MODELING OF LPCVD SILICON NITRIDE PROCESS

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Résumé - Une grande attention a été accordée par divers groupes de recherche et divers auteurs à la modélisation du procédé CVD sous basse pression. Notre modèle a été proposé en 1979 et 1980, puis amélioré et étendu plusieurs fois. La simulation repose sur des formules algébriques faciles à utiliser. Dans nos publications précédentes, *ce modèle a été utilisé avec succés pour le dépôt de silicium polycristallin*. Dans le présent article, il est utilisé dans le cas du dépôt de Si_3N_4. Les résultats théoriques sont en bon accord avec les résultats expérimentaux cités dans la littérature.

Abstract - Much attention has been paid to the modeling of LPCVD process by several research groups and authors. Our simulation model of LPCVD process was proposed in 1979 and 1980, and then improved and extended several times. Our simulation formulae are algebraic, so it is easy to be used. Our model was successfully used for the LPCVD Poly-Si process in our previous papers, and also for the LPCVD Si_3N_4 process in this paper. The theoretical results agree very well with experiments reported in literature.

1 INTRODUCTION

Chemical Vapor Deposition is a widely used process for growing thin films in large scale integrated circuit technology. At low pressure the deposition process becomes essential surface controlled which allows high packing densities of the wafer, see Fig. 1. Much attention has been paid to the modeling of LPCVD process by several research groups and authors. Our simulation model of LPCVD process was proposed in 1979-1980 [1,2], and then improved and extended several times during 1981-1988 [3-11]. As well known, it is most important for any theoretical model that the theoretical results must agree with the experimental ones. In 1986, a comparison with a good agreement was made by us [7] between our theoretical model and LPCVD Poly-Si experiments, reported mainly by van den Brekel,

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Claassen and Kuiper et al. [12-14]. In this paper we make a comparison between our model and LPCVD Si_3N_4 experiments reported by Roenigk & Jensen [15,16].
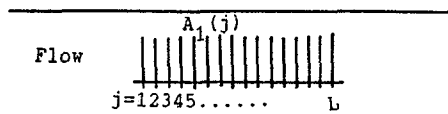

Fig 1. Theoretical model for LPCVD technology.

The kinetics of the reaction in Si_3N_4 process is more complex than that in Poly-Si process. If only the interaction between chlorosilane and NH_3 is under consideration, the calculated results will not agree with the experiments. It can be observed that the experimental deposition rate near the inlet end decreased very quickly along the flow direction and this phenomenon was more obvious at higher temperature. Besides the interaction between chlorosilane and NH_3, the pyrolysis of NH_3 is also one of main causes for this kind of the rate distribution. Based on the kinetics mentioned above, the agreement of our model with many LPCVD Si_3N_4 experiments were obtained. And some inaccuracy of LPCVD Si_3N_4 experimental data in literature were found.

2 DERIVATION OF THEORETICAL EXPRESSION

The main reactions in LPCVD Si_3N_4 process are:

1. Interaction between chlorosilane and NH_3
   $$SiH_2Cl_2 + 4/3\ NH_3 === 1/3\ Si_3N_4 + 2\ HCl + 2\ H_2$$

2. Pyrolysis of NH_3
   $$NH_3 === 1/2\ N_2 + 3/2\ H_2$$

The kinetic expressions of these reactions are:

$$r_1 = \frac{K_s.P_{SiH_2Cl_2}.P_{NH_3}}{1 + K_1.P_{SiH_2Cl_2} + K_2.P_{NH_3}}$$

and

$$r_2 = K_d.P_{NH3}.$$

According to the principles mentioned in our previous papers, the simulation formulae of LPCVD Si_3N_4 can be derived. If no inert gas was used during LPCVD Si_3N_4 reaction, that is, only two reactants, SiH_2Cl_2 and NH_3, were used and the ratio of NH_3 to SiH_2Cl_2 was equal to N, then initial concentrations in mole fraction were:

1. Initial concentration of SiH_2Cl_2, $X_1 = 1 / (N + 1)$,
2. Initial concentration of NH_3 was equal to $N / (N + 1)$.

The initial concentration of NH_3 could be divided into two parts:

1. Stoichiometric NH_3 part was equal to $4/3(N+1)$
2. Excess NH_3 part, $X_2 = (N-4/3)/(N+1)$

When the conversion percentage of SiH_2Cl_2 and the conversion percentage of excess NH_3 were represented by A_1 and A_2, respectively, then
increment of total gas volume,

$$V = 1 + (5/3).X_1.A_1 + X_2.A_2 ;$$

concentration of SiH_2Cl_2,

$$C_1 = X_1(1-A_1)/V ;$$

concentration of NH_3,

$$C_2 = [4X_1(1-A_1)/3 + X_2(1-A_2)]/V;$$

and the kinetic expressions could be written as

$$r_1 = K_s.C_1.C_2.P^2/(1 + K_1.C_1.P + K_2.C_2.P),$$

and

$$r_2 = K_4.C_2.P .$$

That is, at j wafer position

$$r_1(j) = K_s.C_1(j).C_2(j).P^2/(1 + K_1.C_1(j).P + K_2.C_2(j).P),$$

and

$$r_2(j) = K_4.C_2(j).P.$$

Then A_1, A_2 at j+l wafer position

$$A_1(j+1) = \sum_{i=0}^{j} r_1(i).S(i).w/F.X_1,$$

$$A_2(j+1) = \sum_{i=0}^{j} r_2(i).S(i)/F.X_2$$

Here, **w** was the ratio of solid deposit volume to SiH_2Cl_2 gas volume consumed. The pyrolysis of NH_3 is also considered as a surface process, so the consumption of NH_3 pyrolysis was proportional to $r_2(i).S(i)$, as shown in $A_2(j+l)$ equation. In this way two sets of recurrence formulae were obtained. The curves of $r_1(j)$ vs. the wafer position j were the theoretical distributions of growth rate.

3   DISCUSSIONS AND RESULTS

1.   A series of comparison between our simulation model and LPCVD Si_3N_4 experiments were made with very good agreement in tendency, as shown in Fig. 2 to 5. The dotted lines were theoretical ones, the square points were experimental data [17].
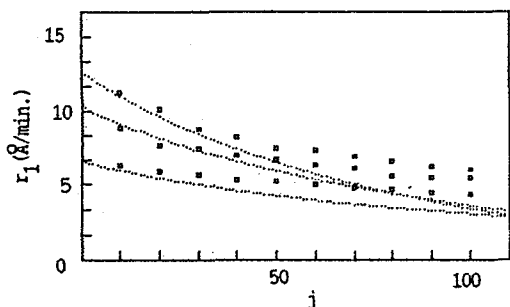

Fig. 2   Comparison between experiments ▪ and our
model..... Experimental parameters:#
800°C, SiH_2Cl_2 10 sccm, NH_3/SiH_2Cl_2
From up to down,   first set: N=15, P=0.95 torr
                    second set: N=10, P=0.65
torr
                    third set: N= 5, P=0.35 torr
Apparent kinetic parameters used in calculation:
$K_s = 3.8\times10^7$ A/min.torr^2 $K_1 = 2.0\times10^5$/torr
$K_2 = 1.8\times10^4$/torr Kd = .005 sccm/torr.cm^2
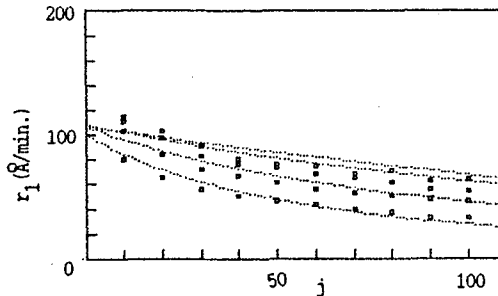
Fig. 3   Comparison between experiments ▪ and our
model.... Experimental parameters:#
800°C, P = 0.95 torr, SiH_2Cl_2 25 sccm,
$N=NH_3/SiH_2Cl_2$
From up to down,   first set: N=12,
                    second set N = 8
                    third set: N = 4
                    fourth set: N = 2
Apparent kinetic parameters used in calculation:
$K_s = 3.8\times10^7$ A/min.torr^2 $K_1 = 2.0\times10^5$/torr.cm^2
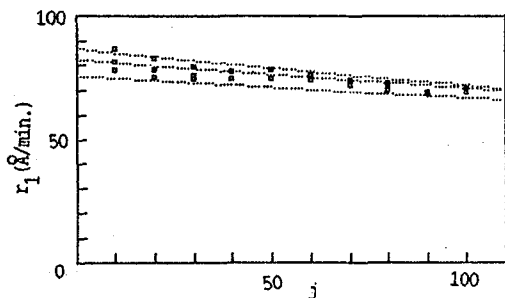$K_2 = 1.8\times10^3$/torr Kd = .005 sccm/torr.cm^2

Fig 4.   Comparison between experiments▪ and our
model... Experimental parameters:#
700°C, P = 0.55 torr, SiH_2Cl_2 25 sccm, N =
NH_3/SiH_2Cl_2
From up to down,   first set: N=2
                    second set: N=3
                    third set: N=4
Apparent kinetic parameters used in calculation:
$K_s = 2.54\times10^5$ A/min.torr^2 $K_1 = 4.0\times10^3$/torr
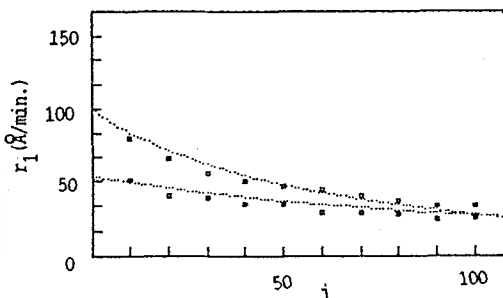$K_2 = 1.2\times10^3$/torr Kd = .0006 sccm/torr.cm^2

Fig 5.   Comparison between experiments ▪ and our
model.... Experimental parameters:#
P = 0.95 torr, SiH_2Cl_2 25 sccm, N = 2, N =
NH_3/SiH_2Cl_2
From up to down,   first set: T = 800°C
                    second set: T = 750°C
Apparent kinetic parameters used in calculation
for 750°C:
$K_s = 3.0\times10^6$ A/min.torr^2 $K_1 = 3.0\times10^4$/torr
$K_2 = 1.7\times10^3$/torr Kd = .002 sccm/torr.cm^2
For 800°C are the same as these in Fig. 3.

2.   The values of theoretical curves at right side (downstream of the gas flow) were mostly lower than those of experimental data (especially in Fig. 2). The area under the experimental growth rate distribution curve (such as solid lines in Fig. 2) was proportional to the total consumption of reactant SiH_2Cl_2, A_1^{total}. It was found A_1^{total} of the solid line in Fig. 2 was near one hundred percent (94.9%). If the consumption before the first wafer and after the last wafer was considered, the value of A_1^{total} would be more than one hundred percent. Of course, it was unreasonable. It must be due to the inaccuracy of experimental data. Maybe, it is due to the corrosion of massflow controller after some time of using chlorosilane. The inaccuracy of experimental data may also be one of the causes of that some adjustment of kinetic parameters were needed for different figures in our calculations.The adjustment of kinetic parameters [2] or even the change of reaction condition values [17] had also been reported.

3.   The consumption before the wafer region was considered in our calculation here as that of the first ten wafers, but not for the Fig. 2.

4.   Our simulation formulae of LPCVD Si_3N_4 are all algebraic, so they are easy to be used. And the agreement between our model and experiments was good.

Geometric parameters of reactor:

| Inside diameter of quartz tube: 130 mm | 110 Wafers loaded |
| Diameter of wafers: 76.2 mm | Wafer spacing   4.8 mm |

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