REFERENCES

- 1. R. K. Ulrich, D. Yi, W. D. Brown, and S. S. Ang, Corros. Sci., 33, 403 (1992).
- 2. A. K. Sinha, H. J. Levinstein, T. E. Smith, G. Quintana, and S. E. Haszko, *This Journal*, **125**, 601 (1978).
- T. J. Cotler and J. Chapple-Sokol, *ibid.*, **140**, 2071 (1993).
 T. J. Cotler and J. Chapple-Sokol, *ibid.*, **140**, 2071 (1993).
 W. A. P. Claassen, W. G. J. N. Valkenburg, F. H. P. M. Habraken, and Y. Tamminga, *ibid.*, **130**, 2419 (1983).
 J. Kanicki and P. Wagner, in *Silicon Nitride and Silicon Diamida Thin Insulating Films*, V. K. Kappen and K. T.
- Dioxide Thin Insulating Films, V. K. Kapoor and K. T.

Hankins, Editors, PV 87-10, p. 261, The Electrochemical Society Proceedings Series, Pennington, NJ (1988).

- 6. R. Chow, W. A. Lanford, W. Ke-Ming, and R. S. Rosler, J. Appl. Phys., 53, 5630 (1982).
- 7. R. E. Rocheleau, Z. Zhang, D. W. Niles, and A. Mason, J. Appl. Phys., 72, 282 (1992).
- 8. R. E. Rocheleau and Z. Zhang, Thin Solid Films, 220, 73 (1992).
- 9. W. A. Lanford and M. J. Rand, J. Appl. Phys., 58, 1248 (1985).

Kinetics of SiO₂ Deposition from Tetraethylorthosilicate

E. A. Haupfear,^a E. C. Olson, and L. D. Schmidt

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

ABSTRACT

The kinetics of the decomposition of tetraethylorthosilicate (TEOS) vapor to form solid SiO₂ in a well-mixed flow reactor at feed pressures from 0.001 to 0.1 Torr have been studied by monitoring reaction rates with a differentially pumped mass spectrometer to determine reactant and product partial pressures. A resistively heated molybdenum foil was used as the deposition substrate to provide surface temperatures up to at least 1300°C. This technique provides rapid measurement $(\sim 10~{
m s})$ of gas composition in a well-mixed flow reactor so that reaction rates could be examined quantitatively. Changes in the partial pressures of TEOS and C_2H_4 were used to probe SiO₂ deposition kinetics. Over a wide range of temperatures and pressures, we observed +1.0 order with respect to TEOS partial pressure and an apparent activation energy of 20.9 ± 0.5 kcal/mol. The effect of C_2H_4 partial pressure on the reaction rate was investigated by including C_2H_4 in the reactor feed. Reaction rates were found to decrease as C_2H_4 partial pressure was increased, with the order with respect to C_2H_4 varying from 0 to -2.0 as C_2H_4 pressure was increased. Also, apparent activation energies were found to increase as C_2H_4 pressures were increased. A Lowrwight increase of a product in phibition decompleted the date were well. were increased. A Langmuir-Hinshelwood model incorporating product inhibition described the data very well, suggesting that the reaction product C_2H_4 adsorbs on the growing SiO₂ surface, blocking adsorption sites for TEOS. Values for model rate parameters were determined by fitting the LH model to both pressure and temperature dependences.

Dielectric films find wide application in integrated circuit technology. Thin films of dielectric material play roles both as passivating layers over devices and insulating layers between interconnect levels. As the area of large scale integration develops, demands on the processing of these dielectric films will continue to become more stringent.

SiO₂ is currently a common dielectric material used in integrated circuit manufacturing.¹ Thin films of SiO₂ can be manufactured to precise specifications using chemical vapor deposition (CVD). A commonly studied precursor for the low pressure chemical vapor deposition (LPCVD) of SiO₂ films is Si(OC₂H₅)₄, tetraethylorthosilicate (TEOS). An overall general deposition reaction is often written as

$$Si(OC_2H_5)_{4(g)} \rightarrow SiO_{2(s)} + 4C_2H_{4(g)} + 2H_2O_{(g)}$$
 [1]

In addition to ethylene and water vapor as products, several other reaction byproducts have been observed including ethanol and acetaldehyde.²

Several studies have focused on understanding the chemical mechanisms and reaction kinetics of the deposition process using TEOS. These studies range from spectroscopic and surface science investigations for identification of reaction intermediates and pathways³⁻⁶ to actual rate measurements for characterizing reaction kinetics.^{2,7,8} These studies have been performed in a variety of reactor geometries over a wide range of operating conditions. One broad classification of experimental deposition reactors is as either hot- or cold-wall, the former being closer to commercial operation but susceptible to homogeneous reactions and reactions on wall surfaces.

Both Desu² and Adams and Capio⁷ have observed in a hot-wall reactor SiO₂ growth rates that were fractional order in TEOS. Pressures used in both these studies were between 0.2 and 0.4 Torr total pressure with TEOS partial pressures between 0.01 and 1.0 Torr, where N_2 was used as

^a Present address: Union Carbide Corporation, South Charleston, WV 25303.

a diluent. Both researchers also observed apparent activation energies of 45 ± 2 kcal/mol. However, Desu observed a decrease in apparent activation energy to ~36 kcal/mol for temperatures greater than 720°C, which was attributed to the onset of mass transfer limitations. Measured growth rates in both studies were typically in the range of 2 to 200 nm/min. A rate expression of the following form was found to describe the kinetics in both of these hot-wall studies

Rate =
$$\frac{kP_{\text{TEOS}}^{0.5}}{1 + KP_{\text{TEOS}}^{0.5}}$$
 [2]

where k and K are rate parameters, and P_{TEOS} is the partial pressure of TEOS.

Different reaction kinetics have been observed in coldwall deposition studies of the TEOS/SiO₂ system. Specifically, Raupp et al.⁸ reported growth rates that were first order with respect to TEOS pressure with an apparent activation energy of 21.5 ± 3.8 kcal/mol. This observation was made for pure TEOS pressures in the range of 0.1-1.0 Torr. Nishimoto et al.⁹ also reported cold-wall kinetic data having an apparent activation energy of ${\sim}22$ kcal/mol. Raupp et al.⁸ proposed that the reported differences between the hot- and cold-wall kinetics are likely due to different ratedetermining steps. Specifically, these differences may be due to different gas-phase temperatures in the hot- and cold-wall reactors. As speculated by Raupp et al., the ratedetermining step in a hot-wall reactor may be a homogeneous process generating some deposition intermediate; in the cold-wall reactor, the rate-determining step is likely a heterogeneous surface reaction. These different ratedetermining processes may account for the observed order and activation energy differences between hot- and coldwall studies.

In describing the reaction mechanism of SiO₂ deposition, it has been proposed that gas-phase deposition products can readsorb on the growing film surface, thus blocking TEOS from surface adsorption sites leading to a rate inhibition.¹⁰ In the works of Raupp *et al.*⁸ and Cale *et al.*,¹¹ the validity of such a product-inhibiting mechanism was tested using a ballistic-transport model to predict stepcoverage profiles for films deposited on patterned substrates in a low-pressure cold-wall reactor. By assuming a heterogeneous mechanism involving product-inhibition, a rate equation of the following form was written and applied in this model to represent the surface kinetics for the simulation

$$Rate = \frac{k' P_{\text{TEOS}}}{1 + K' P_{\text{G}}}$$
[3]

where k' and K' are rate parameters, and $P_{\rm G}$ is the partial pressure of an arbitrary gas-phase product of the reaction. This expression also predicts first order in TEOS, consistent with cold-wall deposition kinetic observations.⁹ The above expression resulted in predicted step-coverage profiles on various substrate geometries that compared very well with profiles of films actually grown in a cold-wall reactor. Profile predictions assuming hot-wall kinetics using Eq. 2 were not as accurate.

As was shown in the ballistic simulations of film growth on features, product inhibition can have potentially significant effects on step-coverage uniformity. Specifically it is important in coating trench-like features where reaction products can accumulate to significant concentrations due to impeded mass transfer out of the trench feature. Therefore, an understanding both qualitatively and quantitatively of reaction kinetics, and specifically inhibition effects, is important to accurately predict optimal operating conditions for the engineering of precise feature coatings.

Although product inhibition in the TEOS/SiO₂ system has been speculated and tested through computer simulations, neither the direct quantification of inhibition kinetics nor the identification of specific inhibition species has been made experimentally. We report here kinetic studies of SiO₂ deposition from TEOS in a low-pressure cold-wall reactor aimed at further characterization of deposition kinetics, particularly product inhibition. The experimental approach involves measuring reaction rates by monitoring changes in the gas-phase composition in the experimental reactor. The kinetics were studied using both pure TEOS and TEOS/C₂H₄ mixtures as feeds.

An experimental approach similar to that reported in this paper has previously been applied successfully to the study of titanium carbide deposition from TiCl₄ and $C_3H_8^{-12}$ and to the study of boron deposition from the H₂ reduction of BBr₃. ¹³ For both these systems, reaction orders were observed that varied from positive to negative values as feed partial pressures changed. Also, for titanium carbide deposition, multiple steady states were observed both *vs.* TiCl₄ partial pressure and *vs.* surface temperature. This experimental approach is complementary to other techniques of studying chemical vapor deposition (CVD) kinetics such as those based on monitoring film thicknesses.

Experimental

The experimental apparatus used for growing silica films and measuring gas composition is similar to that described previously.^{12,13} The CVD chamber consists of a nominal 2 3/4 in. stainless steel six-way cross reactor operated at total pressures between 0.001 and 0.1 Torr pumped by a mechanical vacuum pump having a base pressure of $\sim 10^{-4}$ Torr. A liquid nitrogen trap was placed between the CVD chamber and the vacuum pump to reduce the reactor base pressure and to prevent the air-sensitive reactant TEOS from entering the pump. By adjusting the outlet valve between the CVD chamber and the liquid nitrogen trap, the pump-out rate of the reactor was controlled. Typical residence times in these studies were in the range of 2 to 10 s, depending upon the particular experimental conditions, with longer residence times being used when monitoring slower reaction rates to give detectable conversions. Residence time was also increased to obtain larger TEOS feed pressures in the reactor.

The total reactor pressure was monitored using a capacitance manometer, with the feed partial pressure of TEOS established by adjusting the vapor leak rate into the reactor using a needle valve. TEOS is a liquid at room temperature having a vapor pressure on the order of 1 Torr, and adequate reactor feed pressures were attained by simply maintaining the liquid TEOS source at ~25°C. Freeze-thaw cycles were frequently performed on the liquid TEOS source under vacuum using liquid nitrogen. These cycles removed any nitrogen that was dissolved in the liquid TEOS during storage. Also, the TEOS precursor was heated to degas any decomposition products that accumulated in the vessel. Typically, deposition experiments were performed using a pure TEOS feed, but the effect of ethylene on deposition rate was studied by leaking a known TEOS/ ethylene mixture into the reactor chamber. Ethylene was supplied from a regulated cylinder using a needle valve to adjust the ethylene leak rate into the reactor.

Strips of molybdenum foil were used as deposition substrates in these studies. Each substrate strip was cut approximately 4 mm wide and 2 cm long from a 25 µm thick molybdenum foil. Ends of the foil strip were spot welded to leads of electrical feedthroughs attached to the CVD chamber. The foil could be quickly heated or cooled by adjusting the dc current through the foil using a 20 A power supply. The high melting point of molybdenum (~2900 K) allowed use of high temperatures for cleaning the deposition surface prior to each deposition experiment. Surface temperatures were monitored by an optical pyrometer providing a relative precision of ±2 K for any temperature change. Calibration of the pyrometer for SiO₂ to determine absolute surface temperatures was performed using a Pt/Pt-13%Rh thermocouple spot welded to the molybdenum substrate. Absolute temperatures reported in this paper are believed to be accurate to within ± 40 K. In all data shown here we monitor growth rates of an already nucleated SiO₂ film. Thus, there is no effect of the nature of the substrate and its effect on growth, and results were always found to be reproducible functions of partial pressures and temperature only.

In running a deposition experiment, gases from the CVD reactor were continually leaked into an adjacent chamber which was differentially pumped by a turbomolecular pump with a base pressure of $\sim 10^{-8}$ Torr for residual gas analysis by a quadrupole mass spectrometer. The mass spectrometer was typically operated at $\sim 10^{-6}$ Torr. The mass spectrometer signals were frequently calibrated to correlate changes in mass spectrometer signal with changes in the CVD reactor partial pressures.

A typical experiment involved establishing a steadystate TEOS partial pressure with the substrate at room temperature. The substrate was then quickly heated to a final reaction temperature. Once a steady state was achieved (typically in 10 to 100 s), the changes in partial pressures (*i.e.*, mass spectrometer signal) were recorded, and either the surface temperature or a feed pressure was varied to obtain a new steady state. By writing a mass balance on any gas-phase species i and assuming ideal gas behavior, the changes in partial pressure between the various steady states were correlated with reaction rate using the equation

$$r_{\rm i} = \frac{V(P_{\rm i} - P_{\rm i}^{\rm o})}{\tau_{\rm i} A R T_{\rm g}}$$

$$\tag{4}$$

where r_i is the rate of generation in mol/area \cdot time of species i, V is the reactor volume, P_i is the steady-state partial pressure of species i at reaction conditions, P_i^o is the partial pressure of species i, A is the substrate surface area, R is the gas constant, and T_g is the gas temperature (~300 K). Because of cool reactor walls, low reactor pressures (*i.e.*, low heat transfer from the hot substrate to the gas) and high pumping speeds, the gas-phase temperature was maintained significantly less than the substrate temperature; this lower temperature and low partial pressures of reactants minimize the rate of homogeneous reactions rel-



Fig. 1. (a) Comparison of measured mass 28 (C₂H₄) increases with measured mass 193 (TEOS) decreases during deposition for 0.010 Torr TEOS feed at various values between 800 and 950°C. (b) Total pressure changes mass 28 increases at 0.010 Torr TEOS feed at various values between 800 and 1000°C. (c) Comparison of predicted film thicknesses to measured film thicknesses at 850 and 950°C at 0.040 Torr TEOS. (The solid line represents perfect agreement between predicted and measured thicknesses.) Figures (a), (b), and (c) all have the origin included as a data point to represent the nonreaction case at room temperature.

ative to that of heterogeneous reactions. Also, since the low reactor pressure results in low mixing times (<0.1 s), the reactor composition is well mixed and the surface reactions are not limited by mass transfer to the surface. Hence, rates based on Eq. 4 in this experiment were the surface reaction rates which are in general a function only of the reactor partial pressures and surface temperature. Because of the short time required to reach a steady state, measurements could be done repeatedly on a given substrate. All kinetic results presented here were reproduced on many individual molybdenum substrates.

Calibration

A typical deposition experiment was characterized by an increase in total reactor pressure. Also, major changes in the mass spectrum included a decrease in the mass 193 peak along with an increase in the mass 28 peak. The most intense peak in the TEOS (208 amu) mass spectrum is at mass 193 (*i.e.*, 208 – 15 amu for a -CH₃ group), so changes in this peak are believed to be solely due to TEOS depletion. Mass 28 peak increases are believed to be mostly due to C_2H_4 generation, which is consistent with other reports of C_2H_4 being a major deposition product in the TEOS/SiO₂ system.^{2.5} We also observed other reaction products including H_2 , H_2O , C_2H_5OH , and CH_3CHO as well as traces of C_3 species such as acetone and C_3H_8 .

Because of the 1:1 stoichiometric ratio of TEOS to SiO₂, unambiguous SiO₂ deposition rates can be determined from measured TEOS depletion rates if no other siliconcontaining byproducts are formed. Also, any peak changes that are found proportional to mass 193 peak changes can be used as a reaction rate monitor. Figure 1a compares the measured decreases in the mass 193 peak with the associated increases in the mass 28 peak intensity for SiO₂ deposition at 0.010 Torr TEOS for several surface temperatures between approximately 800 and 950°C. The origin is also included as a data point for the no-reaction condition at room temperature. As shown, the changes in Fig. 1a are linearly proportional to each other, suggesting that TEOS depletion rates are proportional to C_2H_4 generation rates. By (i) assuming that only C_2H_4 generation contributes significantly to mass 28 peak changes, (ii) correcting the peak changes for the species sensitivities in the mass spectrometer, and (iii) measuring the residence time of each individual species, a 5.7:1 ratio in C_2H_4 generation rate to TEOS depletion rate can be estimated. This ratio is approximately 40% (within a factor of two) higher than the maximum predicted ratio of 4:1. Uncertainty in sensitivity factors and residence times could easily account for this discrepancy. However, the data in Fig. 1a suggests that both mass 193 and mass 28 peak changes can be used as a monitor of rate, with uncertainties between each rate being within a factor of two. Also, measured total pressure changes were found to be proportional to mass spectrometer changes. Figure 1b shows total pressure changes vs. mass 28 peak changes. This data was at high conversions to produce measurable total pressure changes. Because of the results in Fig. 1a and b, changes in mass 28, mass 193, and total pressure were all used as a means of confirming and reproducing experimental results.

In CVD processing, film growth rates, of course, are of greater interest than the molar rates directly measured in these studies. However, according to the stoichiometric equation given as Eq. 1, the growth rate of SiO_2 films can be related to the molar reaction rate by

$$r_{\rm t} = \left(\frac{M_{\rm SiO_2}}{\rho_{\rm SiO_2}}\right) r_{\rm R}$$
 [5a]

where $r_{\rm t}$ is a growth rate in thickness/time, $r_{\rm R}$ is the overall reaction rate of Eq. 1 in mol/area \cdot time, $M_{\rm SiO_2}$ is the molecular weight of SiO₂ (60 amu), and $\rho_{\rm SiO_2}$ is the density of SiO₂ (2.3 g/cm³). The overall reaction rate, $r_{\rm R}$, can be determined from the C₂H₄ generation rate, $r_{\rm C_2H_4}$, by the relationship



Fig. 2. (a) Order plot of r_R (and r_l) vs. P_{TEOS} at 770°C (squares), 850°C (open circles), and 950°C (filled circles). The slopes of all lines are 1.0 corresponding to first order. (b) Arrhenius plot at various TEOS pressures of 0.04 Torr (open circles), 0.01 Torr (filled circles), and 0.005 Torr (squares). Lines are drawn corresponding to a 20.9 kcal/mol apparent activation energy.

$$r_{\rm R} = \frac{r_{\rm C_2H_4}}{4}$$
 [5b]

where the factor of 4 arises from the stoichiometric coefficient of C_2H_4 in Eq. 1. Thus, by determining $r_{C_2H_4}$ values from measured $P_{C_2H_4}$ changes using Eq. 4, film growth rates can be readily predicted from Eq. 5a and b. By assuming uniform growth rates, these predicted film growth rates can be multiplied by the respective growth times to predict film thicknesses. By comparing measured film thicknesses with film thicknesses predicted from measured $r_{C_2H_4}$ values using Eq. 5a and b the quantitative accuracy the experimental measurement of $r_{C_2H_4}$ can be evaluated.

Figure 1c compares predicted film thicknesses, as obtained from Eq. 5a, with actually measured film thicknesses at 850 and 950°C grown for 10 min at 0.040 Torr TEOS. The film thicknesses were measured by examining film/substrate cross sections using scanning electron microscopy (SEM); the high contrast between the SiO_2 film and the molybdenum substrate allowed for accurate film thickness measurement. The solid line in Fig. 1c is drawn with a slope of one representing perfect agreement between measured and calculated thicknesses. The error bars on the data are due to the parameter estimations that are involved in calculating a predicted film thickness. The measured and predicted thicknesses in Fig. 1c are in surprisingly good agreement considering the number of parameter estimations and the assumptions of constant and uniform growth rate. Besides confirming the quantitative accuracy of the rate measurement based on Eq. 4, this agreement also confirms that the rates measured in these experiments were surface reaction rates.

Film Quality

The emphasis of this work is on the reaction kinetics of SiO_2 film growth from TEOS. However, film characterization was periodically performed to ensure quality film growth throughout these studies. Deposited SiO_2 films appeared smooth with film growth being confirmed visually

by the presence of refractive fringes. These fringes were present near the end of the foil strips close to the contact points with the feedthrough leads. The fringes are due to a film thickness variation near the ends of the strip caused by a substrate temperature gradient at the feedthrough lead contacts. X-ray photoelectron spectroscopy (XPS) was also used for surface analysis to confirm proper film growth. XPS confirmed a 2 ± 0.1 :1 oxygen to silicon atomic ratio. Also, molybdenum was not detected within the sensitivity of the instrument [≤ 0.5 atom percent (a/o)], confirming that continuous silicon films were deposited on the substrate and that substrate species did not become incorporated in the growing film. The only other species detected was carbon which was present on the surface at an atomic concentration $\sim 5\%$. We believe that this carbon is due mostly to adsorbed TEOS or TEOS fragments remaining on the film surface at the time the substrate was removed from the reactor. This was confirmed by cleaning the surface by argon sputtering. After sputtering ~ 50 Å deep, carbon concentrations reduced to <0.6 a/o.

As previously mentioned, SEM was used to analyze film cross sections for measurement of film thicknesses. Examination of such cross sections confirmed a sharp interface between the substrate and the deposited film. Upon examining the surface morphology with SEM, film surfaces appeared featureless up to at least 10,000 times magnification, suggesting that deposited films were amorphous. The smoothness of the surface confirms that approximating the total surface area (A) as the geometric area of the substrate foil is valid for applying Eq. 4 for rate calculation.

Results

Pure TEOS feed.—Figure 2a shows the overall reaction rate $(r_{\rm R})$ and SiO₂ growth rate $(r_{\rm t}) vs$. TEOS partial pressure, $P_{\rm TEOS}$, for pure TEOS feed at the fixed temperatures of ~770, ~850, and ~950°C. Here, values of $r_{\rm R}$ are calculated from measured $P_{\rm C2H_4}$ changes using Eq. 4 and 5b, where species i in Eq. 4 is C₂H₄. Equation 5a is used to relate the $r_{\rm R}$ ordinate to the $r_{\rm t}$ ordinate in each figure. The lines drawn



Fig. 3. (a) Order plot of r_R (and r_l) vs. $P_{C_{2H_4}}$ at 900°C (open circles), 950°C (filled circles), and 1000°C (open squares). The curves through the data are actual model fits, with the line is drawn to -2.0 reaction order with respect to C_2H_4 . (b) Arrhenius plot at fixed TEOS pressure of 0.010 Torr and various C_2H_4 pressures (open circles, 0.005 Torr; filled squares, 0.010 Torr; open squares, 0.020 Torr; triangles, 0.050 Torr). The filled circles are data for pure TEOS feeds. The curves are actual model fits of Eq. 7 for n = 1 and m = 2.

through the data in Fig. 2a are all drawn with a slope of +1.0 on a log-log plot, suggesting that the reaction rates are all first order with respect to P_{TEOS} . Specifically, at 950°C, we observe a first-order rate dependence with respect to P_{TEOS} over at least two orders of magnitude in TEOS pressure.

Figure 2b is an Arrhenius plot of $r_{\rm R}$ and $r_{\rm t}$ vs. surface temperature ($T_{\rm s}$) at fixed pure TEOS feed pressures of 0.005, 0.010, and 0.040 Torr. The slopes of all lines in Fig. 2b correspond to a 20.9 kcal/mol apparent activation energy. This significant activation energy suggests that the rate is reaction limited, indicating that the observed first-order dependence in Fig. 2a is due to reaction kinetics rather than a flux limit. However, in preliminary studies we observed that at much higher surface temperatures (~1250°C) the onset of a flux limit may occur as indicated by an observed reduction in apparent activation energy.

The experimental results in Fig. 2 suggest that observed reaction rates can be adequately described by the following simple first-order rate expression having Arrhenius temperature dependence

$$r_{\rm R} = k_1 P_{\rm TEOS}$$

where

$$k_1 = k_{1o} \exp\left\{\frac{-E_1}{RT_s}\right\}$$

Here, k_{10} is a pre-exponential factor and E_1 is an effective activation energy. By fitting the above equation to the data in Fig. 2, an apparent activation energy of 20.9 ± 0.5 kcal/ mol and a preexponential factor of 1.7×10^{-3} mol/cm² · s · Torr (or 27,000 µm/min · Torr) are calculated. The lines drawn through the data are the actual predictions of the above first-order expression using these calculated parameters.

For a given temperature and pressure, the absolute SiO₂ growth rates on molybdenum we report are slightly higher than growth rates on silicon reported in most other studies. This comparison, however, is based on extrapolating our results to either higher pressures or lower temperatures using the relationship of Eq. 6. For example, Adams and Capio⁷ report in a hot-wall reactor growth rates of ~7 nm/ min at 0.030 Torr TEOS and 725°C, and ~80 nm/min at 800°C and 0.20 Torr TEOS. For these two sets of conditions, we extrapolate growth rates of 23 and 320 nm/min, respectively, which compare within approximately a factor of four with Adams and Capio. Other extrapolated results also compare within a factor of four with rates reported by Desu.²

Our cold-wall results of observed first order in P_{TEOS} and measured apparent activation energy of 20.9 kcal/mol is consistent with the cold-wall studies of Raupp *et al.*,⁸ which were measured at a higher pressure regime of 0.1 to 1.0 Torr TEOS. By considering the observations of both Raupp *et al.* and of the results reported in Fig. 2a, deposition rates have been confirmed to be first order in TEOS over the range of 0.004 to 1.0 Torr, over almost four orders of magnitude. However, upon extrapolating calculated growth rates to comparable pressures, we predict growth rates almost two orders of magnitude higher than growth rates Raupp *et al.* measured on silicon using ellipsometry.

 $TEOS + C_2H_4$ feed.—The effect of including C_2H_4 in the reactor feed is shown in Fig. 3a and b. Figure 3a shows the effect of $P_{C_2H_4}$ on $r_{\rm R}$ at a fixed $P_{\rm TEOS} = 0.01$ Torr and various fixed substrate temperatures. Specifically, at 950°C (solid circles), we observed that $r_{\rm R}$ decreases as $P_{C_2H_4}$ is increased.

[6]

Table I. Best-fit parameters for Eq. 7.

n 1	m	$k_2 (950^{\circ}\text{C}) (Torr^{-1})$ 34.5	Error ^a	(Torr ⁻¹)	E ₂ (kcal/mol) -20.3	Error ^b 0.780
	2					
$0.5 \\ 0.5 \\ 0.5 \\ 1 \\ 2 \\ 2 \\ 2 \\ 2$	1 2 3 1 3 1 2 3	$\begin{array}{r} 32.5\\ 8.51\\ 4.61\\ 145.3\\ 17.7\\ 2320\\ 404\\ 181\end{array}$	$\begin{array}{c} 9.67 \\ 5.61 \\ 4.05 \\ 2.67 \\ 0.513 \\ 1.70 \\ 8.50 \\ 13.1 \end{array}$	$5.91 \\ 0.659 \\ 0.263 \\ 0.203 \\ 0.00198 \\ 7.44 \times 10^{-6} \\ 2.01 \times 10^{-8} \\ 1.50 \times 10^{-9} \\ \end{array}$	$\begin{array}{r} -4.2 \\ -6.3 \\ -7.0 \\ -16.6 \\ -21.9 \\ -47.9 \\ -58.1 \\ -62.5 \end{array}$	$16.6 \\ 10.0 \\ 7.75 \\ 3.30 \\ 0.853 \\ 2.69 \\ 8.98 \\ 12.2$

^a Error based on fit to 950°C isothermal data in Fig. 3a.

^b Error based on fit to temperature dependence data in Fig. 3b.

As shown by the solid line in Fig. 3a, $r_{\rm R}$ has an order of -2 with respect to $P_{\rm C_2H_4}$ at ~ 0.1 Torr C_2H_4 . At lower $P_{\rm C_2H_4}$, the order with respect to $P_{\rm C_2H_4}$ reduces in magnitude, appearing to approach zeroth order. Also, data at 900 and 1000°C are included as open symbols, indicating similar behavior as observed at 950°C. The curves drawn through the data are actual model predictions which will be described.

The Arrhenius data in Fig. 3b specifically show the effect of varying temperature at various pressures of C_2H_4 at a fixed TEOS pressure of 0.010 Torr. C_2H_4 pressure is varied over an order of magnitude (0.005 to 0.05 Torr). As P_{C_2H4} is increased, there is an observed decrease in reaction rate consistent with Fig. 3a. For reference, rate data for pure 0.010 Torr TEOS is included in Fig. 3b as solid circles. Also, there is an observed increase in apparent activation energy as C_2H_4 is added. Specifically, an activation energy of 37.5 kcal/mol is measured in 0.05 Torr C_2H_4 as compared with 20.9 kcal/mol observed for pure TEOS feed. These experiments were easily reproduced by monitoring both C_2H_4 generation and TEOS depletion rates.

Rate expression.—The results in Fig. 3a and b suggest that a rate expression having the following general functional form may fit the experimental results

$$r_{\rm R} = \frac{k_1 P_{\rm TEOS}}{(1 + k_2 P_{\rm C_2H4}^n)^m}$$
[7]

where *n* and *m* are arbitrary exponents, each ≥ 0 . By including the $k_2 P_{C_2E_4}^n$ term in the denominator, reductions in reaction rate as $P_{C_2E_4}$ is increased can be predicted. Equation 7 predicts zeroth order with respect to $P_{C_2E_4}$ at $k_2 P_{C_2E_4}^n <<1$ varying to $-m \times n$ order at $k_2 P_{C_2E_4}^n >>1$. Based on the data in Fig. 3a, orders ≤ -2 (*i.e.*, $m \times n \geq 2$) must be predicted at large $P_{C_2E_4}$ values. By considering various combinations of values for *n* and *m*, several versions of Eq. 7 can be generated and tested by fitting to the experimental data. For this work we considered all combinations of *n* and *m* for the respective values of n = 1/2, 1, 2 and m = 1, 2, 3, giving nine total combinations. Combinations giving $m \times n < 2$ are included since these combinations give an expression similar in form to the previously examined inhibition expression (Eq. 3).

The constants k_1 and k_2 in Eq. 7 are temperature dependent assuming the Arrhenius form of

$$k_{\mathrm{i}} = k_{\mathrm{i0}} \exp\left\{\frac{-E_{\mathrm{i}}}{RT_{\mathrm{s}}}
ight\}$$
 for $i = 1, 2$

Note that Eq. 7 reduces to Eq. 6 at the limit of $P_{C_2H_4} = 0$. Therefore, the values for k_{10} and E_1 determined from fitting Eq. 6 to the data in Fig. 2 will be assumed, leaving only k_{20} and E_2 remaining unknown in Eq. 7. Different "best-fit" values for k_{20} and E_2 were calculated for each *n*-*m* combination considering in Eq. 7, and these values are summarized in Table I.

In determining k_{2o} and E_2 values, each version of Eq. 7 was initially fit to the 950°C $P_{C_{2H_4}}$ -dependence data (solid circles) in Fig. 3a to determine a k_2 value for each *n*-*m* combination. These fits were essentially single-parameter fits giving "best-fit" k_2 ($T_s = 950$ °C) values which are summarized in Table I. Values for k_{20} and E_2 were then determined by fitting Eq. 7 to the temperature dependence data in Fig. 3b. For each *n*-*m* combination, only a singleparameter fit of E_2 was needed since k_{20} can be written in terms of both E_2 and the predetermined value of k_2 at 950°C.

The fitting procedure consisted of using an optimization code to search for parameters that minimized the error between the experimental and predicted values. The error is expressed as

$$\mathbf{Error} = \sum_{j=1}^{N} \left\{ \ln \left(\frac{r_{j}}{r_{j}^{o}} \right) \right\}^{2}$$
[8]

where r_j° is an experimental measurement of the rate at a particular experimental condition j, r_j is the model prediction of the rate at identical conditions as r_j° , and N is the total number of experimental data points being fit. Since only single-parameter fits were needed, fitting was straight-forward. The minimized error for each model fit is listed in Table I for both the isothermal fit to Fig. 3a and the temperature dependence fit of Fig. 3b.

The best overall fit was found for n = 1 and m = 2. The curves drawn through the data in Fig. 3a and b are the actual model predictions based on Eq. 7 using the parameter values highlighted in Table I. The curve fits are very good considering the few number of parameters involved in predicting both temperature dependence and the pressure dependences of both TEOS and C_2H_4 . Particularly, the model accurately predicts the rate reduction with respect to C_2H_4 along with the associated activation energy increase.

Kinetic Model

In developing a kinetic model, we will assume, by experimental design, that homogeneous reactions play a negligible role relative to heterogeneous reactions in determining the overall kinetics of the reactions measured in these experiments. In particular, the functional form of the general expression used to fit the experimental data (Eq. 7) suggests that Langmuir-Hinshelwood type surface reaction kinetics should give plausible explanations for our experimental observations. In particular, the form of Eq. 7 suggests that the reaction product C_2H_4 may compete with TEOS for adsorption sites on the growing SiO₂ surface. To show this, a simple LH kinetic model will be developed which predicts a rate expression of similar form as Eq. 7.

In deriving a rate expression, we will assume the simple stoichiometry of Eq. 1, although similar rate expressions can be derived assuming a variety of reaction byproducts. We will simplify the notation for TEOS as $Si(OR)_4$, where R represents C_2H_5 . We will assume that the reaction mechanism involves the initial reversible adsorption of $Si(OR)_4$ on a vacant surface site on the growing solid film of SiO_2 . In general, an SiO_2 surface may have a variety of adsorption site types, which may include Si or O atoms, or regions between surface atoms. For this simple model, we will assume only a single type of surface site designated by "*." By assuming adsorption-desorption equilibrium, the adsorption step and respective equilibrium relationship can be written as

$$Si(OR)_4 + * \rightleftharpoons Si(OR)_4^* \qquad \theta_{TEOS} = K_{TEOS}P_{TEOS}\theta_v \qquad [9]$$

where θ_v and θ_{TEOS} are the fractions of vacant sites (*) and TEOS-occupied surface sites, respectively, and K_{TEOS} is an adsorption-desorption equilibrium coefficient.

The surface decomposition of $Si(OR)_4^*$ will be modeled as a sequence of steps each involving the removal of a ligand (R or OR group) from the adsorbed precursor, resulting finally in the eventual incorporation of SiO_2 into the growing film. We will assume the rate-determining step is the initial abstraction of a ligand from the adsorbed precursor by a (or multiple) vacant adjacent site(s)

$$\operatorname{Si}(\operatorname{OR})_4^* + p^* \to \operatorname{SiO}(\operatorname{OR})_3^* + \operatorname{R}''^* \qquad r_{\operatorname{R}} = k_{\operatorname{r}} \theta_{\operatorname{TEOS}} \theta_{\operatorname{v}}^p \quad [10]$$

where $\mathbb{R}^{"}$ represents an arbitrary adsorbed species, k_r is a reaction rate coefficient, and p is the number of vacant sites (*) required for this process.

Subsequent removal of ligands results in various Si-containing TEOS fragments and possibly hydrocarbons and oxygenates adsorbed on the surface. For simplicity, we will assume only C_2H_4 is adsorbed on the surface in significant amounts, and that C_2H_4 in adsorption/desorption equilibrium with the surface

$$C_2H_{4(g)} + * \rightleftharpoons C_2H_4^* \qquad \theta_{C_2H_4} = K_{C_2H_4}P_{C_2H_4}\theta_v \qquad [11]$$

In writing an expression for θ_v we assume that the total number of surface sites at any given time during the growth process is fixed. By assuming that only C_2H_4 coverages are significant

$$\theta_{\rm v} = 1 - \theta_{\rm C_2H_4} \tag{12}$$

By combining Eq. 9–12, the following rate expression can be derived

$$r_{\rm R} = \frac{k_{\rm r} K_{\rm TEOS} P_{\rm TEOS}}{\left(1 + K_{\rm C_2H_4} P_{\rm C_2H_4}\right)^2}$$
[13]

where a value of p = 1 has been assumed (*i.e.*, only a single vacant site is needed in Eq. 10). The $K_{C_{2H_4}}P_{C_{2H_4}}$ term is associated with a relative surface coverage of C_2H_4 . For instance, at very low surface coverages of C_2H_4 , the $K_{C_{2H_4}}P_{C_{2H_4}}$ term will vanish. Equation 13 is identical in form to Eq. 7 for n = 1 and m = 2, the form that best described the experimental data.

Discussion

Based on the above simple model, we can interpret many of our experimental results. First, the observed first order with respect to TEOS can be adequately explained by TEOS requiring only a single-surface site for adsorption (Eq. 9). At high coverages of TEOS, a $K_{\text{TEOS}}P_{\text{TEOS}}$ term would appear in the denominator of Eq. 13, which would therefore reduce the reaction order with respect to TEOS as P_{TEOS} is increased. However, no such order reduction was observed, suggesting that TEOS surface coverages at our experimental conditions of pressure and temperature are low. This is further confirmed by the first-order dependence observed by Raupp *et al.*[§] for pressures up to 1.0 Torr.

The above simple model also suggests that the reduction in reaction rate when $P_{C_{2H_4}}$ is increased may be due to the competitive adsorption between C_2H_4 and TEOS on the growing SiO₂ surface. Since C_2H_4 is a known reaction product, this result suggests that at high enough conversions of pure TEOS feed, rate reduction may occur not only because of TEOS depletion, but also because of significant C_2H_4 inhibiting the reaction. However, in our experiments using pure TEOS feed, the TEOS conversion was too low (typically <20%) to generate significant C_2H_4 inhibition was observed in the pure TEOS studies.

The simple model also gives insight into how C_2H_4 may adsorb on the SiO₂ surface. Based on the above mechanism, the value of exponent *n* in Eq. 7 is determined by how C_2H_4 adsorbs (Eq. 11), and *m* is related to the number of vacant sites involved in the rate-determining process (Eq. 12). When testing various forms of Eq. 7 against the experimental data, n = 1 was consistently a preferred exponent regardless of the value for m. This suggests that C_2H_4 requires only a single vacant site for adsorption, rather than requiring two sites, as would be inferred by an n value of one-half or rather than two ethylene molecules adsorbing on a single site, as would be inferred by an n value of 2. The value of m = 2 suggests a single vacant site may be involved in the rate-determining step.

The simple model can also explain the observed increases in the apparent activation energy as $P_{\rm C_2H_4}$ was increased. This can be illustrated by comparing the limits of $K_{\rm C_2H_4}P_{\rm C_2H_4} << 1$ and $K_{\rm C_2H_4}P_{\rm C_2H_4} >> 1$ (*i.e.*, small and large surface coverages of C₂H₄, respectively). For pure TEOS studies (*i.e.*, $P_{\rm C_2H_4} \sim 0$), the C₂H₄ surface coverage is low, and according to Eq. 13, the rate expression reduces to

$$r_{\rm R} = k_{\rm r} K_{\rm TEOS} P_{\rm TEOS}$$

where the apparent activation energy at low $C_{2}H_{4}$ coverage becomes

$$E_{\rm app}^{\rm low} = E_{\rm r} - \Delta H_{\rm TEOS}$$

where $E_{\rm r}$ is the activation energy of the rate-determining surface reaction (Eq. 10), and $\Delta H_{\rm TEOS}$ is the heat of adsorption of TEOS, where the convention of a positive value of $\Delta H_{\rm TEOS}$ corresponds to an exothermic adsorption.

For the limit of high surface coverages (*i.e.*, high C_2H_4 pressures) of C_2H_4 , Eq. 13 reduces to

$$r_{\rm R} = \frac{k_{\rm r} K_{\rm TEOS} P_{\rm TEOS}}{(K_{\rm C_{2}H_4} P_{\rm C_{2}H_4})^2}$$

having an apparent activation energy of

$$E_{\rm app}^{\rm high} = E_{\rm r} - \Delta H_{\rm TEOS} + 2\Delta H_{\rm C_2H_4}$$

where $\Delta H_{\rm C_2H_4}$ is a heat of adsorption of C₂H₄. Typically, heats of adsorption are exothermic (*i.e.*, $\Delta H_i > 0$ by our sign convention); therefore, $E_{\rm app}^{\rm high} > E_{\rm app}^{\rm low}$ as observed experimentally. Based on the parameter definition of E_2 shown listed in Table I, a $\Delta H_{\rm C_2H_4}$ of ~20 kcal/mol is estimated. This is a relatively large value for a heat of adsorption, suggesting the C₂H₄ is bound in a chemisorbed state.

Conclusion

The kinetics of SiO₂ deposition from TEOS were studied by monitoring changes in reactant and product partial pressures in a well-mixed flow reactor. For experiments using pure TEOS feed, we observed first-order kinetics vs. P_{TEOS} and apparent activation energies of 20.9 kcal/mol over a wide range of feed pressures and surface temperatures. We also investigated the effect of the reaction product C₂H₄, a reaction product, on the rate by including measured amounts of C₂H₄ with the TEOS in the feed. We found that the reaction rate decreased and apparent activation energies increased as P_{CgH_4} was increased. Particularly, we observed -2 order with respect to C₂H₄ at sufficiently high P_{CgH_4} values.

Several rate expressions were considered in testing models to describe the data. Based on curve fitting, a model suggesting that TEOS and C_2H_4 competitively adsorb on the surface was derived. This model suggests that the ratedetermining step is the abstraction of a ligand from an adsorbed TEOS or TEOS fragment by an adjacent vacant site. Also, the model suggests that C_2H_4 adsorbs tightly bound to a single surface site.

It is noteworthy that the pure TEOS experiments showed no detectable rate inhibition due to generated C_2H_4 . This is likely due to the low conversions in these studies. However, whenever C_2H_4 was included in a significant amount in the feed, inhibition could be observed. An understanding of these inhibition kinetics is particularly applicable in situations of high conversions and in the coating of small-scale feature where mass transport effects, for instance in trenches, may lead to built-up of significant concentrations of reaction products. In such situations, reaction inhibition can lead to non-uniform film coatings.

This work was partially supported by DOE undergrant No. DE-FG02-88ER13878-A02.

Manuscript submitted Aug. 16, 1993; revised manuscript received Feb. 17, 1994.

REFERENCES

- 1. S. P. Murarka and M. C. Peckerar, Electronic Materials: Science and Technology, Academic Press, Inc., Boston (1989).
- S. B. Desu, J. Am. Ceram. Soc., 72, 1615 (1989).
 J. E. Crowell, L. T. Tedder, H.-C. Cho, and F. M. Cascarano, J. Vac. Sci. Technol., A8, 1864 (1990).
- 4. L. T. Tedder and J. E. Crowell, ibid., A9, 1002 (1991) 5. L. T. Tedder, G. Lu, and J. E. Crowell, J. Appl. Phys., 69, 7037 (1991).
- 6. T. Okuhara and J. M. White, Appl. Surf. Sci., 29, 223

(1987).

- 7. A. C. Adams and C. D. Capio, This Journal, 126, 1042 (1979).
- G. B. Raupp. F. A. Shemansky, and T. S. Cale, J. Vac. Sci. Technol., B10, 2422 (1992).
- 9. Y. Nishimoto, N. Tokumasu, K. Fujino, and K. Maeda, in Proceedings of the 6th International IEEE VLSI Multilevel Interconnection Conference, T. E. Wade,
- Editor, p. 382, unpublished, 1989. 10. J. Schlote and K. W. Schröder, *This Journal*, **138**, 2393 (1991).
- T. S. Cale, G. B. Raupp, M. B. Chaara, and F. A. She-mansky, *Thin Solid Films*, **220**, 66 (1992).
- 12. E. A. Haupfear and L. D. Schmidt, This Journal, 140, 1793 (1993).
- 13. E. A. Haupfear and L. D. Schmidt, Chem. Engr. Sci., Submitted.

Photoluminescence of Mn²⁺-Activated ZnGa₂O₄

L. E. Shea,^a R. K. Datta,^{*} and J. J. Brown, Jr.*

Center for Advanced Ceramic Materials, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

ABSTRACT

The synthesis and photoluminescence mechanism of $ZnGa_2O_4$: Mn^{2+} are presented. Monitored at 450 nm, $ZnGa_2O_4$ exhibits an absorption band at 245 nm; monitored at 506 nm $ZnGa_2O_4$: Mn^{2+} exhibits absorption bands at 245 and 283 nm. Under 254 nm excitation $ZnGa_2O_4$ exhibits a broad-band emission extending from 360 to 610 nm, peaking at 450 nm. This emission is gradually quenched, as a new band emerges, peaking at 506 nm, as Mn^{2+} is incorporated into the lattice $(Zn_{1-x}Mn_xGa_2O_4)$, where x = 0.006 at maximum intensity. Activator sensitization and host-to-activator energy transfer are suggested.

Gallate phosphors have been well-known for many years for their commercial application in xerography,¹⁻³ and have recently been reported for potential use in vacuum fluorescent displays (VFDs).⁴ Blue-emitting zinc gallate, ZnGa₂O₄ is a possible alternative to the ZnS-based low-voltage cathodoluminescent phosphors presently used in VFDs. The stability of oxide phosphors in high vacuum and the absence of corrosive gas emission under electron bombardment offer advantages over commonly used sulfide phosphors.^{5,6} Manganese-activated zinc gallate, $Zn_{1-x}Mn_xGa_2O_4$ is a green-emitting phosphor that crystallizes in the spinel structure.3,7-9 Information which dephotoluminescence the mechanism of scribes $Zn_{1-x}Mn_xGa_2O_4$ is lacking. The present study attempts to establish $Zn_{1-x}Mn_xGa_2O_4$ both as an activator and host-toactivator sensitized phosphor, where absorbed energy from the Mn^{2+} ions and the $ZnGa_2O_4$ host lattice is transferred to the Mn²⁺ emission centers.

The general formula of spinel is AB_2O_4 , where A and B are metal cations which occupy the tetrahedral and octahedral interstices of the unit cell. In general, all AB_2O_4 spinels can be considerd random, 9 having the formula $(A_{1-x}B_x)^{IV}(B_{2-x}A_x)^{VI}O_4$. Green emission results when manganese occupies the four-coordinating position in the lattice.²

Experimental

Phosphors with the general formula $Zn_{1-x}Mn_xGa_2O_4$ were prepared by solid-state reaction techniques, with xranging from 0 to 0.03. The raw materials ZnO (Aldrich, 99.999%), Ga_2O_3 (Johnson Matthey, 99.999%, metals basis), and MnO (Alfa, 99.5%) were weighed on an analytical balance to an accuracy of ± 0.1 mg, thoroughly mixed under acetone in a glass mortar and pestle, allowed to dry, then air-fired in a CM870901 high temperature furnace at 1100°C for 17 h in covered alumina crucibles. After a light grinding and mixing step, the phosphor powders were

^a Present address: Materials Science Program, University of California, San Diego, La Jolla, CA 92093.

placed in alumina boats, covered, and fired in a reducing atmosphere of 98% N₂-2% H₂ at 900°C for 1 h, with a flow rate of 12 ml/min.

Each $Zn_{1-x}Mn_xGa_2O_4$ powder sample fired, ranged from 6 to 8 g.

The phosphors were characterized by x-ray diffraction analysis using a Phillips PW1729 x-ray diffractometer with CuK α radiation operating at 40 kV, 30 mA, and 3°-2 θ /min scanning rate.

The photoluminescence emission and excitation spectra of polycrystalline samples were obtained using a Perkin-Elmer LS-5B luminescence spectrometer. Up to 0.5 g of a powder sample was placed in a circular cell holder with a fused silica window. The powder holder was mounted at a suitable angle to the excitation and emission beams to give the maximum signal and minimum scatter. Samples were excited with 254 nm radiation from a pulsed xenon discharge lamp. The emission wavelength was scanned from 380 to 600 nm at a scanning rate of 480 nm/min.

For measurements of excitation spectra the excitation wavelength was scanned from 230 to 380 nm at the same scanning rate, and emission monitored at 450 or 506 nm.

An attenuator was used to eliminate second-order Rayleigh scatter of the excitation wavelength. The monochromator on the LS-5B Spectrometer was operated with a slit width of 3 nm.

Results and Discussion

phosphors.—Single Synthesis of spinel phase $Zn_{1-x}Mn_xGa_2O_4$ phosphors after the first firing, in air at 1100°C for 17 h, had a peach body color, and weak green emission due to Mn^{4+} . The second firing in 98% $N_2\text{--}2\%~H_2$ reducing atmosphere for 1 h at 900°C produced powders with a white body color. This, in addition to a bright green emission, indicates that divalent manganese is produced under these firing conditions. Green emission indicates that manganese (Mn²⁺) is in the four-coordinated position in the lattice. For the MgGa₂O₄:Mn²⁺ phosphor, maximum brightness was achieved when the samples were cooled

^{*} Electrochemical Society Active Member.