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**Author**
Gieske, R.J.

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R. J. Gieske, J. J. McMullen, and Lee F. Donaghey

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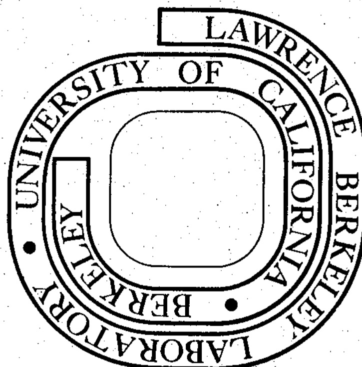


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# LOW PRESSURE CHEMICAL VAPOR DEPOSITION OF POLYSILICON

R. J. Gieske and J. J. McMullen
Tempress Microelectronics
Sunnyvale, California 94086
and
Lee F. Donaghey*
Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Chemical Engineering, University of California,
Berkeley, California 94720

The low pressure chemical vapor deposition of polycrystalline silicon was studied to define the controlling process parameters and the requirements for commercial implementation. Silane, and silane-nitrogen mixtures were utilized as source gases in a tubular reactor containing parallel disk substrates oriented with surface normals in the direction of flow. The results of the study showed that the deposition reaction is surface kinetic reaction controlled over the range of temperature studied, 600 to 700°C, that the reaction is first order with respect to silane, and with an activation energy of $1.33 \times 10^5$ J/g mole. A gradient in temperature along the reactor tube is sufficient to compensate for reactant depletion and to produce a uniform deposition rate.

## INTRODUCTION

The chemical vapor deposition technique has been utilized in the semiconductor industry since its inception. The preparation by chemical vapor deposition (CVD) of semiconducting silicon films by Theurer in 1960 at Bell Telephone Laboratories introduced a major innovation to the industry and initiated the development of cold-wall CVD reactors.[1] Because of wall deposits in hot-wall reactors, however, such reactors were not used in production. The use of silicon dioxide and silicon nitride films in device manufacture led to the natural extension of cold-wall CVD reactors to meet the growing requirements of the semiconductor industry.

The use of hot-wall reactors for polysilicon deposition, or silicon nitride deposition, was minimal until recently, primarily due to the lack of wafer capacity imposed by the mass transport limitations in such reactors at atmospheric pressure. The low-pressure CVD (LPCVD) method applied to hot-wall reactors was then introduced by Chruma and Hilton in 1975.[2] This method minimized mass tranport effects under conditions which allowed surface reaction rate control to dominate.

*Current address: Chevron Research Company, Richmond, CA 94802

The economic advantages derived from a system in which the deposition conditions are such that the rate controlling process is surface reaction limited are considerable.[3] It is estimated that low pressure CVD reactors can save up to 98% of the cost for reactor gases when compared on a per-wafer basis to conventional horizontal or vertical cylinder reactors operating at atmospheric pressure. Additionally, up to 93% of the labor cost, and up to 95% of the capital cost depreciation savings should be achievable with LPCVD reactors. The total cost savings per 3-inch and 4-inch diameter wafers are estimated to be 90 and 94% respectively.[5] The rapid acceptance of LPCVD methods by the semiconductor industry, and the development of high-capacity equipment for production lines in 1976, attest to the economic advantages that can be realized with LPCVD reactors.

The purpose of the present study is to investigate the process parameters involved in the LPCVD process in order to optimize the design of LPCVD equipment and processes. The experimental studies reported concern the deposition of polysilicon from pure silane, and from silane-nitrogen mixtures at low pressures. Generalizations of the results are presented so that extrapolations can be made for other reaction systems.

## THEORY

The mass transport processes in low pressure chemical vapor deposition (LPCVD) are similar to those occuring in catalytic reactors containing solid catalysts. The LPCVD reactors under development for use in the electronics industry consist of a cylindrical tube furnace with densely spaced disk substrates placed parallel to one another, with their surface normals coaxial with the reaction tube.

The process of mass transfer through the annulus between the tube inner wall and the cylindrical stack of disk substrates is analogous to the mass transfer to the surface of a catalyst particle, and can be described in the simplest form by a plug flow model in which the radial concentration gradient is assumed to be negligible.

Flow between the closely spaced disk substrates resembles flow in a catalyst capillary. The concentration profile can be calculated by a stagnant diffusion model with deposition on both walls of the radial channel. The molar concentrations in the cylindrical annulus will be depleted by deposition between the wafers.

The consequences of reduced pressure on mass transport can be appraised by considering the molar flux of a reactant A in a mixture A-B. If

$$N_A = \frac{\mathcal{D}}{\delta RT} (p - p_s) + x_A(N_A + N_B) \qquad (1)$$

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where $\mathcal{D}$ varies approximately with $T^{1.65}$. Under general conditions of flow, the boundary layer thickness can be estimated by a characteristic dimension of the channel, or by a correlation to the kinematic viscosity $\nu$, $\delta \sim \nu^n$. Thus, in the high temperature limit, the molar flux expression becomes:

$$N_A \simeq (\text{const}) \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2} T^{0.65-n} P_{TOT}^{-1} + x_A(N_A + N_B) \ . \qquad (2)$$

This equation shows that the flux varies inversely with the total system pressure, weakly with temperature, and inversely with the square root of molecular weight. The second term accounts for the flux of any second component, which is a carrier gas, or a byproduct of the reaction.

## LPCVD KINETICS

The kinetic regime dominant in low pressure CVD depends upon the temperature range in relation to activation energies of surface reactors. Sugaware has studied the kinetics of silicon deposition from $SiCl_4$ and $H_2$ on a rotating disk substrate.[6] His findings indicate that a transition in deposition rate control occurs at about 1150°C, and that below this temperature the growth is limited by surface reaction kinetics. Since LPCVD processes are carried at temperatures much lower than 1000°C, it can be safely assumed that the deposition reaction is surface reaction rate limited. The uniformity of deposition with low pressure CVD can be improved by operating in the surface reaction controlled regime.

## FLOW IN ANNULAR LPCVD REACTORS

The low pressures utilized in low pressure CVD are sufficiently reduced that the flow lies in the transition range between laminar flow and molecular flow. This regime is termed slip flow, and occurs for the mean free path function $X$ between 0.014 and 1, where $X$ is defined by the following function of the mean free path $\lambda$ and hydraulic diameter $D_H$ :

$$X = \frac{\lambda}{D_H}\sqrt{\frac{8}{\pi}} \ .$$

The conductance of the reactor channels is most conveniently obtained for the slip-flow region by the method of Brown et al.(6) where the true conductance $C$ is obtained from the conductance for laminar flow $C_{lam}$ by

$$C = FC_{lam} \ .$$

The correlation factor for smooth-walled flow channels can be represented parametrically by the following function:

$$F = 3X + (1 + B/2)^{-1} .$$

Then, for the annular flow channel of a LPCVD reactor, the pressure gradient is given by

$$\frac{\partial P}{\partial z} = \frac{8\mu FQ}{\pi R^2} \left\{ (1 - \kappa^4) - \frac{(1 - \kappa^2)^2}{\ln\left(\frac{1}{\kappa}\right)} \right\}^{-1}$$

where $Q$ is the volumetric flow rate for the reactor gas of viscosity $\mu$, and $\kappa$ is the ratio of the inner radius of the annulus, $R_w$, the substrate wafer radius, to the outer radius $R$.

The type of flow expected in an annular LPCVD reactor is determined by the magnitude of the correction factor $F$. For a reactor tube of 6.55 cm radius containing 7.62 cm diameter (3 inch) substrates separated from each other by 0.273 cm, the type of flow expected for several gases is presented in Table I. The table shows that transport is in the slip flow regime near the laminar flow limit, or in the laminar flow regime in the annular channel, and in the mid slip flow regime in the space between the substrate wafers. At the laminar flow limit, the correction factor $F$ has unity magnitude, whereas in the mid slip flow regime, the factor has a magnitude of 2 to 3.

## EXPERIMENTAL

The experimental equipment used for the deposition of films by the LPCVD method consisted of three main components: a resistance heated furnace and quartz reactor tube designed for vacuum use, a gas control system, and a pumping system designed to accommodate the gases used in the process.

These items of apparatus are arranged as shown in Fig. 1. The substrate wafers were loaded vertically in a "ladder" boat and positioned in the quartz reactor tube so that the wafer surface normals were perpendicular to the tube axis.

Figure 2 gives a simplified cross-sectional view of the basic reactor. The quartz reaction tube was 183 cm long with an internal diameter of 101 mm. The wafer holder was a quartz boat 61 cm long. The boat could hold 150 wafers in the stand up position, spaced nominally by 0.25 cm. Temperature measurements were made at both atmospheric and reduced pressure. Pressures were measured by means of a thermocouple gauge installed in the system. Nitrogen was used as the purge gas before and after depositions.

0 0 0 0 4 9 0 2 3 0 4



The wafers were pretreated in the system with HCl prior to deposition in order to etch the surface of growth. The cycle used for deposition consisted of a three min purge with $N_2$ at atmospheric pressure, a reduction of pressure to 10 mTorr, two min purge in $N_2$ during which the reactor pressure was adjusted by means of flow limiting values, deposition of polysilicon for 15 to 45 min, then two min purge with $N_2$ at low pressure, three min purge at atmospheric pressure, then evacuation of the reactor.

Preliminary experiments indicated that the use of a carrier gas with the silicon source gas, $SiH_4$ , was not required for uniform polysilicon films and the addition of a carrier gas added to the capacity required of the pumping system. Therefore, most of the deposition experiments were made using only silane in the system. Most of the experimental data was obtained using flat temperature profiles of 600°C, 650°C, and 700°C in order to study the effect and rate of reactant depletion.

The substrate boat was positioned in the same place for each deposition experiment and the rate data collected were from wafer substrates in identical positions within the boat. The introduction of silane into the heated quartz reactor resulted in deposition on all hot surfaces. As a result, the wafers positioned in the down stream section of the tube were exposed to a mixture of unreacted $SiH_4$ and $H_2$ produced from the reacted $SiH_4$ .

Figure 3 shows the log of the deposition rate on a wafer within the first group of wafers at the entrance end of the tube as a function of reciprocal absolute temperature. The three curves are at different constant silane input flows. The activation energy obtained from Figure 3 is $1.55\times10^5$ J/g mole, (37 kcal/g mole). Hammond and Gieske have quoted similar values for LPCVD of polysilicon.

Figure 4 shows the log of the deposition rate as a function of the log of the silane flow. The three curves are at 600°C, 650°C, and 700°C. The slopes of these curves are 0.53, 0.79, and 0.3 respectively. The apparent order of the reaction cannot be estimated from these curves, however, because the partial pressure of silane was not held constant, and because of the use of $N_2$ in some experiments.

Figure 5 shows the log of the deposition rate as a function of the log of the pressure of silane, without nitrogen added to the system. These results show that the apparent activation energy is nearly unity, over the temperature range from 650°C to 700°C. This result is expected for nonmolecular reaction of silane pyrolysis on the substrate surface.

The yield of polysilicon produced by pyrolysis of silane is shown in Fig. 6 for a system pressure of 0.4 Torr. This figure shows that the reactant yield in the experimental reactor reached a maximum thermodynamic yield above 700°C. At lower temperatures the yield dropped sharply.

The effect of reactant depletion was studied by using a constant temperature over the reactor length. Results under selected conditions are shown in Fig. 7. The reactant depletion effect is significant at 700°C, with the deposition rate falling to low values at the exit end of the reactor. At 600°C, on the other hand, there was essentially no depletion of the reaction, but a smaller reaction rate.

Additional experiments were performed with temperature gradients along the reaction tube. The positive temperature gradient corrected for reactant depletion and achieved increased deposition rates at the exit end of the reactor by enhancing the thermally activated surface reaction. These experiments showed that uniform deposition rates could be achieved over the length of the reactor by carefully adjusting the thermal gradient along the tube for each average deposition temperature. For example, a temperature gradient of 0.328°C/cm is needed for an average deposition temperature of 620°C.

The deposition rate uniformity on test wafers were measured by the groove and stain method and by an optical interference method. In these experiments 7.62 cm (three inch) diameter wafers were used, and deposit thicknesses were measured at five cartesian coordinate points on the wafer spaced by 2.79 cm. These measurements showed that the mean deposition rate variation was 0.42%, with a standard deviation of 0.11%.

DISCUSSION

The expression relating the deposition reaction rate constant to the temperature is:

$$G = A \exp(-\Delta E/RT) \tag{3}$$

where A is the frequency factor, $\Delta E$ is the activation energy, R is the gas constant and T is the absolute temperature. The measured activation energy for polysilicon pyrolysis is $1.33 \times 10^5$ J/g mole (32 kcal/g mole). The rate expression for polysilicon deposited is then

$$G \cong 4.3 \times 10^7 \exp[-133.4/RT] \, p_{SiH_4} \tag{4}$$

where G has the units of nm/s, and $p_{SiH_4}$ has the units of Torr.

The rate expression derived lends itself to a calculation of the temperature profile required in a polysilicon deposition system to achieve uniform deposition rates. The equation must be modified, however, to accommodate the decreasing amount of silane available as deposition occurs down the tube. By knowing the deposition surface area of different wafer sizes and their distribution in the tube, one can adjust the temperature profiles and the silane flows rate to yield deposition rates of better than ±5% over 150 wafers.

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Ogirima et al., have recently described the kinetics of low pressure silicon epitaxial growth from dilute mixtures of $SiH_4$ in $H_2$.[8] Their study was prompted by the suggestion of Deines and Spiro that low pressure epitaxial CVD of silicon could be useful for reducing the autodoping from heavily doped silicon substrates.[9] Ogirima et al., utilized dilute, low pressure mixtures of $SiH_4$ and $H_2$ to show that silicon growth rates and uniformities were extremely dependent on both the pressure in the reaction tube, and on the ratio of $SiH_4$ to $H_2$.

The apparent activation energy of Ogirima et al., $4.6\times10^4$ J/g mole (11 kcal/mole) was measured for pressures between 760 Torr and 150 Torr and $SiH_4/H_2$ in the range from 0.002 to 0.003. This result is in agreement with the previous measurement of $4.2\times10^4$ J/g mole (10). Indicative of a gas-phase homogeneous reaction rather than of a surface reaction is Ogirima's 180 kJ/g mole activation energy measured at 80 Torr.

The effect of reactant depletion indicates some design restrictions for LPCVD of polysilicon. Because reactant depletion is rapid at 700°C, large gradients in deposition rate can be expected on the closely spaced wafer substrates. A stagnant flow model was explored to predict the gradients in deposition rate; the model showed that the deposition rate gradient was largest at the edge of the wafer substrate, and relatively uniform across the center of the wafers, provided that the ratio $kR/\mathcal{D}$ was small, where k is the surface reaction constant, and R is the radius of the wafer. The radial gradient was largest above 675°C, where diffusive effects became large. The radial gradient can be reduced by increasing the wafer separation.

For optimal control of the uniformity, a linear temperature gradient along the reaction tube must be used. Also, reaction temperatures below 650°C maintain both radial and longitudinal gradients below 0.5%. For larger diameter wafers, or longer reactors lower temperatures must be used to achieve the same degree of uniformity.

## CONCLUSION

The low pressure chemical vapor deposition of polysilicon from silane is first order in the pressure of silane, with an apparent activation energy of $1.33\times10^5$ J/g mole. Flow within the space between disk substrate wafers is in the slip flow regime under current reactor conditions. The yield and deposition rates are strongly influenced by temperature, and not strongly influenced by reactant partial pressure. The effect of reactant depletion on the deposition rate uniformity can be controlled by operating the reactor at temperatures below 675°C, and by introducing a temperature gradient along the reaction tube.

## ACKNOWLEDGMENT

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REFERENCES

1. H. C. Theurer, J. Electrochem. Soc., 108, 649 (1961).
2. J. Chruma and P. Hilton, U.S. Patent No. 3,900,597, August 19, 1975.
3. M. Hammond and R. J. Gieske, Low Pressure Chemical Vapor Deposition Impact on the Industry, Presented at Semicon West, May 27, 1976.
4. B. A. Joyce and R. R. Bradley, J. Electrochem. Soc., 110, 1235 (1963).
5. H. W. Markstein, Electronics Packaging and Prod., 17, 5, 31 (1977).
6. G. P. Brown, A. DiNardo, G. K. Cheng and T. K. Sherwood, J. Appl. Phys., 17, 802 (1946).
7. K. Sugawara, J. Electrochem. Soc., 119, 1749 (1972).
8. M. Ogirima, H. Saida, M. Suzuki and M. Maki, J. Electrochem. Soc., 124, 903 (1977).
9. J. L. Deines and A. Shiro, Abstract 62, The Electrochemical Society Extended Abstracts, Spring Meeting, San Francisco, CA, May 12-17, 1974, p. 161.
10. F. C. Farrow and J. D. Filby, J. Electrochem. Soc., 118, 149 (1971).

TABLE I

Flow Properties of LPCVD Reactor Gases

| | | Reactor annulus, $D_H$ = 5.48 cm | | Inter-wafer channel, $D_H$ = 0.546 | |
|---|---|---|---|---|---|
| Gas | $\lambda$(cm), 0°C, 750 Torr | X, 700°C, 0.5 Torr | flow | X, 700°C, 0.5 Torr | flow |
| Ammonia | $5.92\times10^{-6}$ | $9.22\times10^{-3}$ | laminar | $9.25\times10^{-2}$ | slip |
| Argon | $8.98\times10^{-6}$ | $1.40\times10^{-2}$ | slip | 0.140 | slip |
| Hydrogen | $16.00\times10^{-6}$ | $2.49\times10^{-2}$ | slip | 0.250 | slip |
| Helium | $25.25\times10^{-6}$ | $3.93\times10^{-2}$ | slip | 0.394 | slip |
| Nitrogen | $8.50\times10^{-6}$ | $1.32\times10^{-2}$ | laminar | 0.133 | slip |
| Oxygen | $9.05\times10^{-6}$ | $1.41\times10^{-2}$ | slip | 0.141 | slip |

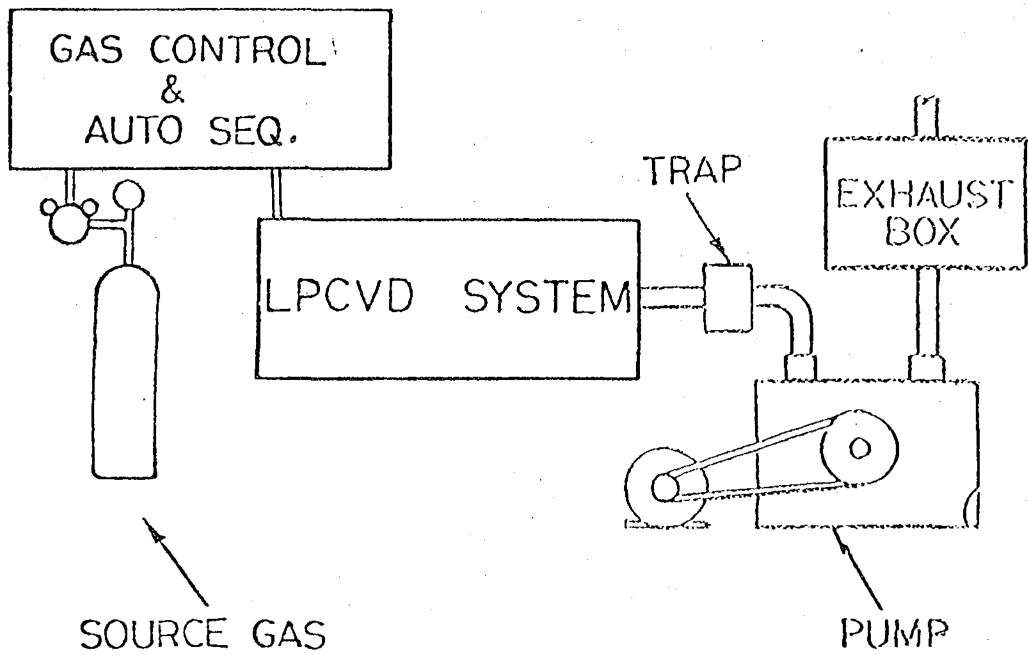


Fig. 1 Schematic of the experimental equipment for low pressure chemical vapor deposition.

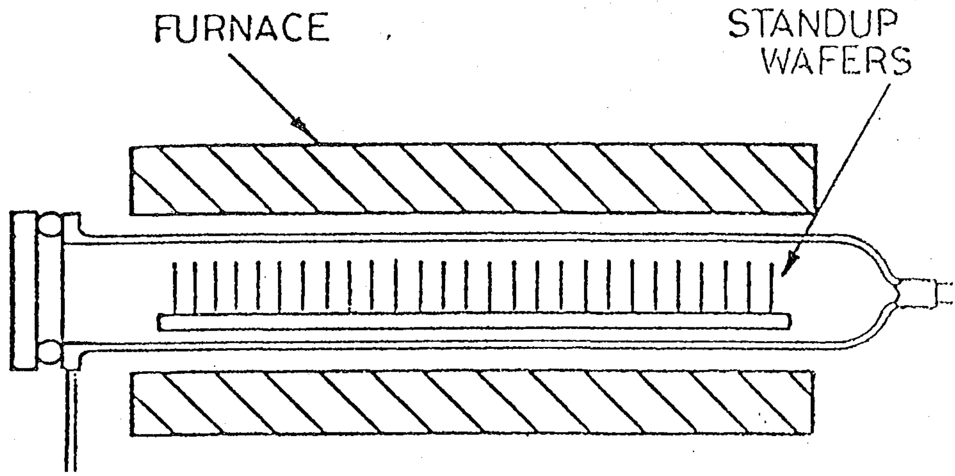


Fig. 2 Cross section of the tubular reactor.

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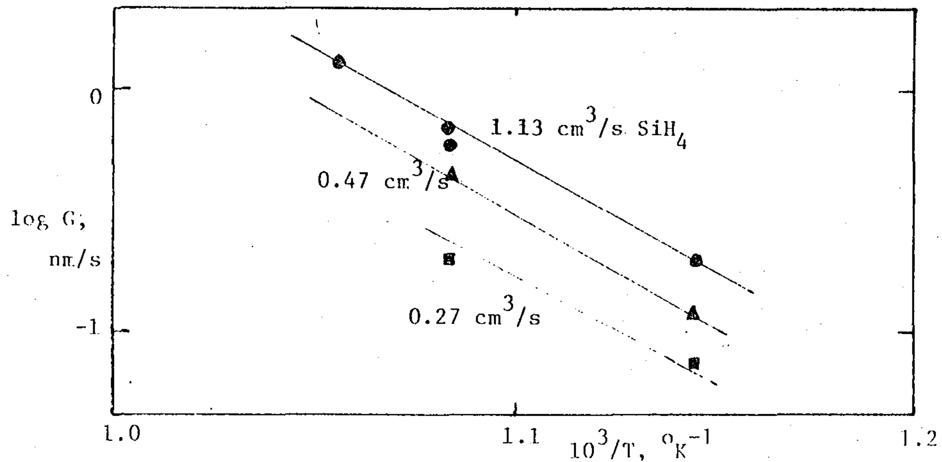


Fig. 3 Temperature dependence of the deposition rate.

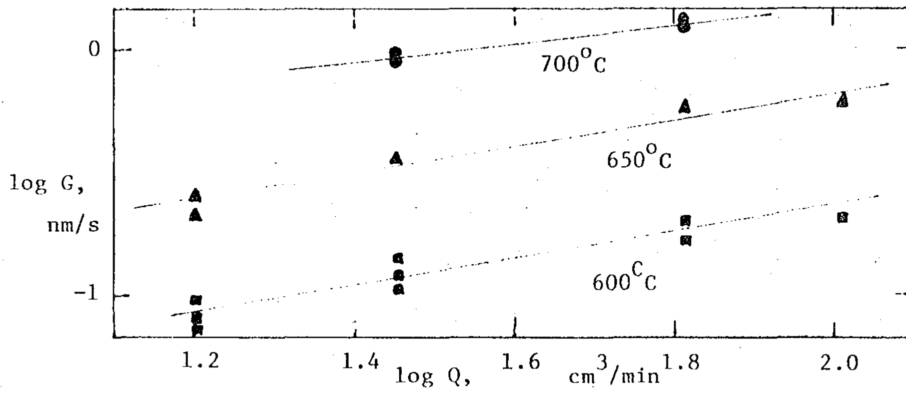


Fig. 4 Dependence of the deposition rate on silane flow rate.

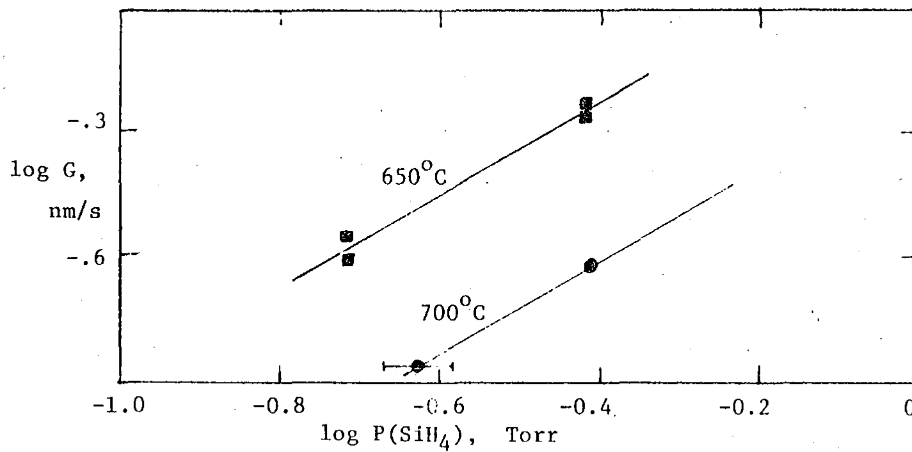


Fig. 5. Dependence of the deposition rate on silane partial pressure.

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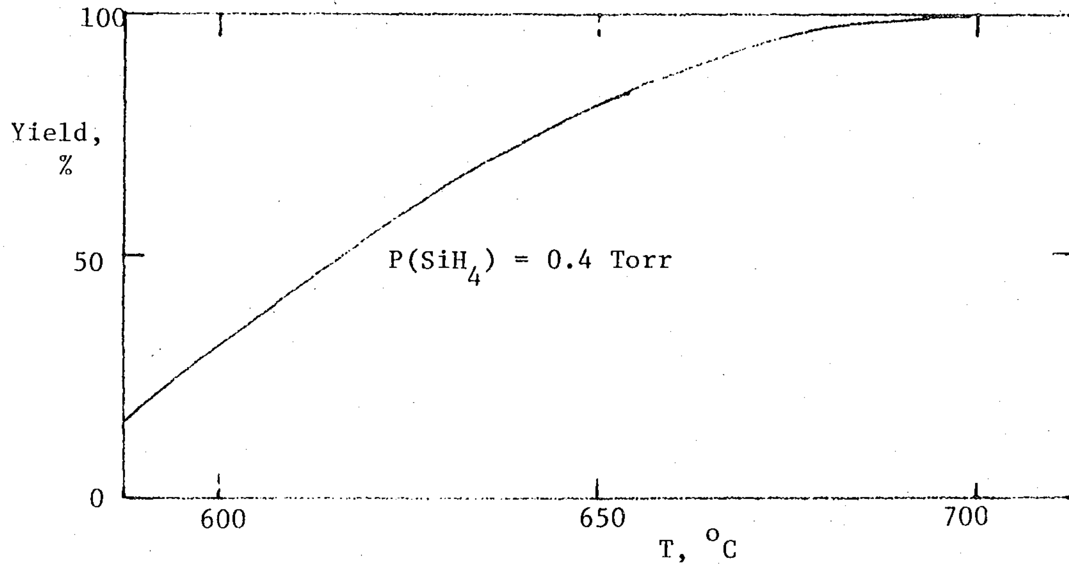


Fig. 6 Yield of polysilicon as a function of temperature.

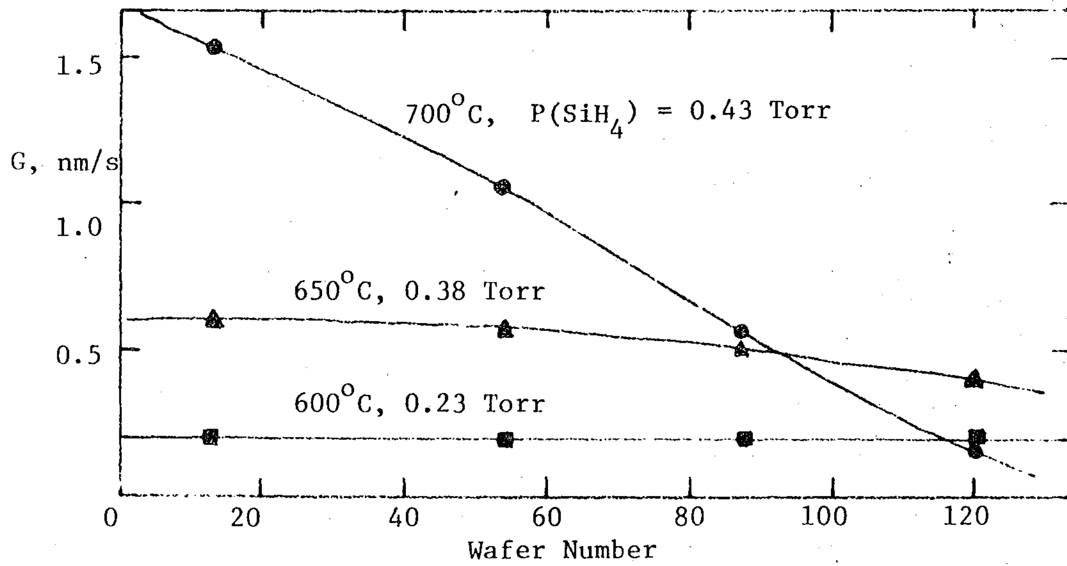


Fig. 7 Effect of reactant depletion on the longitudinal distribution of the deposition rate.

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