



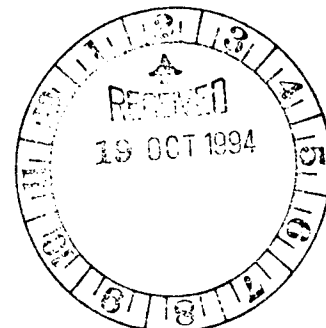
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# EPITAXIAL GROWTH AND CHARACTERIZATION OF $\text{Si}_{1-x}\text{Ge}_x$ MATERIALS AND DEVICES

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## 1. INTRODUCTION

The current program of research was aimed at understanding the issues related to growth and doping of SiGe/Si heterostructures by gas-source MBE, studying the transport properties of the alloys, determining the fundamental material parameters and designing and demonstrating electronic and optoelectronic devices. The specific electronic device is the HBT with high Ge-containing base layers, and the optoelectronic devices are detectors, photoreceivers, and electro-optic modulators. The overall objective is to demonstrate, reliably and reproducibly, the feasibility of integrating SeGe-based optoelectronics with Si-based VLSI technology. We summarize below some of the highlights of the program related to work done in the last year.

## 2. INTERACTION WITH MATERIALS RESEARCH LABORATORY AND WRIGHT LABORATORY, WRIGHT-PATTERSON AFB

We have two ongoing collaborations with researchers in these Laboratories.

1. We have provided devices to Drs. W. C. Mitchel and K. Smith for DLTS and admittance spectroscopy measurements. This joint collaboration resulted in some of the earliest measurement of heterojunction offsets in SiGe/Si and the first determination of deep levels in undoped SiGe alloys.
2. We have grown SiGe/Si superlattices for Dr. M. O. Manasreh for the development of far-infrared detectors. This work is in progress.

## 3. DESCRIPTION OF WORK DONE

The objectives of the current program have been to establish a reliable and reproducible technique for the epitaxy of SiGe alloys (which provides controlled thickness, interfaces, doping levels and doping profiles) and to determine some key electronic and optoelectronic properties of the material for device applications. In the following we will briefly discuss the principal findings of our studies.

### 3.1 EPITAXIAL GROWTH OF SiGe/Si AND GROWTH MODELING

While growth techniques such as ultra high vacuum/chemical vapor deposition (UHV/CVD)<sup>[6]</sup> and rapid thermal chemical vapor deposition (RTCVD)<sup>[7]</sup> have been developed to produce epitaxial  $\text{Si}_{1-x}\text{Ge}_x$  materials, molecular beam epitaxy (MBE)<sup>[8]</sup> is one of the more common techniques to synthesize heterojunction structures with abrupt interfaces. The major difference among these techniques, besides the apparatus used, are the silicon and germanium sources used and the chamber pressures during growth. In RTCVD, dichlorosilane ( $\text{SiH}_2\text{Cl}_2$ ) and germane ( $\text{GeH}_4$ ) are used and the growth pressure is between 1–10 Torr. In UHV/CVD, silane ( $\text{SiH}_4$ ) and  $\text{GeH}_4$  are the sources and the growth pressure ranges from  $10^{-3}$  to  $10^{-1}$  Torr. Molecular beam epitaxy normally uses elemental silicon and germanium sources.

We have studied the MBE growth of SiGe/Si layers using disilane ( $\text{Si}_2\text{H}_6$ ) and elemental Ge for the first time. For a fixed flow rate of  $\text{Si}_2\text{H}_6$ , the functional dependence of germanium content in the  $\text{Si}_{1-x}\text{Ge}_x$  alloys and the germanium cell temperature has been established. Heterostructures and multi-quantum wells with good surface morphology, excellent crystalline quality, and abrupt interfaces are demonstrated, indicating little or no source-related transient effects. Double-crystal x-ray diffraction rocking curves show strong Pendelung oscillations suggesting that the layers are pseudomorphic and of good crystalline quality. A SIMS study confirms that multi-quantum wells with abrupt interfaces can be grown. The surface morphology of the grown layers is nearly featureless. Some characteristics of the grown layers are shown in Figs. 1–4.

#### 3.1.1 Doping of SiGe Alloys

For any growth technique to be successful for heterostructure devices, it is necessary to identify efficient dopant sources that will convert the material to n- and p-type over a wide range of doping. To date, only a few successful doping studies with gas source silicon MBE have been reported.<sup>[9,10]</sup>

We have investigated several solid and gaseous dopant sources to achieve reproducible and high levels of n- and p-type doping. Elemental boron is a well-behaved p-type dopant. At effusion cell temperatures of 1700–1750°C, hole carrier concentrations in the  $10^{20}\text{cm}^{-3}$  range have been obtained (Fig. 5). Elemental antimony doping shows surface segregation problems and the Sb species behave more as surfactants. For uniformly doped layers, the as-grown materials do not show n-type conductivity. Electron concentrations in the  $10^{17}\text{cm}^{-3}$  range were obtained by post-growth conventional and rapid thermal annealing at 900 and 1000°C, respectively. The electron Hall mobility

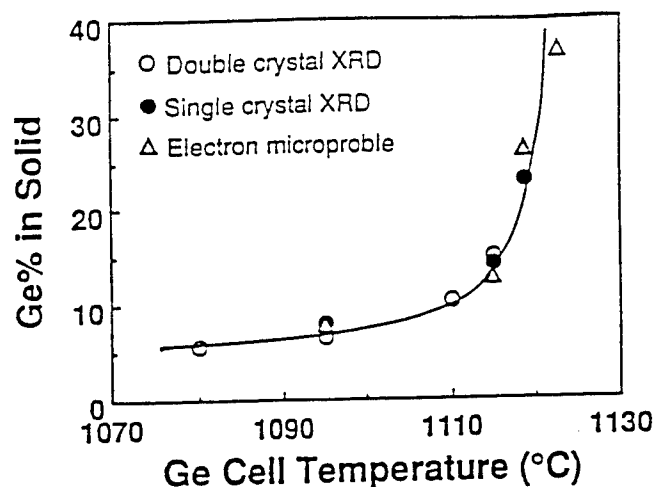


Figure 1: Dependence of germanium content in  $\text{Si}_{1-x}\text{Ge}_x$  alloys as a function of germanium cell temperature. The composition of the layers with low germanium content were obtained by double crystal x-ray diffraction. The composition of layers with high germanium content were determined from electron microprobe. All compositions were confirmed by Rutherford backscattering spectrometry.

improves with optimum annealing time. Delta doping of buried layers exhibits slightly better incorporation behavior although there are still significant surface riding effects. This is shown in Fig. 6. The behavior of solid source As is similar.

Experiments with gaseous  $\text{PH}_3$  show that well-behaved n-type doping characteristics can be obtained. This is shown in Fig. 7. To summarize, solid B and gaseous  $\text{PH}_3$  are the p- and n-type dopants of choice for gas-source MBE of SiGe.

### 3.1.2 Growth Modeling

Gas source or gas/solid source MBE are complex growth techniques. We need to establish whether growth is *mass transport limited* or *surface reaction limited*. In addition, hydrogen desorption may itself be a rate limiting process. In the present study, data on growth rate under different growth conditions were first obtained (Fig. 8). A model has been developed to describe the growth rate behavior of a Si-Ge alloy based on the apparent kinetics of the system. It predicts qualitatively, experimental observations at a range of temperatures. It can thus be fruitfully employed to arrive at optimum growth conditions provided the pressures involved are low enough to assume a surface reaction limited regime. However, this simplified heterogeneous growth model still does not provide an accurate description of the processes taking place. Further kinetics studies will have to be conducted to identify the participating species. Monte Carlo based surface reaction models have proved much better in predicting complex surface phenomena. The advantage of the Monte Carlo approach is its mathematical simplicity and the enormous amount of microscopic insight it provides in understanding surface phenomena. We hope

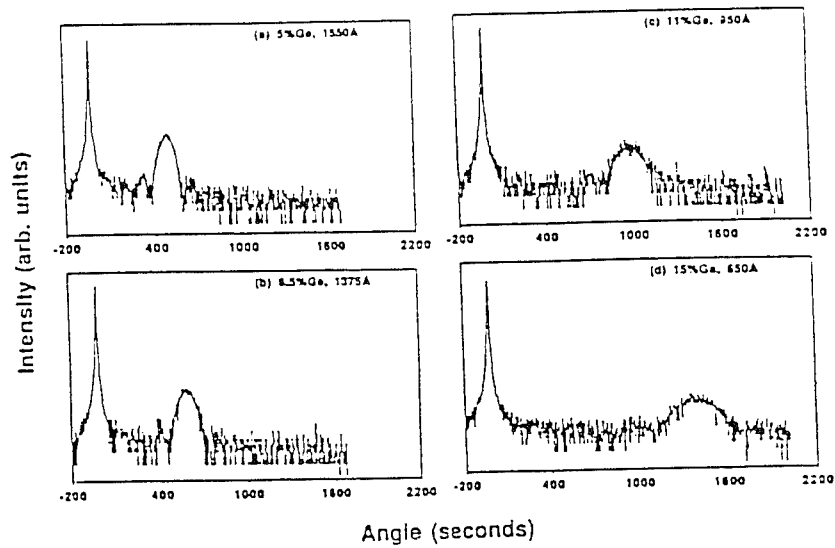


Figure 2: Double crystal x-ray rocking curves for pseudomorphic  $\text{Si}_{1-x}\text{Ge}_x$  layers with various germanium compositions and thicknesses.

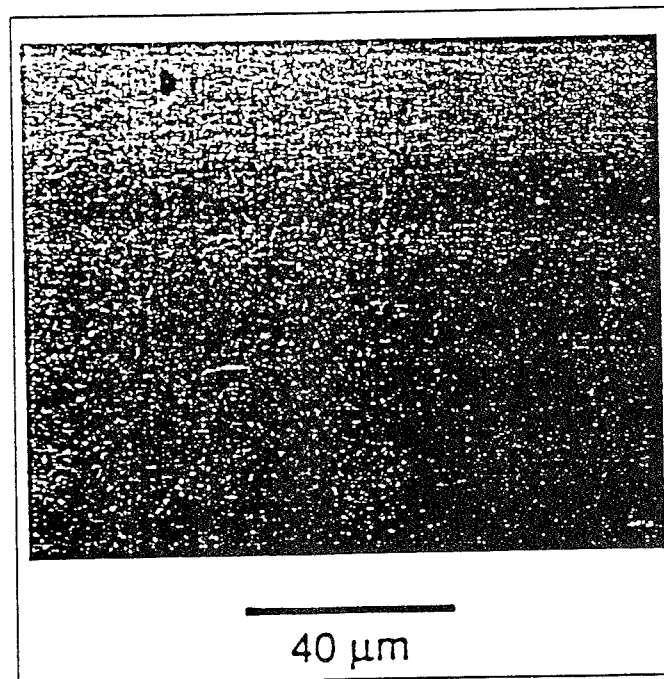


Figure 3: Surface morphology for a thin ( $650\text{\AA}$ ), pseudomorphic  $\text{Si}_{0.85}\text{Ge}_{0.15}/\text{Si}$  layer. Germanium clusters are sometimes observed, as shown in this photomicrograph.

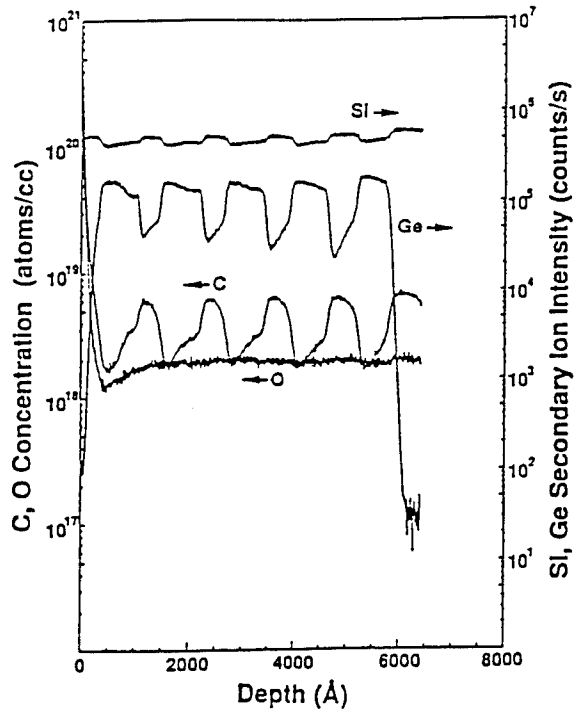


Figure 4: Secondary ion mass spectroscopy data for a five-period  $\text{Si}_{0.9}\text{Ge}_{0.1}$  ( $700\text{\AA}$ )/ $\text{Si}$  ( $500\text{\AA}$ ) multi-quantum well. Silicon and germanium secondary intensities, and carbon and oxygen impurity concentrations are plotted as a function of depth.

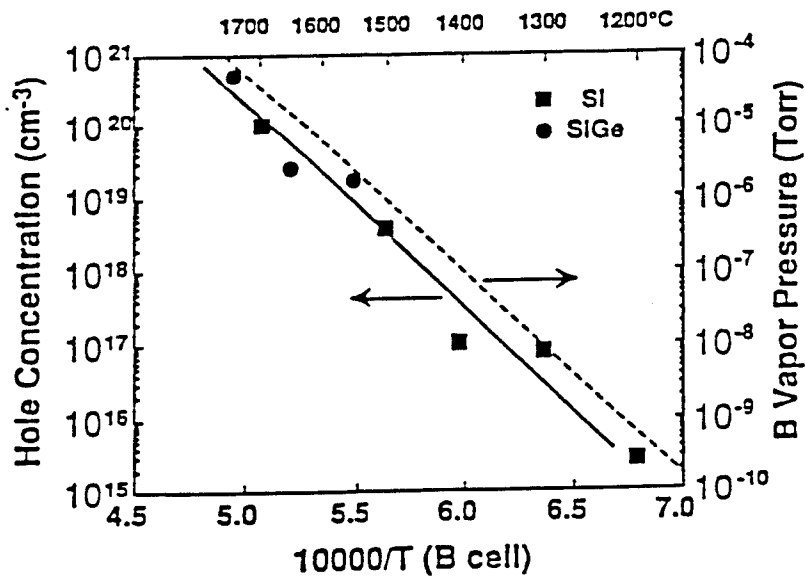


Figure 5: Boron cell temperature dependence of hole carrier concentration in silicon and  $\text{Si}_{0.85}\text{Ge}_{0.15}$ . The growth temperature was  $550^\circ\text{C}$ . The dashed line indicates the boron vapor pressure.

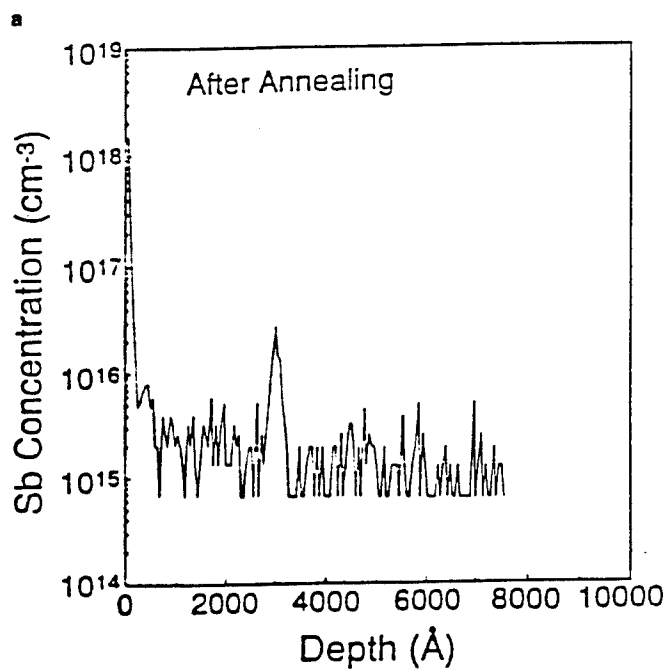
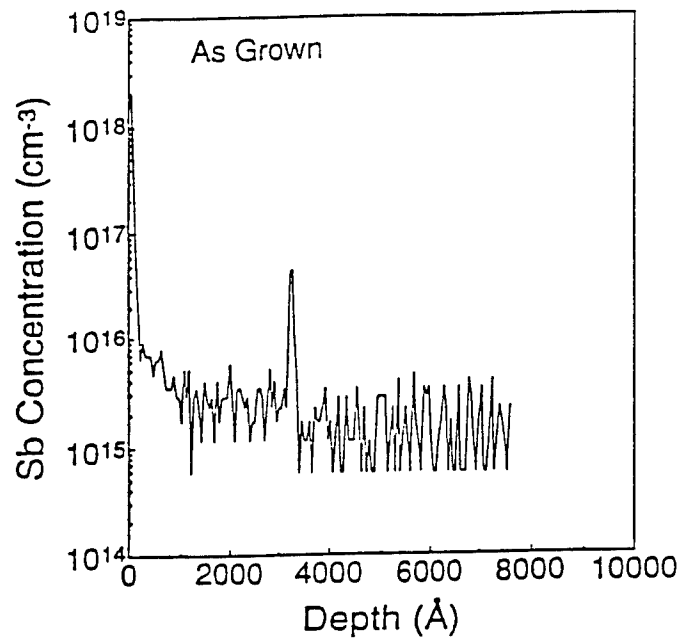


Figure 6: Secondary ion mass spectroscopy of an antimony-delta-doped silicon layer: a) as grown, and b) after RTA at 1000°C for 100 sec.

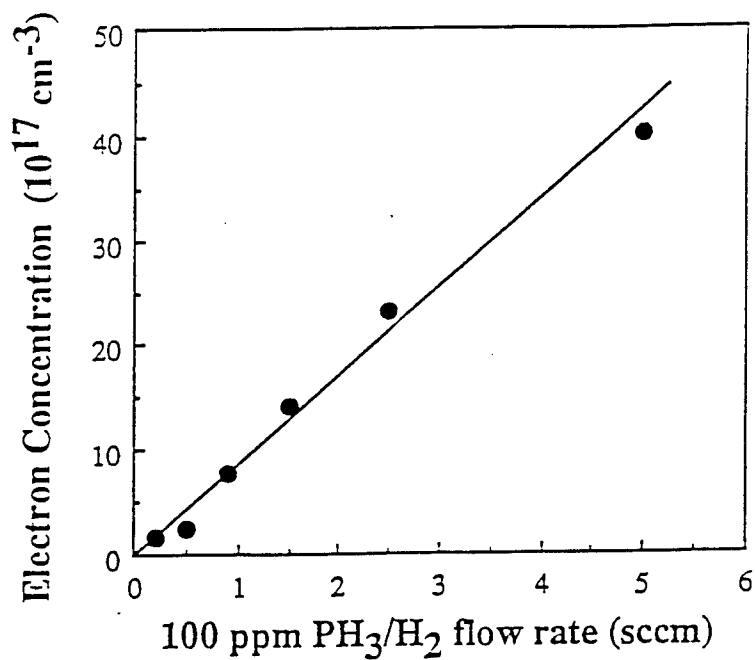


Figure 7: PH<sub>3</sub>/H<sub>2</sub> Flow Rate Dependence of Electron Concentration in Gas Source Si MBE.

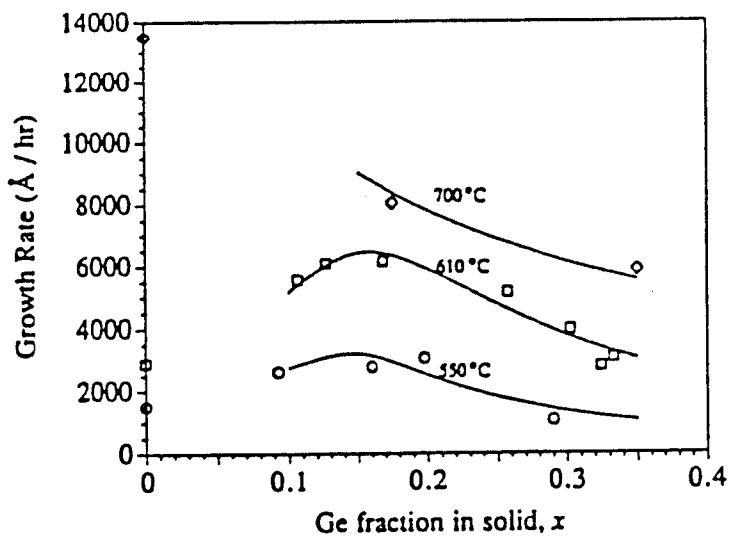


Figure 8: Growth rate of the Si-Ge alloy as a function of Ge composition for different substrate temperatures. The symbols represent raw data and the solid lines are the respective model curve fits.

to perform the Monte Carlo simulations of Si-Ge growth in the near future.

### 3.1.3 Structural Characterization

For materials characterization and device applications, it is important that the grown films are of good crystalline quality. There is not much evidence in the literature of detailed x-ray data of SiGe alloys. We have done detailed double-crystal x-ray measurements of single and multilayered Si/SiGe heterostructures. The intensity and linewidth of the peaks (Fig. 9) and the Pendellosung oscillations confirm the excellent crystalline quality of the materials and interfaces.

We have also done plan-view and cross-section TEM measurements to characterize defect generation and propagation in thick mismatched layers. The ultimate objective is to create nearly defect-free layers by efficient *dislocation filtering*. Some preliminary data are shown in Figs. 10(a) and (b).

## 3.2 ELECTRONIC PROPERTIES OF SiGe/Si HETEROSTRUCTURES

### 3.2.1 Low- and High-Field Transport Properties of SiGe

Bandedge degeneracies in semiconductors are a key reason for poor transport because of the large angle scatterings involved in most inter-band transitions together with a large phase space available for scattering. Thus the improved electron transport in GaAs compared to Si is primarily due to the bandedge being singly degenerate ( $\Gamma$  point) in GaAs and six fold degenerate (near X-point) in Si. Similarly, most semiconductors have poor hole transport due to light hole (LH)-heavy hole (HH) degeneracy. In Si, the situation is worsened because of the very small spin orbit splitting separating the split-off (SO) band.

Growth of pseudomorphic, lattice-mismatched films, provide a viable way to lift bandedge degeneracies, and a host of electronic devices stand to benefit from the improved transport properties. While some work on the measurement of electron and hole mobilities have been reported, there is no report on the high-field transport properties of electrons and holes in the alloys.

The first detailed calculations of in-plane and perpendicular velocity-field characteristics of electrons and holes in these alloys have been made by us<sup>[1]</sup>. The data are shown in Fig. 11, which shows the effects of both composition and the alloy scattering potential.

The velocity-field characteristics of electrons and holes, in relaxed and pseudomorphic SiGe films, were determined from pulsed current-voltage measurements on planar H-shaped devices defined by photolithography and mesa-etching. The measured hole velocity-field characteristics in the relaxed and coherently strained p-Si<sub>1-x</sub>Ge<sub>x</sub> samples are shown in Figs. 12(a) and (b), respectively. The low field mobilities extrapolated from

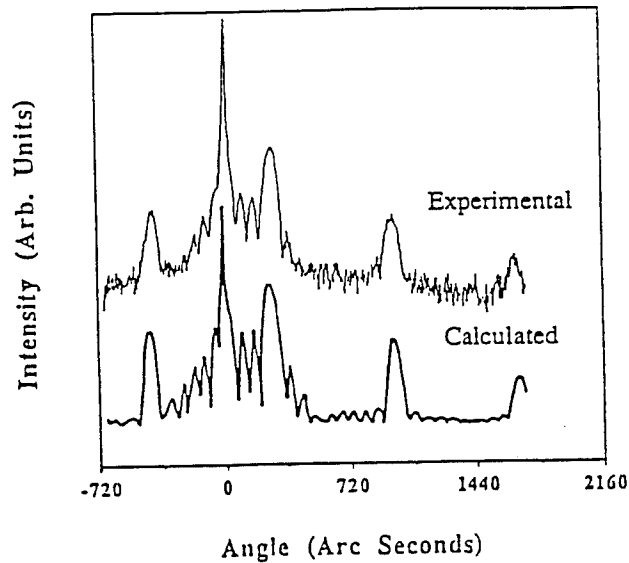


Figure 9: Comparison between experimental and calculated x-ray diffraction spectra: 10-period Si(220Å)/Si<sub>0.9</sub>Ge<sub>0.1</sub>(100Å) MQW.

these data agree fairly well with those obtained from Hall data. Similarly, the measured electron velocities in relaxed SiGe alloys are shown in Fig. 13. It is evident that there is a strong composition-dependent bowing in the hole velocities, which is absent for the electron velocities (Fig. 14). This is an indication of a large alloy scattering potential for holes in these alloys. This aspect is discussed in the next section. These are the first measurements of high-field transport properties of these alloys.

### 3.2.2 Determination of the Alloy Scattering Potential $U_0$ and Hall Factor $r$ in SiGe

The alloy scattering potential is an important parameter in SiGe alloys since it not only affects the velocity-field characteristics for carrier transport, but also allows increased optical transitions by relaxing  $k$ -selection rules. We have estimated the alloy scattering potential from the measured velocity field characteristics by comparing the latter with theoretically calculated ones. The theoretical calculations include a detailed 6-band  $\vec{k} \cdot \vec{p}$  Monte Carlo study of hole transport<sup>[1]</sup>. We find that a value of  $U_0 = 0.6$  eV explains the observed hole transport characteristics. This value is quite large and is different from the value which explains the electron mobility ( $U_0$  for the conduction band is  $\sim 0.2$  eV). This is consistent with the fact that the band offset in the SiGe system is almost entirely in the valence band.

It is important to note that in calculating the relevant parameters from Hall data, the value of the Hall factor  $r$  needs to be known. The value of  $r = 1$  for electrons. However, its value for holes is not known, except in Si and Ge. We have experimentally performed high magnetic field measurements to determine  $r$ . At very high fields  $\mu_H \rightarrow \mu_d$ , the drift mobility and thus the value of  $r$  can be estimated. The measured data are shown in

mobility and thus the value of  $r$  can be estimated. The measured data are shown in Fig. 15, which are in excellent agreement with our theoretical calculations considering a two-band system (light and heavy holes). It is seen that  $r$  in the alloys is a linear interpolation between the values for Si and Ge. These are the first measurements of  $U_0$  and  $r$  in the SiGe alloys.

### 3.2.3 Band Offsets in SiGe/Si Heterostructures

Admittance spectroscopy measurements have been made by Drs. S. R. Smith and W. C. Mitchel at WPAFB on heterostructures grown in our laboratory, and the results have been analyzed to determine the valence band discontinuities. Our data on the band offsets are shown in Figure 16, up to  $x = 0.1$ . The data clearly show that the offset for these heterostructures is primarily in the valence band. Our data also agree with earlier predictions on the trend of the band offsets<sup>[11]</sup>.

### 3.2.4 Deep Levels in Undoped SiGe Alloys

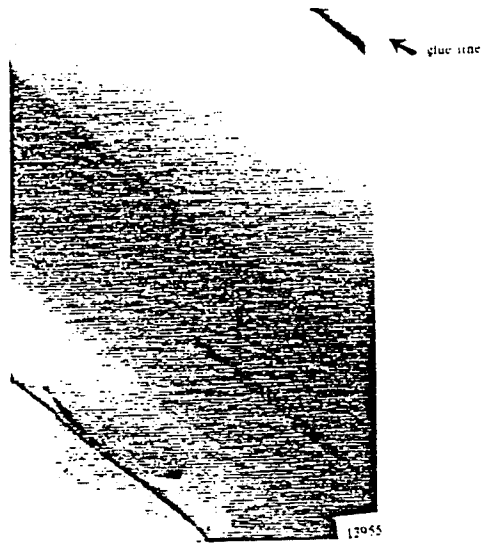
SiGe crystals, like other semiconductors, will have intentional and unintentional impurity species at substitutional or interstitial sites, native defects, or combinations of both, which may give rise to deep levels in the forbidden energy bandgap. Deep levels can act as carrier trapping and recombination centers and are known to degrade the electronic properties and radiative efficiency of semiconductors which will ultimately affect device performance. To our knowledge, there has been no explicit report on the properties of deep levels in undoped SiGe alloys. We have made deep level transient spectroscopy (DLTS) measurements on undoped  $\text{Si}_{1-x}\text{Ge}_x$  ( $0.05 \leq x \leq 0.26$ ) layers grown on Si substrates. We have measured the properties of majority-carrier traps that have been identified in these layers. A typical DLTS signal, Arrhenius plots of majority-carrier traps identified in undoped SiGe are shown in Figs. 17 and 18, and Table 1. Most of these traps originate from native defects.

## 3.3 OPTICAL PROPERTIES OF SiGe

It is of interest to integrate optoelectronic devices, in particular light sources, with Si-based digital or analog integrated circuits. The  $\text{Si}_{1-x}\text{Ge}_x$  alloys are promising materials in this context. In order to realize electroluminescent devices with these alloys, it is important to grow high-quality materials and to understand and characterize their luminescent properties. To this end, some recent reports have been made on the luminescence from  $\text{Si}_{1-x}\text{Ge}_x$  and  $\text{Si}_{1-x}/\text{Si}$  quantum wells<sup>[12-20]</sup> grown by a variety of techniques. In most of these studies the quantum wells were undoped.

In addition to the luminescence intensity itself, it is important to measure the radiative recombination lifetimes in these materials. If the latter are too long, then the possibility of making efficient light sources with these materials is very remote. As a first step, we

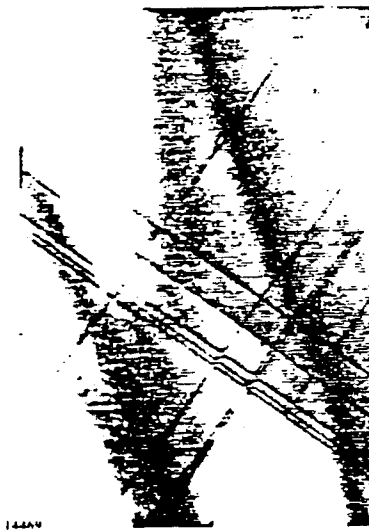
UMS sample 161  
Cross-sectional View



100nm = 1.033cm

(a)

UMS sample 119  
Plan View



(b)

100nm = 0.064cm

Figure 10: (a) Cross-sectional, and (b) plan view TEM of dislocations at  $\text{Si}_{0.8}\text{Ge}_{0.2}/\text{Si}$  interface.

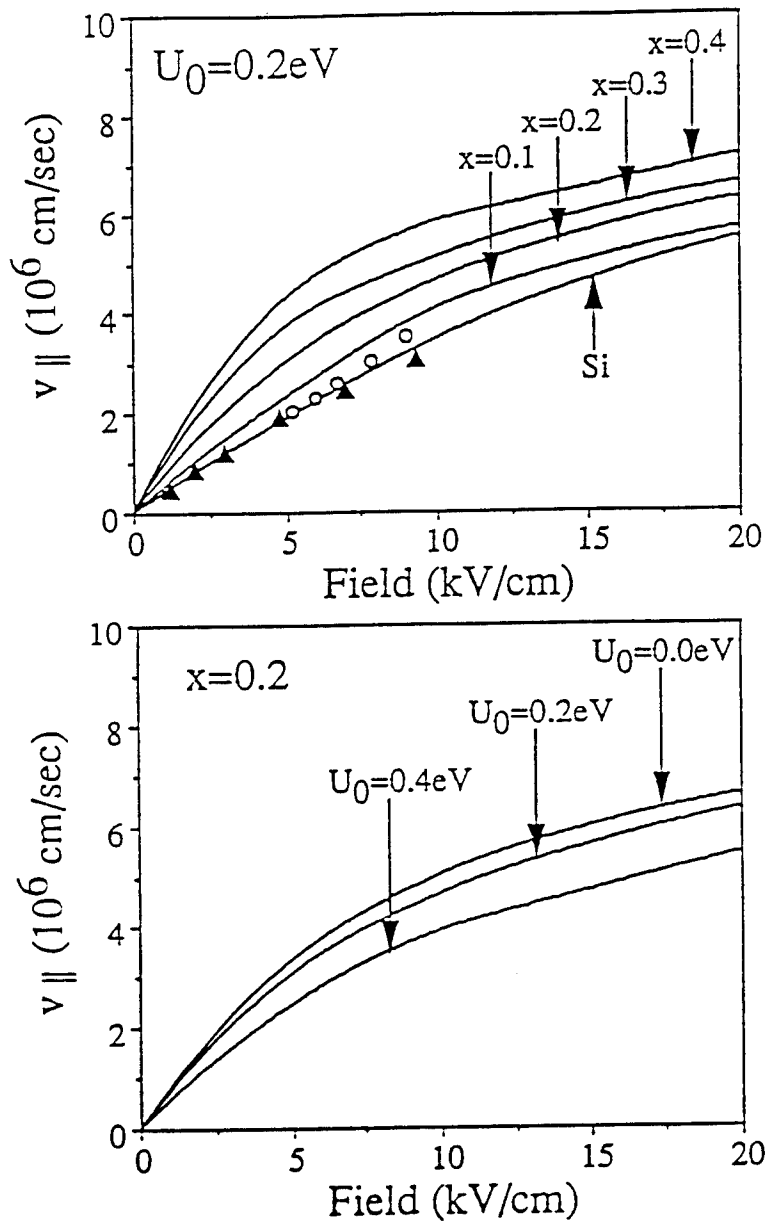
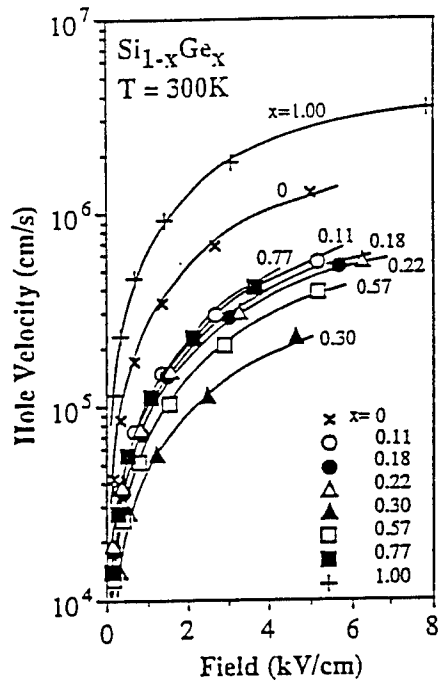
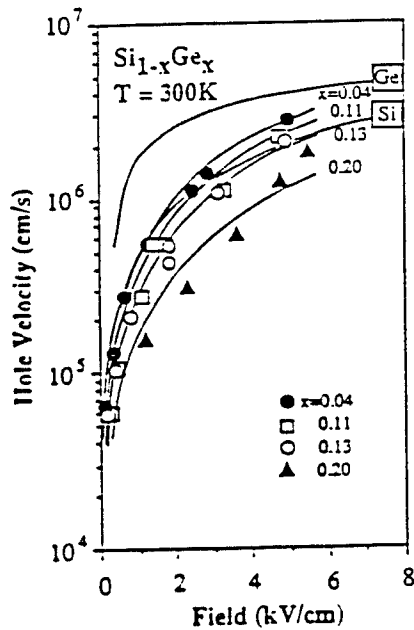


Figure 11: Calculated in-plane velocity-field characteristics (a) for fixed  $U_0 = 0.2$  eV, and (b) in  $\text{Si}_{0.8}\text{Ge}_{0.2}$  for different values of  $U_0$ .



(a)



(b)

Figure 12:  $v/E$  characteristics of (a) relaxed p-type  $\text{Si}_{1-x}\text{Ge}_x$ ; (b) pseudomorphic p-type  $\text{Si}_{1-x}\text{Ge}_x$ .

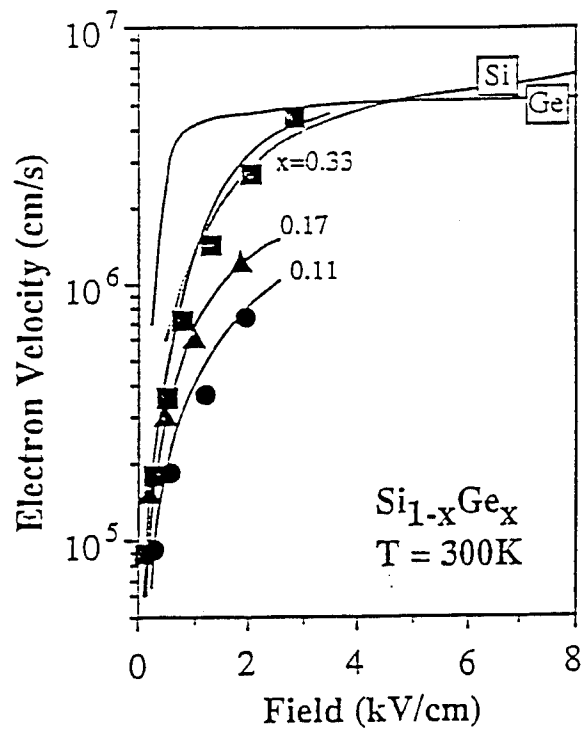


Figure 13:  $v/E$  characteristics of relaxed n-type  $\text{Si}_{1-x}\text{Ge}_x$ .

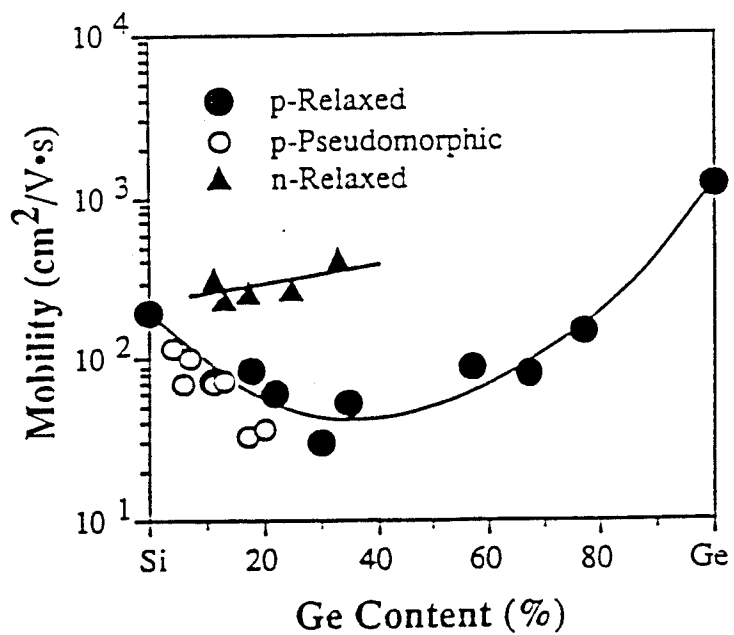
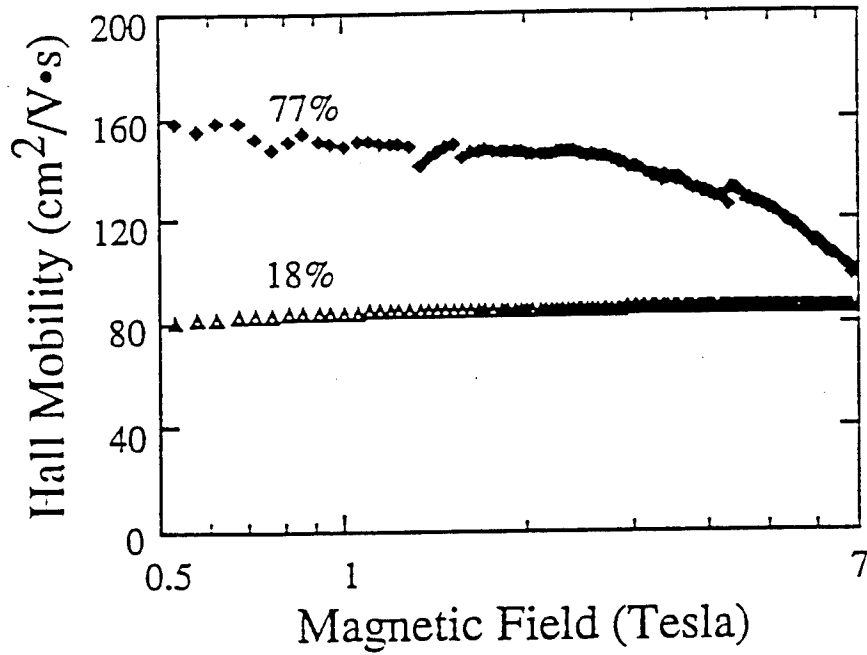
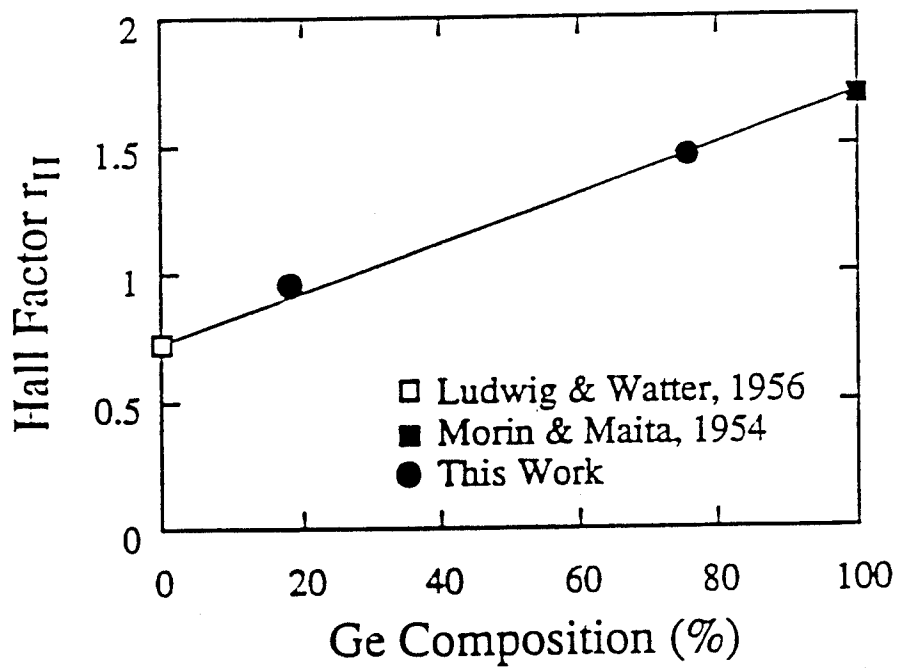


Figure 14: Low-field Hall mobility as a function of Ge content in  $\text{Si}_{1-x}\text{Ge}_x$ .



(a)



(b)

Figure 15: Hall factors of  $\text{Si}_{1-x}\text{Ge}_x$ .

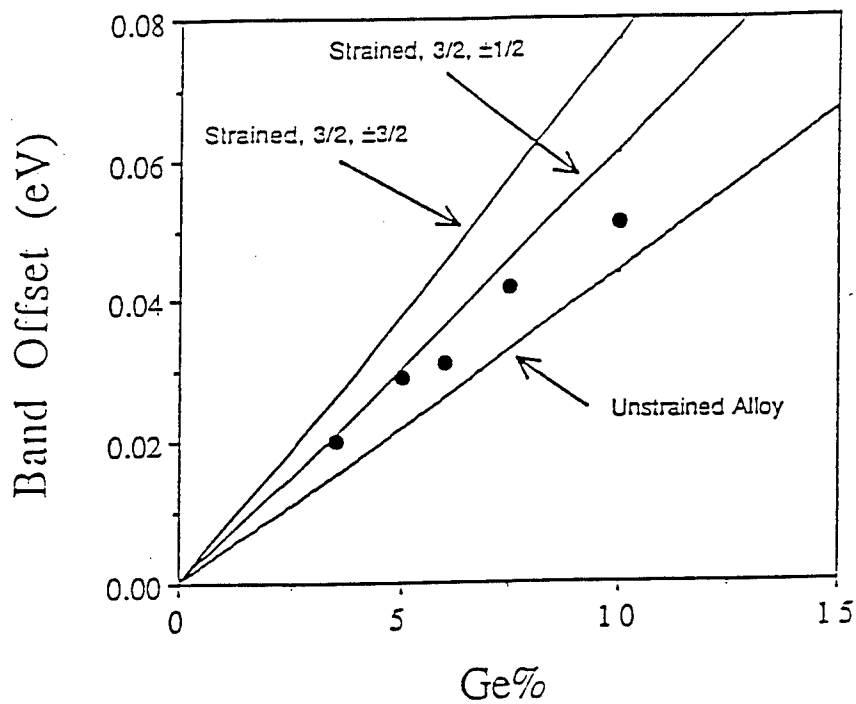


Figure 16: Band offset in Si/Si<sub>1-x</sub>Ge<sub>x</sub> as a function of Ge content.

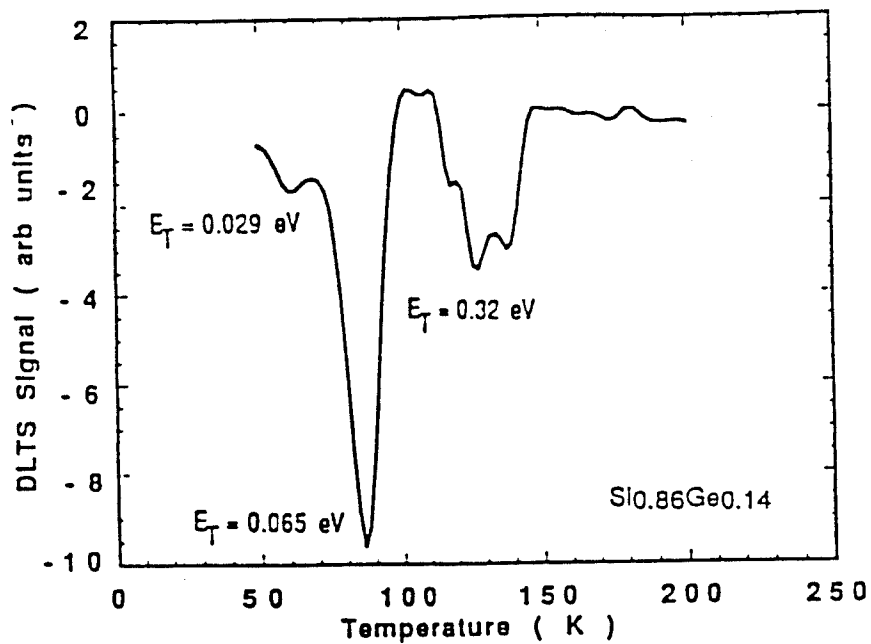


Figure 17: Deep level transient spectroscopy data showing peaks due to hole traps in p-type Si<sub>0.86</sub>Ge<sub>0.14</sub>.

have measured the luminescence intensity in various structures.

Doping by isoelectronic impurities was proven to be a successful technique for enhancing the luminescence in indirect bandgap compound semiconductors such as GaP and GaAsP<sup>[21]</sup>. In the case of these compounds nitrogen (N) was found to be very suitable. Doping with N produced a series of deep levels in the energy bandgap and the k-selection rules for transitions involving these levels were relaxed. There are no suitable isoelectronic dopants in Group IV of the Periodic Table for the SiGe alloys. We therefore chose to investigate the effects of doping with Be(Gr II) and B(Gr III), which is a well-behaved acceptor dopant for these materials. The various luminescence peaks in undoped and doped quantum wells are shown in Figs. 19 and 20.

The PL spectra measured in undoped and doped SiGe/Si MQW and SQW samples suggest that doping in these alloys will not enhance PL efficiencies. No new levels, or enhancement of luminescence is detected in samples which are selectively doped in the well regions, implying that the observed luminescence in the undoped quantum wells is a result of alloy disordering. Improvement of material quality, or other techniques such as disordered quantum wires need to be explored.

### 3.4 HETEROSTRUCTURE ELECTRONIC DEVICES

We have made 0.25 $\mu$ m gate Si(p<sup>+</sup>)/Si<sub>0.8</sub>Ge<sub>0.2</sub> modulation doped heterostructure FETs with a 50Å-thick SiO<sub>2</sub> gate oxide layer grown by ECR-based oxidation. The latter provides the advantages of: a) a high density of reactive radicals; b) low ion energy; and c) slow oxidation rate. The ultra thin oxide has a breakdown field >12 MV/cm and fixed charge density  $\sim 3 \times 10^{10} \text{ cm}^{-2}$ . Leakage current as low as 1 $\mu$ A was obtained with

Table I. Measured Characteristics of Majority-Carrier Traps in Undoped p-Type Si<sub>1-x</sub>Ge<sub>x</sub>

Alloy Comp. (x)	Measured Activation Energy, E <sub>T</sub> (ev)	Trap Concentration (cm <sup>-3</sup> )( $\times 10^{13}$ )	Capture Cross Section $\sigma_{-}$ (cm <sup>2</sup> )
0.06	No traps detected		
0.14	0.029	1.4	$1.96 \times 10^{-20}$
	0.065	3.67	$8.5 \times 10^{-20}$
	0.314	1.3	$1.3 \times 10^{-11}$
0.19	0.041	8.0	$1.6 \times 10^{-20}$
	A deeper trap	not well resolved	
0.26	<0.2	not well resolved	
	0.261	1.2	$8.55 \times 10^{-15}$
	0.45	1.3	$5.0 \times 10^{-9}$

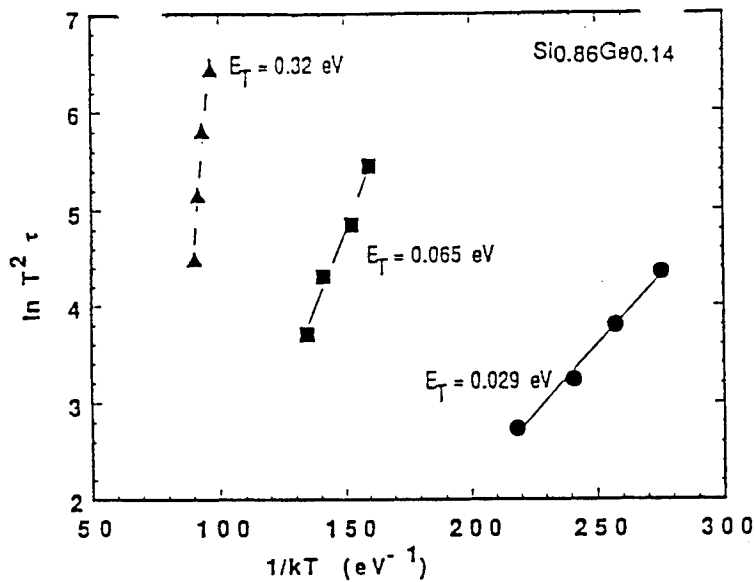


Figure 18: Arrhenius plots of three clearly identified hole traps in Si<sub>0.86</sub>Ge<sub>0.14</sub>.

the gate biased at 4V. The MISFETs typically had a maximum drain current of 41.6 mA/mm and peak transconductance of 21 ms/mm (Figs. 21 and 22).

### 3.5 IMPACT IONIZATION COEFFICIENTS IN Si<sub>1-x</sub>Ge<sub>x</sub>

We have made the first systematic theoretical and experimental determination of the impact ionization coefficients in SiGe alloys. The theoretical calculations were made with a detailed description of the bandstructure. For the experimental determination of  $\alpha$  and  $\beta$ , carrier multiplication measurements were made on relaxed Si<sub>1-x</sub>Ge<sub>x</sub>/Si diodes grown by gas source MBE. It is found that the hole to electron impact ionization coefficient ratio,  $\beta/\alpha$ , varies from 0.3 to 4 in the composition range of  $x = 0.08$  to 1.0.

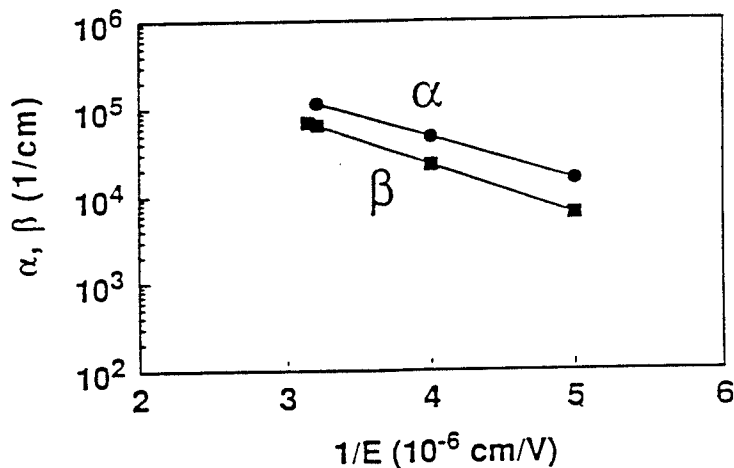


Figure 19: Measured impact ionization coefficients in Si<sub>0.69</sub>Ge<sub>0.31</sub>.

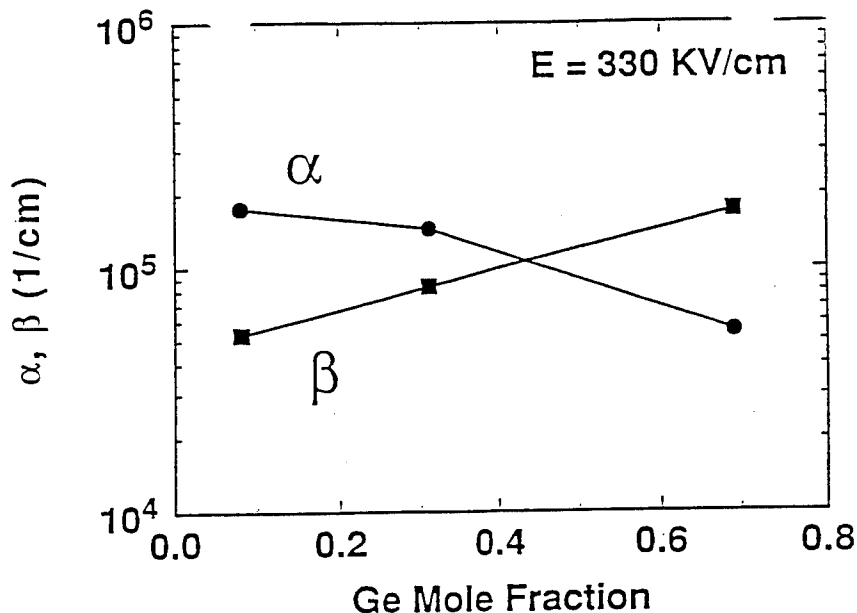


Figure 20: Measured values at  $\alpha$  and  $\beta$  as a function of Ge mole fraction in  $\text{Si}_{1-x}\text{Ge}_x$  at  $E=330 \text{ KV/cm}$ .

#### 4. SUMMARY OF ACCOMPLISHMENTS

Some of the significant results achieved in the last year are:

1. Reproducible and high-level n-type doping of SiGe with phosphine ( $\text{PH}_3$ ). It has been recognized for a while that n-type doping of these alloys is problematic. We are now routinely using  $\text{PH}_3$ -doping to grow junction devices. We have made diodes for DLTS measurements done at the Materials Laboratory, Wright Patterson Air Force Base.
2. Low and high-field transport properties of SiGe and the first theoretical and experimental determination of the alloy scattering potential.
3. The Hall factor for the alloys, which is essential for the measurement of the transport properties, has been measured for the first time. The Hall factor varies from 0.73 to 1.7 from Si to Ge for holes. For electronics it is close to unity.
4. We have experimentally and theoretically determined the electron and hole impact ionization coefficients in  $\text{Si}_{1-x}\text{Ge}_x$  alloys for the first time. Carrier multiplication measurements were made on relaxed  $\text{Si}_{1-x}\text{Ge}_x/\text{Si}$  diodes grown by gas source molecular beam epitaxy. The hole to electron impact ionization coefficient ratio,  $\beta/\alpha$ , varies from 0.3 to 4 in the composition range of  $x = 0.08$  to 1.0. These results are of paramount importance and will affect the design and performance of, HBTs and photodiodes. The results are of importance for every group working with these alloys. Our work has helped to help some of the fundamental material properties of SiGe.

5. We have initiated work on measuring the electro-optic coefficient in SiGe/Si asymmetric quantum wells. Since the refractive index difference between Si and Ge is very large ( $\sim 4\epsilon_x$ ), it is expected that giant electro-optic coefficients will be obtained in these structures, leading to the realization of high-efficiency, low-voltage Si-based electro-optic modulators.

## 5. AWARD/SPECIAL RECOGNITION

Professor Bhattacharya gave an invited talk entitled, "Deep Level Defects, Luminescence, and Electro-Optic Properties of SiGe/Si Heterostructures," at the Materials Research Society Meeting, Boston, December, 1993. This is significant, considering that we had started work with these two alloys only two years ago.

## 6. TECHNOLOGY/INFORMATION TRANSFER TO INDUSTRY

1. The diffusion of phosphorus (P) is a problem in Si technology used for VLSI manufacturing. It has been suggested and shown theoretically that the diffusion of P and some other dopant species can be controlled by the addition of small amounts of Ge. We, therefore, did a joint project with *Dr. Sheldon Aronowitz, National Semiconductors, Santa Clara*, wherein we grew dilute SiGe alloys which were then implanted with P and annealed. The phosphorus diffusion profiles were studied by SIMS. This study shows that the concept of dopant diffusion modified by dopant-dopant interactions can yield a cogent predictive picture of diffusion behavior. The experiments also establish that there is a delicate and intimate relationship between phosphorus diffusion in silicon-germanium alloy films and film composition and thickness. This relationship, anticipated by theory, emphasizes the long range nature of the dopant-dopant interactions.
2. A collaborative program has been established between our theoretical effort and *Dr. Sheldon Aronowitz of National Semiconductor*. An important concern has been identified by National Semiconductor for the next generation Si- devices where gate lengths will start approaching  $0.1\mu\text{m}$ . This is the concern about how breakdown occurs in the devices. The concern would also extend to devices built in SiGe. Extensive field profile data was provided to us by *Dr. Aronowitz* for submicron MOS devices and we studied the impact ionization process in these structures. We found a definite need to abandon the steady state  $\alpha$  vs.  $E$  impact ionization coefficient-field relation as soon as device sizes approached  $0.1\mu\text{m}$ . A path integral approach was developed by using Monte Carlo as a guideline. This approach allows one to use existing codes such as MINIMOS with minimal alterations. Yet the non-local transport effects can be included.

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AFOSR-91-0349

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