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# KINETICS OF THE CHEMICAL REACTION BETWEEN DICHLOROSILANE AND AMMONIA DURING SILICON NITRIDE FILM DEPOSITION

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The applicability of four mechanisms for describing the adsorption stage of the interaction between dichlorosilane and ammonia on a rigid surface during the deposition of silicon nitride films is analysed. It is established that a description of the experimental results in terms of the deposition rate is possible under the assumption of the reagents' adsorption on an energetically heterogeneous surface. When Freundlich's adsorption isotherm is applied, a kinetic equation is derived for determining the rate of the heterogeneous reaction between dichlorisilane and ammonia. The activation energy of the process is also determined. The equation derived also describes fairly well the data of other researchers.

## 1. INTRODUCTION

Thin films of silicon nitride find wide application in the production of electronic elements because of their high dielectric strength and chemical resistivity. They are used for passivation of integrated circuits, as elements in metal–nitride–oxide–semiconductor structures, as diffusion masks in planar technology and for a number of other purposes.

Most frequently, thin films are prepared by chemical vapour deposition. The $SiH_2Cl_2$–$NH_3$ system is widely used; its advantages are comprehensively described in the literature[1].

The basic technological aspects of silicon nitride film deposition are explained qualitatively in a number of experimental investigations[2]. However, papers devoted to the modelling of the process are quite few and insufficient for reliable predictions.

Thermodynamic analysis of the dichlorosilane–ammonia system at low pressure shows[3] that silicon nitride is obtained in a wide temperature range at compositions of the gas phase satisfying the condition Si: $(Si + N) < 0.6$. At the stoichiometric composition of the reacting gas mixture, the main equilibrium gas products are hydrogen and hydrogen chloride. The quantities of nitrogen and $SiCl_4$ are tenfold less. At a temperature of over 800 °C measurable quantities of $SiCl_3$ and $SiCl_2$ appear as well. In excess ammonia, however $(Si:(Si + N) < 0.3)$, only $H_2, N_2$ and HCl exist in the equilibrium gas phase. This means that under these conditions

the reaction

$$3SiH_2Cl_2(g) + 4NH_3(g) \rightarrow Si_3N_4(s) + 6HCl(g) + 6H_2(g) \tag{1}$$

is the basic chemical process and the excess of ammonia decomposes to nitrogen and hydrogen. Under dynamic conditions this decomposition is probably insignificant since Lin[4] has detected by mass spectrometry very small amounts of $N_2$ in a flow of ammonia through a silicon nitride deposition reactor at $800\,^\circ C$ and a pressure of 50–200 Torr.

Morosanu and Segal[5] have found that the deposition of $Si_3N_4$ at atmospheric pressure with low gas mixture flow rates and substantial excess of ammonia ($V_{NH_3}:V_{DCS} = 10^4-10^5$) in the temperature range 700–1100 $^\circ C$ is diffusion controlled. These conditions, however, are of no practical importance, and the description of the process obtained by a model of diffusion through a stagnant gas film[5] is of no real advantage.

It is suggested that at a residual pressure below 1 Torr and temperatures of 700–900 $^\circ C$ the process is kinetically controlled[2,6]. In order to use the models proposed for the determination of the deposited films' uniformity along the reactor[2,7], an equation is needed describing the reaction rate. According to Roenigk et al.[2] the kinetic relationship derived by them does not yield satisfactory results in modelling the complete process in the reactor.

## 2. THEORY

When the process of $Si_3N_4$ film growth is kinetically controlled, the equation describing the deposition rate can be based on the following models[8].

(a) Provided that the interaction between ammonia and dichlorosilane takes place after their adsorption on active centres of the same kind on the surface of the substrate, application of Langmuir's isotherm for multicomponent adsorption yields the following for the surface concentrations of the reactants:

$$\theta_{DCS} = \frac{k_{DCS}C_{DCS}}{1 + k_{DCS}C_{DCS} + k_{NH_3}C_{NH_3} + k_{H_2}C_{H_2} + k_{HCl}C_{HCl}} \tag{2}$$

$$\theta_{NH_3} = \frac{k_{NH_3}C_{NH_3}}{1 + k_{DCS}C_{DCS} + k_{NH_3}C_{NH_3} + k_{H_2}C_{H_2} + k_{HCl}C_{HCl}} \tag{3}$$

The industrial process conditions satisfy the inequality $1 + k_{DCS}C_{DCS} + k_{NH_3}C_{NH_3} \gg k_{H_2}C_{H_2} + k_{HCl}C_{HCl}$ and then

$$J = K_p\theta_{DCS}\theta_{NH_3} = \frac{K_p k_{DCS} k_{NH_3} C_{DCS} C_{NH_3}}{(1 + k_{DCS}C_{DCS} + k_{NH_3}C_{NH_3})^2} \tag{4}$$

It is more convenient to test the applicability of eqn. (4) as a description of experimental data if it is transformed into the form

$$\left(\frac{C_{DCS}C_{NH_3}}{J}\right)^{1/2} = \frac{1 + k_{DCS}C_{DCS} + k_{NH_3}C_{NH_3}}{(K_p k_{DCS} k_{NH_3})^{1/2}} \tag{5}$$

from which it is seen that

$$\left(\frac{C_{DCS}C_{NH_3}}{J}\right)^{1/2} = a + bC_{DCS} + cC_{NH_3} \tag{6}$$

(b) Provided that adsorption takes place on an exponentially heterogeneous surface, Freundlich's isotherm is used. The surface concentrations of the reactants in this case will be power functions of their concentrations in the gas mixture and therefore

$$J = K_p\theta_{DCS}\theta_{NH_3} = K'C_{DCS}^b C_{NH_3}^c \tag{7}$$

The above equation is linearized by taking the logarithm:

$$\lg J = a + b \lg C_{DCS} + c \lg C_{NH_3} \tag{8}$$

(c) If the interaction between NH$_3$ and SiH$_2$Cl$_2$ takes place after adsorption on active centres of different types, the process rate can be expressed using Langmuir's adsorption isotherm:

$$J = K_p\theta_{DCS}\theta_{NH_3} = K_p\frac{k_{DCS}C_{DCS}}{1 + k_{DCS}C_{DCS}}\frac{k_{NH_3}C_{NH_3}}{1 + k_{NH_3}C_{NH_3}} \tag{9}$$

Equation (9) can be rewritten as

$$\frac{C_{DCS}C_{NH_3}}{J} = a + bC_{DCS} + cC_{NH_3} + dC_{DCS}C_{NH_3} \tag{10}$$

which is more convenient for experimental data processing.

(d) Provided that the process takes place as an interaction between adsorbed NH$_3$ molecules and SiH$_2$Cl$_2$ molecules from the gas phase (Rideal and Ely mechanism)

$$J = K_p\theta_{NH_3}C_{DCS} = \frac{K_p k_{NH_3}C_{NH_3}C_{DCS}}{1 + k_{DCS}C_{DCS} + k_{NH_3}C_{NH_3}} \tag{11}$$

Linearization of eqn. (11) results in the expression

$$\frac{C_{DCS}C_{NH_3}}{J} = a + bC_{DCS} + cC_{NH_3} \tag{12}$$

It is easy to show that an equation analogous to eqn. (12) will be obtained if interaction between adsorbed SiH$_2$Cl$_2$ molecules and NH$_3$ molecules from the gas phase is assumed.

The applicability of the corresponding models can be estimated by the determination of the coefficients $a$, $b$, $c$ and $d$ and physical interpretation of the values obtained[8].

## 3. EXPERIMENTAL TECHNIQUE

The experiments were carried out in a horizontal flow reactor with resistive heating of the quartz tube at low pressure. The latter was measured with a vacuum

Pirani gauge with an accuracy of 0.001 Torr and was varied in the range 0.05–1 Torr. The test wafers with a diameter of 0.0762 m were placed in the beginning of the temperature plateau of the reactor where the temperature was maintained constant with an accuracy of 1 °C. The reactants dichlorosilane and ammonia had a purity of 99.998%. Their flow rates were measured with previously calibrated mass flow controllers. By measuring the temperature in the absence and in the presence of a gas flow it was established that the position chosen for the test wafer provides the necessary heating of the reactants. The films of $Si_3N_4$ were deposited on monocrystalline silicon wafers positioned vertically. The films' thicknesses were measured interferometrically with an error of less than 5%. Its variations along the radius of the wafer were within 5%, which confirms indirectly that the process is kinetically controlled. The structure of the films was investigated by electron diffraction.

## 4. RESULTS AND DISCUSSION

The rate of the heterogeneous catalytic process was calculated on the basis of the experimentally determined film deposition rate, using the relationship

$$J \, (\mathrm{kmol\, m^{-2}\, s^{-1}}) = \frac{1}{S} \frac{dN}{dt} = \frac{R_D \rho_{Si_3N_4}}{M_{Si_3N_4}} \tag{13}$$

In order to check the validity of the models, 20 experiments were carried out at a temperature of 770 °C and various molar concentrations of the reactants. The results were processed by the least-squares method[9] in order to determine the coefficients $a$, $b$, $c$ and $d$ in eqns. (6), (8), (10) and (12). It was found that the sets of algebraic equations obtained after differentiating the expressions

$$\sum_{i=1}^{20} (R_i - L_i)^2 \tag{14}$$

with respect to the coefficients $a$, $b$, $c$ and $d$, and making the derivatives equal to zero, have unique solutions. These solutions, estimated numerically[10], are presented in Table I.

The particular forms of eqns. (6), (8), (10) and (12) so obtained were subjected to regression analysis[11]. Two sets of five experiments, each set carried out under the same conditions, were used to evaluate the error variance. Then all coefficients were

TABLE I

COEFFICIENT VALUES FOR THE KINETIC SCHEMES INVESTIGATED ($F_{st}(0.05) \approx 2.6$)

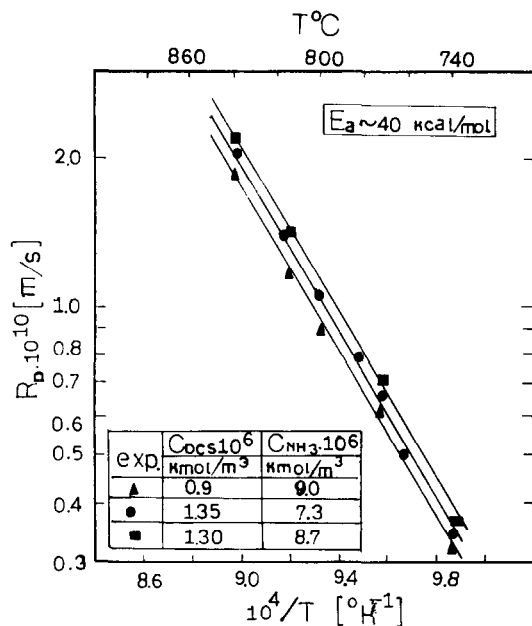| Equation | Coefficient values | | | | Error (%) | | Fisher number |
|---|---|---|---|---|---|---|---|
| | $a$ | $b$ | $c$ | $d$ | Mean | Maximum | |
| (6) | 0.029 | 21640 | 2926 | ... | 6.8 | 20 | 33 |
| (8) | −3.57 | 0.492 | 0.46 | ... | 2.3 | 5.7 | 1.8 |
| (10) | $3.25 \times 10^{-3}$ | −540 | −80 | $46 \times 10^7$ | 3.9 | 10 | 19 |
| (12) | $-1.07 \times 10^{-3}$ | 3111 | 437 | — | 6.2 | 22 | 54 |

Fig. 1. Temperature dependence of the growth rate.

tested using the $t$ criterion of Student and were found to be significant at the 0.05 level.

Since the negative coefficients $a$ in eqn. (12) and $b$ and $c$ in eqn (10) have no physical meaning, these two models must be discarded.

Moreover, eqns (6), (8), (10) and (12) were tested for lack of fit using the Fisher criterion. Only eqn. (8), based on Freundlich's adsorption isotherm, was found adequate. The lowest error of the exponential relation (7) makes it preferable (see Table I).

To describe the temperature relationship of the apparent rate constant, the following equation is recommended[12]:

$$K' = A \exp(-E_a/RT_s) \tag{15}$$

In order to determine $A$ and $E_a$, three series of experiments were carried out, in each one of which the molar concentrations of the reactants was kept constant. The experimental results are shown in Fig. 1. The most probable value of the apparent activation energy in the investigated temperature range (740–840 °C) amounts to 169.4 kJ mol$^{-1}$ (40 kcal mol$^{-1}$). Substitution of this value into the kinetic equation sought yields

$$J = 82\,300 \exp(-20\,375/T_s)C_{DCS}^{0.49}C_{NH_3}^{0.46} \tag{16}$$

Figures 2 and 3 illustrate the influence of the reactants' concentrations on the chemical reaction rate. The lines show the rates calculated from eqn. (16).

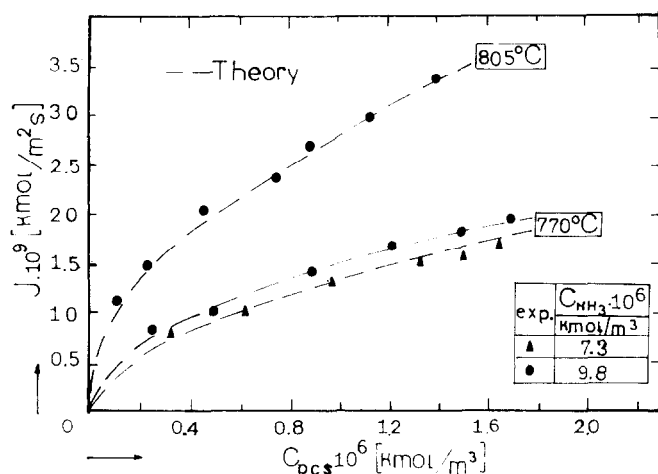Figure 2 also shows that the linear dependence of the growth rate on the

Fig. 2. Growth rate of $Si_3N_4$ vs. concentration of dichlorosilane in the gas mixture.
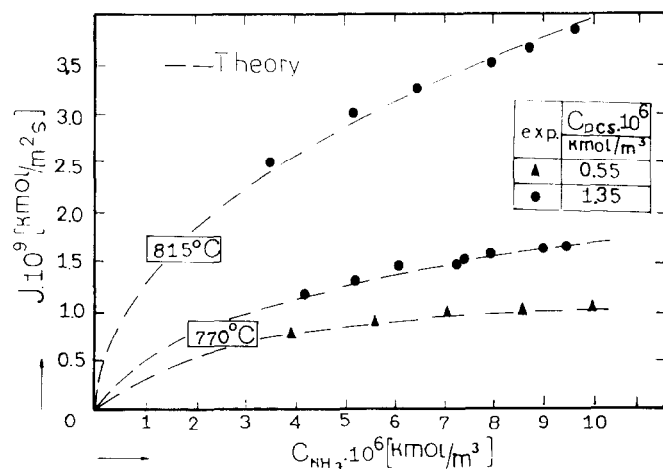


Fig. 3. Growth rate as a function of the concentration of ammonia.

concentration of dichlorosilane which follows from dissociative adsorption of the reagents[6] is not observed.

In Fig. 4 all our experimental data, as well as those of Roenigk et al.[2], are compared with the calculations of eqn. (16). It is seen that there is a good agreement. Our investigation, however, does not confirm the rate decrease above 800 °C observed by Roenigk et al.

Figure 5 displays electron diffraction patterns of $Si_3N_4$ films deposited at 770 and 840 °C. It is evident that under these conditions they have amorphous structure.

Equation (16) describes the process rate in its initial stages (far from its
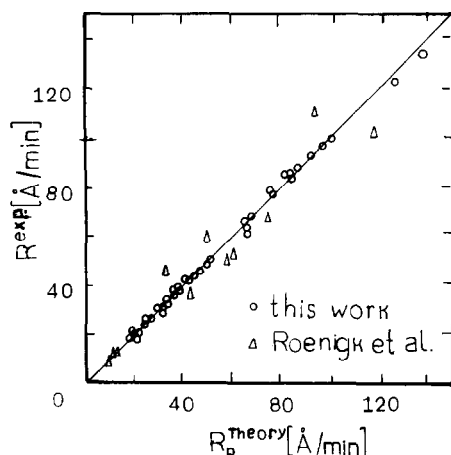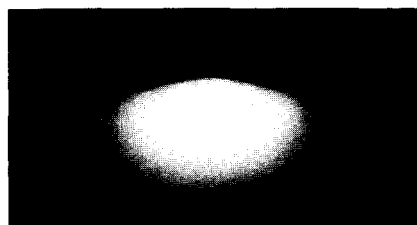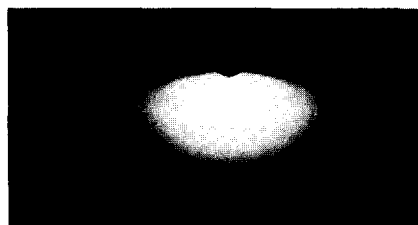
Fig. 4. Comparison between the values of the growth rate obtained experimentally and calculated from eqn. (16).



(a)                                              (b)

Fig. 5. Electron diffraction patterns of silicon nitride films: (a) $T_s = 770\,°C$; (b) $T_s = 840\,°C$.

equilibrium state) and in the excess of ammonia with respect to the stoichiometric quantity. The exhaustion of the reactants, which is accompanied by the production of hydrogen and hydrogen chloride, can result in a change in the process mechanism, including an increase in the part played by the diffusion stage in the total process resistance.

## 5. CONCLUSIONS

The process of silicon nitride film growth from $SiH_2Cl_2$ and $NH_3$ at low pressures (below 1 Torr) with high accuracy (errors below 6%) is described by a power kinetic equation, derived from the prerequisite that the interaction proceeds between reactant molecules adsorbed on an energetically heterogeneous surface.

The apparent orders of the reaction with respect to $SiH_2Cl_2$ and $NH_3$ are approximately identical and equal to 0.5.

The temperature dependence of the apparent rate constant in the range 740–840 °C follows the Arrhenius equation at an activation energy 169.4 kJ mol⁻¹.

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## APPENDIX A: NOMENCLATURE

$a$          coefficient in eqns. (6), (8), (10) and (12)
$A$          pre-exponential factor (eqn. (15))
$b$          coefficient in eqns. (6), (8), (10) and (12)
$c$          coefficient in eqns. (6), (8), (10) and (12)
$C_i$        molar concentration of the $i$th component in the gas phase ($kmol\ m^{-3}$)
$d$          coefficient in eqn. (10)
$E_a$        apparent activation energy of the process ($J\ mol^{-1}$)
$F$          Fisher criterion
$J$          rate of the heterogeneous catalytic chemical reaction ($kmol\ m^{-2}\ s^{-1}$)
$k_i$        equilibrium adsorption constant of the $i$th component (($kmol\ m^{-3})^{-1}$)
$K_p$        rate constant of the heterogeneous catalytic process ($kmol\ m^{-2}\ s^{-1}$)
$K'$         apparent rate constant (eqns. (7) and (15))
$L_i$        values of the expressions in the left-hand sides of eqns. (6), (8), (10) and (12) for the corresponding experiments
$M$          relative molecular mass ($M_{Si_3N_4} = 140.3\ kg\ kmol^{-1}$)
$R_D$        growth rate of the film ($m\ s^{-1}$)
$R_i$        values of the expressions in the right-hand sides of eqns. (6), (8), (10) and (12) for the corresponding experiments
$S$          area of the catalyst ($m^2$)
$t$          duration of the deposition process (s)
$T_s$        temperature of deposition (K)
$\theta_i$   dimensionless surface concentration of the $i$th component
$\rho$       film density ($\rho_{Si_3N_4} = 3180\ kg\ m^{-3}$)