第 29 卷　第 10 期
2008 年 10 月

半　导　体　学　报
JOURNAL OF SEMICONDUCTORS

Vol.29　No.10
Oct.,2008

Growth of SiGe by D-UHV/CVD at Low Temperature*

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Abstract: The temperature is a key factor for the quality of the SiGe alloy grown by D-UHV/CVD. In conventional conditions, the lowest temperature for SiGe growth is about 550℃. Generally, the pressure of the growth chamber is about 10^{-5}Pa when liquid nitrogen is introduced into the wall of the growth chamber with the flux of 6sccm of the disilane gas. We have succeeded in depositing SiGe films at much lower temperature using a novel method. It is about 10^{-2}Pa without liquid nitrogen, about 3 magnitudes higher than the traditional method, leading to much faster deposition rate. Without liquid nitrogen, the SiGe film and SiGe/Si superlattice are grown at 485℃. The DCXRD curves and TEM image show that the quality of the film is good. The experiments show that this method is efficient to deposit SiGe at low temperature.

Key words: SiGe; D-UHV/CVD; low-temperature deposition; DCXRD
EEACC: 4250
CLC number: TN3　**Document code**: A　**Article ID**: 0253-4177(2008)10-1889-04

1　Introduction

SiGe alloy is an important optoelectronic semiconductor material. Because of its modulatory bandgap and compatible characteristics with the CMOS processes, many efforts have been devoted to creating novel optoelectronic devices using strained SiGe/Si heterostructure[1~3]. Nowadays, many novel silicon-based devices have been developed, such as heterostructure bipolar transistors (HBT)[4], high electron mobility transistors (HEMT), SiGe multi-quantum-well infrared photodetectors, SiGe resonant tunneling diodes (RTD), and negative resistance field-effect transistors (NERFET).

The SiGe alloy is traditionally grown by double chamber ultra high vacuum chemical vapor deposition (D-UHV/CVD). Because of the gas sources used in the D-UHV/CVD system, the growth temperature is usually higher than 550℃[5]. The temperature, which seriously affects the SiGe film's growth rate, surface quality, and defects, is an important parameter for the SiGe film growth. The higher the growth temperature is, the higher growth rates are. But with higher growth temperature, the interface interdiffusion will become serious and the SiGe film will have more defects such as dislocations, leading to rough surfaces and depressing the quality of the device. So it is an important aim to decrease the deposition temperature.

In the conventional process of the SiGe deposition by D-UHV/CVD, liquid nitrogen is introduced into the wall of the growth chamber. It maintains the low temperature of the wall and makes the growth pressure very low. In this paper, a novel and efficient method without liquid nitrogen to deposit the SiGe film at much lower temperature is introduced.

2　Experiment

The epitaxy system is ultra high vacuum chemical vapor deposition (UHV-CVD), which is shown in Fig. 1. This system is homemade and has many advantages[6]. It has two growth chambers with a quadrupole mass spectrometer (QMS). The basic pressure of each growth chamber is ultra low, about 2×10^{-8}Pa, and the temperature of the heater in the growth chamber can reach 1000℃.

The substrate is a 100mm-diameter (001) p-type Si wafer with a resistivity of 8～12Ω · cm. The wafer was processed by a RCA cleaning process[7]: it was boiled in $H_2SO_4 : H_2O = 4 : 1$ for 1min, rinsed in de-ionized water tens of times, boiled in $H_2O : H_2O_2 : NH_3 \cdot H_2O = 5 : 2 : 1$ for several seconds, rinsed in HF for 30s, boiled in $H_2O : H_2O_2 : HCl = 7 : 2 : 1$ for seconds, then boiled in $H_2O : HCl = 8 : 1$ for a few seconds, rinsed in $HF : H_2O = 1 : 10$ for several minutes, and finally rinsed in de-ionized water 30 times. After the RCA process, the thin native oxide on the Si wafer surface was removed. When the wafer was dried, it was put into the process chamber and

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* Project supported by the National Natural Science Foundation of China (No. 60336010) and the State Key Development Program for Basic Research of China (No. G2000036605)

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Received 18 April 2008, revised manuscript received 22 May 2008

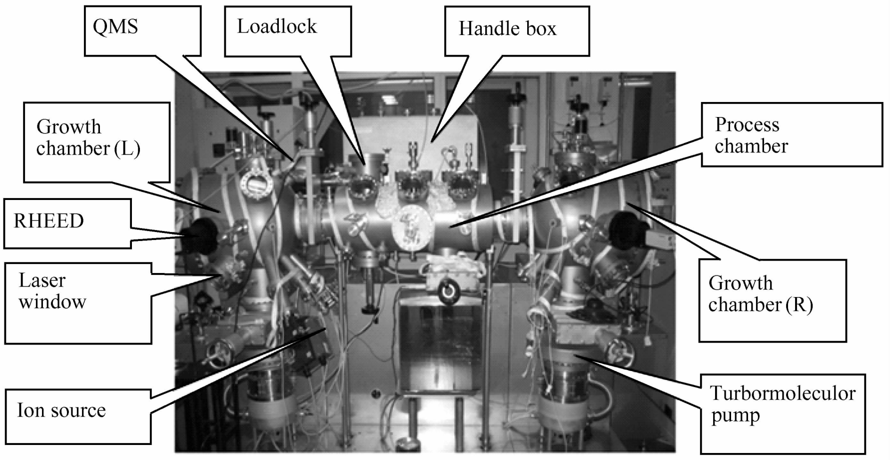

Fig.1 Picture of the homemade D-UHV/CVD epitaxy system

degassed at higher than 300℃ for several hours and then transferred into the growth chamber. The Si substrate was heated to 950℃ to deoxidize for 10mins. When the temperature decreased to the growth temperature, gas sources were imported into the chamber and the deposition process starts according to the procedure.

In the traditional growth process, the liquid nitrogen is introduced into the wall of the growth chamber. It cools down the wall of the growth chamber. Much research has proven that the lowest growth temperature of SiGe alloy is about 550℃. In the conventional condition, we deposited the SiGe film (sample A) for 5min at 500℃. The flux of Si_2H_6 and GeH_4 are 6 and 2sccm, respectively. In contrast, we have used a novel method, without liquid nitrogen, to deposit the SiGe film (sample B) for 5min at 485℃ with the same flux of the gases. A multilayer structure SiGe/Si (sample C) was also grown. To analyze the elements of the surface, we determined the RBS curves of samples A and B. At the same time, we measured the DCXRD curves of samples B and C. The TEM image of sample C was also obtained.

3 Results and discussion

The Rutherford backscattering spectrometry (RBS) can analyze the ingredients of the surface[8]. Figure 2 shows the RBS curves of samples A and B. The RBS spectra prove that there is no germanium element on the substrate of sample A, meaning that no film deposits on it (because the decomposition temperature of Si_2H_6 is higher than GeH_4, if there is some Si film deposited, there must be Ge elements deposited on the sample). There is an obvious Ge peak in the curve of the sample B, proving that there is film grown on it.

Figure 3 is the double crystal X-ray diffraction (XRD) curves of samples B and C, respectively. The

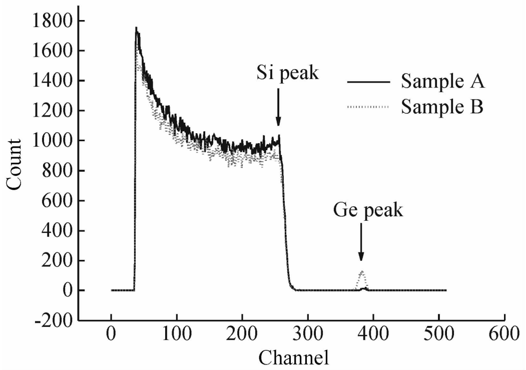

Fig.2 RBS curves of the samples A and B

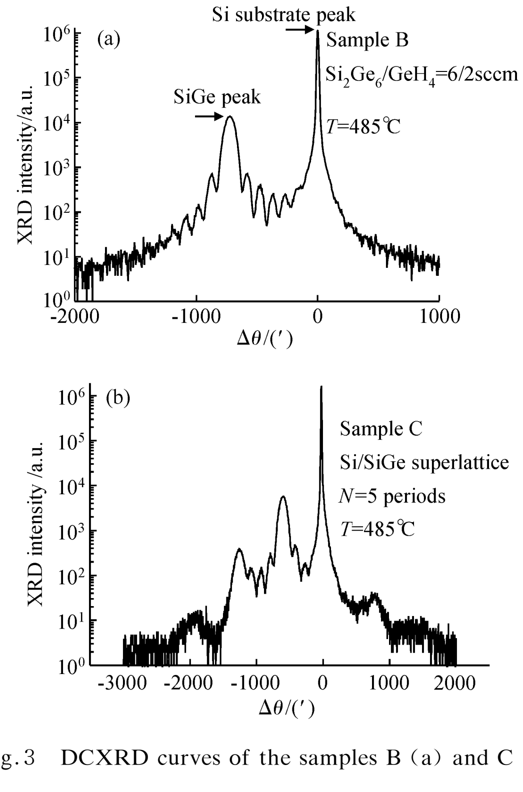

Fig.3 DCXRD curves of the samples B (a) and C (b)

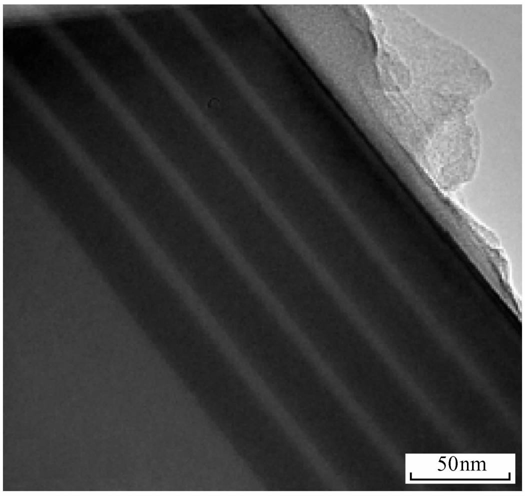

Fig.4　TEM image of the sample C

spectra show that the SiGe film grows on the substrate. Furthermore, the content of the Ge is about 10% according to Vegard's Law[9]. There are Pendellösung peaks with 5 periods in the spectrum of sample C.

Figure 4 is the transmitting electron microscope (TEM) image of sample C. It shows that the superlattice has an abrupt interface, uniform layers, and 5 periods, which is consistent with the DCXRD analysis. The TEM picture and Pendellösung peaks both indicate that the superlattice has good quality.

The Si_2H_6 and GeH_4 gases are pyrolyzed into ions and ion clusters such as SiH_3- and GeH_3- in the growth chamber[10]. The reaction process can be described as the following reaction equations:

$$Si_2H_6(g) + 2\_ \rightarrow 2\,\underline{Si}H_3$$

$$2\,\underline{Si}H_3 \rightarrow 2Si(s) + 3H_2 + 2\_$$

$$GeH_4(g) + 2\_ \rightarrow \underline{Ge}H_3 + \underline{H}$$

$$\underline{Ge}H_3 + \underline{H} \rightarrow Ge(s) + 2H_2(g) + 2\_$$

In fact, the reaction mechanism is more complicated than the above reaction equations. The substrate absorbs the active reactants and they move, interact, and diffuse. Finally, the film comes into being.

In the traditional process, the liquid nitrogen is introduced into the wall of the growth chamber. It keeps the temperature of the wall as low as possible. Therefore, the gas molecules in the chamber are cooled down and absorbed into the wall, which leads to very low pressure in the chamber. When the Si_2H_6 gas comes into the growth chamber, the growth pressure is about 10^{-5}Pa and it is 10^{-3}Pa as the GeH_4 gas is imported. If there is no liquid nitrogen introduced into the chamber wall, when the Si_2H_6 gas comes into the growth chamber, the pressure in the growth chamber is about 10^{-2}Pa and it is about 1Pa when the GeH_4 gas is introduced. Without the liquid nitrogen, the growth pressure can be 3 magnitudes higher.

When the liquid nitrogen cools down the growth wall, the growth pressure is very low. Apparently, the concentrations of the reactants are quite low. In order to deposit the SiGe film, the temperature must be high enough to decompose more source gases. On the contrary, without nitrogen liquid, the reaction pressure increases about 3 magnitudes at the same temperature, which greatly increases the concentration of the reactants. According to the chemical reaction balance principle, the reaction rate will rise significantly. So the SiGe film can be grown at much lower temperature.

4　Conclusion

In the conventional process for SiGe film growth by D-UHV/CVD, the liquid nitrogen is introduced into the wall of the growth chamber. When the flux of Si_2H_6 is 6sccm, the growth pressure is about 10^{-5}Pa and it is 10^{-3}Pa as GeH_4 is imported. The RBS curves indicate that there is no film deposited at 500℃. Without the liquid nitrogen, the growth pressure can increase about 3 magnitudes and result in much higher concentration of the active reactants. Thus, the SiGe film can be deposited at as low as 485℃. A SiGe/Si superlattice was also grown at 485℃. The DCXRD curves and TEM image show that the quality of the superlattice is good. In conclusion, this method is efficient to deposit SiGe film at low temperature.

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D-UHV/VCD系统中SiGe薄膜的低温生长*

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摘要： 生长温度对SiGe合金的性能有重要影响.在双腔超高真空化学气相淀积生长中，通常采用液氮冷却的方法.该生长模式下，通入乙硅烷时腔内的生长气压约为10^{-5}Pa，SiGe的最低生长温度约为550℃.为了降低生长温度，文中采用了不用液氮冷却的模式，腔内生长气压约为10^{-2}Pa，增加3个数量级，并且将生长温度降到了485℃，远低于传统的生长温度.DCXRD测试和TEM图像表明，生长的SiGe薄膜和SiGe/Si超晶格具有良好的晶格质量.结果证明，在UHV/CVD系统中，这是一种有效的实现SiGe低温生长的方法.

关键词： SiGe；超高真空化学气相淀积；低温生长；X射线双晶衍射

EEACC： 4250

中图分类号： TN3　　**文献标识码：** A　　**文章编号：** 0253-4177(2008)10-1889-04

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* 国家自然科学基金（批准号：60336010）及国家重点基础研究发展计划（批准号：G2000036605）资助项目

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2008-04-18收到，2008-05-22定稿