SIPOS Deposition from Disilane: Experimental Study and Modelling

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Abstract. SIPOS films were deposited from a mixture of disilane and nitrous oxide in a tubular hot wall reactor and their thickness and oxygen content were measured. To increase one's knowledge in SIPOS deposition, a detailed chemical mechanism is proposed to represent homogeneous and heterogeneous reactions and the CVD2 model taking into account hydrodynamics and mass transfert with chemical reactions is adjusted to SIPOS deposition. A good agreement between experimental results and model predictions for various operating conditions puts in evidence the representativity of the chosen chemical mechanism. By the use of CVD2 model, the main chemical pathways are identified.

1. INTRODUCTION

SIPOS (Semi Insulating Polycrystalline Silicon) films have been known for several years to meet the requirements for a good passivation behaviour, for instance in planar high voltage transistors. Such films are commonly produced by Chemical Vapor Deposition (CVD), using a mixture of silane (SiH_4) and nitrous oxide (N_2O) as reactant gases. Up to now, no detailed information about the chemical mechanism of deposition has appeared in the literature. A few oversimplified mathematical models have been proposed to explain the observed growth rates but no modelling of the oxygen content dependence on deposition parameters has been undertaken.

This paper reports on a new process for SIPOS thin films fabrication which uses a mixture of disilane (Si_2H_6), instead of silane, and nitrous oxide. For different working conditions, SIPOS thin layers have been realized in a hot wall tubular CVD reactor and the silicon growth rates and the oxygen content of silicon layers have been measured along the wafer load. To explain CVD general behaviour, a chemical mechanism including homogeneous and heterogeneous reactions is proposed with the corresponding rate constants. Using an appropriate adjustment of a two dimensional model, developed in our laboratory to treat the case of polycrystalline silicon deposition and which takes into account hydrodynamics, mass transport and chemical reactions, a comparison between the experimental deposition rates and oxygen contents and the corresponding theoretical predictions is made. Then by the model use, an analysis of the CVD behaviour during SIPOS deposition is realized and the main chemical pathways are put in evidence.

2. EXPERIMENTAL

2.1 Operating conditions

SIPOS films have been realized by pyrolysis of disilane and nitrous oxide in a horizontal hot wall LPCVD reactor (tube diameter, 135 mm, tube length, 1.98 m, see figure 1). Twenty wafers, 100 mm diameter n-type CZ silicon, are arranged on a batch, systematically situated in the center of the heated zone (length, 70cm). Wafer surfaces are normal to the gas flow, injected from the door of the furnace. The distance between two successive wafers is 9.4 mm.

Several deposition parameters have been studied : the temperature from 500 to 570°C and the gas flow ratio $\gamma = Q_{\text{N}_2\text{O}}/Q_{\text{Si}_2\text{H}_6}$ from 10 to 95.

SIPOS thickness has been measured at the wafer center by ellipsometry and also by estimating the step height after etching.

Figure 1 : Schematic view of the LPCVD reactor

The O/Si ratio in the film is assessed by X-ray photoelectron spectroscopy (XPS) and by differential thickness method [1,2] which is based on thickness measurements before and after complete oxidation of SIPOS films.

2.2 Experimental results

Experimental results obtained for various inlet compositions of the gas phase are presented on figures 2 and 3 : growth rate and oxygen content on the fifth and eighteenth wafers of the load are plotted versus the inlet partial pressure of disilane. For all these experiments, the total pressure in the reactor, the deposition temperature and the nitrous oxide flow rate have been kept constant and respectively equal to 580 mTorr, 535 °C and 475 sccm.

From a general point of view, the global growth increases with an increase of the inlet disilane partial pressure when the oxygen content of the silicon layers decreases in the same time. The results are consistent with those observed and reported [2,7] for a gas mixture of silane and nitrous oxide. For the lowest concentrations of disilane in the gas phase, no great differences are noted between the results obtained along the wafer boat : deposition rates and O/Si ratios are nearly the same. But for the highest concentrations, the global growth rate (figure 2) presents a large decrease along the wafer boat with a 50% reduction between the 5th and the 18th positions. The corresponding oxygen contents remain nearly equal (figure 3). This observation constitutes an original result for disilane and nitrous oxide mixtures. We can suppose that the homogeneous reactions certainly play a more important role in the case of disilane than for silane, because of a more important thermal decomposition for disilane.

Figure 2 : growth rate with disilane partial pressure

Figure 3 : Oxygen content with disilane partial pressure

The previous experimental results have been completed by a series of experiments realized for various nitrous oxide flow rates (figures 4 and 5). The same behaviour can be observed for low values of gas flow rates ratio γ (i.e. high partial pressure of disilane), but at γ values higher than 30 no discrepancy of the growth rate along the wafer boat has been put in evidence.

Figure 4 : Growth rate with N2O/Si2H6 ratio

- QN2O=475sccm-5th wafer
- ◆ QN2O=475sccm-18th wafer
- QN2O=240sccm-5th wafer

Figure 5 : Oxygen content with N2O/Si2H6 ratio

- QN2O=475sccm-5th wafer
- ◆ QN2O=475sccm-18th wafer
- QN2O=240sccm-5th wafer

The effect of the deposition temperature on the global growth rate and the oxygen content has also been studied for $\gamma=19$. The measurements obtained for the 5th and the 18th wafers are presented on figures 6 and 7. The total deposition rate increases drastically with temperature, an 70 °C enhancement gives an increase from 10 Å/min to 40-50 Å/min for the growth rate. To represent this behaviour, an Arrhenius law can be used with an enough high apparent activation energy of 71 kJ/mol. Simultaneously, the O/Si ratio in the silicon layers also increases with temperature from 0.3 to 0.6.

For the γ values chosen for this study, a growth rate depletion and an oxygen content enhancement are observed along the wafer boat, but these evolutions are nearly unchanged by a temperature increase.

Figure 6 : Growth rate with temperature

Figure 7 : Oxygen content with temperature

3. MODELLING OF THE REACTOR

3.1 Chemical behaviour

In order to explain these experimental results, a chemical mechanism representative of the chemical behaviour during SIPOS deposition from disilane has been tried to be established. The whole chemical study and constant determination will not be reported in this paper, only the homogeneous and heterogeneous final system is mentioned :

-Three reactions have been selected to represent the homogeneous mechanism :

Table 1 summarizes the corresponding kinetic constants that have been calculated for LPCVD conditions with the QRRK theory [3].

Reaction	Direct constant s^{-1} or $(\text{m}^3.\text{mol}^{-1}.\text{s}^{-1})$	Reverse constant $(\text{m}^3.\text{mol}^{-1}.\text{s}^{-1})$
(V1)	$6.41 \cdot 10^{10} \text{ P exp}(-184970/\text{R/T})$	$2.83 \cdot 10^3 \text{ P}^{0.4} \text{ exp}(+21070/\text{R/T})$
(V2)	$7.14 \cdot 10^7 \text{ P exp}(-197100/\text{R/T})$	$2.00 \cdot 10^2 \text{ P exp}(+900/\text{R/T})$
(V3)	$4.8 \cdot 10^6 \text{ exp}(-90000/\text{R/T})$	none

Table 1 : Kinetic constants for LPCVD conditions with $\text{R}=8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$

-For heterogeneous reactions, the gases injected in the reactor and some chemical species produced by homogeneous reactions can contribute to silicon deposition and/or silicon oxidation. The corresponding chemical equations are supposed to be as follows :

As a first approximation, the deposition rate of disilane has been neglected. Previous studies [4] concerning polysilicon growth from disilane have shown that silicon deposition is mainly due to silane and silylene. The expression given by Wilke and coworkers [5] and commonly used in the case of polysilicon growth from silane can be written as :

$$r_s(\text{SiH}_4) = \frac{k_1 P_{\text{SiH}_4}}{1 + K_S P_{\text{SiH}_4} + K_H P_{\text{H}_2}} \quad (\text{E1})$$

where $k_1 = 3.2 \cdot 10^{-3} \text{ exp}(-6800/\text{T}) \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1}$, $K_H = 4.8 \cdot 10^{-8} \text{ exp}(10000/\text{T}) \text{ Pa}^{-1}$ and $K_S = 0.82 \cdot 10^{-10} \text{ exp}(18000/\text{T}) \text{ Pa}^{-1}$, and T is in Kelvin.

When SIPOS films are deposited from a mixture of silane and nitrous oxide, it is well known that the addition of N_2O in the gas phase induces a decrease of the growth rate and some authors [2,6] have proposed to write this inhibition by using an adsorption-desorption equilibrium constant noted K_N , similar to K_S or K_H and representing a competitive adsorption between SiH_4 and N_2O :

$$r_s(\text{SiH}_4) = \frac{k_1 P_{\text{SiH}_4}}{1 + K_S P_{\text{SiH}_4} + K_H P_{\text{H}_2} + K_N P_{\text{N}_2\text{O}}} \left(\frac{1}{1+x} \right) \quad (\text{E2})$$

On the other hand, the surface of SIPOS layers is certainly not uniform since it will consist of Si sites and O sites. Interactions between molecular species of the gas stream, that is to say SiH_4 and N_2O , and heterogeneous sites will be different according to their nature. In order to take into account this heterogeneity, it can be assumed that reaction of silane deposition takes place exclusively on the sites of highest activity i.e. Si sites and that the fraction of Si sites at the surface for SiO_x is exactly the same as the fraction of Si atoms in the solid bulk i.e. $1/(1+x)$.

According to electronic considerations, we supposed that N_2O reacts on the same sites as SiH_4 and a similar equation has been used to represent silicon oxidation by nitrous oxide :

$$r_s(\text{N}_2\text{O}) = \frac{k'_1 P_{\text{N}_2\text{O}}}{1 + K_S P_{\text{SiH}_4} + K_H P_{\text{H}_2} + K_N P_{\text{N}_2\text{O}}} \left(\frac{1}{1+x} \right) \quad (\text{E3})$$

No data are available in the literature for k'_1 and K_N .

Radical species i.e. SiH_2 and H_2SiO are known to be very reactive [7,8]. Using the equality of the collision speed of the species i with the surface and the integration of the same species in the solid, with a sticking coefficient s , the deposition rate are expressed by :

$$rs(i) = \frac{1}{4} s \sqrt{\frac{8RT}{\pi M_i}} \frac{P}{RT} y_i \quad (\text{E4})$$

3. 2 Adjustment of the CVD2 model to SIPOS case

A few years ago, a two dimensional model called CVD2 has been developed to represent the phenomena involved in an LPCVD hot wall reactor during pure and in situ phosphorus doped polysilicon deposition. The software takes into account hydrodynamics and mass transport equations with homogeneous and heterogeneous chemical reactions.

The flow problem is solved in cylindrical coordinates, for a two dimensional system (no angular dependence) by integration of the well known continuity and motion equations for incompressible, newtonian fluids :

$$\nabla \rho \vec{v} = 0 \quad (\text{E5})$$

$$\rho [\vec{v} \cdot \nabla \vec{v}] = - \nabla p + \mu \nabla^2 \vec{v} + \rho \vec{g} \quad (\text{E6})$$

The deposition rate calculations involve the integration of the mass transport equation :

$$\vec{v} \cdot \nabla c_A - D_{AM} \nabla^2 c_A = R_A \quad (\text{E7})$$

where c_A is the molar concentration of the species A in the gas phase and R_A the production rate by homogeneous reactions.

By lack of place, we do not describe the numerical treatment in details in this paper (see [4] for more precision). The two systems partial differential with the convenient number of boundary conditions have been solved separately by finite difference procedures. A grid, with constant r and z increments has been selected : it involved 121 lines in the radial direction (constant r) and 21 columns in the axial direction (constant z). The values of the different variables and those of their space derivatives have been approximated at each point of the grid by finite series developments of the second order. Calculations involved an iterative Gauss-Seidel type procedure.

To reduce the computing time needed to solve these differential equations written for every chemical species, only a small part of the reactor, i.e. an interwafer spacing has been considered as the modelling zone. Consequently, this domain is considered as isothermal and the physicochemical properties can be supposed independant of the mixture composition but some hypotheses are required to define boundary conditions for the different chemical species supposed to be in this region. But as the concentrations depend on the whole hystory of the gas phase between the reactor inlet and the modelling zone, that is perfectly unknown, some choices are to be made to convey that a dynamic equilibrium is reached.

Generally, two kinds of chemical species can be distinguished : the saturated molecules and the radicals. A saturated molecule presents a high enough concentration with a slow evolution in an interwafer space. All the chemical reactions involving this species contribute weakly to a concentration change, the homogeneous reactions are usually balanced and the consumption or production on solid surfaces have low kinetic rates. The corresponding overall conversion rate through an interwafer space is then identified by an iterative procedure. The ultimate values are next to 0, negative if the species are consumed, and positive if they are produced.

On the contrary, radicals which are very reactive, present very low concentrations and very rapid evolutions. The homogeneous reactions involving these species are of course balanced but the low production or consumption becomes to be important because of the very low concentrations. On solid surfaces, the reactivity of the radical is very high with generally a sticking coefficient equal to one. For radicals, the conversion rate is assigned to be equal to zero, expressing the fact that homogeneous reactions can produce rapidly the part of the radical consumed by heterogeneous reactions.

In the present work, silylene and silanone, i.e. radical species, are supposed to be in dynamic equilibrium, their consumption being perfectly balanced by their production. Their sticking coefficients have been supposed to be equal to unity. The concentrations of disilane, nitrous oxide, hydrogen and nitrogen result from mass balances written for the chemical species Si, O, H and N.

For silane, concentration and conversion rate are determined by trial and error adjustments to fit with the experimental data.

3. 3 Modelling results

3. 3. 1 Identification of unknown parameters and model testing

From the results mentioned above, it has been possible to identify the unknown parameter k'_1 and K_N by adjusting theoretical predictions with experimental results. This identification has been done from values of the global deposition rates and oxygen content in the center of each wafer. For these two constants, Arrhenius expressions have been established from fitting the experimental results : $1.93 \cdot 10^4 \exp(-20563/T)$ mol.m⁻².s⁻¹.Pa⁻¹ and $7.5 \cdot 10^{-11} \exp(16420/T)$ Pa⁻¹ respectively, with T in Kelvin.

Then a complete comparison between experimental results and modelling predictions has been done and a good agreement has been obtained for the various studied working conditions.

To illustrate this comparison, the modelling predictions of the global growth rate and the oxygen content and the corresponding experimental results are reported on figures 8 and 9 for the 5th and the 18th wafers.

The decrease of the total deposition rate along the wafer load is well represented by the model for various values of γ (figure 8). The increase of the oxygen content observed for $\gamma=31.7$ is also well predicted (figure 9).

Figure 8 : Effect of N2O/Si2H6 ratio on deposition rate
T=535°C P=580mTorr

Figure 9 : Effect of N2O/Si2H6 ratio on oxygen content
T=535°C P=580mTorr

Figure 10 : Effect of temperature on deposition rate (P=580mTorr)

Figure 11 : Effect of temperature on oxygen content (P=580mTorr)

The effect of other operating conditions on SIPOS deposition are also well represented by the model including the proposed chemical system. As an example, the temperature influence on the global

deposition rate and the O/Si ratio is presented on figures 10 and 11. A satisfactory agreement can be observed.

By CVD2 model, the total growth rate and the oxygen content are not only calculated at the center of each wafer along the wafer load, but radial variations on a particular wafer can also be predicted. A comparison between calculated and measured radial profiles is presented in figures 12 and 13 for the fifth wafer of the load, at 535 °C and 580 mTorr. A good agreement is observed even at the wafer periphery where great non uniformities have been put in evidence. Let us here recall that the necessary identification of some kinetics parameters has been done for mean values at the wafer center and not along the wafer radius.

Figure 12 : Radial deposition rate profile

Figure 13 : Radial oxygen content profile

3. 3. 2. Detailed description of one modelling result

Among the important results given by CVD2 model for SIPOS deposition, one of the most interesting for the understanding is the concentration distribution of the different chemical species taken into account in the mechanism. On figure 14, the radial evolution of chemical species in the fifth interwafer space is shown for $T=535^{\circ}\text{C}$, $P=580\text{mTorr}$, $\gamma=19$.

Figure 14 : Radial molar fraction profile

□ SiH₄ ♦ SiH₂ ○ H₂ • Si₂H₆
♦ H₂SiO + N₂O □ N₂

Figure 15 : Radial deposition rate profile

□ SiH₄ ♦ SiH₂
♦ H₂SiO + N₂O ○ total

The main chemical species i.e. silane, disilane, hydrogen, nitrogen and nitrous oxide present quite constant values along the reactor radius. On the contrary, for heterogeneous highly reactive species such as silylene (SiH₂) and silanone (H₂SiO), radial concentration profiles are observed with constant low values in the center of the interwafer space and distributed higher values in the annular region between the wafer periphery and the reactor walls. These two different kinds of concentration distribution give two different contributions to total growth rate as illustrated on figure 15. The contributions are constant for silane and nitrous oxide and those of silylene and silanone show non uniformities at the wafer periphery.

By the model use, silylene is identified as the main chemical species that contributes to silicon deposition with a constant contribution of 80% at the wafer surface and a non uniform contribution at the wafer surface.

4. DISCUSSION

The extension of CVD2 model to SIPOS deposition constitutes an useful tool to propose some explanation for the particular behaviour of SIPOS growth from disilane and nitrous oxide mixtures. In particular, the main contribution to silicon deposition is due to silylene (figure 15), a chemical species that is not injected into the reactor but produced by disilane pyrolysis (reaction V1).

At the beginning of the wafer boat, the silylene concentration depends on the reaction V1 advancing. A high concentration of disilane or a high deposition temperature are in favour of a high concentration of silylene and of course of a high global growth rate. This consideration, deduced from CVD2 model is consistent with experimental results (figure 2).

According to CVD2 model, the observed bull's eye effect as for in situ phosphorus doped polysilicon deposition [9] results from radical's contributions to global growth rate and the radial increase of silylene contribution, higher than those of the silanone, explains the radial decrease of the observed oxygen content (figure 13), by remembering that silylene gives only one silicon atom to SIPOS layer while silanone gives both silicon and oxygen atoms.

5. CONCLUSION

In this paper, a chemical system has been proposed to represent the CVD behaviour during SIPOS deposition. The extension of CVD2 model including this mechanism to SIPOS deposition has given predictions close to experimental results expressing a good representation of the chemical phenomena for various working conditions.

The use of CVD2 model has increased our knowledge in SIPOS deposition by CVD technique, putting in evidence the important role played by SiH_2 and H_2SiO .

List of symbols

c_A	molar concentration of the species A in the gas phase (mol.m^{-3})
D_{AM}	mixture diffusion coefficient ($\text{m}^2.\text{s}^{-1}$)
k_1, k'_1	kinetic constants ($\text{mol.m}^{-2}.\text{s}^{-1}, \text{Pa}^{-1}$)
K_S, K_H, K_N	adsorption-desorption equilibrium constants (Pa^{-1})
M_i	molar concentration of the ith species
P	total pressure (Pa)
$rs(i)$	deposition rate of the ith species ($\text{mol.m}^{-2}.\text{s}^{-1}$)
s	sticking coefficient
T	temperature (K)
v	velocity modulus (m.s^{-1})
x	oxygen content i.e. O/Si ratio
y_i	molar fraction of the ith species
μ	dynamic viscosity ($\text{kg.m}^{-1}.\text{s}^{-1}$)
ρ	density (kg.m^{-3})

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