Deposition of Thick Layers, in a New CVD Reactor

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Abstract. This paper presents a new kind of equipment called the annular reactor, which has been designed to treat a great number of substrates with a particularly good uniformity of thickness of deposits on the batch. Furthermore, a small scale pilot plant of this apparatus, called the sector reactor, has been built. It constitutes a very convenient laboratory piece of equipment, particularly useful to perform, at low cost, the unavoidable experimental part of the development of any new application. Theoretical and experimental results obtained with these reactors are presented and compared to those obtained when using tubular reactors. First tests in order to produce cheap thick layers are also reported.

1. INTRODUCTION

In the last two decades, the continuously increasing level of integration of microelectronic circuits has drawn attention of researchers towards thinner and thinner silicon layers and, hence, towards relatively slow deposition procedures, so as to keep a convenient control on thickness.

However, other fields of application like, for example, photovoltaics need thicker layers, one or several microns in thickness. In these cases, the usual procedures and equipments no longer offer convenient results, and it is necessary to develop new technologies and operating conditions.

This paper is devoted to the analysis of a new kind of CVD reactor, the so called annular reactor, and to the search of conditions of use of this equipment producing high enough deposition rates. The final objective is to obtain thick layers at a relatively low cost, which means by rapid treatment of a great number of large wafers, with a convenient thickness uniformity as well on a single substrate as on the batch; for the analysis presented here, the wafers will be 4" wafers, but this size will be increased in the future. It can be added that the theoretical developments, equipments and methods presented here would remain valid if the substrates became square or rectangular flat surfaces, which may be the case for photovoltaic applications.

2. EXPERIMENTAL EQUIPMENT

2.1 The annular reactor

The annular reactor is schematically presented on figure 1. It is a vertical apparatus in which wafers are displayed on an horizontal circular quartz support. The gas inlet is at the top of the reactor and the gas outlet at its bottom. Gas flows parallel to the wafers and each gas element meets only one single surface in its travel from the entrance to the exit; as a consequence each wafer receives an identical treatment, which induces a perfect uniformity on the batch of substrates.

The reactor which has been used in this work is constituted by two coaxial vertical quartz tubes, 0.34 and 0.07 m in diameters and 2 m in height. Heating is provided by six electrical resistances, three

situated inside the inner tube and three outside the external tube. This reactor can treat 90 circular 4" wafers or 90 rectangular flat plates, organized either radially or parallel two by two, on a circular support.

This annular reactor is a large equipment, long and expensive to operate. As a consequence, a small scale pilot plant of this reactor has been designed and built, which constitutes a very convenient equipment to perform representative experiments, at a far lower cost than with the full scale equipment. This small scale pilot equipment has been called the sector reactor.

2.2 The sector reactor

The sector reactor has been made in steel (UL 340). It has a trapezoidal section, 49 mm in long base, 19 mm in short base and 145 mm in altitude. Its height is 1 m. Heating is provided by a three independent zones electrical furnace. It treats only two substrates. This apparatus is schematically represented on figure 2.

Figure 1 The annular reactor

Figure 2 The sector reactor

3. MODELING

First of all, it is necessary to describe briefly the chemical phenomena involved, as well in the gas phase as on solid surfaces, before introducing the general principles used to develop a convenient model.

3.1 Chemistry

Homogeneous reactions

At high temperature, pyrolysis of silane leads to silylene (SiH_2), disilane (Si_2H_6) and higher order silanes. In this study, only the first two reactions have been considered [1] :

The reaction rate equations and constants used throughout this work have been those proposed by Fayolle [2].

Heterogeneous reactions

The homogeneous reactions produce three sources of silicon which are all able to deposit on surfaces. The corresponding global chemical equations are :

The equation used to represent the growth rate from silane has been established by Wilke [3].

It has been supposed that the growth rate from disilane can be neglected [1].

Finally, it has been considered that the growth rate from silylene is first order in silylene and the corresponding rate has been calculated, considering that the reactive sticking coefficient of silylene on surfaces is equal to unity [4].

The general hypothesis selected to build the model used in this work has been to treat separately stable species (SiH_4 , Si_2H_6 and H_2), and radicals, so as to reduce computing times. As a consequence, a 2x1 D piston diffusion type model has been developed; only some boundary conditions must be changed when moving from the annular to the sector equipment.

3.2 Stable species

Concentrations of stable species are supposed uniform on any cross section of the reactor; they depend only of the coordinate value in the flow direction [5]. The continuity equation can then be written:

$$-D \frac{d^2 C}{dz^2} + V_z \frac{dC}{dz} = R_v + R_s S^* \quad (\text{E1})$$

with a V_z component depending on chemical conversion. R_v is the rate of production due to homogeneous reactions and R_s that due to heterogeneous reactions; S^* is a specific surface, calculated per unit area of cross section.

The boundary conditions selected have been :

$$\text{-Entrance of the reactor: } -D \frac{dC}{dz} + V_z C = V_z^0 C^0 \quad (\text{E2})$$

$$\text{-Exit: } \frac{d^2 C}{dz^2} = 0 \quad (\text{E3})$$

3.3 Radical species

For these very reactive species, only transversal variations have been taken into account[5]. With no motion in this direction, the continuity equation can be written :

$$-D \frac{d^2 C}{dx^2} = R_v \quad (\text{E4})$$

The boundary conditions associated with this equation depend on the type of reactor considered.

Annular reactor

The case treated has been that of two parallel wafers. Considering only half of the volume between the two wafers, this results in the calculation domain which is schematically presented on figure 3. The corresponding boundary conditions are :

$$\text{-on the substrate: } -D \frac{dC}{dx} = R_s \quad (\text{E5})$$

$$\text{-on the axis of symmetry: } \frac{dC}{dx} = 0 \quad (\text{E6})$$

Figure 3 Calculation domain for the annular reactor.

Figure 4 Calculation domain for the sector reactor.

Sector reactor

The calculation domain is now limited by an axis of symmetry and by a solid surface representing the lateral wall of the reactor, as indicated on figure 4. The corresponding boundary condition on this lateral surface is similar to that used on the substrate, ie $-D \frac{dC}{dx} = R_s$.

4. RESULTS

A small number of typical results will now be presented and briefly commented.

4.1 Experimental comparison between annular, sector and tubular reactors.

A general comparison has been made at 600°C and 0.3 torr. The Silane flow rate amounted to 200 sccm for the tubular and annular reactors and 6.7 sccm for the sector reactor, in the ratio of the cross section areas.

Figure 5 presents the variations of deposition rate as a function of radial position on a wafer. These results demonstrate, first, that the uniformity in thickness on a wafer is as convenient for deposits made in the new equipment than for those corresponding to the tubular reactor. Then, they clearly demonstrate that deposition phenomena are quite perfectly identical in the annular and sector reactors, but that the common rate for these equipments is between 20 and 30% lower than in a tubular reactor.

Figure 5 Experimental comparison between the annular, sector, and tubular reactors.

It can then be concluded that, at least in the case of deposition of silicon from silane, the sector reactor provides results perfectly representative of the annular reactor and so constitutes a very convenient small scale pilot equipment. As a consequence, in the following, only the sector reactor, which is smaller, easier and cheaper to operate, will be systematically used.

We will now enter a more detailed comparison of the sector and tubular reactors so as to get more insight in the differences of operation and of results between these two equipments.

4.2 Some characteristic modeling results

The tubular reactor has been modeled using a classical software, presented in detail elsewhere [6].

Figure 6 presents the deposition rate variations with axial position in a tubular reactor for the case of a batch of 60 wafers. It is necessary to observe that the deposition rate decreases from the first to the last wafer, from an initial value of 96 Å/min to roughly 89 Å/min; let us recall that these variations constitute a serious limitation of the tubular equipment. The experimental value presented in figure 5, which had been measured on the 10th wafer in the batch, corresponds to a theoretical value of 95 Å/min; model and experiment are then in close agreement.

Figure 6. Calculated growth rate for the tubular reactor.

Figures 7 and 8 present the longitudinal variations of the calculated deposition rate in the sector reactor, respectively on the lateral walls and on the wafer. Again in that case, theoretical calculations are in convenient agreement with experimental data.

Figure 7 Longitudinal variation of deposition on the wall of the sector reactor.

Figure 8 Growth rate predictions for the sector reactor.

Without entering in a detailed discussion, the concentration profiles presented on figures 9 and 10 demonstrate that the two reactors behave in completely different ways, the tubular reactor being much more of the piston type than the sector one. Indeed, on figure 9, concentration regularly decreases in the axial direction. On the contrary, figure 10 suggests that silane (or hydrogen) concentration varies rapidly at the entrance then remains quite perfectly constant all along the equipment; the sector reactor appears like a perfectly mixed equipment.

Figure 9. Calculated molar fraction in the tubular reactor.

Figure 10 Calculated molar fraction in the sector reactor.

Probably due to the strong influence of deposition on parasitic surfaces, as well in the annular as in the sector reactor, silane concentration at the exit appears much less important in these equipments than in the tubular reactor, which results in lower deposition rates.

At that point in the analysis of the behaviour of sector and annular reactors, it has been decided to try to limit the importance of parasitic surfaces and, hence, of silane consumption by designing convenient entrance or exit zones volume reducers.

4.3 Technological improvement of the sector reactor : decrease of dead zones and parasitic deposition surfaces.

Figure 11 Reducer of dead zone in the sector reactor.

As schematically presented by figure 11, dead volumes reducers are metallic pieces introduced in the upper and lower zones of the reactor so as to reduce their volumes. They are in the shape of sectors, with convenient heights. Gases are fed in the central active part by tubes going through these reducers.

So as to treat a case corresponding to unfavourable conditions, these reducers have been tested at relatively high temperature, ie, $T = 635^{\circ}\text{C}$; $P = 0,24 \text{ Torr}$; $Q = 14 \text{ sccm}$.

The mean deposition rate, which was equal to 107 Å/min without reducers, increased markedly, up to 143 Å/min, as a consequence of the reducers use, this last value being quite equal to that obtained in tubular reactors.

After this first step of technological analysis and improvement of the sector reactor, a second part of the analysis has been devoted to the elaboration of relatively thick layers.

4.4 Thick layers elaboration

Of course, elaboration of thick layers asks for high deposition rates so as to limit the operation duration and the corresponding costs. These high deposition rates can be obtained by increasing temperature.

Two particular experimental results are presented on figure 12 and compared with model predictions.

Figure 12 Comparison between experimental and theoretical results for high growth rates in a sector reactor.

The first conclusion is that modeling provides theoretical results in convenient agreement with experiments.

The second observation is that deposition rate remains approximately constant all along the wafer height. This important result suggest that temperatures as high as 660°C, or even more, could be selected to organize mass productions, with deposition rates 2 to 4 times higher than in conventional operations in the microelectronic industries, provided the layers electronic properties are convenient.

4.5 Mechanical stress in deposits

Very often, important mechanical stresses develop in polycrystalline thick silicon layers, resulting in peeling off of the film. As a consequence, a classical stresses determination technic has been implemented, which involves curvature measurements before and after the removal of the silicon film; only a few experiments have yet been performed.

The first observation that must be made is that none of the thick deposits which have been realized in the sector reactor, up to 5 µm in thickness, has ever peeled off.

The second observation is that our first results demonstrate very reasonable stress values of the order of 1 to 4.10⁸ Pa.

5. CONCLUSION

This paper has very briefly summarized a large number of results on a new technology of reactor, able to produce relatively thick layers at low cost with a convenient uniformity.

The annular reactor has been designed to treat a great number of substrates. Moreover, a small scale pilot plant has been built. Experiences demonstrate a good adequation between the two reactors.

Simulation has led to a better understanding of the behaviour of these reactors, and has open on the suggestion of some technological improvements, which have been successfully tested. Finally, thick layers have been deposited.

Our to-day conclusion is that the annular reactor seems very promising for less expensive mass production of films on solid substrates; work is currently going in our laboratory, in several different directions such as the production of polycrystalline films for photovoltaic uses or the deposition of SIPOS layers.

List of symbols

C	molar concentration (mol/m^3)
D	diffusion coefficient (m^2/s)
S*	specific surface (m^2/m^3)
R _v	molar rate of homogeneous phase production (mol/m^3)
R _s	molar rate of heterogeneous production (mol/m^2)
V _z	velocity for z direction (m/s)
P	total pressure (Pa)
T	absolute temperature (K)
Q	total flow rate (sccm)
C ⁰	entrance molar concentration (mol/m^3)
V _z ⁰	entrance velocity for z direction (m/s)
z	axial direction
x	perpendicular direction

References

- [1] Duverneuil P., and Couderc J.P., *J. Electrochem. Soc.*, **139**, (1992), 296-304
- [2] Communal-Fayolle F., Duverneuil P., and Westmoreland P.R., to be published
- [3] Wilke T.E., Turner K.A., Takoudis C.G., *Chem. Eng. Sci.*, **41**, (1986), 643-650
- [4] Meyerson B.S., Scott B.A., and Tsui R., *Chemtronics*, **1**, (1986), 150-155
- [5] Bismo S., Doctorate Thesis, E.N.S.I.G.C, I.N.P.Toulouse, (1993)
- [6] Azzaro C., Doctorate Thesis, E.N.S.I.G.C, I.N.P.Toulouse, (1991)