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Strained-Layer Epitaxy of Germanium-Silicon Alloys

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Summary. Despite the dominant position of silicon in semiconductor electronics, its use is ultimately limited by its incompatibility with other semiconducting materials. Strained-layer epitaxy overcomes problems of crystallographic compatibility and produces high-quality heterostructures of germanium-silicon layers on silicon. This opens the door to a range of electronic and photonic devices that are based on bandstructure physics.

For the last two decades, silicon has been the dominant material in semiconductor electronics (*1*). Its unique position can be attributed to a number of factors: it is the second most abundant material on earth; it can be refined to ultrahigh purity and grown into nearly perfect crystals; its surfaces can be oxidized to form a stable, high-quality dielectric; and it has mechanical properties that make it notable even in the absence of its electrical attributes (*2*).

Despite these qualities, other semiconductors are now finding increasing application in electronics. These "new" materials come primarily from the family of III–V semiconductors (that is, they are composed of equal parts of column III and column V atoms). In certain devices, III–V materials displace silicon because of their unique properties. For instance, unlike silicon, many III–V semiconductors have direct energy bandgaps that facilitate the efficient recombination of electrons and holes to generate light. In other situations silicon is displaced simply because III–V materials offer a wider range of properties that can be advantageously combined within a crystalline semiconductor circuit. For example, III–V materials such as gallium arsenide and aluminum arsenide can be grown in alternate layers or regions of a device to produce local variations of bandgap, refractive index, or carrier concentration for devices such as optical detectors and high electron mobility transistors.

For many years scientists have tried to combine silicon with other semiconducting materials. This work has been limited by two fundamental compatibility problems. First, a successful combination (or heterostructure) of silicon and an alternate semiconductor must involve layers that are crystallographically compatible. That is, because most semiconductor devices depend on high crystalline perfection, a heterostructure is useful only if atomic order is preserved at the interfaces of the components. This generally implies not only that the components must have a similar crystalline structure (such as cubic) but also that atomic spacings must be virtually identical (that is, the materials must be lattice matched). Second, the components of the heterostructure must be chemically compatible. The difficulty here is that the electrical properties of semiconductors depend on the presence of trace amounts of impurity atoms (or dopants). The most electrically affective dopants are those that come from columns of the periodic table immediately adjacent to those of the semiconductor atom. For instance, impurities from columns III and V efficiently dope the column IV material silicon (silicon efficiently dopes III–V semiconductors). The catch-22 is that the only semiconductors crystallographically compatible with silicon come from the family with the worst chemical incompatibility: the III–V materials. Germanium, the material with the best chemical compatibility, has a crystalline structure with atomic spacings 4.2 percent larger than those in the silicon lattice. Although this mismatch may sound small, it is sufficient to disrupt massively the crystalline order, and quality, of a semiconductor device.

Strained-Layer Epitaxy

With two such contradictory rules, the solution is literally to see how much one of the rules can be stretched. Figure 1 illustrates how this is done. In common semiconductors, atoms have four bonds oriented along the four tetrahedral directions (that is, each bond has an angle of 109.5° with the neighboring bond). This bonding leads to so-called diamond or zinc blende face-centered cubic (fcc) crystal structures (*3*). Taking certain liberties, we can represent such fourfold bonded crystals on a two-dimensional page as the square array of atoms shown at the bottom left of Fig. 1. An alloy of two such semiconductors retains the same basic crystal structure but may be dilated if the second semiconductor contains larger atoms (as indicated at the top left of Fig. 1).

If an alloy is grown as an epitaxial layer on a silicon substrate crystal, there are two simple ways in which the layers can bond together. First, as indicated in the top right of Fig. 1, both layers can retain their independent crystal structures. In this situation fourfold bonding cannot be maintained along the interface, and an occasional atom is left with only three bonds. Rows of these improperly bonded atoms form so-called misfit dislocations, which may produce unde-

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sirable electrical activity. Mobile electrons or holes may be trapped at these sites, or the sites may produce leakage across diode junctions.

An alternate bonding arrangement is illustrated at the bottom right of Fig. 1. Because crystalline lattices have a certain elasticity, sufficiently thin epitaxial layers can distort to match the bonding arrangement of the substrate crystal. The more widely spaced epitaxial alloy crystal compresses along the interfacial, or growth, plane such that all atoms retain fourfold bonding (to compensate for that compression, the planes spread slightly farther apart perpendicular to the interface). This strained-layer epitaxy lowers the energy of the interfacial atoms at the expense of stored strain energy within the epitaxial layer. As the thickness of the strained epitaxial layer increases, the stored strain energy builds until at some point the interface shears and reverts to the unstrained structure. The all-important question is whether this higher quality strained-layer epitaxy can be maintained for thicknesses large enough to be useful in electronic devices.

Germanium-Silicon Alloys

Germanium is immediately below silicon in column IV of the periodic table. The two elements not only share valence structure but have the same bonding orbitals (four tetragonal *sp*^{3} hybrids), the same crystal structure (diamond fcc), and similar indirect energy bandgaps. These similarities mean that the materials are chemically compatible and that they can be freely mixed to form crystalline alloys of all compositions with no tendency to segregate into regions of differing structure or composition. Even on an atomic scale the evidence has been that germanium and silicon atoms freely substitute for one another to form a microscopically random alloy.

Germanium and silicon differ in the precise values of their lattice constant, refractive index, dielectric constant, free carrier mobilities, and energy bandgap. The variation of energy bandgap is plotted in Fig. 2. In normal homogeneous unstrained alloys the addition of germanium to silicon narrows the minimum energy bandgap from the value for pure silicon of 1.1 eV toward the value for pure germanium of 0.65 eV. Because of subtleties in the alloy's energy bandstructure, the variation is not linear with composition; in fact, the addition of small amounts of germanium leads to a more gradual narrowing than might be expected (*4*). The shape of this energy bandgap curve is of critical importance. Given the dominant position of silicon technology, we want to synthesize heterostructures of germanium-silicon layers on silicon (GeSi/Si) that can be integrated directly with existing circuits. On the other hand, many heterostructure devices require a variation of 0.1 to 0.2 eV in energy bandgap (*5*). Further, to be compatible with windows for fiber-optic transmission, detectors should have bandgaps of less than 0.85 eV (*6*). Figure 2 indicates that, to produce such a range of bandgaps, GeSi/Si heterostructures must incorporate alloys with no less than 50 percent germanium (denoted $Ge_{0.5}Si_{0.5}$). At this composition the germanium-silicon lattice is more than 2.0 percent larger than that of silicon, a difference that is more than large enough to produce a disastrously high crystal dislocation density at the GeSi/Si interface.

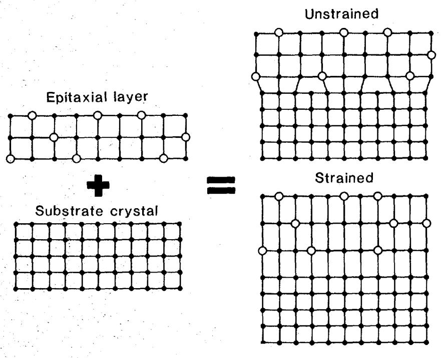


Fig. 1. Alternate modes of semiconductor epitaxy. Component layers are at left. (Top right) Conventional epitaxy where layers are undeformed and lattice mismatch produces dislocations at the interface. (Bottom right) Strained-layer epitaxy where alloy layer deforms to match the atomic spacing of the substrate.

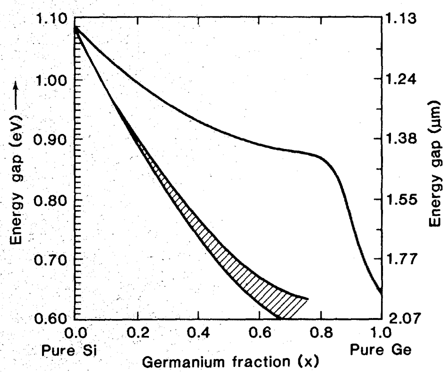


Fig. 2. Energy bandgap for Ge_xSi_{x-1} semiconductor layers. Curves are calculated for unstrained material (upper) and strained-layer epitaxy (lower) on silicon substrates.

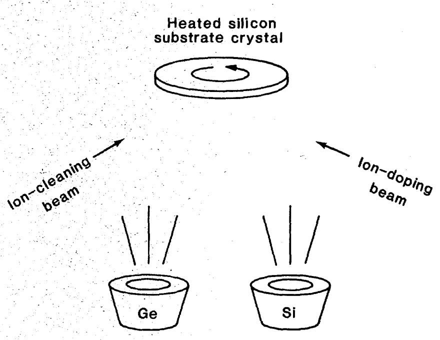


Fig. 3. Simplified schematic for MBE of silicon and silicon alloys (pressure, $<10^{-8}$ atmospheres). Downward-facing substrate is coated by evaporated beams of germanium and silicon generated by electron-beam heating of elemental charges. Additional ion beams are used for substrate cleaning and dopant incorporation.

It is here that strained-layer epitaxy offers a solution. Not only does strained-layer growth eliminate interfacial dislocations but it shifts the energy bandgap. If a germanium-silicon epitaxial layer is compressed to fit a silicon substrate lattice, the energy bandgap narrows more rapidly (*7*). As shown by the cross-hatched curve of Fig. 2, the required shift in bandgap can be achieved in GeSi/Si heterostructures containing only 20 percent germanium. Because the unstrained $Ge_{0.2}Si_{0.8}$ lattice is only 0.8 percent larger than silicon, strained-layer epitaxy is that much easier to achieve. The required 0.8 percent compression nevertheless corresponds to grown-in pressures on the order of 10^5 atmospheres.

Growth by Molecular Beam Epitaxy

Strained-layer epitaxy was modeled theoretically as early as 1949 (*8–12*), and recent experiments in compound semiconductor growth have demonstrated the potential of the technique (*13–15*). However, for growth of germanium-silicon layers on silicon, calculations indicated that strained-layer epitaxy could be sustained for thicknesses of only 10 to 100 Å (*16, 17*). Early experiments supported these calculations (*16–18*). Because these thin layers would be of little use in current devices, the challenge was to see whether equilibrium could be avoided.

For the heterostructure to relax from strained to unstrained growth, bonds along the entire heterostructure interface must be broken. This is a high-energy step that provides a substantial barrier to reaching equilibrium. In actual heterostructures, grown-in crystallographic dislocations provide a means for more gradual relaxation. Dislocations migrate and multiply under the influence of strain, converting small regions of the heterostructure layer from strained to unstrained epitaxy. Therefore, if a metastable strained state is to be maintained, the crystal growth technique must generate layers with virtually no grown-in dislocations. Further, growth should occur at low temperatures where small vibrational energies reduce disorder and interdiffusion. At these temperatures germanium and silicon must arrive as atoms or simple molecules that will readily decompose. Finally, the entire process should occur in vacuum so that low-temperature reactions with ambient gases are eliminated. This is a functional description of the crystal growth technique known as molecular beam epitaxy (MBE) (*19, 20*).

The MBE process is illustrated in Fig. 3. A silicon wafer is placed, polished side down, in an ultrahigh vacuum chamber. It is sputtered briefly with a low-energy argon ion beam to remove any surface contamination. The surface is then reordered by annealing at 800°C for 10 minutes and cooled to the growth temperature of 550° to 750°C. Growth commences when the wafer is exposed to beams of atomic germanium and silicon and ionized doping impurities. Because germanium and silicon have low vapor pressures, intense atomic beams cannot be produced in the resistively heated ovens (called Knudsen cells) used in compound semiconductor MBE (*19*). Instead, shaped germanium and silicon charges are fitted into water-cooled copper crucibles and heated with a 10-keV, 0- to 5-A electron beam. This beam heats the top center of charges to the required 1000° to 2000°C, while the copper crucible keeps the outer edges of the charges solid and cool. The evaporation rates are monitored continuously and controlled by modulating the electron beam current. Further, because atomic germanium and silicon readily condense on any cool surface, growth can be terminated by simply moving refractory metal shutters into the evaporation path (*21*).

Epitaxial films are evaluated by a variety of techniques. One of the most graphic of these is cross-sectional transmission electron microscopy, in which crystals are imaged edge-on to reveal the interfaces between layers. In such images dislocations appear as meandering lines or black and white bands. Figure 4 shows four micrographs of 1000-Å thick germanium-silicon layers grown by MBE on (100) oriented silicon substrates (*19*). The germanium content of the alloys is 10, 20, 50, and 100 percent, corresponding to lattice mismatches with the substrate of 0.4, 0.8, 2.1, and 4.2 percent, respectively. Despite these mismatches, dislocations appear only in the last two layers. The absence of dislocations in the 10 and 20 percent germanium films is clear evidence of strained-layer growth. This may be confirmed by means of techniques such as x-ray reflectance or Rutherford ion backscattering, which can directly measure the shape of the crystalline cell. As indicated at the bot-

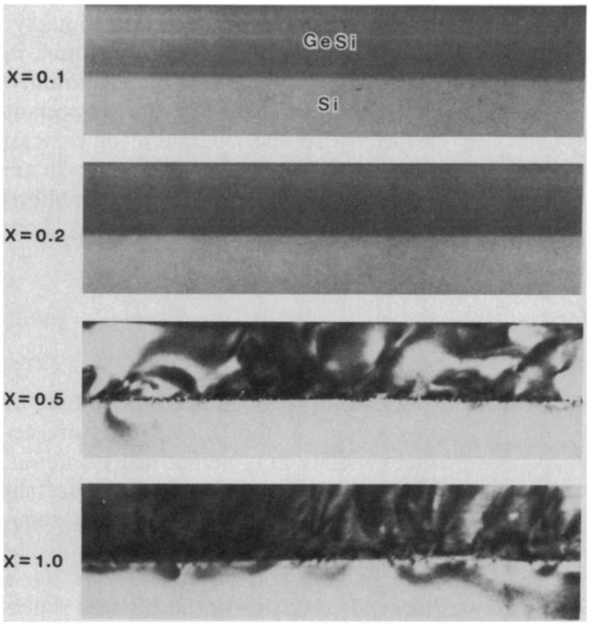
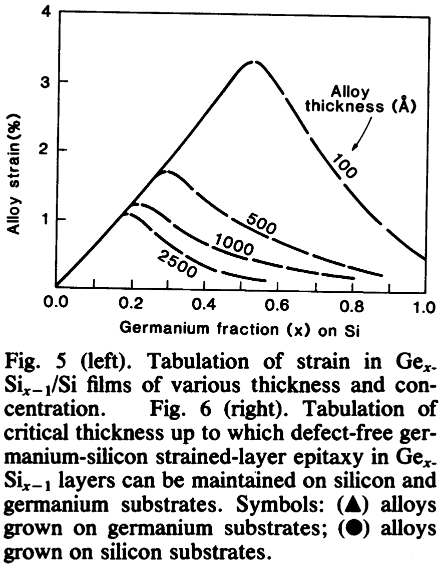


Fig. 4. Cross-sectional TEM micrographs of four Ge_xSi_{x-1} layers on silicon substrates. The absence of dislocations in $x = 0.1$ and 0.2 layers is indicative of strained-layer epitaxy.



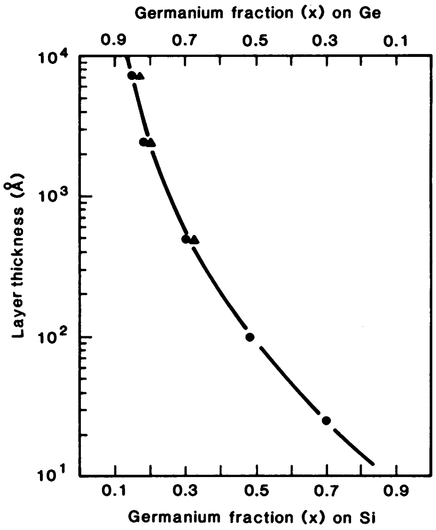


Fig. 5 (left). Tabulation of strain in Ge_xSi_{x-1}/Si films of various thickness and concentration. Fig. 6 (right). Tabulation of critical thickness up to which defect-free germanium-silicon strained-layer epitaxy in Ge_xSi_{x-1} layers can be maintained on silicon and germanium substrates. Symbols: (▲) alloys grown on germanium substrates; (●) alloys grown on silicon substrates.

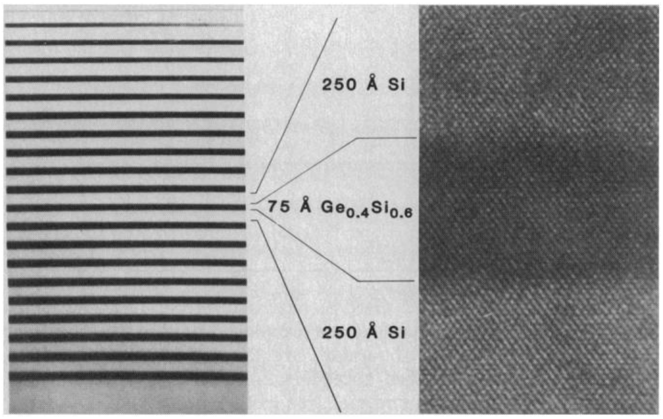


Fig. 7. Cross-sectional TEM micrographs of Ge_xSi_{x-1}/Si strained-layer superlattice (20-period). Enlarged image at right resolves individual atomic rows. [Microscopy by R. Hull and J. M. Gibson]

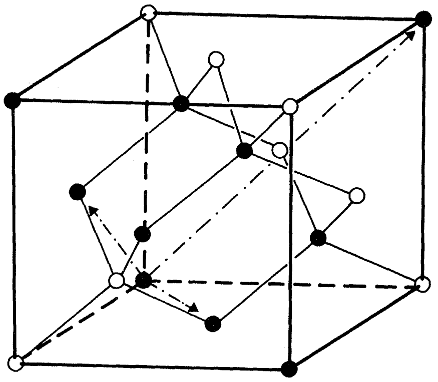


Fig. 8. Microscopically ordered structure produced by annealing of strained germanium-silicon layers. Symbols: (○) silicon atoms; (●) germanium atoms.

tom right of Fig. 1, strained-layer growth produces a rectangular cell. In the GeSi/Si case, the atomic spacing perpendicular to the interface exceeds the spacing parallel to the interface. Strain is defined as the difference in these spacings normalized to average spacing.

Strain has been measured in many GeSi/Si films and is tabulated in Fig. 5 (*22–24*). As the germanium content is increased, strain increases in a more or less linear fashion, then abruptly breaks off the line and begins to diminish. The breakpoint is a function of alloy layer thickness, with thinner films maintaining strain to higher germanium content. This behavior is consistent with models of strained-layer epitaxy: strained growth continues until the cumulative strain energy in the alloy is large enough to force the interface to reorder. Because this energy increases with both germanium content (or mismatch) and film thickness, one can be traded off against the other to maintain strained-layer epitaxy. The breakpoints of Fig. 5 are plotted in Fig. 6 to delineate conditions for strained and unstrained growth. The important result is that the maximum (or critical) thicknesses for strained-layer growth are much larger than predicted by equilibrium theory and are in a range that is likely to be useful in electronic devices.

Superlattices

Although single strained layers are of some interest, most heterostructure devices require not one but many different strained layers. Particularly important are devices based on the repeated, regular alternation between germanium-silicon and silicon layers known as a strained-layer superlattice. These superlattices introduce artificial periodicities that can radically alter the basic physical properties of the materials. It has been postulated that GeSi/Si superlattices might enhance carrier mobilities and lead to the creation of a direct energy bandgap (*25, 26*). Such a bandgap would enhance optical detector sensitivities and could conceivably lead to silicon-based light-emitting diodes that could be added directly to silicon-integrated circuits.

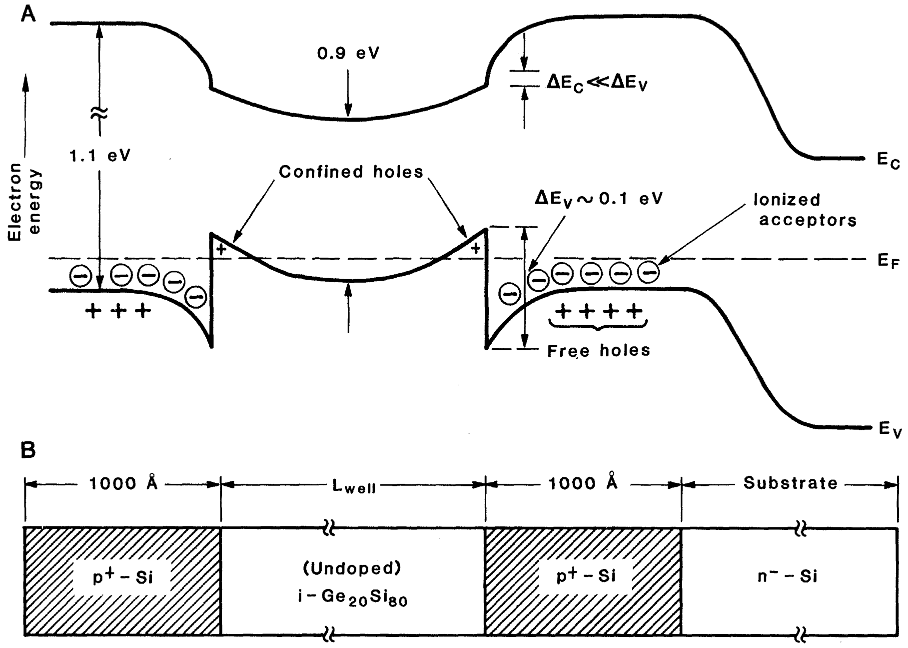


Fig. 9. Modulation-doped GeSi/Si heterostructure. (A) Energy band diagram. (B) Physical structure. Acceptor impurity atoms are placed only in the wider bandgap silicon layers. Holes created near the GeSi/Si boundary are then trapped in the germanium-silicon layer, where interaction with the ionized acceptors is reduced. E_c, E_v, and E_F are the conduction band, valence band, and Fermi energies, respectively. ΔE_c and ΔE_v are the conduction and valence band discontinuities. p^+ and n^- denote regions with high acceptor and low doner doping concentrations. The intrinsically doped region is denoted *i*.

In a GeSi/Si strained-layer superlattice, germanium-silicon and silicon layers may be of comparable thickness, and strain may be distributed over both materials. This not only complicates the strained-layer problem but raises the question of how one maintains lattice matching with the immensely thicker and more rigid silicon substrate. However, germanium-silicon layers were found to be more elastic than even thin silicon layers (*27, 28*). If the silicon layers in a GeSi/Si superlattice are three to five times thicker than the alloy layers, the silicon layers retain an undeformed bulk structure. The strain in adjacent germanium-silicon layers is therefore decoupled, and defect-free superlattices can be designed on the basis of the same critical layer thickness criteria derived in Fig. 6 for single strained layers.

Figure 7 shows cross-sectional TEM micrographs of a 20-period strained-layer superlattice. The left micrograph is a conventional low-magnification view of the entire superlattice. The right micrograph is made in a phase-contrast mode where individual atomic rows and channels are imaged as dark and light dots. Both micrographs show perfect crystalline order, with abrupt planar interfaces between the layers (*29*).

The strain in these superlattices produces another unexpected effect. Despite the differences between germanium and silicon atoms, all indications were that there was no microscopic ordering in germanium-silicon alloys, even when the atoms occur in integral concentration ratios. Apparently the differences between the atoms are so slight that entropy overcomes any energy gain produced by ordering. In strained-layer superlattices the balance can be tipped in the other direction. Recent electron diffraction experiments (*30*) have shown that careful temperature cycling (during or after MBE growth) can produce the regular alternation of atomic planes shown in Fig. 8. This ordering is interesting for a number of reasons. First, it introduces another periodicity into the system that can further alter material bandstructure in potentially useful ways. Second, because the basic crystal cell (or unit) is not centrosymmetric, nonlinear optic, electro-optic, and piezoelectric effects are no longer structurally forbidden.

In GeSi/Si strained-layer superlattices, the total thickness of the germanium-silicon layer can be as much as ten times the critical thickness of the single layer, which in turn is ten times larger than the value derived from an equilibrium theory. This incredible degree of metastability suggests that such structures might be only a laboratory curiosity that would quickly collapse during the harsh processing of integrated circuits. Initial experiments indicate that this is not the case. There is only minor strain relaxation during processing at temperatures as high as 800° to 900°C (*31*). Further, when such relaxation occurs it often has little effect on the lattice structure. For instance, in a strained-layer superlattice, annealing tends to form dislocations only at the substrate-superlattice interface (*32*). This means that the bulk of the superlattice remains free of dislocations.

Electronic Properties and Device Application

Measurements of electronic transport properties and device performance provide a particularly demanding test of material quality. Not only do devices respond to defects invisible to standard analytical techniques, but they are often critically dependent on the properties of interfaces. In strained-layer heterostructures, interfaces are particularly suspect, and indeed, interfacial strain may actually attract degrading metallic impurities. Although GeSi/Si strained-layer device work is new and limited, there have been important initial successes.

Particularly important is the synthesis of modulation doped GeSi/Si heterostructures and their incorporation into selectively doped heterojunction transistors. Modulation doping was first demonstrated in the late 1970's and had been strictly limited to III–V semiconductor structures (*33*). In a modulation-doped device, the electrically active impurities are placed only in the wider energy bandgap layers. These impurities ionize and create either free electrons or holes, which carry the electrical current in the device. Because these carriers can migrate a certain distance from their parent impurities, they will enter the narrower bandgap layers where they will be confined by an energy barrier. In these layers they interact much less strongly with the ionized parent impurity atoms and may thus reach higher speeds (producing faster devices).

Modulation doping was recently demonstrated for holes with the $Ge_{0.2}Si_{0.8}$/Si heterostructures shown in Fig. 9 (*34, 35*). In these heterostructures only the wider bandgap silicon is doped, producing carriers that migrate and are then confined in the germanium-silicon layers. This confinement was evident in both the magnetoresistance characteristics of the material and in the observation of enhanced low-temperature mobilities. Although mobilities do not as yet match the spectacular values achieved in III–V structures, these layers have nevertheless been incorporated into a successful silicon-based heterojunction transistor (*36*). In this transistor the layer sequence consists of a silicon substrate, an undoped silicon layer, an undoped germanium-silicon layer, and a final doped silicon surface layer. This sandwich is oxidized, holes are etched in the oxide, boron is ion implanted, the structure is annealed, and Schottky gate and contact metalization is applied and defined. The structure functions as a *p*-channel transistor and indeed has a transconductance close to that of a state-of-the-art *p*-MOSFET (metal-oxide semiconductor field-effect transistor). Unlike the MOSFET, the conducting channel is buried and as such might be closely integrated with a surface *n*-MOSFET to yield a dense, complementary integrated circuit.

More important than this single device is the fact that this metastable strained-layer heterostructure has successfully withstood a typical integrated circuit-processing sequence. Other silicon-based heterostructure devices, such as bipolar transistors and optical detectors, are therefore possible and are being actively developed.

In the examples above, the goal was to eliminate all dislocations by continuing strained-layer epitaxy throughout the entire structure. In certain situations this is not possible. For instance, in a detector composed of germanium on silicon that is used for fiber-optic communications, the absorbing layer of germanium must be several micrometers thick to capture all the incoming photons. As indicated in Fig. 6, this is much too thick for strained-layer epitaxy to be maintained, and the germanium will relax to its bulk structure. GeSi/Ge superlattices have nevertheless been used successfully as dislocation filters. When such superlattices are grown over a dislocated layer of germanium on silicon, the strain at the superlattice interfaces effectively traps propagating dislocations. The superlattice can then be overgrown with high-quality germanium, which will produce an efficient detector (*37*).

Conclusions

Despite its strong technological position, silicon has been limited by the fact that it is, in the end, only one material with one set of physical properties. Strained-layer epitaxy now provides a way of integrating silicon with another semiconductor. This not only combines the properties of the constituents but leads to phenomena unique to the two-dimensional strained structures. These phenomena range from superlattice effects, to strain-induced bandstructure modification, to the synthesis of microscopically ordered semiconductor alloys. Strained-layer epitaxy thus presents the mature technology of silicon materials with new degrees of freedom of potential use in both fundamental studies and device structures.

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