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Theory of Electronic States and Transport in Graded Mixed Semiconductors*

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Semiconductors which are slowly graded in composition can be shown to have position-dependent band gaps and position-dependent effective masses, describable in terms of an effective Hamiltonian in an effective-mass equation. The effective Hamiltonian previously obtained is, in the present work, rendered Hermitian. Electronic minority-carrier transport for graded systems is described in terms of an effective field which includes the electrostatic field plus a term in the gradient of the band edge and another in the gradient of the effective mass. The local radiative-recombination lifetime and local density of states for inhomogeneous semiconductors are discussed. The equation for the excess minority-carrier concentration in an inhomogeneous semiconductor is deduced and is found to differ from that in an homogeneous system, by the effective field replacing the electric field, by the position dependences of lifetime and mobility, and by terms in the mobility gradient. Some phenomena specific to graded mixed semiconductors are considered on the basis of the theoretical analysis.

I. INTRODUCTION

SEVERAL unique phenomena and device applications have been described for semiconductors which are slowly graded in composition, based on the assumption that such graded systems exhibit graded band gaps.[1–3] Of interest here is the phenomenon of anti-Stokes radiative emission. Van Ruyven and Williams[4] have proposed field-enhanced minority carrier transport and recombination in graded band-gap systems as an anti-Stokes mechanism. The present paper examines theoretically the two basic features of the mechanism and advances the theory of inhomogeneous semiconductors in general. Thus we will be primarily concerned with the concept of a graded band gap and with minority-carrier transport in such systems.

A model one-electron Hamiltonian for graded mixed semiconductors has previously been introduced, and the applicability of the concept of a graded band gap demonstrated by the authors.[5] We considered systems whose components have the same structure and lattice constant. The perturbation Hamiltonian was taken to be $L(x)S(\mathbf{r})$, where $L(x)$ is the slowly varying composition factor varying in one dimension only and $S(\mathbf{r})$ is the difference of the one-electron potentials of the components of the mixed system and is periodic with the same periodicity as the components. The perturbation Hamiltonian is equivalent to assuming a slowly varying virtual crystal, where the virtual-crystal approximation[6] consists of replacing a statistical mixture of unit-cell potentials by averaged unit cells. Our analysis is restricted to a virtual crystal in which the slow variation in average unit cell is entirely in the unit-cell potential with no change in lattice constant.

Assuming that $L(x)$ varies slowly over the spatial extent of the Wannier functions of the homogeneous systems, and that interband coupling of $S(\mathbf{r})$ can be neglected, we obtained an effective masslike equation[5] which is valid for states near each band edge

$$[1/2m_n^*+\beta_n L(x)](-\nabla^2)F_n(\mathbf{r})+\alpha_n L(x)F_n(\mathbf{r})=E_nF_n(\mathbf{r}), \quad (1)$$

where $F_n(\mathbf{r})$ is the effective mass wave function, m_n^* is the unperturbed effective mass, and α_n and β_n are matrix-element components specific to each band and defined by

$$\int \psi_{n,\mathbf{k}}^*(\mathbf{r})S(\mathbf{r})\psi_{n,\mathbf{k}}(\mathbf{r})d\mathbf{r}=\alpha_n+\beta_n k^2+\cdots. \quad (2)$$

Here $\psi_{n,\mathbf{k}}(\mathbf{r})$ is the Bloch function of the unperturbed system.

II. EFFECTIVE HAMILTONIAN

The effective Hamiltonian of Eq. (1) is not, as written, Hermitian. Thus the reality of eigenvalues and the orthogonality of eigenfunctions generated by the effective Hamiltonian are in question. The Hermitic property of an operator is defined, of course, only with respect to a particular class of functions; therefore, the boundary conditions are important. We consider that on each side of the inhomogeneous region in the direction of the grading, $L(x)$ becomes constant, and to be quite specific to insure Hermiticity we take $L(x)$ to be the same constant on both sides, and can thus impose the Born–von Kármán boundary conditions. The lack of Hermiticity is a result of an approximation used in obtaining Eq. (1), and can be readily remedied. The matrix element involved is

$$(LS)_{nn';jj'}\equiv\int a_n^*(\mathbf{r}-\mathbf{R}_j)L(x)S(\mathbf{r})a_{n'}(\mathbf{r}-\mathbf{R}_{j'})d\mathbf{r}, \quad (3)$$

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where $a_n(\mathbf{r}-\mathbf{R}_j)$ is the Wannier function for band n and lattice site $\mathbf{R}_j$. Since $L(x)$ is everywhere positive, the mean value theorem can be applied to the matrix element $(LS)_{nn';jj'}$, yielding

$$(LS)_{nn';jj'}=L(\xi)\int a_n^*(\mathbf{r}-\mathbf{R}_j)S(\mathbf{r})a_{n'}(\mathbf{r}-\mathbf{R}_{j'})d\mathbf{r}\,, \quad (4)$$

where ξ is the appropriate value of the x coordinate of the crystal. We then make use of the localized character of the Wannier functions by assuming that $a_n(\mathbf{r}-\mathbf{R}_j)$ is negligible for $|\mathbf{r}-\mathbf{R}_j|$ greater than some band-dependent critical radius X_n. Then $(LS)_{nn';jj'}$ essentially vanishes for $|\mathbf{R}_j-\mathbf{R}_{j'}|$ greater than $2X_n$ or $2X_{n'}$, whichever is larger; and, in addition, the main contribution to the matrix element comes from the regions near the lattice sites $\mathbf{R}_j$ and $\mathbf{R}_{j'}$.

The statement that $L(x)$ varies slowly is now explicitly taken to mean that

$$2\left|\frac{dL(x)}{dx}\right|X_n\ll 1$$

and

$$2\left|\frac{dL(x)}{dx}\right|X_{n'}\ll 1\,. \quad (5)$$

Then $L(\mathbf{R}_j)$ does not differ appreciably from $L(\mathbf{R}_{j'})$. To make the effective Hamiltonian Hermitian, it is only necessary to make the approximation

$$L(\xi)\approx\tfrac{1}{2}L(\mathbf{R}_j)+\tfrac{1}{2}L(\mathbf{R}_{j'}) \quad (6)$$

instead of the choice, $\xi\approx\mathbf{R}_j$, made in Ref. 5. Equation (1) is now replaced by the following equation:

$$\begin{aligned}[-\nabla^2/2m_n^*-\tfrac{1}{2}\beta_n(\nabla^2L(x)+L(x)\nabla^2)]&\\ \times F_n(\mathbf{r})+\alpha_nL(x)F_n(\mathbf{r})&=E_nF_n(\mathbf{r})\,. \quad (7)\end{aligned}$$

The effective Hamiltonian of Eq. (7) can be shown to be Hermitian by making use of the previously described boundary conditions. Within the scope and approximations of the analysis, the Hermitian Hamiltonian of Eq. (7) appears to be unique.

The expression in the large square brackets corresponds, for a classical system, to $P^2/2m_n^*(x)$, where

$$1/2m_n^*(x)=1/2m_n^*+\beta_nL(x)\,. \quad (8)$$

In going from the corresponding classical to the actual quantum mechanical system one would symmetrize the the product of P^2 and $1/2m_n^*(x)$ because these factors do not commute. One symmetrization corresponds exactly to Eq. (7), as should have been expected from our choice of $L(\xi)$. Other symmetrizations are of course possible.

The effective potential term of Eq. (7) involves the factor α_n which is different for each band, as well as the composition factor $L(x)$. It is this band-dependent potential term that leads to the graded band gap. The fact that α_n is different for each band means that the effective potential an electron experiences depends on the band it occupies. Thus $\alpha_nL(x)$ determines an envelope of classical turning points, and this is the sense in which a position-dependent band edge can be defined. That is, beyond the classical turning point, the effective mass function decreases exponentially. In the quantum mechanical sense, the band edge is "fuzzy" because an electron will have small but nonzero probability of penetrating beyond the classical turning point.

The density of states in a graded system will, similarly, have to be defined in a different sense than applies to homogeneous systems. Since Eq. (7) allows a quasicontinuum of eigenvalues, it is clear that no constraints on density of states have been imposed in the formalism.

While interband matrix elements of $S(\mathbf{r})$ have not been considered here, they can be included in a straightforward generalization.

III. MINORITY-CARRIER TRANSPORT

Our discussion of the minority-carrier-transport equations will treat a nondegenerate, strongly n-type graded mixed semiconductor. The effects of space charge can be separated. For example, it is always possible to grow graded mixed semiconductors that are space charge free in equilibrium by proper inhomogeneous doping.[7] The effects of the Dember field, that is, the field due to the space charge from nonequilibrium charge carriers, can be neglected for low levels of excitation.

The density of minority-charge-carrier states (positive hole states, in this case) near the band edge is assumed to display the usual dependence on energy and effective mass appropriate to parabolic bands:

$$g_v(E)=\text{const}(m_p^*)^{3/2}(E_v-E)^{1/2}\,. \quad (9)$$

Hereafter, m_p^* designates the position-dependent effective mass, and E_v the position-dependent valence band edge as determined through Eqs. (2) and (7). The hole concentration reflects this effective mass dependence, and is taken to be

$$p=\text{const}(m_p^*)^{3/2}\exp[(E_v-E_f)/kT]\,, \quad (10)$$

where E_f is the quasi-Fermi level for holes.

The hole current can be expressed by an effective-field term plus the usual diffusion term, and its component in the direction of the composition gradient is

$$j_p=ep\mu_pF_p-kT\mu_p(dp/dx)\,, \quad (11)$$

where

$$F_p=\mathcal{E}+\frac{1}{e}\left[\frac{dE_v}{dx}+\frac{3}{2}\frac{kT}{m_p^*}\frac{dm_p^*}{dx}\right]. \quad (12)$$

The effective field, which is band-dependent, contains the usual field term plus terms in the band edge and effective-mass gradients. Physically, the term in the

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effective-mass gradient is due to the effect of density of states on diffusion. Kroemer[1] had previously described the band-edge gradient as a "quasifield", and recently Marfaing and co-workers[8] have independently recognized the role of the effective-mass gradient. Both investigators took these gradients to be undetermined material properties, while they have here been related to the matrix element of Eq. (2). A determination of mobility depends on knowing the dominant scattering processes involved in graded mixed systems, which may contain large numbers of scattering centers. In the case of phonon-scattering-limited mobility, a first approximation consists of relating mobility to effective mass (and, hence, position) by the Bardeen-Shockley deformation potential analysis.[9] Such a treatment transfers part of the problem of the position-dependent mobility to the position dependences in the elastic constant and deformation potential parameter. Also, the effects of the anisotropy of these parameters for graded composition materials must be considered.

The other equation fundamental to carrier transport is that of continuity

$$\partial p/\partial t+(1/e)\ \mathrm{div} j_p=-(p-p_0)/\tau_p, \tag{13}$$

where τ_p is the position-dependent radiative recombination lifetime and p_0 is the positive-hole concentration at equilibrium. We neglect all other recombination mechanisms. In every part of the graded system τ_p has the same value as a homogeneous system of the local composition; that is, the band-edge and effective-mass gradients do not influence the local τ_p except, of course, to make it position-dependent. This follows because τ_p is defined in terms of the thermal-equilibrium properties of the system. Thermal equilibrium insures that the effects of these gradients are exactly balanced by a concentration gradient. For nonequilibrium conditions, the excess carriers not only decay with the lifetime τ_p in a particular local region but also have a net flow into or out of that region in accordance with the divergence term of Eq. (13).

The reciprocal lifetime in the nondegenerate, strongly n-type system under consideration is R/p_0, where R is the recombination rate in thermal equilibrium and can be expressed by means of the van Roosbroeck-Shockley analysis[10] in terms of the optical properties of the system. For large band gap or low temperature (conditions, however, for which radiative recombination may be of less importance than other mechanisms of deexcitation) $R\sim\exp(-\Delta E/kT)$. This assumes that band-to-band recombination dominates. Also,

$$p_0=\mathrm{const}(m_p^*)^{3/2}\exp[(E_v-E_f^0)/kT]. \tag{14}$$

Thus, for the special case of the Fermi level E_f^0 at a constant energy from the conduction band edge,

$$\tau_p=\mathrm{const}(m_p^*)^{3/2}\exp[(E_c-E_f^0)/kT]\propto(m_p^*)^{3/2}. \tag{15}$$

When the Fermi level varies rapidly with respect to the conduction band, τ_p varies exponentially with position.

Combining the current and continuity equations, we obtain the following equation for excess minority-carrier concentration as a function of position in the direction of the composition gradient:

$$\frac{\partial\Delta p}{\partial t}+\Delta p\left[\frac{1}{\tau_p}+\mu_p\frac{dF_p}{dx}+F_p\frac{d\mu_p}{dx}\right]+\frac{d\Delta p}{dx}\left[\mu_pF_p-\frac{kT}{e}\frac{d\mu_p}{dx}\right]-\frac{kT}{e}\mu_p\frac{d^2\Delta p}{dx^2}=0. \tag{16}$$

This equation differs from that appropriate to a homogeneous system by the following: the presence of the effective field (which includes the gradients of both the valence band edge and the effective mass); the position-dependence of lifetime and mobility; and the terms in the mobility gradient.

IV. DISCUSSION OF THE CONCEPT OF LOCAL DENSITY OF STATES

It would be desirable to obtain the local density of states for graded systems directly from the formalism of Secs. I and II, rather than having to assume the relation appearing in Eq. (9). We believe that the local density of states is implicitly built into the eigenfunctions of the effective Hamiltonian of Eq. (7). For example, for a one-dimensional system with constant band edge but position-dependent effective mass, the square of the effective mass wave function is found to depend on $[m^*(x)]^{1/2}$. The power of $m^*(x)$ results from the Hermitization. This suggests that the form of the density of states assumed in Eq. (9) may be justified directly from the effective Hamiltonian. The local density of states obtained with this interpretation is consistent with the density of states for the homogeneous material of the same composition as each local region of the graded mixed semiconductor.

V. SOME PHENOMENA SPECIFIC TO GRADED MIXED SEMICONDUCTORS

The concepts and analyses developed in the preceding sections advance the theoretical foundation for understanding the following phenomena specific to graded mixed semiconductors.

The position-dependent band gap and radiative recombination of graded zinc-cadmium sulfide crystals have been determined from position-dependent optical

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absorption and emission[11]; the position-dependence of the band edge for majority carriers with respect to the Fermi level, from position-dependent conductivity and the photovoltaic effect.[12]

Hill and Williams[13] have reported electric-field-dependent luminescence spectra in graded zinc-cadmium sulfide crystals. They have interpreted the linear shift in the edge emission spectrum as field-enhanced minority-carrier transport between regions of different band gaps. Shifts up to 45 Å for band-gap gradients of a few eV/cm were obtained with applied fields of the order of 10^4 V/cm. Solutions of Eq. (16) can be used to determine theoretically the field dependence of emission spectra. Also, the density of states affects the field dependence. From the inequalities (5), it is apparent that much larger shifts can be predicted for mixed semiconductors with larger composition gradients.

Electroluminescence could in principle be achieved by a mechanism specific to graded-band-gap systems, a region of which has a near-zero band gap. Minority carriers thermally generated in the small-gap region would be transported to a region of larger gap by an applied electric field, followed by radiative recombination.[14]

Finally, we propose that the behavior of excitons in graded mixed semiconductors be investigated. For proper systems, the valence and conduction-band gradients can induce motion in the same direction for both electrons and holes. Thus graded-gap systems have unique advantages for the study of exciton transport.

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Radiative Spectra from Shallow Donor-Acceptor Electron Transfer in Silicon[*]

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Radiation associated with shallow donor-acceptor electron transfer in silicon has been examined in the liquid-helium temperature region for various combinations of group-V donors and group-III acceptors. The spectra for all impurities are quite similar, exhibiting TA- and TO-phonon–assisted lines, as well as a no-phonon line in all but the (Sb,B)-doped sample. A (P,In) sample exhibits an unusual extra line which is attributed to an LA-phonon–assisted transition. A theory analogous to that of Thomas, Hopfield, and Augustyniak, modified to take account of anisotropic donor wave functions, is used to analyze the line shapes and determine rate constants and the impurity-pair Coulomb energy for pairs that decay at different times after impurity neutralization. This leads to a direct measurement of the indirect silicon energy gap of 1.166 ±0.0010 eV and an exciton binding energy of 0.0102±0.0015 eV, when combined with infrared-absorption measurements near the indirect gap. The analysis also indicates that optically determined impurity ionization energies are correct, and that the thermally determined impurity activation energies and their concentration dependence probably result from carrier redistribution effects rather than modification of the impurity ionization energies of the majority of the impurities.

1. INTRODUCTION

RADIATIVE spectra and recombination kinetics associated with electron transfer between shallow donors and acceptors have been reported for several semiconductors, among which the most studied are GaP,[1–4] germanium,[5,6] and silicon.[7–10] The luminescence

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