Dielectric response of thick low dislocation-density Ge epilayers grown on (001) Si

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Spectroscopic ellipsometry was used to measure the dielectric functions of epitaxial and bulk Ge at photon energies from 1.5 to 5.2 eV. The epitaxial Ge was grown at 400 °C by molecular beam epitaxy on (001) Si substrates. The optical response and the interband critical-point parameters of Ge on Si were found to be indistinguishable from that of bulk single crystal Ge, indicating high optical quality. Dislocation density measurements using an iodine etch verified low surface defect densities. We conclude that epitaxial Ge grown on Si at relatively low temperatures is suitable for optical device applications. © *1996 American Institute of Physics.* [S0003-6951(96)04352-5]

Because of the large lattice mismatch ($\sim$4%) between Si and Ge and their different thermal expansion coefficients, it is difficult to produce high-quality heteroepitaxial Ge films on Si substrates. On the other hand, the growth of low defect-density Ge[1,2] and $Si_{1-x-y}Ge_xC_y$ alloys[3–5] on Si (001) is of great technological interest to modify transport[3,4,6] and carrier confinement in Si-based devices and to integrate Ge-based optoelectronics (e.g., infrared detectors) with well-developed Si integrated circuit technology. Also, because of the small lattice mismatch of GaAs and Ge, it becomes feasible to integrate III/V devices with Si integrated circuit technology by growing a Ge virtual substrate on Si, followed by GaAs/Ge epilayers.[7]

The initial growth of Ge on Si (001) can be described[8] as Stranski-Krastanow: The first three to six monolayers grow layer-by-layer. After about 10 to 15 Å , islands start to form. Island formation can be suppressed by a surfactant (As), extending the layer-by-layer growth.[8] Because of the local elastic deformation of near-surface layers in the substrate, the onset of dislocations is delayed[8] until the islands have grown to far in excess (500 Å) of the equilibrium critical thickness (10 Å).

This work deals with much thicker layers, where the strain is relieved by misfit dislocations. These dislocations can be studied using plan-view transmission electron microscopy (TEM).[2,4,9] They usually climb to the surface where they deteriorate the transport properties of active device layers (such as a heterojunction bipolar transistor[4]). Using thick compositionally graded layers,[10] it is possible to grow relaxed $Si_{1-x}Ge_x$ layers ($x\sim0.3$) with low threading dislocation densities.

Malta *et al.*[2] have shown that dislocations in Ge on Si can be confined to the epilayer/substrate interface (extending up to 0.7 μm from the interface) by growing with substrate temperatures near the melting point of Ge (937 °C). For samples with a thickness of 2.5 μm, the residual strain was $e\sim2.5\times10^{-3}$ and the etch pit density (EPD), a measure for the dislocation density at the surface, was about 2×10^5 cm^{-2}. Apparently, interfacial Ge melts and subsequently alloys with the Si substrate. Growth at intermediate temperatures (700 °C) does not confine the dislocations, resulting in a higher EPD.

The purpose of this work is to show that slow growth at low temperatures can yield thick Ge films on Si with low surface dislocation densities. This leads to the surprising result that the dielectric function (DF) of Ge on Si is indistinguishable from that of a bulk Ge sample. (The correlation between the DF and of dislocations in group-IV alloys was discussed by Lange *et al.*[11] Thick relaxed $Si_{1-x-y}Ge_xCy$ layers with many dislocations have very broad and weak E_1 peaks, whereas pseudomorphic layers with a low dislocation density have strong and narrow E_1 peaks.)

The Ge layers used in this study were grown[12] by molecular beam epitaxy (MBE). The Ge molecular beam was produced by thermal evaporation from a solid source of zone-refined polycrystalline Ge in a pyrolytic boron nitride crucible. To minimize contamination from the crucible, the cell temperature was kept below 1380 °C. At the cell temperature of 1325 °C used in this experiment, the Ge growth rate was 0.11 μm/h (0.3 Å/s).

Substrates were (001) oriented, 75 mm diameter silicon wafers prepared by degreasing, oxidizing in a solution of H_2O:H_2O_2:HCl (5:3:3), and dipping in HF:H_2O (1:10).[12] The substrates were desorbed at 250 °C in the MBE chamber just prior to growth. The Ge layers were grown at a substrate temperature of 400 °C; they were between 0.3 and 1.1 μm thick (measured by a Dektak) and appeared mirror smooth after growth. Since the mobility of dislocations is limited at lower temperatures[9] and the thermal expansion coefficient of Ge (6×10^{-6}) is about a factor of two larger than that of Si, it is not surprising that growth at low temperatures resulted in high quality layers.

Well resolved reciprocal lattice rods of the substrate were observed by *in situ* reflection high energy electron diffraction (RHEED). After about 10 Å of growth, the lattice rods were less well resolved, but distinct rods still remained. The RHEED pattern gradually improved as the epilayer became thicker. For sample SGC99, a 0.75 μm thick layer of

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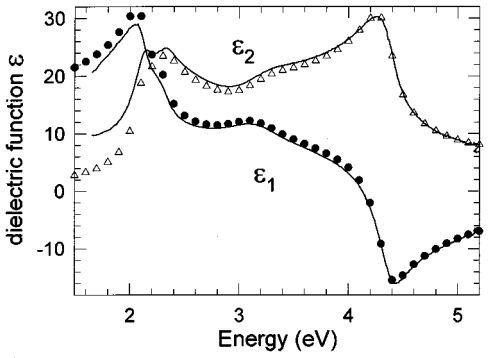

FIG. 1. Lines: Real (ϵ_1) and imaginary (ϵ_2) part of the dielectric function of SGC99 (0.75 μm Ge on Si), corrected for a 10 Å native oxide layer. The data of Ref. 13 for bulk Ge $\langle 111 \rangle$ are shown for comparison (●),(△).

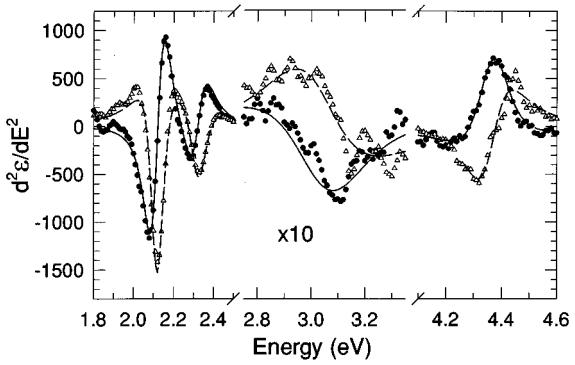

FIG. 2. Numerically calculated second derivatives of ϵ_1 (●) and ϵ_2 (△) for Ge on Si. The lines give the best fit to Eq. (1) with the parameters in Table I. The E_0' region (2.75–3.35 eV) was multiplied by 10 to make it visible on this scale.

Ge on Si grown at 400 °C, the RHEED pattern at the completion of growth was similar in features and intensity to that of commercially available Ge substrates. The RHEED suggested that island formation was partially suppressed at low growth temperatures, and that as growth proceeds islands may coalesce to form single crystal Ge with few defects. We speculate that the low growth rates employed here encourage the formation of reduced defect single crystal Ge over multicrystalline Ge, but further study will be necessary to confirm this.

To find the surface dislocation densities, we used an iodine etch[2] $HF:HNO_3:CH_3COOH:I$ (20 ml:40 ml:44 ml:120 mg) for 1 s to measure the etch pit density (EPD) of the Ge layers. For SGC99, it appeared constant and uniform across the entire area and was consistent between samples and etch times. The average EPD was 4×10^4 cm^{-2}, a factor of five lower than the results of Malta *et al.*[2] The EPDs of thinner layers (<0.3 μm) and those of samples grown at higher temperatures (>500 °C) could not be determined, since the EPD was not uniform or the complete Ge layer was removed by the etch. The EPD of bulk Ge was less than 10^4 cm^{-2}, consistent with data supplied by Eagle Picher. The pit shapes for SGC99 and bulk Ge differed. For the bulk Ge, most pits were circular, about 1 μm in diameter. For SGC99, the pits were squares, approximately $1-3$ μm on each side.

After growth, the dielectric functions (DFs) ϵ in the 1.5 to 5.5 eV photon-energy range were measured *ex situ* with a spectroscopic ellipsometer.[13] The spectra were corrected for a native oxide layer. The thickness of the oxide was determined by matching ϵ_2 at its peak near 4.2 eV with the data of Ref. 13. The lines in Fig. 1 show the real (ϵ_1) and imaginary (ϵ_2) parts of ϵ for sample SGC99, assuming an oxide thickness of 10 Å. Other Ge epilayers grown on Si at the same temperature (not shown in the figure) had similar ϵ. For comparison, we also measured ϵ for a commercial bulk Ge $\langle 001 \rangle$ sample (Eagle Picher). The DF of SGC99 and that of the bulk sample were indistinguishable, except below 1.8 eV, where the accuracy of our instrument decreases. In Fig. 1 we also show the data of Ref. 13 (●), (△) for bulk $\langle 111 \rangle$ Ge. The agreement is good, except for ϵ_2 in the range below 2 eV. (Similar discrepancies were found in Ref. 16.) The DF of SGC99 resembles that of bulk Ge much more than that of thin Ge films enclosed between Si barriers.[14,15]

The spectra show a double-peak structure above 2 eV (E_1, $E_1+\Delta_1$), a shoulder near 3 eV (E_0'), and a third peak near 4.2 eV (E_2). These peaks are interband critical points (CPs) arising from direct band-to-band transitions at various regions in the Brillouin zone.[17] For a further analysis of these CPs, we calculate numerically the second derivative of ϵ with respect to photon energy (shown by the symbols in Fig. 2) and perform a line shape analysis. Following Viña *et al.*,[17] we describe the CPs using a mixture of a 2D minimum and a saddle point represented by

$$\epsilon(\omega) = C - A \ \ln(\hbar\omega - E_g - i\Gamma)\exp(i\phi), \tag{1}$$

where $\hbar\omega$ is the photon energy, E_g the energy of the CP, Γ its broadening, A its amplitude (oscillator strength), and ϕ the phase angle describing the amount of mixing. The parameters obtained from the line shape analysis are given in Table I in comparison with parameters of bulk samples from Viña and co-workers.[17] First, we note that our bulk parameters are, within the error bars, identical to those of Ref. 17 with one exception: Viña and co-workers used a fixed spin-orbit splitting $\Delta_1=187$ meV determined from low-temperature measurements. In our analysis, we treated Δ_1 as

TABLE I. Critical point (CP) parameters for bulk Ge and Ge on Si: amplitude (A), energy (E), broadening (Γ), and excitonic phase (Φ) [see Eq. (1)].

	A (1)	E (eV)	Γ (eV)	Φ (deg)
	Bulk Ge (this work)			
E_1	5.5(3)	2.114(2)	0.058(2)	86(4)
$E_1+\Delta_1$	4.1(6)	2.314(2)	0.076(6)	same
E_0'	3.2(6)	3.05(2)	0.20(2)	−29(12)
E_2	8(1)	4.37(1)	0.107(1)	−193(11)
	Bulk Ge (from Ref. 17)			
E_1		2.111(3)	0.06(1)	71(4)
$E_1+\Delta_1$		2.298(3)	0.07(2)	same
E_0'		3.11		
E_2		4.368(4)	0.109(9)	
	Ge on Si (SGC99, this work)			
E_1	6.2(4)	2.116(2)	0.063(2)	84(4)
$E_1+\Delta_1$	3.7(7)	2.322(2)	0.076(6)	same
E_0'	3.3(5)	3.05(2)	0.21(2)	−29(9)
E_2	8(1)	4.37(1)	0.109(6)	−196(6)

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a free parameter (since it is a measure for the strain in the sample) and found $\Delta_1 = 200$ meV for bulk Ge.

The CP parameters for sample SGC99 are similar to those of bulk Ge. Most importantly, the broadenings, related to defects, are essentially the same. Therefore, the scattering of electrons and holes in SGC99 was mostly due to intrinsic mechanisms such as electron-phonon interactions, not to sample imperfections such as dislocations, grain boundaries, impurities, etc. The spin-orbit splitting parameter for SGC99 was $\Delta_1 = 206$ meV, about 3% larger than in bulk Ge. Using the small-shear approximation described in Ref. 11, we found upper bounds for the hydrostatic and (001) shear strains (e_H and e_S) in SGC99. Since E_1 is the same for bulk Ge and SGC99, we conclude that the hydrostatic and (001) shear shifts for E_1 (ΔE_H and ΔE_S) are approximately equal. Since (the apparent splitting) Δ_1 changes by no more than 6 meV, ΔE_H and ΔE_S are about 3 meV each. We conclude that $|e_H| < 0.03\%$ and $|e_S| < 0.1\%$. Since $\Delta E_H \propto e_H$, whereas $\Delta E_S \propto e_S^2$ our estimate for e_S is less stringent than that for e_H. Using x-ray diffraction, the in-plane strain perpendicular to the growth axis ($e_\perp = e_H - e_S$) was determined for similar samples[5] to be below 0.03%, about three times smaller than the upper limit found here. Although our accuracy is limited, we find less than 3% of the strain expected for a pseudomorphic layer (equal to the lattice mismatch of 0.04). The accuracy of our strain analysis could be improved by measuring ϵ below 100 K (where the broadenings are smaller leading to more accurate CP energies).

In conclusion, we have found that the optical constants (refractive index and absorption coefficient) and their derivatives, related to band structure and transport parameters (CP energies and broadenings), of thick Ge layers on Si are virtually identical to those of bulk Ge. These results are in agreement with RHEED and EPD counts. Therefore, we should expect that electronic and optoelectronic devices fabricated using Ge on Si should have similar (if not superior) characteristics compared to bulk Ge-based devices.

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