Direct optical transitions in indirect semiconductors: The case of Ge twinning superlattices

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The folded direct optical transitions in a recently proposed structure—the twinning superlattice—in germanium are calculated and discussed. The absorption coefficient of this structure is found to exceed the bulk Ge value by at least an order of magnitude, but is still small compared to that for direct-gap semiconductors.

It has been established for quite some time that superlattices made of indirect-gap semiconductors may behave as direct-gap materials, so that direct (not phonon-assisted) optical transitions may occur. The mechanism by which this happens is usually described as band folding. The superlattice periodicity introduced by varying the material composition defines a superlattice Brillouin zone into which the bulk Brillouin zone can be mapped. With a suitably chosen growth direction and superlattice period, the lowest conduction-band valley [at or close to X or L points of the bulk Brillouin zone (i.e., minibands that they form)] may be folded into the center of the superlattice Brillouin zone, thus enabling direct optical transitions to take place, without any need for momentum-compensating phonons to be involved. The most extensively studied superlattice showing this type of behavior is Si/(GeSi),[1] but some other perspective candidates, such as GaP/AlP, have also been suggested.[2] The strain inherent in Si/(GeSi) superlattices actually enhances optical transitions,[1] though it has some drawbacks, for example questioning the long-term stability of these superlattices. Systems lacking periodicity or exhibiting confinement in more than one direction may also provide direct optical transitions. Although there is no formal folding in such cases, it is the wave-function confinement (i.e., modulation) that lifts the $\mathbf{k}$-conservation rule. The most prominent examples of such systems are porous Si quantum wires, where strong luminescence in the visible (even blue) range has been observed.[3] This is suggestive of direct optical transitions, but alternative explanations (defects, surface effects) have also been offered.[4] In view of rather uncontrolled growth of these structures at present, it is not easy to resolve the mechanism of optical transitions. Finally, quantum dots made of indirect semiconductors also show grossly enhanced optical activity on interband transitions, due to confinement-induced indirect-to-direct conversion.[5]

In this paper we consider another way of obtaining folding-mediated direct optical transitions in indirect semiconductor superlattices, specifically in Ge-based twinning superlattices. This is a class of superlattice that we have recently proposed,[6] that relies on the periodic reversal of crystal orientation (by 180°) in a semiconductor which is otherwise, in terms of composition and doping, homogeneous. The structure of a crystal around a single twin boundary may be visualized by looking at the stacking sequence of atoms along the [111] direction. Instead of the $AA'BB'CC'AA'BB'CC'$ sequence of the perfect crystal, one now has $AA'BB'CC'A|A'CC'BB'AA'$, where AA' (or BB' or CC') denote the two basis atoms of the primitive unit cell. In its simplest version, one period of the twinning superlattice might include n and m atomic bilayers of oppositely oriented material, and may thus be called an (n,m) twinning superlattice. Polytypic superlattices[7] may be interpreted as a special class of twinning superlattices in diamond/zinc-blende crystals, but the latter are more general and could also be envisaged in various other crystal systems, provided they allow for twinning.[8]

The essential physics of twinning boundaries is that, although the interface between the two crystal orientations is perfectly lattice matched, the wave functions are highly symmetry mismatched. This leads to large levels of scattering and, where energies are close, to intervalley mixing. A detailed account of the electronic properties of twinning superlattices is given in our previous papers.[6] Since the L valleys, and the minibands they form in the superlattice, are the lowest in the conduction band of germanium, of special interest here are those L points which project onto the $\bar{\Gamma}$ point of the interface Brillouin zone: in twinning superlattices where $m+n$ is even these points are folded into the center of the superlattice Brillouin zone, and so give rise to the possibility of direct optical transitions.

The method used in our calculations is an empirical pseudopotential-based layer method, details of which are described in our previous publications.[6,9] In brief, the complex band structure and wave functions of both the propagating and evanescent states of the two bulk semiconductors on either side of the interface are calculated first. The in-plane ($\mathbf{g}_\parallel$) Fourier components of the eigenfunctions are matched at the interfaces, and then the functions are propagated across the layers. The wave-function propagation and matching is performed using the S-matrix approach, which guarantees high stability against the growth of evanescent states. Once the S matrix of the superlattice period is found, it is recast into the transfer (T) matrix, and the Bloch theorem applied. In spite of its relative simplicity, this method reveals all band-structure-related properties of twinning superlattices arising from band mixing and bulk Brillouin-zone folding. Furthermore, in case of single twinning boun-

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daries and stacking faults, the results obtained from this method show good quantitative comparison to those obtained by more elaborate self-consistent calculations.[10] Numerical calculations have been performed using the empirical pseudopotential form factors from Ref. 11.

The miniband structure of Ge twinning superlattices is essentially determined by finite electron-hole transmission probability through the twin interface, and by the existence of interface bound states. In Ge these interface states exist at the $\bar{\Gamma}$ point both above the valence-band top and below the conduction-band bottom. The valence-band-related state, 27 meV above the valence-band top, has a heavy-hole-like character, and the conduction-band-related state, 39 meV below the conduction-band bottom, has an L-like character. In the periodic superlattice structure these states interact, giving rise to minibands with piecewise-evanescent-like wave functions. Above (below) them are the propagating state electron (hole) minibands, as exist in conventional superlattices. The Γ-L mixing in the conduction-band minibands is extremely small, except for energies close to the Γ valley (but even there it is not large).[6]

In order to calculate the optical absorption in twinning superlattices we tabulate their dispersion $E(\mathbf{k})$ for all the relevant minibands. We are interested here in absorption for only a limited range of photon energies, from about the threshold value for any particular type of absorption to a few hundred meV above. Within the restricted volume of the superlattice Brillouin zone that contributes to the low-energy absorption, the energies for each miniband and the transition matrix elements are tabulated in ~ 80 points of the $\mathbf{k}$ space, and in calculating the absorption interpolation is used for $\mathbf{k}$ points in between this coarse grid.

The calculated interband absorption in the Ge(6,6) superlattice is given in Fig. 1(a). The values of the absorption coefficient are not large when compared to those in direct-band-gap materials like GaAs, but still are an order of magnitude higher than indirect, phonon-assisted absorption in bulk Ge at $T=77-300$ K (e.g., Ref. 12). The largest values of the transition matrix elements amount to $(|p|^2/m_0)\sim 10^{-3}$ eV. By comparing the absorption coefficient or matrix elements obtained here to those stated for Si/(GeSi) superlattices,[1] one can see that Ge twinning superlattices have approximately similar properties, or at least do not lag much behind. It may be that a more suitable Ge(m,n) twinning superlattice in this respect could be found, but we made no attempt toward such an optimization. The example displayed is very convenient for studying the effects that lead to larger folded-direct transition matrix elements. Although it is the folding alone that is sometimes used to explain the indirect-to-direct conversion, it is a necessary rather than sufficient condition for this to take place. Finite values of transition matrix elements in folded direct- (quasidirect-) gap superlattices are really enabled by states mixing, i.e., modulation of bulk wave functions that make up the superlattice wave function (including the appearance of evanescent states), and these effects are usually not so strong as to make a quasidirect-gap superlattice behave like a truly direct-gap superlattice or bulk.

Looking at the structure of the absorption in Fig. 1(a), one can see that there are two types of transitions which are really important. Those between the lowest pairs of minibands in both the conduction and valence bands (specifically $1_{hh}\rightarrow 2_e$ and $2_{hh}\rightarrow 1_e$, others being supressed for wave-function parity reasons) have significant values of matrix elements because they are both interface-related minibands, their wave functions are evanescent-like (hence the $\mathbf{k}$-conservation rule does not strictly apply), and, for the same reason, they have a good overlap. Thus, although the conduction-band states are L derived, there is a finite transition matrix element. Also important are transitions between the lowest pair of hole minibands and the fourth conduction miniband. What gives rise to significant matrix elements here is the fact that this miniband is very close in energy to the Γ valley (which is ~ 0.3 eV above the L valley), Γ-L mixing now becomes non-negligible,[6] and it is actually the small-Γ contribution to the superlattice wave function that makes this miniband optically active. In Fig. 1(b) we give the absorption due only to evanescent state minibands in a Ge(8,8) superlattice, in a limited range of photon ener-

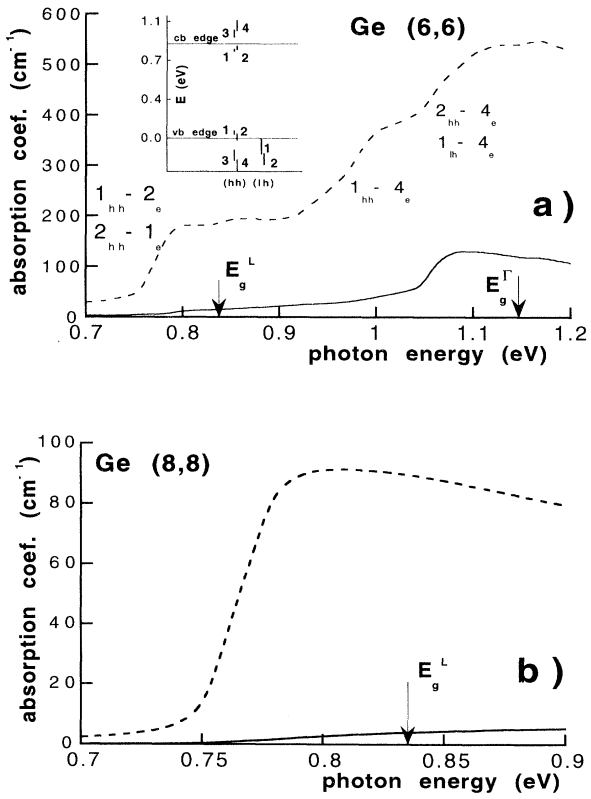

FIG. 1. The absorption due to interband direct transitions in Ge(6,6) (a), and Ge(8,8) (b) twinning superlattices. Solid lines are for light polarized along the z axis, and broken lines for the in-plane (x,y) polarization. The inset in (a) displays the energy range of minibands at the $\bar{\Gamma}$ point of the interface Brillouin zone (energies are measured from the conduction-band edge at that point). The adjacent minibands joined by zero-energy gaps are slightly displaced horizontally, to be distinguishable.

gies. Being primarily the interface-state-related effect, the absorption in this case is lower than in the Ge(6,6) superlattice, because the twinning interfaces are more widely spaced. Indeed, the peak absorption on these transitions in Ge(8,8) is $\sim 50\%$ of what in Ge(6,6) superlattice, close to a rough theoretical estimate of $\frac{12}{16}$.[2] Finally, we may note that because the L states are the ones with the lowest energy, the emission will be rather efficient, since it is these states which will dominate, provided there are no nonradiative relaxation channels.

We note that excitonic effects were not taken into account in this calculation. Compared to the conventional superlattices, e.g., $GaAs/Al_xGa_{1-x}As$, the excitonic binding energy in Ge twinning superlattices would be somewhat increased because of large longitudinal and transverse electron effective masses. However, this effect would be at least partly counterbalanced by the fact that the strong two-dimensional confinement provided by barrier regions in conventional superlattices is absent in twinning superlattices (even the evanescentlike minibands are rather shallow and thus the wave-function decay constants small, unlike the case of conventional superlattices where the low-lying minibands are well below the barrier top). We would thus expect the excitonic effects in twinning superlattices to be similar to those in conventional superlattices. Qualitatively speaking then, excitonic effects would merely change the sharp-rising segments in Fig. 1 to peaklike features.

Twinning, and related phenomena based on it (stacking faults), appear frequently in both natural minerals and artificially grown semiconductor crystals. However, limited efforts have been directed toward their fabrication. A report on growing a high-quality, possibly large-area, single twin boundary in silicon (via the deposition of a submonolayer of boron), has appeared only quite recently.[13] The method may be extended in principle so as to grow superlattices. Another interesting report is the one of Ref. 14, where free-standing GaAs quantum-wire whiskers were found to have the structure of somewhat irregular twinning superlattices, their periods being quite small, in the nanometer range, just as the wire diameters themselves. Although neither of these experiments attempted to obtain similar structures in germanium, the fabrication of a twinning superlattice now seems plausible. Finally, we may note that although the folded direct optical transitions were studied here on the example of Ge, other III-V L-type indirect semiconductors, like the (AlGa)Sb alloy, are also alternative candidates. However, Si is not suitable for this purpose, since none of its X valleys folds into the center of the superlattice Brillouin zone in case of [111] growth.

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