Electronic states of semiconductors with graded periodic inhomogeneities*

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The electronic states of amorphous semiconductors with graded globular inhomogeneities have been previously investigated using perturbation theory for extended states well within allowed bands and effective-mass theory for localized states confined to a globule. In the present analysis we obtain solutions for localized, intermediate, and extended states of systems with sinusoidal grading in one dimension, using effective-mass theory and solutions of the Mathieu equation. The states near the crests of the undulating band edge are obtained for the first time; the earlier analysis for localized states is confirmed. Fine structure in optical spectra is predicted for globular materials. Perturbation theory is used to determine the dependence of the minigaps on the grading function for multilayer films.

I. INTRODUCTION

In a previous publication[1] a model involving graded globular inhomogeneities was proposed for some amorphous semiconductors, and analyses were made of their electronic states. Subsequently, the origin of the graded inhomogeneities in some materials was attributed to spinodal separation.[2] The analyses of the Schrödinger equation for the wave functions were restricted to energies where different approximate solutions could be obtained: one range of energies allowed perturbative solutions (this range was in the middle of an allowed band of the zero-order crystal), and the other range permitted solutions by effective-mass theory for states found to be localized to the central regions of a globule. The band edge was defined to be the locus of the classical turning points of the bound states and was position dependent with a dependence which resembled the grading function. Representative states and the position-dependent band edges are illustrated in Fig. 1. The case shown is the "deformation"-type characteristic of materials with compositional inhomogeneities; the "electrostatic"-type characteristic of inhomogeneous doping has similar individual undulating band edges which however are in phase with each other.

An energy range between those susceptible to these approximations remained unsolved at that time and that energy range and associated wave functions for a particular grading function are the topic of this paper. We have obtained solutions in the effective-mass approximation for states at the energy of the crests of the undulating band edges in the case of periodic grading and for states tightly bound to globular regions. We shall also point out some properties associated with different periodic grading functions. We note that this study is also relevant to multilayer semiconductor films where quantum effects are expected.

In real materials with either globular or laminar inhomogeneities the periodicity will only be approximate. This is the case for spinodal separation[3] and for multilayer films. Any randomness in the interglobule or interlayer distances or in the extrema of the potential undulations will tend to make the amplitudes of the wave functions of specific lower tight-binding electronic states confined to a particular globule or layer and thus localized therein. This provided some of the basis for the earlier calculation of tight-binding states.[1] With the exact periodicity of the present model these states are degenerate from inhomogeneity to inhomogeneity so that the electron or positive hole is no longer localized to a particular inhomogeneity and its wave functions will have equal amplitudes in all equivalent globules or layers. However, with sufficient tight binding the interglobule or interlayer tunneling time is long enough so that self-trapping or localizations by lattice polarization can occur in polar materials. Self-trapping for these states and polaron effects for higher states go beyond the present analysis.

II. SINUSOIDAL GRADING AND THE MATHIEU EQUATION

The particular case which we will treat in detail is that of sinusoidal grading. The Schrödinger equation which must be solved for the case of this grading in one dimension is

$$-(\hbar^2/2m)\nabla^2\psi + V_A\psi + (V_B - V_A)\tfrac{1}{2}(1+\cos 2\pi x/\rho)\psi = E\psi, \tag{1}$$

where V_A and V_B are the unit-cell potentials for the perfect A- and B-type crystals both with lattice constant a, and ρ is of the order of 100 Å. The solutions of Eq. (1) are obtained from working in an effective-mass approximation similar to an earlier analysis[4] for systems with monotonic gradings

$$-(\hbar^2/2m^*)\nabla^2 F_n(\vec{r}) + \tfrac{1}{2}V_0(1+\cos 2\pi x/\rho)F_n(\vec{r}) = EF_n(\vec{r}), \tag{2}$$

where m^* is the effective mass, E is measured from the edge of the band to which the theory is applied,

$$V_0 = \int \psi^*_{n,\vec{k}}(V_B - V_A)\psi_{n,\vec{k}}\, d\vec{r}\,, \tag{3}$$

and

$$\psi(\vec{r}) = u_{n,0}(\vec{r})F_n(\vec{r})\,, \tag{4}$$

where $u_{n,0}(\vec{r})$ is the periodic part of the Bloch functions. We have assumed also that the effective mass is independent of position; this is in general not valid for real systems, however, in the present analysis we are interested primarily in the effects of the sinusoidal potential.

In the usual effective-mass problem we think of the unperturbed particle of mass m^* as free since the only potential involved is the periodic one which has been eliminated. In the present problem, the potential periodic with the lattice distance has been eliminated but the grading produces an effective potential, therefore, the particle of mass m^* is moving in a potential which has the same position dependence as the grading function. We have taken the grading function and thus the potential to be periodic. The globular inhomogeneities arising from spinodal separation are approximately periodic[3] and the multilayer films can, in principle, be made periodic.

Equation (2) separates so that the y and z directions are solved by plane wave solutions. With periodic boundary conditions,

$$E_y = (\hbar^2/2m^*)(2\pi/\alpha)^2\eta_y^2\,, \tag{5a}$$

$$E_z = (\hbar^2/2m^*)(2\pi/\beta)^2\eta_z^2\,, \tag{5b}$$

where η_y and η_z are integers and α and β are the periods involved in the normalization

The equation in the x direction can be put in the form

$$\frac{d^2\Omega}{d\theta^2} + (b - s\cos^2\theta)\Omega = 0\,, \tag{6}$$

where $\theta = \pi x/\rho$ and

$$b = \frac{2m^*}{\hbar^2}\left(\frac{\rho^2}{\pi^2}\right)E_x\,, \quad s = \frac{2m^*}{\hbar^2}\left(\frac{\rho^2}{\pi^2}\right)V_0\,,$$

where E_x is part of a separation constant and can be interpreted as the energy in the x direction so that $E = E_x + E_y + E_z$.

Equation (6) is Mathieu's equation whose solutions have been investigated and partially tabulated.[5] The characteristic values b for which there are stable solutions of Eq. (6) fall into bands. This behavior of E_x is shown in Fig. 2 where we have chosen $\rho = 100$ Å and $V_0 = 0.377$ eV so that $s = 100$. It is seen that the acceptable values of b are discrete for small b; begin to broaden into bands before the value of s is reached; continue to have forbidden ranges for $b > s$ until finally one range

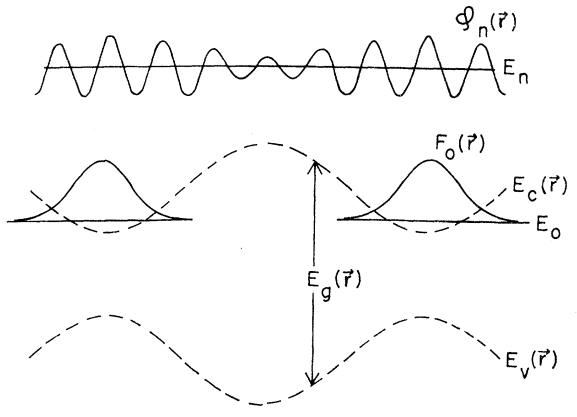

FIG. 1. Representation eigenstates for a "deformation"-type undulating-band-gap semiconductor, including the effective-mass function $F_0(\vec{r})$ for the lowest localized state and the modulated plane wave part $\varphi_n(\vec{r})$ of the eigenfunction of a representative extended state (modified from Ref. 1).

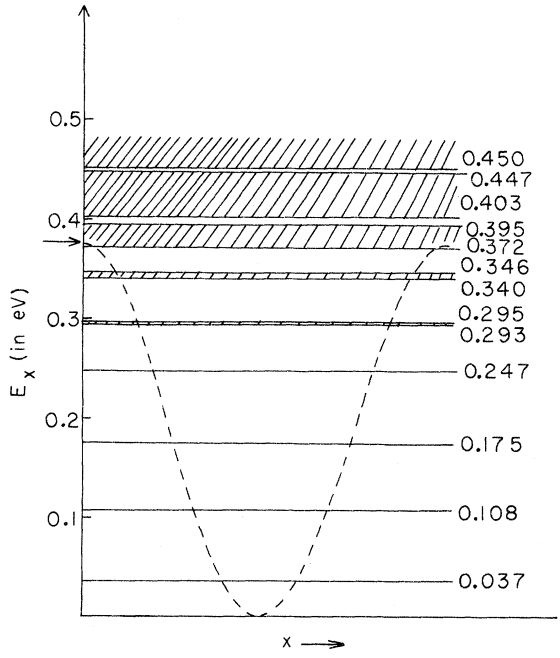

FIG. 2. Energy eigenvalues for a sinusodial perturbation. Dashed line is one period of the perturbing potential with amplitude 0.377 eV and period 100 Å. Cross-hatched areas are allowed bands. ($E = 0$ is the band edge of the component with the lower band edge.)

of acceptable b's becomes adjacent to another and the b values which solve Eq. (6) can be considered continuous. Solutions to Mathieu's equation have earlier been extensively investigated by Slater[6] relevant to the energy bands of perfect crystals.

The effective mass functions[7] which correspond to the characteristic b's are

$$\mathrm{Se}(b,\sqrt{s}\,;\cos\theta)=\sum_{p=-\infty}^{\infty}\gamma_p\cos[(s+2p)\theta]\,, \quad (7a)$$

$$\mathrm{So}(b,\sqrt{s}\,;\cos\theta)=\sum_{p=-\infty}^{\infty}\xi_p\sin[(s+2p)\theta]\,, \quad (7b)$$

where Se and So are even and odd elliptical sine functions, and γ_p and ξ_p are computed by continued fractions and restricted by normalization conditions. It is possible to get approximate expressions for these functions[8] in the limit $b<s$, for which

$$\mathrm{Se}_q(b,\sqrt{s}\,;\cos\theta)\simeq A_q\sum_{p=-\infty}^{\infty}\{\phi_q[s^{1/4}(\theta-\tfrac{1}{2}\pi+2p\pi)] + \phi_q[s^{1/4}(\theta+\tfrac{1}{2}\pi+2p\pi)]\}\,, \quad (8a)$$

$$\mathrm{So}_q(b,\sqrt{s}\,;\cos\theta)\simeq B_q\sum_{p=-\infty}^{\infty}\{\phi_{q-1}[s^{1/4}(\theta-\tfrac{1}{2}\pi+2p\pi)] - \phi_{q-1}[s^{1/4}(\theta+\tfrac{1}{2}\pi+2p\pi)]\}\,, \quad (8b)$$

where

$$\phi_q(\zeta)=e^{-\zeta^2/2}H_q(\zeta)$$

and the $H_q(\zeta)$ are the Hermite polynomials. The index q designates solutions which correspond to increasing b (in the case where the solutions are periodic, q is the number of zeroes in $0<\theta<\frac{1}{2}\pi$). For $q=0$, the solution to Eq. (6) is

$$\mathrm{Se}_0(b,\sqrt{s}\,;\cos\theta)\simeq A_0\sum_{p=-\infty}^{\infty}\{\exp[-\tfrac{1}{2}s^{1/2}(\theta-\tfrac{1}{2}\pi+2p\pi)^2] + \exp[-\tfrac{1}{2}s^{1/2}(\theta+\tfrac{1}{2}\pi+2p\pi)^2]\}\,, \quad (9)$$

which is a set of Gaussian curves centered on $\pm\frac{1}{2}\pi+2p\pi$ with $1/e$ width: $\theta_{1/e}=2\sqrt{2}/s^{1/4}$. This limit was obtained in a different manner in our previous paper[1] where individual globules were solved in three dimensions radially.

This analysis indicates what happens to the states around the band edges—states of the A- and B-type material which are at energies near the energy of the pure A (crest of potential) are rearranged into bands at energies above and below the former A edge and the states near the energy of the pure B edge become tightly bound to the globules.

When a single period describes the grading function the allowed and forbidden bands are sharp. It is expected that when several ρ_i are included in the potential (i.e., several periods) the features of a single period $f(x)$ will disappear and the allowed regions will broaden. The tightly bound states are a consequence of the inhomogeneities in material and should exist wherever there is a concentration of type B (smaller gap) globules which are distributed in the A matrix either periodically or with some randomness. The randomness removes the degeneracy so that the tight-binding states become localized to particular globules.

III. EFFECTS OF THE FORM OF THE GRADING FUNCTION ON ELECTRONIC STRUCTURE

In Sec. II a mathematically simple grading function was treated in detail; in this section we treat two grading functions by approximate methods for purposes of contrasting their effects on electronic states. We will use an abrupt grading which corresponds to layered materials with abrupt heterojunctions and the sinusodial grading treated previously. We will use perturbation theory to get an indication of what is happening as we change from one grading to another; perturbation theory has the advantage of providing analytic answers to problems whose exact solution can be had only numerically but has the disadvantage of being valid only in a restricted range of energies, in this case, those energies in the central region of a band.

We begin by solving the Schrödinger equation

$$-(\hbar^2/2m)\nabla^2\psi+V_A\psi+(V_B-V_A)f(x)\psi=E\psi, \quad (10)$$

where $f(x)$ will remain a general periodic grading function with period ρ until we need to specify it further.

The zero-order wave functions $\psi_1=(1/\sqrt{L})u_{n,k}e^{ikx}$ and $\psi_2=(1/\sqrt{L})u_{n,-k}e^{-ikx}$ are degenerate. We are interested in the effect of the perturbation on these states, and in particular, which states are split. The matrix element connecting unperturbed states is

$$H'_{ij}=\int\psi_i^*(V_B-V_A)f(x)\psi_j\,dx\,.$$

The splitting, H'_{12}, is given by solving the secular equation of degenerate perturbation and yields

$$H'_{12}=\frac{1}{L}\int u^*_{n,k}(x)u^*_{n,k}(x)(V_B-V_A)f(x)e^{-2ikx}\,dx. \quad (11)$$

Examining the H'_{12} for various k values will reveal

what levels have the degeneracy removed (therefore which wave functions need to be generated by degenerate perturbation theory) and which do not, i.e., $H'_{12}=0$. We can expand the terms in the integrand of Eq. (11) in two series with different expansion lengths. The $u^*_{n,k}(x)u^*_{n,k}(x)(V_B-V_A)$ is periodic in x with periodicity a and can be expanded in a set of lattice vectors of the space reciprocal to the space of length a, i.e.,

$$u^*_{n,k}(x)u^*_{n,k}(x)(V_B-V_A)=\sum_{\nu=-\infty}^{\infty} C_\nu e^{2\pi i\nu x/a} \qquad (12)$$

and $f(x)$ is periodic in x with periodicity ρ and can be expanded in a set of lattice vectors of the space reciprocal to the space of length ρ, which is of course an integral multiple of a, i.e.,

$$f(x)=\sum_{\mu=-\infty}^{\infty} D_\mu e^{2\pi i\mu x/\rho}\ , \qquad (13)$$

so

$$H'_{12}=\frac{1}{L}\sum_\nu C_\nu \sum_\mu D_\mu \times\int_0^L e^{2\pi i\nu x/a}e^{2\pi i\mu x/\rho}e^{-2ikx}\,dx\ . \qquad (14)$$

The integral in Eq. (14) where L is an integer multiple of ρ is proportional to a Kronecker δ function, thus

$$H'_{12}=\sum_\nu C_\nu \sum_\mu D_\mu \delta_{k,\pi(\nu/a+\mu/\rho)}\ . \qquad (15)$$

In the general case, therefore, we can say that in the central region of the band in first-order perturbation theory states which are split by the perturbation occur at k values which are integral multiples of π/ρ away from band edges. This is the expected results for a periodic perturbation.

It is important to look at the coefficients in the series to see if in any particular case these states are indeed split. We will first look at the situation of an abrupt grading function

$$f(x)=0,\ (4N+1)\tfrac{1}{4}\rho\leq x\leq(4N+3)\tfrac{1}{4}\rho$$
$$=1,\ (4N+3)\tfrac{1}{4}\rho\leq x\leq(4N+5)\tfrac{1}{4}\rho\ , \qquad (16)$$

where N takes on positive and negative integer values.

Where we work out the Fourier coefficients for this $f(x)$, we find

$$D_0=\tfrac{1}{2}\ \text{ and }\ D_\mu=(1/\pi\mu)\sin\tfrac{1}{2}\pi\mu\ \text{ for }\ \mu\neq 0.$$

This means that only the odd-integer terms survive since for all even μ, $D_\mu=0$. We can rewrite Eq. (15) as

$$H'_{12}=\sum_\nu\sum_{\mu=\text{odd}}\frac{1}{\pi\mu}\left(\sin\frac{\pi\mu}{2}\right)C_\nu\delta_{k,\pi(\nu/a+\mu/\rho)} + \sum_\nu \tfrac{1}{2}C_\nu\delta_{k,\pi\nu/a}\ . \qquad (17)$$

We can contrast this with the expression we obtain with a sinusoidal perturbation. In that case the Fourier expansion of $f(x)$ yields only three terms

$$f(x)=\tfrac{1}{2}+\tfrac{1}{4}e^{2\pi ix}+\tfrac{1}{4}e^{-2\pi ix/\rho}\ .$$

The three k values which leave $H'_{12}\neq 0$ are outside the range of validity of the perturbation theory (they are at the band edge and $\pm\pi/\rho$ away from the band edge), and therefore for the range of energy over which this analysis is valid there are no finite H'_{12} in this order of perturbation theory.

So to first order in the perturbation we find many of the states split in the abruptly graded case and no states split in the sinusoidal case, for the range of energy of the analysis.

The wave functions generated through perturbation theory for the states where it is applicable are given in Ref. 1 neglecting the effect of degeneracy. If we write the perturbed-state wave function as $\psi_k(x)$ then since $H_{11}=H_{22}$ and $H'^*_{12}=H_{21}$ for the degenerate states the proper wave functions are

$$\psi^{\mathrm{I}}(x)=(1/\sqrt{2})[\psi_k(x)+\psi_{-k}(x)]$$

and

$$\psi^{\mathrm{II}}(x)=(1/\sqrt{2})[\psi_k(x)-\psi_{-k}(x)]\ ,$$

with $\psi_k(x)$ taking the form in Ref. 1, Eq. (15).

We thus see the possible consequences of diffusion of materials deposited in layers. To begin with the A- and B-type materials are clearly defined and there are many k values which are substantially split; as time increases diffusion will shift the grading functions to something like a sinusoidal grading and many of the minigaps will disappear. This calculation will be changed if we go to higher orders in perturbation theory. Higher orders will give more, finite H'_{12}. We can observe that if diffusion is complete the material will be a mixed crystal and the situation of no gaps will be an exact solution.

The qualitative features of the above have been pointed out by Esaki and Tsu[9] for both the square well and sinusoidal perturbations. The range of energy of interest in that work was quite close to the band edge. The present work has examined a broader range of energy higher in the band, and shows a decrease in the magnitudes of most of the minigaps as diffusion occurs despite the fact that the diffusion occurs in a way which keeps the

perturbing potential profile periodic in some distance ρ large compared to the period of the lattice.

The structure in the energy states shown in Fig. 2 is specific to E_x. The total energy which includes the continua in E_y and E_z will have less evident structure, and therefore fine structure in the optical spectra is only expected with properly polarized radiation. The lower narrow bands are describable as tightly bound in the x direction. The bound or localized character means that the electronic particle is bound to regions which are rich in the component with the lower band edge but can of course be in those regions in any layer. In addition, as noted earlier, with tunneling times in excess of the periods of lattice modes self-trapping by lattice polarization is to be expected.

For globular inhomogeneities E_x, E_y, and E_z will all be quantized for the lower states and therefore fine structure is predicted in the optical spectra. Transport will involve interglobule tunneling for systems for which the lower band edge lies within the globules; such transport has been shown to involve the well-known $T^{1/4}$ dependence of mobility.[10]

IV. CONCLUSIONS

The electronic states of systems with one-dimensional sinusoidal compositional gradings can be determined by effective-mass theory and solutions of the Mathieu equation. Tightly bound states in the troughs of the undulating band edge are confirmed; modulated extended states near the crests, determined for the periodic case. In first-order degenerate perturbation theory many more minigaps are shown to exist for periodic square-well gradings than for sinusoidal gradings. The latter exhibits additional smaller minigaps in higher order, as in the solutions of the Mathieu equation. Significant features in the optical spectra and electronic transport for systems with globular or laminar inhomogeneities are predicted.

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