Determination of the conduction-band structure of the III-V semiconductors subject to mechanical strain from measurements of the reflectivity spectrum

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In an earlier paper, the authors proposed a model for the conduction-band structure of the III-V semiconductors subject to mechanical deformation. This work presents the theoretical basis for the experimental study of the deformed band structure from measurements of the reflectivity spectrum in the plasma region. The analysis involves two related subjects: the Maxwell equations for optically anisotropic material and the conductivity of the carriers in the deformed solid. The former determines the reflectivity spectrum, whereas the latter furnishes the means by which the carrier eigenstates affect the optical properties. The advantages of this technique are outlined.

I. INTRODUCTION

In an earlier paper,[1] the authors presented a theoretical determination of the effect of mechanical strain on the Γ-point conduction-band minimum in the III-V semiconductors. In this paper we show how these predictions can be checked experimentally from the measurement of the reflectivity spectrum. It should be pointed out that careful design of this experiment can greatly enhance the value of the experimental results. For example, consider first the importance of choosing a proper operating frequency. For sufficiently high frequency, the details of the carrier scattering mechanism become unimportant in many optical phenomena. An upper limit on the frequency is imposed so as to exclude band to band transitions which are not very suitable for the detailed study of a single band. In quantitative terms one wishes to maximize the frequency-relaxation time product without inducing band-to-band excitations. Often frequencies around the plasma minimum adequately satisfy these constraints. A second, experimentally controllable, parameter worthy of consideration is the occupation statistics of the carriers in the band under study. A marked advantage results if degenerate carrier statistics are applicable as one can then study the eigenstates at a fixed energy (the Fermi energy).

In Sec. II, Maxwell's equations for the propagation of electromagnetic radiation in an anisotropic semiconducting solid are considered and the reflectivity spectrum is determined. The influence of the free carriers naturally enters through their electrical conductivity.

In Sec. III a general technique for calculating the transport coefficients for an energy band having only a small deviation from isotropy is presented. In Sec. IV the conductivity of deformed n-type degenerate III-V semiconductors is calculated using this technique. Some semiquantitative considerations are presented which allow one to estimate from a single feature of the reflectivity spectrum the magnitude of the frequency-relaxation time product.

In the following paper,[2] the theoretical considerations presented here are used in the analysis of the shift of the reflectivity spectrum of n-type degenerate InSb subject to uniaxial deformation.

II. REFLECTIVITY SPECTRUM OF ANISOTROPIC CRYSTALLINE SOLIDS

Use of Maxwell's equations allows one to determine the allowed modes of propogation of an electromagnetic wave (frequency ω) in an anisotropic crystalline solid. We define

$$\hat{N}^2 = \hat{\epsilon}/\epsilon_0 - j\hat{\sigma}/\epsilon_0\omega\,, \tag{1}$$

where $\hat{\epsilon}$ is the lattice dielectric constant and $\hat{\sigma}$ is the conductivity of the free carriers. For convenience we choose a coordinate system in which $\hat{N}^2$ is diagonal. We will restrict our attention to plane waves (wave vector $\vec{k}$) propogating in the X-Y plane. Defining $\vec{k} = (\omega/c)\vec{n}$, we can determine the electric field $\vec{E}$ associated with the wave from

$$\begin{vmatrix} (-n_y^2+N_x^2) & n_x n_y & 0 \\ n_x n_y & (-n_x^2+N_y^2) & 0 \\ 0 & 0 & -(n_x^2+n_y^2)+N_z^2 \end{vmatrix} \begin{vmatrix} E_x \\ E_y \\ E_z \end{vmatrix} = 0. \tag{2}$$

Corresponding to (2) there are two independent modes of propogation: The transverse electric mode (TEM) for which $E_x = E_y = 0$ and the transverse magnetic mode (TMM) for which $E_z = 0$.

The reflectivity of the material is found by satisfying the appropriate boundary conditions on the electric and magnetic fields at the interface. Again, assuming the incident wave is propogating

in the X-Y plane, and the interface is an X-Z surface, the ratio E_0'/E_0 of the electric field intensity of the reflected and incident waves is, for TEM,

$$\frac{E_0'}{E_0}=\frac{\cos\theta-(N_z^2-n_y^2)^{1/2}}{\cos\theta+(N_z^2-n_y^2)^{1/2}}, \tag{3}$$

and for TMM,

$$\frac{E_0'}{E_0}=\frac{\cos\theta-(N_x^2-n_y^2)^{1/2}/N_xN_y}{\cos\theta+(N_x^2-n_y^2)^{1/2}/N_xN_y}, \tag{4}$$

where θ is the angle of incidence and $n_y=\sin\theta$. The reflectivity of the surface for either mode is given by

$$R=|E_0'|^2/|E_0|^2. \tag{5}$$

The region of the spectrum for which $\mathrm{Re}N_i^2\simeq 1$ is one in which the free carriers have a pronounced effect on the optical properties of the material. If at the same time the frequency-relaxation time product is large, then only the dynamic properties of the carriers, and not the details of the scattering process, are an important factor.

III TRANSPORT COEFFICIENTS OF ENERGY BANDS HAVING A SMALL ANISOTROPY

General methods (see, for example, Ref. 3) for calculating the transport properties of ellipsoidal bands of the form

$$\gamma(\epsilon)=\sum_{\alpha\beta}a_{\alpha\beta}k_\alpha k_\beta, \tag{6}$$

where γ is an arbitrary function and $a_{\alpha\beta}$ is constant are well developed and have found widespread application. Unfortunately the deformed conduction band in the III-V semiconductors cannot be placed in the form of Eq. (6). In this regard the most notable feature of the deformed conduction band is that the deviation from perfect isotropy is small for strains in the linear elastic region. We develop below a general technique for finding the electrical conductivity of such a band. The extension to other transport coefficients is not difficult.

We assume that the energy band is doubly spin degenerate and write the dispersion relation in the form

$$\epsilon=g(k)+\Delta g(k,\Omega), \tag{7}$$

where Δg depends on the magnitude and direction of $\vec{k}$, $g(k)$ depends only on the magnitude, and $\Delta g\ll g$. The carrier distribution function f is obtained from the Boltzmann transport equation and is given by

$$f=f_0+e(\vec{E}\cdot\vec{v})\frac{\tau}{1+j\omega\tau}\frac{\partial f_0}{\partial\epsilon}, \tag{8}$$

where f_0 is the equilibrium Fermi-Dirac distribution, $\vec{v}=(1/\hbar)(\partial\epsilon/\partial\vec{k})$ is the carrier velocity, and $\vec{E}$ is a small harmonically time varying electric field of frequency ω. The scattering term in the Boltzmann equation is handled by use of the relaxation time (τ) approximation and τ is a function of energy. The current density associated with a doubly spin degenerate band is

$$\vec{J}=-e\int\vec{v}f\frac{2}{(2\pi)^3}d^3k, \tag{9}$$

and the conductivity $\hat{\sigma}$ is given by

$$\sigma_{ij}=-\frac{2}{(2\pi)^3}e^2\int v_iv_j\tau^*\frac{\partial f_0}{\partial\epsilon}k^2\,dk\,d\Omega, \tag{10}$$

where

$$\tau^*=\tau/(1+j\omega\tau). \tag{11}$$

To exploit the properties of $(-\partial f_0/\partial\epsilon)$, it is advantageous to make ϵ, rather than k, a variable of integration in (10). Consequently, we solve (7) for k to first order in Δg. We immediately get

$$k=h-h'\Delta g(h,\Omega), \tag{12}$$

where $h(\epsilon)=g^{-1}$ is the functional inverse of $g(k)$ and the prime on h denotes a first derivative.

Other factors in the integrand (10) can now be expressed as explicit functions of energy:

$$\begin{aligned}v_\alpha&=\frac{1}{\hbar}\left(g'(k)\frac{k_\alpha}{k}+\frac{\partial\Delta g(k,\Omega)}{\partial k_\alpha}\right)\\&=\frac{1}{\hbar}\left(\left[g'(h)-g''(h)h'\Delta g(h,\Omega)\right]\frac{k_\alpha}{k}+\frac{\partial\Delta g(k,\Omega)}{\partial k_\alpha}\right),\end{aligned} \tag{13}$$

$$\frac{\partial\epsilon}{\partial k}=g'(h)-g''(h)h'\Delta g(h,\Omega)+\frac{\partial\Delta g(k,\Omega)}{\partial k}. \tag{14}$$

Thus to first order in Δg, σ_{ij} is given by

$$\sigma_{ij}=-\frac{2}{(2\pi)^3}\frac{e^2}{\hbar^2}\int\tau^*\left(\frac{\partial f_0}{\partial\epsilon}\right)d\epsilon\,d\Omega\,A_{ij}\frac{k_ik_j}{k^2}, \tag{15}$$

where

$$\begin{aligned}A_{ij}&=g'h^2-\left(g''h'\Delta g+\frac{\partial\Delta g}{\partial k}\right)h^2-2hh'\Delta g\\&\quad+\frac{k}{k_i}\frac{\partial\Delta g}{\partial k_i}h^2+\frac{k}{k_j}\frac{\partial\Delta g}{\partial k_j}h^2,\end{aligned} \tag{16}$$

and all functions of k remaining in (16) are to be written as functions of energy through $k=h(\epsilon)$. To evaluate (15) requires specific knowledge of g and Δg. The integration over the solid angle Ω will normally present no problem.

A brief discussion of the relaxation time τ is warranted. Changes in band structure (as represented by Δg) naturally entail changes in the electronic wave functions and hence changes in the scattering transition probabilities. Thus $\tau(\epsilon)$ will depend on Δg but we shall not attempt to determine this dependence quantitatively. To isolate band structure effects, it will be necessary to ensure that the carrier scattering process is not an important factor.

IV. EFFECT OF MECHANICAL DEFORMATION ON THE CONDUCTIVITY OF *n*-TYPE DEGENERATE III-V SEMICONDUCTORS

The conduction-band minimum at the Γ point in most III-V semiconductors exhibits the following well-known nonparabolic but spherical doubly spin degenerate dispersion relation[4]:

$$E'(E'+E_g)(E'+E_g+\Delta)-P^2k^2(E'+E_g+\tfrac{2}{3}\Delta)=0, \tag{17}$$

$$E'=E-\hbar^2k^2/2m_0\,, \tag{18}$$

where E_g is the Γ point band gap, Δ is the spin-orbit splitting of the valence band, and P is a momentum matrix element between states at Γ. The nonparabolicity stems from the strong admixture of s- and p-like Γ-point states required to accurately describe the conduction-band states. The solution of the cubic equation (17) gives the function $g(k)$.

The change in energy produced by a mechanical deformation characterized by the strain tensor $\hat{\epsilon}$ was found in an earlier paper[1] to be

$$\Delta E^{\pm}(\epsilon)=\Delta g=C_1\epsilon-c\epsilon(1-a_c^2)+\frac{b}{2}(2c_c^2-b_c^2)\left(3\sum\epsilon_{ii}k_i^2/k^2-\epsilon\right)+n(2c_c^2-b_c^2)\sum_{i>j}\frac{k_ik_j}{k^2}\epsilon_{ij}-2a_cc_cPk\sum k_i^2\epsilon_{ii}/k^2$$

$$-4a_cc_cPk\sum_{i>j}\frac{k_ik_j\epsilon_{ij}}{k^2}\pm\sqrt{2}\,a_cb_cC_2\left(\epsilon_{xy}^2+\epsilon_{yz}^2+\epsilon_{xz}^2-\frac{1}{k^2}(\epsilon_{yz}k_x+\epsilon_{xz}k_y+\epsilon_{xy}k_z)^2\right)^{1/2}. \tag{19}$$

In this expression, C_1, c, b, n, C_2 are deformation potentials associated with the Γ point states, $\epsilon=\mathrm{Tr}\hat{\epsilon}$, and a_c, b_c, c_c, given below, describe the admixture of s and p like states at Γ necessary to describe the undeformed conduction band eigenfunction at a given $\vec{k}$:

$$a_c=Pk(E'+E_g+\tfrac{2}{3}\Delta)/N\,,$$

$$b_c=\tfrac{1}{3}\sqrt{2}E'\Delta/N, \tag{20}$$

$$c_c=E'(E'+E_g+\tfrac{2}{3}\Delta)/N\,,$$

where N is chosen such that $a_c^2+b_c^2+c_c^2=1$. Since the analysis in Sec. III is linear in Δg, the splitting of the conduction band degeneracy given by the last term in (19) will produce no contribution. We will measure the energy with respect to the band edge in the deformed material and so the first term ($C_1\epsilon$) in (19) will also disappear.

The ac conductivity for the deformed conduction band under strongly degenerate conditions can be calculated using (15). The total number of carriers in the sample is fixed by the number of donor atoms present and so the change in carrier concentration under mechanical strain is given by

$$\Delta N/N_0=-\epsilon. \tag{21}$$

The subscript 0 denotes the unstrained value. We have

$$N=\int f\frac{2}{(2\pi)^3}\,d^3k$$

$$=\int-\left(\frac{\partial f_0}{\partial\epsilon}\right)\frac{1}{3}k^3\,d\epsilon\,d\Omega\,\frac{2}{(2\pi)^3}\,. \tag{22}$$

To proceed analytically, we use the standard approximation

$$-\left(\frac{\partial f_0}{\partial\epsilon}\right)=\delta(\epsilon-\epsilon_F), \tag{23}$$

where ϵ_F is the Fermi energy. Using (12), we find

$$\int\frac{1}{3}k^3\,d\Omega=\frac{4\pi h^3}{3}-h^2h'\int\Delta g(h,\Omega)\,d\Omega\,. \tag{24}$$

From (19),

$$\int\Delta g(h,\Omega)\,d\Omega=4\pi[-c\epsilon(1-a_c^2)-\tfrac{2}{3}a_cc_cPk], \tag{25}$$

Therefore

$$N=\frac{1}{3\pi^2}h^3+\frac{h^2h'}{\pi^2}(c\epsilon+\tfrac{2}{3}a_cc_cPk\epsilon)\,, \tag{26}$$

and the right-hand side of (26) is to be evaluated at $\epsilon=\epsilon_F$. Writing $\epsilon_F=\epsilon_{F0}+\Delta\epsilon_F$, using $N_0=h_0^3/3\pi^2$, expanding (26) to first order in $\Delta\epsilon_F$ and using (21) gives

$$\Delta\epsilon_F=-\tfrac{1}{3}g'_0k_{f0}\epsilon-c\epsilon-\tfrac{2}{3}a_cc_cPk\epsilon\,. \tag{27}$$

Making use of the definitions

$$R=1-a_c^2,\quad S=\frac{2c_c^2-b_c^2}{k^2},\quad T=\frac{4a_cc_c}{k}, \tag{28}$$

we get

$$\frac{\partial\Delta g}{\partial k}=-c\epsilon\frac{\partial R}{\partial k}+\frac{b}{2}\frac{\partial}{\partial k}(Sk^2)\left(3\sum\epsilon_{ii}k_i^2/k^2-\epsilon\right)+n\frac{\partial}{\partial k}(Sk^2)\sum\frac{k_ik_j\epsilon_{ij}}{k^2}$$
$$-\frac{P}{2}\frac{\partial}{\partial k}(Tk^2)\sum\frac{k_i^2\epsilon_{ij}}{k^2}-P\frac{\partial}{\partial k}(Tk^2)\sum_{i>j}\frac{k_ik_j\epsilon_{ij}}{k^2}, \tag{29}$$

$$\frac{\partial\Delta g}{\partial k_\alpha}=c\epsilon\frac{\partial R}{\partial k}\frac{k_\alpha}{k}+\frac{b}{2}\frac{\partial S}{\partial k}\frac{k_\alpha}{k}\left(3\sum\epsilon_{ii}k_i^2-ek^2\right)+\frac{b}{2}S(6\epsilon_{\alpha\alpha}-2\epsilon k_\alpha)+n\frac{\partial S}{\partial k}\frac{k_\alpha}{k}\sum_{i>j}k_ik_j\epsilon_{ij}$$
$$+nS\sum_{j\neq\alpha}\epsilon_{\alpha j}k_j-\frac{P}{2}\frac{\partial T}{\partial k}\frac{k_\alpha}{k}\sum k_i^2\epsilon_{ii}-\frac{P}{2}T\times 2k_\alpha\epsilon_{\alpha\alpha}-P\frac{\partial T}{\partial k}\frac{k_\alpha}{k}\sum_{i>j}k_ik_j\epsilon_{ij}-PT\sum_{\alpha\neq i}\epsilon_{\alpha j}k_j. \tag{30}$$

To calculate $\sigma_{\alpha\beta}$, we must first perform the integration over the angular variable in (15):

$$I_{\alpha\beta}=\int\frac{k_\alpha k_\beta}{k^2}A_{\alpha\beta}\,d\Omega. \tag{31}$$

These angular integrals are algebraically tedious because of the large number of terms involved (approximately 35) but the integrations themselves are simple as they involve only different products, powers, crossproducts, etc., of k_α/k. We find

$$I_{\alpha\alpha}=4\pi g'h^2\left\{1+c\epsilon\left(\frac{g''}{g'^2}+\frac{2}{g'h}\right)-c\epsilon\frac{1}{g'}R'+\frac{b}{2}(3\epsilon_{\alpha\alpha}-\epsilon)\left[-\frac{2}{5}S\left(\frac{g''h^2}{g'^2}+\frac{2h}{g'}\right)+\frac{2}{5}\frac{h^2}{g'}S'+\frac{16}{5}\frac{Sh}{g'}\right]\right.$$
$$\left.+\tfrac{1}{6}Ph^2\epsilon\left(\frac{g''}{g'^2}+\frac{1}{g'h}\right)+\frac{1}{2}Ph(2\epsilon_{\alpha\alpha}+\epsilon)\left(\frac{1}{5}\frac{g''h}{g'^2}T-\frac{1}{5}\frac{hT'}{g'}\right)+\tfrac{1}{2}Ph(3\epsilon_{\alpha\alpha}-\epsilon)\left(-\frac{4}{5}\frac{T}{g'}\right)\right\}. \tag{32}$$

Similarly

$$I_{\alpha\beta}=4\pi(h^3/5)[-(g''/g)(nSh-PTh)+nhS'-PhT'+6nS-6PT],\quad \alpha\neq\beta, \tag{33}$$

therefore

$$\sigma_{\alpha\beta}=\frac{2}{(2\pi)^3}\frac{q^2}{\hbar^2}\int-\frac{\partial f_0}{\partial\epsilon}I_{\alpha\beta}\tau^*\,d\epsilon=\frac{2}{(2\pi)^3}\frac{q^2}{\hbar^2}\tau^*I_{\alpha\beta}\Big|_{\epsilon=\epsilon_F}. \tag{34}$$

To use (34) to describe the change in $\hat{\sigma}$ produced by deformation, one should first include the change in Fermi level with deformation. This means that all zeroth order terms in Δg in $I_{\alpha\alpha}$ must be expanded to first order in $\Delta\epsilon_f$. Denoting $I_0=4\pi g'h^2\big|_{\epsilon_{F0}}$ we find with the use of (27):

$$\frac{\Delta I_{\alpha\alpha}}{I_0}=\epsilon\left[-\frac{1}{3}\left(\frac{g''h}{g'}+2\right)-\frac{1}{6}\frac{PTh}{g'}\right]-c\epsilon\frac{1}{g'}R'+\frac{b}{2}(3\epsilon_{\alpha\alpha}-\epsilon)\left[-\frac{2}{5}S\left(\frac{g''h^2}{g'^2}+\frac{2h}{g'}\right)+\frac{2}{5}\frac{h^2}{g'}S'+\frac{16}{5}\frac{Sh}{g'}\right]$$
$$+\tfrac{1}{2}Ph(2\epsilon_{\alpha\alpha}+\epsilon)\left(\frac{1}{5}\frac{g''hT}{g'^2}-\frac{1}{5}\frac{h}{g'}T'\right)+\tfrac{1}{2}Ph(3\epsilon_{\alpha\alpha}-\epsilon)\left(-\frac{4}{5}\frac{T}{g'}\right), \tag{35}$$

$$\Delta I_{\alpha\beta}/I_0=\epsilon_{\alpha\beta}(h/5g')[-(g''/g')(nSh-PTh)+nhS'-PhT'+6nS-6PT],\quad \alpha\neq\beta. \tag{36}$$

These last two equations are to be evaluated at ϵ_{F0}.

Equations (35) and (36) can be symbolically written in the simpler form

$$\Delta I_{\alpha\alpha}/I_0=a_1\epsilon+a_2\epsilon_{\alpha\alpha}+a_3c\epsilon+a_4b(3\epsilon_{\alpha\alpha}-\epsilon), \tag{37}$$

$$\Delta I_{\alpha\beta}/I_0=a_2\epsilon_{\alpha\beta}+a_4n\epsilon_{\alpha\beta},\quad \alpha\neq\beta, \tag{38}$$

where a_1, a_2, a_3, and a_4 are functions of the undeformed band parameters and Fermi level

$$a_1=(2+g''h/g')(-\tfrac{1}{3})-\tfrac{1}{6}PTh/g'+u-v, \tag{39}$$

$$a_2 = 2u + 3v\,, \tag{40}$$

$$a_3 = -(1/g')R'\,, \tag{41}$$

$$a_4 = \tfrac{1}{5}(h/g')(hS' + 6S - g''hS/g')\,, \tag{42}$$

$$u = \tfrac{1}{2}Ph(g''hT/5g'^2 - hT'/5g')\,, \tag{43}$$

$$v = -2PhT/5g'\,. \tag{44}$$

The conductivity can now be written

$$\sigma_{\alpha\beta} = [2/(2\pi)^3](q^2/\hbar^2)\tau^* I_0(1 + \Delta I_{\alpha\beta}/I_0)\,. \tag{45}$$

Equations (37), (38), and (45) reveal that the second-rank tensors $\hat{\sigma}$ and $\hat{\epsilon}$ are related by a symmetric fourth rank tensor whose components are apparent from (43) and (44). The symmetry of this fourth-rank tensor is typical of all fourth-rank tensors relating two symmetric second-rank tensors in a cubic material. This allows one to express the relationship between $\hat{\sigma}$ and $\hat{\epsilon}$ by a six-dimensional matrix equation in an identical way to which the mechanical stress-strain equation is often handled.[5]

Since $\tau^* = \tau/(1 + j\omega\tau)$, we have

$$\mathrm{Re}\sigma_{\alpha\beta} = (1/\omega\tau)\,\mathrm{Im}\sigma_{\alpha\beta}\,. \tag{46}$$

From (1) we see that, for $\omega\tau \gg 1$, $\hat{N}^2$ and hence the reflectivity spectrum become independent of the relaxation time τ. This implies that the carrier scattering mechanism is no longer a factor. Furthermore, the dependence of the relaxation time on mechanical strain, or even the whole question of the validity of the relaxation time approximation itself, has little or no bearing on the dependence of the plasma region reflectivity on mechanical strain.

The magnitude of $\omega\tau$ can be quite simply estimated from the reflectivity spectrum. For optical isotropy, and normal incidence, Eqs. (1)–(5) give

$$R = [(\mathrm{Re}N - 1)^2 + (\mathrm{Im}N)^2]/[(\mathrm{Re}N + 1)^2 + \mathrm{Im}N)^2]. \tag{47}$$

The minimum reflectivity R_m occurs for $\mathrm{Re}N \simeq 1$, and so $(\mathrm{Im}N)^2 \simeq 4R_m$. It is an easy matter to then show that

$$\mathrm{Im}\sigma_m/\mathrm{Re}\sigma_m = \omega_m\tau = \kappa/4\sqrt{R}_m\,. \tag{48}$$

At optical frequencies, in the III-V semiconductors, $10 < \kappa < 20$. For $R_m \lesssim 0.10$, $\omega_m\tau \gtrsim 10$. Under these conditions the reflectivity spectrum in the plasma region provides a very precise tool for the study of band structure.

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