Structurally Induced Optical Transitions in Ge-Si Superlattices

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Using electroreflectance spectroscopy, we have observed new optical transitions near 0.76, 1.25, and 2.31 eV in an ordered strained-layer Ge-Si superlattice. The possible origins of these transitions are discussed in terms of modification of the electronic band structure by the sample structure.

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Recent developments in silicon molecular-beam epitaxy (MBE) technology have produced dramatic advances in the degree of control and quality of Si and strained Ge_xSi_{1-x} films grown epitaxially on (100) Si.[1-6] Significantly, it has been shown experimentally[7] that the quantum-mechanical formalism for treating the effects of strain on the energy band structure of semiconductors can be extended without modification to treat these new strained-layer structures.

In this Letter we report new electronic energy levels in ordered Ge/Si multilayer structures which are a direct consequence of the individual layer thicknesses which are comparable to the unit cell dimensions. The new levels give rise to three previously unobserved direct optical transitions between 0.7 and 2.4 eV. These multilayer samples are qualitatively different from larger-period (>20 Å) superlattice structures which have been proposed as possibly displaying a quasidirect transition via specific zone-folding schemes related to the bulk Si band structure.[8,9] The new artificially ordered structures discussed in this paper may be best viewed as new semiconducting materials. Our samples were grown in a specially designed MBE system described previously,[4] which allows the precise deposition of layered films under UHV conditions (base pressure $<2\times10^{-11}$ Torr, growth pressure $\sim10^{-10}$ Torr). The substrates were cut from commercial (100) Si wafers and were cleaned by the Shiraki procedure.[3] Prior to growth of the layered structure, a 1000-Å epilayer was deposited (deposition rate 1–5 Å/sec) at substrate temperatures of 600–700 °C. The temperature was then lowered to 480–530 °C for deposition of the Ge-Si multilayers. Finally, portions of the layered films intended for structural studies were capped with a ~140-Å-thick Si layer. The cap thickness over the remainder of the sample, used for electroreflectance measurements, was ~1000 Å. The structure of all films was analyzed *in situ* by reflection high-energy electron diffraction, and, following the deposition, by transmission electron microscopy and Rutherford backscattering and channeling measurements. The reflection high-energy electron diffraction patterns were typically taken after the completion of each layer of a given composition to ensure planar film growth and absence of significant interdiffusion between the layers.

There are upper limits on the number of strained-layer regions which can be accommodated elastically on a given substrate.[10] For the case of germanium grown epitaxially on silicon, the maximum number of germanium monolayers which can be deposited is six.[4] The thickness of the Ge region is calculated from elastic theory, recalling that the in-plane lattice constant $a_{\parallel}$ is forced to be the same as that for Si. The perpendicular lattice parameter of Ge is given by $a_{\perp}=a_0(\mathrm{Ge})[1+k\varepsilon]$, where $k=-2S_{12}/(S_{11}+S_{12})$ and ε is the in-plane lattice mismatch.

Electroreflectance spectroscopy is the technique of choice for measurement of the energies of direct optical transitions between the valence and conduction bands in semiconductors[11-13] because it offers an enhancement of 10^4 over the sensitivity of a simple absorption or luminescence measurement, and it is sensitive only to direct optical gaps. Equally important, electroreflectance measures all the band-to-band optical transitions, whereas absorption or photoluminescence measures only the lowest energy transition. Visible and uv spectra were taken with a Xe arc lamp and S-20 photomultiplier, while infrared spectra were taken with a tungsten source and a cooled PbS photoconductive detector. The data are corrected for the spectral response of the source, monochromator, and optics. Electric field modulation of the sample dielectric constant was applied with a 50-Å semitransparent evaporated Ni Schottky barrier applied to the Si cap layer. Typical modulation voltages were 2–4 V peak to peak at a frequency of 300 Hz.

In Fig. 1, we show schematically an ordered sequence of four monolayers of Ge and four monolayers of Si (4×4 superlattice) repeated five times. The superlattice structure is confined on both sides by a thick region of

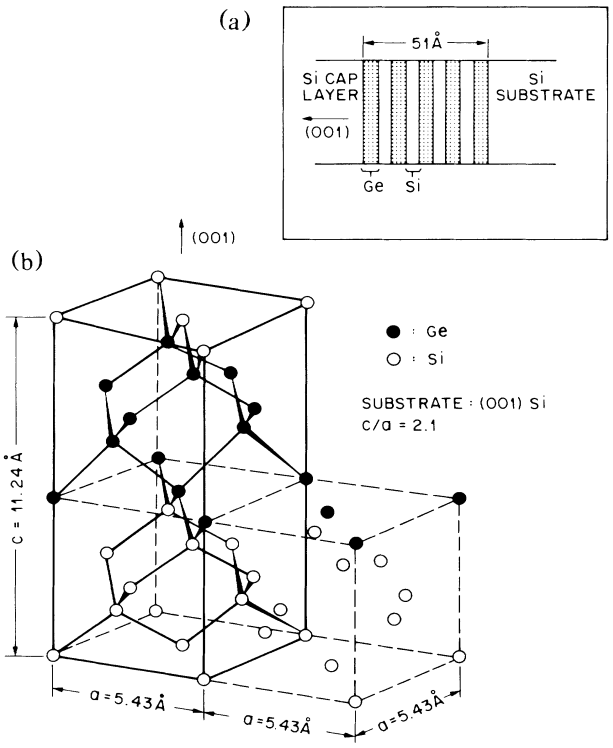

FIG. 1. (a) Alternating four-monolayer sequence of Ge and Si. The boundaries of the superlattice region are defined by the outermost Ge layers and the structure has a total thickness of ~51 Å. (b) Atomic arrangements of the alternating four-monolayer sequence. The new unit cell of the Ge-Si structure is tetragonal.

Si. The effective average composition of the well is approximately $Ge_{0.55}Si_{0.45}$. A more precise determination of the effective composition requires analysis of the wave-function penetration in the Si barrier regions. The total width of this structure is determined to be 51 Å.

Reflection high-energy electron diffraction patterns from this particular sample are qualitatively different, depending on whether they were taken from the top of the Ge or Si sublayers. This result indicates that the sublayers within the superlattice are continuous, and that the film growth indeed proceeds in a planar mode. Moreover, both Rutherford backscattering and transmission electron microscopy lattice imaging indicate excellent crystallinity and strain levels consistent with the pseudomorphic growth. Rutherford backscattering measurement of the total Ge coverage of 20.1 monolayers is also well within the experimental error of the nominal total Ge thickness of 20.0 monolayers.

The electroreflectance spectrum for this sample is displayed in Fig. 2. It is rich in structure and shows components from both the Si overlayer and the Ge-Si superlattice. The 1000-Å cap layer of Si may be considered to be transparent below 3 eV, so that the observed structure below 3 eV originates from optical transitions in the 51-Å superlattice region. The experimentally observed transition energies are determined by fitting the theoretical line-shape function to the data[9]:

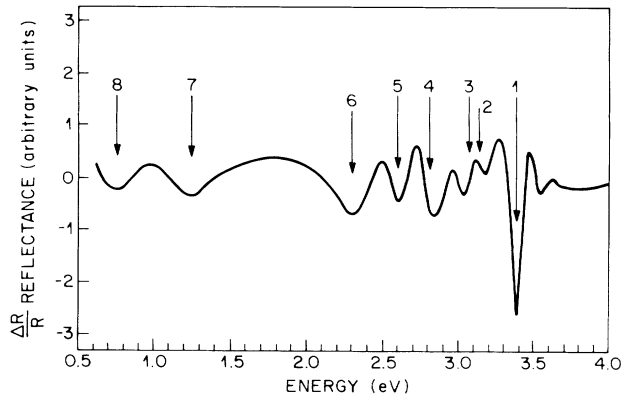

FIG. 2. Direct experimental recording of the electroreflectance spectrum of the Ge-Si/Si alternating four-monolayer structure from 0.6 to 4.0 eV. The spectrum shows transitions occurring both in Si and in the Ge-Si ordered structure. The two lowest-energy Si transitions occur at 3.37 eV, E_1, and 3.13 eV, E_0'. All of the structure at lower energies comes from the 51-Å alternating four-monolayer structure. New transitions are resolved at 0.76, 1.25, and 2.31 eV.

$$\delta R/R = A\Gamma^{-n}e^{i\theta}(E - E_g + i\Gamma)^n. \quad (1)$$

Energy, amplitude, phase, and linewidth (Γ) are adjusted for each transition by a convergence routine developed by Shen and Parayanthal.[14]

The measured transition energies are given in column (a) of Table I and indicated in Fig. 2. The transitions at 3.37 and 3.13 eV are assigned to the E_1 and E_0' gaps, respectively, of Si. They are a common feature in all of our spectra, coming from the 1000-Å cap layer. In column (b) of Table I we show the transitions expected from a pseudorandom alloy of effective composition $Ge_{0.55}Si_{0.45}$. The agreement between theory and experiment in the energy range of 2.4–3.0 eV is not close, quite different from our previous results on Ge_xSi_{1-x} alloy quantum wells of a similar composition and dimension.[7] At energies less than 2.4 eV, moreover, we observe three structures at 0.76, 1.25, and 2.31 eV. The electroreflectance spectrum of a $Ge_{0.55}Si_{0.45}$ alloy should show no transitions below 2.4 eV. The results shown in Fig. 2 present strong evidence for the notion that the 4×4 Ge-Si superlattice has a basic energy-level structure quite different from that of an alloy quantum well of the same thickness and average composition. The level structure is also different from that of Ge in a significant way. The lowest-energy optical transition in pure Ge occurs at 0.8 eV. Compressive strain and quantum confinement by Si would tend to increase this energy. Yet the measured transition at 0.76 eV lies below 0.8 eV.

Our experiments show the existence of new optical

TABLE I. Measured and theoretical transition energies for Ge-Si quantum-well structures. In column (a) the measured transition energies for the five-period Ge-Si superlattice structure are given. A measured amplitude of 7×10^{-5} for $\Delta R/R$ is considered strong; less than 2×10^{-5} is considered weak. In column (b) are the expected transition energies for a strained, single-quantum well of composition $Ge_{0.55}Si_{0.45}$ which is close to the effective average composition of the 4×4 monolayer samples whose transitions are given in column (a).

	(a) Measured transitions for a five-period 4×4 monolayer Ge-Si superlattice			(b) Expected transitions for a strained, 51-Å $Ge_{0.55}Si_{0.45}$ alloy quantum well		
Transition number and identification	Energy (eV)	Linewidth (eV)	Amplitude $\Delta R/R$	Identification	Energy (eV)	Relative strength
1. Si: E_1	3.37	0.13	7×10^{-5}	Si: E_1	3.37	Strong
2. Si: E_0'	3.13	0.15	2×10^{-5}	Si: E_0'	3.10	Weak
3. Ge-Si superlattice	3.06	0.13	1×10^{-5}			
				Ge-Si alloy: $E_1+\Delta_1$	3.035	Weak
4. Ge-Si superlattice	2.81	0.17	7×10^{-5}			
				Ge-Si alloy: $E_0+\Delta_0$	2.80	Weak
				Ge-Si alloy: E_1	2.645	Strong
				Ge-Si alloy: $E_0(2)$	2.59	Medium
5. Ge-Si superlattice	2.58	0.19	7×10^{-5}			
				Ge-Si alloy: $E_0(1)$	2.415	Medium
6. Ge-Si superlattice	2.31	0.24	2×10^{-4}			
7. Ge-Si superlattice	1.25	0.26	5×10^{-5}			
8. Ge-Si superlattice	0.76	0.27	3×10^{-5}			

transitions in the 1.0–2.0-μm range in synthetic, ordered Si-Ge 4×4 superlattices. The origin of these transitions is either extrinsic, that is, due to the presence of a well-defined impurity, or intrinsic, the result of a modification of the electronic band structure induced by the Si-Ge region. We will now consider both of these possibilities.

A well-known example of a quasidirect optical transition created by doping with impurities is the case of GaP:N.[15] If an impurity is the cause of the observed transitions, it could be present either in the Si-Ge superlattice region, or in the Si boundary layers. The band structure of Si, however, makes the probability of such a conjecture unlikely. In addition, such an effect has never been seen in other investigations of bulk Si. We conclude that the new transitions are due to the superlattice structure.

In addition to the 4×4 superlattice, we have investigated the electroreflectance of some closely related structures. These are all single quantum wells of 50-Å width containing (a) alternating single monolayers of Si and Ge, (b) alternating two-monolayers of Si and Ge, and (c) alternating six-monolayers of Si and Ge. All of these samples were grown in the same MBE growth chamber and permit clear resolution of optical transitions originating in the Ge-Si ordered quantum-well region, as well as those coming from the Si cap layer. Each of the samples displays a unique set of transitions that can be related qualitatively to those seen in its neighbors. However, none of these samples shows similar optical activity in the 1.0- to 2.0-μm spectral regime. To generate an effect of the magnitude seen here would require an impurity concentration which is a substantial fraction of the atomic density. This hypothesis appears unlikely because the 4×4 superlattice sample was grown in an MBE reactor with an airlock on a part of the same substrate wafer which was used to grow samples both immediately before and afterwards [samples (a) and (c) mentioned above].

The most apparent structural modification which the 4×4 structure manifests is the loss of cubic symmetry. The unit cell is tetragonal with a c/a ratio ~2.1. In addition, because the Ge part of the unit cell is larger than the Si part, the unit cell is not centrosymmetric. These features suggest that a virtual-crystal approximation of the band structure may not be appropriate. A second important structural feature that we have introduced in these superlattices is the presence of strain. In earlier work on thick, strained, pseudorandom alloys of Ge_xSi_{1-x}, we demonstrated that the effects of strain could be accounted for quantitatively by use of established theory and the virtual-crystal approximation. In the present case, only the Ge part of the unit cell is strained. The modulated strain has the period of the superlattice, but it is asymmetric containing significant higher-order Fourier components. A third important structural modification is the variation inside the unit cell of the atomic potential which is identical in period and asymmetry to the strain potential.

The differences in the electronic energy spectra between the Ge-Si 4×4 monolayer structure and random alloys of similar average composition may be perhaps more simply understood by our treating the ordered

structure as a new semiconducting material rather than as a perturbation of some "virtual-crystal" siliconlike band structure.[16] Following our experimental results, People and Jackson[17] have modeled the 4×4 monolayer structure using the bulk electronic energy levels of Si and Ge, and have treated the superlattice in the Kronig-Penney approximation. This approach shows that the consequence of the tetragonal unit cell is the creation of new, delocalized energy bands in the superlattice region. Recalling the work of Ishibashi *et al.*,[18] good quantitative agreement between experiment and theory for superlattices whose periods are on the order of a unit cell may require a more detailed calculation.[19,20] The intentional ordering of the layered Ge-Si structure has produced a new phase and the measured differences in the electronic spectrum relative to the random alloy are the consequence of its atomic structure.

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