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SILICON DEPOSITION FROM DISILANE : EXPERIMENTAL STUDY AND MODELLING

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Abstract : Undoped silicon films have been deposited from disilane in a tubular hot wall LPCVD reactor and their physical properties have been analyzed. A two dimensional model taking into account a detailed gas phase chemical mechanism has been developed to simulate the growth rate distribution on a wafer. The numerical predictions have been compared with experimental results and a good agreement has been found in various conditions of temperature and pressure. This work has demonstrated that the main contribution to silicon deposition involves the radical silylene in the case of disilane, whereas in the case of silane as a gaseous source it involves silane itself, so suggesting a possible explanation for the very important differences observed in crystalline characteristics of silicon layers. From a more practical point of view, the much larger size of crystals obtained when starting from disilane opens interesting possibilities of industrial developments, in particular for the manufacture of thin film transistors.

1. Introduction :

Several microelectronic specific technologies require either a low silicon deposition temperature or in situ doping by phosphorus. In these two cases, silane, as a source gas, shows limitations : too low growth rates or non uniform thickness on wafers. In the search of an alternative precursor a few analyses have been done and published in the literature, suggesting that disilane could be a relevant candidate.

During the present work, depositions of undoped Si-films from disilane have been performed in a tubular hot wall LPCVD reactor ; the corresponding experimental results have been compared with numerical simulations predictions obtained using a two dimensional model.

2. Experiments :

The films have been deposited from pure Si_2H_6 in an industrial LPCVD reactor, which consisted of a quartz tube which lied horizontally in a three heating zones furnace. The diameter of the tube was 135 mm and the isothermal zone had a length of about 90 cm. Twenty wafers, 4" in diameter (<111> orientation) were stacked normal to the gas flow which was injected from the front door. The distance between consecutive wafers was 5mm. The working conditions and film growth rate results are presented in table 1.

The mean deposition rate ($\langle V_d \rangle$) has been deduced from thickness measurements on the center of the wafers. Consequently, the values of V_d did not take into account the greater thickness that has been found on the edges of the wafers.

Td(°C)	P(torr)	Q(ccm)	Vd(Å/min)	
			from Si ₂ H ₆	from SiH ₄
420	0,2	100	1,6	
450	0,2	100	11,8	
520	0,2	100	83,2	7,2
555	0,2	100	200-300 (powder)	24
555	0,12	25	40,6	
555	0,075	25	23,8	

Tab. 1 : Operating conditions

At 555°C, and a pressure of 200mTorr, it must be added that a production of powder has been observed, a large amount of which deposited on the first and last wafers, and on the edges of the other wafers. We think it also diffused into the interwafers space, probably modifying the layer growth rate and leading to a large uncertainty in thickness measurements.

Nevertheless, it appears clearly that the film growth rate increases rapidly with temperature and pressure. Moreover, the values obtained demonstrate that the deposition rate is much more important when starting, as a gas source, from disilane than from silane. For example, at 520°C and 0.2 torr, the deposition rate from disilane is 12 times higher than the deposition rate from silane.

3. Modeling basic principles

Following the same principles which have already been involved to treat the case of silicon deposition from silane [1], a two dimensional model taking into account hydrodynamics, mass transport and chemical reactions has been developed. In more detail, the general hypotheses of steady state, cylindrical symmetry and the limitation of the modeling region to an interwafer space, have been made to simplify the numerical procedure. Through an interwafer space, the conversion rate of the gaseous phase is sufficiently low to consider the temperature and the gas phase properties as constants, for example $\rho = 2.08 \cdot 10^{-4} \text{ kg/m}^3$ and the diffusivities are precised in table 2

From a technical point of view, the continuity and Navier-Stokes equations (1 and 2) have been solved first, then, for each chemical species k, the mass transport equation with a production term R_k (3) :

$$\text{div } \mathbf{v} = 0 \quad (1)$$

$$\rho D\mathbf{v}/Dt = -\text{grad } p + \mu \Delta \mathbf{v} + \rho \mathbf{g} \quad (2)$$

$$C D y_k / Dt = C \nabla^2 y_k + R_k \quad (3)$$

Boundary conditions on solid surfaces state that the velocity is zero and that mass fluxes are equal to the corresponding deposition (or production) rates. At the entrance and exit sections of the modeling zone, the velocity and concentrations profiles are supposed to have reached a dynamic equilibrium. It means that far from the ends of the wafers line, the phenomena reproduce identical or similar situations from one interwafers space to the following.

From a chemical point of view, disilane, as soon as it has been heated to sufficiently high temperatures ($\approx 300^\circ\text{C}$), it begins to decompose homogeneously into silane and silylene. This last species, a very reactive radical, can combine with stable species to form higher order silanes such as trisilane and tetrasilane. The complete set of homogeneous reactions which have been taken into account in this modeling work for the production term is presented in table 2.

Homogeneous reactions and their kinetic constants [P(Pascal), T(K), R(J K ⁻¹ mol ⁻¹)]		
	direct reaction (s ⁻¹)	reverse reaction (m ³ mol ⁻¹ s ⁻¹)
Si ₂ H ₆ ↔ SiH ₄ + SiH ₂	6.41 10 ¹⁰ P exp(-184970/RT)	2.83 10 ³ P ^{0.4} exp(21070/RT)
Si ₃ H ₈ ↔ Si ₂ H ₆ + SiH ₂	4.75 10 ¹⁵ exp(-221500/RT)	7.08 10 ⁶ exp(-1613/RT)
Si ₄ H ₁₀ ↔ Si ₃ H ₈ + SiH ₂	7.94 10 ¹⁵ exp(-221540/RT)	7.08 10 ⁶ exp(-1613/RT)
SiH ₄ ↔ H ₂ + SiH ₂	7.14 10 ⁷ P exp(-197100/RT)	2.0 10 ² P exp(-900/RT)

Tab. 2 : Homogeneous reactions and their kinetic constants

Kinetic data for these reactions can be found in the literature /2/. For this analysis, the values proposed by Communal et al /3/ and calculated by a quantum RRR method, have been selected (tab.2).

For the silicon deposition on solid surfaces, the decomposition of silylene has been supposed infinitely rapid and those of disilane, trisilane and tetrasilane neglected. For silane, a well known equation has been selected from the literature /4/ :

$$R(\text{SiH}_4) = \frac{320 \exp(-6800/T)}{1 + 4,9 \cdot 10^{-3} \exp(10000/T) P y(\text{H}_2) + 8,3 \cdot 10^{-6} \exp(18000/T) P y(\text{SiH}_4)}$$

The complete set of equations has been solved using a finite differences method and an implicit Gauss Seidel algorithm.

The geometrical and operating parameters, corresponding to the cases treated here, have already been indicated in table 1. The model provides a very great amount of informations which will not all be described and discussed here. The results show that, as a first approximation, silane, disilane, trisilane, tetrasilane and hydrogen concentrations can be considered as uniform in the modeling region ; the corresponding mean values are presented in table 3. On the contrary, silylene concentration varies widely with position and the corresponding results are presented in figure 1. It must be observed, first, that the silylene molar fraction remains everywhere weak, of the order of $1.5 \cdot 10^{-4}$ at its maximum but varies widely from its highest values in the annular region to the lower ones in the interwafers space. A similar distribution has already been observed in the case of silicon deposition from pure silane, but with much lower values, of the order of 10^{-7} (see also figure 1), that is to say two orders of magnitude less.

Characteristics of the gaseous phase (T=555°C ; P=0,2 torr ; Q=100 sccm)			
	from pure silane	from pure disilane	
	molar fraction	molar fraction	diffusivities (m ² /s)
SiH ₄	0,89	0,19	0,2095
Si ₂ H ₆	4,7.10 ⁻³	0,73	0,2155
Si ₃ H ₈	1,4.10 ⁻⁶	2,5.10 ⁻²	0,1175
Si ₄ H ₁₀	2,0.10 ⁻⁹	5,0.10 ⁻⁴	0,0972
SiH ₂	1,3.10 ⁻⁶	1,2.10 ⁻⁴	0,2532
H ₂	0,1	5,5.10 ⁻²	1,0802

Tab. 3 : Molar fractions and diffusivities of chemical species in the gaseous phase

Figure 2 represents the silicon deposition rate variations with radial position on a wafer surface, detailing the contributions due to silane, silylene and the total deposition rate. On the contrary of what has been observed in the case of silicon deposition from silane, the mean contribution to the film growth rate results from silylene, giving rise to the appearance of very strong thickness heterogeneities at the wafer periphery, corresponding to the rapid concentration variations presented on figure 1.

Figures 3 and 4 present the influences on the film growth rate of two important parameters respectively, temperature and pressure.

It can be observed that increases in temperature or in pressure result in increases in growth rate. Without presenting here the corresponding results, it can be added that these growth rate variations are mainly due to increases in the silylene contribution which, in term, result from a more important production of silylene by disilane pyrolysis.

Fig. 1 : Silylene molar fraction spatial variations when starting from (a) pure silane (b) pure disilane

Fig. 2 : SiH_2 and SiH_4 contributions to the silicon growth rate on a wafer

Fig. 3 : Silicon growth rate for various temperatures

Fig. 4 : Silicon growth rate for various pressures

4. Physical properties

With the low temperature values selected in this work, the as grown deposits have been observed to be amorphous. But, it is now wellknown that Si deposits from Si_2H_6 can produce very large grains by annealing at 600°C /5,6/. In particular, grains of about $5\mu\text{m}$ in size can easily grow in films deposited at 450°C , whereas the maximum grain size which can be obtained in annealed, Si films prepared from SiH_4 is about $0.5\mu\text{m}$. It has been suggested /5,6/ that this difference could result from variations in the nucleation rate, N_g , which appear largely lower, and from variations in grains growth rate, V_g , which appear largely higher in the case of a deposit from Si_2H_6 . Nakazawa /6/ proposed that the variations of N_g with the deposition temperature in Si_2H_6 deposits is related to the influence of the temperature both on the deposition rate and on the surface migration. Indeed, he noticed from Raman observations that, the lower the structural disorder is, the higher the nucleation rate is. In turn, the structural disorder increases when deposition rate increases and/or when surface migration decreases (when increasing pressure or decreasing temperature).

The results obtained by numerical simulation and presented in the previous section suggest another explanation. Our opinion is that the important differences between the grain sizes for films obtained starting for silane or disilane must be linked to differences in the deposition mechanisms, the former involving an important contribution of silane and the latter of silylene.

Moreover, and for disilane only, now, table 4 demonstrates that there exists a very strong correlation between silylene concentration in the gas phase (in the center of the interwafer space) and the nucleation rate N_g .

In more detail, our idea is that silane is a less reactive species than silylene and that, when depositing silicon, it leaves more hydrogen in the solid film (Si-H radicals). In turn, during annealing at 600°C, these silicon-hydrogen bounds are broken, leaving free space for the crystal to relax and reorganize ; the more Si-H radicals there are in the film, the more nucleation sites appear and the smaller the resulting grains are.

Td (°C)	gas source	P (torr)	Vd (Å/min)	N_g (cm ⁻³ s ⁻¹)	$\gamma(\text{SiH}_2)$
520	SiH ₄	0,3	8	3 10 ⁹	
555	SiH ₄	0,3	28,5	2 10 ⁹	
450	Si ₂ H ₆	0,2	11,8	1 10 ⁸	2 10 ⁻⁶
520	Si ₂ H ₆	0,2	83,2	5 10 ⁹	4 10 ⁻⁶
555	Si ₂ H ₆	0,2	200-300	> 1 10 ¹⁰	1,2 10 ⁻⁴
555	Si ₂ H ₆	0,12	40,6	5 10 ⁸	7 10 ⁻⁵
555	Si ₂ H ₆	0,075	23,8	< 2 10 ⁵	4 10 ⁻⁵

Table 4 : nucleation rate induced by a 600°C anneal, following depositions in varied conditions

5. Comments

5.1 Comparison between the experimental results and the modeling predictions

The average growth rates experimentally obtained (table 1) and the growth rate distribution calculated by the two dimensional model (fig. 3, 4 and 5) are in good agreement for every temperature and pressure. The selected system for the chemical reactions mechanisms gas phase and solid surfaces seem to be acceptable, and allow us a good representation of the experimental reality.

5.2 Comparison between the silicon depositions mechanisms from silane and disilane

With the same chemical reactions system for the gaseous phase, the two different cases of silicon deposition from silane and disilane can be well represented. The important differences noted between these two cases are : high growth rate and important radial heterogeneities when disilane is used, which can be explained by the change in the main source of silicon deposition. For a pure silane gaseous phase, more than 90 % of the silicon growth rate is due to silane, but when disilane is used as a gaseous source more than 90 % of the silicon growth rate is due to silylene, product of disilane pyrolysis.

5.3 Structural analysis

The analysis of the nucleation rate values that have been measured, (table 4), indicates that the hypothesis of Nakazawa /6/ does not account for the difference between SiH₄ and Si₂H₆, particularly at Td=520 or 555°C, where N_g is of the same order with very different deposition rates. It can neither explain that N_g decreases drastically with the pressure of deposition in the cases Si₂H₆. Indeed, if the nucleation rate decreases when the structural disorder increases, a decrease of pressure and of deposition rate increases the nucleation rate. In fact, we observed the opposite behaviour, with the deposit at 0.075 Torr which does not show any nucleation after 240h of annealing at 600°C (the maximum value of 2.10⁵ cm⁻³.s⁻¹ means that we did not see any nucleis on a surface of 400µm²).

In the present work, nucleation rate values have been measured by direct counts on TEM photographs. For example, a few results in plane views of films annealed during 5 h, in nitrogen, at 600°C are presented on figure 5. For comparison, a few similar results, corresponding to films prepared from SiH₄, at a pressure of 0.3 torr and at temperature of 520 or 555°C are also presented, showing clearly a smaller grain size. Table 4 summarizes the deposition and nucleation rate values, roughly estimated from observations at different times of annealing.

6. Conclusion

To conclude, the first few results presented in this paper seem encouraging. From a practical point of view, the possibility to decrease the deposition temperature by approximately a hundred degrees seems attractive for several important industrial applications (solar panels, flat TV screens, etc...). The drastic change in structural properties that has been noticed seems also promising.

From a more theoretical point of view, the development of a precise two dimensional model appears interesting for the practising engineers which can reduce the number of experiments necessary to design a new equipment. It opens, also, interesting new ideas to analyze the reasons for the changes in structural properties.

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Figure 5 : TEM observations of Si films after annealing at 600°C, 5h in N₂