Pseudomorphic growth of Ge_xSi_{1-x} on silicon by molecular beam epitaxy

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Ge_xSi_{1-x} layers are grown on Si substrates over the full range of alloy compositions at temperatures from 400–750 °C by means of molecular beam epitaxy. At a given growth temperature films grow in a smooth, two-dimensional manner up to a critical germanium fraction x_c. Beyond x_c growth is rough. x_c increases from 0.1 at 750 °C to 1.0 at ~ 550 °C. Rutherford ion backscattering measurements indicate good crystallinity over a wide range of growth conditions. Transmission electron microscopy reveals that in thin films, the lattice mismatch between the Ge_xSi_{1-x} and Si layers can be accommodated by lattice distortion rather than by misfit dislocation formation. This pseudomorphic growth condition can persist to alloy thicknesses as large as 1/4 μm.

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A number of authors have reported growth of Ge_xSi_{1-x} alloys on Si by means of molecular beam deposition.[1-10] Certain studies dealt only with limited alloy compositions (either silicon rich,[1-3] or pure Ge[4,5]) or a limited growth temperature range.[5] Other works employed either substrate preparation procedures or deposition vacuum conditions now known to adversely affect epitaxial layer growth.[4-10] The purpose of this work is to investigate the growth of Ge_xSi_{1-x} alloys on Si for all compositions ($x = 0$–1) over a wide range of growth temperatures (400–750 °C) using the sample preparation procedures and vacuum conditions available in a state-of-the-art molecular beam epitaxy (MBE) system. We examine epitaxial surface morphology, layer defect density, and strain by means of Nomarski optical microscopy, cross-sectional transmission electron microscopy (TEM), and Rutherford ion backscattering and channeling. We find the following: (1) Thin alloy layers grow in a smooth, two-dimensional manner if the alloy composition is less than a critical value x_c. This critical composition is largest at low growth temperatures and equals 1 at $T_{\text{growth}} \lesssim 550$ °C. (2) For alloy compositions $x < x_c$ excellent ion channeling is observed in layers grown from 550–750 °C indicating good epitaxial layer quality. For layers grown at 400 °C, good ion channeling is measured for Ge_xSi_{1-x} grown on Si but not for Si on Si showing that addition of Ge suppresses the minimum epitaxial growth temperature. (3) TEM and off-normal channeling measurements indicate that for $x \lesssim 0.5$ lattice mismatch in thin layers may be accommodated almost entirely by elastic strain rather than by misfit dislocation formation. Depending on the alloy composition, this pseudomorphic growth condition can be maintained for thicknesses up to 1/4 μm. These results are similar to the "strained-layer superlattice" work recently reported in the $GaAs_xP_{1-x}$/GaP system.[11-13]

In this letter Ge_xSi_{1-x} alloy layers were grown on 75-mm-diam *n* and *p*-type (100) Czochralski silicon wafers with resistivities ranging from 0.1–10 Ω cm. Wafers were precleaned in a series of degreasing, reducing, and oxidizing solutions. The wafers were then loaded into the MBE system for *in situ* cleaning and deposition. Details of the apparatus and processing procedures are published elsewhere.[14,15] Briefly, wafers are cleaned by argon ion sputtering followed by a 800–850 °C anneal. A 1000-Å-thick, pure silicon layer is then deposited to ensure a reproducible starting condition. Next a shutter is opened over the germanium source to produce alloy deposition. (Except as noted below, Si and Ge_xSi_{1-x} layers are grown at the same temperature.) The deposition sources are commercial electron beam evaporators; the fluxes are separately sensed and controlled to yield an alloy deposition rate of 5 Å/s. The system base pressure is $\sim 2 \times 10^{-10}$ Torr and rises to $5\text{–}50 \times 10^{-9}$ Torr during deposition. This background pressure is almost entirely hydrogen and helium.

During conventional MBE growth, substrates are rotated to maximize compositional uniformity. In these experiments on growth morphology, a controlled range of compositions was useful. Therefore, substrates remained fixed during deposition and a single shutter was moved in steps across the sample to produce stripes of alloy film with nominal layer thickness of 100, 500, 1000, and 2500 Å. Because Si and Ge sources are both below and to opposite sides of the substrate the alloy composition varied continuously along a stripe from a value about 20% below to a value 20% above the center composition value x. A single wafer thereby yielded a controlled comparison of various thickness and composition values. Film morphology was then examined by Nomarski optical interference contrast microscopy and alloy composition at specific points determined by Rutherford ion backscattering.

At a given growth temperature Ge_xSi_{1-x} alloy films grew in a smooth, two-dimensional manner up to a critical composition value $x = x_c$. Above this value the films grew in discrete, three-dimensional nuclei. This breakup occurred abruptly with the size and density of nuclei changing between $x = x_c$ and $x \simeq x_c + 0.05$, and a relatively constant morphology was maintained for $x_c + 0.05 < x < 1$. The nuclei did not display obvious facets but instead had a random dropletlike appearance. As layer thickness increased the nuclei tended to coalesce and become smooth although coalescence was generally incomplete in the 2500-Å-thick stripes. The shape of the nuclei, their distribution, and coalescence behavior were very similar to that observed in earlier MBE silicon on sapphire work.[16]

A number of samples were grown to define the depen-

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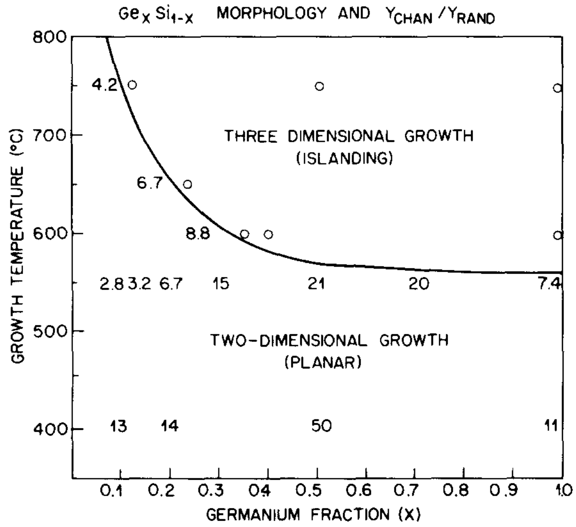

FIG. 1. Plot of film morphology and $y_{\rm chan}/y_{\rm rand}$ vs growth temperature and film composition for 1000-Å-thick alloy films. Rough film produced at points indicated by (O). Smooth films produced at points indicated by numerical values. Numerical values are the ratio of [100] channeling to random backscattering yields ($y_{\rm chan}/y_{\rm rand}$) in percent. Values of 2–3% and 100% would indicate perfectly crystalline and completely disordered films, respectively.

dence of x_c on growth temperature. Results are shown in Fig. 1 where layer growth temperature and composition are plotted as circles for conditions yielding rough growth or $y_{\rm chan}/y_{\rm rand}$ values (discussed below) for conditions yielding smooth growth. The value of the critical or transitional composition increases rapidly as growth temperature decreases and reaches a value of 1 at 550 °C. The shape of this curve leads us to speculate that island formation is energetically favored in $Ge_x Si_{1-x}$ growth on Si. This would be the situation if there were a high energy associated with the alloy/silicon interface or if islanding facilitated relaxation of strain fields in the alloy. In either case islanding would then be avoided only by lowering the growth temperature to the point where atomic surface migration lengths are so short that macroscopic islands cannot form.

If islanding is avoided by reducing surface migration lengths, crystal quality might degrade simultaneously. To investigate this possibility, we evaluated the crystallinity of smooth films by Rutherford ion backscattering and channeling. The ratio of the [100] channeling to nonaligned backscattering yields from the germanium was used as our definition of $y_{\rm chan}/y_{\rm rand}$ (i.e., surface and interface peaks were included.)

As crystalline perfection increases channeling improves and $y_{\rm chan}/y_{\rm rand}$ decreases from a value of 100% for a fully disordered material to a value of 2–3% in a perfect crystalline semiconductor. As shown by the numerical $y_{\rm chan}/y_{\rm rand}$ values in Fig. 1, high crystalline quality is achieved over a wide range of compositions and temperature. At 550 °C, where all alloy compositions grow smoothly, $y_{\rm chan}/y_{\rm rand}$ values range from a perfect 2.8% at $x = 0.10$ to 21% at $x = 0.5$.

Below 500 °C, growth temperatures could not be measured directly by infrared pyrometry. For runs at ~400 °C heater settings were estimated by an extrapolation of heater power versus temperature curves (estimated error, ± 25 °C).

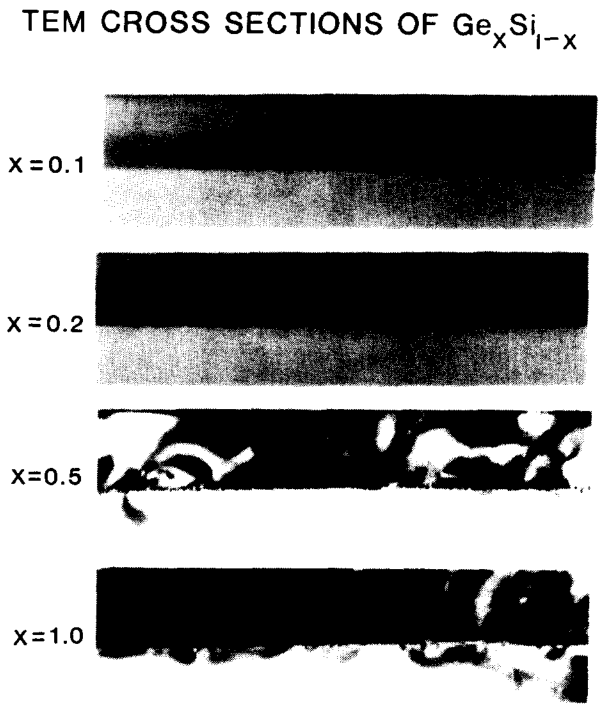

FIG. 2. TEM cross sections of 1000-Å-thick $Ge_x Si_{1-x}$ films grown on (100) Si at 550 °C. Top to bottom $x = 0.1$, 0.2, and 0.5, and 1.0. Top band in each is the alloy film, bottom band is the underlying Si.

In the first set of runs, where the initial 1000-Å Si layer and the alloy layer were grown at the same 400 °C temperature, backscattering indicated that amorphous or disordered growth resulted in both layers. In a second set of runs the 1000-Å Si layer was therefore grown at 550 °C, growth interrupted, and the sample cooled to the 400 °C settings before starting alloy deposition. These alloys were crystalline with the $y_{\rm chan}/y_{\rm rand}$ values shown near the bottom of Fig. 1. These experiments indicate that addition of germanium can actually reduce the minimum epitaxial growth temperature below that observed for pure silicon on silicon growth.

In Fig. 1, for both 400 and 550 °C growth temperatures, $y_{\rm chan}/y_{\rm rand}$ values increase sharply between the germanium fractions of $x = 0.2$ and $x = 0.5$. To understand this behavior, $x = 0.1$, 0.2, 0.5, and 1.0 samples grown at 550 °C were examined in cross section by transmission electron microscopy. The resulting bright field micrographs are shown in Fig. 2 for the 1000-Å-thick stripes. In these micrographs dislocations appear as straight lines (or serrations at the epi-substrate interface) and strain as broad black-white contours. It is evident that the alloy dislocation density does not increase linearly with germanium fraction as one would expect on the basis of lattice mismatch. Instead the dislocation density is ~0 in 10 and 20% films and increases only gradually thereafter. This observation suggests that lattice mismatch in 10 and 20% films is accommodated by strain (i.e., the alloy film is compressed laterally to match the silicon lattice constant).

If pseudomorphic or strain accomodated alloy growth is occurring, one would expect to see a dependence on film thickness. Thinner films would have a lower accumulated strain energy and less of a driving force for dislocation for-

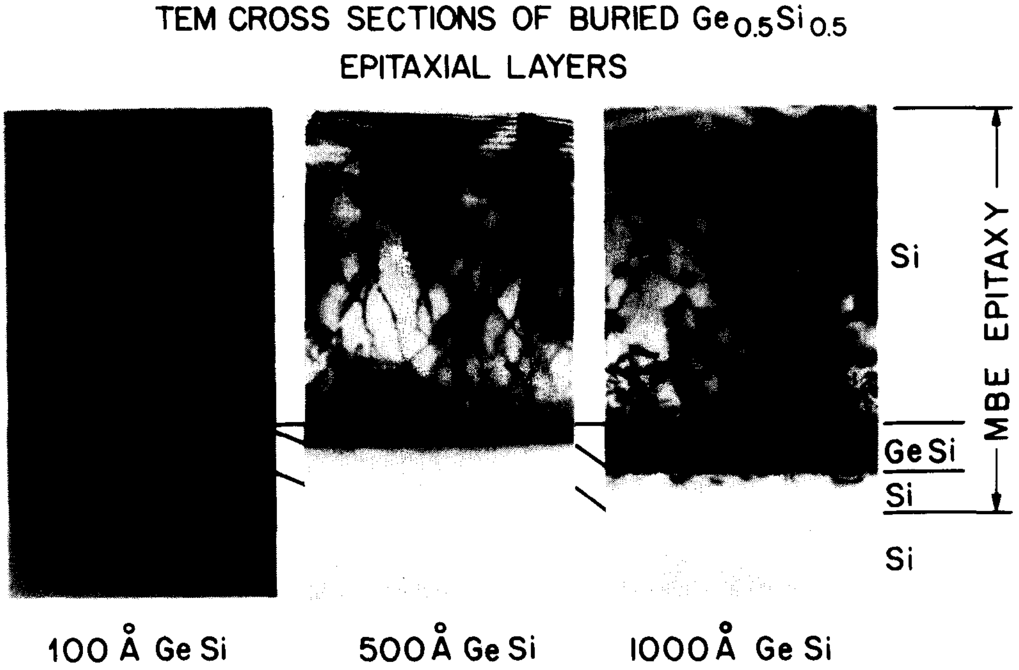

FIG. 3. TEM cross sections of $Ge_{.50}Si_{.50}$ layers of varying thickness grown at 550 °C on (100) Si and capped with $\approx 1\ \mu m$ Si. As alloy layer thickness decreases dislocation density decreases until with a 100-Å-thick $Ge_{.50}Si_{.50}$ layer, lattice mismatch is completely accommodated by strain (i.e., the alloy compresses laterally to match the Si lattice constant).

mation. Indeed in thin enough films, alloys with germanium fractions $\geqslant 0.5$ should grow without dislocations. This point was tested by growing $Ge_{0.5}Si_{0.5}$ films of thickness 100,500, and 1000 Å, the TEM cross sections of which are shown in Fig. 3. In these experiments the alloys were capped by a 1-μm Si layer. Propagation of dislocations into the cap layer would indicate their presence in the thin alloy layer in situations where direct observation would be difficult. Moving right to left in Fig. 3 it is evident that dislocation density decreases to the point where a 100-Å $Ge_{.50}Si_{.50}$ layer can be embedded in silicon with ideal pseudomorphism. Indeed, for the 100-Å layer thickness no dislocations were detected anywhere in the TEM sample. We have examined strain in a large variety of samples using both off-normal backscattering and x-ray measurements[17] and observe near complete accommodation of misfit through strain to layer thicknesses as high as 2500 Å (in an $x = 0.20$ sample). These thicknesses are substantially larger than would be expected from an equilibrium analysis of strain energy and dislocation formation,[18] and suggest a kinetic barrier to dislocation formation. Similar, though smaller, discrepancies were noted in the SiGe work of Kasper and Herzog where a kinetic barrier was also invoked.[3]

In conclusion, we find that smooth Ge_xSi_{1-x} layers of all alloy compositions can be grown on Si by suitable adjustment of MBE growth conditions. As determined by ion backscattering, epitaxial layer quality is high over a wide range of growth conditions. For thin epitaxial layers, lattice mismatch may be accommodated by strain rather than dislocation formation. This pseudomorphic growth condition can be maintained at either alloy compositions or layer thicknesses substantially larger than predicted by equilibrium theory. The growth of defect-free silicon-germanium heterostructures introduces possibilities of exploiting bandgap modulation in manners heretofore restricted to compound semiconductors.

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