Extended Abstracts of the 1993 International Conference on Solid State Devices and Materials, Makuhari, 1993, pp. 225-227

## Invited

# Si<sub>1-x</sub>Ge<sub>x</sub> Epitaxial Growth Using UHV-CVD and Its Device Applications

Toru Tatsumi, Ken-ichi Aketagawa<sup>\*</sup>, K.Miyanaga and Masayuki Hiroi Microelectronics Labs. NEC Corporation, 34, Miyukigaoka, Tsukuba, Ibaragi 305, JAPAN <sup>\*</sup>ANELVA Corporation, 5-8-1, Yotsuya, Fuchu, Tokyo,183, JAPAN

## ABSTRACT

ABSTRACT The conditions under which selective epitaxial growth (SEG) is achieved in UHV-CVD with  $Si_2H_6$  and  $GeH_4$  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. This technique was applied to the self-aligned base fabrication of high speed bipolar transistors. transistors.

## 1. INTRODUCTION

Ultrahigh vacuum chemical vapor deposition (UHV-CVD) using  $Si_2H_6$ ,  $SiH_4$ , or  $SiH_2Cl_2$  has many advantages, including low temperature processing,  $Ge_xSi_{1-x}$  alloy growth, and selective epitaxial growth (SEG).<sup>1</sup>) In these advantages, SEG has become an important technology for become an important technology for fabricating structure of ULSI's. SEG of Si or  $Ge_x Si_{1-x}$  provides very fine self-aligned structures, such as a self-aligned epitaxial base layer of bipolar epitaxial base layer 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<sub>2</sub>Cl<sub>2</sub> 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<sub>2</sub>H<sub>6</sub> or SiH<sub>4</sub> UHV-CVD systems have better growth rates but SEG has yet to be achieved with conventional type UHV-CVD systems, which have hot-wall vet to be achieved with conventional UHV-CVD systems, which have hot-wall isothermal furnace reactors. Hirayama

type UNV-CVD systems, which have not-wall isothermal furnace reactors. Hirayama et al. have reported that low temperature SEG was achieved below 600°C with pure Si2H6 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 critical to the achievement of Si and Si1-xGex SEG on SiO<sub>2</sub> or Si3N4 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 thick 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>H6 molecules. The critical gas amount (Fc), that at which SEG break down and loses its selectivity varied with variations in that at which SEG break down and loses its selectivity varied with variations in growth temperature and in the materials used for, such as  $SiO_2$  or  $Si_3N_4$ . 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 Cl2.

### 2. EXPERIMENTAL

2. EAFERIMENTAL Our UHV-CVD system included a stain-less 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 were masked with 2000A patterns of eitner 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 pro-tective thin oxide layer before loading into the growth chamber. The thin oxide layer on the Si surface was evaporated by a thermal process, during which time the Si<sub>2</sub>H<sub>6</sub> was supplied. The clearing temperature was 8000 c and Si<sub>4</sub>H<sub>6</sub> cleaning temperature was 800°C and Si2H6 was supplied at 5SCCM with 10 sec within the overall cleaning process time of 1 min. Successful SEG condition was confirmed by

RHEED in the growth chamber. The source gas, pure Si<sub>2</sub>H<sub>6</sub>, GeH<sub>4</sub> and Cl<sub>2</sub>, first passed through a mass-flow controller and then into the growth chamber trough a nozzle without precracking. Si<sub>2</sub>H<sub>6</sub> or GeH<sub>4</sub> pressure in the growth chamber was 10<sup>-4</sup> Torr, and Cl<sub>2</sub> pressure was varied from  $10^{-4}$  Torr, and Cl<sub>2</sub> pressure was varied from  $1 \times 10^{-6}$  to  $1 \times 10^{-5}$  Torr.

3. LIMITING CONDITIONS FOR 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. Interval length is inversely pro-portional to gas flow rate, which means that the total amount of gas supplied over the course of an interval will be a constant. This total amount of supplied gas above which poly-Si nucleation occurs is the critical gas amount Fc. Fc can be expressed as Fc = F x tc where F is Si<sub>2</sub>H<sub>6</sub> flow rate and tc is interval length. The condition at which SEG is interrupted can be predicted using this is interrupted can be predicted using this simple fomular. This relation suggests that there is a critical concentration of

adatoms on  $SiO_2$  surfaces which must be reached for poly-Si nucleation to start, since in the region of molecular flow the number of adatoms decomposed from  $Si_2H_6$ number of adatoms decomposed from  $G_{2H_0}$ 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 growth, while on SiO<sub>2</sub> surfaces most of the molecules are reflected and probably only a small portion decomposes to remain as adatoms. So long as the concentration of these adatoms on the SiO<sub>2</sub> surface does not exceed the critical value, SEC will continue Figure 1 shows the SEG will continue. Figure 1 shows the 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 the substrate temperature. With  $SiO_2$  pattern and below 700°C,  $F_C$  decreased with increasing substrate temperature inincreasing substrate temperature in-dependent of the gas flow rate because  $Si_2H_6$  dissociation increased on the  $SiO_2$ surface. Above  $700^{\circ}$  C with SiO<sub>2</sub> pattern, F<sub>C</sub> increases with substrate surface. Above 700°C with SiO<sub>2</sub> pattern,  $F_C$ increases with substrate temperature because of the etching of the SiO<sub>2</sub> surface produced by decomposed Si<sub>2</sub>H<sub>6</sub>. Tabe et al. have reported that at high growth temperatures, Si and SiO<sub>2</sub> reacts as, Si+Si O<sub>2</sub>-SSiO<sub>3</sub><sup>3</sup>) and then adatoms evaporate as

O<sub>2</sub>->SiO,<sup>3)</sup> and then adatoms evaporate as the volatile SiO molecules. With a Si<sub>3</sub>N<sub>4</sub> pattern, F<sub>C</sub> was ten times smaller than that of for SiO<sub>2</sub> and decreased continuously with increasing substrate temperature. This fact suggests that, on a Si<sub>3</sub>N<sub>4</sub> surface, Si<sub>2</sub>H<sub>6</sub> 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<sub>C</sub>) on  $SiO_2$  and  $Si_3N_4$  patterns were 1000A and 100A, Si<sub>3</sub>N<sub>4</sub> patterns were respectively at 650°C.

4. Cl<sub>2</sub> ADDITIONAL EFFECTS When Cl<sub>2</sub> pressure was increased, F<sub>C</sub> increased dramatically, while, there was little decrease in growth rate. Figure 2 shows F<sub>C</sub> 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 3SCCM. With 0.03SCCM Cl<sub>2</sub> addition which is 1/100 of SicHe flow rate twenty times 3SCCM. With 0.03SCCM  $Cl_2$  addition which is 1/100 of Si<sub>2</sub>H<sub>6</sub> flow rate, twenty times larger F<sub>C</sub> was obtained on Si<sub>3</sub>N<sub>4</sub> pattern than that without Cl<sub>2</sub>. Growth rate also decreased but when Cl<sub>2</sub> flow rate was was 0.03SCCM, 50% growth rate of the pure Si<sub>2</sub>H<sub>6</sub> case was obtained. On the Si surface, Cl<sub>2</sub> and Si<sub>2</sub>H<sub>6</sub> are adsorped competitively on the Si surface and the growth rate was

and Si<sub>2</sub>H<sub>6</sub> are adsorped competitively on the Si clean surface and the growth rate was not limited only by Si<sub>2</sub>H<sub>6</sub> gas supply, but Cl desorption on the Si surface. Figure 3 shows F<sub>C</sub> dependence on Si<sub>2</sub>H<sub>6</sub> flow rate at 700°C. Cl<sub>2</sub> flow rate was OSCCM and 0.03SCCM. While F<sub>C</sub> is independent of Si<sub>2</sub>H<sub>6</sub> flow rate without Cl<sub>2</sub> addition, F<sub>C</sub> varied as Si<sub>2</sub>H<sub>6</sub> flow rate when Cl<sub>2</sub> flow rate is 0.03SCCM. This fact is considered to be as follows.

rate is 0.03SCCM. This fact is considered to be as follows. Our model assumes that adatoms which was produced by Si<sub>2</sub>H<sub>6</sub> decomposition on the SiO<sub>2</sub> surface are entrapped on the SiO<sub>2</sub> surface with a mean residence time. When adatoms concentration reached critical adatoms concentration reached critical value (N<sub>C</sub>), poly Si nucliation starts and SEG is interrupted. We may write the kinetic equation for this system as  $dN/dt=K_{I}F-K_{D}N$ 

 $dN/dt=K_1F-K_DN$ where N is the adatom concentration on SiO<sub>2</sub> surface, F is the incident Si<sub>2</sub>H<sub>6</sub> flax, K<sub>1</sub> is the decomposed efficiency of Si<sub>2</sub>H<sub>6</sub> on SiO<sub>2</sub> surface, K<sub>D</sub> is the desorption co-efficent. For case without desorption of adatom, namely K<sub>D</sub>=0, N is simply N=K<sub>1</sub>Ft. When poly Si nucliation starts, N is equal

to Nc and t is inversely proportional to F. The growth without  $Cl_2$  is this case. For case with desorption, N is  $N=(K_1/K_D)F(1-exp(-K_Dt))$ When N is constant, F x t is not constant but varied with F. SEG enhancement effect with  $Cl_2$  is considered to be due to this etching process etching process.

## 5.GROWTH of Si1-x Gex films

5.GROWTH of Si<sub>1-x</sub>Ge<sub>x</sub> films Si<sub>1-x</sub>Ge<sub>x</sub> was grown by use of Si<sub>2</sub>H<sub>6</sub> and GeH<sub>4</sub>. Under the condition of fixed 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 4 shows substrate temperature dependence of the Ge fraction. This result was obtained under the condition that the Si<sub>1-x</sub>Ge<sub>x</sub> growth rate was changed with both the substrate tempera-ture and the source gas flow rate ratio. In this temperature region, the Ge was changed with both the substrate tempera-ture 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. Figure 5 shows growth rate dependence on total flow rate. Si<sub>2</sub>H<sub>6</sub> and GeH<sub>4</sub> flow rate ratio is constant. With GeH<sub>4</sub> addtion, the growth rate at reaction contralled region increases, while decreases at supply contralled region. Figure 6 shows the Arrhenius plots of Si and Si<sub>1-x</sub>Ge<sub>x</sub> epitaxial growth rates. The source gases were supplied in sufficient amounts so that the growth rate would be limited by the substrate temperature, independent of the total flow rate of the source gases. The Si<sub>1-x</sub>Ge<sub>x</sub> growth condition was the same as the condition in Fig.4, where the Ge fraction was 0.13. The activation energy for the Si growth rate and Si<sub>0.87</sub>Ge<sub>0.13</sub> growth rate were 47 and 27 Kcal/mol, respectively. Once we determined the source gas flow rate ratio, the Ge fraction was decided and was independent of substrate temperature, shown in Fig.4, with fraction was decided and was 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.

Indeed, the incorporation processes for Si and Ge are complex and they are considerably different, but Fig.4 shows that the incorporation rates for Si and Ge are nearly the same. We consider then that the common rate limiting step exists in each incorporation process. Therfore, as the film growth rate varies with substrate temperature, the composition ratio is constant. This common rate limiting step is speculated as the hydrogen desorption step from the results of Fig. 5. Liehr et al. reported that the Si growth rate using the SiH<sub>4</sub> system was limited by the hydrogen desorption rate because the activation SiH<sub>4</sub> system was limited by the hydrogen desorption rate because the activation energy for the Si growth rate was 46 Kcal/mol, which corresponded to the activation energy of hydrogen desorption from the Si(100) surface. The activation energy obtained from Fig.5 is extremely close to that of the hydrogen desorption. Then, the Si growth rate using Si<sub>2</sub>H<sub>6</sub> is also thought to be limited by hydrogen desorption. When GeH<sub>4</sub> was added, the Si<sub>1-</sub>  $_{x}$ Gex growth rate was enhanced in the low-temperature region and the activation x Gex growth rate was enhanced in the low-temperature region and the activation energy was reduced, as shown in Fig.5. Meyerson et al. have also observed the same phenomenon and speculate that Ge atoms at the growth interface serve as hydrogen desorption centers and reduce the activation energy for hydrogen desorption.

## 6. CONCLUSION

The conditions critical to the achievement of SEG on SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub> masked with a new water cooled cold-wall type UHV-CVD system. This system allowed us to Si(100) substrates CVD system. This system allowed us to achieve 1000A thich SEG on the  $SiO_2$  masked Si(100) substrate at 650°C gases. Conditions for SEG 650° C without halogen were limited by the total amount of supply Si<sub>2</sub>H<sub>6</sub> molecules.

Acknowledgment

authors The wish to thank Drs. Y.Matsumoto and M.Nakamae for their suggestions and encouragement.

### REFERENCES

B. S. Mayerson, Appl.Phys.Lett.48,797(1986). H. Hirayama, T. Tatsumi, and N. Aizaki, Appl.Phys.Lett.51,2213(1987). M. Tabe, Jpn.J.Appl.Phys.21,534(1982). 1)B. 2)H. 3)M.



Critical gas amount (Fc) for SiO2 and Si3N4 masking Fig. 1 patterns as a function of substrate temperature.



Fig. 2 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 Cl2 flow rate at 650°C. Si<sub>2</sub>H<sub>6</sub> flow rate was 3 SCCM.



Fig. 3 Critical gas amount (F<sub>c</sub>) for SiO<sub>2</sub> dependence on Si2H6 flow rate at 700°C. Cl2 flow rates were 0 and 0.03 SCCM.







Fig. 5 Growth rate dependence on total flow rate.



Fig. 6 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.