Preparation and Properties of SiO₂ Films from SiH₄-CO₂-H₂

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ABSTRACT

This paper presents the results of chemical vapor deposited (CVD) silicon dioxide films on silicon from an SiH₄ + CO₂ + H₂ system. The kinetics of this reaction have been studied with a barrel reactor. The activation energy (ΔE) of the SiH₄, CO₂ reaction in hydrogen is 106.7 J/g mol (25.4 kcal/g mol) in the temperature range 800° -1050°C. The SiH₄ and CO₂ reaction in hydrogen is shown to be a first-order reaction with respect to $SiH_4(CO_2:SiH_4 \ge 20)$. The deposition rates of SiO_2 are dependent only on deposition temperature and on SiH_4 mole fraction. They are independent of the CO_2 : SiH_4 ratio in the experimental range of 7:1-120:1. Electrical characterization was carried out on MOS capacitors of \sim 1300Å dielectric thickness. The breakdown field was found to be $(7.8 \pm 0.1 \times 10^6 \text{ V/cm})$. Measurements of oxide charges, of mobile charges, and of fast surface-state density show that these oxides are stable under positive and negative bias, with maximum shifts of 250 mV after 50 hr stress at 200°C and $\pm 2 \times 10^6$ V/cm electrical field. Postdeposition high-temperature anneal deteriorates the V_{FB} stability under negative-bias temperature stress. The index of refraction depends on the CO₂:SiH₄ ratio, going above 1.46 at a ratio <10. Ratios of CO₂:SiH₄ ≥ 50 give reproducible results at an average index of 1.454 ± 0.001 . Etch rates in "P-etch" for 1000°C deposited samples are $\sim 50\%$ faster than thermal oxides grown at the same temperature.

Chemical vapor deposited (CVD) SiO₂ films have several advantages in planar semiconductor device processing over the oxidation of silicon. Since no silicon of the substrate is consumed, the junction movement, pileup, or depletion of dopants at SiO₂-Si interfaces is minimized. Thick films of SiO2, which may be used in the field region of integrated FET circuits, can be deposited with greater ease than thermal oxidation because the deposition rates are not diffusion-limited in the solid. One application of CVD oxides where the thermal oxide does not compete is the use of CVD oxides as photolithographic masks for films not etched in fluorides, such as silicon nitride. Finally, CVD oxides lend themselves to in situ processing where two or more films are required and one of these films is SiO_2 .

Silica films have been deposited by a variety of chemical systems, at both high and low temperatures (1-10). It was desirable in this case to select a process that would produce SiO₂ films with etch rates close to those of thermal SiO₂, so as to avoid excessive undercutting during etching. Since etch rate is inversely proportional to deposition temperature, the process had to be carried out at a high temperature (1000°C). SiH₄ was preferred over other silicon-bearing compounds (e.g., SiCl₄ or SiBr₄) because of its gaseous nature and resulting ease of metering control. In situ processing also favors SiH_4 because one has only to replace the oxidant with NH₃ to deposit silicon nitride or discontinue the oxidant flow to deposit polysilicon. It was also desirable to use an oxidant that would have a minimal gas-phase reaction with SiH₄ so as to keep the reactor down time to a minimum. This led to the investigation of the SiH₄ and CO₂ reaction. Swann and Payne (4) and Kroll et al. (5) reported on the SiH_4 - CO_2 system. Our purpose is to investigate further the deposition kinetics, to obtain an empirical rate expression, and to examine the physical and electrical properties of the resulting SiO₂ films.

Experimental

Equipment.---The equipment used for the entire experimental investigation was a vertical, cold-wall, barrel-type, induction-heated reactor (11). The silicon "wafers" were placed on an SiC-coated graphite susceptor. Figure 1 gives a schematic cross-sectional view of the reactor. The fused-quartz chamber is 18 in.

* Electrochemical Society Active Member. ¹ Present address: IBM Deutschland Boeblingen (Lab) 0711 Boe-Key words: silicon dioxide, dielectric films, MOS, CVD, thin films.

 $(\sim 45 \text{ cm})$ long, with an internal diameter of 9 in. (~ 23 cm). The susceptor is placed in the chamber so that its leading edge is \sim 5 in. (12.7 cm) from the molybdenum distributor. The susceptor is hexagonal and is divided into three tiers, or "rings." Each of the six faces of the susceptor makes an angle of $\sim 3^{\circ}$ with the central vertical axis. The susceptor is placed on a fused-quartz plate, which in turn is supported by a fused-quartz pedestal. The susceptor, approximately 8.25 in. (21 cm) long, was rotated at about 8 rpm throughout this experimental work. The volume of the annulus between the susceptor and the chamber (i.e., the volume of the deposition zone) is ~ 5 liters.

The temperature was measured with an optical pyrometer.² All temperatures reported were corrected for system transmission losses and for emissivity (12). The reacting and the carrier gases were introduced from the top of the reactor after each had been metered through a separate rotometer. Each rotometer was calibrated. The silane used was a 5% mixture in nitrogen or hydrogen. The SiH₄, CO₂, and the carrier gas (either H_2) or N_2) were filtered (submicron filters) before they passed through their respective rotometers.

Typical deposition conditions and measurement technique.-Three, 2¼ in. (5.7 cm) Si, 11-25 ohm-cm, ptype, <100> wafers were processed in each experimental run, unless otherwise indicated. One wafer each

 $^{\circ}$ The temperature along the susceptor length is $\pm 10^{\circ}C$ of any reported value.



Fig. 1. Schematic cross-sectional view of barrel reactor

was placed in rings 1, 2, and 3, at a predetermined fixed position. The remaining positions on the susceptor were filled with dummy wafers. Before loading in the reactor, wafers were cleaned ultrasonically in hot (85°C) deionized water (for 5 min), followed by H₂SO₄/HNO₃ (3:1, at 120°C) cleaning (for 10 min), followed by 10:1 dilute HF dip (10 sec). The wafers were then rinsed in running deionized water (for 5 min) and subsequently spin-dried. The wafer surface was hydrophobic after this cleaning.

During the experimental work, the carrier gas flow rate (H_2 in most cases) was varied between 60 and 120 liters/min and the SiH₄ flow rate (5% in H_2 or N_2) between 60 and 1000 cm3/min. The SiH4: CO2 ratio was changed between 7:1 and 120:1. The deposition tem-perature range was 800°-1050°C; the deposition time was never less than 5 min or greater than 25 min.

The resulting SiO₂ film thicknesses were measured by CARIS³ (>1500Å) and by ellipsometry (\leq 1500Å). The index of refraction was always measured by ellipsometry. Five thickness measurements were taken per wafer; these five readings cover $\sim 80\%$ of the total wafer area. Peripheral readings were taken 0.125 in. (3.18 mm) away from the edge of the wafer. The typical within-a-run deposition uniformity was $\leq \pm 5\%$ at 1000°C and at a total flow rate of \sim 110 liters/min; the worst case within-a-run uniformity at any temperature and flow (within the experimental range) was $\sim \pm 15\%$. The deposition rates used in this report are therefore average deposition rates over three rings (i.e., 15 measurements); thus, as a first approximation, we neglected the silane concentration variations along the susceptor length.

Experimental Results

Preliminary experiments.-Preliminary experiments were performed using an H₂ and N₂ mixture as a carrier gas at a deposition temperature of 1000°C. The H₂/N₂ ratio was varied from 0.03:1 to 1.5:1, with similar results. The films deposited were dendritic in appearance. When these films were etched in 5:1 diluted HF, a brown film was left on the silicon surface. Swann and Payne (4) reported similar observations when they used argon as a carrier gas. The brown film on the silicon surface was etchable only in I-etch,⁴ suggesting that the brown film is a silicon-rich film (mostly polysilicon).

The use of pure H₂ as a carrier gas prevented the formation of either "dendritics" or the silicon-rich brown film. The SiO₂ films thus deposited were etchable in diluted HF (5:1) and left the silicon surface clean (hydrophobic). The remaining investigations used H_2 as a carrier gas.

Deposition rates $(SiH_4-CO_2-H_2 \text{ system})$.—The parameters whose effect on deposition rate of SiO₂ has been investigated are SiH_4 mole fraction, SiH_4 : CO₂ ratio, deposition temperature, and H_2 flow rate.

Deposition rate vs. SiH_4 mole fraction.—Figure 2 shows the log of SiO₂ deposition rate as a function of silane mole fraction (X_{SiH_4}) , as determined by the entering gas composition. The slope of the graph is very nearly 1, which shows that the SiH_4 -CO₂ reaction in H_2 is a first-order reaction with respect to SiH4. For Fig. 2, the deposition temperature and the H_2 and CO_2 flow rates were kept constant. Note that the CO₂: SiH₄ ratio varied from ~ 20 to 200 during this experiment; however, it is important to point out that only the SiH₄ concentration is a variable for Fig. 2. Hence, Fig. 2 is the result of a classical experiment to isolate the order of the reaction with respect to SiH_4 (13).

Deposition rate vs. SiH₄:CO₂ ratio.-Figure 3 graphs the deposition rate as a function of CO₂/SiH₄ ratio for the two SiH₄ mole fractions. The deposition tempera-



Fig. 2. Deposition rate as a function of SiH₄ mole fraction in the feed. Deposition temperature, H_2 flow, and CO_2 flow kept constant.



Fig. 3. Deposition rate as a function of CO₂:SiH₄ ratio at two silane mole fractions, at 1000°C and at constant H₂ flow rate.

ture and the H_2 flow rate were kept constant. The deposition rate is independent of the CO₂:SiH₄ ratio in the experimental range of 7:1-120:1. Note that, for a fixed SiH₄ mole fraction (e.g., 1.9×10^{-4}), the deposition rate is independent of the CO₂ concentration.

These results are consistent with the classical "method of excesses" or "isolation technique" (14); i.e., when a large excess of one chemical is used as compared with another, the reaction rate is independent of the concentration of the chemical being used in large excess. The lack of dependence of deposition rate on CO₂ concentration, however, is in total disagreement with

³ Constant angle reflection interference spectroscopy. ⁴ I-etch is a mixture of stock solution and HNO₃ in the ratio of 1:5. The stock solution is a mixture of CH₅COOH, HF, HNO₃ in a 1:2:5 ratio, saturated with iodine and allowed to settle overnight (14 hr).

the results reported by Swann and Payne (4) and by Kroll *et al.* (5). Both papers reported an increase in deposition rate with increasing CO₂: SiH₄ ratio. The likely reason for this discrepancy is the difference in reactor design. In both papers, a pedestal or pancaketype reactor was used where the flow of gas is at right angles to the wafer surface. In our reactor, the flow of gases is nearly parallel to the wafer surface. These two very different flow patterns will have a markedly different mass and energy transfer and, hence, possibly, different results.

Deposition rate vs. deposition temperature.—Figure 4 shows the deposition rate as a function of reciprocal temperature at a constant injected SiH₄ mole fraction of 1.9×10^{-4} . Two CO₂: SiH₄ ratios were used, 12 and 40, and the H₂ flow rate was kept constant at 110 liters/min. The activation energy obtained from Fig. 4 is 25.4 kcal/g mol (106.7 J/g mol).

Deposition rate vs. flow rate.—To determine whether the deposition rate of SiO₂ is limited by the surface chemical reaction rate or controlled by mass transfer, an experiment was performed in which the H₂ flow rate was varied from 60 to 115 liters/min. The deposition temperature was kept constant at 1000°C. The SiH₄ and CO₂ mole fractions were also constant at 1.9 × 10^{-4} and 1.14×10^{-2} , respectively. Figure 5 shows the results, with the deposition rate plotted against the square root of the flow rate.

For all practical purposes, the deposition rate is independent of the flow rate, and, hence, the SiH_4 - CO_2 reaction in H_2 is limited by the surface-chemical-reaction rate, with the experimental flow range 60-115 liters/min.

Rate expression (empirical).—Following the standard procedure for obtaining an empirical rate expression for any heterogeneous reaction (13), and knowing that the reaction is (i) independent of CO_2 concentration (Fig. 3), (ii) first order with respect to SiH₄



Fig. 4. Deposition rate as a function of 1/T, at constant H₂ flow rate and SiH₄ mole fraction. Two CO₂:SiH₄ ratios, 12 and 40.



Fig. 5. Deposition rate as a function of square root of flow rate at 1000°C. SiH₄ mole fraction constant at 1.9 \times 10⁻⁴. Constant CO₂:SiH₄ ratio of 60.

(Fig. 2), and (iii) surface-chemical-reaction-limited (Fig. 5), we can arrive at the following rate expression

$$r_{\rm SiO_2} = K_{\rm s} \ C^0_{\rm SiH_4} \ [1 - Y_{\rm SiH_4}]$$
 [1]

where $r_{\rm SiO_2}$ = deposition rate of SiO₂ (moles/min), $C^{0}_{\rm SiH4}$ = silane concentration in the feed (moles/liter), $K_{\rm s}$ = the rate constant for surface chemical reaction (liters/min), and $Y_{\rm SiH4}$ = fraction of silane converted to deposit.

The fraction of SiH₄ converted to SiO₂ can be calculated by mass-balance, and its value is small, *i.e.*, 0.02-0.15, depending on the deposition temperature. Thus, neglecting Y_{SiH_4} and expressing deposition rate in Å/min and concentration as mole fraction, we can rewrite Eq. [1] as

$$d_{\rm SiO_2} = K'_{\rm s} X^0_{\rm SiH_4}$$
 [2]

where $d_{\rm SiO2}$ is the deposition rate in Å/min, $X^0_{\rm SiH4}$ is the mole fraction of silane in the feed, and $K'_{\rm s}$ is the rate constant in Å/min. The value of $K'_{\rm s}$ has been calculated from the data of Fig. 2, at 1000°C, to be approximately equal to 10⁶ Å/min. Now

$$K'_{\rm s} = K'_0 \exp\left[-\Delta E/RT\right]$$
 [3]

where K'_0 is the frequency factor in Å/min and ΔE the activation energy. The activation energy is 25.4 kcal/g mole (Fig. 4), and the calculated value of K'_0 is 2 $\times 10^{10}$ Å/min.

Thus, the empirical rate expression for SiO_2 deposition is

$$d_{\rm SiO_2} = 2 \times 10^{10} \cdot \exp\left[-25\,400/RT\right] \cdot X^0_{\rm SiH_4} \qquad [4]$$

where R is the gas constant (1.98 cal/g mole $^{\circ}$ K) and T is temperature in $^{\circ}$ K.

Physical properties.—Table I lists the physical properties of SiO_2 grown from the SiH_4 - CO_2 - H_2 system as a function of deposition parameters and anneal conditions.

Refractive index.-The refractive index was measured by ellipsometry at 5460Å (mercury-light wavelength). The refractive index of deposited SiO₂ is very close to that of the thermal SiO_2 (1.462) (15). Owing to densification, the annealing treatment increases the refractive index of as-deposited samples. There also appears to be some effect due to the CO_2/SiH_4 ratio. However, although CO_2 : SiH₄ ratios greater than 20:1 do not seem to affect the refractive index within measurement accuracy, for a deposition temperature of 1050°C and a low CO₂/SiH₄ ratio of 12, the refractive index goes up, indicating that the film may be siliconrich. As Table I shows, only the third-place decimal in the refractive index was affected by the CO₂: SiH₄ ratio from 20:1 to 120:1. Ratios of $SiH_4:CO_2 \ge 50:1$ are preferred because the run-to-run refractive index reproducibility is considerably improved (i.e., ± 0.001 run-to-run).

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Deposition temperature (°C)	$\rm CO_2/SiH_4$	Densification in N_2 ambient		D - fun adding	Etch rate in	Etch rate in	D	Sample
		Temp (°C)	Time (min)	index (5460Å)	25°C (Å/sec)	25°C (Å/sec)	(g/cm ⁸)	(µm)
950	12			1.460	3.21	9.5	2.19	0.36
950	12	1100	30	1.462	2.1	7.2	2.28	0.38
1000	12			1.458	2.97	7.9	2.25	0.33
1000	12	1100	30	1.462	2.07	7.2	2.30	0.33
1050	12		_	1.469	_	8.2	2.10	0.21
1050	20	_	—	1.458	2.92	8.5	2.20	0.40
1050	20	1100	30	1.462	2.06	7.2	2.24	0.40
1000	20	_		1.458	_	8.8		0.10
1000	50	_		1.455		8.5	—	0.12
1000	60	-	B	1.454		9.1		0.12
1000	120	_	_	1.453		9.1	_	0.10

Table I. Physical properties of SiO₂ grown from SiH₄-CO₂-H₂.

* By weight loss method.

Infrared absorption spectra of a limited number of as-deposited samples were taken. All samples were deposited at 1000°C. First absorption maxima lay at \sim 1070 cm⁻¹ for all samples.

Etch rate.—Etch rate was determined by etching the samples in P-etch (15) [15 parts HF (49%), 10 parts HNO₃ (70%), and 100 parts H₂O]. Typically, SiO₂ deposited at 1000°C etched ~50% faster than thermal oxide. In P-etch, the etch rate appears to be a function of deposition temperature (Table I). Sample-to-sample variations in etch rate decreased as the deposition temperature was increased. All samples when annealed in N₂ at 1100°C for a half-hour had an etch rate of between 2.1 and 2.06 A/sec. The etch rate in 5:1 diluted HF also showed a drop upon annealing; however, this etchant did not delineate the etch rate as a function of deposition temperature.

Density.—Film density was measured by the weightloss method; *i.e.*, deposited wafers were weighed and then stripped and reweighed. The density of as-deposited samples appears consistently lower than that of annealed samples. The density of all samples varied between 2.1 and 2.3 g/cm³. The density of the annealed sample approached that of thermal oxide (2.27 g/cm³) within measurement accuracy.

Electrical properties.—Several samples were prepared from the SiH₄-CO₂-H₂ system at 1000°C, with the CO₂: SiH₄ ratio varying from 40:1 to 60:1. All wafers were n-type Si, <100>, 8.5-20 ohm-cm, 5.72 cm (2¼ in.) diameter. The total SiO₂ thickness deposited was ~1350Å. Most wafers were split in half after the SiO₂ deposition. One portion of each wafer was then annealed at 1050°C for 15 min in N₂ (standard anneal for thermal SiO₂). Then, clean 20-mil aluminum dots were evaporated on both halves of the wafers. The metallized wafers were annealed at 400°C for a halfhour in N₂.

Following are the results of measurements on MOS capacitors.

Dielectric strength.—Twenty MOS capacitor dots in each sample were biased in accumulation, and the bias voltage was ramped at a rate of approximately 1 V/sec. The capacitor leakage current was monitored with a picoammeter. The dielectric breakdown was considered to have occurred when the leakage was greater than or equal to 2 nA. All samples exhibited the same dielectric breakdown field (E_B) . There was no dependence on CO₂: SiH₄ ratio or the postdeposition anneal. The E_B value obtained was 7.8 \times 10⁶ V/cm, and the breakdown distribution obtained was very tight in every case, with a standard deviation $\sigma_{EB} \leq 0.1$ \times 10⁶ V/cm.

Dielectric constant.—The thickness measured by ellipsometry and C-V measurements agreed within 50Å in all cases. This leads to the conclusion that the dielectric constant lies between 3.8 and 4.0. Annealed halves of wafers were thinner by \sim 30Å than the nonannealed halves. This means that there is densification of the order of 2-3% upon annealing. Oxide fixed charges (Q_{ox}) .—The fixed oxide charges were measured by means of the C-V technique. There was no influence of CO₂: SiH₄ ratio on the fixed charges; however, annealing showed the expected reduction in fixed charges. The Q_{ox} for nonannealed wafers was 2.8 $(\pm 0.2) \times 10^{11}$ cm⁻², and the Q_{ox} for annealed wafers was 1.3 $(\pm 0.5) \times 10^{11}$ cm⁻².

Mobile charges (Q_m) .—Mobile charges were measured by applying $\pm 2 \times 10^6$ V/cm for 10 min at 200°C. This technique is similar to the one used by Kriegler *et al.* (16). The shift in flatband under positive bias was converted into mobile charge. In no case was the shift in the flatband under negative bias taken into account, for two reasons:

1. In most cases, the shift in the flatband under negative bias was negligible (*i.e.*, ≤ 25 mV). This also means that the mobile charges were present at the metal/SiO₂ interface.

2. In some cases, the flatband shift was significant under negative bias (*i.e.*, ≥ 50 mV), but the direction of the shift was wrong, *i.e.*, as if more positive charges were being accumulated at the SiO₂/Si interface. This effect (discussed in greater detail under Stability) is due to fast surface-state generation at the SiO₂/Si interface (17).

There was no measured effect of CO₂: SiH₄ ratio on mobile charge. The annealed wafers had a mobile charge of $<1 \times 10^{10}$, whereas the nonannealed wafers showed a mobile charge of 2.7 (±0.5) × 10^{10} cm⁻². The apparent higher mobile charges in nonannealed wafers are most likely due to run-to-run variations of the Al evaporator. The nonannealed halves of wafers were metallized first. Thermal oxide monitor wafers in the above two metallization runs were checked and showed the same general trend as the CVD oxide wafers.

Fast surface states (N_{FS}).—Fast surface states were determined by the quasistatic technique of Kuhn (18). This technique was modified after Castange (19) and Kerr (20). The modification involved the use of a high-frequency *C*-*V* trace in place of the ideal. The N_{FS} was obtained from accumulation to onset of inversion by comparison of the high- and low-frequency *C*-*V* traces.

$$N_{\rm FS} = \frac{C_{\rm FS}}{q} = \left[\frac{C_{\rm LF} \cdot C_{\rm OX}}{C_{\rm OX} - C_{\rm LF}} - \frac{C_{\rm HF} \cdot C_{\rm OX}}{C_{\rm OX} - C_{\rm HF}}\right] \frac{1}{q} \quad [5]$$

where $C_{\rm FS}$ = capacitance due to fast surface states, $C_{\rm OX}$ = oxide capacitance, $C_{\rm LF}$ = low-frequency capacitance at a given voltage on the metal electrode, $C_{\rm HF}$ = highfrequency capacitance at a given voltage on the metal electrode, and q = electronic charge 1.6 \times 10¹⁹.

Equation [5], in which all capacitances are per unit area, determines $N_{\rm FS}$ as a function of applied electrode voltage. This voltage can be readily converted into surface potential [e.g., Kuhn (18)], so $N_{\rm FS}$, as a function of surface potential, is given in this investigation.

The fast surface-state densities are generally small in all samples. Annealed samples show somewhat higher $N_{\rm FS}$ than nonannealed samples. The difference in the two cases, however, is not considered significant,



Fig. 6. Change of flatband voltage under the influence of temperature-bias stressing.

and all samples measured can be adequately represented by an $N_{\rm FS}$ value of 1.5 (±0.5) \times 10¹⁰ cm⁻² · eV⁻¹ (at mid-bandgap).

Stability-As shown in Fig. 6, 50-hr stress data on some samples were accumulated at 200°C and 2 imes 106 V/cm with both polarities on the metal of the MOS capacitor. The positive-bias data confirm the shortterm stress data. There is a shift in the flatband voltage within the first hour and then a fast leveling off. This can be explained by the movement of mobile ions. Under negative bias, there is again a negative shift, the final value of which is larger for the annealed wafers than for the nonannealed wafers. There was no discernible dependency of $V_{\rm FB}$ shift on the CO₂: SiH₄ ratio. Negative shifts under negative bias are commonly attributed to an increase of fast surface-state density (17). It was not expected that the nonannealed wafers would display fewer fast surface states after temperature bias stressing.

To check the above expectation, several MOS capacitors on both annealed and nonannealed wafers were stressed for 20 hr at $\pm 2 \times 10^6$ V/cm and 200°C. Most of the observed shift in V_{FB} occurs within this time span (Fig. 6). Table II presents the initial and final values of the N_{FS} at mid-bandgap. Note that there is a significant difference between annealed and nonan-

Table II. Fast surface states as a function of temperature-bias stress and postdeposition high temperature (1050°C, 15 min, N_2) anneal

	$N_{\rm FS}~{ m cm}^{-2}~{ m eV}^{-1}$ (at mid-bandgap) $ imes~10^{10}$					
Sample	Initial	After 20 hr of +2 × 10° V/cm and 200°C	After 20 hr of -2×10^{9} V/cm and 200°C			
As deposited Annealed	1.1 (±0.3) 1.8 (±0.2))	1.2 (±0.3) 3.1 (±0.5)	$2.5 (\pm 0.3)$ $6.6 (\pm 0.7)$			

* Note: Values in parentheses are twice the standard deviation.

nealed samples and, contrary to the above expectation, the annealed samples show higher, fast surface-state density after temperature- and negative-bias stressing. The behavior of the annealed samples is much like the dry, O_2 -grown thermal oxides (17), whereas the nonannealed wafers appear to characterize the CVD oxides.

The behavior of the CVD oxides investigated is not believed to be limited to oxides deposited in SiH₄- CO_2 -H₂. This effect is most likely due to the deposition temperature used in this case (*i.e.*, 1000°C). Thus, the high-temperature postdeposition anneal deteriorates the stability of the CVD oxides under temperature- and negative-bias stressing.

Discussion

It has been shown that the SiH_4 -CO₂ reaction is first order with respect to SiH₄. This was determined by using the "method of excesses," or "isolation," technique (14); i.e., CO2 had considerably larger concentration than SiH₄. Therefore, as expected, the reaction rate was independent of the CO₂ concentration. The same technique (i.e., excess SiH_4 compared with CO_2) or the use of molar ratios of SiH_4 and CO_2 cannot isolate the reaction order with respect to CO₂, because, in both cases, silicon-rich films are deposited (i.e., no longer SiO_2). There is no other known technique that would isolate reaction order with respect to CO₂. Thus, the experimental data cannot firmly support a reaction mechanism, and none will be postulated here. However, we shall discuss our results in the light of the mechanism previously postulated.

Tung and Caffrey (1), Steinmaier and Bloem (21), and Rand and Ashworth (8) proposed a two-step kinetic mechanism for SiO_2 deposition from $SiCl_4$ - CO_2 -H₂ and $SiBr_4$ -CO₂-H₂. The first step involves socalled "water-gas" reaction

$$H_2 + CO_2 \rightleftharpoons H_2O + CO$$
 [6]

The second step involves oxidation (hydrolysis) of silicon halides with H_2O . Similar two-step kinetics may also be written for SiH₄, the second step being

$$SiH_4 + 2H_2O \rightarrow SiO_2 + 4H_2$$
[7]

These authors realized that intermediate-reaction steps must exist, *e.g.*, that reactions [6] and [7] may proceed via a free-radical chain mechanism or any other equally probable path. It is also generally accepted that the water-gas reaction is the slower and, hence, the rate-controlling step.

Then, Tingey (22) experimentally determined the forward rate expression of reaction [6] in the temperature range of 800°-1050°C. The experimentally determined activation energy for H_2O formation from H_2 and CO_2 is 78 kcal/g mole (22). Therefore, if the water-gas reaction is rate controlling for SiO₂ deposition from SiH₄-CO₂ reaction in H₂, the observed activation energy should be of the order of 78 kcal/g mole. We have obtained an activation energy of 25.4 kcal/g mole for SiO₂ deposition. These results are inconsistent with the water-gas mechanism. Only the Steinmaier and Bloem (21) results are consistent with water-gas reaction. These authors obtained an activation energy of 82 kcal/g mole for SiCl₄-CO₂-H₂. However, Tung and Caffrey (1), who also studied the SiCl₄-CO₂-H₂ system, reported an activation energy of 51.6 kcal/g mole. Similarly, Rand and Ashworth (8) reported an activation energy of 30 kcal/g mole for the SiBr₄-CO₂-H₂ system in the temperature range of 800°-950°C. Thus, hardly any of the activation energy data involving CO2 and H₂ support the so-called water-gas mechanism.

The inconsistency of the activation energy data led us to perform several experiments, with hopes of answering a two-part question: (i) Does H₂O form in our reactor under the experimental conditions of flow? (ii) What physical evidence would be produced if H₂O were to form in the reactor? It was assumed that, if H₂O were formed, the thermal oxidation of silicon would occur in the absence of SiH₄. In the presence of SiH₄,

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we expected some homogeneous reaction (manifested by reaction-chamber clouding) besides the usual heterogeneous reaction. Several experiments, with results, are presented below.

Cleaned Si wafers were exposed to an H_2 and CO_2 ambient ($\leq 1.2\%$ CO₂) at 1000°C for 1 hr. The wafers were hydrophobic before and after exposure to the H_2 and CO₂ ambient. Ellipsometric measurements showed that the wafers had \leq 15Å of SiO₂ before and after. Now the question arose whether other oxidants produced similar results. This led us to repeat the above experiment with N₂O which resulted in the growth of \geq 600Å SiO₂ on the silicon wafers (23). To check whether the formation of SiO_2 from the N₂O and H₂ reaction was due to the H₂O formation or to the decomposition of N₂O and subsequent oxidation of silicon by oxygen, we repeated the experiment with N_2O and N₂. The resulting film was only ~ 150Å thick (23). Clearly, H₂O is formed when wafers are heated in N₂O and H_2 , whereas H_2O is not likely to form from CO_2 and H₂ under the flow conditions of the reactor. This conclusion is consistent with, and supported by, two facts: (i) when the $SiH_4-N_2O-H_2$ system is used for SiO_2 deposition (850°-1000°C), the reaction chamber clouds very rapidly (23), whereas when the SiH_4 -CO₂-H₂ system is used there is no evidence of reactionchamber clouding; (ii) the deposition rate of SiO_2 from the SiH₄-N₂O-H₂ system is ~ 2-10 times higher than the SiH₄-CO₂-H₂ system, depending on deposition temperature (850°-1000°C) for identical SiH₄ and oxidant mole fraction (23).

Experiments with mixtures of H_2 and O_2 and of N_2 and O_2 showed results similar to those of H_2 and N_2O and of N_2 and N_2O ; *i.e.*, a higher thickness of thermal SiO was grown with the H_2 and O_2 mixture. Clearly, H_2O was being produced by the reaction of hydrogen and oxygen. We then attempted to study the rate of reaction of SiH₄ with H_2O using the SiH₄-O₂-H₂ system. The task, however, was nearly impossible because of the chamber clouding which necessitated reactor cleaning after every run. We were able to obtain deposition-rate data at 800°-850°C, however, before abandoning the effort. The deposition rate of SiO₂ from the SiH₄-O₂-H₂ system was nearly an order of magnitude greater than that obtained from the SiH₄-CO₂-H₂ system for identical temperature, SiH₄, and oxidant mole fractions (24). The results of the experiments with $SiH_4-O_2-H_2$ and $SiH_4-N_2O-H_2$ are at variance with the water-gas mechanism for the SiH₄-CO₂-H₂ system because, if H_2O is produced from CO_2 + H_2 , which subsequently reacts with SiH_4 to produce SiO_2 , then the deposition rate of SiO₂ should not significantly change, irrespective of the source of H₂O.

Finally, Tingey (22) experimentally showed that the water-gas reaction is homogeneous, i.e., that H₂O is produced in the gas phase. This should result in the homogeneous reaction of SiH_4 and H_2O ; yet the SiH_4 - CO_2 -H₂ reaction is singularly characterized by the lack of homogeneous reaction, i.e., no clouding of the reaction chamber by gas-phase reaction. The above experimental and activation energy data neither support nor are consistent with the water-gas reaction mechanism for SiH_4 -CO₂-H₂. It is therefore probable that the SiH₄-CO₂ reaction could proceed via direct oxidation of silane, as suggested by Swann and Payne (4), some complex free-radical chain mechanism, as alluded to by Rand and Ashworth (8), or any other mechanism that does not include water-gas reaction as a step.

Summary and Conclusion

We have presented the results of SiH_4 -CO₂ reaction in H_2 in the temperature range $850^{\circ}-1050^{\circ}C$. We have used a multiple-wafer reactor in sharp contrast to Swann and Payne's single-wafer reactor. Our results should find more application in CVD practice because the flow of gases is nearly parallel to the wafer surface. Unlike Swann and Payne, we have been able to isolate the order of the SiH₄-CO₂ reaction with respect to SiH₄

and the activation energy and frequency factor of the reaction. However, care should be exercised in extrapolating and using these results to predict the SiO₂ deposition rate for SiH₄ concentrations larger than 0.06-0.07% because, at higher concentrations than these, the SiO₂ films become silicon-rich; *i.e.*, codeposition of Si and SiO₂ occurs.

We have shown that the physical and electrical properties of SiO₂ deposited at 1000°C are comparable to those of steam-grown oxide. In fact, the fast surfacestate densities are considerably lower in these CVD oxides than in steam-grown oxides. The low level of fast surface-state density may be attributed to the use of H₂ during deposition. The stability of these oxides under temperature (200°C) and bias \pm 2 \times 10⁶ V/cm has been demonstrated. The negative effects of postdeposition anneal in N_2 at a temperature higher than the deposition temperature have also been shown.

The use of CO₂ does not result in a homogeneous reaction, especially at higher temperatures, *i.e.*, of the order of 1000° C. This is a significant advantage, since it keeps the reactor down time to a minimum. However, the use of CO_2 has often raised the possibility of carbon inclusion. Though we do not have any direct evidence of the presence or absence of carbon in SiO₂ films deposited from SiH_4 -CO₂-H₂, trace quantities of carbon may well be incorporated in these films. None of the measured physical and electrical properties, however, show any unusual or detrimental effects of these trace impurities, if present.

Finally, the CVD SiO_2 film from SiH_4 -CO₂-H₂ could be readily used as a photolithographic mask for films like Si_3N_4 and in the field or the gate region of an integrated FET circuit.

Acknowledgments

The authors are indebted to A. A. Kozul and T. O. Williams for preparing the samples.

Manuscript submitted April 10, 1974; revised manuscript received July 16, 1975. This was Paper 50 pre-sented at the San Francisco, California, Meeting of the Society, May 12-17, 1974.

Any discussion of this paper will appear in a Discus-sion Section to be published in the December 1976 JOURNAL, All discussions for the December 1976 Discussion Section should be submitted by Aug. 1, 1976.

Publication costs of this article were partially assisted by IBM Corporation.

REFERENCES

- 1. S. K. Tung and R. E. Caffrey, *Trans. Met. Soc. AIME*, 233, 572 (1965).

- AIME, 233, 512 (1903).
 2. M. J. Rand, This Journal, 114, 274 (1967).
 3. T. L. Chu, J. R. Szedon, and G. A. Gruber, Trans. Met. Soc. AIME, 242, 532 (1968).
 4. R. C. G. Swann and A. E. Payne, This Journal, 116, 104 (1960). 1014 (1969)
- 5. W. J. Kroll, R. L. Titus, and J. B. Wagner, Abstract 13, p. 31, The Electrochemical Society Extended Abstracts, Spring Meeting, Houston, Texas, May 7-11, 1972.
- M. L. Barry, in "Chemical Vapor Deposition, 2nd International Conference," John M. Blocher, Jr. and James C. Withers, Editors, The Electrochemical Society Softbound Symposium Series, New York (1970)
- 7. T. Miyazaki, I. Yoshida, M. Horiuchi, and T. Tokuyama, ibid., p. 571. 8. M. J. Rand and J. L. Ashworth, This Journal, 113,
- 48 (1966).
- (1966).
 L. V. Gregor, in "Physics of Thin Films," Vol. 3, p. 133, Georg Hass and R. E. Thun, Editors, Aca-demic Press, Inc., New York (1966).
 V. Y. Doo, D. W. Boss, R. Valletta, and W. A. Pliskin, Paper 42, presented at Electrochemical Society New York, New York, Meeting, May 4-9, 1960 1969.
- 11. E. O. Ernst, D. J. Hurd, and G. Seeley, U. S. Pat. 3, 424,629, Assigned IBM Corporation.
- F. G. Allen, J. Appl. Phys., 28, 1510 (1957).
 O. Levenspiel, "Chemical Reaction Engineering," John Wiley & Sons, Inc., New York (1967).

- 14. G. W. Castellan, "Physical Chemistry," p. 607, Addison-Wesley Publishing Co., Inc., Reading, Mass. (1964)
- 15. W. A. Pliskin and H. S. Lehman, This Journal, 112, 1013 (1965).
- 16. R. J. Kriegler, Y. C. Cheng, and D. R. Colton, ibid., **119,** 388 (1972).
- 17. A. Goetzberger, A. D. Lopez, and R. J. Strain, ibid., 120, 90 (1973).
- M. Kuhn, Solid-State Electron., 13, 873 (1970).
 R. Castange, C. Y. Lebd. Se'anc, Acad. Sci. (Paris), 267, 866 (1968).
 D. R. Kerr, Private communication.
- 21. W. Steinmaier and J. Bloem, This Journal, 111, 206 (1964).
- G. L. Tingey, J. Phys. Chem., 70, 1406 (1966).
 R. L. Bratter and A. K. Gaind, Unpublished work.
- 24. R. L. Bratter, Unpublished work.

Fabrication of P-Channel Silicon Gate LSI Devices with Si₁N₄/SiO₂ Gate Dielectric

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ABSTRACT

Processing of p-channel silicon gate devices with a Si₃N₄/SiO₂ gate dielectric is described in detail. Some attractive features of this particular process include polysilicon to silicon contacts, improved metal step coverage obtained with a glass flow anneal, low fast surface-state density for good 1/f noise performance, and high parasitic field threshold voltages obtained by ion implantation of arsenic.

Because of the work function difference between p-type polycrystalline silicon gate electrodes and lightly doped n-type silicon substrates, most p-channel silicon gate devices have been fabricated on <111>oriented silicon substrates. This avoids the possibility of very low threshold or depletion mode devices which can result if <100> oriented substrates are used. This result is a direct consequence of the lower fixed positive charge density at the SiO₂-Si interface of <100>oriented silicon substrates. However, for devices used in analog signal processing, the use of <111> material will degrade the 1/f noise performance of such IGFET'S because of the high fast surface-state density associated with this orientation. To take advantage of the better 1/f noise performance obtained on <100>material and still maintain a reasonable threshold voltage (-1.3V), silicon gate devices can be fabricated with a Si_3N_4/SiO_2 gate dielectric. The desired threshold voltage can be obtained by controlling the amount of fixed positive charge at the nitride-oxide interface formed during the nitride deposition. Other advantages of the dual dielectric structure are: (i) Si_3N_4 is superior to SiO_2 as a boron diffusion barrier (2), (ii) the composite structure has better integrity than a SiO_2 gate, and (iii) higher transconductance FET's result from the higher dielectric constant of Si_3N_4 .

Other attractive features of this particular process are polysilicon-silicon contacts which allow very high packing densities because they take up less area than metal-silicon contacts, improved metal step coverage obtained with a glass flow anneal (4), and high parasitic field threshold voltages obtained by ion implantation of the surface (except active regions) with arsenic.

Process Sequence

An outline of the process is given in the flow chart in Table I. The starting wafer material is 4-8 ohm-cm, <100>, n-type. The first step is the formation of the gate oxide. This is thermally grown in an atmosphere of 10% HCl + 90% O_2 for 13 min at 1000°C. The resulting oxide thickness is about 300Å. This is followed by the deposition of the gate nitride. About 800Å of

* Electrochemical Society Active Member. Key words: polysilicon, insulator, MOSFET, noise.

silicon nitride is deposited at 750°C with an ammonia to silane ratio of 250:1. In the next step, the first photoengraving operation is performed. A mask is applied to define islands of nitride which will ultimately become the active devices. A photoresist mask is used and the silicon nitride is plasma etched (5). The 300Å of oxide under the nitride stops the plasma etching process. With the photoresist still on the wafer, an arsenic implant is next performed at an energy of 80 keV and a dose of 5×10^{11} cm⁻². The photoresist acts as a mask which prevents penetration of the arsenic into active device regions. After photoresist removal, a cross section of a transistor structure appears as in Fig. 1. The transistor gate, source, and drain will be formed in the region defined by the island of silicon nitride. The arsenic implant in the surrounding regions will prevent parasitic transistor action by keeping the surface from inverting at voltages less than -35V. The next processing step forms the field oxide region by steam oxidation at 1100°C.

About 10 kÅ of SiO₂ is grown in 2.5 hr in the regions surrounding the nitride islands. Only about 300Å of the nitride is oxidized. This is removed by dip etching for 30 sec in a 10:1 HF solution. At this point in the process, the structure is annealed in dry O2 for 30 min at

Table I. Process flow chart

- 1. 2. 3. 4.
- 5.
- 6. 7. 8,

- 10.
- Starting material: 4-8 ohm-cm, <100>, n-type Gate oxidation: 300Å (10% HCl + 90% O₂, 13 min at 1000°C) Gate nitride: 800Å (NH₃/SH₄ = 250 at 750°C) Device window mask (plasma etch Si₃N₄) Ion implant arsenic (E = 80 keV, dose = 5 × 10¹¹ cm⁻²) Steam oxidation: 10 kÅ (H₂ + O₂, 150 min at 1100°C) Etch oxidized nitride (~300Å) O₂ anneal (30 min at 1050°C) Polysilicon-silicon contact window mask Polysilicon gate and interconnect mask (plasma etch poly and nitride, chem. etch gate oxide to define self-aligned gate) Boron diffusion (diborane source) a. Deposition: 18 min at 980°C b. Drive: 60 min, O₂ at 1000°C Phosphorus-doped oxide deposition (~5% phosphorus, 15 kÅ) Via and contact window mask Glass flow anneal (02, 20 min at 1050°C) Hydrogen anneal (30 min H₂ at 800°C) Dip etch 30 sec in 10:1 HF (removes oxide from windows in doped glass) Metallization (10 kÅ of Al-Si) Metal interconnect mask 11. 12.
- 13.
- 14. 15. 16.
- 17.
- 18.
- Metal interconnect mask Sinter metal (30 min, N_2 at 500°C) 19. 20.

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