Growth of germanium-carbon alloys on silicon substrates by molecular beam epitaxy

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Metastable $Ge_{1-y}C_y$ alloys were grown by molecular beam epitaxy as homogeneous solid solutions having a diamond lattice structure. The substrates were (100) oriented Si wafers and the growth temperature was 600 °C. We report on measurements of the composition, structure, lattice constant, and optical absorption of the alloy layers. In thick relaxed layers, C atomic fractions up to 0.03 were obtained with a corresponding band gap of 0.875 eV. These alloys offer new opportunities for fundamental studies, and for the development of silicon-based heterostructure devices. © *1995 American Institute of Physics.*

In the past few years, alloys of group IV elements including C, Si, Ge and Sn have been actively investigated for use in heterojunction devices compatible with Si circuit technology.[1] These studies have been complicated by the limited solubility of C in these alloys.[2–6] In thermodynamic equilibrium, the solid solubility of C in Ge, for example, has been estimated to be near 10^8 cm^{-3}.[7] As a result, attempts to synthesize bulk homogeneous solutions of Ge and C by high temperature intermixing have been unsuccessful.[8] On the other hand, *metastable* $Ge_{1-y}C_y$ alloys have been prepared by molecular beam epitaxy (MBE) under non–equilibrium conditions at relatively low growth temperatures with significant C fractions of $y \approx 0.01$.[9–11] $Si_{1-x}C_x$ alloys with C fractions as high as $x \approx 0.2$ have been prepared by MBE,[2] and cubic $Si_{1-x-y}Ge_xC_y$ alloys with $y \leq 0.1$ have been prepared by chemical vapor deposition.[12] We report here on the growth and properties of crystalline $Ge_{1-y}C_y$ alloys which are a new material for fundamental studies and the development of variable band gap semiconductor devices.

The $Ge_{1-y}C_y$ alloys were grown by MBE in an EPI 620 system having six effusion cell ports and a substrate introduction chamber.[11] After bake-out, the base pressure of the growth chamber was less than 5×10^{-11} Torr. During growth a liquid He-cooled cryopump was used and the chamber pressure was typically 5×10^{-9} Torr. A mixture of ethylene glycol and water at a temperature of 15 °C was continuously circulated in the growth chamber cryopanels to avoid thermal cycling which could loosen flakes of dust from the residues of previous growths and thus contaminate growing layers.

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 of the source by B from the crucible, the cell temperature was kept below 1380 °C. At a cell temperature of 1350 °C, the Ge growth rate was 0.07 μm/h.

The C beam was produced by sublimation from a pyrolytic graphite filament which was resistively heated by direct current. The C filament temperature was calculated from the dissipated power and the Stefan-Boltzmann Law ($P = \sigma T^4$) for blackbody radiation using a value of $\sigma = 5.67 \times 10^{-12}$ W cm^{-2} K^{-4}.[13] For our serpentine-shaped filament having a resistance of 0.2 Ω and carrying a current of 38 A, this analysis resulted in a temperature of 2030 °C and a measured effective C growth rate of 0.01 μm/h.

Substrates were (100) oriented, 75 mm diameter Si wafers prepared by degreasing, etching in a solution of $H_2O:H_2O_2:HCl$ (5:3:3), and dipping in $HF:H_2O$ (1:10) to terminate the surface with H.[14] Alloys were grown at a substrate temperature of 600 °C. To enhance the miscibility of C which is related to the strain–induced changes in free energy,[5] we decided to grow the alloys on a thin buffer layer of pure Ge to reduce the layer strain compared to growing the Ge-rich alloys directly onto the Si substrate. During the first 5 min of growth, only the Ge cell was opened producing a Ge buffer layer 6 nm thick. We realized that growing pure Ge on Si produces islands[15] which could affect the overlayer properties, but this is true for any film grown on a supporting substrate. Our goal for the GeC system was to measure bulk, thick film values for the lattice parameters and the optical absorption. As a result, we did not attempt to minimize the dislocation density of the Ge buffer layer. Because of its technological importance and convenience, we used a (100) Si wafer substrate rather than a Ge wafer. Reflection high energy electron diffraction (RHEED) patterns indicated islands during the Ge buffer growth, followed by flat single crystal layers during GeC growth. The surface morphologies of the as–grown GeC alloys appeared specular. Layer thickness was measured by optical interference at an edge step. Transmission electron microscopy (TEM) showed that dislocations accommodated the lattice mismatch with the substrate and that the thick alloy layers were strain–free. The presence of the Ge buffer layer was accounted for in all measurements of GeC alloy layer properties.

TABLE I. Properties of $Ge_{1-y}C_y$ alloy samples including composition measured by AES, RBS and XPS, lattice constant a measured by XRD, band gap E_g measured by FTIR, layer thickness t measured by optical interference, and theoretical C fractions y_{theo} predicted from the optically measured band gaps assuming a linear interpolation of the three conduction band minima versus composition.

Sample	Composition	a (nm)	E_g (eV)	t (μm)	y_{theo} (eV)
SGC-30	$Ge_{0.99}C_{0.01}$	0.56544	0.732	0.582	0.008
SGC-31	$Ge_{0.98}C_{0.02}$	0.56539	0.782	0.139	0.014
SGC-32	$Ge_{0.97}C_{0.03}$	0.56525	0.875	0.136	0.025

The compositions were measured by several techniques including Auger electron spectroscopy (AES), He$^+$ Rutherford backscattering spectrometry (RBS), x-ray photoelectron spectroscopy (XPS), and by estimation from the measured optical band gap using a linear dependence on composition. Measurements made by the different techniques agreed to within experimental error, and the atomic fractions reported in Table I are averages of the measured values. Figure 1 shows a RBS spectrum of backscattered yield versus energy channel number measured using 2 MeV He$^+$ ions. The RBS compositions were determined from the integrated peak heights.[16] Analysis of signals from the Auger KLL fine structure for C at 260 eV indicated that the C formed diamond–type tetrahedral sp^3 bonds with neighboring atoms rather than graphitic sp^2 bonds.[17]

The alloy structure was measured by x-ray diffraction (XRD) at room temperature using a Philips vertical θ–2θ diffractometer and Cu Kα radiation. X-ray line positions were determined by fitting the measured diffraction peaks to a Pearson VII function[18] for the Cu Kα_1/Cu Kα_2 doublet, and applying corrections obtained from the observed (004) Si substrate reflection (including the effects of radial displacement caused by the film thickness).[19]

Scans over a wide range of diffraction angles showed only (004) and (002) reflections from the alloy and (004) and (002) reflections from the substrate and indicated that the
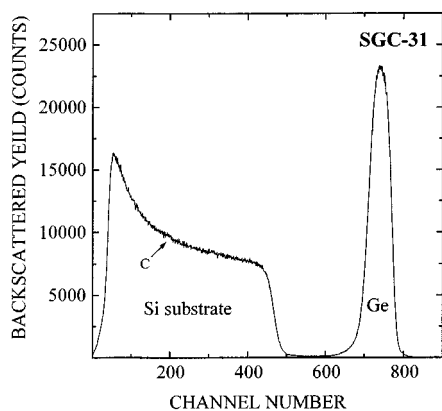

FIG. 1. RBS spectrum of backscattered yield versus energy channel number for alloy SGC-31 on a Si substrate. Peak between channel numbers 700 to 800 is from Ge in the alloy layer. Broad step below channel 500 is from the Si substrate. The C in the alloy layer appears as a low intensity peak on the Si substrate step. The integrated yields versus energy gives the composition.
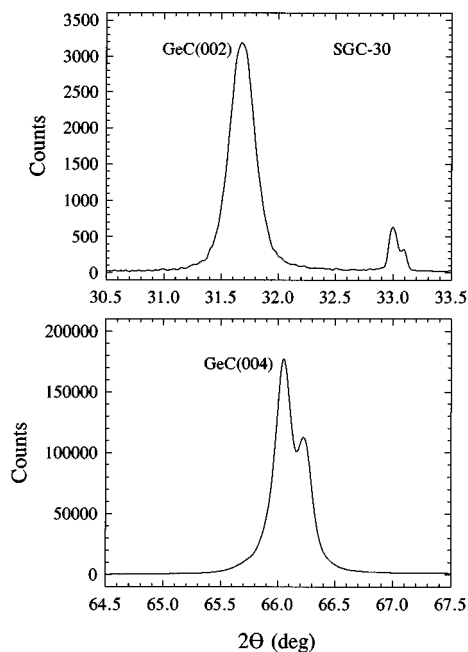

FIG. 2. X-ray diffraction intensity counts versus diffraction angle for sample SGC-30 on (100) Si substrate. The peak near $2\theta=66.1°$ was a (004) reflection of the Cu Kα doublet indicating a lattice constant of 0.56544 nm. The (002) alloy peak near 31.7° was allowed by the structure factor only for an alloy and implied that the Ge atoms and the C atoms occupied the same diamond lattice. The lower intensity peak near 33° was a (002) reflection from the substitutional boron dopant in the substrate.

alloy layers have a diamond structure strongly oriented to the (100) substrate. Figure 2 shows the diffracted x-ray intensity versus scattering angle (2Θ) for a GeC alloy layer. Applying Bragg's Law to the (004) reflection peak near $2\Theta=66.1°$ and to the (002) reflection near 31.7°, yielded the lattice constant given in Table I. The area of the (002) diffraction peak is 1.6% of that of the (004) peak, and its presence implied that both the Ge and the C are substitutional on the same diamond lattice because this reflection is forbidden by the structure factor in a diamond structure crystal with only a single type of atom. In addition, the angular position of this (002) reflection corresponds to the lattice constant of the GeC alloy. The lower intensity forbidden (002) reflection near 33° was caused by the substitutional boron impurity in the doped Si substrate. No other peaks were observed which might indicate misoriented polycrystalline grains, compound precipitation, or oxides.

The optical absorption at photon energies near the band gap was measured at room temperature by Fourier transform infrared spectroscopy (FTIR) in the transmission mode. Figure 3 shows the optical absorption coefficient α versus photon energy for three alloy samples compared with crystalline Ge. Interference effects made it difficult to observe changes in the slope of α at low values so we estimated the band gap E_g as the energy at which $\alpha=30$ cm^{-1}, which was the lowest value that we could measure with confidence, and provided a comparison between samples. The band gaps given in Table I exceed that of Ge and increase with the C fraction, and this was attributed to the alloying effect of C with Ge. The large values of E_g of the alloys compared to Ge implied that the
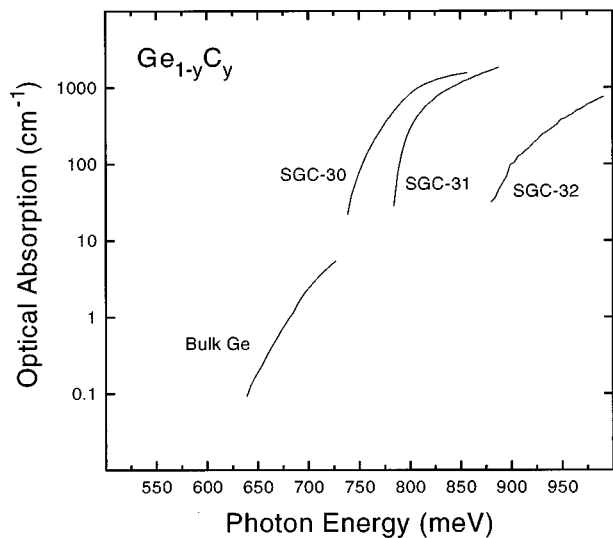
FIG. 3. Measured values of optical absorption coefficient α versus photon energy hν for samples SGC-30 (Ge$_{0.99}$C$_{0.01}$), SGC-31 (Ge$_{0.98}$C$_{0.02}$), and SGC-32 (Ge$_{0.97}$C$_{0.03}$) compared with that of a Ge wafer. The addition of C shifted the absorption edge to higher energies implying alloying with the Ge.

thick layers have relaxed because strain *reduces E$_g$* .[6,20]

The optically measured band gaps E$_g$ in Table I were used to calculate theoretical values for the C fractions by assuming a linear interpolation of the Γ ([000]), L ([111]) and X ([100]) conduction band energy minima versus composition, using known values for Si, Ge, and C as the end points. This interpolation predicted that the GeC alloys had an L minimum for the band gaps measured here, and yielded the theoretical C fractions y_{theo} in Table I which agree well with the measured compositions. This result implied a linear dependence of the Ge$_{1-y}$C$_y$ band gap versus composition for small C fractions, but care must be taken for extrapolations to larger C fractions because departures from linearity have been observed in Si$_{1-x}$C$_x$ alloys,[21] and it is well known that the band gap of cubic 3C–SiC (E$_g$=2.2 eV) is smaller than the value (E$_g$=3.28 eV) predicted by a linear average between diamond and Si.

The alloy lattice constants in Table I are slightly smaller than for pure Ge. It is not yet clear why these values were not as small as might be expected by Vegard's Law of the linear dependence of lattice constant on composition. We speculate that there was significant local strain near the C atoms as has been reported,[10] or perhaps the perpendicular lattice plane spacing has not completely relaxed due to residual tetragonal distortion in the alloys layers. This latter explanation, how-

ever, is inconsistent with our observation of a linear increase of band gap with composition, which implied strain-free layers.

In conclusion, the nonequilibrium, low temperature growth conditions of molecular beam epitaxy have produced crystalline Ge$_{1-y}$C$_y$ alloys having a cubic diamond lattice oriented to the (100) Si substrate. Measurements on thick relaxed alloy layers showed that up to 3 at. % C was incorporated, which reduced the lattice constant and increased the energy band gap compared to bulk Ge. These alloys open up an exciting new region for group IV semiconductor heterostructure physics and device possibilities.

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