Mass spectrometry study of the gas phase reactions in the CVD of Si and in situ-phosphorus doped Si in order to explain the different growth rates

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Abstract : The experiments have been carried out in a vertical impinging jet type reactor in order to have a kinetically controlled growth. Two types of heating modes were used : hot wall reactor (HWR) and cold wall reactor (CWR). The gas phase compositions have been determined by coupling the reactor to a quadrupole mass spectrometer (QMS), while the growth rates were measured versus temperature and phosphine to disilane molar ratio in order to determine the species responsible for the deposits. Disilane draws a decrease in the inhibition of the growth rate which is 4 times less than in the case of monosilane as starting product. In contrast, phosphorus incorporation, which is in the range $1,5 \cdot 10^{19}$ - $8 \cdot 10^{20}$ atom cm^{-3} , keeps the same order of magnitude.

1 - Introduction

The use of SiH_4 is widespread in the manufacturing of electronic devices but presents some disadvantages with the reduction of the components sizes (inhomogeneity of growth). Moreover, the growth rate suffers a strong decrease when phosphine is added to silane in order to obtain in situ doped films. For these reasons disilane Si_2H_6 is now considered as a promising alternative source of silicon. The pyrolysis of disilane has been studied under various experimental conditions (1-5) and different mechanisms of decomposition have been proposed. Therefore, we have decided to study the decomposition of disilane by mass spectrometry analysis of the gas phase of the LPCVD reactor during the deposition and to measured in the same time the growth rates. Moreover two types of reactors, cold wall reactor (CWR) and hot wall reactor (HWR) have been used in order to vary the ratio gaseous volume/hot surfaces and modify the relative importance of homogeneous and heterogeneous reactions. The same process of investigation has been applied to $\text{Si}_2\text{H}_6/\text{PH}_3$ mixtures used for the elaboration of in situ P-doped silicon films.

2 - Experimental

The reactor is a vertical impinging jet type (figure 1) which provides kinetically controlled CVD reactions.

Fig.1. - Representation of the LPCVD apparatus showing the two modes of heating and the position of sampling capillary (SP) in each case

The sampling of gases is realized by passing through a stainless steel capillary tube (i.d. 0,16 cm). A part of this flow is then admitted into the QMS through a second tube (i.d. 100 Mm, 30 cm long) coated with silica. The working pressure in the QMS is between 10^{-4} - 10^{-5} Pa.

Figure 2 shows the position of the sampling in the both used configurations (CWR and HWR).

Analysis were performed using Balzers type QMG 420 mass spectrometer with a cross beam ion source and a 17 stages, 90° off axis electron multiplier.

The electronic grade gases admitted are controlled by mass flow regulators (AFC 260 ASM). The pressure is lowered by a 40 m³ h⁻¹ pump and regulated by using absolute capacitive manometer fitted with a butterfly valve. The flow rates of about 7 sccm (standard cubic centimeter) of disilane (diluted with nitrogen in the cases of depositions) give pressures between 10 and 10^4 Pa.

The substrate temperature is varying in the range 200-1000 °C in the cold wall configuration and 200-600°C in the hot wall configuration and the working pressure is 67 Pa.. Phosphine (5 % in Nitrogen) is added in the gas phase in the case of in-situ doped films. δ , defined by the phosphine to disilane partial pressure ratio, represents the quantity of phosphine injected in the reactor. δ is varying between 0 and $5 \cdot 10^{-2}$.

The thickness of the films is measured by profilometry after chemical etching. Phosphorus concentration is determined by SIMS analysis.

3 - Results and Discussion

The thermal dissociation of Si_2H_6 has been extensively studied and let suggests that homogeneous reactions play an important part .

Two types reactions lead to the deposition of silicon starting from disilane : homogeneous and heterogeneous. The main homogeneous reactions are listed belows.

The following stage is the adsorption of the gaseous species on the silicon surface and desorption of hydrogen (heterogeneous reactions).

Undoped silicon

Gas phase analysis were done by following the QMS signal evolution of some specific ionic fragments The fragment $m/q = 60$ ($[\text{Si}_2\text{H}_4]^+$) has been chosen as representative of disilane. The mass $m/q = 30$ ($[\text{SiH}_2]^+$) has been selected to follow the evolution of monosilane. Figure 2 shows the evolution versus temperature

Fig.2. - Comparison of the evolutions versus temperature of monosilane ($\blacksquare$) and disilane ($\circ$) signals in HWR (full symbols) and CWR (empty symbols). $P = 67$ Pa, molar fraction of $\text{Si}_2\text{H}_6 = 1$.

of the abundance of $m/q = 60$ and $m/q = 30$ fragments in both heating modes. The abundance of disilane begins to decrease at about 400 °C, while that of monosilane increases, corresponding to the reaction R1. Silylene radicals cannot be detected by mass spectrometry, but they are formed on the same scale than SiH_4 . Monosilane increases up to 520 °C in the HWR and up to 625 °C in the CWR, and then decreases while the disilane decreases throughout the whole range. The differences existing between the two configurations are attributed to the consumption of the gaseous species by the hot surfaces (reactions R7 and R8) and a higher dissociation rate of Si_2H_6 in the homogeneous phase (reactions R1 and R5) in the HWR case.

Higher silanes, which are formed by silylene insertion (reactions R2 to R4), have not been detected in HWR. In CWR, polysilanes, like tri-, tetra- and pentasilane (m/q) were significantly detected. Their evolutions are the same as that of SiH_4 and their relative quantities decrease by a factor 10 with each added silicon atom.

Fig.3. - Growth rates of silicon versus temperature. Comparison between HWR (■) and CWR (□). $P = 67$ Pa, molar fraction of $\text{Si}_2\text{H}_6 = 10^{-2}$

Growth rates versus reciprocal temperature are reported in the figure 3. They follow an Arrhenius type law and the activations energies are about 159 kJmol⁻¹ and 184 kJmol⁻¹ in HWR and CWRT respectively. These values agree with those of NAKAZAWA [6]. In the HWR, deposition rates are 3 to 5 higher than in CWR. The deposition of silicon starting from Si_2H_6 begins at lower temperature than starting from SiH_4 and at a given temperature the growth rate is about 10 times higher (HWR).

These results are to be linked to the difference of the concentration of the silylene radicals. In the case of disilane they point out, the importance of the homogeneous gas phase reactions which, more numerous in HWR, imply higher dissociation rate and higher growth rate.

In situ P. doped silicon

A preliminary gas phase analysis of PH_3 has shown that, in HWR, phosphine adsorption occurs as soon as 330°C , but there is not significant dissociation until 600°C . In contrast in CWR, phosphine begins to dissociate in the homogeneous phase above 550°C and gives P_2 and P_4 gaseous species (7). In the case of in situ doping we have recorded the gas phase evolution with T starting from $\text{PH}_3/\text{Si}_2\text{H}_6$ mixtures. Fig. 4 reports the comparisons of SiH_4 amounts when PH_3 is added to Si_2H_6 in CWR and HWR.

Fig.4.- Comparison of the amounts of SiH_4 (signal $m/q = 30$) in the gas phase when feeding the reactor either with pure disilane (133 Pa) (□) either with a mixture (disilane (133 Pa)/phosphine 5 % in nitrogen (133 Pa) (■)
 a CWR b HWR

In both configurations the amount of SiH_4 is greater in the presence of PH_3 . The concentration of Si_2H_6 remaining in the gas phase follows the same variation but with a lesser importance. These behaviours can be explained by the adsorption of PH_3 which prevents that of the other species (8) and reduce the growth rate. In the case of CWR the amounts of tri and tetrasilane decrease when PH_3 is added in the gas phase meaning that reactions of insertion of SiH_2 in silane are less numerous. In the same way we have compared the quantity of PH_3 in the gas phase with and without Si_2H_6 : the presence of Si_2H_6 causes a decrease of PH_3 concentration attributed to its consumption by reaction with silylene radicals. These observations tend to prove the formation of gaseous compounds which contain phosphorus and silicon atoms like monosilyl phosphine these compounds are difficult to detect by mass spectrometry because of their small concentrations and the overlapping of their mass spectra with those of other components. The evolution of the growth rate versus γ is presented on in fig. 5.

In both cases, the presence of phosphine carries a decrease in the deposition rate. The influence of phosphine is more important in the CWR and can be linked to the quantities of the silylene radicals present in the gas phase. In the HWR, SiH_2 radicals are sufficiently numerous to compensate the

unadsorption of SiH_4 molecules. The reduction of the growth rate is quickly limited and leaves off when γ exceeds $8 \cdot 10^{-3}$. In the CWR, SiH_2 species are less numerous and the influence of PH_3 spreads over the whole variation range of γ . In both cases, the inhibition of the growth rate is lower than in the use of SiH_4 (80 % against 20 and 60 % respectively in the HWR and CWR).

Fig.5. - Growth rate versus $\text{PH}_3/\text{Si}_2\text{H}_6$ ratio. $P = 67$ Pa, molar fraction of $\text{Si}_2\text{H}_6 = 210^{-2}$, temperature of the substrate 520°C for the HWR ($\bullet$), 550°C for the CWR ($\circ$)

These results agree with those published by Ahmed and Meaking [9].

The solid-phase phosphorus concentration, determined by SIMS analysis, increases linearly with γ

Fig.6. - Phosphorus concentration in the films versus $\text{PH}_3/\text{Si}_2\text{H}_6$ ratio. $P = 67$ Pa, temperature of the substrate 520°C in HWR ($\bullet$), 550°C in the CWR ($\circ$)

(fig. 6). The phosphorus concentration varies between $1.5 \cdot 10^{19}$ and $7-8 \cdot 10^{20} \text{ cm}^{-3}$ in the HWR (deposition conditions are 520°C and 2 % Si_2H_6) and from $4 \cdot 10^{19}$ to $5 \cdot 10^{20} \text{ cm}^{-3}$ in the CWR ($T_d = 550^\circ\text{C}$). In the later case phosphorus incorporation seems to be higher than in the former one.

4 - Conclusion

We used disilane gas to successfully deposit undoped and in-situ P doped silicon layers. Gas phase analysis points out the formation of gaseous species like higher silanes (tri and tetrasilane) and silylphosphine. We showed the difference between the two heating modes and correlate them to the amount of SiH_2 radicals and also, to the importance of homogeneous reactions. The growth rate evolutions, in the presence of phosphine, are linked to the amounts of SiH_2 radicals.

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