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SiGe/Si Heterostructures

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The conditions under which selective epitaxial growth (SEG) is achieved in UHV-CVD with Si$_2$H$_6$ are determined by the amount of Si$_2$H$_6$ molecules being supplied, and there is a critical gas supply amount (F$_c$) beyond which SEG will break down and lose its selectivity. The value of F$_c$ is itself determined by two factors, growth temperature and the material used for masking, i.e. SiO$_2$, Si$_3$N$_4$. We found that this limiting factor of F$_c$ was increased through the addition of a small amount of Cl$_2$, and that after such addition, the resulting decrease in growth rate is minimal.

1. INTRODUCTION

Ultrahigh vacuum chemical vapor deposition (UHV-CVD) using Si$_2$H$_6$, SiH$_4$, or SiH$_2$Cl$_2$ has many advantages, including low temperature processing, Ge$_x$Si$_{1-x}$ alloy growth, and selective epitaxial growth (SEG). In these advantages, SEG has 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 transistors. Successful achievement of SEG has been reported for a SiH$_2$Cl$_2$ system. However, the growth rate with this SiH$_2$Cl$_2$ system was very low at low temperature below 700°C because the maximum growth rate was limited by the desorption of Cl$_2$ from the Si surface. Si$_2$H$_6$ or SiH$_4$ UHV-CVD systems have better growth rates but SEG 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°C with pure Si$_2$H$_6$ 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 10Å/min.1 We report here on the conditions critical to the achievement of SEG on SiO$_2$ or Si$_3$N$_4$ 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 1000Å thick SEG on the SiO$_2$ masked Si(100) substrate at 650°C. Conditions for SEG were limited by the total amount of supply Si$_2$H$_6$ molecules. The critical gas amount (F$_c$), 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$_3$N$_4$. It was considered that the selectivity was made possible by the fact that with the cold-wall type UHV-CVD, few of the Si$_2$H$_6$ 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

Our UHV-CVD system included a stainless steel growth chamber, a water cooled jacket, and separate nozzles for Si$_2$H$_6$ and Cl$_2$. A 1000l/s turbo-molecular pump reduced background pressure on the growth chamber to 1.5x10$^{-6}$ Torr. 6-inch (100) Si wafers were masked with 2000Å patterns of either SiO$_2$, or Si$_3$N$_4$. Wafers were precleaned with a chemical solution (NH$_3$/OH:H$_2$O$_2$:H$_2$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 thermal process, during which time the Si$_2$H$_6$ was supplied. The cleaning temperature was 800°C and Si$_2$H$_6$ was supplied at 5SCCM with 10sec 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$_2$H$_6$, GeH$_4$ and Cl$_2$, first passed through a mass-flow cont roller and then into the growth chamber through a nozzle without precracking. Si$_2$H$_6$ and GeH$_4$ pressure in the growth chamber was 7x10$^{-4}$ Torr, and Cl$_2$ pressure was varied from 1x10$^{-6}$ to 1x10$^{-8}$ 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$_2$H$_6$ 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 will be a constant. This total amount of 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 \( \text{Si}_2\text{H}_6 \) flow rate and \( t_c \) is interval length. The condition at which SEG is interrupted can be predicted using this simple formula.

This relation suggests that there is a critical concentration of adatoms on \( \text{SiO}_2 \) surfaces which must be reached for poly-Si nucleation to start, since in the region of molecular flow the number of adatoms decomposed from \( \text{Si}_2\text{H}_6 \) molecules is closely proportional to the volume of gas supplied without adatoms desorption. On \( \text{Si} \) surfaces, a few percent of \( \text{Si}_2\text{H}_6 \) molecules decompose and contribute to epitaxial growth, while on \( \text{SiO}_2 \) 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 \( \text{SiO}_2 \) surface does not exceed the critical value, SEG will continue.

Figure 2 shows the critical gas amount \( (F_c) \) for \( \text{SiO}_2 \) and \( \text{Si}_3\text{N}_4 \) masking patterns as a function of the substrate temperature. With \( \text{SiO}_2 \) pattern and below 700°C, \( F_c \) decreased with increasing substrate temperature independent of the gas flow rate because \( \text{Si}_2\text{H}_6 \) dissociation increased on the \( \text{SiO}_2 \) surface. Above 700°C with \( \text{SiO}_2 \) pattern, \( F_c \) increases with substrate temperature because of the etching of the \( \text{SiO}_2 \) surface produced by decomposed \( \text{Si}_2\text{H}_6 \).

With a \( \text{Si}_3\text{N}_4 \) pattern, \( F_c \) was ten times smaller than that of \( \text{SiO}_2 \) and decreased continuously with increasing substrate temperature. This fact suggests that, on a \( \text{Si}_3\text{N}_4 \) surface, \( \text{Si}_2\text{H}_6 \) dissociation efficiency is ten times larger than that on an \( \text{SiO}_2 \) surface and there is no reaction, which produce volatile molecules, between adatoms and substrate. Using pure \( \text{Si}_2\text{H}_6 \), the maximum SEG thickness (\( t_c \)) on \( \text{SiO}_2 \) and \( \text{Si}_3\text{N}_4 \) patterns were 1000Å and 100Å, respectively at 850°C.

4. \( \text{Cl}_2 \) ADDITIONAL EFFECTS

When \( \text{Cl}_2 \) 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 \( \text{Cl}_2 \) flow rate at 850°C. \( \text{Si}_2\text{H}_6 \) flow rate was 3SCCM. With 0.03SCCM \( \text{Cl}_2 \) addition which is 1/100 of \( \text{Si}_2\text{H}_6 \) flow rate, twenty times larger \( F_c \) was obtained on \( \text{Si}_3\text{N}_4 \) pattern than that without \( \text{Cl}_2 \). Growth rate also decreased but when \( \text{Cl}_2 \) flow rate was 0.03SCCM, 50% growth rate of the pure \( \text{Si}_2\text{H}_6 \) case was obtained.

Figure 4 shows \( F_c \) dependence on \( \text{Si}_2\text{H}_6 \) flow rate at 700°C. \( \text{Cl}_2 \) flow rate was 0.03SCCM and 0.3SCCM. While \( F_c \) is independent of \( \text{Si}_2\text{H}_6 \) flow rate without \( \text{Cl}_2 \) addition, \( F_c \) varied as \( \text{Si}_2\text{H}_6 \) flow rate when \( \text{Cl}_2 \) flow rate is 0.03SCCM.

5. GROWTH of \( \text{Si}_{1-x}\text{Ge}_x \) films

\( \text{Si}_{1-x}\text{Ge}_x \) was grown by use of \( \text{Si}_2\text{H}_6 \) and \( \text{GeH}_4 \). Figure 5 shows the source gas flow rate ratio dependence of the Ge fraction \( x \) of \( \text{Si}_{1-x}\text{Ge}_x \). Under the condition of fixed...
total source gas flow rate and substrate temperature, the Ge fraction \( x \) increased monotonously as the GeH\(_4\) 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.

Figure 7 shows the Arrhenius plots of Si and \( Si_{1-x}Ge_x \) 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 \( Si_{1-x}Ge_x \) 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 \( Si_{1-0.2}Ge_{0.8} \) growth rate were 47 and 27 Kcal/mol, respectively. Once we determined the source gas flow rate ratio, the Ge fraction was decided according to Fig.3 and was independent of substrate temperature, shown in Fig.4, at 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 \( SiO_2 \) or \( Si_3N_4 \) masked \( Si(100) \) substrates were examined closely with a newly water cooled cold-wall type UHV-CVD system. This system allowed us to achieve 1000A thick SEG on the \( SiO_2 \) masked \( Si(100) \) substrate at 650°C without halogen gases. Conditions for SEG were limited by the total amount of supply \( Si_2He \) molecules. The selectivity was made possible by the fact that with the cold-wall type UHV-CVD, few of the \( Si_2He \) fragment formed by thermal dissociation and interrupted SEG were irradiated on the \( SiO_2 \) surface. We also found that \( Pc \) can be increased with minimal decrease in growth rate by the addition of a small amount of Cl\(_2\). Under 7x10^{-6} Torr Cl\(_2\) pressure at 650°C, ten times larger \( Tc \) was obtained with 50% growth rate of the pure \( Si_2He \) case.

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REFERENCES