

Control of Oxygen Incorporation and Lifetime Measurement in  
 $\text{Si}_{1-x}\text{Ge}_x$  Epitaxial Films Grown by  
Rapid Thermal Chemical Vapor Deposition

J.C. Sturm, P.V. Schwartz, E.J. Prinz, and C. Magee\*

Department of Electrical Engineering  
Princeton University, Princeton, N.J. 08544

\*Evans East, Inc., Plainsboro, N.J.

### ABSTRACT

Oxygen levels in epitaxial  $\text{Si}_{1-x}\text{Ge}_x$  films grown by rapid thermal chemical vapor deposition (RTCVD) have been reduced to under  $2 \times 10^{18} \text{ cm}^{-3}$ , and the source of oxygen in films with higher oxygen concentration has been identified. Films with low oxygen levels have minority carrier lifetimes in the  $\mu\text{s}$  range, and Si/ $\text{Si}_{1-x}\text{Ge}_x$ /Si heterojunction bipolar transistors (HBT's) fabricated with low oxygen levels have near-ideal base currents which do not depend on the base composition.

### INTRODUCTION

Rapid thermal chemical vapor deposition has been shown to be a useful technique for the growth of high quality silicon-germanium films on silicon substrates. However, films grown in the 625-640 °C range have been found to contain oxygen levels on the order of  $10^{20} \text{ cm}^{-3}$ , roughly two orders of magnitude larger than the maximum oxygen solid solubility in silicon, and these high oxygen levels have been suspected of reducing the lifetimes of the films [1]. This paper describes work to identify and then remove the source of the oxygen contamination. The lifetimes of the resulting low-oxygen SiGe films have been measured, and HBT's with near ideal performance have been fabricated.

### GROWTH REACTOR

All films grown in this work were grown in a quartz-walled RTCVD system heated by tungsten-halogen lamps. The gases are supplied by a computer controlled distribution system, and five-ported valves are used so that mass flow controller flows can be stabilized before gases are switched into the growth chamber. The vacuum technology consists of a two-stage rotary vacuum pump (30 cfm) and viton O-ring seals as in a usual LPCVD system. The leak rate of the chamber when these experiments were performed was on the order of  $10^{-5}$  torr/min. Typical deposition pressures were 6 torr with a hydrogen carrier. Dichlorosilane was used as the silicon source gas (partial pressure  $\sim 60$  mtorr) and germane was used as the germanium source (partial pressure  $\sim 2$  mtorr) for the growth of  $\text{Si}_{0.8}\text{Ge}_{0.2}$  films.

The first epitaxial films grown in a system similar to ours were grown by the Limited Reaction Processing (LRP) method [2]. In the LRP method, the reactive process gas flows

are initiated and stabilized while the wafer is cold (no growth), and rapid ramps in the sample temperature are used to control the actual growth times. For the growth of multiple layers, the process gases are changed while the wafer is cold between cycles. In our work, to avoid extended time at low temperature between the growth of adjacent layers, we have not used the LRP approach. Rather, the gas flows, rather than the sample temperature, are used to control the start and stop of layer growth. The sample is brought to the growth temperature before the reactive gas flows are started, and the wafer is not cooled between the growth of adjacent layers.

## CONTROL OF OXYGEN INCORPORATION

Low-temperature  $\text{Si}_{1-x}\text{Ge}_x$  layers grown by LRP to date have had high concentrations of oxygen, on the order of  $\sim 10^{20} \text{ cm}^{-3}$  [1]. These concentrations are nearly two orders of magnitude higher than the maximum solid solubility of oxygen in silicon [3], and nearly three orders of magnitude higher than the solid solubility of the growth temperature ( $\sim 625\text{-}640^\circ \text{C}$ ). Similar results were seen in initial films grown in our lab at  $625^\circ \text{C}$ . Shown in fig. 2 is a SIMS profile of the oxygen concentration in a multilayer sample grown without a load lock, i.e. the growth chamber was vented to atmospheric pressure to load each sample. The oxygen in the silicon is at the SIMS resolution limit, but the oxygen level is large in the  $\text{Si}_{0.8}\text{Ge}_{0.2}$  grown at  $700^\circ \text{C}$  ( $\sim 5 \times 10^{18} \text{ cm}^{-3}$ ) and still larger in the  $625^\circ \text{C}$   $\text{Si}_{0.8}\text{Ge}_{0.2}$  ( $\sim 2 \times 10^{19} \text{ cm}^{-3}$ ). Other SiGe samples grown in this reactor at  $625^\circ \text{C}$  have shown oxygen levels between  $10^{19} \text{ cm}^{-3}$  and  $5 \times 10^{20} \text{ cm}^{-3}$ . Although the microstructural arrangement of the oxygen is not known, TEM measurements have shown the SiGe films to be free from both threading and misfit dislocations. The films also were free from stacking faults, which is very surprising since any oxygen contamination in high temperature (e.g.  $1000^\circ \text{C}$  silicon epitaxy results in stacking fault formation well before the oxygen level in the film rises significantly above  $10^{18} \text{ cm}^{-3}$ .

Two conclusions may be drawn from the SIMS data of fig. 1. First, by comparing the  $700^\circ \text{C}$  SiGe and Si growth, one sees that the oxygen concentration is higher in SiGe layers. Second, one notes an increased oxygen concentration at lower growth temperatures. The second observation can be explained by increased thermodynamic stability of oxygen on silicon surfaces at lower temperatures [4]. Indeed, it is this fact which makes vapor phase epitaxial growth more difficult at low temperatures. The higher oxygen concentration in the  $\text{Si}_{1-x}\text{Ge}_x$  can be explained by one of two hypotheses. First, the germane source gas used for  $\text{Si}_{1-x}\text{Ge}_x$  growth could be contaminated with oxygen or water vapor. Alternatively, the oxygen could come from somewhere else, and the germane flow or germanium in the solid could somehow enhance the incorporation into the solid.

To distinguish between these possibilities, a load-lock was added to the growth reactor. This enables samples to be loaded and unloaded without exposing the growth chamber to outside air. Structures grown with the load-lock show oxygen levels in  $625^\circ \text{C}$   $\text{Si}_{0.8}\text{Ge}_{0.2}$  reduced to the SIMS background levels of  $\sim 10^{18} \text{ cm}^{-3}$  (fig. 2). This reduction in oxygen concentration of two orders of magnitude shows that the oxygen source was not the germane source gas, but rather is related to the sample loading procedure. When loading samples without a load-lock, the chamber was vented with nitrogen from the house supply.

Presumably this nitrogen was not pure and contained water vapor or some oxygen and/or wafer vapor diffused back from the air into the reactor and adsorbed onto the quartz reactor walls when the chamber was open. This oxygen and/or water then desorbed during the growth to contaminate the sample. Loading samples with the load-lock avoided the introduction of oxygen and/or wafer vapor into the chamber and hence the subsequent contamination.

A more difficult question is that if the oxygen source is related to sample loading, why is the silicon-germanium more susceptible to oxygen contamination than the silicon? Since the SiGe growth rate at 700 °C in fig. 1 was larger than that in the silicon (200 vs 30 Å/min), from kinetic arguments one would expect a decreased, not increased, oxygen concentration in the SiGe compared to that in the Si. One possibility is that the sticking coefficient of oxygen or wafer to germanium on the SiGe surface is higher than that to silicon. Although no such direct data exists, this hypothesis is extremely unlikely since the Si-O bond is much stronger than the Ge-O bond (e.g., compare 8.0 vs 6.9 eV for the bond strength of diatomic SiO vs GeO [5], or a bond strength for each Si=O in SiO<sub>2</sub> of 9.6 eV vs 7.3 eV for each Ge=O in GeO<sub>2</sub> [6]). Despite the weaker Ge-O bonds compared to Si-O bonds, preferential oxygen adsorption could still take place at Ge sites if the silicon surface were predominantly hydrogen-covered, and the open sites for adsorption were Ge. The Ge-H bond is indeed slightly weaker than the Si-H bond (3.0 vs 3.3 eV [7]). This difference is small, however, compared to the difference in the Si-O and Ge-O bond, so that preferential absorption of O-containing species at Ge sites is not a likely explanation for the increased oxygen levels in the SiGe films compared to Si.

A second option is that the presence of the GeH<sub>4</sub> source gas somehow leads to a higher partial pressure of the contaminating species in the reactor. (This is not due to contamination of the GeH<sub>4</sub> source gas, however, since with the load lock, oxygen contamination is avoided). For example, GeH<sub>4</sub> might aid in the desorption of oxygen containing species from the reactor walls (which were adsorbed during loading). Investigation of such processes is currently in progress.

### LIFETIMES IN Si<sub>1-x</sub>Ge<sub>x</sub> EPITAXIAL LAYERS

Although the main applications of Si<sub>1-x</sub>Ge<sub>x</sub> layers at present are for minority carrier devices such as HBT's and p-i-n diodes for infrared detectors, to date there have been no direct measurements of the lifetimes in these films. Lifetime measurements in thin films are very difficult since it is usually difficult to separate generation/recombination within the film from generation/recombination outside of the film. This is especially so in the case of strained Si<sub>1-x</sub>Ge<sub>x</sub> films since they typically are less than 1000 Å in thickness to avoid misfit dislocations. We have measured the generation lifetime in SiGe films by observing the recovery from deep depletion in MOS capacitors fabricated on SiGe films. P-type Si<sub>0.82</sub>Ge<sub>0.18</sub> layers of ~30 nm thickness were grown on a p-type substrate at 625 °C, followed by the growth of a 30 nm p-type Si capping layer. On some samples the capping layer was subsequently oxidized, and on some samples an oxide was formed by plasma CVD (fig. 3). Control samples included bulk wafers and a 700 °C Si epitaxial layer (no Ge). The top silicon layer was employed to give an oxide/silicon interface since the oxide/silicon-germanium interface is known to be of poor electronic quality.

The capacitors were then pulsed into deep depletion and the recovery times (which represent carrier generation) were observed. When analyzing the data [8], it is very important to insure that the measurement conditions really measure the generation lifetime  $\tau_g$  in the SiGe films. According to Shockley-Read-Hall theory, the generation rate  $G$  is equal to its usually assumed value of  $n_i/\tau_g$  only when both  $p$  and  $n$  are less than  $n_i$  in the generation region. The region where this occurs is substantially smaller than the depletion region. If both  $n$  and  $p$  are not less than  $n_i$ , the generation will be artificially suppressed and the lifetime will be overestimated. Simulations were done during various parts of the capacitance transient to insure that this condition for maximum generation in the SiGe was satisfied (fig. 4) [9]. When analyzing the data, it is also important to note that because of the smaller bandgap,  $n_i$  will be larger in the SiGe than the usual  $1.4 \times 10^{10} \text{ cm}^{-3}$  value assumed for Si. The generation leading to the capacitance recovery could occur in either the Si or SiGe layers. However, in the analysis, the worst case assumption was made that all of the generation occurred in the SiGe. The results are summarized in fig. 5. Typical generation lifetimes for the SiGe and for the 700 °C silicon are 1-2  $\mu\text{s}$ . The lifetimes of these samples and of the control bulk wafers did not depend on the type of oxide, leading one to conclude that surface generation had a minor effect on these results. One also notes for similar lifetimes, the SiGe capacitors had shorter recovery times ( $\tau_{\text{rec}}$ ). This is because of the smaller bandgap in the SiGe which leads to faster generation for the same concentration of traps.

The oxygen levels in the SiGe layers of the above capacitors were measured by SIMS to be  $2 \times 10^{18} \text{ cm}^{-3}$  or less (limited by SIMS background). The measurement of lifetime in SiGe layers with high levels of oxygen is currently in progress.

#### BASE CURRENTS IN HETEROJUNCTION BIPOLAR TRANSISTORS

In Si/Si<sub>1-x</sub>Ge<sub>x</sub>/Si npn HBT's, the base bandgap is changed as the base composition is varied. In such devices (as contrasted to varying the emitter bandgap), the effect of the narrow gap base should be an increased collector current. The base current should not depend on the base composition. Initial results with HBT's fabricated by RTCVD (LRP) [1] had near ideal collector current performance, but the base currents were also observed to increase by several orders of magnitude as the base composition was changed. One possible explanation of these increased base currents given by the authors was a low lifetime in the SiGe base (caused by the high oxygen levels) which would lead to increased base recombination. We have fabricated HBT's with base compositions varying from a base that is graded from 0 to 20% Ge across the base, to devices with a constant base composition of 20% Ge [10]. The samples were grown in the system described above with a load lock, and the SiGe layers are thought to contain low levels of oxygen. Shown in fig. 6 is the Gummel plot of four devices between these extremes. As the total amount of Ge in the base is increased, the collector current increases rapidly as expected. However, despite the varying base compositions in the four devices, the base currents in all four devices are nearly identical. Since the base currents have a near ideal slope of 62 mV/decade, this suggests that the base currents are limited by emitter efficiency as in the ideal case, and not by base recombination caused by a low lifetime.

## SUMMARY

High quality  $\text{Si}_{1-x}\text{Ge}_x$  films have been grown by RTCVD without UHV conditions at temperatures as low as 600 °C. Despite these low temperatures and modest vacuum conditions, the oxygen levels in these films is under  $2 \times 10^{18} \text{ cm}^{-3}$ . For reasons that are not yet clear, SiGe films do appear inherently more sensitive to oxygen contamination than low temperature Si films, however. In low-oxygen SiGe films, generation lifetimes in the  $\mu\text{s}$  range have been measured, and HBT's have been fabricated in which the base currents are controlled hole injection into the emitter, not by base recombination.

## ACKNOWLEDGEMENTS

The support of ONR (N00014-J-90-1316), NSF, and Texas Instruments, IBM, and the N.J. Commission on Science and Technology is gratefully appreciated.

## REFERENCES

1. C.A. King, J.L. Hoyt, and J.F. Gibbons, IEEE Transactions on Electron Devices **TED-36**, 2093 (1989).
2. J.F. Gibbons, C.M. Gronet, and K.E. Williams, Appl. Phys. Lett. **47**, 721 (1985).
3. H.J. Hrostowski and R.H. Kaiser, J. Phys. Chem. Solid **9**, 214 (1959).
4. G. Ghidini and F.W. Smith, J. Electrochem. Soc. **131**, 2924 (1984).
5. R.C. Weast, ed., **Handbook of Chemistry and Physics**, (Chemical Rubber Company, Cleveland), p. F200, 1973.
6. Calculated from heats of formation of  $\text{GeO}_2$ ,  $\text{SiO}_2$ , bond energy of  $\text{O}_2$ , and cohesive energies of Si and Ge.
7. Calculated from heats of formation of  $\text{SiH}_4$ ,  $\text{GeH}_4$ , bond energy of  $\text{H}_2$ , and cohesive energies of Si and Ge.
8. D.K. Schroeder and J. Guldberg, Solid State Elect. **14**, 1285 (1971).
9. P.V. Schwartz and J.C. Sturm, Appl. Phys. Lett, to be published.
10. E.J. Prinz and J.C. Sturm, Tech. Dig. IEDM, to be presented, 1990.

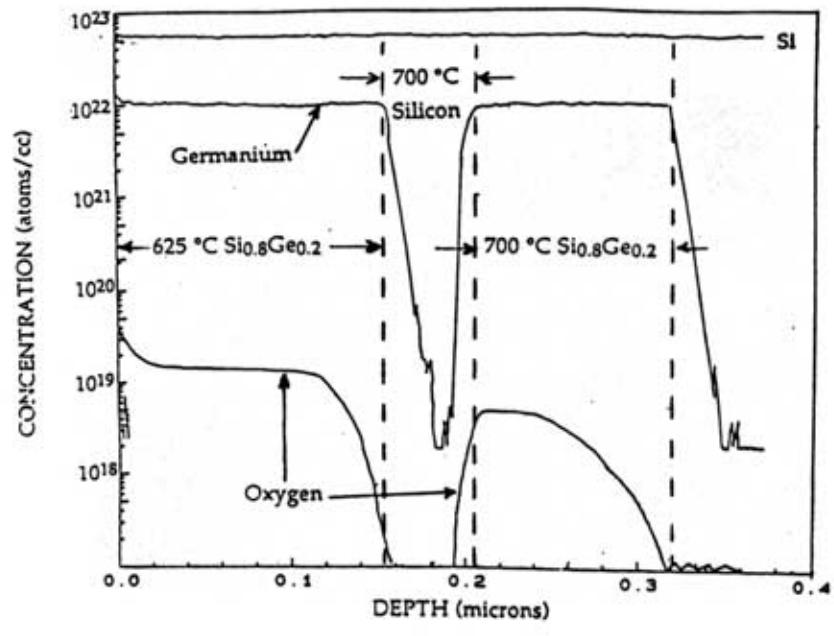


Fig. 1. SIMS profile of oxygen concentration in a multilayer Si<sub>1-x</sub>Ge<sub>x</sub> sample grown without a lock-lock.

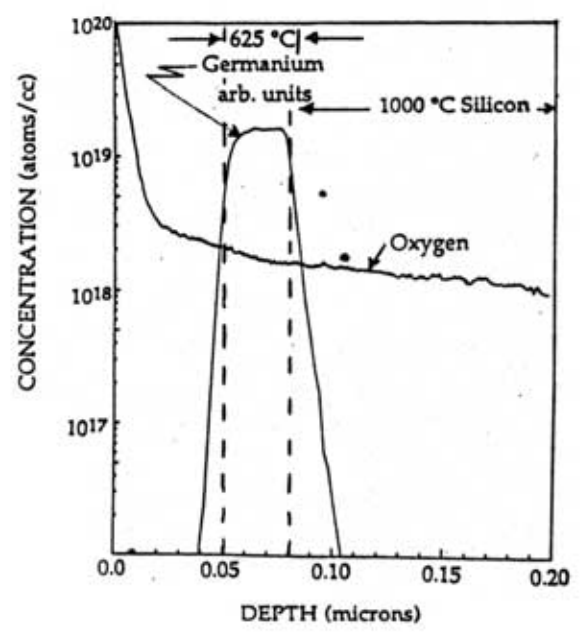


Fig. 2. SIMS profile of oxygen concentration in a multilayer Si<sub>1-x</sub>Ge<sub>x</sub> sample grown with a load-lock.

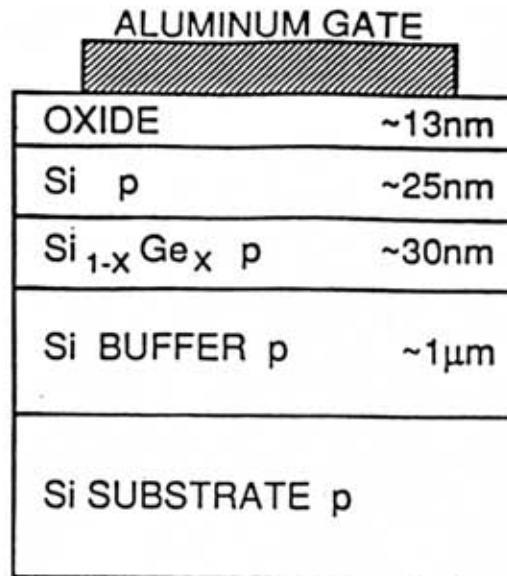


Fig. 3. Sample device structure for a buried layer silicon-germanium capacitor with a thermal oxide insulator. A voltage pulse applied between the gate and the substrate forces the capacitor into deep depletion with the depletion region residing primarily in the Si<sub>1-x</sub>Ge<sub>x</sub> layer.

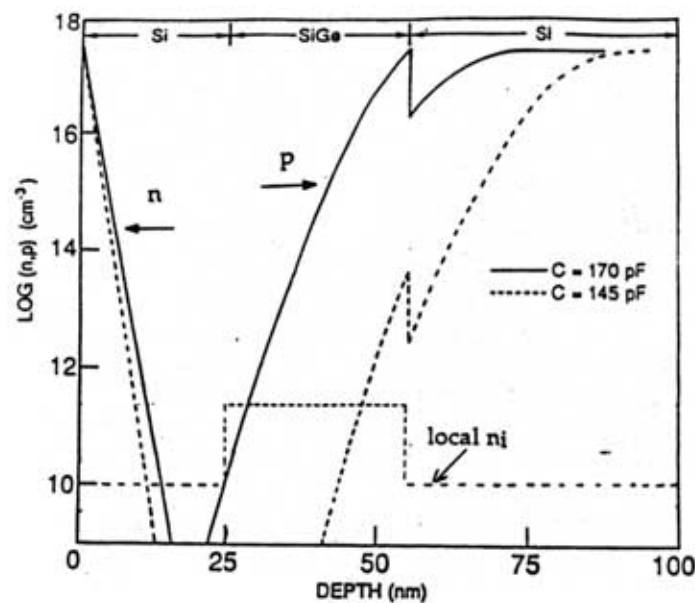


Fig. 4 Logarithm of the carrier profiles as a function of depth into the device for the buried layer Si<sub>1-x</sub>Ge<sub>x</sub> capacitor at two points during its recovery from deep depletion to inversion. For C > 170 pf, the generation in the SiGe is not depressed by high carrier levels. The discontinuity of the hole concentration reflects the discontinuity of the valence band at the Si/Si<sub>1-x</sub>Ge<sub>x</sub> interface.

SAMPLE	DOPING	OXIDE	$\tau_g$ ( $\mu$ s)	$\tau_{rec}$ (sec)
<100>Cz Si	$5 \times 10^{14}$	THERMAL	9.2	325
<100>Cz Si	$5 \times 10^{14}$	DEPOSITED	7.7	275
700°C Si	$2 \times 10^{17}$	THERMAL	2.1	400
SiGe	$3 \times 10^{17}$	THERMAL	1.4	26
SiGe	$2 \times 10^{17}$	DEPOSITED	1.1	19

Fig. 5 Table of generation lifetime data. The  $Si_{0.82}Ge_{0.18}$  lifetimes ( $\tau_g$ ) were calculated assuming an  $n_i$  of  $2.6 \times 10^{11} cm^{-3}$ .  $\tau_{rec}$  is the measured deep depletion recovery time.

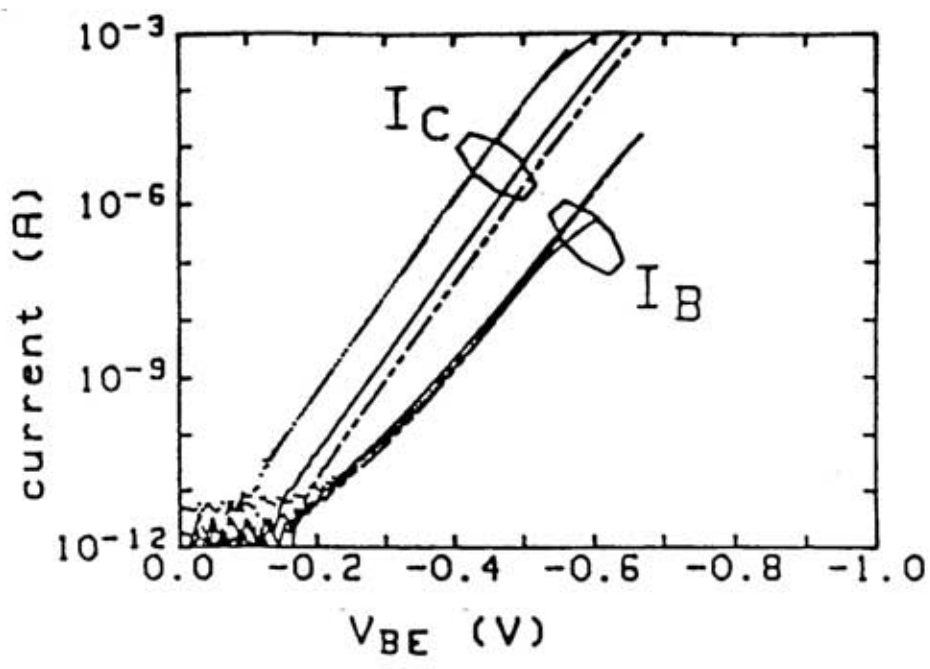


Fig. 6 Room temperature Gummel plots of npn Si/SiGe/Si graded base HBT's with varying base compositions. 0-20% Ge, dot-dash; 7-20% Ge, solid; 13-20%, dashed; and 20% Ge, not graded, dotted.