

## Electrical and optical properties of phosphorus doped $\text{Ge}_{1-y}\text{C}_y$

M.W. Dashiell<sup>a,\*</sup>, R.T. Troeger<sup>a</sup>, K.J. Roe<sup>a</sup>, A-S. Khan<sup>a</sup>, B. Orner<sup>a</sup>,  
J.O. Olowolafe<sup>a</sup>, P.R. Berger<sup>a</sup>, R.G. Wilson<sup>b</sup>, J. Kolodzey<sup>a</sup>

<sup>a</sup>Department of Electrical Engineering, University of Delaware, Newark, DE 19716, USA

<sup>b</sup>Hughes Research Laboratory, Malibu, CA 90265, USA

### Abstract

In situ n-type doping was investigated for  $\text{Ge}_{1-y}\text{C}_y/\text{Si}$  heteroepitaxial layers ( $y \sim 0.001$ ) for a potential optoelectronic material compatible with Si. Using a solid GaP sublimation source for phosphorus doping, epitaxial  $\text{Ge}_{1-y}\text{C}_y$  films were in situ doped on Si(100) substrates during solid source molecular beam epitaxy and we compare their electrical and optical properties with those of epitaxial Ge on Si. Infrared absorption revealed red shifts in the absorption of visible light with increasing P doping for both  $\text{Ge}_{1-y}\text{C}_y$  and Ge. The index of refraction decreases for  $\text{Ge}_{1-y}\text{C}_y$  layers compared with Ge. Free carrier absorption increased with increasing phosphorus concentrations, following a wavelength dependence of  $\sim \lambda^{3.1}$  in the region of 10–20  $\mu\text{m}$  for heavily doped material. Addition of C did not affect the incorporation of P donors in the grown layers or the electrical activation of the donors. An increase in the electron mobility for heteroepitaxial  $\text{Ge}_{1-y}\text{C}_y$  layers compared with Ge was observed for the doping levels studied. © 1998 Elsevier Science S.A. All rights reserved

**Keywords:** Germanium carbon; Phosphorus; Doping; Optical; Electrical; Molecular beam epitaxy

### 1. Introduction

Binary and ternary alloys of Si, Ge and C are currently under investigation for use in heterostructure and optoelectronic devices [1,2]. Because of the low solubility of C in Si ( $\sim 3 \times 10^{18} \text{ cm}^{-3}$ ) and Ge ( $\sim 1 \times 10^8 \text{ cm}^{-3}$ ) these alloys are typically grown far from equilibrium by molecular beam epitaxy (MBE) [3,4], chemical vapor deposition (CVD) [5] and solid phase epitaxy (SPE) [6]. Carbon concentrations far in excess of the equilibrium solubility have been reported for both  $\text{Si}_{1-y}\text{C}_y$  [7] and  $\text{Ge}_{1-y}\text{C}_y$  [8].

Significant development efforts are now concentrated on an understanding of C on the structural, optical and electrical properties of the  $\text{Si}_{1-y}\text{C}_y$  and  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys. Most of these efforts focus on the Si-rich alloy, due to the ability to strain compensate the layer, so that thick, dislocation free  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  layers may be grown on Si substrates [9]. The germanium rich spectrum of the alloy has not been as thoroughly investigated because of the large lattice mismatch between the epitaxial layer and silicon substrates. The large mismatch results in critical thicknesses of  $\sim 20$  monolayers

or less for Ge/Si epitaxy, depending on the growth parameters [10].

Despite the large lattice mismatch between Ge and Si, the development of group IV heterostructures using germanium-rich alloys opens a wide variety of possible device applications on silicon substrates, such as infrared photodetectors, modulation doped field effect transistors (MOD-FETs) and optical waveguides. Significant Ge fractions ( $x \geq 0.50$ ) are necessary for efficient infrared detection of 1.3 and 1.55  $\mu\text{m}$  light for fiber optic communication. Low dislocation density  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y/\text{Si}$  pin photodiodes with  $x = 0.60$  have been fabricated with external quantum efficiencies of 1% at 1.3  $\mu\text{m}$  [11]. Higher Ge concentrations are expected to increase the quantum efficiency due to the corresponding decrease in bandgap. Adding small amounts of carbon to epitaxial germanium may reduce the total defect density associated with lattice mismatch, surface roughness and interfacial defects during the heteroepitaxy of germanium-rich alloys on silicon. Fukami [12] reported a 6-fold decrease in reverse leakage current with implantation of C atoms in SiGe/Si heterostructure diodes. The decrease in leakage current was attributed to improvement in crystalline quality due to C doping. Band structure modifications by alloying carbon with germanium may be possible as has been demonstrated for  $\text{Si}_{1-y}\text{C}_y$  and  $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$  alloys

\* Corresponding author. Tel.: +1 302 8318959; fax: +1 302 8314316; e-mail: dashie@ee.udel.edu

[13]. Strained two-dimensional  $\text{Ge}_{1-y}\text{C}_y$  layers with enhanced C solubility ( $y = 0.01$ ) grown on Si(100) in the presence of surfactants have been demonstrated by MBE [10].

Vital to the success of any new semiconductor material is the ability to precisely control the carrier concentrations by introducing dopant atoms. We are unaware of any experimental study of n-type doping in  $\text{Ge}_{1-y}\text{C}_y$  epitaxial films on Si(100). We report on the electrical and optical properties of P-doped ( $N_D \sim 10^{18} - 10^{20} \text{ cm}^{-3}$ )  $\text{Ge}_{1-y}\text{C}_y$  epitaxial layers grown by MBE on Si(100) substrates. High doping levels such as these are necessary for development of such devices as the  $\text{Ge}_{1-y}\text{C}_y$  Esaki tunneling diode on Si. Of the group IV elements, Ge Esaki diodes exhibit the highest peak to valley current and packaged configurations exhibit switching speeds as high as 22 ps. Germanium Esaki diodes are not monolithically integrated into silicon based technology due to the large lattice mismatch between the two elements.

## 2. Experimental

In this paper we discuss the results of in situ phosphorus doping of epitaxial  $\text{Ge}_{1-y}\text{C}_y$  films grown on Si(100) substrates. Samples were grown on 7.6-cm Si(100) substrates in an EPI-620 MBE chamber [3]. Pure Ge samples were epitaxially grown under equivalent conditions for comparison. All samples were grown at a substrate temperature of 400°C. Sharp streaks on the reflection high energy electron diffraction (RHEED) screen indicated a flat, single crystalline surface.

Zone refined germanium was thermally evaporated, at 0.20 Å/s, from a pyrolytic boron nitride (pBN) crucible contained in a standard EPI effusion cell. Carbon was introduced into the molecular beam by passing current through a high purity, pyrolytic-graphite filament. Phosphorus doping was achieved by in situ evaporation of GaP from a pBN crucible at temperatures from 650 to 750°C with  $\text{P}_2$  being the dominant species in the beam [14]. A pBN gettering module is employed to minimize residual gallium in the beam. The epitaxial layers were 1  $\mu\text{m}$  in thickness. Previous work has shown that thick Ge on Si grown at 400°C demonstrates a low density of defects at the surface, determined by etch pit densities and spectroscopic ellipsometry [15].

Secondary ion mass spectrometry (SIMS) using a CAMECA 4f-sector magnet (Charles Evans and Associates) measured the phosphorus content and many other residual elements associated with the sources and their respective crucibles. A 14.5-KeV Cs primary beam was used for Si, Ge and P and an 8.0-KeV  $\text{O}_2$  beam was used to measure the B and Ga concentrations. Phosphorus levels varied from  $10^{18}$  to  $10^{20} \text{ cm}^{-3}$ . Concentrations of boron from the pBN crucible were less than  $10^{16} \text{ cm}^{-3}$ , the detection limit of the measurement. Due to insufficient gettering of Ga from the GaP sublimation cell, a significant concentration of Ga was incorporated into the epitaxial layer (between  $1 \times 10^{16} \text{ cm}^{-3}$  and  $1 \times 10^{17} \text{ cm}^{-3}$ ), similar to previous studies for SiGe

MBE [16]. Carbon concentrations were estimated from X-ray rocking curves of the (004) symmetric and (224) and (511) asymmetric reflections. Rutherford backscattering spectrometry using a 4.23-MeV  $^4\text{He}^{++}$  ion beam detected C signal near the detection limit of the system ( $\leq 0.003$ ). The C concentration estimated by the relaxed lattice parameter of the  $\text{Ge}_{1-y}\text{C}_y$  layer is  $y \sim 0.001$ . Room temperature infrared absorption spectroscopy did not reveal an absorption mode attributed to substitutional C in Ge. This mode was observed by Hoffman [8] for  $y \sim 0.007$  using low temperature (9 K) infrared spectroscopy. The small C concentration and thickness for our samples may however, produce vibrational signal below the room temperature sensitivity of our instrument.

Optical transmission of the epitaxial layers was measured with a Nicolet 740 Fourier transform infrared spectrometer (FTIR). Absorption due to the Si substrate was corrected by subtracting the absorption spectra of a reference Si substrate. Hall effect measurements of P-doped epitaxial  $\text{Ge}_{1-y}\text{C}_y$  and Ge layers were carried out using a standard van der Pauw structure under a magnetic field of 3.3 kG. Measurements were taken for two polarities of magnetic fields to eliminate the misalignment voltage of the Hall contacts.

## 3. Results

### 3.1. Carrier concentration and Hall effect

SIMS measurements revealed that phosphorus concentrations ranged from  $10^{18}$  to  $10^{20} \text{ cm}^{-3}$ . Phosphorus concentrations for epitaxial  $\text{Ge}_{1-y}\text{C}_y$  and Ge layers did not differ for equivalent P cell temperatures. This indicates that small C fractions do not affect the incorporation of P into the grown layer. Electron concentrations measured by the Hall effect correlated well with SIMS, indicating the complete activation of P donors for both  $\text{Ge}_{1-y}\text{C}_y$  and Ge epitaxial layers. We can conclude that P incorporates on substitutional sites during  $\text{Ge}_{1-y}\text{C}_y$  and Ge epitaxial growth, i.e. for small amounts, C is electrically neutral in  $\text{Ge}_{1-y}\text{C}_y$ . Faschinger [17] demonstrated for  $\text{Si}_{0.99}\text{C}_{0.01}$  alloys that the incorporation and activation of extrinsic donors (Sb) is very similar to that in pure Si. Their group also demonstrated the important result that electron mobility in strained  $\text{Si}_{1-y}\text{C}_y$  with  $N_D \sim 10^{16} \text{ cm}^{-3}$  is not limited by scattering at lattice deformations induced by C, but rather by ionized impurity scattering.

Fig. 1 shows the room temperature Hall mobility for Ge and  $\text{Ge}_{1-y}\text{C}_y$  layers for two different donor concentrations. An increase in the room temperature mobility is observed for heteroepitaxial  $\text{Ge}_{1-y}\text{C}_y$  films compared to Ge films grown under equivalent conditions. X-ray diffraction of the epitaxial layers revealed an average decrease of 30% of the full width at half maximum (FWHM) for  $\text{Ge}_{1-y}\text{C}_y$  compared with Ge suggesting a reduced defect density for

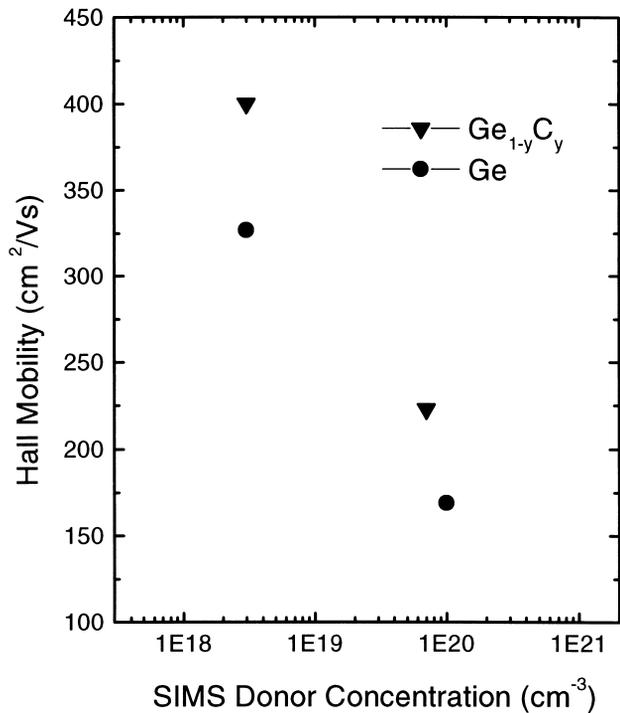


Fig. 1. Hall mobility of phosphorus doped Ge<sub>1-y</sub>C<sub>y</sub> (▼) and Ge (●) epitaxial layers on Si(100) at 296 K.

Ge<sub>1-y</sub>C<sub>y</sub> epitaxial layers. The findings of Fukami [12] and Shao [18] describing the reduced reverse leakage current and increased reverse breakdown voltages for Si<sub>1-x-y</sub>Ge<sub>x</sub>C<sub>y</sub> and Ge<sub>1-y</sub>C<sub>y</sub> diodes with introduction of C support this observation.

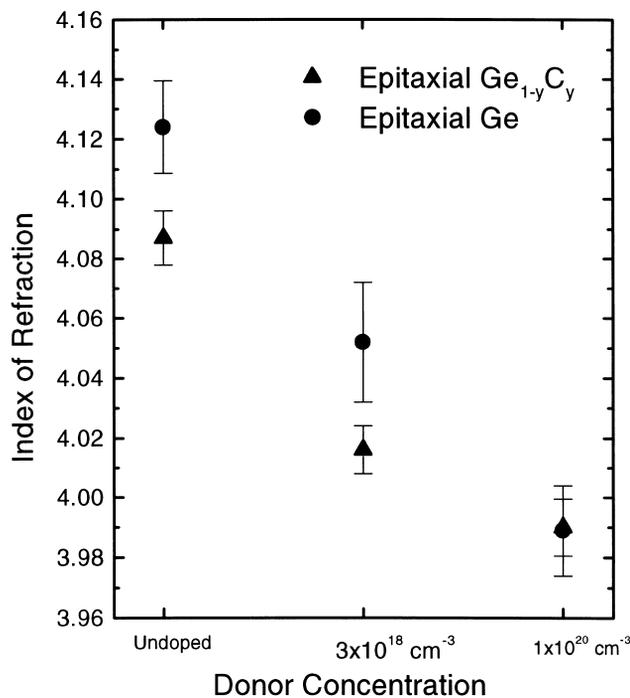


Fig. 2. Refractive index versus donor concentration for Ge<sub>1-y</sub>C<sub>y</sub> (▲) and Ge (●) epitaxial films on Si(100). The refractive index was computed from the interference fringes of the transmission spectrum.

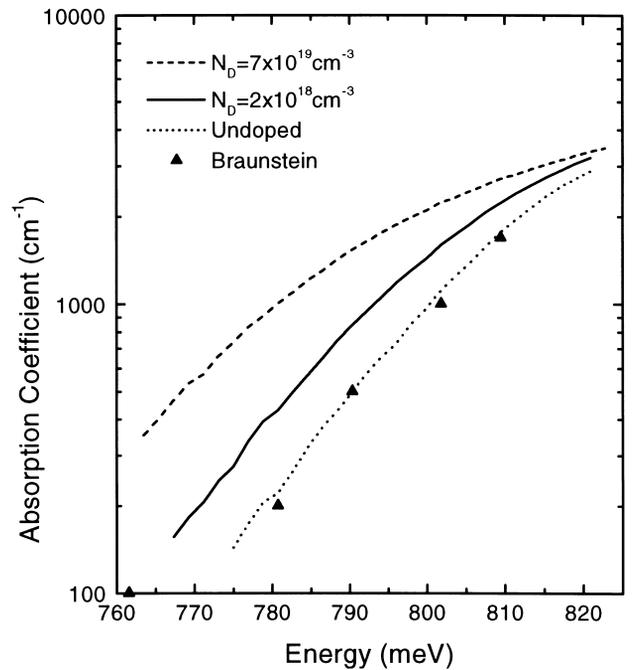


Fig. 3. Absorption coefficient versus photon energy of Ge<sub>1-y</sub>C<sub>y</sub> layers on Si(100) for  $N_D = 7 \times 10^{19} \text{ cm}^{-3}$  (dashed line),  $N_D = 2 \times 10^{18} \text{ cm}^{-3}$  (straight line) and undoped (dotted line). Included are values for intrinsic bulk Ge [22].

### 3.2. Optical transmission

Transmission spectroscopy was performed in the visible and infrared regions to observe the near band edge absorption spectra and free carrier absorption of the epitaxial films. For energies below the bandgap the optical constants and thickness of the epitaxial layers were determined by curve fitting interference fringes resulting from multiple reflections at the air/film and film/substrate interface [19].

By fitting the measured transmission spectra of the Ge<sub>1-y</sub>C<sub>y</sub> and Ge films in the region of 560–700 MeV we determined the thickness of the epitaxial film and the index of refraction at energies near the bandgap. Fig. 2 shows the index of refraction of the epitaxial Ge<sub>1-x</sub>C<sub>x</sub> as a function of donor concentration and compares them to Ge epitaxial layers grown under identical conditions. Introducing carbon into epitaxial Ge films doped with P decreases the refractive index near the absorption edge.

Absorption coefficients above the band edge were computed from the measured transmission spectra and the optical constants as described in reference [20]. Fig. 3 illustrates the absorption coefficients ( $\alpha$ ) of phosphorus doped Ge<sub>1-y</sub>C<sub>y</sub> films grown epitaxially on Si(100) for  $\alpha > 100 \text{ cm}^{-1}$ . The absorption edge experiences a red shift with increasing phosphorus concentrations for both Ge<sub>1-y</sub>C<sub>y</sub> and Ge films. Included in the graph is published data on high purity Ge [21]. Note that undoped Ge<sub>1-y</sub>C<sub>y</sub> epitaxial layers exhibit the same absorption coefficient as does intrinsic bulk germanium for  $\alpha > 100 \text{ cm}^{-1}$ , thus a significant band structure modification was not observed by optical absorption for these C concentrations. Because of the thickness of the epi-

taxial layers, absorption coefficients less than  $100 \text{ cm}^{-1}$  can not be accurately measured, thus the minimum indirect energy gap was not determined by this method. The absorption coefficient of Ge for  $\alpha > 100 \text{ cm}^{-1}$  is expected to have transition contributions from the direct conduction band valley at  $\Gamma$  and from indirect valleys at L and X. Our results are consistent with those of Pankove [22] who reported a shrinkage of the energy gaps at  $k = (111)$  and the direct valley at  $k = (000)$  with heavy doping of bulk Ge.

### 3.3. Free carrier absorption

Absorption coefficients of phosphorus doped  $\text{Ge}_{1-y}\text{C}_y$  and Ge epitaxial layers were calculated in the regions from 2.5 to 25  $\mu\text{m}$  from transmission data. Free carrier absorption of heavily doped  $\text{Ge}_{1-y}\text{C}_y$  and Ge layers follows a wavelength dependence of  $\alpha \sim \lambda^{3.1}$  for  $N_D \sim 10^{20} \text{ cm}^{-3}$ . For lighter doping a weak wavelength dependence was observed for both materials. No significant change was observed with the addition of C. This behavior supports the observation that C is electrically neutral in Ge and does not change the dominant room temperature scattering mechanism.

### 3.4. Conclusions

Optical and electronic properties of epitaxial  $\text{Ge}_{1-y}\text{C}_y$  layers on Si(100) Si were investigated and compared with epitaxial Ge on Si. SIMS and Hall effect analysis indicate that C does not affect the incorporation of P into the film and that C is electrically neutral in  $\text{Ge}_{1-y}\text{C}_y$  for  $y \sim 0.001$ . Full activation of P donors is observed by close agreement between SIMS and electron concentration measurements. X-ray and high energy electron diffraction indicate a single crystalline structure. A decrease in the bulk lattice constant compared to pure Ge was observed with the addition of carbon ( $y \sim 0.001$ ). A strong alloying effect due to C was not observed in the optical absorption of  $\text{Ge}_{1-y}\text{C}_y$  for  $\alpha \geq 100 \text{ cm}^{-1}$ , although a decrease in the index of refraction may indicate a change in the dielectric properties with addition of C. We conclude that small alloy concentrations of C during the heteroepitaxial growth of  $\text{Ge}_{1-y}\text{C}_y$  on Si have enhanced the electronic properties of epitaxial  $\text{Ge}_{1-y}\text{C}_y$ . Initial results indicate that the enhancement may be due to

a change in the structural properties of the heteroepitaxial layer due to carbon, rather than a modification of the band structure. These results indicate that  $\text{Ge}_{1-y}\text{C}_y/\text{Si}$  heteroepitaxy is an interesting new material system that may be applicable for optoelectronic device applications, particularly for infrared detection at 1.3 and 1.55  $\mu\text{m}$ .

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