Photo-Enhanced Boron-Doping in Low-Temperature Silicon Epitaxy and Its FTIR Study

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Low-temperature silicon epitaxy in a $Si_2H_6/B_2H_6/H_2$ gas system using ultraviolet (UV) light was investigated. By adopting a CVD model for the growth of polysilicon to this system, it was found that UV irradiation during growth and doping extracted the hydrogen atom in the ≡Si-H bond at the surface, which produced free surface sites for the adsorption of boron compound and enhanced the incorporation and/or the migration of adsorbed silicon compounds.

Introduction

Low-temperature silicon epitaxy is key technology to develop high-grade VLSI/ULSI devices. Many attempts to grow such devices using MBE[1], LPCVD[2], and plasma-[3] and photo-enhanced CVD[4] have been made. Photo-enhanced CVD using ultraviolet (UV) light sources seems to be the most promising in reducing the epitaxial growth temperature and improving crystal quality.

Recently, the authors[5] showed that using incoherent UV light sources were produced excellent doping characteristics, i.e., the activation ratio of the boron atom in the epitaxial growth film was 100% up to a carrier concentration of 1.2×10^{20} cm^{-3} without crystallographic defects under UV irradiation in a $Si_2H_6/B_2H_6/H_2$ system at the low temperature of 680°C. Interests are now focusing how UV irradiation affects growth and doping at low temperatures. The authors investigated the relationship between the silicon film growth rate and diborane partial pressure and the boron and hole concentration in the film. The gas phase under growing conditions was also analyzed.

Experiments

N-type silicon wafers with resistivities from 10 to 20 ohm-cm and (100)-oriented surfaces cleaned by the conventional wet treatment were used in the experiments. Before epitaxial growth, the wafer temperature was held at 930°C in a hydrogen ambient for 10 minutes to remove a native oxide on the wafer surface. Silicon films were grown in a photo-epitaxy reactor using a $Si_2H_6/B_2H_6/H_2$ gas system. The silicon wafer in the reactor was irradiated by high-pressure Hg lamps with intensity of 1 W/cm^2 ($\lambda < 300$ nm). Growth temperature was 680°C at a total pressure of 2.7×10^4 Pa, for a growth thickness of 400-500 nm. The boron concentration of boron in the silicon film was determined by secondary ion mass spectroscopy (SIMS). The gas in the reactor was sent through a quartz capillary to a cell and studied by Fourier transform infrared (FTIR) spectroscopy.

Results and discussion

1. Epitaxial silicon growth rate and boron doping

Figure 1 shows the silicon growth rate, G_{Si}, at 680°C as a function of diborane partial pressure, P_{B2H6}. With or without UV, the growth rate is increased slightly by adding diborane except at higher P_{Si2H6} and higher P_{B2H6}, where P_{Si2H6} is disilane partial pressure. It should be noted that, as P_{Si2H6} increased, the effect of UV irradiation on the growth rate grows. Figure 2 shows the dependence of the boron concentration, C_B, on P_{B2H6}. The C_B value increases with P_{B2H6} and is inversely proportional to P_{Si2H6}. With increasing P_{B2H6}, boron concentration in the grown epitaxial silicon film with UV irradiation becomes less than that without.

The activation ratio of the boron atoms in the film, C_{hole}/C_B, where C_{hole} is the hole concentration, is shown in Fig. 3. Boron atoms, doped in situ under UV irradiation, were completely activated up to 1.2×10^{20} cm^{-3}. However, without UV irradiation, the activation ratio was low. It should be noticed that boron was not activated beyond 1.2×10^{20} cm^{-3}, which may correspond to its solid solubility, for above a P_{B2H6} of 1.3×10^{-1} Pa, even with UV irradiation.
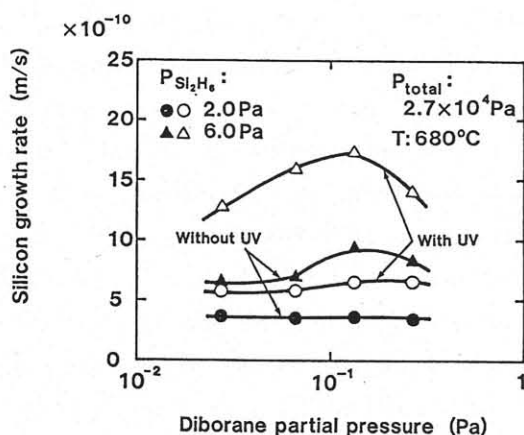
Fig. 1. Silicon growth rate at 680°C as a function of diborane partial pressure.

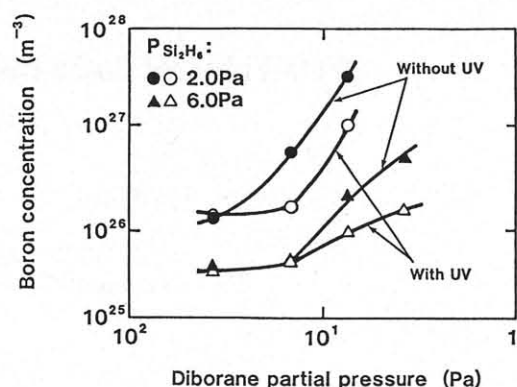## 2. Gas-phase analysis and surface reaction mechanism

Fig. 2. Boron concentration in the grown silicon film as a function of diborane partial pressure.
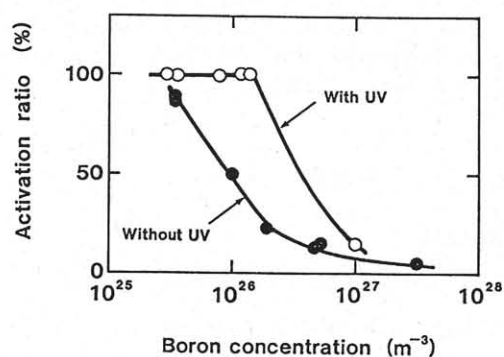
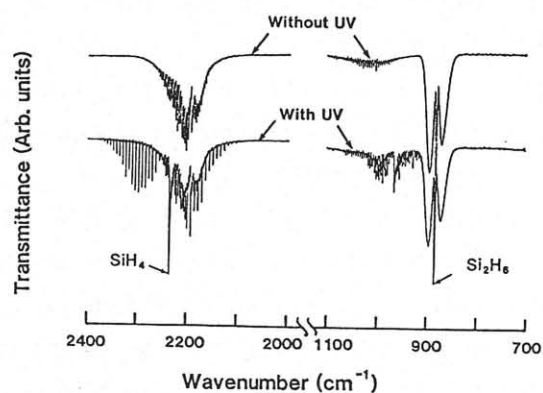Fig. 3 Activation ratio of the boron atoms in the silicon film.

Fig. 4 Photodissociation of disilane molecule by UV light.

Figure 4 shows that several ten of percent of disilane molecules are photodissociated by UV irradiation and become monosilane molecules stable at room temperature. Diborane molecules did not become photodissociated, however. These results show that the photo-dissociation cross section for disilane is more than ten times that for diborane.

This photo-enhanced CVD process cannot

be explained completely due to the lack of information on radicals generated by UV irradiation and on the electric characteristics of the wafer surface under UV irradiation. The above process can be simplified, however, using a well-known CVD formula, if CVD parameters are effective. That is, the effects of the photo-generated radicals and the surface electric characteristics are included with parameters shown below.

The authors propose that disilane molecules will be adsorbed on the surface:

(1) $*_s + Si_2H_6 \longleftrightarrow Si_2H_6^*$,
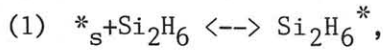
where $*_s$ is a free surface site. The adsorbed disilane will migrate over the surface to a kink, where it will be incorporated into the silicon lattice and hydrogen desorbed,

(2) $*_k + Si_2H_6^* \longrightarrow 2Si + 3H_2 + *_k$,
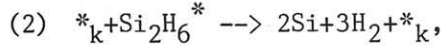
where $*_k$ is the surface site at a kink. Reaction (1) is in thermal equilibrium and has the equilibrium constant K. The growth rate, G_{Si}, is expressed in the following equation:[6]

$$1/G_{Si} = 1/k + 1/(kKP_{Si2H6}),$$

where k is the reaction rate constant. This is also applied to boron doping. The growth rate of holes, G_{hole} ($= G_{Si} \times C_{hole}/C_{Si}$), where C_{hole} and C_{Si} are the concentrations of holes and silicon in the film, must be defined. The values of k and K are estimated using Figs. 5 and 6 for cases with and without UV irradiation and summarized in Tables 1 and 2.

In silicon growth, the value of k with the UV irradiation is slightly larger than that without, as shown in Table 1. This means that the chemical reaction between the surface and silicon-compounds is enhanced by UV irradiation. UV irradiation affects boron doping differently, however. The adsorption of boron compound is enhanced by
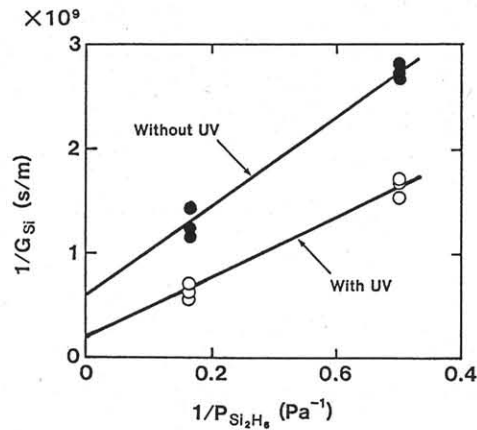

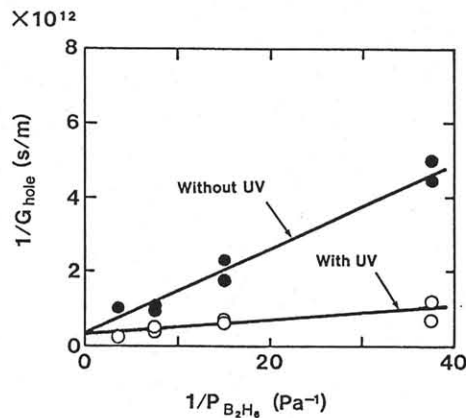Fig. 5. Reciprocal representation of data in Fig. 1.

Fig. 6. Reciprocal of the hole growth rate as a function of the reciprocal diborane partial pressure.

Table 1. Rate and equilibrium constants k and K, calculated from Fig. 5.

	With UV	Without UV
k(s/m)	5×10^{-9}	2×10^{-9}
K(Pa⁻¹)	0.1	0.1

Table 2. Rate and equilibrium constants k and K, calculated from Fig. 6.

	With UV	Without UV
k(s/m)	3×10^{-12}	3×10^{-12}
K(Pa⁻¹)	20	3

UV irradiation despite the fact that the chemical reaction is not affected, as shown in Table 2.

The amount of diborane molecules presented in the reactor was measured by FTIR technique at 680°C for both with and
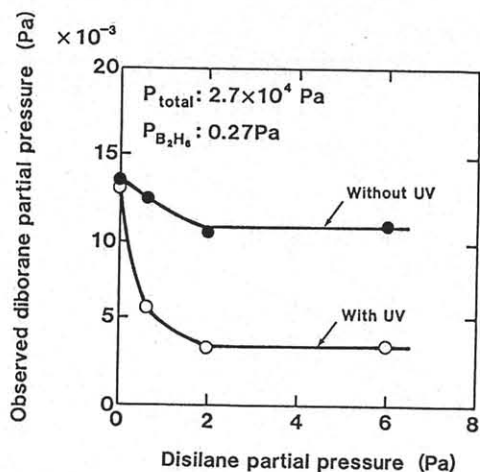
Fig. 7. Diborane partial pressure observed by FITR as a function of disilane partial pressure.

without UV irradiations. The value is shown in Fig. 7 as a function of disilane partial pressure. With disilane partial pressure is increased, the amount of diborane is decreased steeply. This suggests that the adsorbed boron compound increases with the presence of disilane and the UV irradiation.

From these results, the steady-state growth and doping is explained as follows: Without UV irradiation, the wafer surface in the $Si_2H_6/B_2H_6/H_2$ gas system at 680°C is thought to be occupied mainly by silicon compounds, such as Si_2H_6 and SiH_4, partly by boron compounds, $\equiv Si-H$ bonded atomic hydrogen that may impede the adsorption and migration of adsorbed compounds, and free surface sites able to adsorb compounds. The film is grown by the chemical reaction of the adsorbed compounds and extraction of atomic hydrogen from the adsorbed compounds. The sites of silicon and boron, then, become the free surface sites and adsorb the silicon and boron compounds. With UV irradiation, the extraction of atomic hydrogen in the growth above is enhanced by UV irradiation. This means that the mobility of the adsorbed compounds and/or the reaction speed between the adsorbed compounds and the lattice becomes faster, and that the free surface sites for

adsorption of boron compound increase as atomic hydrogen is eliminated. Thus, the growth rate and activation ratio of boron are increased by UV irradiation. The model proposed here explains the excellent doping characteristics under UV irradiation up to a hole concentration of 1.2×10^{20} cm^{-3}.

Conclusion

Low-temperature silicon epitaxy in a $Si_2H_6/B_2H_6/H_2$ gas system using ultraviolet (UV) light sources was investigated. It was shown by gas-phase analysis that disilane molecules, but not diborane molecules, were dissociated by UV irradiation. By adopting a CVD model for polysilicon growth to this system, UV irradiation during growth and doping was found to extract the hydrogen atom in the $\equiv Si-H$ bond at the surface, which produced free surface sites for the adsorption of boron compound and enhanced the migration of adsorbed silicon compound.

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