INTERNAL FRICTION IN INTRINSIC
AND N-TYPE GERMANIUM AND SILICON

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The dependence of the high temperature internal friction of germanium and silicon, intrinsic and highly n-type, has been measured as a function of temperature, frequency, dislocation density, and dopant concentration. Two features found in the internal friction spectrum were investigated.

At moderate temperatures in both materials, when not too highly doped, there appears a peak, the features of which are independent of dislocation density, due to the acousto-electric effect. The acousto-electric peak in both germanium and silicon was found to agree well with the theory of Weinreich.³¹ The mechanism believed to be responsible for the excess free charge carrier lifetime in both materials is Auger band-to-band recombination; however, the theoretical and experimental treatments of Auger recombinations are as yet insufficient for a positive identification.

The high-temperature dislocation-dependent damping in intrinsic and intrinsic behaving germanium and silicon was found to agree well with most previous studies.^{13,14,15,16,18,19,20} If deformed at high temperature and allowed to anneal highly doped, n-type material behaved intrinsically due to preferential precipitation at dislocations. If deformed at minimum temperatures and not allowed to anneal, a greatly enhanced dislocation-dependent internal friction was found which depended upon the extrinsic carrier concentration.

A theory was developed for the dislocation damping in semiconductors and was found to agree well with experimental results. The model is based upon electronic viscous damping of dislocations by excess current carriers whose lifetimes are controlled by Auger recombination processes.

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I. INTRODUCTION

The elemental semiconductors germanium and silicon are the highest quality materials available for experimental research today. Large single crystals that are nearly perfect or even dislocation free, with extremely low point defect concentration, are routinely produced not only for scientific study as is generally the destination of high quality monocrystals but also for the mass production of electronic devices. The high quality of these crystals and their strong resistance to plastic flow at room temperature make them almost ideal materials from an experimental standpoint for the study of plastic flow.

Germanium and silicon, however, are definitely not structural materials, and therefore studies of their mechanical properties provide little direct benefit to applied technology. What they do represent though is a "model" material for the understanding of many of the much more complicated high strength, high temperature materials of today.

The extremely strong, highly directional covalent bonding in these crystals is responsible for the presence of a relatively large Peierls potential. As a result of this, dislocations are expected to move by the processes of double-kink nucleation and the subsequent lateral migration of abrupt kinks. The relative importance and the details of the specific mechanisms of these two processes, however, are not well understood. This is especially true for the process of lateral kink migration along the dislocation.

It is generally believed that during internal friction measurements, at least at KHz frequencies and above, not enough energy is supplied to a dislocation from the acoustic wave for the process of double-kink nucleation to occur. Dislocation-related internal friction therefore is thought to arise from either the individual or collective lateral motion of grown-in kinks along the dislocation.

The following is a report of an extensive experimental study of the high temperature dislocation damping present in deformed crystals of both germanium and silicon as a function of temperature, dislocation density, frequency, and n-type dopant concentration. A qualitative theoretical model based upon the interaction of a moving dislocation with its electronic environment is developed and supported by the results of this study. During the course of the research it became apparent that the acousto-electric peak found in these materials may provide some insight into the mechanisms of the high temperature, dislocation damping and therefore the dependence of this peak upon various parameters has also been studied.

II. REVIEW

A typical example of the high temperature internal friction spectrum found in deformed crystals of both germanium and silicon is provided by the 40 Ω cm, bent germanium data of figure 1. With increasing temperature the first damping encountered is the non-dislocation related, acousto-electric peak. As the temperature is increased a damping arises that is proportional to dislocation density, inversely proportional to measurement frequency, and exponentially increasing with temperature.

This chapter is designed to provide the reader with a minimal amount of specific background material believed helpful in understanding the study of the high temperature internal friction in germanium and silicon reported here. We will begin by a discussion of the general form and origins of the dislocation related damping believed applicable in germanium and silicon, and of various theoretical models proposed to explain the damping. In general, previous experimental work on intrinsic material agrees well with the form of the internal friction spectrum of figure 1 and therefore will be discussed later in comparison to the present study. Section B of this chapter will be a discussion of the acousto-electric peak whereas section C will be concerned with electrical effects of dislocations in semiconductors. Throughout this report we will be referring specifically to 60° edge-type dislocations unless otherwise stated.

A. Dislocation Damping

The bonding of germanium and silicon occurs through the presence of strong, highly direction covalent bands. Electron microscopic^{1,2} and X-ray topographic^{3,4} studies in these materials have revealed an extremely strong tendency for dislocations to lie along the $\langle 110 \rangle$, close-packed directions. Peierls potential barrier calculations^{5,6} have predicted the presence of a relatively

Figure 1. Typical specimen data for high temperature internal friction measurements. The data were taken on a deformed 40 Ω cm germanium crystal at 50 KHz. The background damping has been subtracted.

large Peierls barrier in monopolar semiconductors. On the basis of such evidence as that mentioned above dislocation motion in germanium and silicon is believed to occur through the mechanism of double-kink nucleation and subsequent lateral abrupt kink migration⁷. Measurements of dislocation velocities^{8,9,10,11} using the Johnston and Gilman¹² etch pit technique have found a close correspondence between the activation energy of long range dislocation motion and the calculated energies of double-kink nucleation. Since the Peierls barrier calculations^{5,6} have predicted a relatively small ($< .1$ ev) migrational energy for kink motion along the line, the correspondence of measured and calculated energies have led many authors^{8,9,10,11} to conclude that long range dislocation motion is controlled entirely by double kink nucleation.

Measurements of the high temperature, dislocation dependent internal friction found in germanium^{13,14,15,16,17} and silicon^{14,18,19,20} have smaller activation energies than those found by etch pit measurements (~ 1.1 ev as compared with 1.6 ev for germanium and ~ 1.6 ev as compared with ~ 2 ev for silicon). Because of this many authors^{7,16,19,20,21} have concluded that the energy supplied to the dislocation by an acoustic wave during KHz internal friction measurements is too small for the nucleation of double-kinks and therefore that the form of motion studied is that of lateral migration of "grown-in" kinks along the line. The dislocation dependent internal friction in germanium and silicon therefore arises from frictional losses occurring as a result of lateral motion of abrupt kinks acting either individually, or collectively. By individually we mean losses that may occur by some kink inhibition confined to the dislocation core, whereas collective kink action losses may be interpreted as arising from motion of the dislocation as a whole. Both of these concepts have been used in the past to interpret high temperature dislocation damping, and particular treatments will be discussed after an additional,

useful simplifying assumption is made through application of the Granato-Lücke²² theory.

The Granato-Lücke²² theory of dislocation damping has proved to be an extremely useful tool for the interpretation of dislocation-related internal-friction measurements in a great variety of materials. Its applicability in the case of germanium and silicon where dislocation motion under high temperature KHz internal friction conditions is generally believed to occur solely through the motion of grown-in kinks along the line, has been indicated by several authors.^{19,23} The model draws an analogy between a dislocation and a damped, elastic string and predicts a maximum in the frequency dependence of the dislocation-dependent internal friction. At low frequencies a dislocation is underdamped and moves as depicted in figure 2a. The damping in this case is proportional to frequency. At high frequencies however the dislocation behaves in an overdamped manner (figure 2b), and damping is proportional to the inverse of the frequency. In an overdamped condition the dislocation can be viewed as moving as a straight line, and the magnitude of the damping is controlled entirely by viscous drag, independent of line tension and pinning length.

Previous measurements,^{14,15,16,19,20} in agreement with the study reported here, have shown that the KHz frequency range dislocation dependent damping is proportional to inverse frequency and independent of strain amplitude. This allows us, under assumption of the validity of Granato-Lücke²² theory, to ignore the presence of pinning points or line tension and conclude that the measured damping is due entirely to viscous drag. This simplified approach will be taken in the following discussion.

Such authors as Kessler,²⁴ Southgate and Attard,¹⁹ and Nonomiya, Thomson and Garcia-Moliner²¹ have proposed models that have been applied to the high temperature dislocation damping in germanium and silicon. Kessler²⁴ has

Figure 2. Schematic of dislocation displacement under Granato-Lücke theory;²² a) low frequency, underdamped; b) high frequency, overdamped.

suggested a model in which small vibrations of dislocation line segments cause displacements in the point defect distribution (Cottrell atmosphere²⁵) surrounding the dislocations. The energy lost through the motion of the point defects, which were concluded to be vacancies, then gave rise to the mechanical damping. Kessler's theory was developed however before the frequency dependence of the high temperature damping was known. To achieve the proper temperature dependence, i.e. increasing logarithmic decrement with increasing temperatures, it was necessary under Granato-Lücke theory to assume the undamped case. If Kessler's model is applied to an overdamped dislocation, as applicable in these materials, damping should decrease with increasing temperature which is certainly not the case.

Southgate and Attard¹⁹ attributed the damping as due to the lattice resistance to the lateral motion of a single abrupt kink along the line. They suggest that the movement of an abrupt kink from one Peierls barrier of the second kind²³ to another may involve some sort of bond breaking and therefore may require migrational energies comparable to that of the covalent bond energy. Under this model migration becomes a rather difficult process resulting in relatively slow velocities. This of course disagrees with the view of high kink velocities taken by many authors during the interpretation of studies of dislocation etch pit velocities^{8,9,10,11} and with the behavior predicted through Peierls potential barrier calculations.^{5,6} It is also quite difficult for their model to account for the strong dependence of dislocation damping upon electrically active dopant concentration found during the present study and described in detail in a later section.

Ninomiya, Thomson, and Garcia-Moliner²¹ have proposed a model based upon the interference of lateral kink motion caused by the presence of mobile dragging points located on the dislocation. This model also predicts a rather low

resultant kink velocity and also encounters difficulties in explaining the strong dopant concentration dependence found here.

B. Acousto-Electric Peak

Relatively little work has gone into the investigation of the acousto-electric effect in monopolar semiconductors. This is in contrast to the extensive effort centered around the measurement of the same effect in piezoelectric semiconductors such as the III - V compounds where the effect is much larger (for an excellent review the reader is referred to McFee²⁶). Much of the work that has been done in germanium or silicon has been concerned primarily with the coupling of shear waves to free electrons through intervalley scattering below room temperature.^{27,28,29} The only investigation of acousto-electric effect at high temperature in monopolar semiconductors that the author is aware of is the work of Southgate³⁰ who was primarily concerned with dislocation damping. This peak, found originally in germanium by Kessler¹³ was identified by Southgate.³⁰

The term "acousto-electric effect" refers specifically to the appearance of a d.c. electric field along the direction of propagation of a traveling acoustic wave in a medium containing mobile charges, but we shall use the term to describe the general effects of the interaction of acoustic waves with current carriers. The development of the theory in monopolar semiconductors is primarily due to Weinreich, et al.,^{27,31} and their analysis will be followed here.

As a simple explanation of the effect we can consider the following picture proposed by Weinreich, et al..²⁷ With a spatially variable potential supplied by the acoustic wave through the deformation potential, the current particles will tend toward an equilibrium distribution which favors the regions of lower energy. The exact attainment of this distribution is, however, precluded by the fact that the wave is in motion and a finite time is required for the particles to reach

equilibrium. The particle distribution will therefore always lag behind the equilibrium distribution. For very low values of $\omega\tau$, where ω is the wave frequency and τ the relaxation time of the distribution, the distribution will be very close to equilibrium, whereas for high values the distribution will be almost unaffected by the acoustic wave.

Fortunately since attainable acoustic wavelengths are much larger than carrier mean-free-paths and the periods much longer than mean-free-times we can treat the problem classically. Specifically we can use the macroscopic current equation with the continuity equation to calculate the redistribution of carriers which takes place when an external field is applied in the form of an acoustic wave and then determine the effect of the nonequilibrium carrier distribution on the acoustic wave through the wave equation.

To avoid space-charge difficulties Weinreich³¹ considered not only the deformation potential, but also the force exerted by electric fields resulting from the redistribution of charges. In metals, since there is only one type of carrier available, the electric field essentially cancels the deformation field resulting in extremely small acousto-electric effects. However, in semiconductors since both positive and negative current carriers are present rather large nonequilibrium distributions of excess carriers can occur. Therefore Weinreich³¹ uses the common approximation, which is valid when the period of the wave is much longer than the dielectric relaxation time and the acoustic wavelength much larger than a Debye length, that charge neutrality is maintained exactly, and that the electric fields necessary for this purpose are set up automatically and instantaneously.

Using the above scheme Weinreich²⁸ calculates the logarithmic decrement, δ , in the KHz frequency range and with zero applied electric field as,

$$\delta = \frac{q^2 \pi}{kT} \frac{s}{1+s} n_i \left(\frac{\omega \tau}{1+(\omega \tau)^2} \right) \quad (1)$$

where $q = q_n + q_p$ = the sum of the effective acoustic charge of electrons and holes, $S \equiv n_o/p_o$ where n_o and p_o are the equilibrium concentration of holes and electrons and n_i is the intrinsic carrier concentration.

In 1960 Southgate³⁰ reinvestigated the peak originally found in germanium by Kessler¹³ and discovered a complementary peak in silicon. These peaks, located around 650°C in silicon and 400°C in germanium at 100 KHz (56% of the melting point in both materials) were identified by him as due to the acoustic-electric effect.

To analyze the experimental data according to equation (1) Southgate³⁰ assumed that the total carrier lifetime was made up of an intrinsic, temperature dependent lifetime, τ_i , of the form,

$$\tau_i = \tau_o e^{E_{\tau}/kT}$$

and extrinsic excess carrier lifetime, τ_e , of the form of the Shockley-Read³² type trapping mechanism which is only slowly temperature dependent. The total excess carrier lifetime, τ_t , is then given by,

$$\frac{1}{\tau_t} = \frac{1}{\tau_i} + \frac{1}{\tau_e}$$

On the low temperature side of the peak, if $\tau_e \ll \tau_i$, τ_e will control the damping and it will have a temperature dependence described by $\exp(-E_g/kT)$, where E_g is the band gap energy. If $\tau_e \gg \tau_i$ the low temperature damping will have the form $\exp[-(E_g + E_{\tau})/kT]$. On the high temperature side of the peak and at the peak temperature it is unlikely that $\tau_e < \tau_i$ (except in the case of extremely low room temperature excess carrier lifetime, i.e. $\tau_e < 1/\omega$). If this is indeed

the case the peak temperature is not dependent upon the extrinsic excess carrier lifetime and this was indeed found to be the case in most of the germanium and silicon samples used by Southgate³⁰ and in the germanium samples of Calzecchi, et al.^{15,16}

The activation energy for the intrinsic excess carrier lifetime in silicon, as determined by the slope of the high temperature side of the acousto-electric peak, was found by Southgate³⁰ to be 1.45 ev. However, Southgate³⁰ expressed some concern over the accuracy of this value since it had been obtained by curve-fitting over a fairly small temperature range because of the interference of the high temperature oxygen peak occurring in many of his specimens. In germanium the excess carrier lifetime determined by the same curve fitting procedure by Southgate³⁰ was 1.15 ev. Through measurements of the temperature shift of the peak with applied vibration frequency Kessler¹³ and Calzecchi, et al.^{15,16} have found an activation energy of 1.1 ev. Therefore much more confidence can be placed in the germanium value.

Southgate³⁰ was not able to determine from the measured activation energies in both germanium and silicon what the mechanism of intrinsic excess carrier lifetime was. Unfortunately no measurements of the high temperature excess carrier lifetime were available (which to the author's knowledge is still true) and he was not able to identify these activation energies with any theoretical models.

C. Electrical Properties of Dislocations

Although it had been known for some time that defects strongly influence the electrical properties of semiconducting materials, it wasn't until 1952 that Gallagher,³³ while showing that both germanium and silicon could be plastically deformed at elevated temperatures, also noted that in the deformed regions of

n-type germanium the resistivity was increased and the lifetime of photo-injected carriers was sharply reduced. Shortly after this, the development of etch pit techniques in germanium by Vogel, Pfann, Cory and Thomas³⁴ provided an experimental tool which brought the prospects of studying the electrical effects of various controlled arrays of dislocations in semiconductors.³⁵

Schockley³⁶ then proposed his dangling bond model to account for the electrical effect of dislocations in semiconductors. Until recently, this model has dominated the interpretation of most of the experimental results. The model proposed, based largely on geometrical arguments, the existence of a row of unsatisfied or "dangling bonds" located along each atomic position of the bottom of the extra half-plane associated with a pure edge or 60° edge dislocation. These dangling bonds introduce acceptor-like states from the valence band into the band gap. The acceptor centers associated with the dangling bond of an edge-type dislocation differ from other acceptor centers, such as the group III impurities, in that they are not uniformly distributed throughout the lattice but form a line of acceptors, spaced only a few angstroms apart. This opens the possibility of a one dimensional band of "edge-states" analogous to the two-dimensional surface state bands and negates the use of the normal occupation statistics for acceptors due to the electrostatic interaction of electrons occupying the dislocation acceptor states.

As opposed to an edge-type dislocation a perfect screw dislocation contains no dangling bands and therefore should remain electrically neutral in the semiconductor. However, in real crystals, screw dislocations will possess a certain number of edge-type kinks which contain dangling bands. Therefore the electrical properties of imperfect screw dislocations in semiconductors may be somewhat like that of "weak" edge-type dislocations depending upon their degree of perfection.

Pearson, Read, and Morin³⁷ performed the first controlled experiments on the electrical effects of dislocation arrays introduced by plastic bending at elevated temperature in germanium. Measurements were made of conductivity, Hall effect, and excess carrier lifetime in n and p-type specimens with various dislocation densities. They found that n-type material was strongly affected by dislocations while a negligible effect occurred in p-type material. From this it was concluded that deformation introduces acceptor type energy levels in the vicinity of .2 ev below the conduction band, and that these levels are probably associated with Shockley's dangling bands³⁶ on edge dislocations.

Following this such authors as Read,^{38,39,40,41} Broudy and McClure,⁴² and Broudy⁴³ began the development of theoretical models concerning the occupation statistics and effects of dislocations on the free carrier mobilities in semiconducting materials. An edge type dislocation was viewed, under the Shockley dangling band model³⁶ as having a single level or very narrow band. As the dislocation acceptors accept electrons, the dislocation line becomes negatively charged and a space charge region develops around the dislocation. If we imagine that a dislocation is suddenly introduced into n-type material where the Fermi level lies above the energy level of the dislocation acceptors, then the acceptors will begin to fill. Initially the decrease in the free energy of the system will be proportional to the number of electrons that have dropped from the conduction band into the dislocation acceptors. The electrostatic energy of the negatively charged line is proportional to the square of the number of accepted electrons in the line. Thus eventually the acceptors become filled to a point where the increase in electrostatic energy makes it energetically unfavorable to add more electrons to the dislocation.

At non-zero temperatures the various models differ in the entropy term of the free energy. They all, however, fall between the values of the following two extreme approximations. The minimum energy approximation, approached at

sufficiently low temperature or high f , assumes the electrons all take their minimum energy position (i.e., even spacing along the line) and therefore the entropy vanishes (since there is only one configuration of even spacing). Whereas the above approximation provides a measure of the minimum occupation, a maximum value of occupation can be obtained by assuming maximum entropy (labeled Fermi statistics by Read) which is valid at sufficiently high temperature and low occupation. Under this approximation the entropy is calculated assuming completely uncorrelated occupation (i.e., no interaction between neighboring electrons) whereas the enthalpy is the same as before and does consider the electrostatic interaction energy. The various models for the occupation statistics were designed under a low temperature approximation in that the screening of the dislocation charge is assumed to occur entirely through the presence of ionized impurity atoms. At high temperatures however screening will occur primarily from the presence of free charge carriers; unfortunately a treatment of the occupation statistics for this case has not been attempted.

A rather extensive effort employing such experimental techniques as conductivity, Hall effect, optical absorption, intrinsic and extrinsic photoconductivity and magneto resistance has gone into the search for the position of the dislocation acceptor energy level, based on the Schockley dangling bond model. A tremendous disagreement between various authors exists, and reported values for the location of the dangling bond level are scattered throughout the band gap. However recent measurements when using the dangling bond acceptor model seem to be converging on a location slightly below the center of the band gap in both Ge and Si.

Before leaving the Schockley dangling bond model of dislocation acceptor states it should be pointed out that the existence of a donor level may also be rationalized under the dangling bond scheme. Just as it is reasonable to expect

that an electron paired with a dangling bond would have an energy less than a conduction electron but higher than a valence electron and therefore give rise to an acceptor state in the band gap, in theory the dislocation could also act as a donor³⁹ because a single unpaired dangling bond would be less tightly bound than a normal valence electron. Although some authors^{38,44} have reported little or no effect of dislocations on electrical properties of p-type material (where the Fermi level would be expected to be below the dislocation level and the acceptor states unoccupied) some^{45,46,47} have indeed reported possible donor activity in lightly p-type samples at low temperatures with an apparent dislocation donor level within a few tenths of an electron-volt of the valence band.

The Schockley dangling bond approach to electrical effects has been used quite extensively to interpret experimental results. Recently, however, the theory has had some strong opposition with the suggestion, made as early as 1958 by Chynowith and Pearson⁴⁸ and later stated more directly by Celli, et al.,⁴⁹ that the strain field of the dislocation, through its effects upon the band gap in a semiconductor (deformation potential), should actually be held accountable for the electrical effects of dislocations in semiconductors. In fact, Güth has argued that the fact that the optical absorption line at 0.1 eV^{51,52} has a very distinct polarization parallel to the Burgers vector cannot be explained by the Schockley theory but is a direct consequence of the spatial effects of the deformation potential upon the band gap. Güth's suggestion,⁵⁰ which is similar to that of Celli, Gold, Thomson,⁴⁹ is that only in the very close environment of the dislocation line is the crystal appreciably distorted. It is uniaxially dilated and compressed below and above the dislocation line and only in this region is there an appreciable perturbation of the band structure. The perturbation is such that in the region of dilation the energy of the valence band edge is lifted whereas the edge of the conduction band is lowered, and therefore one expects discrete energy levels above the valence band

and below the conduction band along the dislocation. The roughly .4 to .5 eV transition found by photoconductivity^{53,54} and in the past suggested as a transition from the dangling bond ground state to the conduction band is then actually a transition between the conduction and valence band in the close proximity of the dislocation.

III. EXPERIMENTAL TECHNIQUE AND PROCEDURES

The experimental plan generally followed during this study consisted of initial material characterization and preparation, internal friction measurements on undeformed specimens, deformation of specimens, and finally, internal friction measurements on deformed specimens. The particular techniques used are discussed below.

A. Materials and Specimen Preparation

Characterization data such as resistivity, concentration of electrically-active impurities, dopant, and source of the various germanium or silicon monocrystals used in this study are given in table I. The crystals were all $\langle 111 \rangle$ axis Czochralski grown with initial $\{111\}$ etch pit densities in the neighborhood of $10^3/\text{cm}^2$ for the germanium and 10^2 to $10^3/\text{cm}^2$ for silicon boules.

Individual specimens were cut on a diamond wafering saw in the form of 3/16 inch square bars with $\langle 111 \rangle$ axis and faces perpendicular to $\langle 110 \rangle$ and $\langle 112 \rangle$ directions having lengths in excess of that required for the particular half-wavelength longitudinal resonant frequency needed. Specimen sides were then ground with oil-lubricated carbide paper with final lapping on 0 grade paper to 1/8 inch square using aluminum jigs to insure cross-sectional uniformity. Both ends of the bars were similarly ground to a final length very slightly in excess (the excess was to allow for $\sim .2\text{mm}$ material removal during etching) of that required for frequency matching. This procedure was followed by a modified CP-4 (bromine excluded) etch of 3 minutes during which constant specimen motion by tapping with a pair of teflon-coated tweezers was required to eliminate "scarring" of the specimen surfaces from the flow of gas formed during the etching process. Surface perfection of these specimens was found to be extremely important primarily because extraneous peaks appear

TABLE I
MATERIALS CHARACTERIZATION

Element	Resistivity	Dopant	Concentration ^a	Source
Ge	40 Ω cm	--	--	Ventron
Ge	1 Ω cm	Sb	2×10^{15}	
Ge	.030 Ω cm	Sb	10^{17}	Eagle-Picher
Ge	.003 Ω cm	As	1.6×10^{18}	Eagle-Picher
Si	100 Ω cm	--	--	Ventron
Si	4 Ω cm	P	1.2×10^{15}	Mansanto
Si	.400 Ω cm	P	1.6×10^{16}	Mansanto
Si	.025 Ω cm	P	1.5×10^{18}	Mansanto

a) Estimated from resistivity through references 55 and 56.

during internal friction measurements of the temperature-dependent logarithmic decrement in poorly-prepared specimens. For example, figure 3 shows the measured logarithmic decrement, δ , as a function of temperature for a lightly etched (45 seconds), undeformed 40 Ω -cm germanium specimen and for the same specimen after an additional three minute etch in modified CP-4. A possibly similar surface effect has been found at low temperatures in germanium by Halworth, Mattas, and Birnbaum⁵⁷ working in the low KHZ frequency range. These authors found a peak in the temperature dependence of the logarithmic decrement in the vicinity of 200°K in undeformed specimens with abraded surfaces. Similar peaks found by various authors^{58,59,60} between 100°K and room temperature have in the past been attributed to dislocation mechanisms such as a Bordini type peak; however, Halworth, et al.⁵⁷ were able to correlate the appearance or disappearance of the peak in undeformed and deformed material with surface conditions. From the etching behavior and the disappearance of the peak with annealing at temperatures as low as 473°K Halworth, et al.⁵⁷ suggest that hydrogen migration, possibly associated with the presence of dislocations, could be responsible for the peak.

One can also speculate, however, that the surface grinding peak of Halworth, et al.⁵⁷ could be due to the acousto-electric effect through the reduction of excess carrier lifetime by surface recombination. To calculate a typical excess carrier lifetime, τ , assuming all carriers reaching the ground surface recombine, a typical specimen thickness, t , for the flexural resonant mode of 0.2 cm, and an electron mobility, μ , of 10⁴ cm²/volt sec with the formula⁵⁶

$$\frac{1}{\tau} = \frac{\pi^2}{4} \frac{\mu k T}{e} \frac{1}{t^2},$$

we obtain at 200°C, $\tau = 9.4 \times 10^{-5}$ sec which should be compared to the value of $1/\omega = 7.96 \times 10^{-5}$ sec at 2 KHZ. The peak condition is of course $\omega \approx 1$.

Figure 3. Internal friction data showing peaks due to poor surface preparation. Data taken on undeformed 40 Ω cm germanium at 50 KHz; solid line after 45 sec. etch; broken line after additional 3 minute etch.

B. Electrical Measurements and Specimen Purity

Electrical resistivity of all specimens was measured before and after every elevated temperature exposure during the course of this study to guard against specimen contamination by electrically-active impurities. Resistivity profiles were taken on freshly lapped and cleaned surfaces by passing a current from a constant current source through the length of a bar and measuring the voltage between spring loaded probes separated by .1 inches. As expected the resistivity of deformed intrinsic germanium and silicon was found to be lowered by the increased density of dislocations introduced during 4-point bending. The resistivity decrease was found to be compatible with that seen by previous authors^{34,45,96} and its variation along the length of intrinsic specimens followed the variation of dislocation density produced by four-point bending (figure 4). No measurable additional change in resistivity was detected in intrinsic specimens after high temperature internal friction measurement on undeformed or annealed, deformed specimens.

To verify that the resistivity changes encountered after deformation of intrinsic specimens was indeed due to increased dislocation densities two relatively standard experiments were performed. First, a 40 Ω -cm germanium and 100 Ω -cm silicon specimen were placed in the deformation furnace and taken through the standard temperature cycle without deformation. No change in their electrical resistivity could be detected. Secondly a 40 Ω -cm germanium specimen was gold plated on four sides and deformed. After removal of the plating by lapping the resistivity change was found to be comparable with that of unplated specimens.

In highly doped specimens, for example 0.003 Ω -cm germanium, no detectable change in electrical resistivity was found after deformation if the deformation temperature and time were kept to a minimum. This is entirely reasonable since the maximum dislocation electron occupation is far less than

Figure 4. Resistivity measured along the length of a deformed $40\ \Omega\ \text{cm}$ germanium specimen.

the $> 10^{18}$ free electrons available and the effects of ionized donors on electron mobility should exceed that of the charged dislocations.^{46,56} However, after high temperature internal friction measurements or if the deformation temperature is relatively high, the electrical resistivity of highly doped specimens was found to increase due to what we believe to be preferential precipitation at dislocations. This effect will be discussed in chapter IV.

Possible contamination of semiconductors by such fast-diffusing interstitials as copper or oxygen which generally cannot be seen by electrical resistivity measurements unless present in high concentrations has concerned many investigators of both electrical and mechanical properties. Interference in dislocation damping measurements by preferential precipitation of these impurities on dislocations or some type of defect drag mechanisms is a possible danger. There is some evidence however that these contaminants in moderate concentrations have little or no effect on high-temperature dislocation-related internal friction. A Snoek type relaxation peak, dependent upon oxygen concentration, with activation energy of 2.55 ev, has been found by Southgate³⁰ in the $\langle 111 \rangle$ vibration axis in silicon. However, Southgate and Mendelsen²⁰ have shown that dissolved oxygen in concentrations as high as 10^{18} per cm^3 has little or no effect on high temperature dislocation damping in silicon. In intentionally copper-doped germanium, Calzecchi, Gondi, and Martavani^{15,16} have found no effects in the dislocation related damping although copper does affect the height and position of the mid-temperature, acousto-electric peak probably through its trapping properties.

Periodic spectrographic analysis of specimens failed to reveal any copper or oxygen contamination in any specimen although the technique's oxygen resolution is quite poor and moderate oxygen concentration, especially in silicon, is to be expected in Czochralski grown crystals.

C. Deformation

Dislocations were introduced into the specimens by means of four-point bending in the high temperature vacuum furnace shown in figure 5. The deformation temperatures used were 600 to 625°C for germanium and 900 to 925°C for silicon. The system was such that when precipitation effects were to be avoided in the highly doped material, a specimen could be heated, deformed and cooled so that the total time spent within 150°C of the deformation temperature could be kept under 15 minutes. High purity, high strength ZTA graphite was used for the sliding blocks while polished tungsten rods were used to contact the specimens. Stainless steel was used for the rest of the deformation rig, which was contained in an Al_2O_3 tube furnace wrapped with Mo wire and surrounded by Ta heat shields. The system was placed in a water-cooled, stainless steel vacuum chamber which employed a mechanical pump with molecular seive, a Ti sublimation pump and a VacIon pump. Pressure was determined from the current of the VacIon pump. After initial construction of the deformation rig and furnace, and periodically throughout its use, the system was subjected to a 1200°C, 24-hour purification anneal and when not in use the internal parts were stored in a dessicator. Typical values of vacuum obtained were on the order of 5×10^{-6} torr at the 900°C deformation temperature of silicon down to below 5×10^{-7} torr at room temperature after deformation.

Average dislocation densities of 6×10^5 to 2×10^6 per cm^2 were introduced into the central 3/4 inches of various specimens. These values calculated from the radius of curvature in this portion of the crystals with the formula⁶¹

$$\bar{\rho} = \frac{d}{R\bar{b}},$$

where $\bar{\rho}$ is the average dislocation density, d is specimen thickness, R is the radius of curvature, and $\bar{b}$ is the magnitude of the dislocation Burgers

Figure 5. High temperature, 4-point bending deformation furnace.

vector resolved along the specimen axis. The radius of curvature was computed from the amount of vertical displacement, Z , of the vertical plunger, assuming zero elastic strain, by the formula,

$$R \approx \frac{\sqrt{3} \ell' (\ell - \ell')}{4Z},$$

where ℓ is the distance between outside bending points, and ℓ' the distance between inside bending points.

Etch pit counts of dislocation density were not taken; however, it has been shown by various authors^{61, 62} that reasonably accurate values of dislocation density can indeed be calculated from the deformed radius of curvature. Etch pitting with CP-4 revealed qualitative agreement with deformation patterns expected in four-point bending (as did resistivity measurements); i.e., increasing dislocation density from outside to inside rod, constant density between inside rods, and maximum density at the top and bottom surfaces with a neutral plane in the center.

The $\langle 110 \rangle$ bending axis was primarily used; however, no discernible difference in high temperature internal friction of annealed specimens was found when the $\langle 112 \rangle$ direction was used as the bending axis.

To investigate the possible influence of specimen curvature on the high temperature, internal friction measurements, two intrinsic germanium specimens were rotated 180° after initial deformation, reheated, and straightened. Except for a slight increase in the magnitude of the high temperature, dislocation-related damping no change was found in the logarithmic decrement.

Occasionally the portion of the specimen surface in contact with the polished tungsten rods developed scars which could be correlated with extraneous peaks, smaller but similar to those produced by poor surface preparation. To avoid this problem, deformed specimens were carefully

checked for surface flaws after deformation and when found these flaws were ground off and the specimen re-etched.

D. Internal Friction Measurements

Continuous measurement of the internal friction was obtained in this study by use of a regenerative feedback loop in conjunction with a Marx composite oscillator.⁶³ The composite oscillator was chosen over other techniques which may be more sensitive to low values of the logarithmic decrement because of its high strain capabilities and comparative ease of automation. The resolution of the Marx technique is limited by the background decrement of the composite and the relative masses of background components and specimen, which in this case give a lower limit of about 1×10^{-5} .

Most workers who have used the composite oscillator technique for studying internal friction have employed electronics similar to those described originally by Marx.⁶³ This system requires that the experimenter keep the composite oscillator at resonance by manually adjusting the input frequency to the driver crystal while recording three variables simultaneously. Since the system must be monitored constantly, much time is consumed, and it is impossible to make accurate measurements when the internal friction is changing rapidly.

A more suitable system for such measurements is a regenerative one, which allows for continuous measurement of internal friction while automatically adjusting to the resonance frequency. Other regenerative systems have been described for non-composite oscillator techniques such as the eddy-current drive used on metallic specimens by Thompson and Glass.⁶⁴ French, Sinclair, and Pollard⁶⁵ discussed a composite oscillator regenerative system;

however the present system has the advantages of greater control, stability, and simplicity.

1. THE MARX COMPOSITE-OSCILLATOR TECHNIQUE

The composite oscillator technique as developed by Marx⁶³ consists of bonding quartz driver and gauge piezoelectric crystals to a specimen for the production and detection of a standing longitudinal resonance wave. Each component is of such a length that its longitudinal resonant frequency is closely matched to the other component. The system is then driven by use of the drive transducer at its resonant frequency, and the resultant vibrational amplitude is measured in the gauge crystal. In experiments where the driver-gauge transducers must be isolated from a hostile specimen environment, an Al_2O_3 buffer rod, also closely frequency-matched, can be placed between specimen and transducers.

The equation for the total decrement of the composite is,

$$\delta_T = \frac{NS}{2\ell_d f_d^2 m_t} \left(\frac{V_d}{V_g} \right), \quad (1)$$

where N and S are constants involving resonator dimensions, piezoelectric constants, and capacitance values of the transducers and measuring circuit, m_t is the total mass of the resonator, and ℓ_d and f_d are the length and resonant frequency of the driving transducer. The total decrement is therefore simply proportional to the ratio of the driver crystal voltage to the gauge crystal voltage, i.e.

$$\delta_t = K \frac{V_d}{V_g}$$

The proportionality constant, K, can then be calculated by means of equation (1) or directly determined experimentally by interrupting the driver

signal and photographing the decay of the gauge crystal voltage on an oscilloscope. The specimen decrement, δ_s , is then calculated from the relation,

$$\delta_s = \frac{m_t}{m_s} \delta_T - \frac{m_B}{m_s} \delta_B,$$

where m_t , m_s , and m_B are the mass of the total composite, the specimen and the composite oscillator without the specimen, respectively. The quantity δ_B is the background decrement, or decrement of the composite oscillator without the specimen present. The resonant frequency of the specimen, and therefore the modulus, can be found by a similar set of relations.

2. GENERAL DESCRIPTION OF THE APPARATUS

The regenerative feedback loop consists primarily of a closed loop containing an amplifier and a resonant element with a feedback circuit to control the gain of the amplifier.

The resonant element in this case is the driver-gauge combination of piezoelectric crystals. The particular crystals used (purchased by Blily Electronics) were of 1/8th inch square cross-section and had lengths which gave resonant frequencies of from 35 to 160 kHz. These crystals have full-length evaporated gold electrodes for drivers and 2/3rd length for gauge crystals. Grooves of approximately 0.003 inches deep were placed at vibration nodes of the crystals to accept 0.003 inch-diameter tungsten wires which acted as both mounting and electrical-contact wires. Driver and gauge crystals were cemented together, with electrodes at right angles to reduce electrical pickup, using Eastman 910 adhesive. The bond between the Al_2O_3 buffer rod and the transducers was also made with Eastman 910. These bonds made no appreciable contribution to the background internal friction of the composite oscillator. The monocrystalline Al_2O_3 buffer

rods used were of 1/8 inch-square cross-section and closely matched to each particular set of driver-gauge transducers at a particular temperature. The total lengths of the rods were chosen to be from eight to eleven inches to provide thermal insulation for the transducers while keeping the mass of the background composite weight as low as possible for maximum sensitivity. Specimens, again closely frequency-matched, were cemented to the buffer rod using a high-temperature ceramic adhesive. The technique used to bond the specimen to the buffer rod will be discussed in detail in a later section.

3. CIRCUITS

A block diagram of the complete composite-oscillator regenerative feedback loop is shown in figure 6. The signal from the gauge transducer, produced by the resonant strain wave in the composite, is fed to a pre-amplifier (Hewlett-Packard 465A) which is placed as close to the gauge as possible to minimize cable loss. The strength and frequency of the signal are then measured by an AC voltmeter (Hewlett-Packard 400E) and a frequency counter (General Radio 1191-B). A variable attenuator is then placed in front of the automatic gain control amplifier (Motorola MC1590G) to keep the input signal to this component low enough to avoid the distortion produced by overloading. The signal is extracted between the attenuator and the automatic-gain-control amplifier, fed into an additional amplifier, rectified, filtered and used as the control signal of the automatic-gain-control amplifier. The push-pull output of the automatic-gain-control amplifier is fed into a variable phase shift network to compensate for the $\pm 90^\circ$ phase shift of the composite oscillator (depending on whether the first or third harmonic of the transducers is used), any small phase shift which may occur in the individual electronic components, and the small phase shift caused by

Figure 6. Block diagram of regenerative feedback loop for use with the Marx composite oscillator.

the modulus defect. A power amplifier then follows the variable phase shifter to compensate for the relatively low power capability of the automatic-gain-control amplifier. Signal strength is then measured by another AC voltmeter and the signal is applied to the driver transducer. For calibration purposes a switch is placed in the driver-transducer input line. This switch can interrupt the driver signal while triggering an oscilloscope for photographing the gauge transducer decay. Also employed in the circuit on both input and output lines are a pair of high-pass filters to reduce low frequency noise. Although it has not been required in this research, the need for a high Q band-pass filter may arise when measuring very high specimen decrements. A circuit diagram for the automatic-gain-control amplifier, control signal, and variable-phase-shift network is given in figure 7.

For strain-independent decrement measurements, the total decrement of the composite oscillator is simply proportional to the input signal of the driver transducer. Therefore by recording the input signal strength, the resonant frequency, and other experimental variables under consideration, complete continuous information on the system can be obtained. However, during strain-dependent measurements, since the total decrement is found from the ratio of the input to output voltages, both must be recorded. As an alternative to simply recording both of these voltages and then taking ratios manually later, both signals can be fed into a standard divider circuit, such as that formed by a Motorola MC 1595L linear four-quadrant multiplier integrated circuit used in conjunction with a pair of operational amplifiers.⁶⁶ Recording the output of this circuit and the output signal of the gauge transducer gives the experimenter a continuous record which is proportional to both the total composite decrement and the dynamic strain.

4. OPERATION OF THE SYSTEM

The composite oscillator is placed vertically in a high temperature vacuum furnace with drive and gauge crystals above the specimen and held in place with the taut 0.003 tungsten wires. Power is then applied to the signal's amplifier or the gain-control resistance (R_{AGC} of figure 7) is reduced until the desired strain is reached in the composite oscillator. The latter method, although more convenient, is not preferred because the sensitivity of the automatic gain-control amplifier is dependent upon R_{AGC} . Adjustment of the phase shift is now made to give the lowest driver transducer input voltage. This condition corresponds to the maximum system response and therefore to resonance. "Motorboating" of the system is occasionally encountered because of too large a capacitance in the gain-control filter circuit but is easily eliminated by using a filter time-constant smaller than that of the composite-oscillator decay.

The measurement parameter of interest can now be varied while the regenerative feedback loop provides a continuous record of both the internal friction and modulus. The resistance furnace used in this particular experiment is dc powered to avoid Hz noise and is controlled by a motor-driven Variac. Temperature is swept at a slow enough rate to avoid thermal lag and is measured by a thermocouple placed near the specimen. Calibration runs have been made with an additional thermocouple in contact with the specimen to ensure accurate temperature measurement. Strain-dependent measurements are easily made by varying R_{AGC} and the input attenuator while keeping in mind the input and output limitations of the MC 1590G. The input and output signals are constantly monitored on an oscilloscope, especially during strain-dependent measurements, to reveal the occurrence of any distortion in either signal.

5. CALIBRATION OF THE SYSTEM

A suggestion of the maximum obtainable response of this system may be gained from a consideration of the variation of the amplifier gain to automatic gain control signal (Fig. 8). When R_{AGC} is chosen as zero the amplifier is capable of greater than 4% control of the composite oscillator dynamic strain during a decrement change of an order of magnitude. A performance test indicating the response of the loop under typical operating conditions is shown in figure 9. These data were obtained by placing a variable attenuator in series with a constant-decrement composite oscillator specimen. Varying the attenuation has the effect of varying the apparent specimen decrement. This result can be compared to a similar test reported by French, Sinclair, and Pollard⁶⁵ on their system (dotted line of figure 9).

The strain amplitude in the composite can be swept in a matter of seconds from less than 10^{-8} to 10^{-4} . This range generally corresponds to a gauge-crystal output voltage range of the order of 1 mV to 10 volts. Beyond strains of 10^{-4} the danger of shattering the quartz driver and gauge transducers places a practical upper limit on the strain. Furthermore, in this range the background decrement becomes strain-dependent primarily through slippage of the mounting wires, a result which greatly reduces the accuracy of the specimen-decrement measurements at these high strain levels.

6. BONDING AND BACKGROUND

Buffer rods of 1/8th inch square cut from Czochralski grown, single crystal Al_2O_3 were obtained from Union Carbide Corporation's Materials Systems Division. They were cut to slightly larger length than needed with a diamond wafering saw and ground on carbide paper (down to 600 mesh) so that they were frequency-matched between 400°C to 500°C with a particular set of driver and

Figure 8. Variation of MC1590G automatic-gain-control amplifier
with control signal variation.

Figure 9. Effect of decrement changes on gauge control level;
solid line, present work; dotted line, French, Sinclair,
and Pollard.⁶⁵

gauge crystals. After repeated use it was found that the buffer rod decrement would increase slightly, due possibly to a coating of evaporated Ge or Si. This effect was easily controlled by grinding slightly with 600 mesh carbide paper and etching in CP-4 before bonding.

By far the most difficult problem with the use of the Marx composite oscillator technique at temperatures far from R.T. is obtaining a reliable bond between the specimen and buffer rod. The ideal requirements of the bond are: strength through the entire temperature range of room temperature to 1000°C, little or no contribution to the background internal friction, ability to be cycled between high and low temperature, and ease of forming. Of the many high-temperature ceramic bonding materials tested Aremco's, Ultra-Temp 516 ceramic adhesive provided the best results when used carefully. The bonding process consisted of forming the bond in an alignment rig and holding for at least 2 hours at room temperature. A 250 watt infrared lamp was then placed about 5 cm away for at least 12 hours to insure complete drying. During this treatment the specimen was in contact with a large block of Al in an effort to prevent excessive heating of the specimen. The major portion of the specimen was again etched in CP-4 for approximately 15 seconds and then washed in alcohol and deionized water. Care was taken at this point to avoid moistening the bond, and therefore the last centimeter of the crystal was not re-etched and re-cleaned. The Al_2O_3 buffer rod and transducer were also washed in alcohol and deionized water over the full length except in the area of the ceramic bond. The specimen was then placed in the internal friction furnace, heated slowly to approximately 150°C and held for about 1 hour. Finally, the chamber was evacuated and then the experiment begun. The composite could then be cycled from the maximum temperature ($\sim 1000^\circ\text{C}$) to a lower temperature; however, upon cooling below about 200°C, the bond would generally break.

It was found that an increase in the strength of the bond and therefore an increase in the ability to cycle from high to low temperatures could be obtained by lapping the specimen end with 2/0 paper before bonding. In undeformed specimens, however, the number of dislocations introduced at the ground end surface was sufficient to increase the dislocation dependent damping at high temperature. To avoid this, the bonding ends of undeformed specimens were not ground as they were in deformed specimens.

Another major difficulty with Marx composite oscillator is the relatively high background damping and fluctuation of the background damping between successive mountings and bondings of the oscillator.

A typical measurement of the composite oscillator background damping made by not bonding a specimen to the composite is shown in figure 10. In all background measurement the decrement was found to decrease slightly approximately linearly with temperature and was independent of frequency in agreement with the results obtained by Huber et al.,⁶⁷ who also used the composite oscillator and an Al_2O_3 single crystal, and who found a slow decrement decrease that continued up to temperatures $> 1800^\circ\text{C}$ depending upon the dislocation density. Much of the background damping, however, can be traced not to the Al_2O_3 buffer rod but to the quartz transducers. Room temperature measurement of damping in the transducers alone gives typical values of 2×10^{-5} whereas room temperature values with buffer rod attached $\sim 1.5 \times 10^{-5}$.

A variation of as much as 100% in background was found with variations of such parameters as mounting wire tension and alignment.

Additional slight variation in background damping was found to arise from bonding. By bonding a dummy specimen of Al_2O_3 cut to the proper length to the composite a decrement variation of as much as 50% could occur even though identical bonding and mounting procedures were followed.

Figure 10. Typical data of background measurement for 50 KHz transducers with only buffer rod attached.

It is believed that the above difficulties with the technique have led some authors (i.e., Paddock,⁶⁸ Welsh, et al.¹⁷) using the composite oscillator at frequencies greater than 50 KHz to report a high temperature "plateau" independent of temperature, frequency, doping or dislocation density in the damping spectrum. Other authors such as Southgate,¹⁴ Southgate, et al.^{19, 20} using other techniques find that the damping above room temperature which is not associated with the acousto-electric peak, or with the high temperature dislocation dependent damping have found no such plateau. The work of Haworth, Mattas, and Birnbaum⁵⁷ at frequencies of 2 KHz and temperatures below 400°C have been able to account almost completely for the damping by the calculated thermoelastic damping which is entirely consistent with the lack of a "plateau" at the higher frequencies and thicker specimens used in composite oscillator measurements.

With the above in mind it was decided by the author that the background damping could be determined by extrapolating the non-peak or dislocation-dependent composite oscillator damping through the peak and dislocation-dependent region rather than by independently measuring the background. The consistency of the results at low specimen damping was found to be greatly improved by using this method.

For measurements of the acousto-electric peak in undeformed germanium it was found that the specimen could be bonded directly to the quartz transducer and heated to temperatures up to 400°C with little degradation of the transducer parameters. A special furnace was used for this so that only the top 1/2 inch of the gauge crystal was in the hot zone. By attaching several thermo-couples along the specimen length a specimen temperature gradient of less than 5° at 350°C was found. Reduction of the background mass by elimination of the buffer rod increased the sensitivity of the technique so that the relatively small values of acousto-electric damping could be more accurately

measured.

All data reported in the remainder of this study will already have the background damping subtracted with the exception of figure 11.

IV. RESULTS

The results of measurements of the dependence of the logarithmic decrement upon temperature, frequency, and n-type dopant concentration in both undeformed and deformed germanium and silicon are reported in this chapter. The data reported here represent studies on more than 30 different specimens. Data from several additional specimens have been rejected because of erratic behavior, such as the appearance of large, irreproducible peaks. This erratic behavior in a particular specimen could usually be correlated with the existence of flaws such as previously-undetected, deep microcracks formed during deformation, or occasionally deep surface irregularities which may have been impurity clusters or oxide precipitates.

The germanium and silicon crystals studied showed qualitative similarity between the two semiconductors, differing only in the values of various parameters. Typical of these measurements are the data for an intrinsic germanium specimen, shown before and after light deformation in figure 11. The background damping has not been subtracted from these data. With increasing temperature the first detectable damping is that of the small acousto-electric peak, which will be discussed in section A. In undeformed specimens, at much higher temperatures, there is in addition a relatively erratic, temperature-dependent decrement. This portion of the damping in undeformed specimens is most likely due either to dislocation damping through grown-in dislocations or possibly to the oxygen-concentration dependent Snoek peak found by Southgate.³⁰ Because of its erratic behavior no attempt was made here to obtain any quantitative data on the high temperature damping in undeformed material.

In deformed material, at temperatures generally just past that of the acousto-electric peak, there appears damping proportional to dislocation density that increases logarithmically with inverse temperature. At high

Figure 11. Typical internal friction data for 40 Ω cm germanium
at 50 KHz; solid line deformed, broken line undeformed.

dislocation densities in highly doped n-type material the dislocation damping is often too large to reveal the presence of the acousto-electric peak. The data for dislocation damping are presented in section B of this chapter.

A. Acousto-Electric Peak

Typical data from the acousto-electric damping are shown in figure 12 for an intrinsic germanium specimen at resonant frequencies of 50, 100, and 150 KHz. In germanium, the moderate-temperature nature of the peak permitted the bonding of specimens directly to driver and gauge crystals, as previously mentioned in chapter III. The 50 and 150 KHz measurements were taken by using the first and third harmonics of a single set of driver and gauge transducers, while the 100 KHz measurements used the same specimen with a set of transducers having a first harmonic of 100 KHz. In the silicon measurements, taken at 70 and 140 KHz, because of the higher temperatures required it was not possible to bond the specimens directly to the driver and gauge transducers. A short (as compared to the buffer rods used with deformed specimens) buffer rod of approximately two inches was used for the acousto-electric peak measurements. This rod was frequency matched to individual 70 and 140 KHz transducers.

Figure 13 is a plot of the inverse temperature of the peak maximum as a function of the logarithm of the resonant frequency for germanium, while figure 14 presents similar data for silicon. Figures 15 and 16 present the values of peak height as a function of inverse peak maximum temperature in germanium and silicon respectively. The graphs contain data from both intrinsic and lightly doped, n-type material. In n-type material, if the doping was such that the material was essentially intrinsic at the peak temperature, no difference could be detected in the acousto-electric peak between n-type and intrinsic material. In highly doped material

Figure 12. Acousto-electric peak in undeformed 40 Ω cm germanium
at 50, 100, and 150 KHz.

Figure 13. Logarithm of resonant frequency as a function of the inverse temperature of the acousto-electric peak maximum for several 40 Ω cm undeformed germanium specimens.

Figure 14. Logarithm of resonant frequency as a function of the inverse temperature of the acousto-electric peak maximum for several 100 Ω cm undeformed silicon specimens.

Figure 15. Logarithm of the acousto-electric peak maximum height as a function of inverse temperature of the peak maximum for several undeformed 40 Ω cm germanium specimens.

Figure 16. Logarithm of the acousto-electric peak maximum height as a function of inverse temperature of the peak maximum for several undeformed 100 Ω cm silicon specimens.

(i.e. $0.003 \Omega \text{ cm}$ germanium and $0.025 \Omega \text{ cm}$ silicon) no acousto-electric peak could be detected. Measurements on four moderately n-type doped germanium specimens ($.03 \Omega \text{ cm}$) which are only slightly extrinsic at the peak temperatures gave data for the peak which was slightly lower in magnitude and about 10°C lower in temperature than intrinsic material. Figure 17 is a comparison of the 50 KHz acousto-electric peak in $.03 \Omega \text{ cm}$ germanium with that of intrinsic material.

From the slopes of figures 13 and 14 an activation energy for the peak (assuming that $\omega\tau =$ a particular constant as the condition for the peak maximum) of 1.1 ev for germanium and 1.55 ev for silicon can be calculated. The value for germanium is in good agreement with the work of several authors, while the 1.55 ev activation energy in silicon can be compared with the 1.45 ev value obtained by Southgate,³⁰ which is the only previously reported value.

B. Deformed Material

1. ANNEALING

The high-temperature, dislocation-dependent damping in deformed germanium and silicon shows relatively strong annealing effects, the magnitude of which depends upon the condition of deformation. This effect can be seen in figure 18 by the difference found between the first heating and cooling curves for the intrinsic deformed specimen shown there. It was not uncommon for the magnitude of the dislocation damping to drop by as much as a factor of two in specimens rapidly cooled after deformation. As expected the rate of annealing becomes appreciable during the first heating associated with internal friction measurements above the deformation temperature. If higher deformation temperatures are used, or if the specimens are held at temperature in the deformation furnace, the annealing occurring during the

Figure 17. Comparison of 50 KHz acousto-electric peak in undeformed
40 Ω cm and .03 Ω cm germanium.

Figure 18. Example of annealing effects present in deformed $40\ \Omega\ \text{cm}$ germanium. First cooling curve and second heating and cooling curves are identical.

Initial heating of internal friction runs are greatly reduced or eliminated. In the present study, once specimens were heated above 650°C for germanium or 950°C for silicon in either the deformation or internal friction apparatus, very little additional annealing took place and a stable, temperature-dependent damping with constant activation energy was found.

The annealing effects are most likely due to the motion of freshly introduced dislocations toward stable equilibrium network. A similar effect has been reported by Southgate and Attard.¹⁹ Direct observation techniques such as electron microscopy^{1,2} and X-ray topography^{3,4} have been able to show the strong tendency of dislocation in both germanium and silicon to lie along $\langle 110 \rangle$ directions. This is primarily a direct result of the extremely deep Peierls valleys believed to exist in these materials. The direction of dislocations in freshly deformed material can be viewed as, to a certain degree, random because of dislocation interaction during deformation, with increasing "randomness" occurring with increasing dislocation density. If the material is allowed to stand at high enough temperatures, however, the perfection of the dislocation network increases with time and the total dislocation length contained by a specimen decreases.

Similar annealing effects have been found in studies of the electrical properties of dislocations. For example, Collins and Miles,⁷⁰ while studying the electrical resistivity of twisted germanium were able to show that the magnitude of the dislocation density is not as important as the arrangement of the dislocations. It was found that the most ideal arrays of screw dislocations, and therefore the least disturbance of the electrical properties, were produced when higher deformation temperatures or longer annealing times were employed. Another noteworthy result, which was also observed by Meyer *et al.*,⁴⁴ was that for best results samples should not be deformed past the end of the easy glide region. In the present study

because of the relatively low dislocation densities used, it was seldom necessary to leave the easy glide region during the four-point bending.

Welsh et al.,¹⁷ reporting on internal friction measurements of germanium deformed in tension, have recently found a spectrum of activation energies for high-temperature, dislocation damping which ranges from .7 to 1.0 ev. The higher deformation samples tended to give the lower activation energies. Since his reported data appear to be those taken during the first heating of the damping measurements, and because of the extremely high dislocation densities introduced into his specimens (up to about 10^8 cm^{-2}) this spread of activation energies, which has not been found in this study or by previous authors, could possibly be attributed to annealing effects.*

The data on intrinsic dislocations damping in both germanium and silicon presented in the following section will represent effects occurring after a stable, temperature dependent damping had been achieved. In highly extrinsic material however, difficulties with what is believed to be preferential precipitation of dopant impurities at dislocations when held at temperatures slightly above the deformation temperature presented special problems and will be discussed later.

2. DISLOCATION DAMPING IN "INTRINSIC" MATERIAL

The data reported here is for the dislocation damping of material which "behaves" like intrinsic germanium and silicon. This includes not only 40 $\Omega \text{ cm}$ germanium and 100 $\Omega \text{ cm}$ silicon but the n-type material also. In

*Because of the high dislocation densities used by Welsh et al.¹⁷ the possibilities of overlapping between electronic screening of adjacent, charged dislocations might also have caused the spread of activation energies if the mechanisms proposed in Chapter V are operative.

lightly doped, n-type material ($< 10^{17} \text{ cm}^{-3}$ for both germanium and silicon), where dislocation damping is present the intrinsic carrier concentration is greater than the number of donor impurities and therefore the material is intrinsic. In more heavily doped material, as discussed in detail in the next section, preferential precipitation of the dopant at dislocations is believed to increase the resistivity in the deformed areas of the specimens so that it also behaves intrinsically. An anneal of heavily doped, deformed material at say 100°C above the deformation temperature is sufficient to bring about the transition from extrinsic dislocation damping behavior to intrinsic damping behavior.

In agreement with several authors it has been found that the logarithmic decrement, δ , of the dislocation damping in intrinsic-behaving material can be described by the empirical relationship,

$$\delta = \frac{N\delta_0}{f} e^{-E_i/kT} \quad (1)$$

where N is the dislocation density, f the frequency, δ_0 a constant, E_i the intrinsic activation energy, and kT has its usual meaning.

The results of the internal friction measurements on a large variety of specimens, deformed to dislocation densities of .65, 1.3, and 1.95×10^6 , and preformed at resonant frequencies of 50, 100, and 150 KHz for germanium and 70 and 140 KHz for silicon are presented in tables II and III. The average values of E_i and δ_0 obtained here are compared with those of previous authors in table IV.

TABLE II

INTRINSIC DISLOCATION DAMPING PARAMETERS FOR GERMANIUM

Specimen Number	Resistivity (Ωcm)	Resonant Frequency (KHz)	Dislocation Density (cm^{-2})	Activation Energy (ev.)	δ_0 ($\text{cm}^2\text{sec}^{-1}$)
106	40	50	6.5×10^5	1.10	9.4
107	40	50,100,150	6.5×10^5	1.15	9.3
108	40	50,100,150	13.0×10^5	1.09	8.6
109	40	50	13.0×10^5	1.05	9.6
210	40	50	19.5×10^5	1.12	9.0
211	40	50	13.0×10^5	1.08	9.5
212	40	50	19.5×10^5	1.10	10.6
213	.003	50	6.5×10^5	1.08*	9.2*
214	.003	50	6.5×10^5	1.08*	9.8*
216	.003	50,150	13.0×10^5	1.11*	9.7*
217	.003	50,150	13.0×10^5	1.10*	9.6*
219	.03	50	13.0×10^5	1.10	9.6
220	.03	50	13.0×10^5	1.12	9.7
222	1.	50	13.0×10^5	1.10	9.3
223	1.	50	13.0×10^5	1.09	9.0

*After high temperature anneal

TABLE III

INTRINSIC DISLOCATION DAMPING PARAMETERS FOR SILICON

Specimen Number	Resistivity (Ωcm)	Resonant Frequency (KHz)	Dislocation Density (cm^{-2})	Activation Energy (ev.)	δ_0 ($\text{cm}^2\text{sec}^{-1}$)
105	100	70	6.5×10^5	1.58	31.7
108	100	70,140	13.0×10^5	1.60	30.2
109	100	70,140	19.5×10^5	1.57	32.6
211	.025	70,140	13.0×10^5	1.62*	31.5*
212	.025	70	6.5×10^5	1.61*	31.0*
213	.025	70	13.0×10^5	1.61*	33.0*
215	.4	70	13.0×10^5	1.63	30.1
216	.4	70	13.0×10^5	1.61	31.6
217	4	70	13.0×10^5	1.57	31.1
218	4	70	13.0×10^5	1.61	31.9

*After high temperature anneal

TABLE IV
COMPARISON OF PRESENT RESULTS WITH OTHERS

Material	Present Study		Kessler ¹³		Southgate <u>et al.</u> ²⁰		Calzecchi <u>et al.</u> ¹⁶		Welsch <u>et al.</u> ¹⁷	
	E_i (ev)	δ_o (cm ² sec ⁻¹)	E_i (ev)	δ_o (cm ² sec ⁻¹)	E_i (ev)	δ_o (cm ² sec ⁻¹)	E_i (ev)	δ_o (cm ² sec ⁻¹)	E_i (ev)	δ_o (cm ² sec ⁻¹)
Germanium	1.1	9.46	1.1	5.41*			1.1	69.8	.7 to 1.1	.170*
Silicon	1.6	31.5			1.61	6.68				

3. EXTRINSIC DISLOCATION DAMPING

Measurements of the temperature dependence of the logarithmic decrement in deformed, highly extrinsic n-type germanium and silicon depend a great deal on specimen history. For example, if a $.003 \Omega \text{ cm}$ ($\sim 1.6 \times 10^{18} \text{ cm}^{-3}$ arsenic atoms) is deformed at 675°C and held there for 10 minutes before cooling, the measured logarithmic decrement will be identical with that of intrinsic material. Upon measuring the electrical resistivity of this specimen along its length one finds that in the heavily deformed areas the room temperature resistivity will have increased by as much as 100%; whereas the resistivity of the specimen ends where little deformation has taken place may be identical with the pre-deformation resistivity. The increase in resistivity cannot be explained by the reduction of electron carrier concentration through dislocation acceptors or by the reduction of electron mobility through dislocation scattering effect. In material containing say $1.3 \times 10^6 \text{ cm}^{-2}$ dislocations, the maximum dislocation electron occupation should be less than 10^{13} cm^{-3} and therefore have no effect upon the $> 10^{18} \text{ cm}^{-3}$ conduction band electrons present. Measurement of electron mobility in deformed, $25 \Omega \text{ cm}$ material, for example by Podor,⁷¹ shows only a few percent reduction in the room temperature electron mobility at dislocation densities as high as 10^7 cm^{-2} .

If an undeformed $.003 \Omega \text{ cm}$ specimen is subjected to the same anneal as that of the deformed specimen discussed above, no change in electrical resistivity can be detected. This is entirely compatible with measurements of arsenic solubility in as-grown material which find a solubility limit of $> 10^{19} \text{ cm}^{-3}$ at 600°C in germanium^{72,73} - a value that can easily be preserved by rapid cooling. However, electron microscopy⁷³ has shown preferential precipitation of arsenic at dislocations and therefore it is not surprising that dopant solubility is greatly reduced in highly dislocated crystals.

Fortunately, by using the minimum deformation temperature ($\sim 600^{\circ}\text{C}$ for germanium and 900°C for silicon) and minimum deformation time at temperature (~ 10 min.) we were able to produce highly doped, deformed specimens with little or no detectable change in resistivity in the deformed regions of the crystal, indicating that little or no dopant precipitation had taken place. A measurement of the temperature dependence of the logarithmic decrement of such a specimen is shown in figure 19. This specimen was brought through an internal friction measurement cycle of R.T. to 750°C to 400°C to 750°C to R.T. On first heating this specimen shows a greatly enhanced lower temperature damping than found in intrinsic material of the same dislocation density. As the deformation temperature is passed, a combination of what is most likely dislocation annealing and dopant precipitation causes the damping to level off or in some cases decrease slightly before a stable, intrinsic-like dislocation damping is reached. Upon cooling and after the second heating and cooling the specimen behaves intrinsically. Electrical measurements taken after the run show increased resistivity in the deformed region.

Attempts to solution heat-treat specimens, after dopant precipitation has taken place, at 850°C (the temperature of maximum arsenic solubility⁷²) for one hour proved fruitless, and very little reduction, if any, in the increased resistivity could be found (internal friction run on such material also showed intrinsic behavior).

By deforming highly extrinsic material at minimum temperatures and times as discussed above, and by not heating the specimen during internal friction runs to within 50°C of the deformation temperature a reproducible, stable logarithmic decrement could be measured.

A strong temptation exists to attempt to correlate the enhanced damping found in extrinsic material with the increased electron concentration. We shall

Figure 19. Example of internal friction data for a .003 Ω cm germanium specimen deformed quickly at 600°C. The first cooling curve and second heating and cooling curves are identical.

first assume that the damping is of the form,

$$\delta = \frac{N\delta_o}{f} e^{-E_i/kT} \left(\frac{n_o}{n_i}\right)^m,$$

where n_o is the equilibrium electron concentration and n_i the intrinsic carrier concentration. If we now plot $\ln\delta f \exp(E_i/kT)N$ vs $\ln(n_o/n_i)$ calculated from semiconductor data,⁵⁶ m is determined from the slope and δ_o is given by the y-intercept. This has been done for the data of figure 19 and is presented in figure 20, whereas table V presents the values of m and δ_o for all extrinsic behaving specimens. The data show that the extrinsic damping is proportional to dislocation density and inversely proportional to frequency as was the intrinsic damping. The value of m found is slightly greater than 2 for both materials. The values of δ_o in table V are slightly larger than those found for intrinsic behaving material (tables II and III), however, this discrepancy is most likely caused by the lack of dislocation annealing during extrinsic measurements.

4. STRAIN-DEPENDENCE

The data reported above were taken at dynamic resonant strains of the order of 10^{-6} to 10^{-5} . Throughout this study the logarithmic decrement was periodically checked for the presence of strain-dependence in both the acousto-electric peak and the dislocation-dependent damping. This could be done rather easily and quickly with the regenerative feedback loop as described in Chapter II. These measurements have shown that there is no detectable strain-dependence up to dynamic strains of the order of 5×10^{-4} in any of the damping studied here.

Strain-dependence in the dislocation-dependent logarithmic decrement of silicon has been reported in the past by two authors; however, in both cases the experimental conditions were such that the existence of strain

Figure 20. Comparison of extrinsic data with extrinsic carrier concentration.

TABLE V

EXTRINSIC DISLOCATION DAMPING PARAMETERS

Material	Specimen Number	Resistivity (Ω cm)	Resonant Frequency (KHz)	Dislocation Density (cm^{-2})	δ_0 Pre-anneal ($\text{cm}^2 \text{sec}^{-1}$)	m
Ge	213	.003	50	6.5×10^5	13.2	2.12
Ge	214	.003	50	6.5×10^5	12.1	2.16
Ge	216	.003	50,150	13.0×10^5	12.5	2.25
Ge	217	.003	50,150	13.0×10^5	13.0	2.10
Si	211	.025	70,140	13.0×10^5	42.3	2.25
Si	212	.025	70	6.5×10^5	37.0	2.27
Si	213	.025	70	13.0×10^5	39.7	2.20

dependence at least in the KHz range and above is questionable. Southgate and Mendelson,²⁰ in a special "tuning-fork" specimen, with resonant frequency of 560 Hz found a strain-dependent logarithmic decrement at strains as low as 10^{-6} . Paddock and Carpenter,⁶⁸ using the composite oscillator technique at 50 KHz in silicon, found a rather large strain dependence in highly doped, undeformed specimens; however, their strain-independent studies completely disagree with this study and all previous studies and therefore causes this author to question their strain-dependent findings.

V. DISCUSSION

A. Acousto-Electric Peak

The acousto-electric peak was carefully studied in this work and was found to be well described by the theory of Weinreich.³¹ Southgate³⁰ originally identified the peak during his studies on intrinsic germanium and silicon, and the present work agrees reasonably well with his results. Calzecchi, et al.,^{15,16} working after Southgate,³⁰ attempted to analyze the peak on the basis of the dislocation damping theory of Ninomiya, Thomson and Garcia-Moliner.²¹ However their analysis required the rather dubious assumption of inverse proportionality between kink separation and dislocation density.

We shall start our discussion of the peak by outlining the reasons for its correlation with acousto-electric damping, as originally proposed by Southgate³⁰ and reaffirmed here.

(i) The peak height is independent of dislocation density.

(ii) The peak height and location are independent of type and concentration of impurities except in cases where the concentration of electrically active impurities is large enough to affect excess carrier recombination time or electron distribution at the peak temperature.

(iii) As the resonant frequency is changed, the temperature dependence of the peak height is that of the charge carrier density.

The equation for the logarithmic decrement, δ , from the acousto-electric theory of Weinreich³¹ when employed for the temperature and frequency ranges used herein,

$$\delta = \frac{q^2 \pi}{kT} n_i \frac{s}{1 + s^2} \frac{\sqrt{\omega \tau}}{1 + (\omega \tau)^2} \quad (1)$$

where $q = q_n + q_p$ = the sum of the effective charges for electron on holes, $s \equiv n_0/n_i$, τ = excess carrier lifetime, and other constants have their usual

meaning.

In intrinsic material, $s = 1$ and equation (1) becomes

$$\delta = \frac{q^2 \pi}{2kT} n_i \frac{\omega \tau}{1 + (\omega \tau)^2} \quad (1)$$

The excess carrier lifetime at elevated temperature can be assumed to originate from some sort of band-to-band transition and therefore for intrinsic material can be described by

$$\tau = \tau_0 e^{E_T/kT} \quad (3)$$

where τ_0 is the pre-exponential term and E_T the activation energy for the particular band-to-band process responsible for the lifetime.

E_T and τ_0 can be determined from the slopes and y-intercepts of the $\ln \omega$ vs $1/T_{\text{peak}}$ plots of figures 13 and 14. The values of q can be determined from the y-intercept of the $\ln \delta_{\text{max}}$ vs $1/T$ plots of figures 15 and 16, and the slopes of these plots should be comparable to one-half the band gap for the respective material. The values determined in this study are compared to those found by previous authors and, where possible, to those found by other experimental techniques, in table VI.

There is some difficulty in determining the mechanism responsible for the excess carrier lifetime. Considering the experimental difficulties involved (and lack of interest by device people), it is not surprising that no direct measurements of excess carrier lifetime at elevated temperature have been made. However, it is generally agreed⁷⁴ that at high enough temperature Auger recombination will be the process responsible for excess carrier recombination. This assumption is supported somewhat by room temperature measurements which indicate the presence of Auger recombination at high doping^{75,76} or high carrier injection levels.^{77,78,79}

TABLE VI
COMPARISON OF ACOUSTO-ELECTRIC PARAMETERS

Parameter	Determination from Acousto-Electric Peak Measurements						Determined in Other Ways	
	Present Study		Kessler ¹³		Southgate ³⁰		Calzecchi et al. ¹⁶	
	Ge	Si	Ge	Ge	Si	Ge	Calculated from Theory	
E_T (ev.)	1.1	1.55	1.08	1.15	1.45	1.1	1.09 (80)	1.58 (80)
							.78 (84)	1.21 (84)
							From Room Temperature Recombination Data with use of E_T from Present Study	
τ_o (sec) $\times 10^{15}$	3.90	2.65	14.0	4.12	14.5	3.5	6.33 (76)	2.95 (75,77)
								8.23 (78)
							Piezoresistance Measurements	
q (ev.)	5.23	4.96	3.5	6.5	2.3	---	7.0 (91,92)	1.9 (93)

The theory of Auger recombination and its complementary process, impact ionization, has been developed for direct band gap semiconductors (a class which does not include germanium and silicon) by Beattie and Landsberg^{80,81,82}. Auger recombination, a radiationless process which can take place without the use of thermal phenomena, actually involves two processes occurring in parallel. One involves electron-electron collisions and the other hole-hole collisions. In a semiconductor containing heavy holes such that $\mu \equiv m_c/m_v < 1$ (m_c and m_v equal electron and hole effective masses, respectively), electron-electron processes will dominate in both intrinsic and n-type material; therefore we shall neglect hole-hole processes.

The electron-electron Auger process can be described schematically with the help of figure 21. Recombination (figure 21a) occurs by the finite probability that two electrons, 1 and 2, in the conduction band may collide in such a fashion that 1 drops to the empty state 1' in the valence band while 2 assumes the recombination energy and advances to the empty state 2' high in the conduction band. The complimentary process of electron generation, i.e. impact ionization, is simply the reverse of the above process. An electron high in the conduction band, 2' of figure 21b, collides with an electron in the valence band, 1', in such a manner as to create an additional electron hole pair in the semiconductor.

The excess carrier lifetime when Auger processes are in control and only electron-electron collisions are considered is of the form,

$$\tau = \tau_0 \left(\frac{n_i}{n_0} \right)^2 e^{E_T/kT}, \quad (4)$$

In direct band gap semiconductors according to the theory of Beattie and Landsberg⁸⁰ E_T is given by $(1 + 2\mu) E_g / (1 + \mu)$, where E_g is the gap energy. In direct band gap semiconductors such as tellurium⁷⁴ or InSb⁸³ where Auger recombination has been observed at room temperature the agreement between theory

Figure 21. Schematic representation of Auger electron-electron processes;
a) recombination; b) generation.

and experiment is quite good.

It is interesting to note that if we blatantly ignore the fact that germanium and silicon are indirect band gap semiconductors and apply the theory of Beattie, et al.⁸⁰ we get $E_T = 1.58$ ev for silicon and 1.09 ev for germanium -- values which are in extremely good agreement with the activation energies determined here for the acousto-electric peak. A precedent for this result has been established by Blinov, Bobrova, Vavilov, and Galkin⁷⁹ who applied the theory of Beattie, et al.⁸⁰ to silicon with modest success to explain their room temperature recombination data during high photoexcitation levels. Huldt⁸⁴ has strongly criticized this treatment however and has developed a theory for Auger recombination in indirect band gap materials which predicts an activation energy of about the size of the band gap or .78 ev for germanium and 1.21 ev for silicon.

Landsberg⁸⁵ has pointed out the possibility that there may not be a great difference in the rate of Auger processes between direct and indirect band gap semiconductors as Huldt⁸⁴ suggests. Landsberg concludes this from the experimental result that the drop of the quantum efficiency in $\text{GaAs}_{1-x}\text{P}_x$ in the range $0.4 < x < 0.5$ ⁸⁶ can be explained from the drop in the radiative recombination rate as the material becomes indirect. Thus little change occurs in the non-radiative rate, which is controlled by Auger processes, between direct and indirect band gap material.

The only firm conclusion that can be drawn from the above discussion is that not enough is known concerning Auger recombination to identify the activation energies of 1.1 and 1.55 ev determined in this study with the Auger process. If Landsberg's⁸⁵ assertion that there is not a great deal of difference in the Auger recombination rate for direct and indirect band gap semiconductors is correct, then the theory of Beattie, et al.⁸⁰ can be used and the measurements here are in very good agreement with that theory. On the other hand if Huldt's⁸⁴

theory for indirect band gap semiconductors describes the high temperature Auger recombination rate, our measurements cannot now be explained.

In closing we note that applying equation (4) with the values of table VI to the prediction of acousto-electric peak behavior in extrinsic material, i.e. equation (1), agrees with the disappearance of the peak in .003 Ωcm germanium and .025 Ωcm silicon, and with the magnitude of the reduction of peak temperature and peak height in .03 Ωcm germanium.

B. Dislocation Damping

The empirical expression for the logarithmic decrement of the high temperature dislocation damping in both germanium and silicon as developed in chapter IV is,

$$\delta = \frac{\delta_o N}{f} \left(\frac{n_o}{n_i} \right)^m e^{-E_i/kT}, \quad (5)$$

with experimentally determined values for the various constants appearing in tables IV and V. The agreement of the magnitude of the various parameters of equation (1) determined here and by previous studies on intrinsic material is in the author's view quite good (table IV). There is a large variation in the experimentally determined values of δ_o but this is most likely explained by the difficulties of determining accurate values of the dislocation densities.

The theoretical interpretation of these data however is another matter. None of the available treatments of high temperature dislocation damping in semiconductors has been very well accepted as an explanation of the damping found in intrinsic material. It is even more difficult for these treatments to account for the $(n_o/n_i)^m$, with $m \geq 2$, dependence of the damping found in extrinsic material. Previous theoretical models have been based upon either the interaction of abrupt kinks with the lattice¹⁹ or dragging points²¹ or with the interaction of a dislocation with surrounding lattice defects.²⁴ A

potentially more successful approach, which is taken here, may be to design an explanation for the high temperature dislocation damping in semiconductors based upon the electronic environment of the electrically-active dislocations. The possibility that dislocation damping in semiconductors is electronically controlled is greatly strengthened by the experimental finding that the damping is insensitive to impurity concentration, or type, unless the impurity affects the relative population of electron and holes in the conduction and valence bands.

When possible mechanisms of electronic control of dislocation damping are considered, the temptation is quite strong to attempt a correlation of the mechanism responsible for the acousto-electric peak with that of dislocation damping. The rather close correspondence of the activation energies of the acousto-electric peaks and dislocation damping in a particular material, the initial appearance of dislocation damping at temperatures in the vicinity of the acousto-electric peak, and the $(n_o/n_i)^{-2}$ dependence of extrinsic dislocation damping are some of the reasons for attempting such a treatment.

It is quite unfortunate however that although much effort has gone into the measurement of the electrical effects of dislocations in semiconductors, the mechanisms are only qualitatively understood. The greatest difficulty we will encounter in the following is in determining an expression for the electron occupation probability of the dislocation. The dangling band theory of Schockley³⁶ which in the past has dominated the interpretation of electrical measurements related to dislocation effects has recently been highly questioned by such authors as Güth.⁵⁰ These authors have suggested that the deformation potential model, outlined originally by Celli, et al.,⁴⁹ explains dislocation electrical properties in greater detail than the dangling bond model. Unfortunately the high temperature occupation statistics have not been theoretically or experimentally studied for either model. In the following we will use the

deformation potential model and are forced to use an approximation of the dislocation electron occupation probability which although valid for slightly extrinsic material might be quite poor in highly extrinsic material.

In order to design an electronic theory for dislocation damping in semiconductors based upon a dislocation interaction with its electronic environment we must first present at least a qualitative picture of how the presence of a dislocation disturbs this environment. We are fortunate here in that the frequency-dependence of dislocation damping is that of an overdamped oscillator, and therefore upon assumption of the Granato-Lücké is completely viscous in nature. Dislocation line tension and possible effects of pinning points can therefore be completely ignored. The inverse frequency dependence is not surprising from an electronic damping point of view because the electronic relaxation time should be much shorter than the inverse of frequencies used here (dislocation damping usually appears just after the acousto-electric peak with increasing temperature). The dislocation will therefore be viewed as a straight line moving viscously through the lattice. The presence of abrupt kinks may be completely ignored at distances larger than the kink separation distance.

At sufficient distances the only effects of the dislocation in the semiconductors will be a change in the width of the forbidden band gap by the dislocation deformation potential. Shear effects of the dislocation will be considered secondary.

We therefore have a relatively long range, radial electron and hole potential energy described in a plane perpendicular to the dislocation with x-axis lying in the slip plane by,

$$\phi_i = q_i \Delta_0 \frac{\sin \theta}{r} \quad (6)$$

where,

$$\phi_i = \phi_n \text{ or } \phi_p$$

Φ_n = dilation related conduction band electron potential energy

Φ_p = dilation related valence band hole potential energy

$q_i = q_n \text{ or } q_p$

q_n = deformation potential conduction band electron effective charge

q_p = deformation potential valence band hole effective charge

$$\Delta_0 = - \frac{\sqrt{3} (1-2\nu)b}{4(1-\nu)}$$

ν = Poisson's ratio

b = magnitude of 60° dislocation's Burgers vector

θ = angle from x-axis

r = radial distance from the dislocation

If this was the only effect present and we could ignore the fact that the dislocations have a charged core, then the potential energy of an electron in the conduction and valence bands could be represented as is done in figure 22a for an electron along a line parallel to the slip plane and perpendicular to the dislocation (the sign of the potential energy charge depends upon whether one is above or below the slip plane). The dilation of the band gap will produce a redistribution of the equilibrium free current carriers around the static dislocation, which for intrinsic material is shown in figure 22b. For an expansion of the band gap there is a reduction in the free carrier concentration in the vicinity of the dislocation, and an increase for a band gap contraction.

If the dislocation is now forced to move at a constant velocity, $\vec{v}$, the disturbance in electron and hole concentrations will move with it; at high temperature this occurs primarily by electron-hole recombination or generation. However the net rate of recombination is dependent upon the excess carrier concentration and therefore the steady state electron-hole distribution will lag behind the equilibrium distribution as in figure 22c. Since we now have an

Figure 22. Schematic representation of excess electron dislocation damping in semiconductors; a) band gap dilation, b) free charge carrier concentration for static dislocation, c) solid line free charge carrier concentration for moving concentration; dotted line free charge carrier concentration for static dislocation, d) effect of screening on free charge carrier concentration.

unsymmetrical carrier distribution riding upon a symmetrical, nonuniform potential energy, a net back force acts upon the dislocation. If we now apply a force on the dislocation rather than a constant velocity the dislocation would accelerate until the excess carrier concentration builds up enough to produce a back force of equal and opposite magnitude and a constant velocity is reached. This force is considered here to be the viscous damping force and is determined by the recombination and generation rates of excess electron and hole pairs.

In the above discussion however we have neglected the fact that the dislocation has a charged core. If we assume a negative charge, free current carriers will screen the dislocation charge by reducing the electron concentration and increasing the hole concentration close to the dislocation as in figure 22d. The screening potential acts in an abrupt manner when compared to the gradient of the deformation potential. At distances larger than r_0 , therefore the carrier concentration will be assumed to be controlled entirely by the deformation potential. At distances smaller than r_0 , the screening potential will control the carrier concentration. In the region where the screening potential controls the carrier concentration, it acts in such a way as to affect electron and hole concentration in an opposite sense (i.e., increase holes, decrease electrons). Recombination or generation cannot compensate for this. We will therefore assume that r_0 acts as an abrupt cut-off parameter.

We can now try to find an expression for the viscous dragging force consistent with the above discussion. In the following development the treatment we use is a continuum approach. At the temperatures encountered for the presence of dislocation damping, the free electron mean-free-path is on the order of 100 Burgers vectors. Outside the screening radius the deformation potential is relatively slowly varying and dislocation separation is on the order of 25,000 b; therefore, little difficulty should be encountered. The screening radius, however, at very high temperature or high dopant concentration can be

on the order of the electron mean-free-path. In this treatment we will ignore this possible problem and use a continuum approach with the sharp cut-off parameter, r_0 .

To begin we must first determine the equilibrium electron and hole populations in the vicinity of a static dislocation. For this and the rest of the derivation we define the following symbols:

n, p = electron, hole local density

n_e, p_e = equilibrium electron, hole local density

n_o, p_o = bulk electron, hole density

n_s, p_s = screening electron, hole local density

δ_n, δ_p = excess electron, hole density

Φ_n, Φ_p^o = equilibrium "excess" electron, hole potential energy

$\Delta = \Delta_o \frac{\sin\theta}{r}$, Δ_o defined earlier

e = electronic charge

ϵ = electric permittivity of the solid

$\rho_n, \rho_p = q_n/e, q_p/e$

V_o = electric potential from non-equal carrier density charge

V_s = electric screening potential

$S = n_o/p_o$

$\rho_o = (Sp_n - \rho_p)/(1 + S)$

$\vec{j}_n, \vec{j}_p$ = electron, hole current

μ_n, μ_p = electron, hole mobility

γ = increased electron occupation probability of dislocation energy level

N = dislocation density

N_s = number of dislocation energy levels per unit distance

N_c, N_v = density of states at conduction, valence band edge

E_c, E_v = energy of conduction, valence band edge

E_F = fermi level

E_g = band gap

E_T = distance of dislocation level from band edge

The equilibrium electron and hole populations around a static dislocation, under the Boltzmann approximation, will be given by,

$$n_e = n_o e^{-e\Phi_n^\circ/kT} \approx n_o \left(1 - \frac{e\Phi_n^\circ}{kT}\right), \text{ if } \frac{e\Phi_n^\circ}{kT} < 1 \quad (7)$$

$$p_e = p_o e^{-e\Phi_p^\circ/kT} \approx p_o \left(1 - \frac{e\Phi_p^\circ}{kT}\right), \text{ if } \frac{e\Phi_p^\circ}{kT} < 1$$

where

$$\Phi_n^\circ = \rho_n \Delta - V_o, \text{ and } \Phi_p^\circ = \rho_p \Delta + V_o \quad (8)$$

V_o can be determined from the solution of Poisson's equation,

$$\nabla^2 V_o = - \frac{4\pi e}{\epsilon} \left[(p - n) - (p_o - n_o) \right], \quad (9)$$

as

$$V_o = \frac{S\rho_n - \rho_p}{1 + S} \Delta = \rho_o \Delta \quad (10)$$

Therefore from (7), (8), and (10),

$$n_e = n_o \left[1 - \frac{e\Delta}{kT} (\rho_n - \rho_o) \right] \quad (11)$$

$$p_e = p_o \left[1 - \frac{e\Delta}{kT} (\rho_p + \rho_o) \right]$$

With equation (11) for the equilibrium, static carrier concentration, we can now calculate the excess free carrier concentration around a dislocation moving with velocity $\vec{v}_d = v_d \hat{x}$, where $\hat{x}$ lies in the slip plane perpendicular to the dislocation. We let the carrier concentrations become,

$$\begin{aligned} n &= n_e + \delta_n \\ p &= p_e + \delta_p \end{aligned} \quad (12)$$

and make the common assumption $\delta_n = \delta_p$ to avoid space charge difficulties. This essentially assumes that charge neutrality of excess carriers is maintained exactly, the electric fields necessary for this purpose being set up automatically and instantaneously. We shall also assume that $\delta_n \ll n_o$ or p_o and $\vec{\nabla} \delta_n \ll \vec{\nabla} n_e$ or $\vec{\nabla} p_e$.

The excess carrier concentrations can now be determined from simultaneous solution of the current equation,

$$\vec{j}_n = - \mu_n (n \vec{\nabla} \phi_n + \frac{kT}{e} \vec{\nabla} n) \quad (13)$$

$$\vec{j}_p = - \mu_p (p \vec{\nabla} \phi_p + \frac{kT}{e} \vec{\nabla} p)$$

and continuity equations,

$$\frac{\partial n}{\partial t} + \vec{\nabla} \cdot \vec{j}_n + \frac{\delta n}{\tau} = 0 \quad (14)$$

$$\frac{\partial p}{\partial t} + \vec{\nabla} \cdot \vec{j}_p + \frac{\delta p}{\tau} = 0$$

Combining equations (11), (12), (13), and (14) and by using the various assumptions one can find that an approximate solution for δ_n is given by,

$$\delta_n = \frac{S}{1+S} \frac{p_o v_d \tau}{kT} \hat{x} \cdot \vec{\nabla} \Delta \quad (15)$$

To determine the viscous force-velocity law for the electronically damped dislocation we note that the force on the dislocation from the applied stress is equal and opposite to the x-component of the excess carrier force on the dislocation. If σ is the shear stress resolved in the $\hat{x}$ direction, for a 60° dislocation,

$$\begin{aligned} \frac{\sqrt{3}}{2} b\sigma &= \int_V q\delta_n \hat{x} \cdot \vec{\nabla} \Delta dV \\ &= \frac{S}{(S+1)} \frac{p_o q^2 \Delta_o^2 v_d \tau}{kT} \int_0^{2\pi} \int_{r_o}^{\infty} (\hat{x} \cdot \vec{\nabla} \frac{\sin\theta}{r})^2 r dr d\theta \end{aligned}$$

where the cut-off parameter r_o has been used. Upon integrating and solving for the dislocation velocity we have,

$$v_d = \frac{\sqrt{3} (S+1) r_o^2 kT b \sigma}{\pi S p_o^2 q^2 \Delta_o^2 \tau} \quad (16)$$

Equation (16) gives us the dislocation velocity as a function of stress. In order to interpret this however we must first estimate the magnitude of the cut-off parameter, r_o . The spacial dependence of the free charge carrier distribution due to the presence of a charged dislocation is given by,

$$\begin{aligned}
 n_s &= n_o e^{+eV_s/kT} \approx n_o \left(1 + \frac{eV_s}{kT}\right) \\
 p_s &= p_o e^{-eV_s/kT} \approx p_o \left(1 - \frac{eV_s}{kT}\right)
 \end{aligned}
 \tag{17}$$

where the assumption has been used,

$$\left| \frac{eV_s}{kT} \right| \ll 1
 \tag{18}$$

V_s can now be found through the use of equation (17) and the solution of Poisson's equation, (9), with the appropriate boundary conditions as,

$$V_s = - \left(\frac{2eN_s\gamma}{\epsilon} \right) K_0(r/\lambda)
 \tag{19}$$

where $K_0(r/\lambda)$ is the zero order, modified Bessel function, the term in the brackets was determined by normalization, and λ , the two-dimensional Debye screening length given by,

$$\frac{1}{\lambda^2} = \frac{4\pi e^2}{\epsilon kT} (n_o + p_o)$$

We can now assume that r_o is given by the distance where the disturbance of the free carrier distribution due to dislocation charge screening becomes appreciable. This shall occur in the vicinity of the breakdown of assumption (18), arbitrarily picked as $|eV_s/kT| \approx 1.0$. To keep the solution analytical we shall also approximate the modified Bessel function by λ/r . With these assumptions we have,

$$r_o = \frac{2e^2 N_s \gamma \lambda}{\epsilon kT}
 \tag{20}$$

All we need now is an expression for γ , the dislocation electronic charge occupation probability. To calculate this expression we shall assume the Celli, et al.⁴⁹ - Güth⁵⁰ model where γ represents the net increase in the electron occupation probability at the dislocation's core as energy levels are pulled out of the conduction band and valence band into the band gap by the dislocation. We shall use the energy level scheme of figure 23, which is consistent with Celli, et al.⁴⁹ - Güth,⁵⁰ where the levels are pulled equal amounts from conduction and valence bands, E_T , where equal numbers of levels are pulled out, and where all energy levels at the dislocation core are raised by E_S the extra electron interaction energy. For a conduction band level, assuming Boltzmann statistics, the charge in the electron occupation probability is given by,

$$e^{-(E_C + E_S - E_T - E_F)/kT} = e^{-(E_C - E_F)/kT},$$

and for a valence band level,

$$\left[1 - e^{-(E_F - E_V - E_S - E_T)/kT} \right] = \left[1 - e^{-(E_F - E_V)/kT} \right].$$

The dislocation electron occupation probability is equal to the sum of these and is given by

$$\gamma = 2 e^{-E_g/2kT} \left[e^{-E_S/kT} \sinh(\Phi + E_T/kT) - \sinh \Phi \right], \quad (21)$$

where $\Phi = \sinh^{-1}(N_d/2n_i)$.

The calculation of an expression for E_S at high temperature has not been made. This is primarily for the lack of an analytical expression for the high temperature screening potential accurate at small distances from the dislocation. Computer calculations⁸⁷ for the screening potential have been done but their incorporation into E_S has not. However, Read³⁸ has argued on the basis of his

Figure 23. Dislocation energy level scheme under Celli, et al.⁴⁹ -
Güth⁵⁰ theory with addition of dislocation accepted
electron interaction energy.

low temperature approximation for E_S , that at high temperatures, it may be ignored if $\gamma < 0.1$ as expected here. An approximate expression for equation (21), for values of Φ and E_T/kT that are not too large is therefore,

$$\gamma = \frac{E_T}{kT} e^{-E_g/2kT} \quad (22)$$

Equation (22) predicts that the occupation probability is insensitive to dopant concentration. This result occurs because of the rather rough approximations used to obtain it. In reality one would expect an increase in γ with increasing donor concentration (if $N_d > n_i$); however, it would be much less than the linear dependence of a normal acceptor level.

Using equations (16), (20), and (22) the expression for dislocation velocity becomes,

$$v_d = \frac{\sqrt{3}}{\epsilon} \left(\frac{eN_S E_T}{\pi q \Delta_o kT \sqrt{N_c N_v}} \right)^2 \frac{b\sigma}{\tau} \quad (23)$$

The logarithmic decrement defined as the energy absorbed per cycle divided by twice the maximum stored energy of the acoustic wave is therefore,

$$\delta = \frac{\sqrt{3}G}{2\epsilon} \left(\frac{eN_S E_T b}{\pi q \Delta_o kT \sqrt{N_c N_v}} \right)^2 \frac{N}{f\tau},$$

or with equation (4), the Auger excess carrier lifetime,

$$\delta = \frac{N\delta_o}{f} \left(\frac{n_o}{n_i} \right)^2 e^{-E_T/kT} \quad (24)$$

where,

$$\delta_o = \frac{\sqrt{3}G}{2\epsilon\tau_o} \left(\frac{eN_S E_T b}{\pi q \Delta_o kT \sqrt{N_c N_v}} \right)^2$$

Equation (24) is to be compared to the empirically determined expression for the logarithmic decrement, equation (5). The measured value of m in equation (5) is slightly greater than two, which is the power of (n_0/n_i) in equation (24). This was to be expected however according to the discussion after equation (22). The values of δ_0 from equation (24) can be calculated as $6.1 \text{ cm}^2 \text{ sec}^{-1}$ for germanium and $5.8 \text{ cm}^2 \text{ sec}^{-1}$ for silicon by using τ_0 and q determined by the measurements of the acousto-electric peak, by assuming $N_s \approx 1/b$ and $E_T \approx 0.1 \times E_g$ and by using table values for the other parameters. These values are in fair agreement with the experimental values $9.5 \text{ cm}^2 \text{ sec}^{-1}$ for germanium and $31. \text{ cm}^2 \text{ sec}^{-1}$ for silicon. The fact that the activation energy for Auger recombination measured by the acousto-electric peak is slightly lower than that measured by dislocation damping (1.55 as compared to 1.6 ev.) may also be due to the assumption behind equation (22) however the agreement is within our experimental accuracy.

In closing we might comment on the recent speculation concerning the possibility that dislocation motion is controlled by some mechanism involving partial dislocations.⁸⁸ Electron microscopic observation^{89,90} has recently shown that both the 60° edge and screw dislocation are indeed split. This should not affect equation (24) however unless some stronger damping mechanism involving partial dislocations becomes operative.

VI. SUMMARY

The temperature, frequency, dislocation density, and n-type dopant concentration dependence of the high temperature internal friction in deformed and undeformed germanium and silicon has been measured.

At moderate temperatures a peak is present in not too highly doped material, independent of dislocation density and due to the acousto-electric effect. The acousto-electric peak was shown to be well described by the theory of Weinreich.³¹ The mechanism responsible for the excess carrier lifetime at the peak temperatures is most likely that of Auger band-to-band processes, however the experimental and theoretical treatments of Auger processes in germanium and silicon are as yet insufficient to make a positive identification.

The dislocation-dependent internal friction measurements made here on intrinsic material agree well with those of most previous authors.^{13-16,18-20} For the first time internal friction measurements in highly doped, n-type, deformed material have been made and a strongly enhanced dislocation-dependent damping has been found in extrinsic-behaving material.

A theoretical model for the high temperature dislocation damping has been developed and shown to agree well with the data. This model is based upon the viscous damping of dislocations in semiconductors by excess current carriers whose lifetimes are controlled by Auger band-to-band recombination processes.

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