Phosphorus doping of Si and Si$_{1-x}$Ge$_x$ grown by ultrahigh vacuum chemical vapor deposition using Si$_2$H$_6$ and GeH$_4$

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100 ppm PH$_3$ diluted in hydrogen is used as the n-type dopant gas in Si and Si$_{1-x}$Ge$_x$ epilayers grown by ultrahigh vacuum chemical vapor deposition (UHVCVD) using Si$_2$H$_6$ and GeH$_4$. The phosphorus concentration in Si increases linearly at a small PH$_3$ flow rate and becomes nearly saturated at higher flow rates, while the phosphorus concentration in Si$_{1-x}$Ge$_x$ only shows a nearly linear behavior with PH$_3$ flow rate. The growth rates of Si and Si$_{1-x}$Ge$_x$ epilayers decrease seriously (~50%) and slightly (~10%) with the increase of PH$_3$ flow rate, respectively. These results can be explained by a model based on the enhancement of hydrogen desorption rate at smaller PH$_3$ flow rates and different levels of the effects of phosphorus blocking of surface-activated sites between Si and Si$_{1-x}$Ge$_x$ epilayers at higher PH$_3$ flow rates. © 1996 American Institute of Physics.

The fabrication of new high performance devices, such as Si/Si$_{1-x}$Ge$_x$ modulation-doped field effect transistors (MODFETs), SiGe channel metal-oxide-semiconductor field effect transistors (MOSFETs), and heterojunction bipolar transistors (HBTs), has placed the strong requirement of low temperature Si/Si$_{1-x}$Ge$_x$ epitaxial technologies. Consequently, several low temperature epitaxial techniques that include Si molecular beam epitaxy (Si-MBE), ultrahigh vacuum chemical vapor deposition (UHVCVD), and ultralow pressure CVD (U-LPCVD), have been proposed to grow Si/Si$_{1-x}$Ge$_x$ heterostructures. Device-quality Si/SiGe strained epilayers and high performance devices have been demonstrated and fabricated by UHVCVD at temperature as low as 550 °C. Therefore, UHVCVD appears to be the most promising method for low temperature Si/Si$_{1-x}$Ge$_x$ epitaxy.

For conventional UHVCVD invented by Meyerson, the system utilizes a hot wall isothermal furnace, and silane (SiH$_4$) and germane (GeH$_4$) are used as the source gases. Although the quality of the epilayers is good enough for device applications, it shows a very low Si growth rate and some limits in selective epitaxial growth (SEG) application. Recently, a novel UHVCVD process with a water-cooled cold wall reactor using disilane (Si$_2$H$_6$) and germane (GeH$_4$) source gases has been proposed to get high quality Si/Si$_{1-x}$Ge$_x$ epilayers and successful SEG capability. Therefore, this technique was used to grow Si/Si$_{1-x}$Ge$_x$ epilayers in this study.

n-type Si and Si$_{1-x}$Ge$_x$ epilayers are very important for MODFET and HBT applications. As usual, phosphine (PH$_3$) is used as the doping gas in the UHVCVD process. However, it was well known that the growth rate of Si will be depressed greatly with the introduction of a large amount of PH$_3$. There are very few reports dealing with n-type doped Si/Si$_{1-x}$Ge$_x$ epilayers grown by UHVCVD using Si$_2$H$_6$, GeH$_4$, and PH$_3$. In this letter we report on the phosphorus doping characteristics of UHVCVD-grown Si/Si$_{1-x}$Ge$_x$ epilayers using Si$_2$H$_6$ and GeH$_4$ source gases. We also demonstrate the dependence of growth rate and phosphorus concentration of Si/Si$_{1-x}$Ge$_x$ epilayers on the PH$_3$ flow rates. A simple model based on the enhancement of hydrogen desorption rate and phosphorus blocking of surface-activated sites due to PH$_3$ introduction is proposed to explain the experimental results.

The UHVCVD system includes a water-cooled cold wall stainless steel reaction chamber, a loading chamber, separate nozzles for process and doping gases, and a computer-controlled gas switching box. The growth chamber is pumped by a 1000 l/s turbomolecular pump and a base pressure of $2 \times 10^{-10}$ Torr was obtained. The chamber pressure is also maintained below $1 \times 10^{-3}$ Torr during the epitaxial process by this pump. Si substrates were subjected to a precleaning process with a hydrogen passivation technique. After the cleaning step, the substrates were loaded into the loading chamber and then the chamber was pumped down to $10^{-6}$ Torr as soon as possible. Then, the substrate was transferred into the growth chamber. During the transfer process, the temperature of the heater is kept at 200 °C. A base pressure of $10^{-9}$ Torr was routinely obtained within 1 min after the wafer transfer process. Then, the heater was lowered and the substrate was heated to the deposition temperature at a ramp rate of approximately 150 °C/min. Pure Si$_2$H$_6$, GeH$_4$, and 100 ppm PH$_3$ diluted in H$_2$ are introduced into the growth chamber for the growth of n-type Si and Si$_{1-x}$Ge$_x$ epilayers at growth temperature. Before the Si and Si$_{1-x}$Ge$_x$ epilayer growing process, a thin Si buffer layer was grown by introducing 0.2 sccm Si$_2$H$_6$ flow into the reaction chamber during the heater ramping-up period. The flow rates of the reactants were controlled precisely by STEC mass flow controllers. The growth rates of Si and Si$_{1-x}$Ge$_x$ are measured by double crystal x-ray rocking curves and the surface depth profiles of the selectively grown epilayers. The phosphorus concentrations of Si and Si$_{1-x}$Ge$_x$ epilayers are...
determined by calibrated secondary ion mass spectrometry (SIMS).

The dependence of the Si growth rate on the PH$_3$ flow rate is shown in Fig. 1. The growth temperature is 600 °C and the Si$_2$H$_6$ flow rate is 2 sccm. As demonstrated, the growth rates increase slightly with increasing the phosphine flow rate at a smaller flow rate (<2 sccm) and then decrease seriously (~50%) with the increase of the phosphine flow rate. To verify the accuracy of the variation tendency, we have checked the dependence of the Si growth rate on PH$_3$ flow rate at different growth temperatures of 550, 600, 650, and 700 °C. All of the Si growth rates at different temperatures show the same variation tendency and the measurement error is within 2 A/min. The decrease of the growth rate with the higher PH$_3$ flow rate is attributed to the blocking of the surface-activated sites by phosphorus. However, the increasing tendency of the Si growth rate at smaller PH$_3$ flow rate was not observed. This result is first presented here and may be due to the slight increase of the hydrogen desorption rate of the Si epilayer surface which results in the Si growth rate enhancement by introducing a small volume of PH$_3$ flow. The growth rates of Si$_{1-x}$Ge$_x$ epilayers as a function of phosphine flow rate is also shown in Fig. 2. The growth temperature is 600 °C and the flow rates of Si$_2$H$_6$ and GeH$_4$ are 1 and 3 sccm, respectively. The Ge fraction of the Si$_{1-x}$Ge$_x$ epilayers evaluated by experimental and theoretical calculated double crystal x-ray rocking curves is 0.157 in this study. It also shows that the Ge fraction is independent on the PH$_3$ flow rates. The growth rates also increase slightly with phosphine flow at a smaller flow rate and may be due to the same mechanism. However, it only shows a slight decrease (~10%) with the phosphine flow at a higher phosphine flow rate. This signifies that the surface-activated sites blocking effect of the Si$_{1-x}$Ge$_x$ epilayer due to a large volume of PH$_3$ introduction is not so severe as that of the Si epilayer.

In order to evaluate the incorporation rate of phosphorus, the phosphorus doping profiles of Si and Si$_{1-x}$Ge$_x$ epilayers with different phosphine flow rates were characterized by SIMS profiling. SIMS measurements were performed in a Cameca IMS 5F apparatus. There is not any significant oxygen spike at the interface of the epilayer and the substrate. We also find a drop in the oxygen level in Si and Si$_{1-x}$Ge$_x$ epilayers compared to the Si substrate. It implies that the growth process and environment are suitable for high quality Si and Si$_{1-x}$Ge$_x$ epitaxial processes. The phosphorus concentrations have been calibrated by phosphorus-implanted Si and Si$_{1-x}$Ge$_x$ standard samples for precise evaluation. The measured phosphorus concentration in Si as a function of phosphine flow rate is shown in Fig. 3. The growth condition is the same as that of Fig. 1. The phosphorus concentration was found to increase linearly at a smaller phosphine flow rate and becomes nearly

FIG. 1. Growth rate of the Si epilayer as a function of the phosphine flow rate.

FIG. 2. Growth rate of the Si$_{1-x}$Ge$_x$ epilayer as a function of the phosphine flow rate.

FIG. 3. Phosphorus concentration of Si as a function of the phosphine flow rate.
FIG. 4. Phosphorus concentration of Si1−xGex as a function of the phosphine flow rate.

saturated at a higher phosphine flow rate. The highest phosphorus concentration is about 6.5×10^{18} \text{ cm}^{-3} in this case. Combining Figs. 1 and 3, we found that the saturation of phosphorus concentration at higher PH3 flow accompanied the strong depression of the Si growth rate, and both are attributed to the activated surface site blocking effect by phosphorus. Figure 4 shows the dependence of phosphorus concentration in Si1−xGex epitaxial films on the phosphine flow rate with the same growth conditions described in Fig. 2. The phosphorus concentration shows a nearly linear increasing behavior with phosphine flow rate and does not become saturated at a higher phosphine flow rate. The highest phosphorus concentration obtained in this case is about 5×10^{19} \text{ cm}^{-3}, which is nearly one order of magnitude greater than that of Si epilayers. This variation tendency is also consistent with that of the Si1−xGex growth rate.

In conclusion, in situ phosphorus-doped Si and Si1−xGex epilayers have been grown by UHVCVD using SiH\textsubscript{4}, GeH\textsubscript{4}, and PH\textsubscript{3}. The growth rates and phosphorus concentrations of Si and Si1−xGex epilayers as a function of PH\textsubscript{3} flow rate have been characterized and discussed. Compared to the undoped epilayers, the growth rates of Si and Si1−xGex increase slightly at a small PH\textsubscript{3} flow rate (<2 sccm). This may be due to the slight increase of the hydrogen desorption rates of the growing surfaces, resulting in the Si growth enhancement by a small volume of PH\textsubscript{3} incorporation. Then, the growth rates decrease seriously (~50%) and slightly (~10%) with an increase of the PH\textsubscript{3} flow rate, respectively. This indicates that the level of the phosphorus blocking effect of Si1−xGex is smaller than that of Si epilayers. Phosphorus concentration in Si increases linearly with PH\textsubscript{3} flow rate at a small PH\textsubscript{3} flow rate and becomes nearly saturated at a higher PH\textsubscript{3} flow rate, while the phosphorus concentration in Si1−xGex only shows a nearly linear behavior with the PH\textsubscript{3} flow rate and does not become saturated at a higher PH\textsubscript{3} flow rate. As is known, the epitaxy of Si and Si1−xGex at low temperature is controlled by a hydrogen desorption mechanism. The hydrogen desorption rate is enhanced by germanium incorporation for the Si1−xGex epitaxial process. Therefore, a higher vacant activated surface site fraction is exposed during the Si1−xGex epitaxial process for phosphorus compound adsorption and results in a lower phosphorus blocking effect. This effect can be used to explain the fact that greater phosphorus concentration and a smaller decrease in the growth rate of Si1−xGex epilayers occurs at a higher PH\textsubscript{3} flow rate.

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