Hot Carrier Concentration in *n*-Type Germanium —a Suggested Experiment

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The anisotropy character of the microwave conductivity of a many-valley semiconductor in the presence of a high dc field is discussed. The propagation of microwave signals through this anisotropic medium is briefly studied and a microwave experiment is suggested for determining the elements of the conductivity tensor. It is shown that an analysis of the data obtainable from the experiment would enable one to find out whether the ⟨100⟩ valleys in *n*-type germanium are populated under hot-electron conditions. It is also shown that if the ⟨100⟩ valleys are found to be insignificantly populated, one may determine the anisotropy factor K and the carrier population in the different ⟨111⟩ valleys from these data.

1. INTRODUCTION

THE experimental hot-electron characteristics of *n*-type germanium below the saturation region are explained qualitatively by the assumptions of intravalley acoustic and optical-phonon scattering.[1,2] A quantitative agreement between theory and experiment may also be obtained[3,4] below the saturation region when the effect of intervalley phonon scattering in causing a repopulation of carriers in the different ⟨111⟩ valleys is taken into account. The characteristics in the saturation region are not, however, understood[5] even when the scattering to the equivalent valleys is taken into account. It has been suggested[6] that in this region transition of carriers occurs to the ⟨100⟩ minima. Evidences have been put forward[7] from the data on optical and pressure experiments in support of this suggestion. It has, however, been pointed out by Schweitzer and Seeger[8] that the characteristics in the saturation region do not show any perceptible effect of this repopulation. The role of intervalley scattering may be clarified if the carrier populations in the different valleys, especially in the ⟨100⟩ valleys, can be determined experimentally.

Methods for the determination of carrier population from analysis of the conductivity characteristics have been outlined by Paige[9] and Nathan.[10] The carrier concentration has been evaluated by Paige for the electric field applied in the $[1/\sqrt{2}\ 1/\sqrt{2}\ \sqrt{3}]$ direction by using Koenig's[11] experimental data on the longitudinal conductivity and the anisotropy angle. The carrier distribution has been assumed to be Maxwellian and the temperature in the three hot valleys identical. Strictly speaking, this assumption is not justified since the effective fields in the three valleys are not equal. A theoretical relation between mobility and electron temperature and an empirical relation between intervalley relaxation time and electron temperature have also been assumed. The concentrations given by this method are therefore correct only if the above assumptions are valid. In addition, an indication of the population in the ⟨100⟩ minima cannot be obtained by this method because only two independent sets of data are used in the analysis.

In the method of Nathan[10] the carrier concentrations are obtained from a phenomenological analysis of the conductivity data for the ⟨100⟩ and ⟨111⟩ directions. The mobility at any effective field is obtained from the conductivity data for ⟨100⟩ directions, for which all the valleys are equally populated and the conductivity data are explained by one relaxation time. The carrier concentrations for the ⟨111⟩ direction of the applied field are then chosen so that the experimental data may be fitted by using the values of mobility for different effective fields in the different valleys, calculated from the conductivity for ⟨100⟩ direction of the field. These carrier concentrations are then used to calculate the intervalley scattering rate at any effective field and enable one to calculate the carrier populations for other directions of applied field. Since three independent sets of data are analyzed in this method, in principle, it should be possible to detect population in the ⟨100⟩ valleys through involved calculations. However, the accuracy of the method is limited by the amount of anisotropy in the conductivity. The data for the temperature of 77°K indicate significant repopulation, but at 298°K no repopulation is indicated. Hence, for small anisotropy as at room temperature, the effect of nonequivalent intervalley scattering would be very difficult to assess.

Microwave methods for the determination of the conductivity of semiconductors provide a powerful tool for obtaining the values of the components of the conductivity tensor, and may provide data for the resolution of the discrepancies, discussed above, in the roles attributed to intervalley scattering. It is the purpose of this paper to discuss the possibilities of a

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TABLE I. Components of the conductivity tensor for various field directions.

Directions of the coordinate axes[a]	σ_{xx}	σ_{yy}	σ_{zz}	σ_0
x [001] y [010] z [100]	$(e^2n\tau/m_c)(1+0.2128\phi)$	$(e^2n\tau/m_c)(1+0.2128\phi)$	$(e^2n\tau/m_c)(1+\phi)$	$e^2n\tau/m_c$
x [110] y [001] z [1$\bar{1}$0]	$(e^2/m_c)[n_h\tau_h(1.0746)+n_c\tau_c(2.92)]$	$(2e^2/m_c)[n_h\tau_h+n_c\tau_c(1+0.5425\phi_c)]$	$(e^2/m_c)[2.92n_h\tau_h(1+\phi_h)+1.0746n_c\tau_c(1+\phi_c)]$	$(e^2/m_c)[2.92n_h\tau_h+1.0746n_c\tau_c]$
x [1$\bar{1}$0] y [11$\bar{2}$] z [111]	$(e^2/m_c)[n_h\tau_h(2.5346+0.4082\phi_h)+n_c\tau_c(1.46)]$	$(e^2/m_c)[n_h\tau_h(2.5346+0.6930\phi_h)+n_c\tau_c(1.46)]$	$(e^2/m_c)[3.9186n_h\tau_h\times(1+\phi_h)+1.46n_c\tau_c(1+\phi_c)]$	$(e^2/m_c)[3.9186n_h\tau_h+1.46n_c\tau_c]$

[a] The high dc field is assumed to be applied in the z direction.

microwave method in determining whether scattering to ⟨100⟩ minima occurs in the saturation region and also in the determination of carrier concentrations in the ⟨111⟩ valleys below the saturation region with an accuracy better than what has been possible from an analysis of the dc data.

2. MICROWAVE CONDUCTIVITY UNDER HOT-ELECTRON CONDITIONS

Let us assume that the high dc field F_0 is applied in the z direction and the microwave field, applied along any arbitrary angle to the dc field, has the components F_x, F_y, F_z along the directions of the three coordinate axes. We shall assume that intervalley energy relaxation is negligible so that the heating of the carriers in any valley is determined by the effective field $F_{\rm eff}$ in the valley. The effective field $F_{\rm eff}$ is given by $(\mathbf{F}\cdot\boldsymbol{\alpha}_v\cdot\mathbf{F})^{1/2}$, where $\boldsymbol{\alpha}_v$ is the normalized reciprocal effective-mass tensor[6] in the valley and $\mathbf{F}$ is the total electric field applied. The effective field in the presence of a microwave signal is given by

$$F_{\rm eff}=F_0(\alpha_{zzv})^{1/2}\left[1+\frac{\alpha_{xzv}}{\alpha_{zzv}}\frac{F_x}{F_0}+\frac{\alpha_{yzv}}{\alpha_{zzv}}\frac{F_y}{F_0}+\frac{F_z}{F_0}\right]. \quad (1)$$

In the above expression, the second-order terms involving the squares or the products of the microwave field components have been neglected. Since the carrier concentration n_v and the relaxation time τ_v for each valley is determined by its temperature and hence by the effective field in the valley, the product $n_v\tau_v$ in the presence of the microwave field may be written as[12]

$$n_v\tau_v=(n_v\tau_v)_0\left[1+\phi_v\left(\frac{\alpha_{xzv}}{\alpha_{zzv}}\frac{F_x}{F_0}+\frac{\alpha_{yzv}}{\alpha_{zzv}}\frac{F_y}{F_0}+\frac{F_z}{F_0}\right)\right], \quad (2)$$

[12] E. Erlbach, Phys. Rev. 132, 1976 (1963).

where

$$\phi_v=\frac{1}{(n_v\tau_v)_0}\frac{\partial}{\partial F}(n_v\tau_v)_0F_0.$$

The subscript 0 in $n_v\tau_v$ or its derivative is used to indicate the value in the absence of the microwave field. It should be noted that the above expression for $n_v\tau_v$ is obtained when it is assumed that the product of the microwave frequency ω and the internal-energy relaxation time[13,14] τ_ϵ is small for each valley. In the general case, however, there would appear a multiplying factor of the form $1/(1+i\omega\tau_\epsilon)$. The components of the microwave conductivity tensor in the presence of a high dc field are hence given by

$$\sigma_{xx}=\frac{e^2}{m_0}\sum_v(n_v\tau_v)_0\alpha_{xxv}\left[1+\phi_v\frac{\alpha_{xzv}^2}{\alpha_{zzv}\alpha_{xxv}}\right], \quad (3)$$

$$\sigma_{yy}=\frac{e^2}{m_0}\sum_v(n_v\tau_v)_0\alpha_{yyv}\left[1+\phi_v\frac{\alpha_{yzv}^2}{\alpha_{zzv}\alpha_{yyv}}\right], \quad (4)$$

$$\sigma_{zz}=\frac{e^2}{m_0}\sum_v(n_v\tau_v)_0\alpha_{zzv}(1+\phi_v), \quad (5)$$

$$\sigma_{xy}=\sigma_{yx}=\frac{e^2}{m_0}\sum_v(n_v\tau_v)_0\alpha_{xyv}\left[1+\phi_v\frac{\alpha_{xzv}\alpha_{yzv}}{\alpha_{zzv}\alpha_{xyv}}\right], \quad (6)$$

$$\sigma_{yz}=\sigma_{zy}=\frac{e^2}{m_0}\sum_v(n_v\tau_v)_0\alpha_{yzv}(1+\phi_v), \quad (7)$$

$$\sigma_{zx}=\sigma_{xz}=\frac{e^2}{m_0}\sum_v(n_v\tau_v)_0\alpha_{zzv}(1+\phi_v). \quad (8)$$

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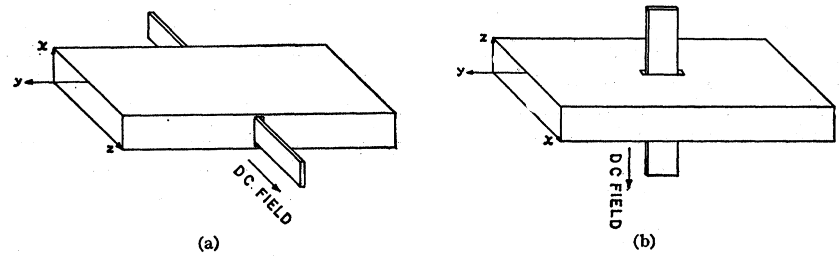

FIG. 1. Experimental arrangement for the determination of the components of the conductivity tensor. (a) Microwave field perpendicular to the dc field. (b) Microwave field in the same direction as dc field.

In the particular case, when the dc field is along one of the directions of symmetry, i.e., along ⟨100⟩, ⟨110⟩, or ⟨111⟩ directions,

$$\sigma_{xz}=\sigma_{zx}=\sigma_{yz}=\sigma_{zy}=0. \quad (9)$$

If the microwave field be in the plane perpendicular to the dc field, the microwave conductivity tensor will be given by

$$\sigma=\begin{bmatrix}\sigma_{xx} & \sigma_{xy}\\ \sigma_{yx} & \sigma_{yy}\end{bmatrix}. \quad (10)$$

3. MICROWAVE PROPAGATION IN A SEMICONDUCTOR HAVING CONDUCTIVITY ANISOTROPY

A linearly polarized microwave signal having the electric vector along the dc field will propagate as a linearly polarized wave and the medium will present a conductivity σ_{zz}. However, if the microwave electric field be in the plane perpendicular to the dc field, its propagation characteristic may be complicated. For a medium having the conductivity given by Eq. (10), Maxwell's equation for a linearly polarized wave propagating in the z direction may be written as

$$\partial^2E_x/\partial z^2=i\omega\mu(i\omega\epsilon+\sigma_{xx})E_x+i\omega\mu(\sigma_{xy})E_y, \quad (11)$$

$$\partial^2E_y/\partial z^2=i\omega\mu(\sigma_{yx})E_x+i\omega\mu(i\omega\epsilon+\sigma_{yy})E_y, \quad (12)$$

where ϵ and μ are the permittivity and permeability of the medium. If the signal propagates in the medium with a propagation constant Γ, then Γ is given by

$$(-\omega^2\mu\epsilon+i\omega\mu\sigma_{xx}-\Gamma^2)(-\omega^2\mu\epsilon+i\omega\mu\sigma_{yy}-\Gamma^2)-(i\omega\mu)^2\sigma_{xy}\sigma_{yx}=0. \quad (13)$$

Thus, Γ has the solutions

$$\Gamma^2=\tfrac{1}{2}(\Gamma_{xx}^2+\Gamma_{yy}^2)\pm\tfrac{1}{2}[(\Gamma_{xx}^2-\Gamma_{yy}^2)^2+4\Gamma_{xy}^2\Gamma_{yx}^2]^{1/2}, \quad (14)$$

where

$$\Gamma_{xx}^2=-\omega^2\mu\epsilon+i\omega\mu\sigma_{xx}, \quad (15)$$

$$\Gamma_{yy}^2=-\omega^2\mu\epsilon+i\omega\mu\sigma_{yy}, \quad (16)$$

$$\Gamma_{xy}^2=i\omega\mu\sigma_{xy}, \quad (17)$$

$$\Gamma_{yx}^2=i\omega\mu\sigma_{yx}. \quad (18)$$

Also,

$$\frac{E_y}{E_x}=-\frac{1}{\Gamma_{xy}^2}[\tfrac{1}{2}(\Gamma_{xx}^2-\Gamma_{yy}^2)\mp\tfrac{1}{2}\{(\Gamma_{xx}^2-\Gamma_{yy}^2)^2+4\Gamma_{xy}^2\Gamma_{yx}^2\}^{1/2}]. \quad (19)$$

Thus in the general case, only plane waves with the tip of the electric vector describing a tilted ellipsoid may propagate in the medium. The focus of the electric vector is different for the two senses of rotation.

It is evident that a linearly polarized wave would propagate in this medium without any change of polarization when $\Gamma_{xy}=\Gamma_{yx}=0$. In this case, $\Gamma^2=\Gamma_{xx}^2$ or Γ_{yy}^2. This means that the x component of the electric vector propagates with the propagation constant Γ_{xx} and the y component with the propagation constant Γ_{yy}. In general, if the conductivity of the sample is large enough to affect the phase constant, for nonequal values of σ_{xx} and σ_{yy} the x and y components of the signal will suffer different phase shift and attenuation in propagating through the semiconductor and the emerging wave will be elliptically polarized. If on the other hand, the conductivity is small the attenuation of the two signals will be different and the emerging wave will be linearly polarized but the direction of the electric field of the emerging wave will be rotated with respect to that of the incident wave. It is also evident that linearly polarized waves having the electric field in the x or y directions will propagate, respectively, with the propagation constants Γ_{xx} and Γ_{yy}.

4. THE MICROWAVE CONDUCTIVITY OF n-TYPE GERMANIUM WHEN ONLY THE ⟨111⟩ VALLEYS ARE POPULATED

The mass factors for the different valleys when the dc field is applied in the directions of symmetry have been given by Das and Nag.[15] Table I has been prepared, using these data and gives the conductivity components for these directions of the dc field. In all these cases $\sigma_{xy}=\sigma_{yx}=0$. The subscripts c and h are used to indicate, respectively, the values for cold and hot valleys. m_c is the conductivity effective mass. In evaluating the different components of conductivity tensor given in Table I, it has been assumed that the value of the anisotropy factor K is 20. From Table I it may be observed that for [100] direction of the dc field, $\sigma_{xx}=\sigma_{yy}$; but for the other two directions, all the conductivity components are unequal.

5. EXPERIMENTAL ARRANGEMENT

A suitable experimental arrangement for obtaining the conductivity components is shown in Fig. 1. The

[15] P. Das and B. R. Nag, Proc. Phys. Soc. (London) 82, 923 (1963).

sample is prepared in rectangular shape with a length greater than the broad dimension of the waveguide. For obtaining σ_{xx} and σ_{yy}, it is inserted in a rectangular guide through nonradiating slots in the narrow sides (shown in the figure) so that the plane of the sample is perpendicular to the axis of the waveguide [Fig. 1(a)]. The sample is so cut that the length and the breadth of the sample coincide, respectively, with one set of z and x directions of Table I. The faces and sides of the sample are to be insulated from the guide walls.

A microwave signal is made incident on the sample and pulsed dc fields are applied along the length of the sample. The microwave signal would propagate as a linearly polarized wave and the attenuation and phase shift suffered by the signal may be measured by the conventional techniques. These data would give Γ_{xx} and hence σ_{xx}. The conductivity along the y direction may be obtained from a similar experiment with the sample so mounted that its length and breadth coincide, respectively, with the z and y directions of Table I.

The conductivity along the z directions may be obtained by mounting the sample through nonradiating slots in the broad dimension of the waveguide so that the plane of the sample is parallel to the direction of propagation [Fig. 1(b)]. The sample is cut so that the length of the sample is identical to z direction of Table I. The measured attenuation and phase shift would give σ_{zz}. σ_0 may be obtained from the dc data, if one end of the sample is made thick enough to eliminate injection effects.

6. ANALYSIS OF THE EXPERIMENTAL DATA

Assuming that the population of the carriers is confined only to the ⟨111⟩ valleys, carrier concentration in the different valleys may be obtained from an analysis of the experimental data for the dc field applied along the three symmetry directions of the crystal. For electric field in the [100] direction, the value of τ for any applied field may be obtained from the values of σ_0. If the microwave frequency is high enough to make $\phi/(1+i\omega\tau_\epsilon)$ much too small, the values of σ_{xx}, σ_{yy}, and σ_{zz} are expected to be identical to σ_0 which then provide three extra sets of data and may be used to improve the accuracy in determining the value of τ. If on the other hand the microwave frequency is such that the contribution of ϕ is not negligible, τ may be obtained from the values of σ_{xx}, σ_{yy}, or σ_{zz} using the following relation which is derived from the expression for these quantities given in Table I.

$$\tau=\frac{m_c}{ne^2}\frac{1}{\alpha_i}F_0^{-1/\alpha_i}\int\sigma_{ii}F_0^{(1-\alpha_i)/\alpha_i}dF;\quad i=x,y,z,\qquad(20)$$

where

$$\alpha_x=\alpha_y=0.2128,\quad\alpha_z=1.$$

In this case also, there are available three sets of extra independent data giving the value of τ.

In the experiment with the dc field along the [111] or [110] direction, there are four independent sets of data available which may be used to obtain the values of the unknowns $n_h\tau_h$, $n_c\tau_c$, $n_h\tau_h\phi_h$, and $n_c\tau_c\phi_c$. τ_h and τ_c may be obtained from an analysis of the ⟨100⟩ data following the method of Nathan[10] and concentration in the different valleys may hence be obtained. It may be noted that the values of the conductivity components used for this analysis correspond to identical experimental conditions and hence the difference between the conductivities would be very sensitive to carrier repopulation. On the other hand, in the dc experiments for the same applied field in the two directions, the effective fields in the valleys are altered and hence τ_h and τ_c are changed, which in effect makes the data insensitive to carrier repopulation.

It is also of interest to note that if the contribution of ϕ_c to σ_{yy} for the [110] experiment is negligible (this may occur when there is insignificant carrier repopulation, since the effective fields in the cold valleys are small), there are three sets of independent data available for determining $n_h\tau_h$ and $n_c\tau_c$. Hence if one treats the anisotropy factor K as an unknown quantity, its value may be obtained from an analysis of these data and this would provide an experimental method for obtaining K under hot electron conditions. The value of K thus obtained is independent of the ⟨100⟩ data and hence of any assumption about τ_h and τ_c.

In the above discussion, it has been assumed that the population of the valleys is confined to the ⟨111⟩ valleys and, as a result the values of τ obtained from the analysis of the four sets of ⟨100⟩ experimental data discussed earlier, are expected to be identical. However, if the ⟨100⟩ valleys are also populated, the following terms will be added to the values of σ_{xx}, σ_{yy}, σ_{zz}, and σ_0 given in Table I:

$$\begin{aligned}\sigma_{xx}&=(e^2/m_c)(0.912n_h'\tau_h'+0.76n_c'\tau_c'),\\ \sigma_{yy}&=(e^2/m_c)(0.912n_h'\tau_h'+0.76n_c'\tau_c'),\\ \sigma_{zz}&=(e^2/m_c)[0.76n_h'\tau_h'(1+\phi_h')+n_c'\tau_c'(1+\phi_c')],\\ \sigma_0&=(e^2/m_c)(0.76n_h'\tau_h'+n_c'\tau_c'),\end{aligned}\qquad(21)$$

where the primes refer to the values in the ⟨100⟩ valleys.

On considering Eq. (21), it is evident that if the ⟨100⟩ valleys are populated, the values of τ obtained from the ⟨100⟩ experiments would not be equal. Also, the following relation will not be satisfied:

$$\sigma_{xx}=\sigma_{yy}=\sigma_0+0.2128(\sigma_{zz}-\sigma_0).\qquad(22)$$

The inequality in τ or a deviation from Eq. (22), if observed, would serve as a definite evidence of the population in the ⟨100⟩ valleys at high electric fields. Unfortunately, however, the effect of this population is of such form that the exact values of the carrier population in the ⟨100⟩ valleys can not be obtained from the experimental data.

7. CONCLUSION

A microwave experiment has been suggested for obtaining the components of the conductivity tensor under hot electron conditions in *n*-type germanium. It is found that it would be possible to determine the carrier repopulation with good accuracy and also to obtain a definite indication about the population of the ⟨100⟩ valleys from a theoretical analysis of the obtainable data. In regions where the ⟨100⟩ valleys are not poputated, the available data may be used for determining the anisotropy factor (K) under hot electron conditions.

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Electrical-Transport Measurements on Synthetic Semiconducting Diamond

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Four-probe electrical-conductivity measurements have been made on a series of General Electric aluminum-doped and nominally boron-doped synthetic semiconducting diamonds in the temperature range 223 to 323°K, and the results compared with those obtained from a natural semiconducting diamond (type IIb). These results, together with those obtained from optical-absorption, recombination-radiation, and chemical-impurity measurements on the same set of specimens, show that the same acceptor center, namely aluminum, is responsible for the semiconducting properties of both natural diamond and synthetic semiconducting diamond presently available. The large range of activation energies reported by other workers is considered to be due to the onset of impurity conduction at progressively higher temperatures with increasing concentrations of neutral acceptor centers.

INTRODUCTION

ELECTRICAL–transport,[1–6] optical-absorption,[7] and extrinsic recombination-radiation measurements[6] on natural semiconducting diamonds (type IIb) have shown that the semiconducting properties can be explained in terms of one definite invariant acceptor center with an activation energy of ~0.37 eV. This acceptor center has been identified with substitutional trivalent aluminum by comparing acceptor concentrations derived from Hall data with aluminum concentrations measured by neutron-activation analysis.[6] The analysis of the Hall-effect data indicates partial compensation of the acceptor concentration by deep-lying donors, with compensation ratios varying typically between 0.03 and 0.3.[2] The donor center is thought to be nitrogen at isolated substitutional sites with a donor binding energy of ~4 eV.[8]

The extrinsic features in the recombination-radiation spectra of natural semiconducting diamonds have been associated with the decay of excitons bound to the neutral acceptor center.[6] The recombination-radiation spectra obtained from both aluminum-doped and nominally boron-doped semiconducting synthetic diamonds[9] are virtually identical with those obtained from natural semiconducting diamond, except that the intensity of the extrinsic features relative to the intrinsic features is much stronger in the synthetic specimens.[6] These results suggest that the same acceptor center, namely aluminum, is responsible for the semiconducting properties of both natural and synthetic diamonds presently available, independent of the nominal dopant in the latter. Recombination-radiation measurements on more recent batches of semiconducting synthetic diamond,[9] including nominally undoped, boron-doped, and aluminum-doped specimens prepared using various catalysts, confirm this general picture.[10] Infrared-absorption measurements have also been made on a selection of aluminum-doped and nominally boron-doped synthetic diamonds.[11] The features in the line spectra associated with

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