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GROWTH AND DOPING KINETICS OF $Si_{1-x}Ge_x$ STRUCTURES BY LIMITED REACTION PROCESSING

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ABSTRACT

We have investigated the growth rate and boron doping of $Si_{1-x}Ge_x$ epitaxial films grown by Limited Reaction Processing The growth experiments were carried out at a pressure of 6.0 torr with growth temperatures ranging from 625ºC to 1000ºC. The growth rate increases rapidly upon the additon of a small germane flow to the dichlorosilane in the reaction-rate-limited growth regime, and can not be explained simply by germanium incorporation. The presence of germane can increase the silicon growth rate by up to a factor of one hundred. Boron doping was also studied at high concentrations of boron in Si and $Si_{1-x}Ge_x$ epitaxial films as a function of diborane flow and growth rate supports a simple kinetic model rather than an equilibrium model.

INTRODUCTION

Strained $Si_{1-x}Ge_x$ has been investigated over the past several years for application of heterojunctions to Si based device structures[1]. One succesful method for growing high quality $Si_{1-x}Ge_x$ is LRP (Limited Reaction Processing)[2]. The growth and doping kinetics of these epitaxial films is of interest from both a scientific and technological (device structures) point of view.

LRP is a novel combination of chemical vapor deposition (CVD) and rapid thermal processing (RTP). The growth chamber consists of a round quartz tube in which a 4" wafer is supported, without a susceptor, on 3 quartz pins. The wafer temperature is adjusted by a bank of microprocessor controlled tungsten-halogen lamps, and the system is surrounded by a water-cooled gold-plated reflector.

The $Si_{1-x}Ge_x$ layers are grown at 6.0 torr using 26 sccm dichlorosilane (DCS) in 3.0 slpm H_2 carrier gas along with varying flows of germane (GeH_4) and diborane (B_2H_6). Shown in figure 1 is the growth rate of Si (no GeH_4 flow) under these conditions from 700ºC to 1000ºC. One clearly notices the mass flow limited regime (above 800ºC) and the reaction rate limited regime (below 800ºC). In this low temperature regime the growth rate is determined by the actual chemical reaction rate. These low temperatures are also desirable to minimize interdiffusion between layers. This paper will focus on work in this regime. All work was done on Si <100> substrates.

Growth rates were calculated using layer thicknesses measured by Rutherford Backscattering or Secondary Ion Mass Spectroscopy(SIMS). Boron doping was determined with SIMS using implant standards.

DISCUSSION AND RESULTS

Ge_xSi_{1-x} Growth

As small amounts of GeH_4 (1-2 sccm compared to 26 sccm DCS) are added to the gas flow a marked enhancement is seen in the growth rate of epitaxial layers at 700ºC (figure 2). With Si alone the growth rate is 30Å /min but it increases to over 300Å /min upon the addition of 2 sccm of GeH_4 to the 26 sccm of DCS. Two sccm of GeH_4 yields a film with composition $Si_{0.8}Ge_{0.2}$This growth rate enhancement may not simply be accounted for by considering the additional germanium growth. When the total growth rate is broken down into Ge and Si components (figure 2) we see that the Ge growth rate is linear with GeH_4 flow following simple first order growth kinetics. However the Si growth rate is tremendously enhanced by the GeH_4, up to 10 times the growth rate without GeH_4.

Growth at 700ºC yielded epitaxial films, but "island" (3-dimensional) growth resulted in rough surfaces. Growth at 625ºC however yielded surfaces that looked perfectly smooth when viewed via Nomarski microscopy. At 625ºC we see similar results (figure 3) except that the Si growth rate enhancement is even more dramatic (up to 100x). The Ge component growth rate is virtually identical to the Ge component growth rate at 700ºC and is also linear with GeH_4flow. Since the Si growth rate at 625ºC is substantially lower (even for GeH_4 enhanced growth) this leads to an increased Ge concentration in the epitaxial layer for a given GeH_4 flow. Similar results have been seen using SiH_4 by Uram et. al. at IBM [3].

Some films were grown at 900ºC where mass transport, rather than reaction rate, determines the growth rate in our reactor. As expected the Si growth rate in the mass flow limited growth regime is unaffected by GeH_4 flow.

One possible approach to explaining the large Si growth rate increase is that the silicon surface bonds are mostly terminated by hydrogen, and that competitiion between hydrogen and the growth species for the available bonding sites limits the reaction rate. Because the Ge-H bond is weaker than the Si-H bond, the presence of Ge in the film would lead to faster hydrogen desorption, more open sites, and faster growth. If this were indeed true, the growth rate of pure Si (no GeH_4) should be strongly dependent on the hydrogen partial pressure and/or the DCS/H_2 ratio. Controlled experiments were carried out at 700ºC varying the DCS/H_2 ratio (see Table I). The results show a negligable change in the growth rate while the DCS/H_2 ratio was changed by a factor of six. This suggests that hydrogen-desorption is not a limit to Si growth rate and not involved in the enhanced Si growth as Ge enters the epitaxial film.

Boron Dopant Incorporation

The boron dopant incorpoation as a function of diborane flow (11ppm in H_2) was investigated for Si at 700ºC and 800ºC. As may be seen in figure 4 the boron doping was linear with B_2H_6 flow. We see that this linearity extended above the solid solubility for 700ºC silicon (2e19 cm-3) [4] suggesting a kinetic dependence for the boron incorporation rather than an equilibrium dependence. Equilibrium growth would set an upper limit to the doping levels (solid solubility).

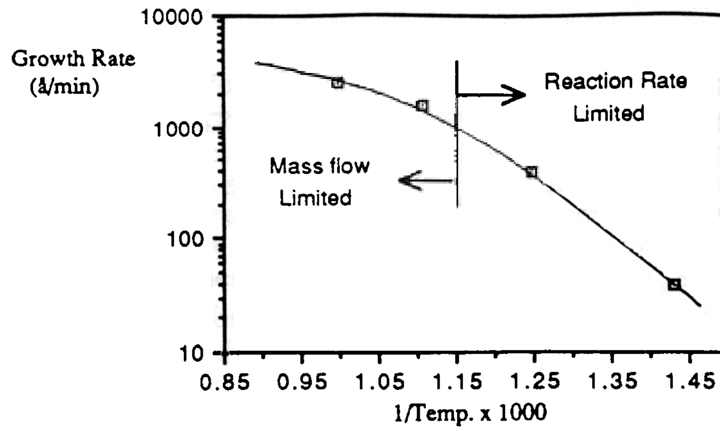

Figure 1 Growth rate of Si vs inverse temperature The DCS flow was 26 sccm, the hydrogen flow was 3.0 slpm, and the pressure 6.0 torr

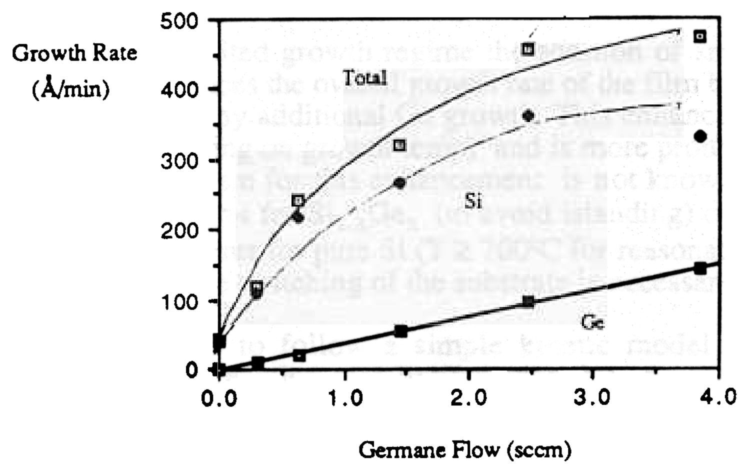

Figure 2 Total growth rate at 700°C. as a function of germane flow for fixed DCS flow. The growth rate has been divided into Ge and Si components.

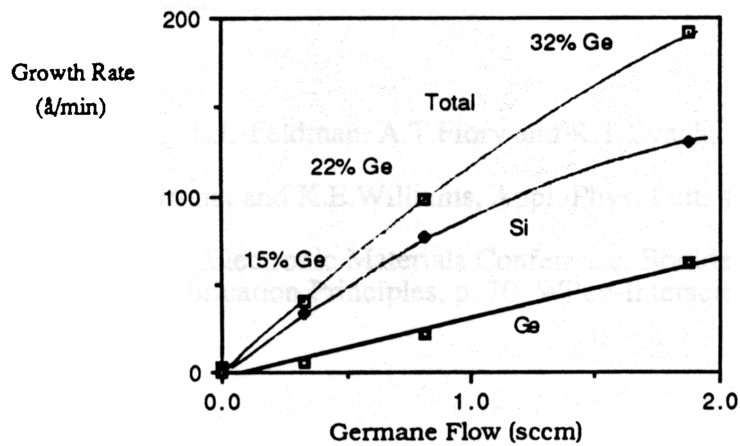

Figure 3 Total Growth Rate at 625°C for various germane flows (DCS flow fixed). The growth rate has been divided into the Si and Ge components.

A simple kinetic model for dopant incorporation would suggest that for a fixed boron (B_2H_6) flux impinging on the substrate an increased film growth rate would lead to a decreased boron density in the growing epitaxial film. Thus the final doping density of the film should be inversely proportional to the film growth rate. Comparing 800ºC Si epi relative to 700ºC epi we observe that the 10x increase in growth rate is matched by a 10x decrease in boron incorporation. This is further evidence for a simple kinetic model. Similar results for Ge_xSi_{1-x} films grown at 625ºC have also been observed. Further evidence of the inverse relationship between concentration and growth rate was demonstrated by changing the GeH_4 flow with DCS flow fixed.As shown earlier, this significantly increases the growth rate. As seen in figure 5 as the growth rate increases, boron concentration decreases.

CONCLUSIONS

In the reaction rate limited growth regime the addition of small amounts of germane flow greatly enhances the overall growth rate of the film by catalyzing the Si growth rate, not simply by additional Ge growth. This enhancement is a large effect (10x to 100x depending on growth temp) and is more pronounced at lower temperatures. The mechanism for this enhancement is not known, however.The necessity of low temperatures for $Si_{1-x}Ge_x$ (to avoid islanding) coupled with the high temperature requirements for pure Si ($T \geq 700$ºC for reasonable growth rate) imply that rapid temperature switching of the substrate is necessary for the growth of multilayer structures.

Boron doping seems to follow a simple kinetic model rather than an equilibrium model in the reaction rate limited growth regime for both Si and Ge_xSi_{1-x} epitaxial films.

ACKNOWLEGEMENTS

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Table Effect of H2 Partial Pressure on 700ºC Si Growth Rates

DCS partial P (torr)	H2 partial P (torr)	Growth Rate (Å/min)
.0507	5.95	24.2
.0502	17.95	27.4
.0507	1.95	21.5

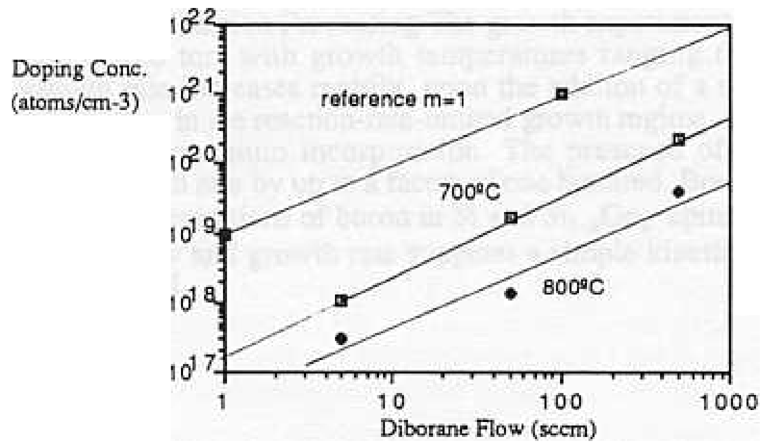

Figure 4 Boron concentration as a function of diborane flow for Si growth at 700ºC and 800ºC. The reference line indicates the slope of a linear relationship

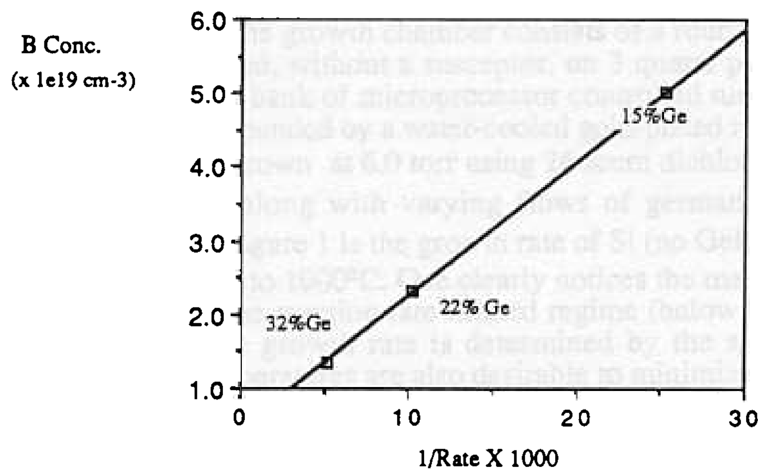

Figure 5 Boron concentration vs inverse growth rate for germanium/silicon alloy films grown at 625ºC. The growth rate was altered by varying the germane flow rate