s = PJ = \frac{N_x}{\lambda} J = \dot{\epsilon} n J \ .$$

When citing the work of Ham and Seitz, Lee and Maddin (14) reported the production rate of vacancies to be independent of temperature but dependent on dislocation geometry effects; also the number of lifetime jumps increased with temperature, thus aiding diffusivity.

Darby et al. (15) reported results contradictory to Lee and Maddin, in their self-diffusion studies of single crystal silver while undergoing plastic tensile and compressive straining. They reported no decisive enhancement within the limits of experimental error. It was concluded by Darby et al. that the number of excess vacancies created by deformation is insignificant to the number generated by temperature alone. Their results indicated the ratio of (D_s/D_u) to be on the order of 1.5 as compared to 100/1 for Lee and Maddin. The experimental results of Darby et al. indicate that the number of vacancy jumps per cc per 1% strain was less than 10^{32}. The number of vacancies produced per cc per 1% strain is approximately 10^{17} for face centered cubic materials. Further studies show the number of lifetime jumps to be 10^{10} as determined by annealing studies of quenched in vacancies. Thus, at low temperatures the number of vacancy jumps per 1% strain per cc is 10^{27}, a factor of 10^5 lower than the experimentally calculated maximum value of 10^{32} at higher temperatures. It is not expected that thermal energy would account for this difference and certainly not account for additional jumps required for the Lee and Maddin D_s/D_u of 100. In view of this Darby et al. discounted their 1.5 ratio as being the result of experimental error.

Darby et al. (16), in their negative result attempt to duplicate the torsional experiment of Lee and Maddin (14), presented the following equation relating the number of extra strain-induced vacancy jumps required per 1% strain for the corresponding strained (D_s) and unstrained (D_u) diffusivities:

$$N_\epsilon(1\%) = D_u[(\frac{D_s}{D_u}) - 1][\frac{48}{100a^5\dot{\epsilon}}] .$$

In this equation, (a) is the lattice parameter in Å and $(\dot{\epsilon})$ is the strain rate. Accordingly, using the data of Lee and Maddin, 5×10^{32} extra jumps per cc per 1% strain are required for their 100/1 diffusivity ratio. Again this is an unreasonably large number to expect, in comparison to the 10^{27} extra jumps/cc/1% strain near room temperature.

In view of the above discussion it is the author's contention that an excess of point defects could be responsible for enhanced diffusivity with high ultrasonic strain rates. As an illustrative example consider an acoustical transmission line operating at 40 Kcps with a half wavelength excursion of .001". This would have an average strain of approximately .0006 giving a maximum sttain of nearly .001. At 40 Kcps the period of one cycle is $.25 \times 10^{-4}$ seconds with the maximum strain occurring in 1/4 of a cycle or in $.0625 \times 10^{-4}$ seconds. It is evident that the maximum strain rate would exceed 160/sec ($\dot{\epsilon}_v$). By applying this strain rate to Darby's analysis for the number of excess vacancies required for enhancement, as in the above equation, the number required with ultrasonic straining can be approximated by (N_{xu}) below.

$N_x = 5 \times 10^{32}$ for Lee and Maddin with $\dot{\epsilon} = 25 \times 10^{-5}$/sec

but

$$\frac{N_{xu}}{N_x} = \frac{\dot{\epsilon}}{\dot{\epsilon}_v} ;$$

thus, $N_{xu} = \dfrac{(5 \times 10^{32})(25 \times 10^{-5})}{160} = 0.8 \times 10^{27}$/cc/1% strain.

Thus, with ultrasonic straining the number of excess vacancies required per cc per 1% strain is of the order 10^{27}. This is of the order of magnitude expected at room temperature as discussed above in the work of Darby et al. (16). It is therefore reasonable to expect the high strain rate associated with ultrasonics to be capable of introducing an excess of vacancies for supporting a 100-fold increase in diffusivity.

Three extensive reports by Balluffi and Ruoff (17) (18) (19) were written in an attempt to clarify the contradictions of Darby and Lee and Maddin. It is suggested that within each grain or single crystal there exist subgrains possessing a negligible dislocation density with a boundary of high dislocation density. If within the subgrain a homogeneous array of screw and climb type jogs existed with an equilibrium between the source and sink actions of the boundary; a small applied stress could override the balance to the point where excessive production occurs. This is the model generally accepted for the explanation of possible enhancement of diffusion by plastic straining.

After a final analysis of some fourteen experiments Ruoff and Balluffi have concluded that there has been no evidence of enhanced diffusivity due to the creation and annihilation of point defects; other parameters were responsible for past results. These remarks hold for strain rates used in past work up to the maximum of 25 × 10^{-5}/sec, applied by Lee and Maddin (14) but not necessarily for ultrasonic strain rates approaching 160/sec.

EXPERIMENT DESIGN

In view of the hypothetical explanations of expected enhancement of diffusivity, this investigation was designed with the intention of checking for point defect, temperature, and geometric effects of ultrasonics. There are several general requirements which would aid in the selection of materials for this study: (1) a high diffusivity diffusion couple, requiring short penetration times, would minimize most heating and control problems associated with the ultrasonic equipment; (2) the examination technique of determining the concentration gradient should be accurate, versatile, and available; (3) a single crystal is required to eliminate possible anisotropic effects of diffusion in the various grains of a polycrystalline specimen and short circuiting of diffusing atoms along grain boundaries; and (4) information should be available concerning the unaided diffusivity and its probable mechanism.

Material Selection

Shewmon (20) and Crank (21) have developed a thin film solution, for the accurate determination of the diffusivity of substitutional atoms which uses the following relationship:

$$\frac{\delta \ell n\ C(x,t)}{\delta x^2} = -\frac{1}{4Dt} = m\ .$$

It is therefore possible to calculate the diffusivity (D) from the slope (m) of a plot of the natural logarithm of concentration (C) versus the square of the penetration distance (x^2) for a given time (t).

In order to eliminate excessive heating of the ultrasonic equipment and to reduce experimental time, a maximum time of 1800 seconds was selected. For macroscopic diffusion a minimum x value of 0.1 cm is required to reduce surface effects. In achieving good resolution of solute concentration a minimum of one order magnitude change is acceptable. With these parameters and the thin film analysis it was calculated that a diffusivity of $.6 \times 10^{-6} \text{cm}^2/\text{sec}$ is required. A literature review indicated most D values for the diffusion of metals were of the order 10^{-10} to 10^{-12} cm^2/sec, a value much smaller than desired.

Higher diffusivities are obtained with the semiconductor family of materials such as silicon and germanium. According to Boltaks (22) elements such as gold, silver, zinc, copper and iron form substitutional solid solutions in germanium while lithium is interstitial. At 800°C the diffusivities, into germanium, of Groups I and VIII of the Periodic Table are larger by a factor of 10^6 to 10^8 than those of Groups III and V. Specifically at 800°C: D of copper, Group I, is $2.8 \times 10^{-5} \text{cm}^2/\text{sec}$, and that of indium, Group III is $2 \times 10^{-13} cm^2/sec$. Thus, the first requirement of high diffusivity is fulfilled with the couple of copper into germanium.

Through consideration of the fundamental properties of semiconductor physics the second requirement of easy measurement was solved, since diffusivities can be determined from conductivity data. Copper behaves as an acceptor in a substitional solid solution with germanium. Hence, when filling vacancy sites in the germanium lattice, each copper atom accepts an electron which leaves behind a positive hole, causing the germanium to be p type. By doping germanium with a donor impurity such as antimony, an n-type extrinsic semiconductor material is obtained with an excess of electrons over that of intrinsic germanium. If copper is diffused into the n-type germanium the holes soon outnumber the electrons in the vicinity of copper atoms and the carrier type is reversed. A narrow but distinct junction is formed between the two types of carriers; this is designated a p-n junction. By measuring the conductivity of the germanium the concentration of copper acceptors can be determined. In the experiments to be cited below, the diffusivity of copper into germanium as determined from the acceptor concentration, just described, has had excellent agreement with the radioactive tracer method. This method has been used most frequently for its precision and agreement with Fick's laws.

Other added advantages to using this particular diffusion couple are related to the requirements proposed. The results of this study can be discussed in terms of the wealth of information available on this system, accumulated since the early 1950's. A correlation exists between the electrical properties, impurity concentration, and crystal perfection (dislocation concentration). Common etch pit techniques of dislocation counting are available and single crystal specimens are readily available.

Cu-Ge Diffusion Studies

Germanium was found to undergo a reversal of carrier type when n-type was heated to 800°C and rapidly cooled. The new p type would reverse back when heated at 500°C for a prolonged period. Fuller et al. (23) investigated the cause of this conversion and found an advancing p-n junction, indicating the diffusion of impurity acceptors into the germanium. The diffusivity of these acceptors was found to be of the order $10^{-5} cm^2/sec$ near 750°C, and their concentration was assumed to be equal to: (1) the reduction of n carriers in n-type material, (2) the number of n electrons of the original material at the junction and (3) the sum of the original n carriers plus the added holes in the converted material.

Fuller and Struthers (24) found the diffusivities of the thermal acceptors and copper to agree within the limits of experimental error when diffused into germanium at 654 to 919°C. Copper was diffused into n-type germanium from a thin film deposited from a copper nitrate solution, and the concentration gradient was measured with both radioactive tracer and conductivity techniques. During a 48 hour anneal at 500°C the copper precipitated out of solid solution and changed the germanium back to n-type of nearly the original resistivity. Slichter and Kolb (25) verified the equality of copper and thermal acceptors. Germanium examined at various stages during and after crystal growth were found not to convert when reheated. Exposure to air or doubly distilled water following growth had no influence, but after immersion in a dilute solution of copper nitrate (0.001 atomic percent) excessive conversion was found. Again the ratio of radioactive copper atoms to hole carriers was found to be approximately one.

In an analysis similar to that used in this study, Fuller et al. (26) found an average diffusivity of $2.8 \pm .3 \times 10^{-5} cm^2/sec$ for the temperature range of 700-900°C. Solubility studies verified the close agreement between the conductivity and radioactive techniques of measuring diffusivity below 700°C. The maximum solubility occurred at 875°C with 4×10^{16} holes or copper atoms per cc. This agrees with the peak value of 8×10^{-5} atomic percent of Thurmond and Struthers (27). Due to the scatter of the diffusivity results, the temperature dependence of diffusivity was not accurately determined; however, by a statistical analysis of the data, a maximum activation energy of 4100 cal is obtained. Accordingly, the following temperature-dependent Arrhenius equation was developed by Fuller et al. (26) for the 700 to 900°C range:

$$D = 0.00019 \exp(-4100/RT) \;.$$

Their attempts to measure diffusivity below 650°C indicated a much lower diffusivity. It is their opinion that this may be due to a lack of equilibrium below this eutectic temperature. Esaki (28) has reported a higher activation energy of 35,000 cal for thermal acceptors below 650°C; this leads to a lower diffusion coefficient. Fuller et al. (26) suggest that the low activation energy and high diffusivity, 2.8×10^{-5} at 700-900°C, indicate an interstitial mechanism of diffusion. Also, atoms known to enter germanium substitutionally had very low diffusion coefficients of the order 10^{-12} cm^2/sec. However, as with normal interstitial diffusion of acceptors, the copper should diffuse as a negative ion, since it has an added electron. It is found that the diameter of the negative ion is greater than 1.5Å which is larger than the interstitial site of 1.22Å. It was thus suggested that the copper diffuses interstitially as Cu^0 or Cu^+ at high temperatures and takes on an acceptor level at lower temperatures. This was based on the evidence that in the presence of a dc field copper diffuses as a positive ion at 850°-900°C and as an uncharged atom at 700°C.

The possibility of interstitial diffusion with a return to a substitutional lattice site has been critically examined by van der Maesen and Brenkman (20). They developed the concept that both Cu_i and Cu_s (i = interstitial and s = substitutional) exist together and are in temperature-dependent equilibrium, with only Cu_s acting as an acceptor. This is written as follows, where Q is the energy of reaction:

$$Cu_i \rightleftarrows Cu_s + Q \ .$$

Prolonged heating at 500°C allows excess Cu_i to precipitate with Ge as a second phase of Cu_3Ge. This is shown as:

$$3Cu_i + Ge \rightleftarrows Cu_3Ge \ .$$

The Cu_3Ge is formed from interstitial copper since it moves freely in the lattice and as it is formed the interstitial copper is replenished by the substitutional copper.

From an analysis of the concentration gradient of copper diffused into germanium, van der Maesen and Brenkman (29) found that the concentration (c) and copper diffusivity (D) were not related by the common error function:

$$\frac{c}{c_0} = 1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} .$$

In this equation c_0 is the surface concentration while (x) and (t) are the diffusion distance and time, respectively. It was concluded that the diffusivity was not a constant but instead a function of the copper concentration. This was verified by applying an analysis developed by Hall (30) for variable diffusivities. Hall, in his analysis, assumed the fundamental relationship of Boltzman which required the concentration to be a function of the diffusion time (t) and distance (x) as described by the following:

$$c = c\left(\frac{x}{\sqrt{t}} \right) .$$

It was shown by van der Maesen and Brenkman that c was not a pure function of $(x/\sqrt{t})$ but included some unknown factors. Thus the validity of the Hall analysis is questionable. In their opinion the analysis of concentration gradients for diffusivity is complicated by the interaction of interstitial and substitutional modes of diffusion.

The above theory was expanded by Frank and Turnbull (31) who included the requirement of a supply of vacancies for the conversion of interstitial to substitutional copper in germanium. The apparent high diffusivity of substitutional copper is easily achieved in imperfect germanium, since an excess of vacancies exists at the dislocations. However it was theorized that, in a perfect crystal structure, substitutional copper atoms near the surface must dissociate into vacancies and interstitial atoms. With each diffusing independently and subsequently recombining, the high apparent diffusivity can be obtained. It was therefore concluded that the diffusivity of copper into germanium was highly structure-dependent.

Fuller and Ditzenberger (32) confirmed the deviation of Cu-Ge diffusion from the basic Fick's Law as reported by van der Maesen, and proceeded to study the effects of structural defects on the diffusivity of copper. Their thoughts were closely related to the theory of Frank and Turnbull in that a wide range of diffusitives which are generated at surfaces and dislocations, i.e., D would vary even within the same crystal with an inhomogenous dislocation array. In the first phase of their investigation copper was diffused into bent and unbent specimens of germanium at temperatures of 760°C to 875°C. The samples were from the same crystal and bent at room temperature. The results indicated a greater rate of saturation with deformation and a more pronounced effect at lower temperatures. The diffusivity increased from the order 10^{-7} to 10^{-5} cm^2/sec due to deformation. In the bent germanium the copper rapidly becomes an acceptor by combination of interstitial copper and the abundant vacancies introduced by the dislocations, but in the unbent the copper essentially remains interstitial for a longer time. Acceptor formation and eventual saturation was more rapid in high etch pit count samples, 13,000 etch $pits/cm^2$, when compared to a medium count of 1800 etch $pits/cm^2$. This verified the relationship between deformation, dislocations and diffusivity. Another study indicated that the acceptor concentration is less than the total amount of radioactive copper. The discrepancy decreases with both an increase in time to saturation and temperature. Finally, evidence from autoradiographs, etch pit patterns, and p-n junctions conclusively prove the mutual existence of Cu^{64}, etch pits, and copper acceptors in proportions corresponding to the diffusion rates and concentration gradients.

Frank and Turnbull (31) suggested the following relationship for the acceptor diffusivity (D_s) for dislocation free germanium, where recombination of Cu_i and vacancies depend on vacancies entering from the surface.

$$D_s = \frac{D_v(C_v)}{C_v+C_s}$$

In this equation D_v is the vacancy diffusivity; C_v and C_s are the vacancy and acceptor concentrations, respectively. In germanium of high dislocation count the copper diffuses interstitially to the internally generated vacancies resulting in the following equation:

$$D_s = D_i \frac{C_i}{C_i+C_s} \; .$$

In this case D_i is the interstitial copper diffusivity and C_i is the interstitial copper concentration. It should be evident that in the actual crystal both processes may occur simultaneously.

It is the opinion of Fuller and Ditzenberger (32) that this mechanism may apply to solid state diffusion in other conventional solid crystals. This also provides a method for long-range transport of substitutional atoms with a dependence on the dislocation array involved.

Equipment

The ultrasonic equipment designed for this study, shown schematically in Figure 1, is of a versatile nature and hence can be adapted to other studies involving the effects of ultrasonic energy on the physical properties of materials. Basically it requires no metallurgical joining of the specimen involved to the acoustical transmission line. In this respect, the 40 Kcps ultrasonic driver, shown as part (1) and the full wavelength follow-up section (2) clamp the specimen (3) in position by means of the constant pressure air cylinder located at (5). The one limitation to this arrangement is that the specimen cannot be placed in tension, but in a comparative study this may not be necessary. The transmission line, composed of members (1), (2), and (3), has a standing wave with stress nodes and antinodes as illustrated.

The other significant features of this equipment layout are: the vertically movable furnace (8), cooling heat exchangers (7), and the nitrogen quench supply jets (9). At (4) a soft iron segment, attached to the titanium transmission line (2), supports the magnetic field of the permanent magnet incorporated in the amplitude detector. The magnetic flux passing through a variable air gap permits the calibration and measurement of the excursion of the end of member (2) by a commercial Hall cell. An estimated 30% loss of acoustical energy was noted at the velocity node of member (2), hence the excursion of the half wavelength specimen is larger than that measured by the Hall cell by a factor of 1.43. A photograph of the actual equipment is shown in Figure 2.

The conductivity measuring equipment consisted of a Dumas four-point probe, of .025" point spacing, a one milliampere constant current source, and an Electronics Associates Incorporated digital voltmeter. A 10:1 voltage amplifier was required to increase the measured voltage such that ±2% accuracy could be obtained when reading less than 10 millivolts. By using various combinations of ±2% deviation in actual measured data, less than ±2% error was obtained in the subsequent diffusivity calculations; this is believed to be of sufficient accuracy for this study.

Experimental Procedure

In view of the literature available on the couple chosen it is expected that the effects of ultrasonics on diffusion may be determined. Temperature and geometric influences should also be apparent. The diffusion procedure and analysis used by Fuller et al. (26) was followed and the basic format of this study consists of diffusing copper into germanium with and without ultrasonics under the conditions of constant temperature, pressure, orientation, and time. This will permit a comparative study of the behavior of this diffusion in the presence of ultrasonic energy.

Single crystal germanium having the following properties was used throughout this study. It was zone leveled, n-type, and grown parallel to the [100] direction with a dislocation density of 2000 to 4000 counts/cm^2. The resistivity of 3 ohm - cm ±20% was obtained by doping with antimony. The crystal was cut into parallelepipeds .250" square by 2.500" long with the 2.500" length parallel to the [100] direction. All faces were cut to be {100} crystallographic planes and were lapped by the supplier to remove saw damage. The acoustical half wavelength was determined to be 2.43" at 40 Kcps frequency by the following relationship given by Mason (33):

$$\frac{\lambda}{2} = \frac{V[100]}{2f} = \frac{\sqrt{C_{11}/\rho}}{2f} .$$

For a longitudinal wave in germanium with the strain and wave velocity in the [100] direction a stress constant C_{11} is given by Mason as being 1.292×10^{12} dynes/cm^2. In this relationship λ is the wavelength, V is the velocity of sound, ρ is the density of germanium (5.323 gm/cm^3) and f is the 40 Kcps driving frequency. A length of 2.500" was used since the slightly shorter length at an elevated temperature could not be accurately predicted, and several temperatures from 450 to 700°C were to be used.

The bars of germanium are hand lapped successively on dry Aloxite abrasive paper of 320, 400 and 600 grit. After each step they are washed in doubly distilled water and finally cleaned in Freon. This was found to be both necessary and sufficient to eliminate surface contamination effects during diffusion. Following this, a copper nitrate solution, 2% by weight, was applied with an eyedropper on one .250" by 2.500" surface. After 2 to 4 minutes the excess was carefully removed with the edge of a blotter. Without touching this surface, the specimen was loaded into the acoustical equipment for diffusion.

The diffusion time was taken as the time from insertion into the furnace to removal from the furnace and start of quench. No correction factor was applied to this time interval since the objective was not to determine a precise value of diffusivity but rather a comparison with and without ultrasonics. The assumption was made that the heat-up time approximately equals the cooling time; this offsets most of the time-temperature error. A nitrogen gas jet was used as the quench and it was assumed that this was sufficiently repeatable for the comparative study and also rapid enough to avoid precipitation of copper acceptors from solution. Since it had been reported that the diffusivity is much lower below 650°C, the nitrogen must in reality suppress the precipitation for a drop of about 100°C, as from 725°C to 625°C. This is valid if diffusion is the mode of atom transport during precipitation.

For examination of the copper acceptor concentration, the bars were cross-sectioned, with a diamond saw, parallel to the longitudinal direction and perpendicular to the surface of applied copper. After sawing, the germanium surface was lapped as before to remove saw damage to the surface. The surface was then probed for conductivity measurements with a four-point probe. This analysis is to be discussed in a later section.

A typical specimen was used for temperature calibration of the furnace. Five holes, .017" diameter and .062" deep, were abrasively drilled at equal spacing along the longitudinal length of the bar. Thermocouples were placed in these holes to check the temperature contour relative to a surface thermocouple used for the furnace temperature controller. The controller was found to maintain a temperature variation with ±8°C when set for 715°C and the variation appeared to be cyclical. Figure 3 illustrates the temperature contours used for various settings of the controller. It is to be noted that although a rather steep gradient exists due to cooling from the associated equipment, the .750" central portion varies by about 10°C maximum. The germanium was noted to reach operating temperature in less than 40 seconds at all settings. This was due mainly to the transmission characteristics of germanium to infrared radiation from the glow-bars of the furnace, which enhanced deep and uniform heating of the specimen.

Dew-Hughes (34) reports that germanium creeps above 400°C and gives the tensile curves for 650°C. His creep results at 650°C indicate a strain of .03 after 5 minutes under a stress of 1.28 Kg/mm^2. Since the specimen is under a compressive load in the acoustical equipment it is necessary to stay below the yield point and to minimize creep for experiments of 10 minutes time duration. Based on the data of Dew-Hughes, an applied pressure of 1200 PSI (.845 Kg/mm^2) was assumed to be reasonable at 700°C.

Although copper-germanium diffusion has not been studied in the presence of a compressive stress or thermal gradient, it is expected that these effects, if present, should be eliminated by this comparative study.

Diffusivity Calculations

The thin film analysis developed by Shewmon (20) and Crank (21) was used; a Fortran program was written which allowed the use of an IBM 1620 computer for the computations. In this analysis it is assumed that Fick's Laws are obeyed and consequently (D) the diffusivity is constant. This was found not to be true by van der Maesen and Brenkman (29) who used the Hall analysis for a variable diffusivity solution. However, as previously described in the discussion of the Cu-Ge diffusion couple, there was an uncertainty in the application of Boltzman's rule for variable D in the Hall analysis for this couple. Since the object is not to find a precise value of D, but to use a comparative study, it is even more reasonable to use the basic thin film analysis. It can be shown that a semi-infinite system can be assumed for this .250" diffusion distance for diffusivitives as high as $8.9 \times 10^{-5} cm^2/sec$ if 3% reflection is allowed.

The copper acceptor concentration is determined from the conductivity data as follows. The four points of the probe are held parallel to the initial copper surface, at a distance L from the surface. With a point spacing of S the resistivity ρ is found as follows, as developed by Valdes (35).

$$\rho = \frac{V}{I} S\pi F_3(\frac{L}{S}) .$$

In this equation, V is the measured voltage in millivolts with a constant current I in milliamperes; $F_3(L/S)$ is a surface correction factor given as follows:

$$F_3(\frac{L}{S}) = \frac{1}{1 + \frac{2}{\sqrt{1 + (\frac{2L}{S})^2}} - \frac{1}{\sqrt{1 + (\frac{L}{S})^2}}} .$$

The number of carriers, either holes or electrons, is found from the relationship shown below:

$$n = \frac{1}{q\mu_n\rho} \quad \text{or} \quad p = \frac{1}{q\mu_p\rho} .$$

In the case of n-type material, n equals the number of electrons having a mobility μ_n equal to 3900 $cm^2/volt$ sec. With p-type germanium, p is the number of holes of mobility μ_p equal to 1900 cm^2/volt sec. The choice of mobility values agrees with the work of Prince (36) when no scattering of carriers from the copper is found. The value of the charge of the carriers is given by $q = 1.60 \times 10^{-19}$ coulombs.

In this study with unconverted n-type germanium the copper concentration is found from the following equation, when assuming one copper acceptor for each added hole:

$$\text{Cu acceptors} = N_i + N_f \quad \text{(for n-type Ge)} .$$

It is merely the difference between the initial (N_i) and final (N_f) electron carrier concentration. If the germanium converts from n-type to p-type, the copper acceptor concentration equals the sum of the original electron concentration (N_i) and the final hole concentration (P_f) as shown below:

$$\text{Cu acceptors} = N_i + P_f \quad \text{(for p-type Ge)} .$$

The final part of the calculations involves the thin film solution. This required the slope (m) of the ℓn c vs. distance x^2 curve which was related to the diffusivity (D) and diffusion time (t) as follows:

$$m = \frac{\delta \ln c}{\delta x^2} = - \frac{1}{4Dt}$$

and

$$D = - \frac{1}{4mt} \quad .$$

The minimum concentration level was subtracted from the concentration data, to provide a normal concentration gradient, which would reduce to zero as x approaches infinity. This solution was used by Fuller et al. (26). This corrected value of concentration was used in the thin film solution, and a linear regression analysis was performed on the $\ln c$ versus x^2 data to find the best value of slope m.

RESULTS AND DISCUSSION

The calculated diffusivities and important concentration data are presented in Tables I and II and averaged results are summarized in Table III. Also, typical copper acceptor concentration gradients are given in Figure 4. The diffusivities of copper acceptors in the temperature range of 692°C to 699°C, as shown in Table I, did not appear to significantly change with the applied ultrasonic straining. Figure 4 illustrates the consistency of the surface copper acceptor concentration and the similarity of the concentration gradients, for this temperature range, with and without ultrasonics. It is apparent that no significant increase in the surface acceptor concentration is caused by ultrasonics and therefore, this can be interpreted as no increase in substitutional copper atoms. The lack of response to ultrasonics can be explained by either no increase in vacancy concentration or no change in the recombination rate of vacancies and interstitial atoms. The increase in the minimum concentration level with ultrasonics will be examined in a subsequent discussion.

A substitutional copper solubility study was performed in order to determine possible changes in vacancy concentration and temperature of the germanium due to the applied ultrasonic straining. Fuller (32) found the ratio of copper acceptors to total copper to be a linear function of temperature. In particular, a 24% increase in this ratio occurs with a 50°C temperature increase from 700°C. In view of this, two bars of germanium were dipped into a 4% by weight copper nitrate solution for five minutes. One bar was diffused for one hour at 695°C without ultrasonics, while the second bar was diffused in the same manner with ultrasonic straining at a measured amplitude of 0.15 mils excursion. By using the four-point probe and a resistivity analysis, the original n carrier, final p carrier, and total acceptor concentrations in both bars were found to be uniform across the sections perpendicular to the longitudinal direction of the acoustical transmission line. This indicates even heating across these various sections. In all measurements, at various temperatures (i.e., longitudinal positions) the copper acceptor solubility with ultrasonics was equal to or less than the solubility without ultrasonic straining. This result leads to two important deductions. First, no additional vacancies are introduced since interstitial copper should combine with them to increase the acceptor concentration. Secondly, with no increase in the acceptor concentration the temperature rise must be insignificant, in view of the temperature dependence of the ratio of copper acceptors to total copper expressed by Fuller (32).

At a distance of 0.3 to 0.4 cm, the acceptor concentration reaches a, non-zero, minimum value as in Figure 4 for 695°C. An increase in this minimum level occurs with applied ultrasonics, the difference being 170% and 220% for a measured ultrasonic amplitude of 0.1 and 0.2 mils, respectively, for the average results of Table III. An increase in interstitial copper diffusivity, as explained below, may account for this.

According to Fuller (26), this minimum level is due to residual copper diffusing from the various exposed surfaces of the specimen. In spite of careful specimen preparation, it is possible that during previous manufacturing steps, traces of copper may have diffused into the germanium and precipitated during the zone refining heating and slow cooling cycles. Reheating of this type of material would result in diffusion of the copper from the precipitate in a homogeneous manner throughout the specimen. Homogeneous diffusion of copper from this source has been observed by Fuller (26) and the author suggests that this phenomenon may also account for the minimum level of copper acceptors observed without ultrasonics.

Based on the work of Frank and Turnbull (31), another explanation of this minimum level is possible. The effective copper diffusion in germanium is composed of both interstitial and substitutional modes of diffusion, where vacancies are required for the conversion of the interstitial to substitutional copper. Accordingly, it was stated by Frank and Turnbull that the interstitial copper diffusivity was $4 \times 10^{-3} cm^2/sec$, which is nearly two orders of magnitude higher than the effective diffusivity at 700°C. This high interstitial diffusivity accounts for the deviation from Fick's law at the depths beyond the p-n junction. Upon checking the conductivity type along the concentration gradient, using the conventional Seebeck effect, it was found that the p-n junction occurred at the minimum concentration value. Hence, it is assumed that the acceptor concentration obtained at depths greater than the p-n junction is due mostly to the high diffusivity interstitial copper.

According to an analysis of the thin film solution for these specimens of 0.250" diffusion depth after 480 seconds at 700°C, pure interstitial diffusivities of $4 \times 10^{-3} cm^2/sec$ would result in 74% of the interstitial copper being reflected from the surface opposite the original thin film. Reflection is due to the impermeable boundary (the opposite surface) for the diffusing interstitial copper atoms at this depth and a resulting build-up of interstitial copper concentration within the specimen. Hence, in effect, 74% of the interstitial copper is increasing the apparent concentration within the specimen rather than diffusing to an infinite distance as in the theoretical thin film analysis. This phenomenon is mathematically treated as a reflected diffusion gradient. The reflection of interstitial copper would tend to occupy vacancies in a near homogeneous manner throughout the sample and result in the minimum level as shown in Figure 4 without ultrasonics. Following this concept it is reasonable that ultrasonics would enhance the interstitial diffusivity of copper and thus increase the minimum levels as experienced during this study. The increase in the minimum level of approximately 4×10^{14} acceptors/cc is about 16% of the surface concentration and hence the effect of this increase is to some extent masked by the variances of the data at higher concentration due to experimental error. However, in Figure 4, a nearly homogeneous increase in acceptor concentration of this magnitude is observed for 695°C with 0.2 mils ultrasonic amplitude, while the surface concentration essentially remains constant as discussed before.

A study of acceptor diffusion at 496°C also can be interpreted as evidence of the enhancement of interstitial diffusion with ultrasonics. As shown in Figure 4 for 496°C, the concentration gradient is grossly different with applied ultransonics and the calculated diffusivity is greater by a factor of five (Table III). However, these diffusivity values are questionable since a thin film solution is not strictly valid. The concentration curve of Figure 4 shows a near constant concentration of acceptors up to a distance of 0.2 cm before a reduction occurs and appears as a constant source. However, the gradient at a depth greater than 0.2 cm appears to have a slope similar to the other diffusion gradients, with and without ultrasonics at both 496°C and 695°C. Hence it is deduced that the effective diffusivity is not altered significantly with ultrasonics at 496°C. It is also apparent from Figure 4 that an order of magnitude greater concentration is reached at a depth of 0.2 cm when ultrasonics is applied. This concentration of the order of 3×10^{14} acceptors/cc is greater than the solubility of 1×10^{14} atoms/cc found by extrapolating Fuller's (26) data at 496°C. However, his solubility data below 650°C was determined from concentration data obtained from a study of diffusion by the motion of the p-n junction and thus the validity of the 1×10^{14} atoms/cc value is questionable. The slight increase in surface concentration as shown in Figure 4 could arise from an enhancement of equilibrium with ultrasonics, but in general the concentration increase is deduced to be a result of enhanced interstitial diffusivities as examined previously for 695°C. A minimum concentration level for 496°C was not measured due to the poor resolution by the equipment used at this acceptor level. It is thus proposed that ultrasonic energy enhances the pure interstitial diffusivity of copper to the point that saturation is reached during the time of the experiment as a result of the low solubility at 496°C. This can explain the change in shape of the concentration curve with ultrasonics in Figure 4.

It is apparent that the interstitial diffusion of copper in germanium is enhanced with ultrasonics. Since no increased temperature or vacancy concentration was caused by ultrasonics during the acceptor solubility study, it is unlikely for diffusion to be enhanced by an excess of vacancies created by the high strain rate of ultrasonics or from local temperature effects. Therefore, a change in lattice parameters is suggested as the mechanism of interstitial diffusivity enhancement, as discussed in the "Hypothetical Explanations" section of this study.

Boltaks (22) reports his work with Sozinov, whereby the diffusivity is studied with radioactive copper from 600°C to 900°C. It is shown that above 700°C, D is of the order $10^{-5} cm^2/sec$ while below this temperature D varies from $10^{-11} cm^2/sec$ at 600°C to $10^{-9} cm^2/sec$ at 700°C. It is thus indicated that a sharp discontinuity exists from substitutional to interstitial at 700°C. However, the data obtained in this study supports van der Maesen and Brenkman (29) who suggest the continuous transition from substitutional to interstitial copper with an increase in temperature. As illustrated in Table III, the acceptor diffusivity decreased to $0.661 \times 10^{-5} cm^2/sec$ upon decreasing the temperature to 496°C with a reduction in surface concentration. It is noted that the order of magnitude of effective diffusivity is still $10^{-5} cm^2/sec$, suggesting that interstitial copper diffusivity is still operative down to 496°C. No measurable acceptor diffusivity was found at 445°C, indicating that interstitial diffusivity was either not operative or not detectable with the equipment used.

SUMMARY

It was the objective of this endeavor to achieve a better understanding of the effects of ultrasonics on solid state diffusion. The selection of the copper-germanium diffusion couple was beneficial in many respects because of its unique characteristics. In this respect the effects of ultrasonic energy on the temperature and structural properties of germanium during diffusion of copper were either measured or deduced from the experimental data. However, because of the interaction of many physical properties of this system, the validity of the conclusions listed below should be checked with more conventional materials. One apparent disadvantage of this couple is that the direct analysis of either interstitial or substitutional diffusion is not obtained. The acceptor diffusivity measured is the sum of an interstitial and substitutional component of copper diffusion.

The following remarks are restricted to the diffusion of copper into germanium in the temperature range of 500°C to 700°C. Where ultrasonic energy was applied, the maximum strain amplitude was approximately 0.001 at 40 Kcps.

(1) It is concluded that ultrasonic straining had no significant effect on the diffusivity of copper acceptors. Evidence of this was shown

in the similarity of diffusion gradients of samples diffused with and without ultrasonic energy and also through a comparison of results of the thin film analysis.

(2) It was demonstrated that the solubility of copper acceptors is not increased by the application of ultrasonic energy. This was verified with a solubility study and the similarity of surface concentrations of the diffusion gradients.

(3) It is postulated that ultrasonics did not introduce point defects in an amount sufficient to enhance substitutional copper diffusion and thus dislocations were not introduced or caused to intersect to any significant degree. This indicates that an excess of vacancies is not generated as a result of the high strain rate associated with ultrasonics. The basis for this proposition was the acceptor solubility and diffusion data obtained for this system which had been reported to be extremely structure-sensitive.

(4) From a consideration of the copper acceptor diffusion gradients and a solubility analysis, it was deduced that there was no significant temperature increase in the germanium due to ultrasonic cyclic straining of the crystalline lattice. This was based on the work of Fuller and Ditzenberger (32), whereby an increase in temperature of the germanium during diffusion resulted in a proportional increase in the ratio of copper acceptors to the total number of copper atoms.

(5) It is suggested that ultrasonic energy enhances the interstitial diffusion of copper by altering the lattice parameters of the germanium crystal structure. This was described as a geometric and probability effect and was illustrated by an increase in the minimum acceptor concentration level by ultrasonics.

(6) The copper acceptor diffusivity was determined to be of the order $10^{-5} cm^2/sec$ for temperatures from 700°C to 496°C. No measurable acceptor diffusivity was found at 445°C. Hence there

appears to be no step function for the change from substitutional to interstitial diffusion of copper in germanium at 700°C as suggested by Boltaks (22). Acceptor diffusivity of this magnitude down to 500°C supports the concept of van der Maesen and Brenkman (29) whereby a continuous transfer from substitutional to interstitial diffusion occurs with the quantity of each mode varying with temperature.

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Table I

Diffusion and Concentration Data for $T > 600$°C at 480 sec

Specimen Number	Position from end 1"	1¼"	1½"	Hall Amplitude mils	Surface Concentration	Minimum Concentration	Diffusivity
	Temp °C 692	699	692		(Cu-Acceptors/cc) × 10^{15}		$\text{cm}^2/\text{sec} \times 10^{-5}$
1	*			---	2.30	0.18	1.700
		*		---	2.50	0.14	1.980
			*	---	2.10	0.14	1.907
2	*			---	2.35	0.21	1.765
		*		---	2.30	0.17	1.936
			*	---	1.95	0.14	2.156
3	*			0.1	2.15	0.45	1.508
		*		0.1	2.30	0.26	1.819
			*	0.1	1.95	0.15	2.187
4	*			0.1	2.25	0.60	1.084
		*		0.1	2.65	0.60	1.208
			*	0.1	2.35	0.58	0.996
5	*			0.2	2.45	0.45	1.773
		*		0.2	2.40	0.37	1.648
			*	0.2	1.98	0.45	1.899
6	*			0.2	2.35	0.65	1.179
		*		0.2	2.45	0.48	1.577
			*	0.2	2.00	0.33	2.028
7	*			0.2	2.40	0.62	1.189
		*		0.2	2.35	0.64	1.347
			*	0.2	1.95	0.68	1.428

Table II

Diffusion and Concentration Data for T < 600°C at 480 sec

Specimen Number	Position from end 1"	1¼"	1½"	Temp. °C	Hall Amplitude mils	Surface Conc. (Cu-Acceptors/cc × 10^{14})	Conc. at 0.2 cm (Cu-Acceptors/cc × 10^{14})	Minimum Conc. (Cu-Acceptors/cc × 10^{14})	Diffusivity cm^2/sec × 10^{-5}
8	*			586	----	9.3	3.10	0.95	1.710
		*		589	----	9.3	3.50	0.55	2.800
			*	586	----	7.7	3.50	1.55	1.845
9	*			528	----	2.8	0.80	0.45	1.025
		*		531	----	2.6	0.80	0.45	1.218
			*	528	----	2.0	0.90	0.37	1.704
10	*			494	----	---	----	----	-----
		*		499	----	1.0	0.20	0.04††	1.385†
			*	494	----	1.0	0.15	0.10††	0.741
11	*			494	----	2.2	0.25	0.10††	-----
		*		499	----	2.6	0.25	0.10††	0.468
			*	494	----	2.6	0.25	0.10	0.774
12	*			494	0.20	3.0	0.80	0.50	1.017
		*		499	0.20	3.0	0.80	0.50	1.126
			*	494	0.20	---†	0.80	0.10††	-----†
13	*			494	0.20	---†	2.50	0.10††	-----†
		*		499	0.20	2.8	2.50	0.10††	2.720
			*	494	0.20	2.8	2.00	0.10††	3.590
14	*			494	0.20	2.9	1.70	0.10††	4.770
		*		499	0.20	2.2	0.80	0.10††	4.780
			*	494	0.20	2.3	0.80	0.10††	-----†
15	*			440	----	---	----	----	-----
		*		448	----	---	----	----	-----
			*	440	----	---	----	----	-----
16	*			440	0.17	---	----	----	-----
		*		448	0.17	---	----	----	-----
			*	440	0.17	---	----	----	-----

†Scatter in Data ††Estimated Values

Table III

Average Values of Significant Results

Temperature °C	Hall Amplitude mils	Surface Conc.	Conc. at 0.2 cm	Minimum Conc.	Diffusivity $cm^2/sec \times 10^{-5}$
		Cu-Acceptors/cc × 10^{14}			
445	----		No apparent diffusion		
445	0.17		No apparent diffusion		
496	----	1.9	0.22	0.09	0.661
496	0.20	2.7	1.40	0.10	3.000
530	----	2.5	0.83	0.42	1.320
587	----	8.8	3.40	1.01	2.120
695	----	22.5	----	1.63	1.907
695	0.10	22.8	----	4.40	1.467
695	0.20	22.6	----	5.19	1.563

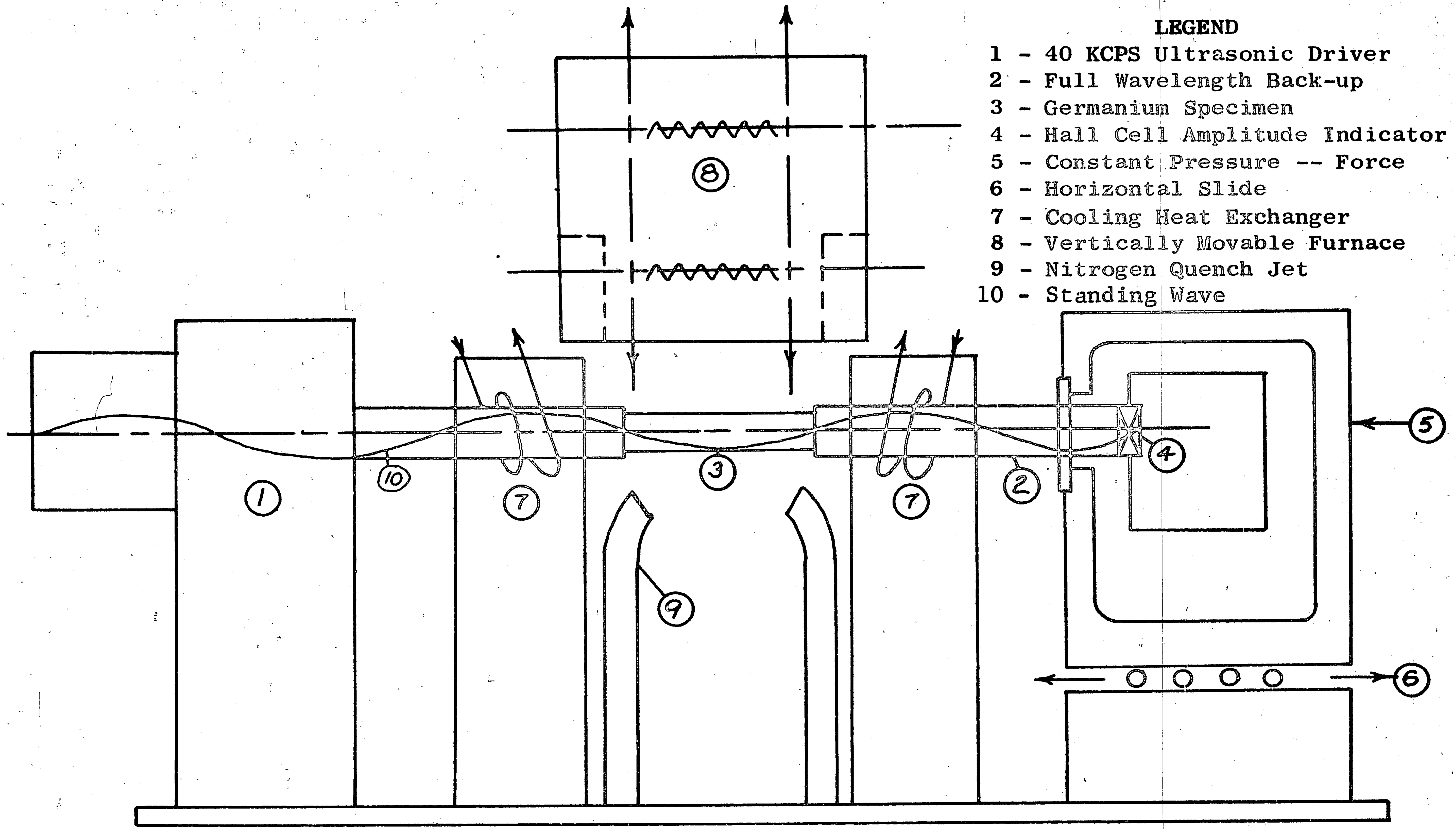

Figure 1

Schematic Illustration of Ultrasonic Diffusion Equipment

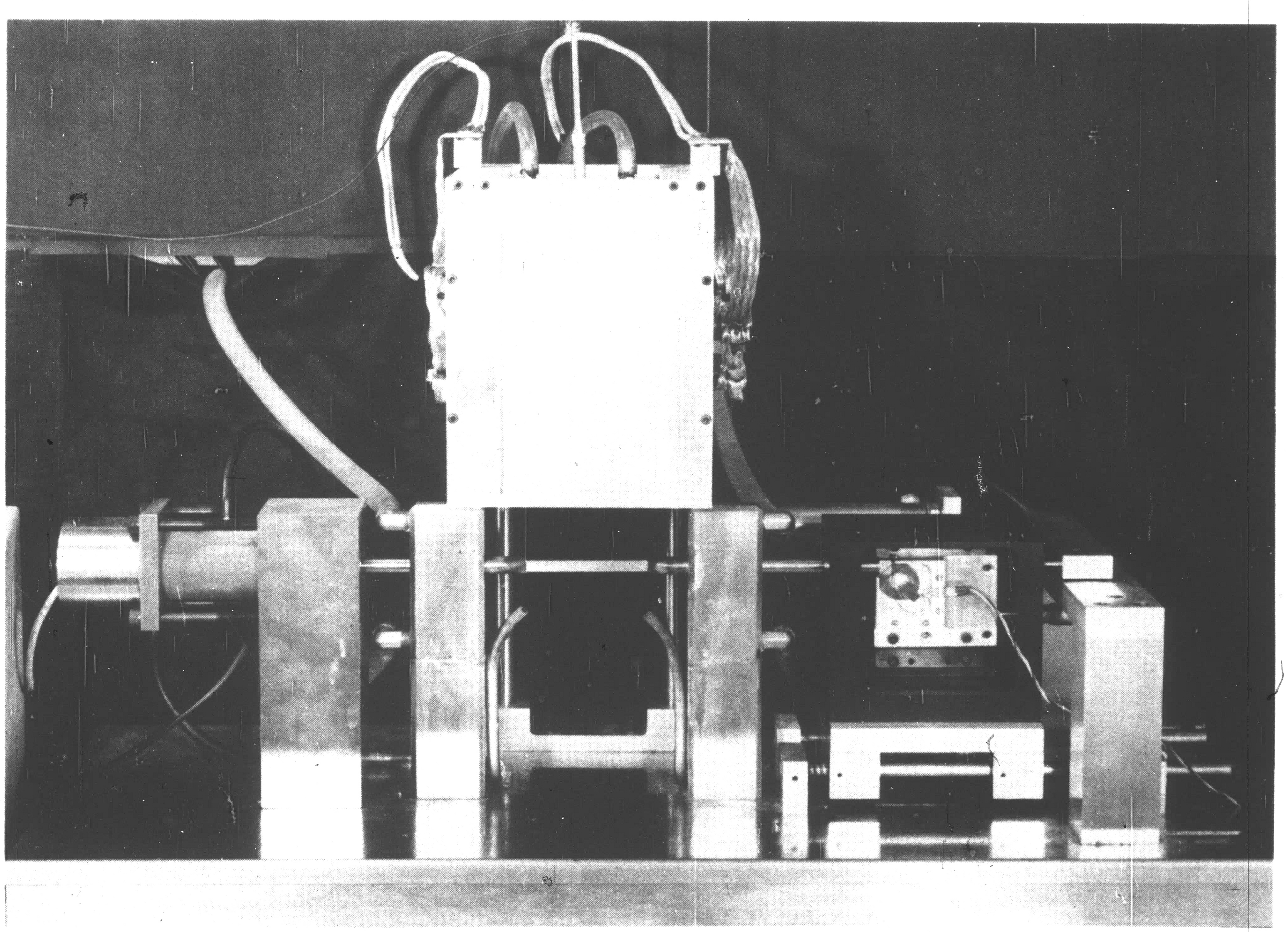

Figure 2

Ultrasonic Diffusion Apparatus Used with Furnace in Raised Position

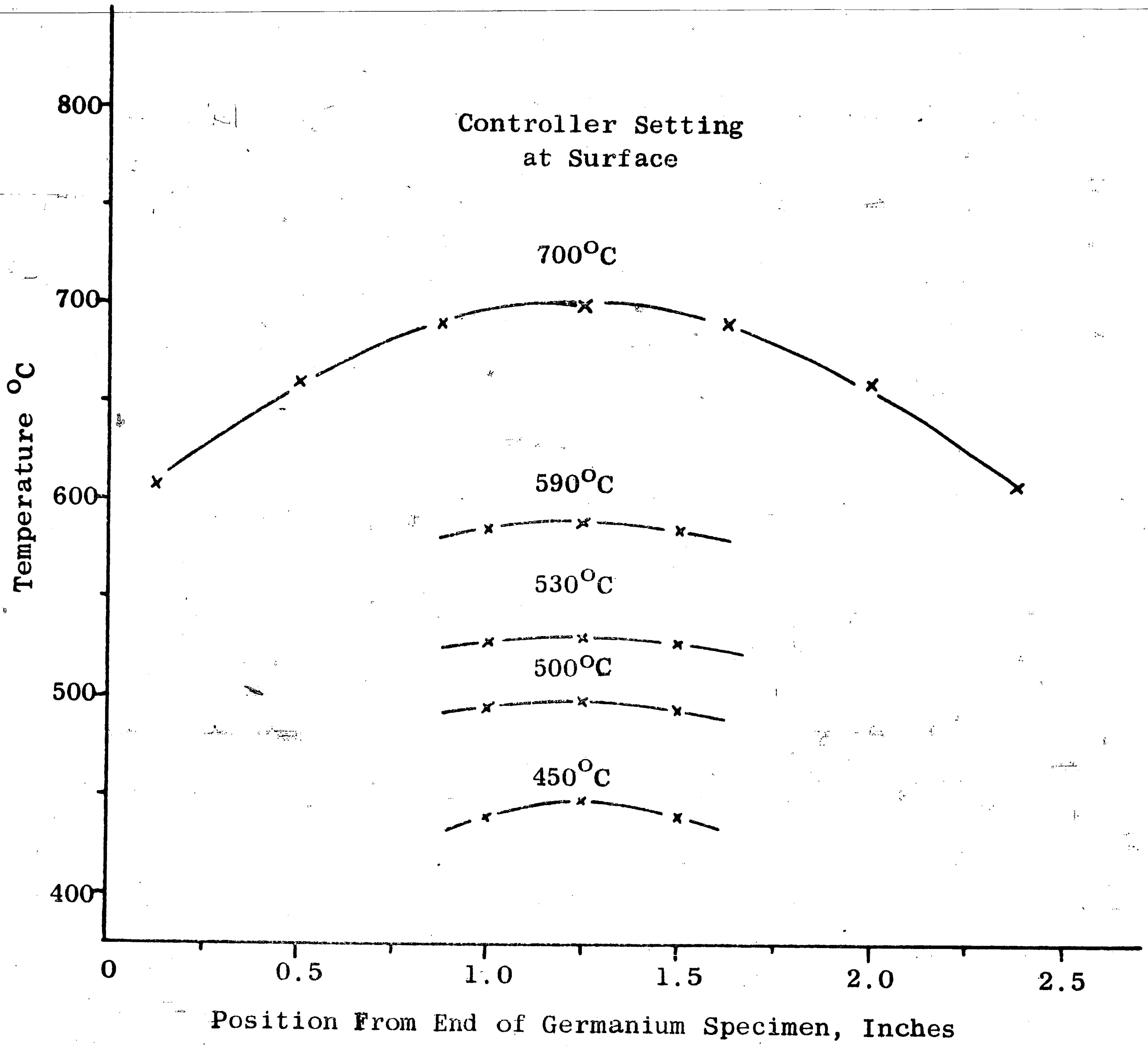

Figure 3

Specimen Temperature Gradients for Various Controlled Temperature Settings

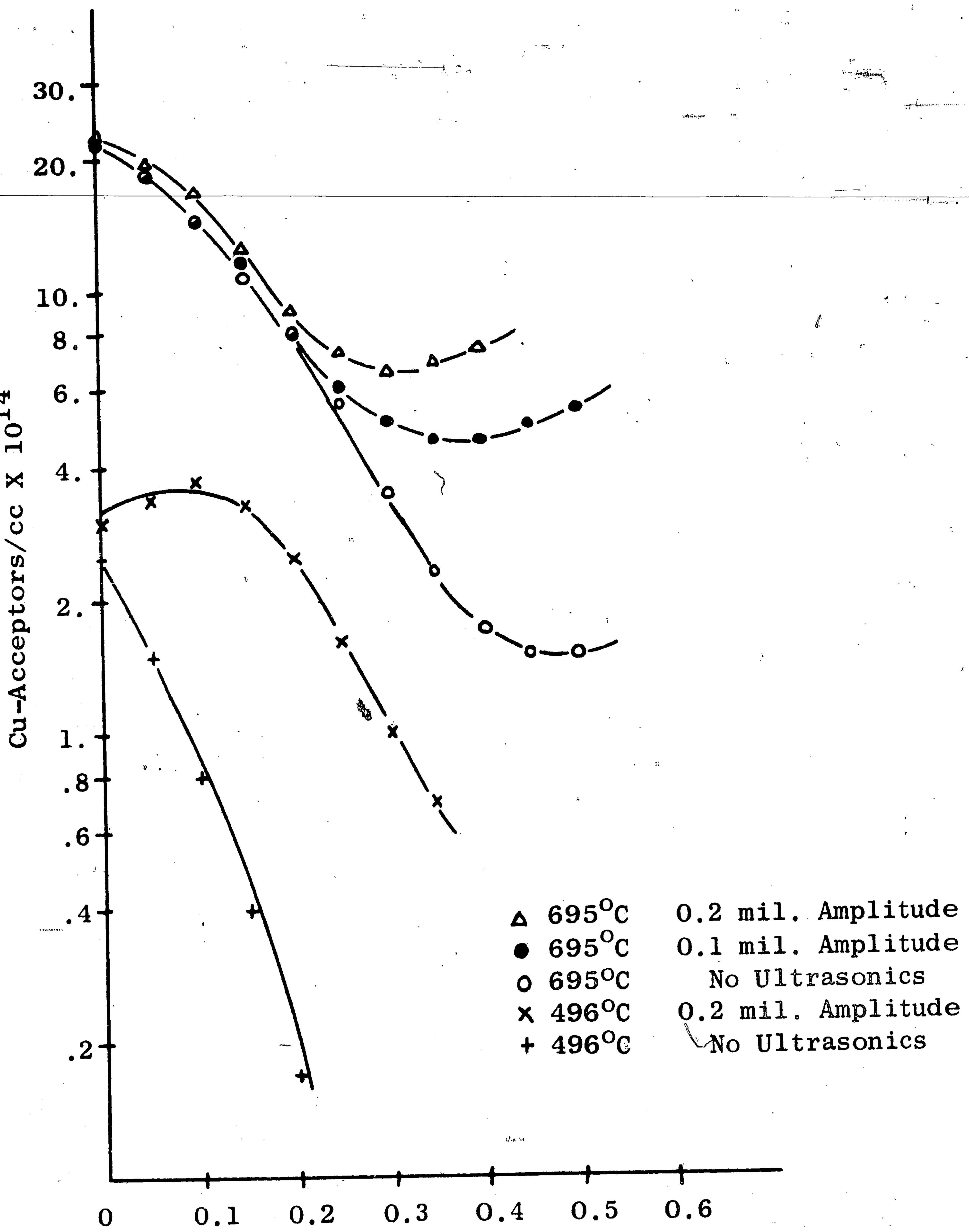

Figure 4

Typical Acceptor Concentration Gradients
With and Without Ultrasonics at 695°C and 496°C

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