Structure and Optical Properties of Strained Ge-Si Superlattices Grown on (001) Ge

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Ge-Si strained-layer superlattices have been synthesized on (001) Ge with unit-cell periodicity of ten atomic monolayers along the growth direction. Microstructural characterization establishes extended planar superlattice layering. X-ray diffraction is used to measure the superlattice composition. Optical reflectance spectra show new optical transitions at energies theoretically predicted for superlattice-induced direct optical transitions at the center of the Brillouin zone.

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Ge-Si superlattices with periodicities of a few atomic monolayers have been the subject of considerable theoretical and experimental interest following the discovery of new electronic energy band structures induced by the superlattice periodicity.[1,2] Studies of valence-band offset and the well-understood properties of uniaxial strain in Si and Ge have established that the conduction-band edge in these structures is formed from ⟨100⟩-oriented Si states. Commensurate, strained-layer epitaxy of a Ge-Si superlattice on a (001) Ge substrate imposes a compressive uniaxial strain along the superlattice (SL) growth direction.[3] Under these conditions of strain, the conduction-band edge lies only along the SL axis, and it will be mixed by the SL potential with zone-center states,[4-14] raising the possibility that the SL might be a direct-band-gap material.[15-18]

We have investigated two such samples: One with a unit cell consisting of seven monolayers of Ge and three monolayers of Si repeated 5 times in the growth direction (Ge_7Si_3), and a structure consisting of six monolayers of Ge and four monolayers of Si (Ge_6Si_4). The conduction-band energy minimum in bulk Si lies about $\frac{4}{5}$ the distance from the zone center Γ to the zone edge at X. Imposing a SL periodicity equal to 5 times the primitive cell dimension will fold the Brillouin zone so that this energy minimum appears at the zone center. Since the Si basis consists of two atoms, ten atomic monolayers is the shortest-period SL that will achieve the required folding of the Brillouin zone. The concept of zone folding, while it may appear too simple at first glance, has been proven to give an accurate picture of the effect of SL periodicity on the band structure.[4,9,13]

The basic SL structure of 44 monolayers is repeated 20 times by placing a 250-Å Ge buffer between each unit to moderate the average strain in the epitaxial layer to a level below the threshold for dislocation formation. Details of the growth procedure will be presented elsewhere.[19] Transmission electron microscopy of the layers shows the presence of dislocations at the level of 10^7–10^8 cm^{-2} in our structure. While this level is too large for some kinds of device applications, it is much too low to have an effect on the electronic band structure of the SL. The average distance between the dislocations is 1 μm, while the total SL structure is about 0.6 μm thick. Evidence of structural uniformity and periodic layering for these samples can be seen clearly in the transmission electron diffraction pattern and bright-field image[20] of the cross section shown in Fig. 1. It is quite clear from this image that the nanostructure of the Ge-Si SL is not significantly perturbed by the dislocation density.

The high-resolution x-ray diffraction (HRXRD) measurements were carried out with a previously described

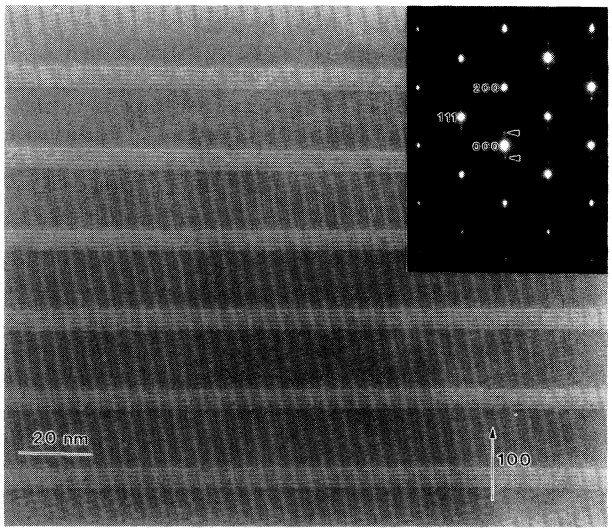

FIG. 1. Transmission electron micrograph (TEM) of Ge_6Si_4/Ge superlattice using the (004) bright-field condition near a ⟨100⟩ zone axis. The cross-sectional TEM shows extended planar layering of the superlattice and the Ge spacer layers used to separate the superlattice regions. The total integrated superlattice thickness is about 1000 Å. Inset: Zone-axis TEM diffraction pattern. Superlattice spots along [001] are clearly in evidence showing a fivefold superperiodicity.

TABLE I. Structural parameters of two ten monolayer Ge-Si/Ge superlattices.

	Λ (Å)	$N_{Ge\text{-}Si}$	N_{Ge}	$a^{\perp}_{Ge\text{-}Si}$ Expt. (Å)	$\epsilon^{\perp}_{Ge\text{-}Si}$ (%)	$t_{Ge\text{-}Si}$ (Å)	t_{Ge} (Å)	$a^{\perp}_{Ge\text{-}Si}$ Calc. (Å)	$a_{Ge\text{-}Si}$ Relax. (Å)	x_{Si} Composition
Ge_7Si_3	272.7	44	150	5.522	−2.4	60.7	212	5.518	5.581	0.34
Ge_6Si_4	247.2	44	132	5.479	−3.2	60.2	187	5.475	5.556	0.45

x-ray geometry[21] consisting of a compact four-crystal monochromator,[22] which produces a parallel, monochromatic Cu $K\alpha$ x-ray beam, with the sample as the fifth crystal and an open-end detector. This arrangement, which is run in a θ-2θ mode, is adapted to a Huber 424/511 four-circle diffractometer and aligned with a Rigaku-300 rotating-anode x-ray source.

In order to determine the periodic structural parameters along the [001] growth direction, x-ray spectra were taken in the vicinity of the Ge [004] reflection. The periodicity of the Ge-Si SL structure, under net hydrostatic expansion, generates an x-ray satellite pattern around the [004] diffraction peak which can be analyzed by a computer simulation based on a kinematical diffraction step model.[23] Analysis of the data allows us to calculate the number of monolayers $N_{Ge\text{-}Si}$ in the Ge-Si SL cell and N_{Ge} in the Ge buffer, and their corresponding d spacings, $d_{Ge\text{-}Si}$ and d_{Ge}, between subsequent monolayers along [001].[24] [The parameter d_{Ge} can be assumed to be equal to the bulk value, $a_0/4$, where $a_0(\mathrm{Ge}) = 5.6576$ Å.] Once these structural parameters are extracted from the step model, the thickness of the Ge-Si SL, $t_{Ge\text{-}Si}$, and that of the buffer layer, t_{Ge}, are calculated giving the period of the SL plus buffer structure, Λ, and the strain, ϵ. The results of this procedure are given in Table I.

In both samples, the Ge-buffer-layer thickness is ~200 Å, about 20% less than the nominal thickness of 250 Å. The strain $\epsilon^{\perp}_{Ge\text{-}Si}$ in the Ge_6Si_4 structure is 33% larger than in the Ge_7Si_3 SL, in agreement with the difference in Si concentration which is about 33% higher in the Ge_6Si_4 structure. The kinematical model shows that both SL structures are composed of 44 monolayers in excellent agreement with the intended structures. For Ge_7Si_3 the layer sequence of (373737373) has 43 monolayers, and for Ge_6Si_4 the sequence (464646464) has 44 monolayers. The nominal concentrations of Si are 0.35 and 0.46, respectively. The combination of TEM and x-ray analysis is sufficient to prove that the samples discussed in this paper are ordered, extended, planar superlattices with no evidence of strain relaxation, the compositions of which correspond to the nominal composition within one monolayer. These results are necessary to the interpretation of the optical spectra.

The uniaxial strain imposed by the substrate splits the valence band of Si into three components and lowers the [001] conduction band below the $\langle 111 \rangle$ minima of Ge, so that it forms the SL conduction-band minimum. The ten monolayer SL periodicity folds the Brillouin zone of the Ge-Si SL so that this minimum appears at Γ. Because the valence-band maximum for both Si and Ge already occurs at Γ, the SL periodicity has no additional effect on modifying the energy-band structure at the valence-band edge. The relatively large valence-band offset between Ge and Si means that both the Ge_6Si_4 and Ge_7Si_3 heterostructures have a type-II band alignment. This situation is diagramed in Fig. 2. Starting with the offset determined by Van de Walle and Martin,[25] the splitting of the Si valence band is calculated using the full strain-dependent Hamiltonian.[3] The results give a single uppermost level separated by about 500 meV from two nearly degenerate lower-lying levels. These are indicated by the solid lines in Fig. 2 in the Si valence-band region. There is a single level in the conduction band. Ge levels are unaffected by the strain. We modeled the SL structure using the Krönig-Penney approximation in order to calculate the energies of the three valence- to conduction-band transitions.[2] The solutions of this calculation for the Ge_6Si_4 SL are shown as dashed lines in Fig. 2, and the transition energies are given in heavy type in this figure and in Table II. Relative to the Ge_6Si_4 SL,

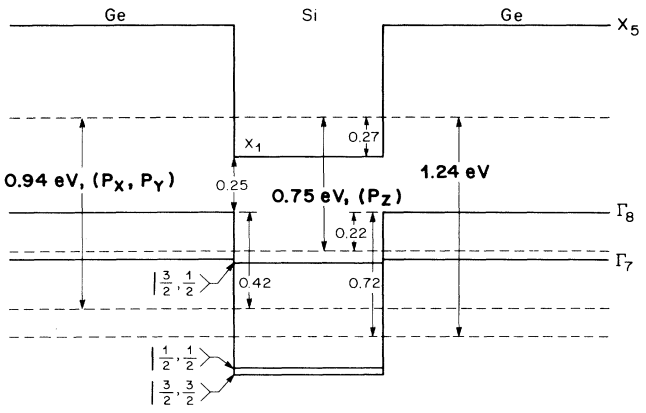

FIG. 2. Schematic representation of the band-alignment model used to calculate the transition energies in a Ge_6Si_4 SL grown on (001) Ge. First the bands of unstrained Ge and Si are aligned. Next the effect of strain on the energy band of Si 1s calculated leading to the solid lines shown in the figure. These levels are used as the basis for a Krönig-Penney calculation that gives the delocalized levels indicated by the dashed lines. Transition energies between these levels are indicated in the diagram.

TABLE II. Optical transition energy parameters deduced from 40-K line-shape analysis.

Transition number	Energy (eV)	Amplitude ($\Delta R/R$)	Linewidth (eV)	Krönig-Penney energy (eV)	Identification
(a) Bulk Ge					
1	0.88	7.1×10^{-4}	0.04		Ge: E_0
2	1.19	1.3×10^{-4}	0.04		Ge: $E_0+\Delta_0$
(b) Ge_6Si_4/Ge(001)					
1	Not observed	...	...	0.745	SL: p_z
2	0.88	1.6×10^{-4}	0.017	...	Ge: E_0
3	0.96	8×10^{-5}	0.015	0.94	SL: p_x,p_y
4	1.18	9.4×10^{-6}	0.024	...	Ge: $E_0+\Delta_0$
5	1.22	8×10^{-6}	0.020	1.24	SL: split off
(c) Ge_7Si_3/Ge(001)					
1	Not observed	...	...	0.780	SL: p_z
2	0.89	6×10^{-6}	0.017	...	Ge: E_0
3	0.93	6×10^{-6}	0.014	0.93	SL: p_x,p_y
4	1.20	5×10^{-7}	0.016	...	Ge: $E_0+\Delta_0$
5	1.25	3×10^{-7}	0.013	1.24	SL: split off

the Ge_7Si_3 structure has a more narrow conduction-band "well," raising the conduction-band state, but a wider Ge valence-band "well," also raising the energy of this state. As a result, the band-to-band transition energy, which depends on the difference, does not change very much. In a type-II SL the transition energies are not a strong function of superlattice subcomposition, and the electroreflectance spectra of the two SL structures are expected to be similar.

The lowest-energy transition at $E=0.75$ eV corresponds to the direct band gap. However, this transition has p_z polarization symmetry and cannot be excited in our experimental geometry where only p_x and p_y polarizations are possible. The transitions calculated at 0.94 and 1.24 eV can be measured, and their observation is experimental evidence confirming the existence of the zone-folded conduction-band minimum at Γ. While the Krönig-Penney method gives the band-gap energy accurately, it says nothing about the character of the band gap. Satpathy, Martin, and Van de Walle[9] have studied the band structure of Ge-Si SL structures in the local-density approximation, and have shown that an absolute conduction-band minimum is expected at Γ in ten-period SL structures grown on Ge. Further theoretical investigations by Gell[11] show that these transitions are allowed, and that the optical matrix element is substantially larger than that characteristic of indirect transitions.

Electroreflectance spectra taken at 40 K are shown in Fig. 3. In Fig. 3(a) we show the spectrum of the Ge substrate, and in Fig. 3(b) we show the spectra taken under the same modulation conditions ($V_{ac}=200$ mV p.p.; $V_{dc}=-200$ mV) for the two SL structures. All three spectra show distinct features at 0.88 and 1.18 eV corresponding to the E_0 and $E_0+\Delta_0$ transitions for Ge.[2] However, the SL spectra are more complex, showing additional structure near 0.94 and 1.24 eV. These transition energies, summarized in Table II, are extracted from the spectra using a nonlinear fitting routine that gives the amplitude and linewidth, as well as the energy, of each feature.[2,26] Comparison of the E_0 and $E_0+\Delta_0$ transition energies in these three cases gives a fair evaluation of the accuracy of our measurement and analysis procedure. The fine structure in the Ge E_0 transition, apparent in all three spectra, is a well-understood excitonic effect that has been observed previously in GaAs.[27] We observe this feature when the ac modulation amplitude is less than the band gap.

The two SL spectra are quite similar to each other, even though x-ray analysis shows the compositions and strain levels to be distinct. This result confirms experimentally the type-II nature of the band alignments. The measured transition energies are in excellent agreement with those calculated in our model. The amplitude and linewidths of the SL transitions are similar to direct transitions measured in the Ge substrate and buffer regions. These measurements therefore confirm the existence of a zone-folded conduction-band state in the superlattice. The direct band gap is formed between this state and the upper valence-band level with a transition energy of about 0.75 eV (depending on the precise structure). This transition is not measured in our experiment because of polarization selection rules. However, it has been observed by Abstreiter *et al.* in a much thicker Ge_4Si_6 superlattice grown by the strain symmetrization method.[18]

In this work we have shown that Ge-Si SL structures with ten monolayer periods can be characterized to confirm the structure, strain, and subcomposition within one monolayer. Optical measurements by electroreflectance are in agreement with all the expected properties of these superlattices, confirming in particular the formation of a zone-folded conduction-band minimum leading to superlattice transitions in excellent agreement with theory. We believe that our results offer convincing evidence for

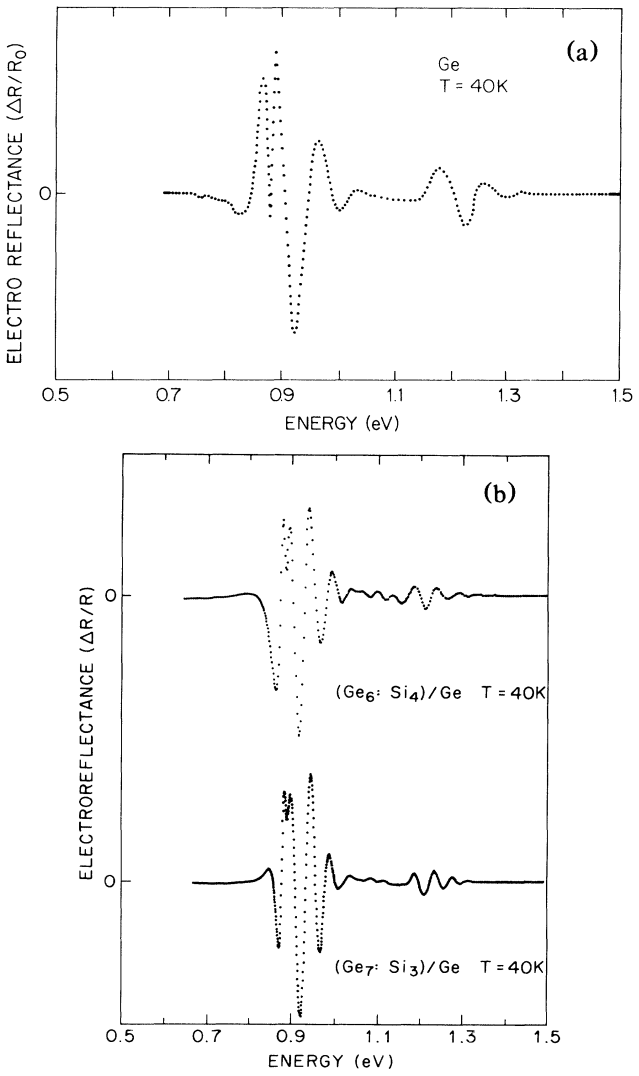

FIG. 3. Electroreflectance spectra at 40 K. (a) Electroreflectance spectrum of the bulk Ge substrate in the region of the E_0 and $E_0+\Delta_0$ transitions. Transition energies are determined from a line-shape fitting procedure and are given in Table II(a). (b) Electroreflectance spectra of the Ge_6Si_4 (upper) and Ge_7Si_3 (lower) SL's in the same spectral range and under the same modulation conditions as in (a). The two spectra are similar because of the type-II band alignment. Both samples show an additional strong oscillation near 0.95 eV not seen in the Ge spectrum. This feature is the superlattice transition near 0.95 eV. Precise values for the SL transitions as well as the Ge transitions in these samples are determined by line-shape analysis and given in Table II(b) and II(c).

the formation of a direct gap in a superlattice composed of two indirect-band-gap semiconductors by using principles of strain and symmetry in crystalline materials.

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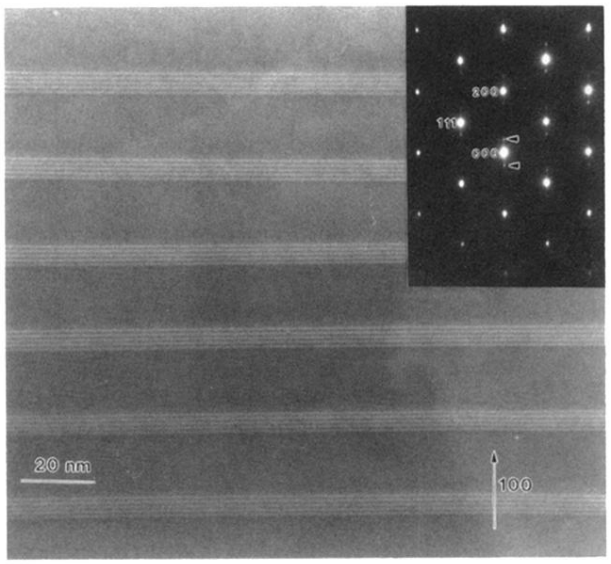

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