Interband Transitions in Strain-Symmetrized Ge₄Si₆ Superlattices

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We present experimental as well as theoretical data for the linear optical response of symmetrically strained Ge₄Si₆ [001] superlattices. *Ab initio* calculations show that they have a direct gap. The complex dielectric function has been measured ellipsometrically. Agreement of the experimental second-derivative spectrum $d^2\epsilon_2/d\omega^2$ with the theory is obtained, both for the shape and position of bulklike transitions and for new superlatticelike transitions, after including lifetime effects in the calculated curves through Lorentzian convolution.

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Ge/Si strained-layer High-quality superlattices (SLS's) have been grown up to a thickness of 200 nm on thin homogeneous $Ge_x Si_{1-x}$ buffers, ¹ causing the strain to be equally distributed in the Ge and the Si layers ("strain symmetrized"). A stimulus for the investigation and growth of Ge/Si SLS's is the hope to obtain new materials with a direct or quasidirect gap that can be integrated on well-established silicon technology. This was suggested long ago,² and recently confirmed with the local-density, pseudopotential method³ for an overall period of 10 monolayers (ML) and a minimum amount of tensile strain in the Si layers, and demonstrated experimentally by Pearsall et al.⁴ and Zachai et al.,⁵ although the details of their interpretation are still under debate.⁶ For device applications, the optical response over a wide energy range is of great importance. We present such experimental data here, as well as theoretical calculations that allow a detailed analysis of the observed structures in terms of interband transitions. For the freestanding Ge₄Si₆ [001] SLS studied here we find various strain-split peaks that can be ascribed to bulklike transitions, not only in the calculations but also in the spectrum measured with the spectroellipsometric method. From the shape and the magnitude of the various peaks, we can estimate the effects of lifetime broadening on these transitions. In addition, we observe several new peaks that can be ascribed to "superlattice" transitions, such as zone-folded transitions that originate from the k_{τ} direction $(\hat{\mathbf{z}} \parallel [001])$.

The calculations are performed within the localdensity approximation (LDA) by means of the linearmuffin-tin-orbitals (LMTO) method.⁷ Corrections for the LDA "band-gap problem" were made by adding external potentials on the atomic sites.^{8,9} These sharply peaked potentials are included self-consistently in the calculation and yield the correct conduction bands and deformation potentials of the bulk materials Si and Ge.⁹ When these correction parameters are transferred to the SLS's, our calculated direct transition energies agree within ≈ 0.1 eV with electroreflectance^{4,10} and photoreflectance¹¹ experiments. The SLS structure has been relaxed with a valence force-field scheme.^{12,13}

The Ge₄Si₆ SLS has orthorhombic symmetry¹⁴ [space group $D_{2h}^{28}(Imma)$], although the unit cell is biaxial. As the difference of the eigenvalues along the two inequivalent [100] and [010] directions is small,¹³ we use in Fig. 1 the notation of the tetragonal Brillouin zone (BZ).⁸ The calculated lowest band gap of the Ge₄Si₆ SLS (E_d) is direct, with an energy of 1.1 eV. For a discussion of this value and the interpretation of photoluminescence experiments,⁵ see Ref. 6. We have chosen the lattice constant in the plane so as to meet the requirement of minimum elastic energy¹⁵ ("free-standing" case): $a_{\parallel} = 5.51$ Å, which yields a lateral strain in the Si



FIG. 1. Calculated electronic band structure (including spin-orbit splitting) of the "free-standing" Ge_4Si_6 SLS along lines of high symmetry. The notation of the points in **k** space is taken from Ref. 8.



FIG. 2. Imaginary part $\epsilon_2(\omega)$ of the dielectric function of the Ge₄Si₆ SLS, as measured at T = 10 K (solid line) and as calculated (dashed line) with a Lorentzian of $\Gamma = 50$ meV. The calculated values below ≈ 2 eV are shown without any lifetime-broadening effects, magnified by a factor of 1000.

layers of 1.4%. In the calculation of the dielectric function,¹⁶ the **k**-space integration has been performed by means of the tetrahedron method¹⁷ based on 638 **k** points in the irreducible part of the BZ. Because of the large index of refraction of the SLS's, the electric field is polarized mainly perpendicular to the growth direction, so that the measured dielectric function corresponds (with the orientation of the sample used) to $\epsilon_2^{xx}(\omega)$ or $\epsilon_2^{yy}(\omega)$. The optical anisotropy perpendicular to the growth direction expected for orthorhombic crystals is small in this case¹³ and has been neglected earlier.¹⁸ In addition, the presence of monatomic steps in the SLS is expected to destroy this small effect, which was not detectable. We thus compare in Fig. 2 the experimental spectrum with the average of ϵ_2^{xx} and ϵ_2^{yy} .

The measurements have been performed at T = 10 K and at room temperature (RT) in the energy range between 2.5 and 5.0 eV with a rotating analyzer ellipsometer as described in Ref. 19. The various SLS's of ≈ 0.2 μ m thickness were grown by molecular-beam epitaxy on Si(001) substrates. Strain symmetrization was achieved similarly to previous work¹ by growing the SLS's pseudomorphically on partially relaxed buffers (GeSi alloy and pure Ge). The strain distribution is near that of a free-standing SLS, as assumed in the calculation. Small changes in the strain and individual layer thickness (which may vary up to 1 ML) affect our spectra only negligibly.¹³ The dislocation density in the samples is still large ($\approx 10^{9}/\text{cm}^{2}$). Misfit dislocations, however, are expected to affect mainly the photoluminescence spectra of the direct transitions, and not so much the absorption coefficient at higher energies, which we measure in ellipsometry. Some of the samples were n-doped (Sb) to a degree²⁰ ($\approx 10^{18}$ /cm³) which is known to be about



FIG. 3. Second derivative spectrum $d^2 \epsilon / d\omega^2$ as obtained from the experiment (lower two spectra at T = 10 and 300 K) and as calculated with the inclusion of various lifetime broadenings. Note that the scale of the theoretical results has been shifted by 0.1 eV in order to facilitate the comparison.

2 orders of magnitude below the detection limit in ellipsometry. $^{\rm 21}$

We see in Fig. 2 qualitative agreement between the experimental and calculated $\epsilon_2(\omega)$. Below 2.7 eV, the measured $\epsilon_2(\omega)$ is dominated by strong oscillations produced by interference²² with the beam reflected at the substrate surface. As in the bulk materials, the calculated magnitude of the E_1 peak at about 3 eV is strongly underestimated due to many-body and excitonic effects, which are neglected in our calculation.¹⁶ In addition, the existence of a surface overlayer and a thin Si cap layer of about 1 nm may affect the spectrum unfavorably. For these reasons we decided to compare the second derivatives of the measured and calculated $\epsilon_2(\omega)$, which are less influenced by the conditions discussed above. This is also the preferred representation for the critical-point analysis.

Figure 3 shows the second derivative of the experimental spectrum $d^2\epsilon_2/d\omega^2$ at T=300 K and T=10 K (lower two spectra), in comparison with the corresponding theoretical spectra, for which the effect of lifetime broadening has been included by folding with Lorentzians of $\Gamma=50$ and 100 meV FWHM (upper two spectra). We have chosen these values of Γ as they reflect the experimental broadenings of various transitions which lie in the 30-130-meV range for Si and Ge.²³ We should, however, keep in mind that Γ , which is determined by the self-energy of electrons interacting with phonons,^{23,24} depends considerably on temperature, imperfections, and the character of the transition, and that is different for each transition.

Nevertheless, the agreement of these smoothened spectra with the experimental ones is excellent. Strong absorption starts at ≈ 2.3 eV and is due to transitions from the valence band top (v1) to the lowest conduction band (c1) at $k \approx \frac{1}{2}N$ (E^a₁ peak). N corresponds to the folded L-point of the diamond BZ.⁸ The absorption due to quasidirect transitions originates from matrix elements that are 3-4 orders of magnitude smaller than those originating from the E_0 transitions, and thus are negligible in our study, although they are of fundamental interest.⁴⁻⁶ The small magnitude of their oscillator strengths can be studied in Fig. 2, where the energy region from 1 to 2 eV has been blown up by a factor of 1000. The E_{\perp} transition typical for bulk materials is split into various contributions $(E_1^i, i=a,b,c)$, originating from various strain-split bands along Γ -N, as listed in Table I. Two different E_1 peaks in Ge_nSi_m SLS's have already been observed with resonant Raman scattering.²⁵ The E_1^d transition at ≈ 3.0 eV is smeared out and amplified in the experiment via excitonic interaction. The excitonic character of these transitions has already been observed for Si.²³ The position of this peak is rather sensitive to the exact composition of the SLS's, owing to the large difference ($\approx 1.2 \text{ eV}$) in the E_1 energies of the constituting bulk materials, in analogy to $Ge_x Si_{1-x}$

TABLE I. Interband transition analysis of the various examined structures. The conduction bands are labeled c_1, c_2, \ldots with increasing energy, and the valence states v_1, v_2, \ldots from the top with decreasing energy. Experimental data refer to T = 10 K. The notation of the k space is compatible with the one used in Fig. 1.

Struc-	Energy	(eV)		≈ k space
ture	Theory	Expt.	Transitions	region
E	≈ 2.3		$v \rightarrow c 1$	$\frac{1}{2}N$
E_0	2.64		$v 1 \rightarrow c 7$	Г
E_{1}^{b}	2.75		$v \rightarrow c 3, c 5$	$\frac{1}{3}N$
<i>E</i>	3.0		$v2, v3 \rightarrow c1$	$\frac{3}{4}N$
E^{d}_{1}	3.11	3.01	$v 2 \rightarrow c 2$	$\frac{3}{4}N$
S_{\perp}	3.28	3.22	$v 2 \rightarrow c 3$	$\frac{1}{3}(X+2Z)$
S_2	3.41	3.38	$v 3 \rightarrow c 3$	$\frac{1}{4}(X+2Z)$
S_3	3.63	3.51	$v 2 \rightarrow c 4$	$\frac{1}{2}(X+N+Z)$
S_4	3.90	3.68	$v 3 \rightarrow c 1$	$\frac{1}{2}(X+Z)$
S_5	4.08	3.97	$v \rightarrow c 2$	$\frac{1}{2}(X+Z)$
S_6	4.21	4.09	$v \rightarrow c 1$	$\frac{1}{2}(X+N+Z)$
E_2^q	4.36	4.26	$v \rightarrow c 2$	$\frac{4}{5}X, \frac{4}{5}P$
	4.40	4.29	$\begin{array}{c} v & 2 \longrightarrow c \\ v & 1 \longrightarrow c \end{array}$	$\frac{4}{5}X$
E	4.62	4.53	$v \rightarrow c 4$	$\frac{1}{2}(X+N+Z)$
ES	4.70	4.62	$v2 \rightarrow c4$	$\frac{1}{2}(X+N)$
E	4.90	4.78	$v1 \rightarrow c5$	$\frac{1}{2}(X+N)$

alloys.²⁶ This is not the case for the E_2 transitions, which also split into various components. The contribution that can be related to unstrained bulk transitions, E_{2}^{a} , is the dominant one and is split into two components. While this splitting is not clearly visible in the theoretical spectrum with $\Gamma = 100$ meV and in the T = 300 K experiment, it becomes evident for $\Gamma = 50$ meV and T = 10 K. Thus, we also get some rough estimate of the temperature dependence of Γ for the E_2^a transition, which should be around 100 meV at 300 K, comparable to that for Si.²³ The amplitude of this peak ($\approx 400-600 \text{ eV}^{-2}$ for various SLS's at RT) is close to the average magnitude of the corresponding transitions in Si ($\approx 1000-1200$ eV⁻²) and Ge ($\approx 200-300$ eV⁻²), and to the calculated peak with $\Gamma = 100$ meV. The remaining three E_2^i peaks (i=b,c,d) are associated with transitions to higher conduction states (c4, c5). In the experimental spectrum, appreciable noise above ≈ 4.8 eV prevents further assignment of peaks.

In addition to the bulklike transitions discussed above we observe a multitude of weak structures originating from zone-folded bands. We have designated the maxima of these peaks with S_i , i = 1-6. Only at T = 10 K can these peaks be clearly observed, although the assignment to the calculated peaks has to be somewhat tentative due to their small strength. We believe that the structure of these peaks can be used as an indication for the quality of the sample. In the spectrum taken at RT (lowest curve in Fig. 3), the peaks are less pronounced, but their spectral positions do not seem to show any appreciable temperature dependence. This may be due to final conduction states interacting with phonons via conduction states located at lower energy and conversely for holes via higher-energy valence states. These secondorder "Fan" terms²⁴ should compensate the decrease in the gap with increasing temperature commonly observed. In contrast to the S_i , the main E_1 and E_2 transitions shift by about 0.1 eV when the temperature is decreased from 300 to 10 K, practically the same shift as observed for bulk Si (Ref. 23) and Ge.¹⁹

In conclusion, we have given a detailed experimental and theoretical analysis of interband transitions in a free-standing Ge₄Si₆ SLS, including both bulklike as well as zone-folded transitions. Keeping in mind sample imperfections such as diffusion at the interface, interface roughness, misfit dislocations, changes in the composition, strain distribution, etc., the agreement between experiment and theory (≈ 0.1 eV for the peaks of the various structures) is excellent.

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