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Recent progress of low temperature Si epitaxy

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In this paper, we summarize the recent progress of low-temperature Si epitaxy focused on the cleaning procedure. Then the low-temperature Si epitaxy by the mercury-sensitized photo-CVD is described and we demonstrate the heavily phosphorus doping (>$10^{21}cm^{-3}$) by photo-CVD.

1. INTRODUCTION

In the high-temperature processes, typically 1000°C, the auto-doping effect and the unintentional impurity diffusion are serious and practical problems. Therefore, a large demand for the development of low-temperature silicon epitaxial technology has been increased with shrinking both the lateral and vertical dimensions of ultra-large scale integration (ULSI) devices.

In this paper, recent progresses of the low-temperature Si epitaxial technology, such as molecular beam epitaxy (MBE), plasma-chemical vapor deposition (plasma-CVD), ultra-high vacuum CVD (UHV-CVD) and photo-chemical vapor deposition (photo-CVD), will be first summarized. Then we will demonstrate the low-temperature Si epitaxy by photo-CVD.

2. RECENT PROGRESS OF LOW-TEMPERATURE Si EPITAXY

Recent reports on the low-temperature Si epitaxy are summarized in Table I. A variety of methods have been applied and many researchers succeeded in the epitaxial growth of Si in the temperature range around 700°C or 300°C.

For the realization of Si epitaxy at low temperature, cleaning procedure before the growth is most important. B.S.Meyerson pointed out that the background pressure of both oxygen and water vapor in the system affects the epitaxial growth of Si[6]. From the basic surface investigation of the $Si/O_2/H_2O/SiO_2$ equilibrium system[21], the silicon is effectively etched by those species through the following reactions:

$$Si(s) + O_2 \rightarrow 2SiO(g)$$
$$Si(s) + H_2O \rightarrow SiO(g) + H_2(g).$$

Therefore, extrapolating Ghiddini's data for water vapor downward in temperature, it can be estimated that one must maintain a partial pressure of H_2O less than 10^{-8}Torr in order to achieve an oxide free surface at 800°C. Therefore, several researchers carried out there works under ultra-high vacuum or ultra-clean conditions[5, 6, 7, 8, 12, 14, 20].

In plasma-CVD, T.Ohmi[12] and L.Breaux[14] found that the H_2 plasma cleaning was favorable for lowering the growth temperature and we added the halogenated silane gas in our photo-CVD system to remove the native oxide on the growing surface[11, 17].

As a new cleaning procedure of Si wafer, hydrogen termination of Si surface by HF dip[22] or exposure to HF vapor[23] was demonstrated and it was shown that these treatments were very effective to maintain the clean Si surface and to lower the growth temperature.

Table I. Reports on low-temperature Si epitaxy

Method	Source Gas	Temperature (°C)	Author	Ref.
gas-source MBE	Si_2H_6	630	H.Hirayama	1
gas-source MBE	Si_2H_6	490-680	S.M.Mokler	2
MBE	-	350	K.D.Hobard	3
MBE	-		Y.Shiraki	4
low-pressure CVD	SiH_4	600-850	T.Ohmi	5
UHV-CVD		750-850	B.S.Meyerson	6
atomos.-pressure CVD	SiH_4	650-750	T.S.Kuan	7
ArF laser-CVD	Si_2H_6	330	S.Lian	8
ArF or XeF laser-CVD	Si_2H_6	600-650	A.Yamada	9
photo-CVD	Si_2H_6	600	T.Ito	10
photo-CVD	SiH_2F_2, Si_2H_6	200	A.Yamada	11
ECR plasma-CVD	SiH_4	R.T.	T.Ohmi	12
ECR plasma-CVD	SiH_2Cl_2	650	N.Kasai	13
remote plasma-CVD	SiH_4	150	L.Breaux	14
plasma-CVD	SiH_4	775	R.Reif	15
plasma-CVD		800	L.M.Williams	16
plasma-CVD	SiF_4, SiH_4	250	A.Yamada	17
rapid thermal-CVD	SiH_4	450-700	M.Liehr	18
rapid thermal-CVD	SiH_4	600-800	M.L.Green	19
sputtering	-	250	T.Ohmi	20

3. LOW-TEMPERATURE PHOTO-CVD PROCESS

In this section, we will discussed the low-temperature Si epitaxy by the photo-CVD technique based on our results. First of all, the mercury-sensitization method will be described in brief. Then we will demonstrate the low-temperature Si epitaxy with SiH_2Cl_2.

3.1. Mercury-sensitized process

There are several processes for the excitation of reactant molecules. One of them is the transition with the counter-excitation of another molecule (intermolecular energy transfer). This process enables a molecule to excite without any absorption of photons. The photosensitization methods have been used in the field of photochemistry in order to obtain the photochemical reaction of a molecule which has no absorption against given photons. For example, SiH_4 can not be directly decomposed by the UV irradiation with a low-pressure mercury lamp which has resonance lines of 253.7 and 184.9nm since SiH_4 has a fundamental absorption edge at a wavelength of 160nm[24].

A mercury photosensitization method, using mercury atoms as the sensitizer, is one of the easiest to deal with among them. The primary step for a mercury photosensitization using 253.7nm resonance line is given as follows:

$$Hg(^1S_0) + h\nu(253.7nm) \rightarrow Hg(^3P_1)$$

and excited mercury atom, $Hg(^3P_1)$, reacts with SiH_4 molecule and decomposes it through the following reaction:

$$Hg(^3P_1) + SiH_4 \rightarrow Hg(^1S_0) + SiH_3 + H.$$

Therefore, SiH_3 radical which has a relatively long life time can be selectively produced by the mercury-sensitized method.

The probability of the energy transfer from the excited mercury atom depend on the gas species, and it is called "quenching cross section". The typical quenching cross sections for several molecules are summarized in Table II. It is noticeable that H_2 molecule has also large cross section, therefore, it is expected that H radicals could be easily produced by the mercury-sensitized photo-CVD.

Table II. Typical quenchin cross sections for several compounds.

SiH_4	26	B_2H_6	?
Si_2H_6	60-100	PH_3	26.2
CH_4	0.06	AsH_3	very large
C_2H_2	23	H_2	6
C_2H_6	0.1	H_2O	1
GeH_4	140	O_2	13.9
NH_3	2.94	CO_2	2.48

By using this novel method, we have realized a low-temperature Si epitaxy at a substrate temperature as low as 250°C with a gas mixture of Si_2H_6 + SiH_2F_2 + H_2[11]. Furthermore, the heavily phosphorus doping has been successfully realized by the photo-CVD technique[25]. In this paper, we will discuss the low-temperature Si epitaxy with SiH_2Cl_2.

3.2. Low-temperature Si epitaxy by the photo-CVD method with SiH_2Cl_2 gas

A schematic diagram of the photo-CVD apparatus is shown in Fig.1. The deposition system consists of a main reactor and a load-lock entry. The main chamber was evacuated with a diffusion pump to a pressure of $4x10^{-6}$Torr. Si(100) substrates were cleaned in organic solvents, followed by a HF (5%) dip prior to the growth. Other special treatments, such as conventional heat treatment, were not carried out.

The mercury sensitized method was used to enhance dissociation of the reactant gases. A $40mW/cm^2$ low-pressure mercury lamp was employed as an UV source, radiating intense 184.9 and 253.7nm resonance lines. A gas mixture of SiH_4, H_2 and SiH_2Cl_2 was introduced into the reactor with a very small amount of mercury vapor. Table III shows the main growth conditions.

Table III. Typical growth conditions

SiH_4 flow rate	4.6sccm
SiH_2Cl_2 flow rate	1-4.5sccm
H_2 flow rate	50-120sccm
Pressure	1Torr
Tsub.	100-300°C

Figure 2 shows a dependence of the film crystallinity and the deposition rate on SiH_2Cl_2 flow rates at a substrate temperature of 250°C. The film crystallinity was assessed by RHEED measurement. The flow rates of SiH_4 and H_2 were 4.6sccm and 90sccm, respectively. In the figure, the deposition rate decreases with an increase of SiH_2Cl_2 in gas phase. The partial pressure of SiH_4 is almost invariant in this experiment due to high H_2 flow rate. Therefore, a decrease of the deposition rate implies that an etching of the growing surface

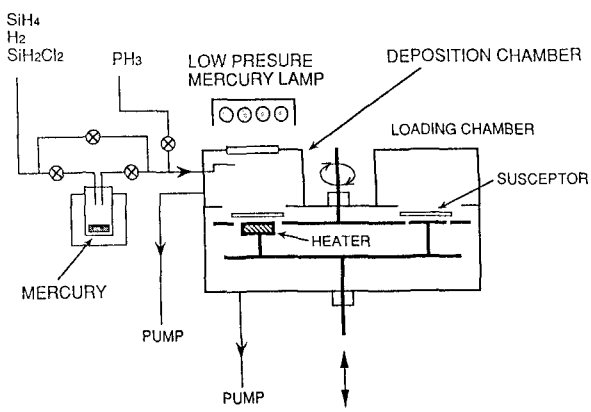

Fig. 1 Schematic diagram of photo-CVD system.

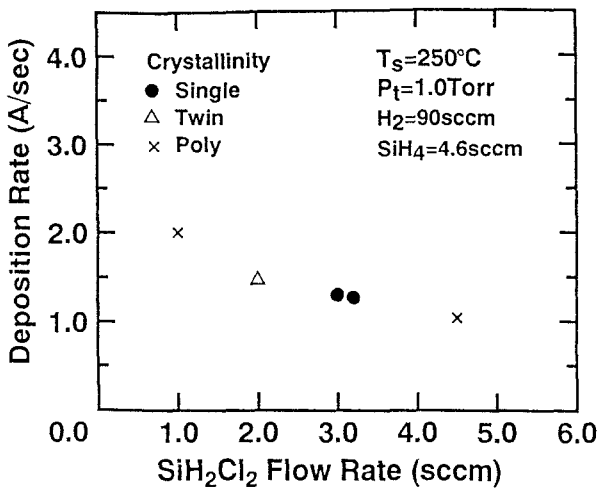

Fig. 2 Deposition rate and film crystallinity as a function of the SiH_2Cl_2 flow rate.

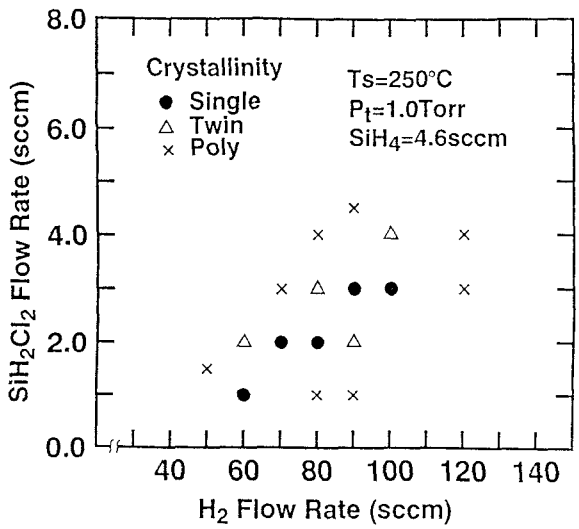

Fig. 3 Dependence of film crystallinity on both H_2 flow rate and SiH_2Cl_2 flow rate.

might occur during the growth with the introduction of SiH_2Cl_2. At a SiH_2Cl_2 flow rate of 3.0sccm, epitaxial Si film was obtained.

Figure 3 shows film crystallinity as a function of the flow rates of SiH_2Cl_2 and H_2. The flow rate of SiH_4 was fixed at 4.6sccm. The epitaxial Si films were obtained in the conditions indicated by the closed circles. It has been shown in the figure that the film crystallinity is sensitive to both SiH_2Cl_2 and H_2 flow rates.

From these experiments and our previous reports[11], the growth mechanism of the low-temperature Si photo-epitaxy is summarized as follows. The H atoms cover the growing surface, resulting in an enhancement of migration of film precursors such as SiH_3 radicals. The Cl-related radicals etch the growing surface and remove native oxides or weakly bonded Si atoms. Thus, the epitaxial temperature is drastically reduced. H atoms which cover the surface may be also removed by the Cl-related radicals. Therefore, there is a strong correlation between the SiH_2Cl_2 and H_2 flow rates to obtain the Si epitaxial film.

3.3. Heavily phosphorus doping by photo-CVD

The reduction of contact resistance should be minimized to realize the high-speed devices. Therefore, the heavily doping technique is strongly necessitated to demand this requirement. Since the epitaxial growth of silicon by the photo-CVD proceeds under the non-thermal equilibrium conditions, it could be expected that the heavily doping would be realized without the solid- solubility limitation. Therefore, we have carried out the heavily phosphorus doping by the photo-CVD method with SiH_2F_2 gas.

Figure 4 shows the dependence of the carrier concentration on doping quantity (PH_3/SiH_4). In the figure, the samples grown at 250°C, 200°C and 180°C are indicated by circles, squares and triangles, respectively. The phosphorus concentration measured by SIMS is also shown in the figure and indicated by

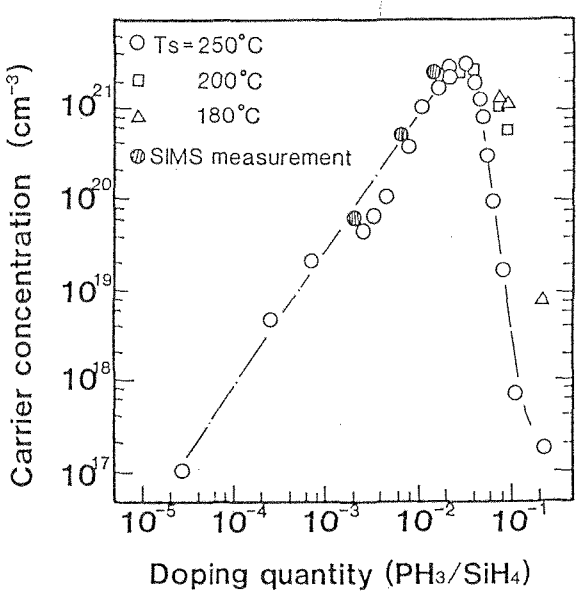

Fig.4 Dependence of carrier concentration on doping quantity.

closed circles. The electron concentrations were determined by Hall measurements using van der Pauw techniques at room temperature with magnetic flux density of 0.8T. The phosphorus concentration was measured by the SIMS method using a cesium ion beam accelerated to the energy of 14.5keV. When the doping quantity is less than about 4%, the electron concentration has a linear dependence on the doping quantity and it agreed fairly well with the incorporated phosphorus concentration, which suggested 100% activation of the phosphorus atoms even at the high concentration of about $10^{21}cm^{-3}$. However, for the doping quantity higher than 4%, the electron concentrations show a tendency of decrease and the deterioration of film quality was observed. Thus far, the maximum electron concentration of about $3x10^{21}cm^{-3}$ and resistivity of $1.8x10^{-4}\Omega cm$ were obtained at doping quantity of 4%. To our knowledge, this is the highest value reported for an epitaxial P-doped silicon films. In the more heavily doped samples, a remarkable deactivation of the dopant was verified. Furthermore, it was found that at higher doping region (doping quantity higher than 5%), the carrier concentration was increased with decreasing the growth temperature. We found from a further study of these supersaturate films that a new defect complex, v-P_4 in which one vacancy is surrounded by four phosphorus atoms, is formed after an annealing at 600°C[26].

4. CONCLUSIONS

In this paper, we summarized the recent progress of low-temperature Si epitaxy focused on the cleaning procedure. Then the low-temperature Si epitaxy by the mercury-sensitized photo-CVD was described. In the last section, we demonstrated the heavily phosphorus doping ($>10^{21}cm^{-3}$) by photo-CVD.

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