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# Invited

# SiGe/Si Heterostructures

## Toru Tatsumi, Ken-ichi Aketagawa<sup>\*</sup>, Masayuki Hiroi, and Junro Sakai<sup>\*</sup>

Microelectronics Labs. NEC Corporation, 4-1-1, Miyazakidai, Miyamaeku, Kawasaki, Kanagawa 213, JAPAN \* ANELVA Corporation, 5-8-1, Yotsuya, Fuchu, Tokyo,183, JAPAN

The conditions under which selective epitaxial growth (SEG) is achieved in UHV-CVD with  $Si_2H_6$  are determined by the amount of  $Si_2H_6$ molecules being supplied, and there is a critical gas supply amount (F<sub>c</sub>) beyond which SEG will break down and lose its selectivity. The value of F<sub>c</sub> is itself determined by two factors, growth temperature and the material used for masking, i.e.  $SiO_2$ ,  $Si_3N_4$ . We found that this limiting factor of F<sub>c</sub> was increased through the addition of a small amount of Cl<sub>2</sub>, and that after such addition, the resulting decrease in growth rate is minimal.

### 1. INTRODUCTION

Ultrahigh vacuum chemical vapor deposition (UHV-CVD) using Si<sub>2</sub>H<sub>6</sub>, SiH<sub>4</sub>, or SiH<sub>2</sub>Cl<sub>2</sub> has many advantages, including low superature processing,  $Ge_x Si_{1-x}$  alloy growth, and selective epitaxial growth become technology become important an for fabricating structure of ULSI's. SEG of Si or  $Ge_X Si_{1-x}$  provides very fine self-aligned structures, as a layer d such self-aligned epitaxial base of bipolar transistors. Successful achievement of SEG has been reported for a SiH<sub>2</sub>Cl<sub>2</sub> system. However, the growth rate with this  $SiH_2Cl_2$  system. However, the growth rate with this  $SiH_2Cl_2$ system was very low at low temperature under 700°C because the maximum growth rate was limited by the desorption of Cl from the Si surface.  $Si_2H_6$  or  $SiH_4$  UHV-CVD systems have better growth rates but SEG has ver to be achieved with converting has yet to be achieved with conventional type UHV-CVD systems, which have hot-wall isothermal furnace reactors. Hirayama et al. have reported that low temperature SEG was achieved below  $600^{\circ}$ C with pure Si<sub>2</sub>H<sub>6</sub> in gas source Si-MBE with a liquid nitrogen shroud, but this low temperature SEG produced a consequently limited low growth rate, in the range of about 10A/min.<sup>2)</sup> We report here on the conditions

We report here on the conditions critical to the achievement of SEG on SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> masked Si(100) substrates with a new cold-wall type UHV-CVD system. This water cooled cold-wall type growth chamber allowed us to achieve 1000A thich SEG on the SiO<sub>2</sub> masked Si(100) substrate at 650° C. Conditions for SEG were limited by the total amount of supply Si<sub>2</sub>H<sub>6</sub> molecules. The critical gas amount (F<sub>C</sub>), that at which SEG break down and loses its selectivity varied with variations in growth temperature and in the materials used for, such as SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub>. It was considered that the selectivity was made possible by the fact that with the cold-wall type UHV-CVD, few of the  $Si_2H_6$  fragment formed by thermal dissociation and interrupted SEG were irradiated on the  $SiO_2$  surface. We also found that  $F_C$  can be increased with minimal decrease in growth rate by the addition of a small amount of  $Cl_2$ .

#### 2. EXPERIMENTAL

UHV-CVD Our system included а Our UHV-CVD system included a stainless steel growth chamber, a water cooled jacket, and separate nozzles for Si<sub>2</sub>H<sub>6</sub> and Cl<sub>2</sub>. A 10001/s turbo-molecular pump reduced background pressure on the growth chamber to  $1.5 \times 10^{-9}$  Torr. 6-inch (100) Si wafers were masked with 2000A patterns of either SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub>. Wafers were precleaned with a chemical solution (NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O=1:6:20) to form a protective thin oxide layer before loading into the growth chamber. The thin oxide layer on the Si surface was evaporated by a layer on the Si surface was evaporated by a thermal process, during which time the SieHe was supplied. The cleaning Si2H6 was supplied. The cleaning temperature was 800° C and Si<sub>2</sub>H<sub>6</sub> temperature was  $800^{\circ}$ C and  $Si_2H_6$  was supplied at 5SCCM with 10 sec within the was overall cleaning process time of 1 min. Successful SEG condition was confirmed by RHEED in the growth chamber.

The source gas, pure  $Si_2H_6$ ,  $GeH_4$  and  $Cl_2$ , first passed through a mass-flow cont roller and then into the growth chamber trough a nozzle without precracking.  $Si_2H_6$  and  $GeH_4$  pressure in the growth chamber was  $7x10^{-4}$  Torr, and  $Cl_2$  pressure was varied from  $1x10^{-6}$  to  $1x10^{-5}$  Torr.

### 3. LIMITING CONDITIONS FOR OF SEG

In our cold-wall type UHV-CVD system, poly-Si nucleation did not begin immediately. There was first a short period during which SEG was achieved. Figure 1 shows the length of this interval as a function of the  $Si_2H_6$  flow rate at growth temperature of 650 °C. Interval length is inversely proportional to gas flow rate,

which means that the total amount of gas supplied over the course of an interval be a constant. This total amount of will supplied gas above which poly-Si nucleation occurs is the critical gas amount  $F_c$ .  $F_c$ can be expressed as  $F_c = F \times t_c$  where F is  $Si_2H_6$  flow rate and  $t_c$  is interval length. The condition at which SEG is interrupted predicted using this simple be can fomular. This relation suggests that there is a critical concentration of adatoms on surfaces which must be reached for SiO<sub>2</sub> poly-Si nucleation to start, since in the region of molecular flow the number of adatoms decomposed from  $Si_2H_6$  molecules is closely proportional to the volum of gas supplied without adatoms desorption. On Si surfaces, a few percent of Si<sub>2</sub>H<sub>6</sub> molecules decompose and contribute to epitaxial epitaxial growth, while on SiO<sub>2</sub> surfaces most of the molecules are reflected and probably only a portion decomposes small to remain as adatoms. So long as the concentration of these adatoms on the  $SiO_2$  surface does not SEG exceed the critical value, will continue.

Figure 2 shows the critical gas amount (F<sub>c</sub>) for SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> masking patterns as a function of the substrate temperature. With  $SiO_2$  pattern and below 700°C,  $F_C$  deincreasing creased with increasin temperature independent of substrate gas flow increased rate because Si<sub>2</sub>H<sub>6</sub> dissociation Above 700°C with SiO2 on the SiO<sub>2</sub> surface. pattern, Fc increases with substrate temperature because of the etching of the  $SiO_2$  surface produced by decomposed  $Si_2H_6$ . Tabe et al. have reported that at high growth temperatures, Si and SiO<sub>2</sub> reacts as,  $Si+SiO_2->SiO_3$  and then adatoms evaporate the volatile SiO molecules. as

With a  $Si_3N_4$  pattern,  $F_C$  was ten times smaller than that of for  $SiO_2$  and decreased continuously with increasing temperature. This fact suggests substrate that, on a surface, Si2H6 Si3N4 dissociation efficiency is ten times larger than that on a SiO<sub>2</sub> surface and there is no reaction, which produce volatile molecules, between adatoms and surface. Using pure  $Si_2H_6$ , the maximum SEG thickness  $(T_C)$  on  $SiO_2$  and on SiO<sub>2</sub> 1000A patterns 100A, Si3N4 were and respectively at 650°C.

#### 4. Cl<sub>2</sub> ADDITIONAL EFFECTS

When  $Cl_2$  pressure was increased,  $F_C$ increased dramatically, while, there was little decrease in growth rate. Figure 3 shows  $F_C$  and growth rate dependences on  $Cl_2$ flow rate at 650 °C.  $Si_2H_6$  flow rate was 3SCCM. With 0.03SCCM  $Cl_2$  addition which is 1/100 of  $Si_2H_6$  flow rate, twenty times larger  $F_C$  was obtained on  $Si_3N_4$  pattern than that without  $Cl_2$ . Growth rate also decreased but when  $Cl_2$  flow rate was was 0.03SCCM, 50% growth rate of the pure  $Si_2H_6$ case was obtained.

Figure 4 shows  $F_C$  dependence on  $Si_2H_6$ flow rate at 700°C.  $Cl_2$  flow rate was OSCCM and 0.03SCCM. While  $F_C$  is independent of  $Si_2H_6$  flow rate without  $Cl_2$  addition,  $F_C$ varied as  $Si_2H_6$  flow rate when  $Cl_2$  flow rate is 0.03SCCM.

# 5.GROWTH of $Si_{1-x}Ge_x$ films

 $Si_{1-x}Ge_x$  was grown by use of  $Si_2H_6$  and GeH<sub>4</sub>. Figure 5 shows the source gas flow rate ratio dependence of the Ge fraction x of  $Si_{1-x}Ge_x$ . Under the condition of fixed







Fig. 2. Critical gas amount  $(F_c)$  for SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> masking patterns as a function of substrate temperature.



Fig. 3. Critical gas amount  $(F_c)$  for SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> patterns and growth rate dependences on Cl<sub>2</sub> flow rate at 650°C. Si<sub>2</sub>H<sub>6</sub> flow rate was 3 SCCM.



Fig. 4. Critical gas amount ( $F_c$ ) for SiO<sub>2</sub> dependence on Si<sub>2</sub>H<sub>6</sub> flow rate at 700°C. Cl<sub>2</sub> flow rates were 0 and 0.03 SCCM.

total source gas flow rate and substrate temperature, the Ge fraction x increased monotonously as the GeH<sub>4</sub> flow rate ratio increased until x=0.3.

Figure 6 shows substrate temperature dependence of the Ge fraction. This result was obtained under the condition that the  $Si_{1-x}Ge_x$  growth rate was changed with both the substrate temperature and the source gas flow rate ratio. In this temperature region, the Ge fraction depended only on the source gas flow rate ratio without the dependence on substrate temperature.

dependence on substrate temperature. Figure 7 shows the Arrhenius plots of Si and  $Si_{1-x}Ge_x$  epitaxial growth rates. The source gases were supplied in sufficient so that the growth rate would be amounts by substrate temperature. limited the independent of the total flow rate of the source gases. The  $Si_{1-x}Ge_x$  growth condition the same as the condition in Fig.4, was the Ge 0.13. The fraction where was activation energy for the Si growth rate and Sig.87Geg.13 growth rate were 47 and 27 Kcal/mol, respectively. Once we determined flow rate ratio, source gas the Ge the fraction was decided according to Fig.3 and was independent of substrate temperature, shown in Fig.4, inspite of the increase in growth rate with temperature, as in Fig.5. Taking advantage of this relationship, the Ge fraction can be controlled precisely by the control of the source gas flow rate ratio in this system.

#### 6. CONCLUSION

The conditions critical to the achievement of SEG on SiO2 or Si3N4 masked Si(100) substrates were examined closely with a new water cooled cold-wall type UHV-This us CVD system. system allowed to achieve 1000A thich SEG on the SiO<sub>2</sub> masked Si(100) substrate at 650°C without halogen Conditions for SEG were limited by gases. the total amount of supply Si<sub>2</sub>H<sub>6</sub> molecules. The selectivity was made possible by the fact that with the cold-wall type UHV-CVD, few of the  $Si_2H_6$  fragment formed by thermal and dissociation interrupted SEG were irradiated on the SiO<sub>2</sub> surface. We also found that  $F_C$  can be increased with minimal decrease in growth rate by the addition of a small amount of  $Cl_2$ . Under  $7 \times 10^{-6}$  Torr a small amount of  $Cl_2$ . Under  $7 \times 10^{-6}$  Torr  $Cl_2$  pressure at 650°C, ten times larger  $T_C$  was obtained with 50% growth rate of the pure Si<sub>2</sub>H<sub>6</sub> case.

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Fig. 3. Source gas flow rate ratio dependence of the Ge fraction. The Ge fraction was increased monotonously with the GeH<sub>4</sub> flow rate ratio.



Fig. 4. The substrate temperature dependence of the Ge fraction. The Ge fraction was independent of the substrate temperature and depended only on the source gas flow rate ratio.



Fig. 5. Arrhenius plots of Si and  $Si_{1-x}Ge_x$  epitaxial growth. Epitaxial growth was carried out under the condition that the growth rate was independent of total gas flow rate.