E_1-Like Optical Transitions in Ge/Si Heterostructures Studied by Electroreflectance and Photoreflectance

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We report low temperature (77 K) electroreflectance and photoreflectance measurements of tlie E_1-like optical transitions on a. series of Ge/Si heterostructures (superlattices and quantum wells). Por single and double quantum wells of any thickness, as well as for thick-layer superlattices (period $\sim$ 100 Å) the spectra can be understood in terms of quantum confined bulk-Ge E_j states. For thin ($\sim$ 10 Å) multiple quantum wells and superlattices zone folding effects dominate the spectra.

I. Introduction

The study of the electronic states in pseudomorphically grown Ge/Si heterostructures poses many challenging questions, such as folded electronic states, tlie quasidirect gap induced by superperiodicity and the higher energy transitions in these materials[1,2]. In particular, band structure calculations show tliat the E_1-like transitions in Ge/Si strained layer superlattices (SLS) constitutes a. multiplet[3,4] that seems to be a fingerprint of the microstructure[5]. The components of this multiplet has been observed using electroreflectance in Ge/Si SLS grown on Si(001)[6], while a splitting of tliese transitions could be resolved by resonant Raman scattering only for samples with periods larger than 20 monolayers[7]. Recently Rodrigues et al.[8] have shown that this multiplet evolves to Ge-like and Si-like transitions when the period of tlie SLS goes from $\sim$ S to $\sim$ 30 monolayers. On the other hand, for a single layer of Ge grown on Si(001) Tsang et al.[9] have observed one confined E_1-like struture in samples witli only $\sim$ 5 monolayers of Ge.

Here we present low temperature (77 K) photoreflectance and electroreflectance measurements on a series of Ge/Si heterostructures in the spectral region of the E_1-like transitions. Our samples can be divided into two groups accorcling to the thickness of the Ge layers (d_A). For samples with thick Ge layers ($d_A \sim$ 100 Å) me observe a. shift of the E_1 peak to higher energies, suggesting that the electronic states responsible foi this transition suffer quantum confinement effects. The behavior of the E_1 structure for samples with thin Ge layers ($d_A \sim$ 7 Å) depends strongly on the number of Ge layers. However, for a single and a double Ge layer the E_1-like transitions can also be understood *qualitatively* in terms of simple quantum confinements models.

The samples were grown by molecular beam epitaxy at low substrate teinperature with thicknesses smaller than tlie critical thickness for the Ge/Si system[10]. The samples with thick Ge layers were grown on Ge(001) substrates and are made up of alternating layers of pure Ge and Ge_xSi_{1-x} alloy. The relevant structural parameters for all samples are summarized in Table I. The samples with thin Ge layers were grown on Si(001) substrates. The sarnple SQW7 is a "single quantum well" of Ge while the samples 2QW7 and 6QW7 are a. "double" and a "sextuple" quantum well, respectively. In each of tliese samples the well is composed of five monolayers of Ge, while the barriers in the sam-

Table I - Relevant structural parameters for the samples studiec. The column $d_A(d_B)$ lists tlie thickness of the Ge (Ge_xSi_{1-x}) layers, x is the Ge concentration in tlie alloy Ge_xSi_{1-x}, ϵ^{Ge} is the percentage variation of the in-plane lattice parameter of the heterostructure and that of bulk Ge, while N is the number of times tlie structure d_A/d_B was repeated.

Sample	d_A (Å)	d_B (Å)	x	$10^2\epsilon^{Ge}$	$N^{(a)}$
SQW250	$250^{(a)}$	$400^{(a)}$	$0.8^{(a)}$	$0^{(a)}$	1
111/32	$111^{(b)}$	$32^{(b)}$	$0.7^{(b)}$	$\sim 0^{(b)}$	20
102/34	$102^{(b)}$	$34^{(b)}$	$0.7^{(b)}$	$\sim 0^{(b)}$	15
SQW7	$7.3^{(a)}$	0	0	$-4.01^{(a)}$	1
2QW7	$7.3^{(a)}$	$6.8^{(a)}$	0	$-4.01^{(a)}$	2
6QW7	$7.3^{(a)}$	$6.8^{(a)}$	0	$-4.01^{(a)}$	6

(a) Nominal value.
(b) Experimental value. See ref. [11]

ples 2QW7 and 6QW7 are five monolayers of pure Si. Tlie structure (single, double or sextuple quantum well) was repeated 10 times in each sample, separated by thick (~ 300 Å) Si layer. The thick samples were characterized by x-ray, Raman scattering and photoreflectaiice measurements[11]. Tlie values listed in Table I for these samples are tlie ones determined experimentally. Tlie thin samples were characterized by Raman spectroscopy[12]. The spectra of the optical phonons for the Ge-Ge, Ge-Si and Si-Si vibrations are compatible with tlie nominal structural parameters listed in Table I.

The electroreflectance (ER) and photoreflectance (PR) measurements were performed at 77 K with the samples immersed in liquid nitrogen, using a standard set-up[13,14]. For ER measurements a Schottky barrier was created by depositiiig a $\simeq$ 100 Å thick Ni- film on the sample siirface. The modulation was accomplished by biasing externally tlie Schottky barrier with an ac voltage of 3 V peak to peak. For PR measurements, the secondary (inodulatioii) beam conies from a 10 mW He-Cd laser attenuated by neutral filters aiid mechanically chopped at 200 Hz. Tlic experimental spectra were fitted with a third derivative line shape[14]:

$$\frac{\Delta R}{R} = \sum_j Re\left\{\frac{C_j e^{i\theta_j}}{[(\hbar\omega - E_j) + i\Gamma_j]^n}\right\}, \qquad (1)$$

where j is tlie transition number, C_j the relative amplitude, θ_j the phase, Γ_j the phenomenological broadening parameter, and E_j the transition energy. We used $n = 3.0$ which corresponds to two-dimensional critical points.

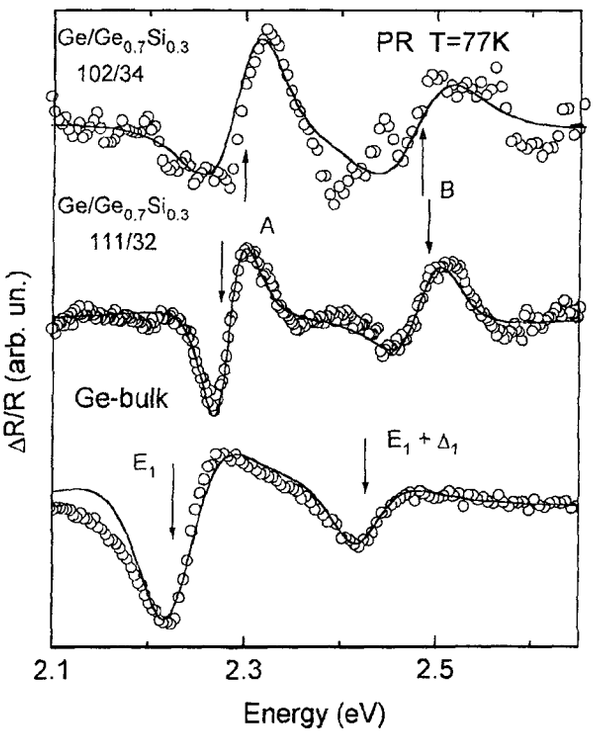

Figure 1: Photoreflectance (samples 102/34 and 111/32) and electroreflectance (Ge bulk) spectra in the range of the E_1, $E_1+\Delta_1$ transitions. Open circles are experimental data. Tlie arrows are tlie transition energies obtained by tlie fitting procedure (continuous lines).

Fig. 1 displays the PR spectra (open circles) for the samples 102/34 and 111/32 together with the one for a bulk Ge sample, in the spectral region of the E_1, $E_1 + \Delta_1$ transitions. The transition energies obtained by fitting (continuous lines) tlie experimental data to eq. (1) are indicated by arrows in Fig. 1 and listed in Table II. Tlie spectrum of the bulk Ge sample shows two structures whose energies correspond to the E_1, $E_1+\Delta_1$ transitions in pure Ge [15]. The spectra for the sarnples 102/34 and 111/32 have only two structures (peaks A and B in the Fig. 1) whose energies are slightly higher than those for the bulk Ge. We assign these structures to the E_1, $E_1 + \Delta_1$ transitions from the Ge layers. The spectrum for the sample SQW250 (not shown in Fig. 1) contains structures whose energies are in good agree-

Table II - Transition energies (TE) and assignment for tlie E_1-like transitions observed in the Photoreflectance spectra of thick Ge/Si heterostructures. The last two columns show the experimental shift (Exp.) of the E_1 transition in the heterostructures, iii relation to tlie bulk Ge value, and the confinement energy predicted by an infinite quantum well model (Inf. Well).

Sample	TE (eV)	Assignement	Shift (meV)	
			Exp.	Inf. Well
	2.300 A	E_1(Ge)	72 ± 15	53
102/34				
	2.480 B	$E_1 + \Delta_1(Ge)$		
	2.280 A	$E_1(Ge)$	52 ± 10	45
111/32				
	2.490 R	$E_1 + \Delta_1(Ge)$		
	2.230	$E_1(Ge)$	2 ± 10	9
SQW250	2.400	$E_1 + \Delta_1(Ge)$		
	2.510	$E_1(Ge_{0.8}Si_{0.2})$		
	2.610	$E_1 + \Delta_1(Ge_{0.8}Si_{0.L})$		
	2.228	E_1		
Ge- bulk				
	2.420	$E_1 + \Delta_1$		

ment with the values for the E_1, $E_1 + \Delta_1$ transitions of bulk Ge. The results displayed in Fig. 1 and listed in Tahle II show that the E_1 transition from the Ge layers in thiclr Ge/Si heterostructures are shifted to higher energies, in relation to the corresponding transition of bulk-Ge. This shift dccreases with increasing Ge layer thickness, suggesting that the electronic states responsible for tlie E_1 transition suffer quantum confinement effects. In order to estimate the confinement energy we have calculated tlie eigen energies of a particle with mass μ in an infinite quantuin well. We have used the measured reduced interband mass[15] along the direction $\Gamma - L$ of bulk-Ge. The shifts predicted for tlie E_1 transition using this simple inodel, as well as those found experiinentally are listed in Table II. Given the simplicity of this model and the large volume of the Brillouin zone[16] involved in the E_1 transition, the reasonable agreement between the theoretical and experimental shifts (see Table II) may be fortuitous. However, this comparison supports the suggestion that the electronic states responsible for the E_1 transitions suffers quantum confinement effects. Ellipsometric[17] and Raman scattering[18] experiments performed on superlattices based on 111-V materials reach a similar conclusion. Although the experimental results indicate that quantum confineinent effects play a role in the E_1-like transitions, the theoretical description of these effects is not trivial due to the large volume of the Brillouin zone involved in the E_1 transition.

Let us turn to the thin layer heterostructures. In Fig. 2 we display the ER spectra of the samples SQW7, 2QW7 and 6QW7, together with the ones from bulk Si and a sample of $Ge_{0.5}Si_{0.5}$ alloy not strained. The spectra of the Ge "quantum wells" can be divided in three regions. In the spectral range $\hbar\omega \leq 2.4$ eV there is an oscilatory pattern produced by interferences due to the multiple reflections in the heterostructure/substrate interface. This pattern is also reported in ER[8] and ellipsometric measurements[5] on strain-symmetrized Ge/Si superlattices. For $\hbar\omega \simeq 3.2-3.4$ eV the spectrashow an intense structure, easily identified with the $E_1 - E_0'$ complex of bulk Si[19]. Finally, in the region $\hbar\omega = 2.4 - 3.1$ eV the spectra contain peaks related to the Ge/Si heterostructures.

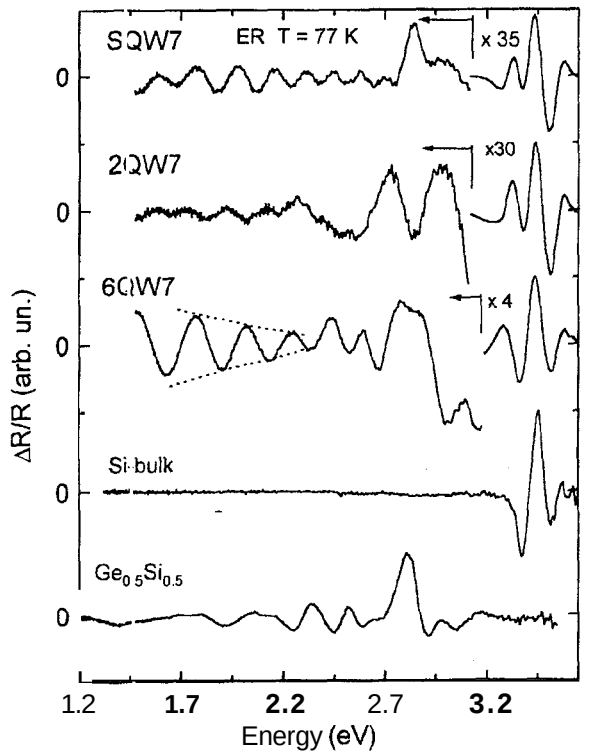

Figure 2: Electroreflectance spectra of the Ge quantum wells grown on Si(OO1), bulk Si and the $Ge_{0.5}Si_{0.5}$ alloy. Tlie dotted lines in tlie spectrum of tlie 6QW7 are meant as a guide to tlie interference pattern.

Fig. 3 shows the best fit (continuous lines) to the experimental data (open circles) in the spectral region $\hbar\omega \sim 2.4 - 3.1$ eV. The individual line shapes composing the fit ar: shown below each spectra. Tlie arrows, labeled by capital letters, indicate the transition energies obtained by tlie fitting procedure. Tlie results from this fit and tlie assignment given to pealis A - D in Fig. 3 are listed in Table III. In addition to the interference pattern, the spectrum of tlie SQW7 shows only one structure located at 2.83 eV (peak A in Fig. 3). Since tlie bulli Si does not have any structure in this spectral range, we conclude tliat this transition comes from tlie Ge layer. This line has two possible origins: tlie E_0-like or the E_1-like transition from the Ge layer. The ER spectra of the Ge/Si superlattices show that the E_1-lilíe transitions are much stronger than tlie E_0 ones[8]. Hence, we identify peak A with the E_1-like transition of the Ge layer. This interpretation is suported hy the ellipsometric and resonant Raman scattering results of Tsang et al.[9], who observed an E_1-like transition in samples with Ge layers as thin as 7 Å. Peak A in the spectrum of the SQW7 is shifted to higher energies (490 meV) in comparison with the corresponding transition in the strained bulli Ge[20]. Qualitatively, this shift can be accounted for by quantum confinement effects. However, an infinite quantum well calculation of the confinement energy greatly overestimates this shift. Tlie spectrum of the 2QW7 in the spectral range $\hbar\omega \sim 2.6 - 3.0$ eV shows two structures (labeled A aiid B in Fig. 3) with almost the same intensities. Based on similar arguments as those for the sample SQW7, we assign the peaks A and B to E_1-like transitions of the 2QW7. The most striking change in the ER spectra when we go from the SQW7 to the 2QW7 is the splitting of the E_1-like transitions. This splitting suggests that the two peaks in the 2QW7 spectrum may be associated with transitions between symmetric and antisymmetric states in a double quantum well. This assignment, although not corroborated by additional evidence, is consistent with the overall explanation of the E_1-like structures in these samples, as we shall see next. Finally, the spectrum of the 6QW7 (lower curve in Fig. 3) is qualitatively different from those discussed above. The appearance of four structures suggests that tlie spectrum of the sample 6QW7 is similar to that for a real Ge_5Si_5 superlattice (five monolayers of each constituent repeated inany times)[8]. The calculated band structure for a infinte strain-syminetrized Ge_5Si_5 superlattice [4] predicts the existence of four E_1-like critical points. The ER spectra for a Ge_5Si_5 sample with —150 repetitions is compatible with this prediction[8]. Also, differences in the strain profile is expected to change slightly the transition energy of each critical point, not altering the number of critica1 points. Therefore, we assign the structures A, B, C and D present in spectrum of sample 6QW7 to the E_1^a, E_1^b, E_1^c and E_1^d transitions predicted by the theorical calculation.

In Fig. 4 we show the experimental energy of the E_1-like transitions for the samples SQW7, 2QW7 and 6QW7 as a function of the number of Ge layers (N). This Figure also shows the corresponding transition energies for a strain-symmetrized Ge_5Si_5 superlattice,

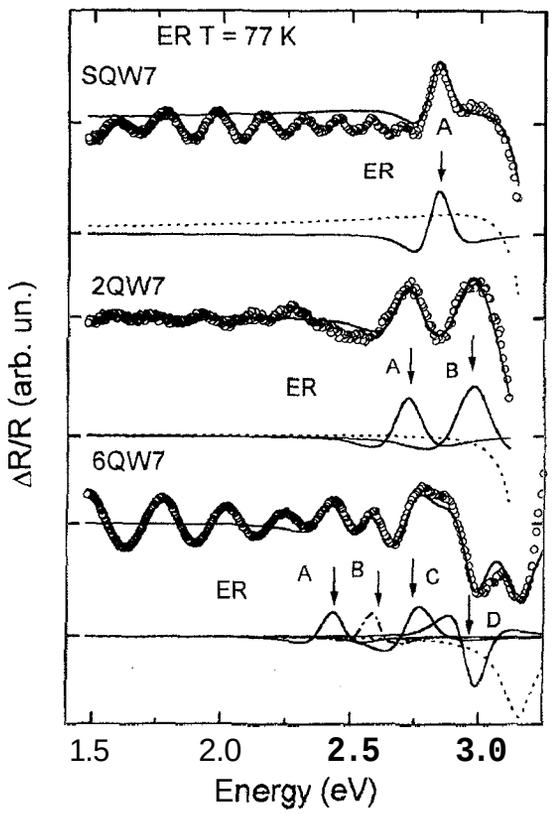

Figure 3: Fittings (continuous lines) of the electroreflectance spectra foi the samples SQW7, 2QW7 and 6QW7. The arrows indicate tlie transition energies obtained by tlie fitting procedure. The dotted lines are the functions fitted to the low energy side of the $E_1 - E_0'$ bulk-Si complex.

Table III - Transition energies (TE) and assignment of tlie E_1-like transitions observed in the electroreflectance spectra of thin Ge/Si quantum wells.

Sample	Experimental ER (77K) TE (eV)	Assignment
SQW7	2.83 A	E_1
2QW7	2.72 A	E_1^+
	2.98 B	E_1^-
6QW7	2.43 A	E_1^a
	2.59 B	E_1^b
	2.74 C	E_1^c
	2.97 D	E_1^d

taken from Ref. [8]. The arrows at the right side indicate thc position of the relevant electronic transitions in bulk Ge (compressed) and bullí Si (not strained). Notice in Fig. 4 the rcasonable agreement between the transition energies for tlie E_1-like structures in the sample 6QW7 and a real Ge_5Si_5 superlattice. This agreement is particularly good if we consider that the two samples have different strain profiles.

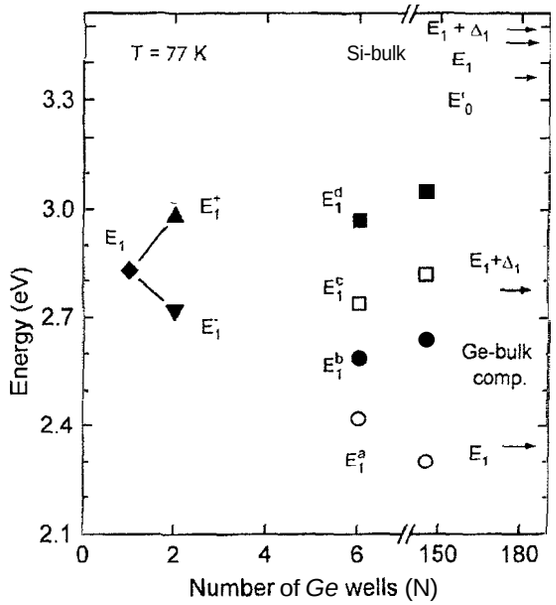

Figure 4: Dependeuce of the E_1-like transition energies with tlie number of tlie Ge quantum wells (N). The data for N = 145 were taken from Ref. [8]. Kotice the break in the horizontal scale. The arrows at tlie right side indicate the position of the relevant electronic transitions in biilk-Ge (compressed) and bulk-Si (not strained).

Fig. 4, together with the results for the thick Ge/Ge_xSi_{1-x} sainples (see Table II) suggest the following picture of the E_1-like transitions in the Ge/Si system. For a single layer (or a single quantum well) of Ge tlie electronic states responsible for the E_1-like transition suffer quantum confinement effects, shifting the corresponding structure in the optical spectra to higher energies (the shift is negligible for Ge layers —250 Å thick). Also, quantum confinement effects seems to explain the E_1-like transitions in superlattices with thick (—100 Å) Ge layers. The concept of double quantum well and states symmetric and antisymmetric qualitatively explain the spectral features observed in a sample containing two layers of Ge separated by one layer of Si (each layer —7 Å thick). As the number of QW's

increases and the sample evolves into a Ge_nSi_m superlattice, zone folding effects begin to dominate this region of the spectrum, resulting in a multiplicity of E_1 structures, as explained in Ref. [8]. Within these superlattices, as the layer thickness increases, this E_1-like multiplet resolve into two sets: Ge-lilíe and Si-like E_1, $E_1 + \Delta_1$ structures. Finally, once tliese Ge- and Si-lilre structures are built, quantum confinement concepts can be again qualitatively applied.

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