Spectroscopic Ellipsometry of E_1-Like Transitions in Nanometer-Thickness Ge Layers

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Spectroscopic ellipsometry of epitaxial Ge in bulk Si(100) has been used to study the effects of strain and layer thickness on the Ge-derived E_1 transitions. Although a 4-Å-Ge layer exhibits no Ge-like E_1 structure, localized E_1-like transitions are observed for 7-Å-Ge layers showing the E_1 transition is a robust probe of the Ge-like behavior in ultrathin layers.

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The ability to fabricate structures composed of subnanometer-thickness layers of group-IV semiconductors such as Ge has prompted considerable interest about electronic states in ultrathin layers and superlattices of these materials. The optical properties of such systems have been the object of considerable recent study.[1-3] Spectrocopic ellipsometry has been widely employed to describe multilayer systems,[4-7] using known dielectric response functions to model the experimentally derived $\epsilon_1(\omega)+i\epsilon_2(\omega)$. The effective dielectric functions for quantum wells[8,9] and for superlattices[9] have also been determined by this technique, which offers the most direct and accurate approach to obtaining dielectric functions from such thin layers. In this paper, we show how spectroscopic ellipsometry can be used to derive $\epsilon(\omega)$ for a single, subnanometer-thickness layer grown on an optically dense, large-index-of-refraction substrate. We describe the behavior of the Ge-derived E_1 and $E_1+\Delta$ gaps ($E_1-E_1+\Delta$) at nanometer layer thicknesses and consider the effects of epitaxial growth and finite layer thickness on these transitions. The Ge character of these transitions was also verified by resonant Raman scattering.

The dominant contributions to the dielectric response of bulk Ge for photon energies below 3 eV stem from direct transitions across the $E_1-E_1+\Delta$ gaps along the (111) direction of the Brillouin zone; we show that similar transitions can be identified by spectroscopic ellipsometry in Ge layers only 7 Å thick. For such thin epitaxial layers, we expect significant changes in the electronic structure of the thin Ge layer (as compared with bulk Ge) due to the strain of pseudomorphic growth, alloying, and the confinement of the electronic states in the quantum well. Yet the E_1-like transitions remain identifiable as long as there is multilayer Ge bonding.

The samples studied were all grown by molecular-beam epitaxy[10,11] on Si(100) substrates. Ge layers were grown on Si buffer layers and covered by Si(100) overlayers. Growth temperatures were held below 350 °C. The samples were measured as received, and were covered by a thin native oxide. An electron micrograph of the 17-Å-Ge layer in Si(100) is shown in Fig. 1. The Ge layer is smooth and continuous with no islanding even though the layer thickness exceeds the critical thickness, as determined by considerations of mechanical equilibrium,[12] during growth. More detailed examination of this micrograph shows that the growth is pseudomorphic with no dislocations at the interfaces. Thinner Ge layers were below the critical thickness, and all Raman spectra were consistent with the presence of continuous strained layers.

The ellipsometric data were obtained using a custom-made system described previously.[4,5] The system was operated for photon energies between 1.4 and 5.4 eV. The resonant Raman data were obtained using a multichannel Raman-scattering system which has been previously described.[10] The Raman spectra were excited at photon energies between 1.9 and 2.7 eV.

In Fig. 2, we show $\epsilon_1(\omega)+i\epsilon_2(\omega)$ experimentally obtained for our 4-, 7-, and 17-Å-thick Ge layers. Also shown (solid line) are the ellipsometric results of Aspnes[14] for $\epsilon(\omega)$ of bulk Ge. The thin-layer results in Fig. 2 were generated in a multistep process. Initially, the bulk dielectric functions[13-15] of Si, Ge, SiO_2, and amorphous Si were used to model the experimentally obtained values for the ellipsometric parameters, based on the sample geometry shown schematically in Fig. 2. The fit obtained from the bulk dielectric functions to the experimentally obtained ellipsometric response was optimized[4] over the full spectral range using the thicknesses and compositions of the layers shown in Fig. 2 as parameters. For several of our samples, Rutherford back-

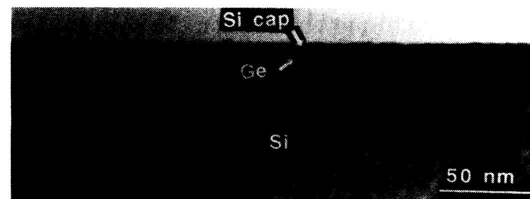

FIG. 1. An electron micrograph of a 17-Å-Ge layer grown on Si(100) by MBE at 350 °C and covered by an Si(100) cap layer.

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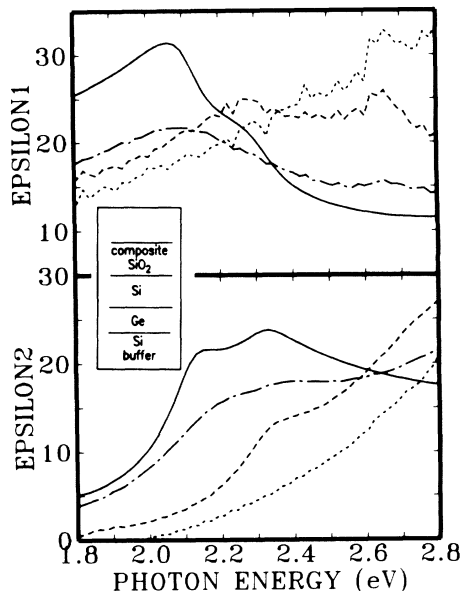

FIG. 2. The ellipsometrically derived values of $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ for a 17-Å (dot-dashed curve), a 7-Å (dashed curve), and a 4-Å (dotted curve) -Ge layer grown in Si(100) at temperatures below 350 °C. The bulk dielectric response of Ge is shown by the solid line. Inset: The laminar structure assumed in the extraction of these values from the data.

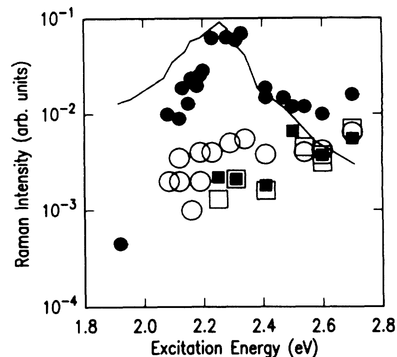

FIG. 3. The resonant-Raman profiles for the Ge-Ge Raman scattering from the two samples studied in Figs. 1 and 2. The solid line is the resonant profile of bulk Ge. The solid circles are resonant profile of the Ge line for the 7-Å layer while the open circles are the resonant profile of the Ge-Si line for this sample. The solid squares are the resonant profile of the Ge line for the 4-Å sample while the open squares are the resonant profile of the Ge-Si line for this sample.

scattering (RBS) provides a crosscheck for thicknesses determined by our method; in all cases, the discrepancy between the equivalent areal atom density from RBS and the ellipsometric analysis was < 15% or 1 Å. The spectroscopic and backscattering results on the 17-Å sample are consistent with the electron micrograph of this sample shown in Fig. 1.

The parameters obtained from this modeling were then used with the bulk $\epsilon(\omega)$'s of Si, SiO_2, and amorphous Si and the experimental results to derive an $\epsilon(\omega)$ for the Ge layer that fully accounts for the observed ellipsometric response. This is again done through a least-squares minimization of the error parameter, varying only the real and the imaginary parts of the dielectric function for this layer. In this approach all deviations from the model dielectric response are ascribed to the optical response of the single layer; the errors included in such measurements and models become magnified if ascribed to a layer so thin as to account for only a small portion of the overall optical response. The most severe impact of the substrate response on the derived Ge-layer response occurs for energies above 3.0 eV where there are strong Si resonances, which causes us to limit our ellipsometric results to energies below 3 eV.

We tested the sensitivity of these results to alterations in layer thickness and alternative models, including a physical mixture of pure Ge clusters embedded in a silicon matrix. The detailed spectral shape was insensitive to such details, although minor variations in relative intensity and small shifts (of order tens of meV) in spectral features were inferred.

In the spectral region shown in Fig. 2, the Ge-derived structure in the 7- and 17-Å layers can be compared to the $E_1-E_1+\Delta$ structure of bulk Ge. Bulklike structure in ϵ_1 and ϵ_2 is observed from the 17-Å-Ge layer. The intensity of the structure in the Ge layer is weaker than in the bulk. Two samples of this approximate thickness were measured, the other being about 15 Å thick. Calculating $d^2[\omega^2\epsilon(\omega)]/d\omega^2$ for these samples shows that the 17- (15-) Å film response stems from a pair of transitions at 2.13 and 2.33 eV (2.15 and 2.35) with damping Γ's of 90 to 140 meV, a relative amplitude ratio of 4.3:1 (2.3:1), and a phase Φ of 4.03 (4.11). The energies and phase are close to the bulk $E_1-E_1+\Delta$ values: energies of 2.12 and 2.32 eV, damping Γ of 0.075 eV, intensity ratio of 2:1, and phase of 3.93. The ellipsometrically obtained dielectric functions for the 7-Å-Ge layer in Fig. 2 show a single line at 2.32 eV. Γ is 127 meV for this transition and $\Phi=3.99$. The apparent structure near 2.6 eV which is seen in all of our spectra has been traced to the reference spectrum used for the Si layers in our calculations. No Ge-derived structure between 1.8 and 2.8 eV is observed from the 4-Å-Ge layer.

In Fig. 3, we show the resonant Raman profiles of our 4- and 7-Å-Ge layers for their Ge-Ge and Ge-Si Raman modes in these samples. The solid line is the $E_1-E_1+\Delta$ resonance for bulk Ge which also describes the resonant Raman profile of the 17-Å sample. The Raman spectrum of the Si-Ge system arises from localized or quasi-localized Si-Si, Ge-Ge, and Ge-Si modes so that resonant Raman scattering from these phonons measures the local electronic structure of the layers.[1] The Raman intensity of the Ge-Ge vibration shows a strong enhancement at 2.3 eV for the 7-Å sample. The intensity of this vibrational mode shows no enhancement for the 4-Å sample.

In contrast, the resonant Raman profile of the Ge-Si mode in the 7-Å sample shows only a very weak enhancement compared to the Ge-Ge mode at 2.3 eV. The agreement between the resonant Raman peaks and the peaks of the Ge-layer ϵ_2 in Fig. 2 confirms that our decomposition of the ellipsometric data provides an accurate measurement of the Ge-layer dielectric response for the 7- and 17-Å samples and shows that the same transitions are observed. Our failure to see a significant enhancement of the Ge-mode Raman-scattering intensity between 1.9 and 2.7 eV in the 4-Å-Ge layer is also consistent with the ellipsometric results which show no Ge-related structure in this energy range.

For narrow wells of Ge in Si, electronic structure near 2 eV can be attributed to strain- and confinement-shifted levels derived from electronic states responsible for either the bulk E_0 transitions or the $E_1-E_1+\Delta$ transitions or from completely new transitions.[1,16] The quantitative similarities between the transition strengths, spectral widths, phase shifts, and electron–Ge-LO-phonon coupling of the layer transitions and the bulk $E_1+E_1+\Delta$ transitions and their localized character are consistent with their derivation from the bulk-Ge $E_1-E_1+\Delta$ transitions are largely inconsistent with the parameters describing the bulk E_0 and E_2 gaps. In our ultrathin layers, the electronic transitions will be perturbed by their pseudomorphic growth on Si(100) and by the finite thickness of the layers themselves.

We expect that the 4-Å-Ge layer will not show bulklike Ge behavior. The Raman spectrum of this sample strongly resembles the Raman spectrum of the alloy rather than that of a thick Ge layer.[1] This is understandable since the Si-Ge interfaces are more than an atomic layer in thickness. The 4-Å-Ge layer is only three atomic layers in thickness so that intermixing of the Si and Ge atoms at the monolayer level will produce alloylike bonding for the Ge atoms in the layer with few Ge atoms bonded tetrahedrally to four other Ge atoms. Si-Ge alloys show a continuous evolution of the $E_1-E_1+\Delta$ structure from 2.2 eV in bulk Ge to 3.4 eV in bulk Si.[17] For $Ge_{0.5}Si_{0.5}$, E_1 is near 2.8 eV. The strain of pseudomorphic growth will shift the transition to about 2.6 eV, but confinement of the relevant electron and hole wave functions would shift it about 2.7 eV, outside our spectral range.

Our ellipsometric results for the 7-Å layer show a single transition at 2.32 eV. The derivative spectra of $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ obtained on the 7-Å-Ge layer resemble the E_1 structure observed in bulk Ge, with the larger damping expected given the presence of the Ge-Si interfaces. Theoretical treatments of these transitions in Ge_4Si_4 superlattices predict that E_1-derived transitions will occur near 2.5 eV.[18] The one-electron band-structure calculations do not include the exciton effects which are significant for E_1 in the bulk.[19] We therefore believe this peak to be related to E_1 of bulk Ge. However, the characteristic doublet seen in the bulk due to the spin-orbit splitting of the valence band is not observed in this sample. This results from the large uniaxial stress inherent in pseudomorphic growth. Extrapolating the results of Chandrasekhar and Pollak,[19] we find that the pseudomorphic growth of bulk Ge on Si(100) (corresponding to a strain $X \sim 10^{11}$ dyn/cm^2, an order of magnitude larger than the experimentally applied strains in Ref. 19) will result in $E_1=1.8$ eV and $E_1+\Delta=3$ eV. The layer energies would be shifted up by confinement effects so the spin-orbit split transition would be outside our spectral range.

In contrast to the single transition observed in the 7-Å sample, we observe two transitions separated by 0.2 eV in $\epsilon(\omega)$ for our 15- and 17-Å-Ge layers. This bulklike behavior is confirmed in resonant-Raman-scattering studies on this sample which show a peak in the Raman cross section for Ge-Ge scattering near 2.25 eV, similar to the bulk resonant Raman spectrum. However, we cannot trivially associate the pair of transitions to the spin-orbit split valence-band states since Raman scattering and electron microscopy both show that the layer is fully strained. While strain and confinement effects will both shift and split the E_1 and $E_1+\Delta$ transitions explaining the observation of an E_1 transition below 2.5 eV as seen in the 7-Å layer, $E_1+\Delta$ should still be separated by over 1 eV for a fully strained 17-Å layer.

The finite thickness of the Ge layer modifies the bulk electronic structure in several ways. The replacement of the three-dimensional band structure by a series of subbands in the layers can modify the spin-orbit splitting of the valence bands through changes in the symmetries of the valence-band wave functions. The confinement of the valence-band states can also enhance the electron-hole exchange interaction which splits the E_1 transition by about 4 meV in the bulk.[19] Such effects have been observed for the hydrogenic excitons in III-V quantum wells where order-of-magnitude increases in the exchange energy occur as the well width becomes significantly smaller than the exciton radius.[20] For our situation, the enhancement of the exchange interaction by strain and confinement would have to be very large, $\simeq 50$, to explain the doublet at 2.13 and 2.33 eV in the 17-Å sample. Finally, calculations of the band structure of a Ge-Si superlattice predict a multiplicity of E_1 transitions in this energy range due to zone-folding effects. New, previously forbidden transitions can be observed in a finite-thickness layer where translational symmetry in the direction normal to the layer plane is lost. The relative strengths of these new transitions for thin layers will depend on the details of the band structure and the layer thicknesses. A similar splitting of E_1 in GaAs-AlAs superlattices has been reported by Garriga *et al.*[21] and attributed to zone folding.

In conclusion, we have used spectroscopic ellipsometry to derive the dielectric response of ultrathin Ge layers in Si(100) bulk materials. The existence of the Ge-derived E_1 gaps derived from the spectroscopic ellipsometry

studies are confirmed by resonant-Raman results for samples with Ge layers greater than 7 Å. Our results are consistent with experimental studies on disordered Ge which showed that the E_1 transitions depend only on the presence of the local Ge bonding order and are quite insensitive to disorder effects on the longer scale.[22] The E_1-derived transition is a very characteristic signature of Ge even for Ge layer thicknesses as small as a nanometer. The E_1 transitions represent an interesting test of our ability to fabricate microscopic structures in Si and Ge. For example, our results raise questions about our ability to fabricate atomically abrupt Si-Ge structures where the layer thicknesses are below 4 Å.

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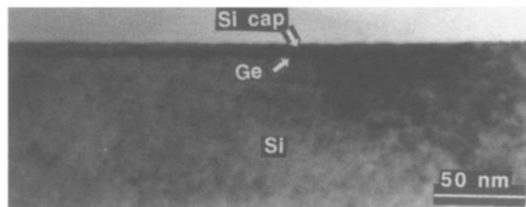

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