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Superlattice and Negative Differential Conductivity in Semiconductors*

Abstract: We consider a one-dimensional periodic potential, or "superlattice," in monocrystalline semiconductors formed by a periodic variation of alloy composition or of impurity density introduced during epitaxial growth. If the period of a superlattice, of the order of 100Å, is shorter than the electron mean free path, a series of narrow allowed and forbidden bands is expected due to the subdivision of the Brillouin zone into a series of minizones. If the scattering time of electrons meets a threshold condition, the combined effect of the narrow energy band and the narrow wave-vector zone makes it possible for electrons to be excited with moderate electric fields to an energy and momentum beyond an inflection point in the E-k relation; this results in a negative differential conductance in the direction of the superlattice. The study of superlattices and observations of quantum mechanical effects on a new physical scale may provide a valuable area of investigation in the field of semiconductors.

Introduction

We consider theoretically a one-dimensional periodic potential, or "superlattice," in monocrystalline semiconductors. This superlattice potential would be obtained by a periodic variation of alloy composition or of impurity density introduced during epitaxial growth. This technique would enable one to vary arbitrarily the amplitude and periodicity of the superlattice potential over a range of values, although one period probably could not be made much shorter than 100Å (about 20 times as long as the lattice constant of the host crystal). If this distance, which is comparable to the junction width in a tunnel diode,[1] is shorter than the electron mean free path, one may expect to observe strong energy dispersion effects in the proposed structure. These effects would allow observation of familiar quantum mechanical properties in a new domain of physical scale, due to very narrow allowed and forbidden energy bands associated with a series of minizones in the Brillouin zone, not seen in the host crystal. It should be possible to obtain a novel class of man-made semiconductor materials, at least as far as electronic properties are concerned, and one expects the properties to depend not only on the band parameters of the host crystal, but also on the characteristics of the superlattice.

We have analyzed the dynamics of conduction electrons in a superlattice structure which, we think, is realizable with techniques described here. Although the one-dimensional lattice per se is an elementary subject, the results contain important implications for the direction of experimental effort. We have found that, in the direction of the superlattice (perpendicular to the superlattice planes), the narrow wave-vector zones and the narrow energy bands make it possible for electrons to be excited beyond the energy corresponding to an E-vs.-k inflection point with moderate electric fields. The resulting negative conductance could lead to new ultra-high-speed devices.† These devices would have virtually no frequency limitation except when the energy quantum for the frequency involved is a significant fraction of the width of the narrow energy band. Since the potentials envisioned are small compared with band gap energies of the host semiconductors, and since the properties depend on a sustained periodic variation, the structure should be viewed as a perturbed bulk crystal rather than as a series of junctions.

Materials

The achievement of a well-defined superlattice structure with a period of, say, 100Å will require considerable effort even with the use of the most advanced epitaxial thin-film technologies. The materials should be well-known semiconductors and their alloys; for examples, Ge, Si, Ge-Si alloys, III–V compounds and their alloys, II–VI com-

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* Research sponsored in part by the Army Research Office, Durham, North Carolina under Contract DAHCO4-69-C-0069.

† H. Krömer proposed using the heavy hole band in Ge, Si and other semiconductors for a negative mass amplifier, wherein transverse effective masses were said to become negative for excited electrons (actually holes) [*Phys. Rev.* **109**, 1856 (1958)]. Application of the effect, however, has not turned out to be practical.

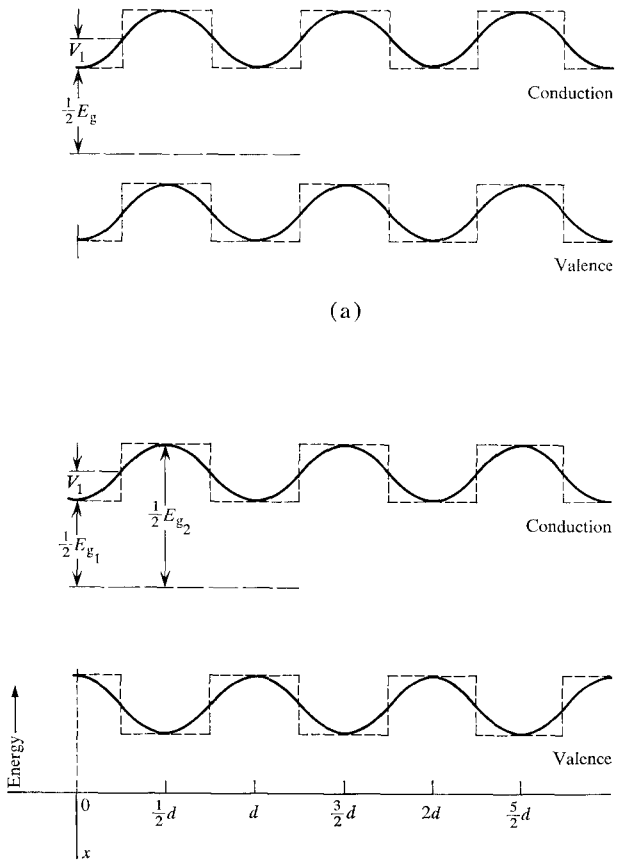


Figure 1 Electron energy in the valence and conduction bands as a function of distance in the direction of the superlattice for (a) alternation of donor and acceptor impurities and (b) periodic variation of alloy composition. Solid and dashed lines represent sinusoidal and periodic square-well potentials, respectively. The E_g are the magnitudes of the energy gap in the semiconductor materials used and V_1 is the amplitude of the periodic superlattice potential.

pounds and their alloys, etc. There may be a number of ways to form a superlattice structure.* We considered two methods: (1) a periodic variation of donor or acceptor impurities, alternately, in a single semiconductor; and (2) a periodic variation of alloy composition, introduced during the crystal growth. Both methods could be used simultaneously and it would be advantageous to carry out the epitaxial growth at a relatively low temperature[2] to minimize the thermal diffusion of impurities or alloy constituents, which would tend to wash out the desired potential profile. In this context, it is more desirable to apply method (2) because of the lower diffusion coefficients in alloys.

* Some crystals such as hexagonal SiC have a number of different structural forms known as polytypes, in which one sees a kind of one-dimensional superlattice structure. The periods range from 15 to 53Å, depending on the type of crystal. The potential amplitude and resulting energy gap are probably too small to demonstrate any of the effects described here.

In the alternating impurity system (Fig. 1a), the peak-to-peak amplitude of the periodic potential can be chosen, in principle, as any value up to that of the energy gap, whereas, in the alternating alloy composition system (Fig. 1b), the value would be limited to about half of the difference between the energy gaps of the two materials involved. It would not be possible to obtain the desired superlattice structure (with a 100-Å period and a 0.1-eV potential amplitude) with relatively light doping because of space charge effects.

We considered two potential functions, a sinusoidal wave and a periodic square wave, as illustrated in Fig. 1, and two typical values of effective mass, $0.025m_0$ and $0.07m_0$, which are applicable to the InAs-based alloy and GaAs-based alloy systems, respectively. The Ge-GeSi system is also attractive, particularly from an experimental point of view. We would choose relatively pure elemental or binary compound semiconductors as the narrower gap semiconductor, corresponding to the valleys in the potential profile, to obtain a favorable electron scattering time.

Band structure

We are concerned with the energy bands in a one-dimensional superlattice represented by a periodic potential $V(x) = V(x + nd)$ with a period d typically 10 to 20 times greater than the lattice constant a in the host crystal. The usual Brillouin zone will be subdivided into minizones as shown in Fig. 2a. Since we are interested only in the first minizone, because of low carrier concentrations we may assume that the E-k relation in the directions parallel to the superlattice planes is parabolic as usual. For the sinusoidal potential $V(x) = V_1 [\cos (2\pi x/d) - 1]$, the wave equation in the direction of the superlattice, denoted by x, has the form of Mathieu's equation and has been studied in great detail by Slater.[3]

The reduced energy and amplitude of the perturbing periodic potential are defined by $\eta = \eta(k_x) \equiv (E_x - V_1)/E_0$ and $\gamma \equiv V_1/E_0$, respectively, where V_1 is the amplitude of the periodic superlattice potential and $E_0 \equiv \hbar k_d^2/2m$; here $k_d = \pi/d$ and m is the effective mass. In Fig. 2b we plot η vs. γ for the sinusoidal potential, using a parameter $\beta \equiv k_x/k_d$. The allowed solutions of the wave equation are represented by the non-shaded regions, while the forbidden solutions fall in the shaded regions. For the case of $\gamma = 0.5$, η vs. β is plotted in Fig. 2a.

We also calculated the energy-momentum relation for the periodic square-well potential,[4] using the expression given by Smith.[5] A comparison of the E-vs.-k curves for the two potentials is shown in Fig. 3, where $d = 100$Å, $V_1 = 0.1$eV, and $m = 0.025m_0$ (Fig. 3a) and $0.07m_0$ (Fig. 3b). The zeros of the energy scales in Fig. 3 are set at the bottom of the conduction band in the narrower energy-gap material. Therefore the first band is moved up by an amount slightly less than V_1. In the case of

alternating impurities, the energy gap is narrowed slightly by the introduction of the superlattice structure.

The energy band width $E_1 \equiv E(\pi/d) - E(0)$ decreases as γ increases from 0.667 to 1.85; i.e., electrons are progressively more localized in the direction of the superlattice as the periodic perturbing potential increases. At $\gamma = 4$, E_1 is only one-tenth the unperturbed energy band width in the first minizone, which means that the effective mass in the superlattice direction is ten times greater than the unperturbed value. This trend leads to virtually a two-dimensional electron gas system.[6]

For large γ, and particularly for the periodic square-well potential, the E-k relation can be approximated by a sinusoidal form, $E_x \approx \frac{1}{2}E_1(1 - \cos k_x d)$; the inflection point is located at the center, $\pi/2d$, of the first minizone. In general, each carrier with a definite effective mass interacts with the superlattice and generates a corresponding set of energy bands. Therefore, whenever more than one effective mass is involved, the total population of carriers is redistributed among the respective bands.

Transport properties

We used a simplified path integration method[7] to obtain a relation between the applied field F in the direction of the superlattice and the average drift velocity v_d. The equations of motion are

$$\hbar\dot{k}_x = eF \text{ and } v_x = \hbar^{-1}\partial E_x/\partial k_x; \tag{1}$$

the velocity increment in a time interval dt is

$$dv_x = eF\hbar^{-2}(\partial^2 E_x/\partial k_x^2)\, dt. \tag{2}$$

The average drift velocity, taking into account the scattering time τ, is written as

$$v_d = \int_0^\infty \exp(-t/\tau)\, dv_x$$

$$= eF\hbar^{-2}\int_0^\infty (\partial^2 E_x/\partial k_x^2)\exp(-t/\tau)\, dt. \tag{3}$$

Using the sinusoidal E-k approximation, we obtain

$$v_d = g(\xi)[\hbar k_d/m(0)] \tag{4}$$

and

$$g(\xi) = \xi/(1 + \pi^2\xi^2), \tag{5}$$

where $\xi = eF\tau/\hbar k_d \equiv k_\tau/k_d$; the effective mass $m(0)$ is determined by the curvature of $E(k)$ and is equal to $2\hbar^2/E_1 d^2$. The function $g(\xi)$ (shown as the dashed curve in Fig. 4) has a maximum at $\xi = 1/\pi$ and thereafter decreases, corresponding to a decreasing average drift velocity, which results in a negative differential conductance because the current is proportional to v_d. At high fields the current is proportional to $(F\tau)^{-1}$. The value $\xi = 1/\pi$ corresponds to $eF\tau d/\hbar = 1$. This threshold

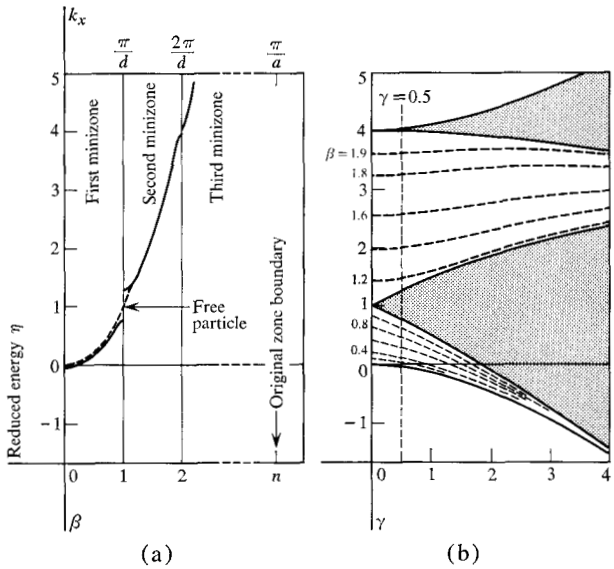
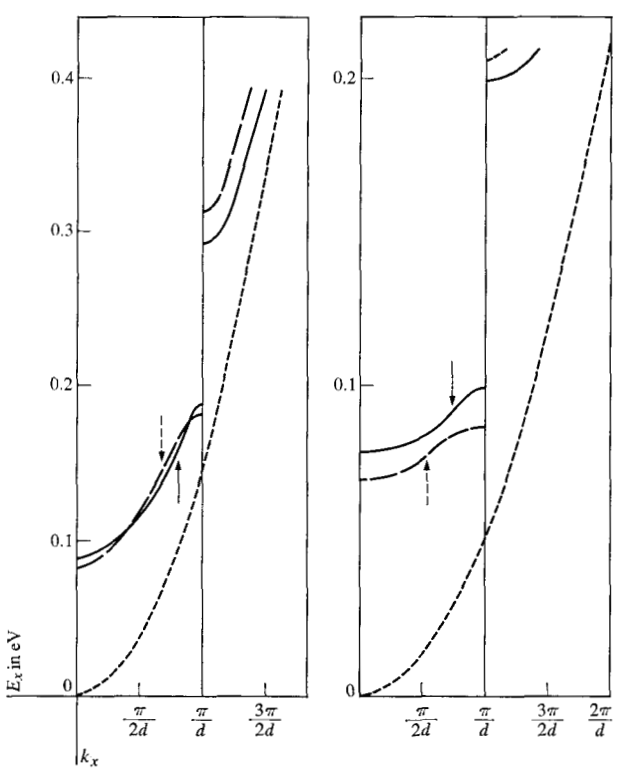


Figure 2 Reduced energy η as a function of (a) wave vector k_x or reduced wave vector β for $\gamma = 0.5$ and (b) reduced amplitude γ of the sinusoidal superlattice potential; $\eta \equiv (E_x - V_1)/E_0$, $\gamma \equiv V_1/E_0$ and $\beta \equiv k_x/k_d$.

Figure 3 Electron energy E_x as a function of wave vector k_x in the direction of the superlattice. Solid curves are for the sinusoidal potential, long-dash curves are for the periodic square-well potential, and the short-dash curves are for the unperturbed cases. The arrows refer to the points of inflection. Values of the parameters are $V_1 = 0.1$ eV and (a) $m = 0.025m_0$, $\gamma = 0.667$; (b) $m = 0.07m_0$, $\gamma = 1.85$.



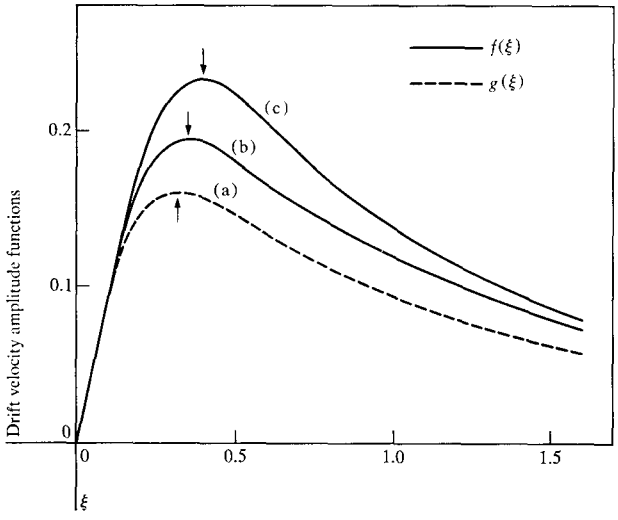


Figure 4 Drift velocity amplitudes as functions of the reduced parameter $\xi = 2eF\tau d/h \equiv k_\tau/k_d$: (a) sinusoidal potential; (b) periodic square-well potential for $k_i/k_d = 0.5$; and (c) periodic square-well potential for $k_i/k_d = 0.82$. Here k_i is the wave vector at the inflection point of the E-k curve. Arrows indicate the peaks of the drift velocity functions.

condition can be achieved with an electric field strength $F = 10^3$ V/cm and a scattering time $\tau = 0.67$psec.

For small γ, when $E(k)$ is not a sinusoidal function, the E-k relation was approximated by sections of two parabolas of opposite curvature, joined at the inflection point (E_i, k_i). For the average drift velocity in this case we obtained

$$v_d = f(\xi)[\hbar k_d/m(0)]$$

and

$$f(\xi) = \xi\left[1 + \frac{2k_d}{k_d - k_i}\frac{\sinh(k_i/k_d\xi)}{\exp(2/\xi) - 1} - \frac{k_d}{k_d - k_i}\exp(-k_i/k_d\xi)\right]. \quad (7)$$

The function $f(\xi)$ is plotted in Fig. 4 for $k_i/k_d = 0.82$ ($\gamma = 0.667$) and 0.50 ($\gamma = 1.85$). These curves also indicate the existence of negative conductance, but the threshold value, $\xi \geq 0.4$ or $eF\tau d/h \geq 1.26$ for the top curve, is slightly greater than for the sinusoidal E-k relation. Since the inflection point is shifting toward the minizone boundary, it is understandable that higher fields or longer scattering times are required to obtain negative conductance.

As the applied voltage is increased, however, effects such as Zener tunneling, avalanching and impact ionization set in; eventually the negative conductance would be offset by these effects. The possibility of Zener tunneling to the second minizone when electrons reach the first minizone boundary could be a dominant factor in the case of small amplitude of the periodic potential. If, however, the amplitude V_1 is of the order of 0.1eV and the applied field is of the order of 10^3 V/cm, the tunneling probability can be kept negligibly small. If the electron scattering time is sufficiently long, electrons will undergo rf oscillation due to the reflection at the minizone boundaries, the so-called "Bloch oscillation." This occurs for $eF\tau d/h > 2\pi$, which is several times the threshold value for negative conductance. The frequency of the Bloch oscillator is $eFd/h = 250$ GHz for $F = 10^3$V/cm and $d = 100$ Å. The scattering time then should be greater than 4 psec.

Discussion

In obtaining the solutions for the average drift velocity, Eqs. 4 and 6, we made two assumptions; namely, that $k_x = eFt/\hbar$ and that τ is time-independent. The former assumption implies that $k_x \approx 0$ at $t = 0$, which is justifiable in relatively lightly doped semiconductors.[8] The latter assumption is a reasonable approximation in the case in which the allowed band width is made narrow. In the two examples, $m = 0.025m_0$ and $0.07m_0$, the smaller mass case requires an electron temperature close to 1000°K, whereas the larger mass case requires only 100°K, to reach the negative differential conductivity region. This electron temperature, which is also a function of the amplitude and the profile of the periodic potential, could be kept very low with proper design of the structure. In such cases the specimen could be operated with low electric fields at cryogenic temperatures; lower temperatures are helpful in obtaining longer scattering times.

Using the Heisenberg uncertainty principle we estimated the values of electron scattering time τ and the mean free path l that are required for these quantum mechanical effects. For $\Delta E \approx 0.1E_1 \approx 0.003$ eV and $\Delta k \approx 0.1k_d \approx 3 \times 10^5$ cm^{-1}, the inequalities are $l \geq 330$ Å and $\tau \geq 0.22$ psec. This indicates that the mean free path should be at least three times as long as the superlattice spacing. The scattering time here is about one-third of that previously estimated for obtaining a negative differential conductance.

The scattering time is an important factor in the effects described and more-detailed calculations are being made to verify the model. If the superlattice were perfect, the scattering time would be infinite, as is the case with an ideal crystal lattice. Small deviations from the perfect periodic potential, even when the long-range order is preserved, act as localized scattering centers. If the superlattice structure is prepared by a periodic variation of alloy composition, there will be unavoidable random variations in the magnitude of the thereby introduced superlattice potential maxima (at $x = d/2, 3d/2, \cdots$). However, the probability density of conduction electrons in the superlattice structure of the sinusoidal potential indicates that electrons in the conduction band would be bunched

in the potential minima at $x = 0, d, 2d, \cdots$. Therefore, small variations in the magnitude of the potential maxima, where the electron probability distribution has minima, would have little effect.

If the deviation from an ideal superlattice becomes so large that the long-range order is no longer preserved, a disordered system will be obtained, which might be called a disordered one-dimensional superlattice. Even this structure, however, may provide a testing ground for mathematical models used in the study of one-dimensional disordered systems.[9] Correlation between theory and experiment on a disordered superlattice would lead to better understanding of a three-dimensional disordered system, i.e., an amorphous substance. Although it may be a formidable task to construct the proposed superlattice, we believe that efforts directed to this end will open new areas of investigation in the field of semiconductor physics.

Acknowledgments

The authors are pleased to acknowledge W. E. Howard and R. Ludeke for their contributions and P. J. Stiles for stimulating discussions. The Bloch oscillator described here is an outgrowth of discussions with W. E. Howard.

References

1. L. Esaki, *Phys. Rev.* **109,** 603 (1958).
2. R. N. Thomas and M. H. Francombe, *Appl. Phys. Letters* **13,** 270 (1968). Vapor growth at ultra-high vacuum may be suitable for this purpose.
3. J. C. Slater, *Phys. Rev.* **87,** 807 (1952).
4. R. de L. Kronig and W. J. Penney, *Proc. Roy. Soc.* **A130,** 499 (1930).
5. R. A. Smith, *Wave Mechanics of Crystalline Solids,* John Wiley and Sons, Inc., New York 1961, Chap. 4.
6. F. Stern and W. E. Howard, *Phys. Rev.* **163,** 816 (1967).
7. R. G. Chambers, *Proc. Phys. Soc.* (London) **A65,** 458 (1952); A. B. Pippard, *The Dynamics of Conduction Electrons,* Gordon and Breach Science Publishers, Inc., New York 1965.
8. P. A. Lebwohl and R. Tsu showed that the use of the path integration method gives exact results under these conditions (private communication).
9. See, for instance, E. H. Lieb and D. C. Mattis, *Mathematical Physics in One Dimension,* Academic Press, Inc., New York 1966, and J. Hori, *Spectral Properties of Disordered Chains and Lattices,* Pergamon Press, Oxford 1968.

Received September 3, 1969