

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

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-Received 20 April 1995; accepted for publication 22 July 1995!

Metastable $\text{Ge}_{1-y}\text{C}_y$ alloys were grown by molecular beam epitaxy as homogeneous solid solutions having a diamond lattice structure. The substrates were $\sim 100^\circ$ 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

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 K α radiation. X-ray line positions were determined by fitting the measured diffraction peaks to a Pearson VII function¹⁸ for the Cu K α ₁/Cu K α 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

alloy layers have a diamond structure strongly oriented to the (100) substrate. Figure 2 shows the diffracted x-ray intensity versus scattering angle (2 θ) for a GeC alloy layer. Applying Bragg's Law to the (004) reflection peak near 2 θ =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

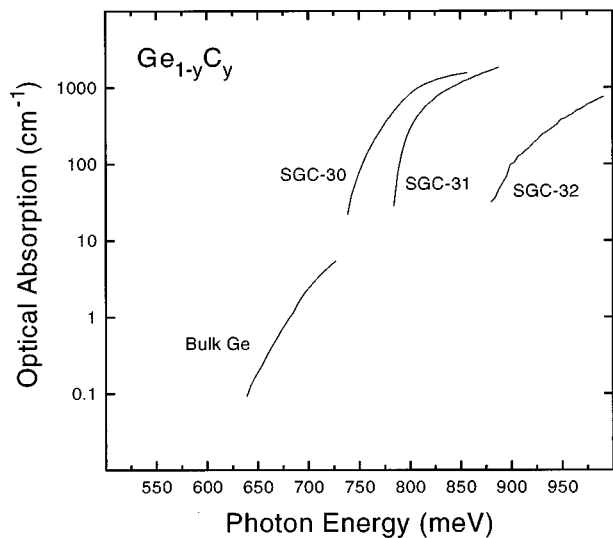


FIG. 3. Measured values of optical absorption coefficient α versus photon energy $h\nu$ for samples SGC-30 ($\text{Ge}_{0.99}\text{C}_{0.01}$), SGC-31 ($\text{Ge}_{0.98}\text{C}_{0.02}$), and SGC-32 ($\text{Ge}_{0.97}\text{C}_{0.03}$) compared with that of a Ge wafer. The addition of C shifted the absorption 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 G $\sim 100\%$, L $\sim 111\%$ and X $\sim 100\%$ 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 $\text{Ge}_{1-y}\text{C}_y$ 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 $\text{Si}_{1-x}\text{C}_x$ 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 $\text{Ge}_{1-y}\text{C}_y$ 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.

We gratefully acknowledge P. Berger for TEM, G. DeSalvo for MBE design and instrumentation, and J. Kramer for AES. This work is supported by AASERT Grant No. F49620-92-J-0340, by AFOSR Grant No. AFOSR-91-0370, and by ONR Grant No. N00014-93-1-0393.

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