

REPORT DOCUMENTATION PAGE		Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.			
1. AGENCY USE ONLY (Leave blank)		3. REPORT TYPE AND DATES COVERED FINAL 1 Sep 93 - 31 Aug 94	
2. REPORT DATE		5. FUNDING NUMBERS 61102F 2305/FS	
4. TITLE AND SUBTITLE SiGeC Alloys for Optoelectronic Devices		6. AUTHOR(S) James Kolodzey	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Dept of Electrical Eng Univ of Delaware Newark, DE 19716		8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-95-0282	
9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NE 110 Duncan Avenue Suite B115 Bolling AFB DC 20332-0001		10. SPONSORING MONITORING AGENCY REPORT NUMBER AFOSR-91-0370	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED		12b. DISTRIBUTION CODE DTIC SELECTED JUN 19 1995 F	
13. ABSTRACT INFORMATION SEE FINAL REPORT ABSTRACT 19950615 075 DTIC QUALITY INSPECTED 8			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UNCLASSIFIED

SiGeC Alloys for Optoelectronic Devices

1993-1994 Annual Technical Report for Contract AFOSR-91-0370

Air Force Office of Scientific Research/NE

110 Duncan Avenue

Bolling AFB, DC 20332-0001

Attn: Lt. Col. Gernot S. Pomrenke

James Kolodzey

Department of Electrical Engineering

University of Delaware

140 Evans Hall

Newark, DE 19716

(302) 831-1164

FAX: (302) 831-4316

Internet: kolodzey@ee.udel.edu

Accession For	
NTIS CRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

This third annual technical report covers the time period from 1 September, 1993 to 31 August, 1994.

1 Growth of SiGeC Alloys

$\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$, alloys have been actively investigated for use in heterojunction devices compatible with Si. Using the following values for the lattice constants of Si, Ge and C: $a_{\text{Si}} = 0.357 \text{ nm}$, $a_{\text{Ge}} = 0.357 \text{ nm}$ and $a_{\text{C}} = 0.357 \text{ nm}$, and assuming Vegard's Law, we obtain the condition on the ratio of Ge and C atomic fractions for lattice-matching to Si: $x/y = 8.2$. For $\text{Ge}_{1-y}\text{C}_y$, binary alloys, the composition $\text{Ge}_{0.89}\text{C}_{0.11}$ is predicted to be lattice-matched to Si.

In thermodynamic equilibrium, the solid solubility of C in Ge has been estimated to be less than 10^{19} cm^{-3} . Metastable alloys, however, can be successfully prepared by molecular beam epitaxy (MBE) at relatively low growth temperatures. Our $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys were grown in an EPI 620 MBE system having six effusion cell ports and a substrate introduction chamber. The growth chamber base pressure was below 5×10^{-11} Torr. During growth a liquid He-cooled cryopump and an ion pump were used and the typical chamber pressure was 5×10^{-9} Torr. A chilled mixture of ethylene glycol and water continually circulated in the growth chamber cryopanel to avoid thermal cycling which could loosen flakes of dust from the residues of previous growths and thus contaminate growing layers.

The Si source used a novel crucible of TiB_2 ceramic coated on the outside with W, and used in a high temperature effusion cell. The intention was to avoid possible irradiation damage during electron beam evaporation. The Ge molecular beam was produced by thermal evaporation from a solid source of zone-refined polycrystalline Ge loaded into a pyrolytic boron nitride crucible. To avoid contaminating the Ge with B from the crucible, cell temperatures were kept below 1380°C . At a cell temperature of 1350°C , the Ge growth rate was $0.07 \mu\text{m/hr}$. The C beam was produced by sublimation from a pyrolytic graphite filament which was resistively heated by direct current. The temperature of the C filament was calculated from the dissipated power based on the Stefan-Boltzmann Law ($P = \sigma T^4$) for blackbody radiation and a value of $\sigma = 5.67 \times 10^{-12} \text{ W cm}^{-2} \text{ K}^{-4}$ for C. For our serpentine-shaped filament having a resistance of 0.2Ω , a current of 38 A gave a temperature of 2030°C and an effective C growth rate of $0.01 \mu\text{m/hr}$.

Substrates were (100) oriented, 75mm diameter Si wafers prepared by degreasing, followed by cleaning in a (5:3:3), solution of $\text{H}_2\text{O} : \text{H}_2\text{O}_2 : \text{HCl}$, and then a (1:10) $\text{HF} : \text{H}_2\text{O}$ dip to terminate the surface with H. Alloy films were deposited at substrate temperatures of 400°C and 600°C . During growth of the Ge-C alloy, the reflection high energy electron diffraction (RHEED) pattern indicated flat layers and the resulting Ge-C film surface morphologies appeared specular.

Transmission electron microscopy (TEM) of the layer-substrate interface showed misfit dislocations which accommodate the lattice mismatch so that the bulk regions of the layer and the substrate are strain-free. We concluded that the alloys were grown thick enough to be strain-free so that properties such as the lattice constant and the bandgap have relaxed to

their bulk values.

2 Alloy Characterization

Compositions were determined by a variety of techniques including Auger electron spectroscopy (AES), He^+ Rutherford backscattering spectrometry (RBS), and growth conditions calibrated to the variation of vapor pressure versus temperature. The compositions obtained by the different techniques agreed to within ± 0.01 in atomic fractions.

Structure was measured by X-ray diffraction (XRD) at room temperature using a Philips vertical $\Theta - 2\Theta$ diffractometer and $\text{Cu K}\alpha$ radiation. X-ray line positions were determined by fitting measured diffraction peaks to a Pearson VII function for the $\text{Cu K}\alpha_1/\text{Cu K}\alpha_2$ doublet, and applying corrections obtained from the observed (400) Si substrate reflection and including the effects of radial displacement caused by the film thickness. Applying Bragg's Law to the XRD measurements gave lattice constants which were slightly smaller than for pure Ge due to the incorporated Si and C.

Table I. Measured properties including sample number, composition, lattice constant a , bandgap E_g , and layer thickness t measured by optical interference. The calculated minimum bandgaps, $E_g(\text{calc})$, were determined by linear interpolation versus composition of the Γ , X , and L bands (as in Figure 2), are for comparison. T_{sub} is the substrate growth temperature.

Sample	Composition	a (nm)	E_g (eV)	t (μm)	$E_g(\text{calc})$ (eV)	T_{sub} ($^{\circ}\text{C}$)
SGC-19	$\text{Si}_{0.08}\text{Ge}_{0.90}\text{C}_{0.02}$	0.56348	1.046	0.49	1.024	400
SGC-20	$\text{Si}_{0.08}\text{Ge}_{0.91}\text{C}_{0.01}$	0.56394	0.998	0.47	0.917	400
SGC-30	$\text{Ge}_{0.98}\text{C}_{0.02}$	0.56544	0.732 eV	0.582	0.87	600
SGC-31	$\text{Ge}_{0.94}\text{C}_{0.06}$	0.56539	0.782 eV	0.139	1.2	600

SiGeC alloys are attractive because their lattice constants, energy gaps (E_g 's) and conduction and valence band offsets (ΔE_V and ΔE_C , respectively), vary over the full range of

compositions. The optical absorption at photon energies near the bandgap was measured at room temperature by Fourier Transform Infrared Spectroscopy (FTIR) in the transmission mode. Figure 1 shows a blue shift in the absorption coefficient α versus photon energy with increasing C atomic fraction corresponding to an increase in the energy gap E_g . Interference effects made it difficult to observe changes in the slope of α at low values so we estimated the bandgap E_g as the energy at which $\alpha = 0.5 \text{ cm}^{-1}$, which gives E_g for Ge. The bandgaps given in Table I *exceed* that of Ge and this is attributed to the alloy-effect of substitutional C rather than to the effects of strain which *reduce* E_g [9].

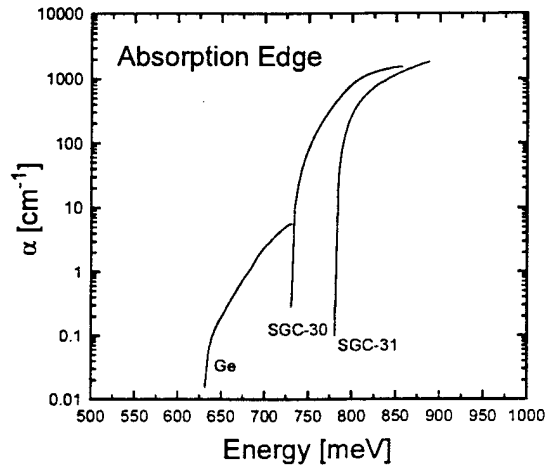


Figure 1: Measured values of optical absorption coefficient α versus photon energy $h\nu$ for samples SGC-30 ($Ge_{0.98}C_{0.02}$), and SGC-31 ($Ge_{0.94}C_{0.06}$) compared with that of a crystalline Ge wafer. Larger fractions of C shift the absorption edge to higher energies implying that C is alloying with the Ge.

The measured bandgaps were smaller than expected from a linear interpolation of the measured compositions, Ge and C, as shown in Figure 2. The reason for the disagreement may be either that the atomic fraction of *substitutional* C is smaller than the total fraction, or that the dependence of bandgap versus composition is strongly non-linear. We conclude that the bandgaps and lattice constants of the alloys have a weak dependence on the atomic fraction.

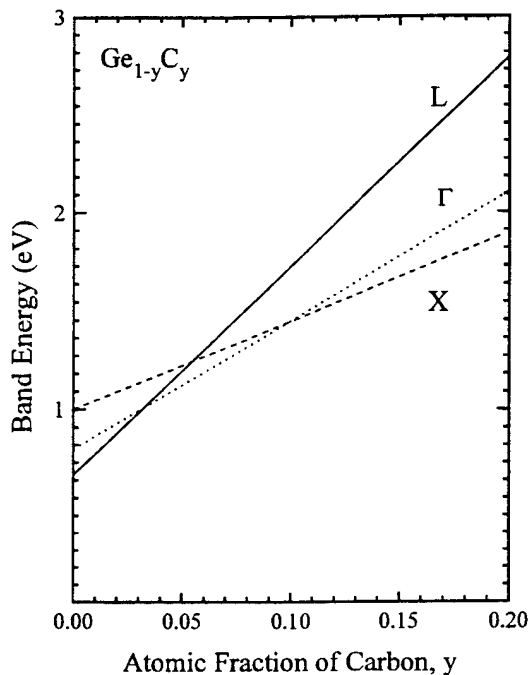


Figure 2: Theoretical values of conduction band critical energies by linear extrapolation from critical energies measured for Ge and C(diamond). The direct bandgap for C atomic fractions in the range $0.03 \leq y \leq 0.1$ is an unexpected result that may have a tremendous impact on optical emitters compatible with Si.

We have observed photoluminescence (PL) from SiGeC and GeC alloys over a range of temperatures as an indication of the quality of our MBE material. An example of our PL capability is shown in Fig. 3 for the case of $\text{Si}_{0.08}\text{Ge}_{0.9}\text{C}_{0.02}$ on Si (SGC-19) at 11 K. The high energy peak appears to be attributed to the no-phonon (NP) emission of the bulk alloy. It occurs at 1.0458 eV with a full width at half maximum (FWHM) of 2.7 meV. The lower energy peaks are 42 meV, 60 meV and 101 meV below the NP peak, and are likely due to transverse optical (TO) phonon replicas from $X_{\text{Ge-Ge}}^{\text{TO}}$, and $X_{\text{Si-Si}}^{\text{TO}}$, and $X_{\text{C-C}}^{\text{TO}}$, respectively. The labeling of the $X_{\text{C-C}}^{\text{TO}}$ is tentative at this time, but is higher in energy than known SiGe TO phonon replicas, and therefore most likely due to a carbon complex.

The University of Delaware has developed an expertise in the characterization of $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloys using PL. The PL setup uses a 200 mW air-cooled argon ion laser for photoexcitation, an open-cycle cryostat which allows temperature control from 4.2 K to above room tempera-

ture, and a 1 meter spectrometer for high resolution of radiative transitions. Detection of the PL signal uses a liquid nitrogen-cooled Ge detector (North Coast, long time constant) with internal amplifier circuitry, a chopper and lock-in amplifier for increased signal-to-noise ratio, and an IEEE interface with a 386-based personal computer for data acquisition. Data can be downloaded to a SUN workstation network for data manipulation, archival storage and plotting.

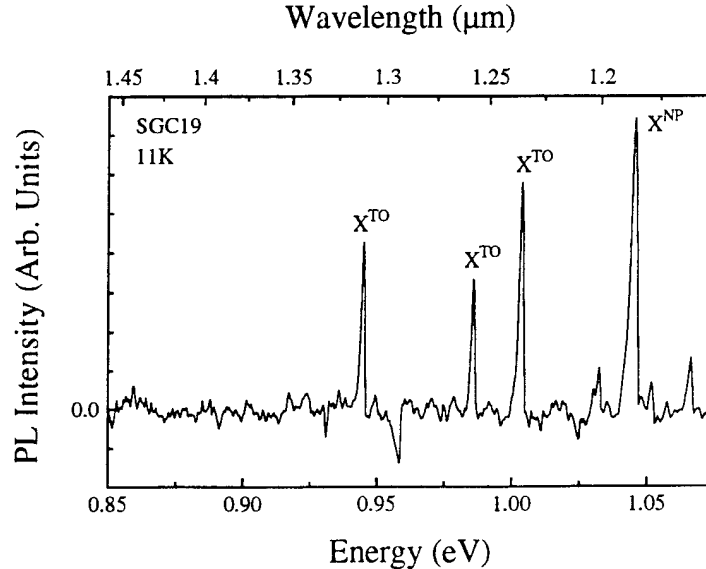


Figure 3: Photoluminescence measured at 11 K of MBE-grown alloy on Si substrate: $\text{Si}_{0.08}\text{Ge}_{0.9}\text{C}_{0.02}$ (SGC 19). Intensity peaks were attributed to no-phonon (NP) exciton recombination and to associated optical phonon (TO) replicas at lower energies. Measurements made in collaboration with Prof. P. Berger.

3 Energy Band Offsets

We have begun measurements of the valence band offsets of SiGeC alloys using X-ray photoelectron spectroscopy (XPS) which is widely considered to be the most accurate and least ambiguous technique. These offsets are not yet known for SiGeC alloys.

Since X-ray photoelectron spectroscopy gives information about both the valence band and

the core electron levels, by correlating the two it is possible to calculate the band offset. Our approach is to obtain high resolution spectra of the valence band and the core levels. Any of the core level peaks can be used for this purpose, i.e., Si, Ge, or C. Both Ge and Si core levels are well defined and conveniently identifiable whereas C levels are complicated by adventitious C that is inevitably present on the surfaces of samples. The difference in the valence band maximum, E_V , and the core level, E_{CL} , will be measured for each of the samples. The valence band maximum itself can be easily identified by comparing the XPS results with the theoretically calculated density of states (using the muffin-tin orbital method and density functional theory) [7]. The differences between the core levels ΔE_{CL} on the heterojunctions of SiGeC alloys with Si can then be measured. The valence band discontinuity can then be calculated by:

$$\Delta E_V = (E_V - E_{CL})_{SiGeC} - (E_V - E_{CL})_{Si} + \Delta E_{CL} \quad (1)$$

From the change in the optical band gap ΔE_g versus composition, obtained from optical transmission measurements, the conduction band offset (ΔE_C) for the samples can be calculated:

$$\Delta E_C = \Delta E_g - \Delta E_V. \quad (2)$$

4 Summary

1. We have designed, purchased and installed an MBE system for growing the ternary alloy: $Si_{1-x-y}Ge_xC_y$,
2. We have designed, installed, and tested software for a PC computer system to control MBE growth conditions, including shutter position, and temperature.
3. We have found that the non-equilibrium, low temperature growth conditions of molecular beam epitaxy can produce crystalline $Si_{1-x-y}Ge_xC_y$ alloys in which the C and Ge atoms are substitutional on silicon lattice sites oriented to the (100) Si substrate,
4. We have also grown the binary alloy GeC,
5. We have measured the lattice constant of the alloys by X-ray diffraction (XRD),

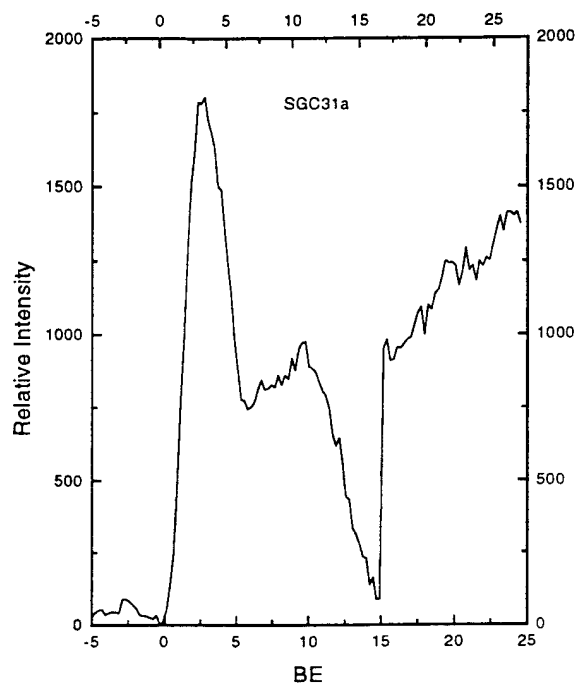


Figure 4: Valence band density of states versus binding energy in eV (extending below valence band edge) of sample SGC-31 ($Ge_{0.94}C_{0.06}$) measured by X-ray photoelectron spectroscopy (XPS). The band edges and core levels can be obtained by fitting DOS features to known critical points. Measurements were made in collaboration with Dr. S. Ismat Shah.

6. We have found that the addition of C to Ge shifts the absorption edge to higher energies,
7. In collaboration with Dr. S.S. Iyer at IBM, we have been measuring the optical bandgap of SiGeCSn alloys,
8. In collaboration with Prof. Paul Berger, we have begun photoluminescence (PL) and transmission electron microscopy (TEM) studies,
9. We have found that SiGeC has strong PL at 11 K, with sharp distinct peaks comparable to the best results obtained with SiGe alloys grown by the CVD technique,
10. In collaboration with Dr. S. Ismat Shah of DuPont Corp., we have begun to measure the band offsets in SiGeC and GeC alloys using X-ray photoelectron spectroscopy (XPS),

We gratefully acknowledge P. Berger for TEM, G. DeSalvo for MBE design and instrumentation, J. Kramer for AES, and S.I. Shah for X-ray photoelectron spectroscopy.

5 Publications

Due to the time spent on extensive equipment building in our start-up effort, we have only recently begun submitting publications to refereed journals. We realize the importance of publishing and have begun working on manuscripts as the following list shows.

1. J. Kolodzey, J. Krajewski, R. Shekhar, M. Barteau, R. Schwarz, T. Muschik, F. Wang, R. Plaettner, and E. Guenzel, "Optoelectronic properties of amorphous SiGeC:H alloys," *Amorphous Silicon Technology - 1992*, A. Madan, Y. Hamakawa, M. Thompson, E.A. Schiff, and P.G. LeComber, eds., *Mat. Res. Soc. Symp. Proc.*, vol. 258, pp. 637-642, 1992.
2. J. Kolodzey, S. Zhang, P. O'Neil, E. Hall, R. McAnnally, and C.P. Swann, "Growth of GeC alloys by molecular beam epitaxy," *Proc. 5th Int. Conf. on Silicon Carbide and Related Materials*, Washington, DC, 1993, *Inst. Phys. Conf. Ser. No. 137*, Chapter 3, pp. 357-360.
3. J. Kolodzey, P.A. O'Neil, S. Zhang, B. Orner, K. Roe, J. Pickett, D. Hits, F. Chen, P. Berger, A. Khan, X. Shao, S.I. Shah, M. Waite, C.P. Swann, and K.M. Unruh, "Growth and properties of SiGeC alloys," *1994 North American Conference on Molecular Beam Epitaxy*, Urbana, IL, to be presented, October, 1994.
4. J. Kolodzey, P. A. O'Neil, S. Zhang, B. Orner, K. Roe C. P. Swann and K. M. Unruh "Growth of Germanium-Carbon Alloys on Silicon Substrates by Molecular Beam Epitaxy," to be submitted to *Phys. Rev. Lett.*, 1994.
5. J. Kolodzey, P. Berger, P.A. O'Neil, S. Zhang, B. Orner, A. Khan, and X. Shao, and K.M. Unruh, "The Molecular Beam Epitaxy of SiGeC Alloys on Si Substrates," to be submitted to *Appl. Phys. Lett.*, 1994.
6. J. Kolodzey, P.A. O'Neil S. Zhang, B. Orner, F. Chen, P. Thompson, P. Colombo, "The Growth of Silicon by Molecular Beam Epitaxy Using a Solid Source Thermal Effusion

Cell," in preparation, 1994.

7. J. Kolodzey, B. Orner, P.A. O'Neil, "Cracking pattern of C evaporated from a hot filament," in preparation, 1994.
8. J. Kolodzey, B. Orner, F. Chen, M. Waite, S.I. Shah, "Valence Band Alignments in SiGeC and GeC Alloys," in preparation, 1994.
9. J. Kolodzey, B. Orner, K. Unruh, "Interdiffusion in annealed GeC/Si Superlattices," planned, 1994.

6 Bibliography of Recent SiGeC Publications

1. R.A. Soref, Proc. IEEE **81**, 1687 (1993).
2. A.R. Powell and S.S. Iyer, Jpn. J. Appl. Phys. **33**, 2388 (1994).
3. Z. Altzman, A.E. Blair, E.J. Jaquez, J.W. Mayer D. Chandrasekhar, D.J. Smith, R.L. Hervig, and McD. Robinson, Appl. Phys. Lett. **65**, 2559 (1994).
4. P. Boucaud, C. Francis, F.H. Julien, J.-M. Lourtioz, D. Bouchier, S. Bodnar, B. Lambert, and J.L. Regolini, Appl. Phys. Lett. **64**, 875 (1994).
5. B. Dietrich, H.J. Osten, H. Rücker, M. Methfessel, and P. Zaumseil, Phys. Rev. B **49**, 17185 (1994).
6. S. Im, J. Washburn, R. Gronsby, N.W. Cheung, K.-M. Yu and J.W. Ager, Appl. Phys. Lett. **63**, 2682 (1993).
7. G. He, M.D. Savellano, and H.A. Atwater, Appl. Phys. Lett. **65**, 1159 (1994).
8. J. Weber and M.I. Alonso, Phys. Rev. B **40**, 5683 (1989).
9. J. Kolodzey, S. Zhang, P. O'Neil, E. Hall, R. McAnnally, and C.P. Swann, *Inst. Phys. Conf. Ser. No. 137, 1993*, Chap. 3, p. 357.
10. P.E. Thompson, M.E. Twigg, D.J. Godbey, K.D. Hobart, and D.S. Simons, J. Vac. Sci. Technol. B **11**, 1077 (1993).

11. H.J. Osten, E. Bugiel, and P. Zaumseil, *J. Crystal Growth* **142**, 322 (1994).
12. J.W. Strane, H.J. Stein, S.R. Lee, B.L. Doyle, S.T. Picraux, and J.W. Mayer, *Appl. Phys. Lett.*, **63**, 2786 (1993).
13. P. Boucaud, C. Francis, F.H. Julien, J.M. Lourtioz, D. Bouchier, S. Bodnar, B. Lambert, and J.L. Regolini, "Band-edge and deep level photoluminescence of pseudomorphic $Si_{1-x-y}Ge_xC_y$ alloys," *Appl. Phys. Lett.*, vol. 64, pp. 875-877, 1994.
14. J.L Regolini, F. Gisbert, G. Dolino, and P. Boucaud, "Growth and characterization of strain compensated $Si_{1-x-y}Ge_xC_y$ epitaxial layers" *Materials Letters*, vol. 18, pp. 57-60, 1993.
15. J.L Regolini, S. Bodnar, J.C. Oberlein, F. Ferrieu, M. Gauneau, and B. Lambert, "Strain compensated heterostructures in the $Si_{1-x-y}Ge_xC_y$ ternary system," *American Vacuum Society Meeting*, 1993.
16. A. Gupta, Yao-Wu Cheng, Jianmin Qiao, M.Mahmudur Rahman, Cary Y. Yang, Seongil Im, Nathan W. Cheung, and Paul K.-L. Yu "Characterization of Ge and C implanted SiGe and SiGeC layers," *Materials Research Society Symposium Proceedings*, v. 298, 1993, p. 135-138.