

## 원격 플라즈마 화학기상 증착법으로 성장된 미세 결정화된 SiGe 박막 형성

김도영<sup>a</sup>

울산과학기술대학교 전기전자공학부

### The Formation of Microcrystalline SiGe Film Using a Remote Plasma Enhanced Chemical Vapor Deposition

Doyoung Kim<sup>a</sup>

School of Electrical and Electronics Engineering, Ulsan College, Ulsan 44022, Korea

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**Abstract:** SiGe thin films were deposited by remote plasma enhanced chemical vapor deposition (RPE-CVD) at 400°C using SiH<sub>4</sub> or SiCl<sub>4</sub> and GeCl<sub>4</sub> as the source of Si and Ge, respectively. The growth rate and the degree of crystallinity of the fabricated films were characterized by scanning electron microscopy and Raman analysis, respectively. The optical and electrical properties of SiGe films fabricated using SiCl<sub>4</sub> and SiH<sub>4</sub> source were comparatively studied. SiGe films deposited using SiCl<sub>4</sub> source showed a lower growth rate and higher crystallinity than those deposited using SiH<sub>4</sub> source. Ultraviolet and visible spectroscopy measurement showed that the optical band gap of SiGe is in the range of 0.88~1.22 eV.

**Keywords:** Silicon germanium, Silicon chloride, Silane, Germanium chloride, Raman spectroscopy, Optical bandgap

## 1. INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) is tremendously used for various industrial applications such as thin film transistors (TFTs) for liquid crystal display (LCD), and optoelectronic devices like a thin film solar cells [1]. However, a-Si:H is required to improve the film quality because of low crystallinity and optical defect originated from localized states in the middle of bandgap [2]. Especially, a-Si:H has a low light absorption performance

in the infrared wavelength that is unsuitable for many applications [3]. One way to solve the optical problems is what choose the microcrystalline Si ( $\mu\text{c-Si}$ ) instead of a-Si:H due to high photovoltaic quality [4]. Several microcrystalline silicon studies have been proposed in order to overcome these problems and use in various applications [5,6].

From previous report [7], the bandgap of active films can be controlled by alloying Ge with Si. With the increase of Ge concentrations, the band gap of SiGe film becomes narrower. It is well-known that microcrystalline SiGe thin films are studied for potential candidates for electric and optoelectronic applications [8,9]. For synthesis microcrystalline SiGe film, chemical vapor deposition has many advantages. Especially, the remote technique has an

a. Corresponding author; [dykim@uc.ac.kr](mailto:dykim@uc.ac.kr)

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inherent advantage of no direct exposure to the plasma during the deposition process. This eliminates the damage to the film surface from energetic particles in the plasma.

In this paper, we performed the deposition and evaluations of microcrystalline SiGe films as a function of Ge concentrations using a remote plasma enhanced chemical vapor deposition (RPE-CVD). And we used two sources of SiH<sub>4</sub> and SiCl<sub>4</sub> for Si source. They were comparatively studied with GeCl<sub>4</sub> as Ge source. The growth characteristics and the electrical properties and the optical transmittance spectra of SiGe film were discussed too.

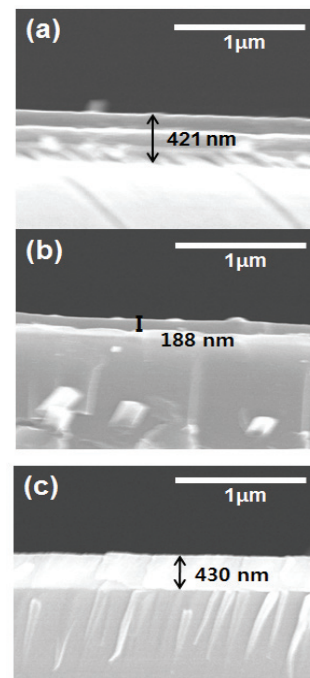
## 2. METHOD FOR EXPERIMENT

In this experiment, the SiGe films were deposited by RPE-CVD method. This equipment consisted of chamber and cylindrical cavity connected with RF power generator to create plasma away from the samples. Maximum 8 inch sample can be loaded and the vacuum of the chamber was set by low vacuum pump and the base pressure is 30 mTorr. Hydrogen gas for plasma was passed through the cavity directed to the sample holder and its flow was kept to 70 sccm by mass flow controller. The source synthesized SiGe film was used the chemical of SiCl<sub>4</sub>, GeCl<sub>4</sub>, and the gas of SiH<sub>4</sub>. In order to control the flow rate of sources, the needle valve was applied without bubbling because of their enough vapor pressure at room temperature. With these flow, the chamber pressure increased to about 10 mTorr at standard growth condition. The temperature of gas lines were maintained higher than source canister for prevent of the chemical source condensation. The coming glass was used for substrate, and RF power and deposition temperature and time were fixed to 300 W, 400 °C and 20 min, respectively.

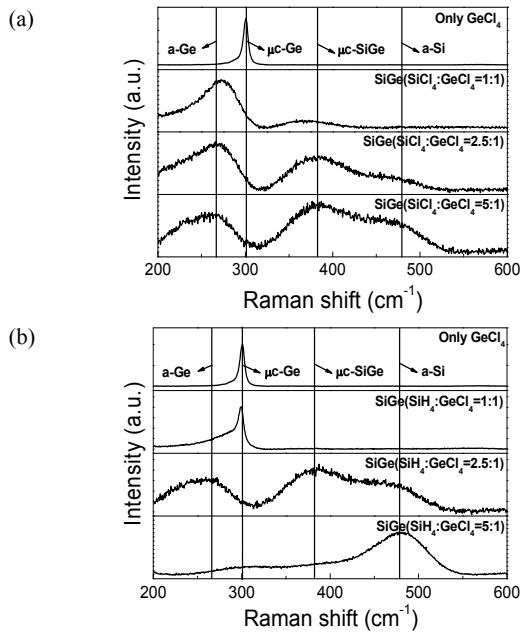
The microstructure and structural properties of SiGe films were analyzed by SEM (JSM-6700F), and Raman spectroscopy (LabRam HR, Ar-ion laser, 514 nm). Also the changes in SiGe optical band gap and film resistivity depending on Ge concentration were studied using UV-VIS (PerkinElmer Inc., Lambda 35) and Hall effect measurement (Eopia HEM-2000), respectively.

## 3. RESULTS AND DISCUSSIONS

SiGe film was deposited at 400 °C with the environment of H<sub>2</sub> plasma. The sources of SiGe are used SiH<sub>4</sub> with GeCl<sub>4</sub> and SiCl<sub>4</sub> with GeCl<sub>4</sub>, respectively. When chemical and source gas supplied to the chamber, the base pressure maintained 40 mTorr. The partial pressure of SiH<sub>4</sub> and SiCl<sub>4</sub> fixed 30 mTorr. That of GeCl<sub>4</sub> fixed as 10 mTorr. Figure 1 exhibited vertical images of SiGe films using a SEM. In using a SiH<sub>4</sub> and GeCl<sub>4</sub> of Fig. 1(a), SiGe film was deposited 421 nm with the growth rate of 30.5 nm/s. In using a SiCl<sub>4</sub> and GeCl<sub>4</sub> of Fig. 1(b), SiGe film was deposited 188 nm with growth rate of 10.6 nm/s. Single Ge film without Si source was deposited 430 nm (growth rate = 30.6 nm/s) as shown Fig. 1(c). In this case, Cl atom also has an influence on reduce the growth rate of SiGe film. From SEM observation, the Cl has larger binding energy with Ge (390.8 kcal/mol) than hydrogen (263.2 kcal/mol). Although the decomposition energy of chlorine on the Ge surface is not reported yet, large binding energy of Cl had a big



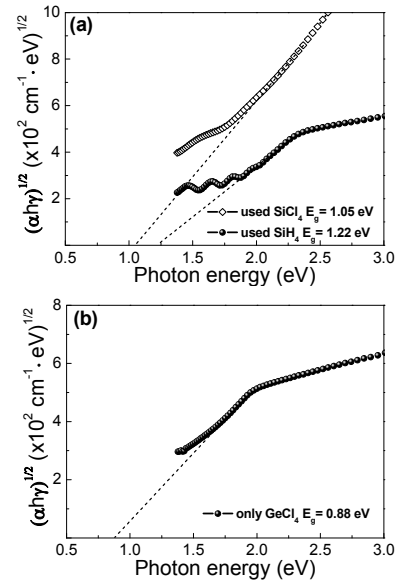
**Fig. 1.** SEM image of SiGe films with H<sub>2</sub> plasma at 400 °C : (a) using SiH<sub>4</sub> and GeCl<sub>4</sub>, (b) using SiCl<sub>4</sub> and GeCl<sub>4</sub>, and (c) using only GeCl<sub>4</sub>.



**Fig. 2.** Raman spectra of Si films deposited as a function of (a) the rate of partial gas pressure of  $\text{SiCl}_4$  and  $\text{GeCl}_4$  and (b) the rate of partial gas pressure of  $\text{SiH}_4$  and  $\text{GeCl}_4$ .

influence on the suppression of chlorine decomposition on SiGe film surface. Therefore, additional Cl passivation effects to decrease the growth rate of films deposited by  $\text{SiCl}_4$  and  $\text{GeCl}_4$ .

SiGe films were deposited as a function of Si and Ge partial gas pressure rate from 1:1 to 5:1 to same working pressure of 40 mTorr. Figure 2 shows the change of Raman spectra of SiGe films. In Fig. 2(a), the narrow peak located at  $300 \text{ cm}^{-1}$  shows crystalline structure of Ge film deposited by only  $\text{GeCl}_4$  without any Si source. However, with increasing rate of  $\text{SiCl}_4$  source, the intensity of Ge peak is decreased due to the increasing of Ge amorphous phase. And additional peaks appear at around  $380$  and  $480 \text{ cm}^{-1}$  due to Si-Ge and Si-Si bonds [10]. When the rate of partial gas pressure is 1:1, the film is still formed amorphous Ge film although crystallization is suppressed by Si atoms. With increasing the partial pressure of Si source, the peak intensity of Ge-Ge band decreases and that of Si-Si band increases. This means the formation of microcrystalline SiGe films at the condition of the rate of  $\text{SiCl}_4$  and  $\text{GeCl}_4$  of 5:1. SiGe was also deposited by a  $\text{SiH}_4$  and  $\text{GeCl}_4$  source as shown in Fig. 2(b). The peak of Ge-Ge was strongly



**Fig. 3.** Optical band gap of (a) SiGe films and (b) only Ge film by  $\text{GeCl}_4$ .

dominant at around  $300 \text{ cm}^{-1}$  when the rate of  $\text{SiH}_4$  and  $\text{GeCl}_4$  is 1:1. This means Ge film doped Si is formed because of low  $\text{SiH}_4$  source concentration. Ge film has high crystallinity because the peak is little shifted to the low frequency and low full width half maximum. The SiGe film was formed as an increasing rate of Si partial gas pressure, but the peaks of SiGe disappeared when the rate of  $\text{SiH}_4$  and  $\text{GeCl}_4$  is 5:1. It expects the most of Si film is formed high  $\text{SiH}_4$  gas partial pressure because of higher decomposition rate of  $\text{SiH}_4$  gas than  $\text{GeCl}_4$  source.

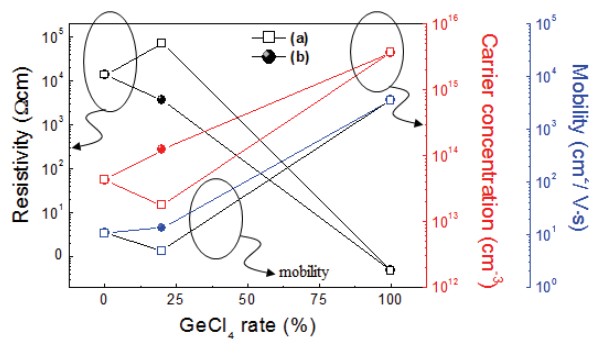
The optical properties of SiGe films were measured by ultraviolet-visible (UV-VIS) wavelength spectroscopy. From these results, the optical band gap ( $E_g$ ) could be calculated using a following equation [11]:

$$(\alpha h\nu)^{1/2} = A(h\nu - E_g) \quad (1)$$

Where  $\alpha$  is the absorption coefficient,  $h$  is Planck's constant,  $\nu$  is the photon frequency,  $A$  is a constant, respectively. The values of  $(\alpha h\nu)^{1/2}$  were plotted as a function of photon energy ( $h\nu$ ) as shown in Fig. 3, and then  $E_g$  can be determined by extrapolation of the linear part. The optical band gap was evaluated to be 1.05, 1.22 eV for SiGe films deposited to be used  $\text{SiCl}_4$  source and to be used  $\text{SiH}_4$ , respectively. From this results, we could

**Table 1.** Summary of physical and optical performances as a function of Si and Ge source.

Source type	Thickness	Optical Eg	Crystallinity
SiCl <sub>4</sub> +GeCl <sub>4</sub>	188 nm	1.05 eV	Microcrystalline
SiH <sub>4</sub> +GeCl <sub>4</sub>	421 nm	1.22 eV	Amorphous
only GeCl <sub>4</sub>	430 nm	0.88 eV	Microcrystalline

**Fig. 4.** Electrical performance of SiGe film (a) using SiH<sub>4</sub> and GeCl<sub>4</sub> and (b) using SiCl<sub>4</sub> and GeCl<sub>4</sub> by Hall measurement.

know that the SiGe film used SiCl<sub>4</sub> was more cooperated with Ge than that used SiH<sub>4</sub> because the Eg of only Ge is lower than SiGe. That value using only GeCl<sub>4</sub> was 0.88 eV. This result supports that the optical Eg of Ge film is lower than SiGe film. We summarized physical and optical performances as a function of Si and Ge source as shown in Table 1.

In order to evaluate the electrical performance of the SiGe film as a function of GeCl<sub>4</sub> rate, we tried the Hall effect measurement as shown in Fig. 4. As increasing of input GeCl<sub>4</sub> rate, carrier concentration and mobility was increased simultaneously. Above these results, resistivity was decreased. However, the resistivity of film used SiCl<sub>4</sub> as the Si source was faster decreased than the case of SiH<sub>4</sub>. This result might be considered that SiGe film used SiCl<sub>4</sub> source had a lower defects than used SiH<sub>4</sub>.

#### 4. CONCLUSION

Microcrystalline SiGe films were deposited by remote plasma enhanced chemical vapor deposition with several

GeCl<sub>4</sub> concentrations and two Si sources of SiCl<sub>4</sub> and SiH<sub>4</sub>. The crystallinity of SiGe films deposited to be used SiCl<sub>4</sub> source had better than SiH<sub>4</sub> source with low GeCl<sub>4</sub> concentration condition. The optical band gap of SiGe films was lower than that of Si and it can be changed with incorporation of SiCl<sub>4</sub> and SiH<sub>4</sub> source. The electrical properties of SiGe showed the resistivity was decreased with GeCl<sub>4</sub> source concentrations.

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