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Oxygen Incorporation during Low Temperature Chemical Vapor Deposition Growth of Epitaxial Silicon Films

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ABSTRACT

We have studied the incorporation kinetics of oxygen during the chemical vapor deposition (CVD) growth of epitaxial silicon and silicon-germanium layers at temperatures between 700 and 750°C. In this temperature range, the incorporation of oxygen into the growing film is a kinetically driven process and is not governed by equilibrium conditions. Oxygen concentrations exceeding the solid solubility for interstitial oxygen in silicon can be incorporated into the epitaxial layers. We determine an effective sticking probability for oxygen on the surface of silicon under CVD growth conditions and find it to be 100 times lower than that found in ultrahigh vacuum experiments. This reduction in sticking is due to both hydrogen surface coverage and boundary layer effects. We also have determined the maximum oxygen contamination level allowed in the gas stream for the CVD growth of low oxygen content silicon films.

The role of oxygen in the silicon has been studied extensively since the beginning of the semiconductor era. Characteristics of oxygen in bulk silicon emerged in the middle 1950s with the infrared absorption work of Kaiser *et al.*[1,2] Many properties of oxygen in Czochralski grown silicon were found to be beneficial, such as the added mechanical strength[3] and metallic gettering properties[4,5] due to oxygen precipitates. The interaction of oxygen with the silicon surface also has received endless attention because of the importance of SiO_2 to the electronics industry (Ref. 6 contains an extensive reference list of work in this area). Surface scientists have concentrated on the initial formation of chemical bonds and the stability of oxygen on silicon surfaces over a wide range of temperatures.[7,8]

Here, we investigate the surface interaction of oxygen and silicon during low temperature CVD by studying the incorporation of oxygen during the growth of epitaxial silicon layers. This study is to determine the conditions for the growth of high quality silicon (and silicon-germanium) epitaxial layers by CVD performed at temperatures <800°C. To determine conditions for the growth of high quality films, we must study the characteristics of oxygen incorporation during CVD. With this information we can determine the effective sticking coefficient for oxygen under growth conditions and proceed to determine the conditions for growing low oxygen content films.

Background

For any crystalline growth technique, a clean defect-free surface is needed for epitaxial growth. During silicon epitaxy, surface oxide formation can break the pattern of the silicon surface and cause noncrystalline growth and highly defective films through the formation of stacking faults and hillock structures.[9,10] Experimental results of oxygen stability on the silicon surface have been used as guidelines by which operating points for epitaxial reactors are designed. Figure 1 describes the stability of oxygen on clean (100) silicon in 600 to 1000°C and is from the experiments of Lander *et al.*[8] The work demonstrates the competing processes of adsorption of oxygen to form SiO_2 and desorption of oxygen as SiO with the following reactions

$$\frac{1}{2}O_2 \rightarrow O(ads) \qquad [1]$$

$$Si + 2\ O(ads) \rightarrow SiO_2 \qquad [2]$$

$$Si + SiO_2 \rightarrow 2SiO(g) \qquad [3]$$

where Eq. 1 and 2 describe the adsorption of oxygen and the formation of SiO_2, and Eq. 3 describes the desorption of oxygen in the form of SiO. Similar experiments were performed by Ghidini *et al.*[7,11] to extend the results to higher substrate temperatures and oxygen pressures.

According to the Lander study, as the partial pressure of oxygen in the chamber increases and the substrate temperature decreases, oxygen remains more stable on the silicon surface. The result is the formation of SiO_2. The sticking probability of oxygen on the clean silicon surface (no passivating layer) has been determined as approximately 0.01 [12] and relatively independent of temperature. Under the conditions of high substrate temperature and low oxygen pressures, the surface remains free of oxygen due to the desorp-

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tion of SiO from the substrate surface. This condition creates a clean crystalline surface on which to grow epitaxial silicon layers. The pair of lines in Fig. 1 delineates the regimes of oxide-stable and oxide-free surface conditions. Historically, these experimental results have dictated the conditions for epitaxial growth of silicon. Our main focus here is to show that these conditions are overly pessimistic for growth by CVD. The reports of sticking coefficients in the range of 10^{-8} to 10^{-4} (pre- and postincubation period measurements) by Agnello *et al.*[13,18] illustrate this argument. Here, we also find the sticking coefficient for oxygen on the surface of silicon to be reduced by almost two orders of magnitude during CVD growth.

The data of Fig. 1 indicate that to obtain an oxygen-free silicon surface at 700°C, the partial pressure of oxygen in the growth environment must be $<10^{-8}$ Torr. Consequently, for a growth pressure of 1 atm (760 Torr), the source gases must be purified to a level <0.01 ppb (parts O_2 per billion parts source gas). This is beyond the range of gas purifiers available on the market today. To circumvent this restriction on gas purity, the technique of ultrahigh vacuum (UHV)/CVD was developed.[14] By reducing the growth pressure to 10^{-3} Torr, as done in UHV/CVD, the restriction on gas purity is relaxed several orders of magnitude. With a growth pressure of 10^{-3} Torr, the source gas purity need only be <10,000 ppb of oxygen to remain < the 10^{-8} Torr of oxygen required for a clean silicon surface at 700°C. UHV/CVD growth conditions yield high quality epitaxial films as demonstrated by the excellent electronic performance of devices fabricated in such material.[15] However, our central point is to demonstrate that such low growth pressures (and UHV) are not required for low temperature silicon CVD. Since the advent of UHV/CVD in 1984, it has been demonstrated that high quality oxygen-free silicon films may be grown at 700°C and a pressure of 6 Torr by CVD,[16] and later others have grown high quality epitaxial silicon at 750°C and atmospheric pressure,[17] without gas purity of 0.01 ppb. Clearly, the criteria imposed by the UHV clean surface experiments are too pessimistic when dealing with CVD growth conditions. Similar arguments can be made for water vapor (which in practice may be worse than O_2), but we give arguments and experiments relating to oxygen, keeping in mind the principle relates to water vapor as well. We chose to study O_2 in these experiments because the reactor memory is much shorter for oxygen that it is for water vapor. Once the oxygen source is extinguished, the partial pressure of O_2 decreases rapidly and contamination in subsequent layer growth is minimized.

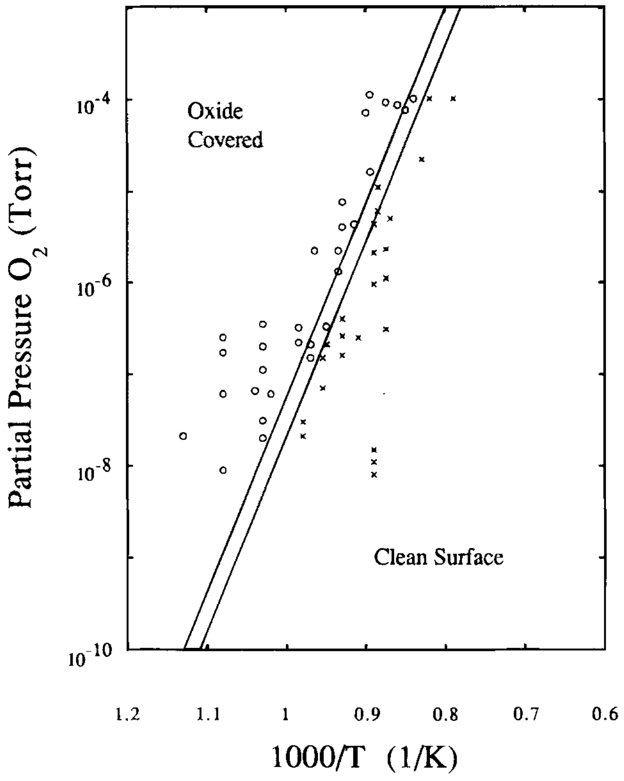

Fig. 1. Oxygen stability data of Lander and Morrison[8] for (100) Si. As the partial pressure of oxygen is increased and the substrate temperature decreased, oxygen is made more stable on the silicon surface. As the temperature is increased and the oxygen partial pressure decreased, the surface remains clean; (○) oxide covered, (×) oxide free.

We first determine experimentally the incorporation rate of oxygen in the growing films as a function of growth conditions. We then model this incorporation taking into account both boundary layer mass-transport effects and the effect of hydrogen surface coverage on the sticking probability. Oxygen incorporation, both onto a static surface (no growth) and during epitaxial growth in a CVD environment has been studied recently by Agnello and Sedgwick[13,18] and work by Greve[19] has covered many aspects of low temperature CVD including oxygen incorporation during growth. The work by Agnello *et al.*[13,18] demonstrates the effect of a hydrogen passivation layer on the incubation period (and hence sticking coefficient) before oxide formation on a silicon surface becomes significant. In our work, oxygen incorporation during CVD growth between 700 and 750°C is studied. Our results give further evidence to the reduced sticking of oxygen to silicon in a hydrogen ambient, and we also determine a linear relationship between the oxygen in the gas flow and the oxygen concentration in the epitaxial film.

Experiment and Results

The growth experiments were performed in a single-wafer load-locked rapid thermal chemical vapor deposition (RTCVD) system described in detail elsewhere.[20] The system base pressure is approximately 10^{-8} Torr and is determined by pumping the unit overnight with a turbomolecular pump. All growth, however, is performed at 6 Torr using a mechanical pump. Assuming infinitely pure source gases, the oxygen contamination level due to the reactor background at the growth pressure is calculated to be at most 1 ppb. This satisfies the conditions for a clean silicon surface at 700°C as imposed by the UHV experiments discussed above.

The oxygen-doped layers (Si:O) were grown on (100) float zone silicon substrates which were chemically cleaned in a bath of H_2O_2:H_2SO_4 followed by a rinse in dilute hydrofluoric acid prior to loading into the growth chamber. Float zone substrates were employed to minimize the contribution of oxygen from the substrate when determining the oxygen content of the epitaxial layers. The wafers were then cleaned *in situ* at 1000°C in a 250 Torr H_2 ambient for 60 s. The system pressure was then reduced to 6 Torr for the growth of a high temperature (and hence a low oxygen content) 1.5 μm buffer layer using dichlorosilane (DCS) as the silicon source gas. The temperature was then reduced for the growth of the Si:O layer in 700 to 750°C. At this point, silane replaced DCS as the silicon source gas and the flow was allowed to stabilize before the oxygen was introduced to the growth environment. The wafer temperature during the oxygen-doped silicon growth was controlled precisely by a closed-loop measurement system based on optical transmission of infrared radiation.[21] Control of the wafer temperature in this range is critical because the growth rate of the epitaxial films depends exponentially on temperature.

The oxygen is introduced to the growth environment in an argon carrier through a calibrated mass flow controller. The incorporation data are shown in Fig. 2. The different curves correspond to different growth temperatures and hence growth rates and the source gas is assumed to be silane except where noted. The growth rates range from 13 nm/min at 700°C to 50 nm/min at 750°C. The oxygen concentrations were determined by Fourier transform infrared spectroscopy measurements calibrated by secondary

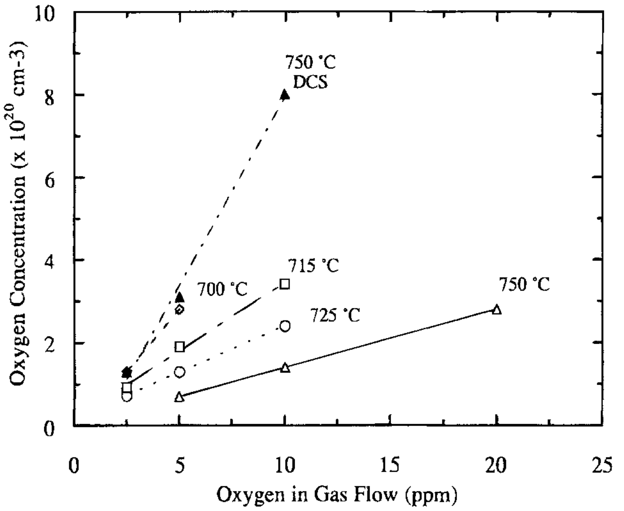

Fig. 2. Oxygen content of epitaxial silicon layers as a function of gas concentration. The oxygen concentrations in the solid are linear with the gas-phase concentrations and exceed the peak solid solubility for oxygen in silicon. The different lines correspond to various growth temperatures and growth rates. The source gas is silane except where dichlorosilane (DCS) is indicated.

ion mass spectrometry (SIMS). We see from Fig. 2 that the oxygen incorporation is linearly proportional to the oxygen concentration in the gas flow and decreases at high temperature as the growth rate increases. This linear relationship is different from the superlinear relationship seen in Ref. 13. If one defines an effective oxygen incorporation efficiency, η, as

$$\eta = \frac{[\mathrm{O}]_s}{p_{\mathrm{O}_2}} \cdot G \qquad [4]$$

where $[\mathrm{O}]_s$ is the concentration of oxygen in the solid and G is the growth rate. p_{O_2} is defined as the average partial pressure of O_2 in the reactor (this assumes a uniform distribution of O_2 in the reactor). η has the units of $\mathrm{cm}^{-2} \cdot \mathrm{Torr}^{-1} \cdot \mathrm{s}^{-1}$, and one sees that η is independent of temperature (Fig. 3). This suggests that we are in a simple kinetic regime for oxygen incorporation where a fixed fraction of oxygen reaching the surface sticks and that the desorption is not significant. Although the growth from a DCS source had slower growth rate and a higher oxygen concentration than growth from a silane source, η was similar. This implies that the chlorine from the DCS does not affect the oxygen incorporation. Further evidence of a kinetic regime of oxygen incorporation is given since oxygen incorporation levels of 5×10^{20} cm^{-3} can be achieved at 700°C, while the solid solubility is only 5×10^{16} cm^{-3} at that temperature.

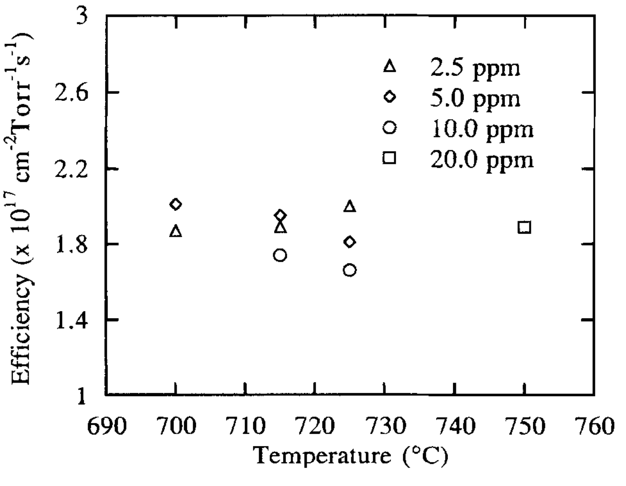

Fig. 3. Effective oxygen incorporation efficiency as a function of temperature. The incorporation efficiency is relatively independent of temperature which suggests a kinetic process for oxygen incorporation.

The oxygen-doped layers exhibit specular reflection from the wafer surface with no signs of haze due to defect formation for oxygen concentrations up to approximately 10^{20} cm^{-3}. A microscopic study of the films is being performed currently by transmission electron microscopy. We have characterized the films both electronically and structurally and reported the results elsewhere.[22] The films are semi-insulating due to trap levels introduced into the semiconductor bandgap, and exhibit classic characteristics of space charge limited current in trap-filled insulators. Even though the oxygen concentrations exceed the peak solid solubility, the films remain crystalline. The crystallinity was determined from x-ray diffraction techniques and electron channeling patterns on crystalline material grown directly on the semi-insulating layer.

We have neglected the desorption of oxygen from the silicon surface in our model for oxygen incorporation under the assumption that we are well below the desorption temperature for SiO. The pair of lines in Fig. 1 (the Lander and Morrison data) corresponds to the situation where the desorption rate of SiO equals the sticking rate of oxygen. Under UHV conditions, the hit rate of oxygen is governed by the kinetic theory of gases. Therefore, we can estimate the desorption rate of oxygen from the silicon surface using the data of Lander and Morrison. The oxygen flux incorporating in the layers of our experiment is approximately 1×10^{13} cm^{-2} s^{-1}. According to the Lander experiment, the desorption temperature to accommodate this flux is approximately 850°C. At 750°C, the desorption flux is approximately 7×10^{11} cm^{-2} s^{-1}. Thus we see that our assumption of negligible desorption below 750°C is valid.

Being in a kinetic regime implies that the atomic oxygen incorporation rate, R (atom cm^{-2} s^{-1}), can be defined as

$$R = 2 S_{\mathrm{eff}} v_{\mathrm{th}} C_{\mathrm{fs,O_2}} \qquad [5]$$

where v_{th} is the thermal velocity of O_2 just above the wafer surface (assuming a gas temperature at the wafer surface equal to the wafer temperature), $C_{\mathrm{fs,O_2}}$ is the free stream concentration of oxygen and is calculated assuming the gas percentages in the free stream are those introduced into the reactor. That is

$$C_{\mathrm{fs,O_2}} = 1.1 \times 10^{19} \left(\frac{\mathrm{K}}{\mathrm{cm}^3\ \mathrm{Torr}}\right) \frac{f_{\mathrm{O_2}}}{f_{\mathrm{Total}}} \frac{P_{\mathrm{Total}}}{T_{\mathrm{gas}}} \qquad [6]$$

where $f_{\mathrm{O_2}}$ and f_{Total} are the oxygen and total gas flow into the reactor, P_{Total} is the total gas pressure in the reactor and T_{gas} is the average gas temperature in the free stream. S_{eff} is an effective sticking coefficient which differs from the true sticking coefficient since $C_{\mathrm{fs,O_2}}$ differs from the true O_2 concentration just above the growth surface (as is modeled in detail later).

If our data is modeled according to the simple kinetic process described above (Eq. 5 and 6), one extracts an effective sticking coefficient, S_{eff}, of approximately 10^{-4}. This value is nearly two orders of magnitude below the accepted UHV value and was found by assuming an average gas temperature based on the wafer temperature and the reactor wall temperature and is consistent with other reported data.[13] These assumptions are discussed later.

Modeling

We develop a model of oxygen incorporation that is linear with oxygen concentration in the growth environment, consistent with the simple kinetic limit described earlier. Although the experimental levels of oxygen are far above those acceptable in high quality epitaxial layers (due to the intentional introduction of oxygen), we assume the results can be extrapolated to low oxygen concentrations as well. For example, the oxygen incorporation flux for 10 ppm O_2 in the gas flow at 6 Torr is found experimentally in our CVD work to be approximately 1.1×10^{13} atom cm^{-2} s^{-1}. If the effective sticking coefficient were 10^{-2}, as in the UHV clean surface condition, we would have expected the oxygen in-

Table I. Oxygen-doped silicon incorporation data.

Sample	Gas source	Wafer temperature T (°C)	$[O_2]$ ppm	$[O]_s$ (cm^{-3})	Growth rate (Å/min)	M	S_{CVD}
676	DCS	750	5	3.1×10^{20}	100	0.21	2.4×10^{-4}
685	DCS	750	2.5	1.3×10^{20}	100	0.17	1.9×10^{-4}
826	SiH_4	750	10	1.4×10^{20}	485	0.22	2.7×10^{-4}
858	SiH_4	750	5	7.0×10^{19}	485	0.22	2.7×10^{-4}
855	SiH_4	725	5	1.2×10^{20}	235	0.20	2.3×10^{-4}
856	SiH_4	725	10	2.4×10^{20}	235	0.20	2.3×10^{-4}
967	SiH_4	700	5	2.8×10^{20}	133	0.24	2.9×10^{-4}
968	SiH_4	700	2.5	1.3×10^{20}	133	0.21	2.4×10^{-4}
969	SiH_4	715	2.5	9.1×10^{19}	183	0.22	2.7×10^{-4}
970	SiH_4	715	5	1.9×10^{20}	183	0.23	2.8×10^{-4}

corporation flux to be approximately 10^{15} atom $\cdot$ $cm^{-2} \cdot s^{-1}$, approximately a factor of 100 greater. This reduction of the incorporation flux is extremely fortuitous for CVD and explains why conditions for epitaxy inferred from UHV experiments are overly pessimistic for CVD. To explain this, we examine CVD kinetics and find that this is due to (*i*) the slow nature of the mass transport of oxygen across a CVD boundary layer and (*ii*) the hydrogen passivation of the silicon surface.

Mass transport/boundary layer effects.—Gas flow and mass transport are complicated issues in CVD reactors. The simplest possible picture is the stagnant film model to describe the conditions for mass transport during CVD growth. In this model, the gas phase is separated into two regions, one which is well mixed and flows freely past the solid surface (free stream) and the other a stagnant layer (boundary layer) of thickness δ adjacent to the substrate surface which separates the free stream from the wafer. The boundary layer exists because of the frictional drag on the gas as it passes the surface of the wafer. The transport of gas across this boundary layer is by diffusion alone, with the following boundary conditions: (*i*) the gas concentration at the boundary-layer/free-stream interface is the free stream concentration, C_{fs}; and (*ii*) the concentration of gas just above the wafer surface is C_{surf}. The properties of boundary layer are determined by the carrier gas and are the same for all species in the gas flow.

We describe the incorporation kinetics for oxygen using a simplified Grove model for CVD.[23] For CVD, there are two rate-limiting steps: (*i*) gas transport to the substrate surface by diffusion across a boundary layer and (*ii*) the chemical reaction which occurs on the substrate surface to create the growing film. Step *ii* includes surface adsorption and all else that occurs on the wafer surface.

The transport of oxygen to the substrate surface is governed by Fick's first law which is repeated here to introduce reaction coefficients and is expressed as

$$F_{d,O_2} = h_{h,O_2} \cdot (C_{fs,O_2} - C_{surf,O_2}) \qquad [7]$$

where F_{d,O_2} is the net flux of oxygen atoms toward the substrate surface and h_{g,O_2} is the mass transfer coefficient for oxygen. The net consumption of oxygen by the surface is assumed to be linearly proportional to the oxygen concentration just above the surface and is represented as

$$F_{s,O} = 2v_{th}C_{surf,O_2}S_{CVD} = 2k_s \cdot C_{surf,O_2} \qquad [8]$$

where $F_{s,O}$ represents the flux of oxygen atoms consumed by the growing film, S_{CVD} is the true sticking coefficient of oxygen at the surface, and k_s is the surface reaction rate constant. The extra factor of two is to account for the two oxygen atoms per oxygen molecule. S_{CVD} differs from S_{eff} since C_{surf,O_2} (true near-surface concentration) is different from C_{fs,O_2} from Eq. 6. In steady state, the flux of oxygen atoms consumed by the surface and the flux of oxygen atoms diffusing toward the surface must be equal, or $2F_{d,O_2} = F_{s,O}$. From Eq. 7 and 8, we obtain the familiar expression for the near-surface concentration of oxygen, C_{surf,O_2}

$$C_{surf,O_2} = \frac{h_{g,O_2}}{k_s + h_{g,O_2}} \cdot C_{fs,O_2} \qquad [9]$$

The flux of silicon atoms consumed at the surface is the product of the growth rate (G_{Si}) and the atomic density of silicon atoms in the silicon crystal (5×10^{22} cm^{-3}). The silicon flux can be determined experimentally at any temperature. From the silicon flux and Eq. 8 and 9, we determine the density of oxygen atoms in the growing film by way of a simple burying process as

$$[O]_s = \frac{k_s h_{g,O_2}}{k_s + h_{g,O_2}} \cdot \frac{2C_{fs,O_2}}{G_{Si}} \qquad [10]$$

which is equivalent to taking the ratio of the oxygen and silicon fluxes consumed at the surface to be equivalent to the ratio of oxygen atoms to silicon atoms in the solid film. The factor of two is introduced to account for the two oxygen atom per oxygen molecule. Equation 10 is the starting point for determining the sticking coefficient for oxygen during CVD growth.

The effective CVD sticking coefficient, or the probability that the oxygen atom at the silicon surface sticks to the silicon surface during CVD growth, is contained within k_s as defined in Eq. 8. By using Eq. 10 and the data of Fig. 2, the surface reaction rate constant can be extracted. The measurable quantities of Eq. 10 are C_{fs,O_2}, G_{Si}, and $[O]_s$. We determine the oxygen concentration in the gas flow, C_{fs,O_2}, from the flow rate into the reactor, and after growth we determine the growth rate of the film by beveling and staining techniques. The oxygen concentrations in the film were measured by SIMS and FTIR. The mass-transfer coefficient for oxygen does not depend on the sticking probability and can be modeled ideally as

$$h_g = D_g/\delta \qquad [11]$$

where D_g is the diffusivity of the gas and δ is the mean thickness of the boundary layer formed above the growth surface, determined by the large H_2 flow. In general the mass-transfer coefficient, h_g, is difficult to calculate for real reactor geometries. C_{fs,O_2}, h_{g,O_2} however, can be obtained experimentally from the silicon growth rate in the mass flow limited regime, and noting the similar masses of SiH_4 and O_2 (Appendix A).

We now reconfigure Eq. 10 to represent a measurable quantity to determine the cause of the reduced effective oxygen sticking coefficient by rewriting Eq. 10 as

$$\frac{k_s}{k_s + h_{g,O_2}} = \frac{G_{Si}[O]_s}{2C_{fs,O_2}h_{g,O_2}} \overset{\Delta}{=} M \qquad [12]$$

The center term in Eq. 12 consists entirely of experimentally known quantities and working with the term $C_{fs,O_2}h_{g,O_2}$ (as opposed to just h_{g,O_2}) does not require knowledge of the actual C_{fs,O_2} in the free stream. $M = 0$ implies a relatively slow surface reaction (low sticking coefficient), so that boundary layer effects do not affect the net rate of oxygen flow to the surface. For $C_{surf,O_2} = C_{fs,O_2}$, $M = 1$ implies a regime where the surface reaction was infinitely fast, and hence oxygen incorporation is determined solely by boundary layer transport. In this case, $C_{surf,O_2} = 0$.

Table I lists the values of the ratio, M, for the data presented in Fig. 2 for the growth temperatures ranging from

700 to 750°C. An average for M of 0.21 is found. Therefore, the oxygen incorporation occurs in neither a purely mass flow limited regime ($M = 1$, implying $h_{g,O_2} \approx 4\ k_s$) nor a surface reaction limited regime ($M = 0$). Although not limited purely by mass transport across the boundary layer, this layer still severely restricts the oxygen reaching the silicon surface. From Eq. 12, it can be seen that if the surface reaction were infinitely fast (implying $M = 1$), the oxygen incorporation rate would be five times its actual value, and still approximately well over ten times less than without boundary layer effects as calculated in the section on Experiment and Results.

Surface sticking coefficient effects.—Having established that the oxygen incorporation is suppressed in part by the slow diffusion of oxygen across the boundary layer, one can continue to extract the actual oxygen sticking coefficient under CVD conditions, S_{CVD}. This can be accomplished through the surface reaction rate (defined as $v_{\mathrm{th}}C_{\mathrm{surf,O_2}}S_{\mathrm{CVD}}$ in Eq. 8), and extraction of k_s from Eq. 12. However, knowledge of h_{g,O_2} is required, not just $C_{\mathrm{fs,O_2}}h_{g,O_2}$ which was determined in Appendix A and used to find M. To estimate $C_{\mathrm{fs,O_2}}$, we assume (*i*) the reactor walls are at 200°C and (*ii*) that $C_{\mathrm{fs,O_2}}$ can be approximated by the ideal gas equation using an average gas temperature defined as the average of the wall and wafer temperatures. The extracted values of S_{CVD} are listed in Table I for each growth temperature. They are all on the order of 10^{-4}, roughly 50 times lower than the sticking coefficient of oxygen on a clean silicon surface. This is a true surface effect and not a boundary layer effect since S_{CVD} is defined using the actual oxygen concentration $C_{\mathrm{surf,O_2}}$.

We associate the reduction of the oxygen sticking coefficient to the hydrogen passivation of the silicon surface. It is well known that a hydrogen-terminated surface has greatly reduced sticking coefficient for contaminants compared to a bare silicon surface. The hydrogen reduces the number of available sites on the surface with which contaminants can react (*i.e.*, chemisorb).[24] Hydrogen is available during CVD from the carrier gas as well as in the silicon source gases themselves, and the hydrogen overpressure can lead to a hydrogen passivated surface at temperatures in excess of the hydrogen desorption temperature of 510°C.[25]

Hydrogen passivation and its effects on the CVD growth temperature in oxygen-free environments has been studied by several researchers,[26,27] yet little work has been directed to study the hydrogen passivation of silicon when a hydrogen overpressure exists from a hydrogen carrier. The effect of a hydrogen overpressure has been determined to increase the incubation period before oxide precipitates form on a silicon surface.[13] The H_2 interaction with silicon has been studied sufficiently, however, to determine the equilibrium hydrogen coverage on Si (100) as a function of hydrogen pressure and temperature. The Si (100) surface is terminated by a single hydrogen atom, yet desorption occurs as hydrogen molecules

$$H_{2(g)} \leftrightarrow 2H_{(a)} \qquad [13]$$

where $H_{(a)}$ is adsorbed hydrogen and the equilibrium rate constant is given as $K_{\mathrm{eq}} = k_a/k_d$ (k_a and k_d are the adsorption and desorption rates, respectively) and is related to the Gibb's free energy by $K_{\mathrm{eq}} = \exp\ (-\Delta G/k_B T)$. Since $\Delta G = \Delta H - T\Delta S$, where ΔH is the enthalpy of reaction (~ -2 eV) and ΔS is the entropy (~ -1.2 meV/K),[28] a value for K_{eq} can be approximated. The fraction of surface coverage of atomic hydrogen (θ_H) as a function of H_2 pressure (p_{H_2}) is found according to a Langmuir adsorption isotherm as

$$\theta_H = \frac{[K_{\mathrm{eq}} \cdot p_{H_2}]^{1/2}}{1 + [K_{\mathrm{eq}} \cdot p_{H_2}]^{1/2}} \qquad [14]$$

where p_{H_2} is in Torr.

Figure 4 shows the approximate value for hydrogen surface coverage (θ_H) as a function of temperature under our standard growth conditions of 6 Torr H_2. For example, although hydrogen desorbs rapidly from a silicon surface at 510°C, due to the abundant supply of hydrogen for re-adsorption, in equilibrium the surface remains approximately 99.5% covered at 750°C. If one makes the assumption that the sticking coefficient for oxygen is proportional to the number of nonpassivated (open) sites, one expects a reduction of sticking coefficient compared to the UHV case by a factor of 200. This is reasonably consistent with the measured reduction in sticking coefficient of 50 (from 10^{-2} to 2×10^{-4}). That the reduction is not as large as predicted by a first-order Langmuir model may be due to the physisorption of oxygen on passivated sites, and subsequent migration to open sites for reaction. This leads to a weaker dependence of sticking coefficient with hydrogen coverage.[29]

Discussion

We have described two effects in low temperature CVD for the reduction of oxygen incorporation: the boundary layer which reduces the number of oxygen molecules which can reach the surface and the reduction of the actual sticking coefficient due to hydrogen passivation. The relative importance of these two effects is determined by the ratio, M, of Eq. 12. Since M was found to be approximately 0.2 both effects are important to our experiments. Since their effects on the sticking are additive in nature and not multiplicative, they both have an effect of reducing the sticking coefficient by a factor on the order of 100. For instance, if the surface reaction were to occur infinitely fast ($k_s = \infty$) and the mass transport (h_g) is fixed at the measured value, the incorporated oxygen concentration increases by only a factor of approximately five. If the mass transfer were infinitely fast ($h_g = \infty$), which means no boundary layer effects, and the surface reaction rate retains its measured value, Eq. 12 predicts that the incorporated oxygen level increases by only 25%.

That $M \neq 0$ demonstrates that we do not have a uniform distribution of oxygen in the reactor and the distribution is affected by the size of the boundary layer. The effect is to raise the free stream concentration of oxygen above the average concentration which was assumed in our model. Since an experimentally determined value of $C_{\mathrm{fs,O_2}}h_{g,O_2}$ was used in our calculation, the value determined for M remains unchanged. However, the calculated value of h_{g,O_2} is reduced since the free stream concentration was over estimated. The final result is that the calculated sticking coefficients are lower than shown in Table I. A rough calculation shows the boundary layer in our reactor to be less than 50% of the critical dimension of the reaction chamber. The assumption of a uniform distribution of oxygen in the reactor gives us a conservative estimate (an upper end) of the effective sticking coefficient.

As described in the Background section, UHV experiments showed the sticking probability of oxygen on the

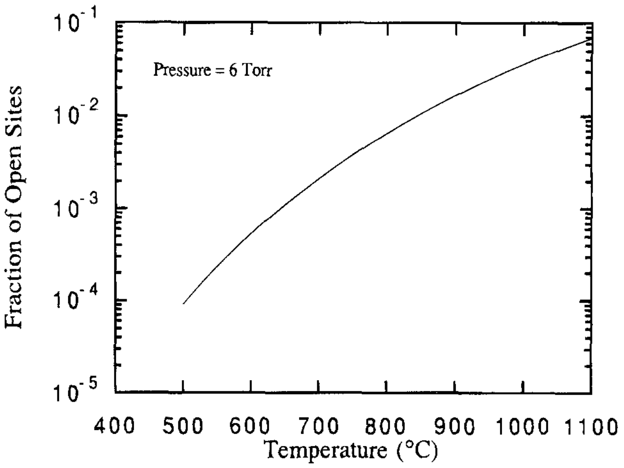

Fig. 4. Calculated hydrogen coverage of a silicon surface as a function of temperature with a hydrogen overpressure of 6 Torr. At 750°C, the surface remains approximately 99.5% hydrogen passivated.

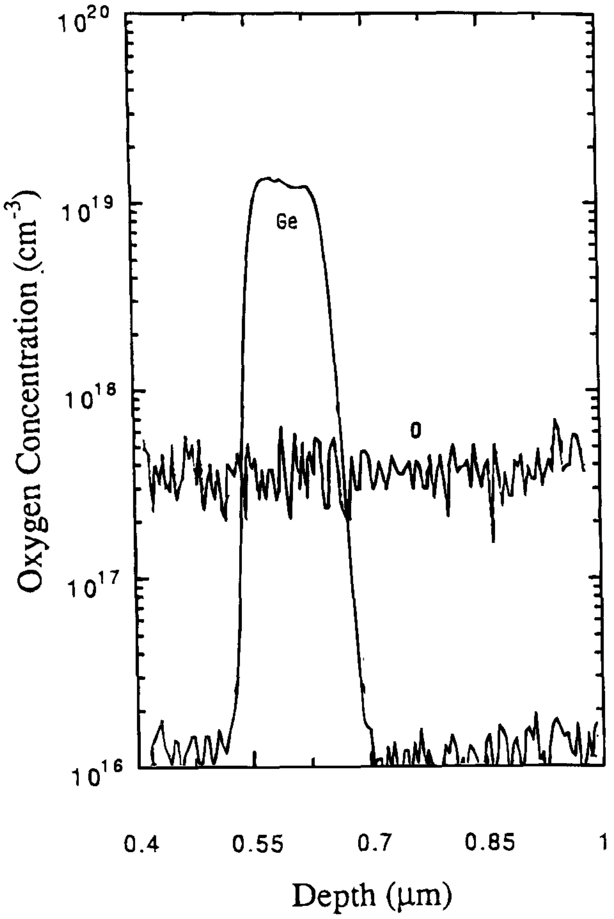

Fig. 5. SIMS plot of a silicon-germanium layer grown at 625°C. The oxygen concentration in the silicon-germanium layer is limited by the resolution of the measurement. Germanium concentration is in arbitrary units.

(100) surface of silicon to be approximately 0.01 over a wide range in temperature. We find under our standard growth conditions that the sticking coefficient is effectively reduced by approximately two orders of magnitude. This reduction in the sticking coefficient has significant effects on the electronic performance of devices fabricated in materials grown by low temperature CVD.

Although our work was performed with oxygen, the same mechanisms for the reduction of contamination are expected to apply to water vapor, which in practice may be more significant than oxygen. Even if the sticking coefficient for water vapor is substantially larger than for oxygen, the net incorporation is still limited by the boundary layer transport to a value limited to that observed in our work with oxygen.

From our experimental results, one can extrapolate to low oxygen levels to determine the necessary conditions for the growth of high purity ([O] < 2 × 10^{18} cm^{-3}) epitaxial films by CVD. For example, to grow a silicon (or silicon-germanium) film at 750°C (growth rate of 50 nm/min) at 6 Torr, one may tolerate 100 ppb oxygen in the gas stream. Oxygen concentrations below this level are easily obtained with gas purifiers available on the market today. 10 ppb oxygen concentration are guaranteed routinely, which means a growth rate of 5 nm/min (typical of DCS growth rate at 700°C) may be used to obtain less than 2 × 10^{18} cm^{-3} oxygen in epitaxial silicon. Such low oxygen concentrations are achieved routinely in our reactor when oxygen is not intentionally introduced. For example, Fig. 5 shows a SIMS plot of an epitaxial $Si_{0.8}Ge_{0.2}$ layer grown at 625°C (100 Å/min) with a structure similar to $Si/Si_{1-x}Ge_x$ heterojunction bipolar transistors. The oxygen concentration is below the resolution of the measurement which is near 5 × 10^{17} cm^{-3} with this sample. The UHV surface cleanliness criteria described earlier in the paper requires an unrealistic oxygen concentration (<1 ppb) for successful growth at 700°C. This demonstrates conclusively that the conditions for successful low temperature silicon epitaxy by CVD are not as stringent as previously thought from the results of the clean silicon surface, an extremely fortuitous result for manufacturing.

One also can extrapolate the results of our model to support the results reported for successful low temperature silicon CVD growth at atmospheric pressure,[17] a pressure which is two orders of magnitude higher than that of our work (6 Torr). A first order Langmuir adsorption implies a reduction in the number of nonpassivated surface sites by two orders of magnitude, and hence reduces the true sticking coefficient (S_{CVD}) by a similar amount. Assuming a similar boundary layer thickness (on the order of 10 cm), the higher pressure decreases the mass-transport factor by 100 times due to a reduced diffusion coefficient. These effects hence decrease the effective oxygen sticking coefficient (S_{eff}) by two orders of magnitude compared to our results. Therefore, for the same fractional oxygen contamination (~10 ppm O_2 in the gas flow), the same rate of oxygen incorporation is expected even though the partial pressure of oxygen is higher. Since atmospheric pressure (AP) CVD growth rates are similar to ours, this implies the gas purity requirements for APCVD are similar to those required for our work.

Summary

Oxygen incorporation into epitaxial silicon layers during low temperature CVD growth in a hydrogen ambient is suppressed by a limitation in the amount of oxygen which can reach the surface and by hydrogen passivation of the growth surface. This reduction is two orders of magnitude, at 6 Torr compared to UHV conditions, in a range between 700 and 750°C. The reduction is probably even larger at higher growth pressures. The actual sticking coefficient is reduced by a similar amount. This effect enables the low temperature growth of high quality epitaxial silicon and silicon-germanium with gas purities within the range of commercial gas purifiers.

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APPENDIX A

Direct calculation of h_g using Eq. 11 is difficult because of uncertainties in the exact boundary layer thickness in a real CVD reactor and because of the gradients in gas temperature from the wafer (700 to 1000°C) to the reactor walls (estimated to be approximately 200 to 300°C). Rather the mass-transfer coefficient for oxygen can be estimated by measuring the mass-transfer coefficient for silicon in our growth reactor and correcting for the mass difference between O_2 and SiH_4 ($D_g \propto m^{-1/2}$). Since the masses of O_2 and SiH_4 are equal (32 g/mol), however, the value obtained experimentally for h_g is nearly equal for both molecules. The mass-transfer coefficient for silane can be determined from the growth parameters for silicon in the mass-flow limited regime. Agnello *et al.*[18] have studied in some detail the complications of knowing the gas-phase concentration of oxygen just above the silicon surface under the conditions where mass transport is a limiting factor, but we determine the mass-transfer coefficient from our silane growth measurements.

The silane growth rate in our reactor for 0.5% SiH_4 in H_2 at 1000°C for a reactor pressure of 6 Torr is 0.15 μm/min. This corresponds to growth limited by mass transport across the boundary layer (not surface reactions) since the growth rate in this regime depends little on temperature. The corresponding flux of silane molecules toward the surface in this mass-flow limited regime is $h_{g,si}C_{fs,si} = 1.2 \times 10^{16}\ \text{cm}^{-2}\ \text{s}^{-1}$. This is consistent with an order of magnitude calculation of the flux from tabulated data in Ref. 30 $(D_gC_{fs}/\delta = (80\ \text{cm}^2\ \text{s}^{-1} \cdot 10^{15}\ \text{cm}^{-3}/4\ \text{cm} \approx 2 \times 10^{16}\ \text{cm}^{-2}\ \text{s}^{-1}$ as determined with an ambient pressure of 6 Torr. (δ is estimated from Eq. 1.14 of Ref. 30.) Due to the similar masses of O_2 and SiH_4, for the condition of 0.5% O_2 in the gas stream at 1000°C, one can estimate $h_{g,O_2}C_{fs,O_2} \approx 1.2 \times 10^{16}\ \text{cm}^{-2}\ \text{s}^{-1}$. For other oxygen levels in the gas stream, one expects little change in h_g, since the bulk of the gas in the reactor is hydrogen. Therefore $h_{g,O_2}C_{fs,O_2}$ is expected to scale linearly with the oxygen flow introduced into the reactor. Finally, the h_gC_{fs} product is only weakly dependent on temperature ($\sim T^{-1/4}$). Therefore using this value at other temperatures (*e.g.,* 700°C) introduces little error. (The exact gas temperature is a complicated issue in coldwall reactors since a temperature gradient is established between the wafer surface and the reactor walls.) With the considerations given above, the value of $C_{fs,O_2}h_{g,O_2}$ of $1.2 \times 10^{16}\ \text{cm}^{-2}\ \text{s}^{-1}$ at 0.5% O_2 in 6 Torr of H_2 is used for our calculations (scaled to the appropriate O_2 gas flow).

LIST OF SYMBOLS

δ	boundary layer thickness
η	oxygen incorporation efficiency
θ_H	H_2 surface oxygen
C_{fs,O_2}	free stream concentration of oxygen
C_{surf,O_2}	gas-phase concentration of oxygen at the growing surface
D_g	gas diffusivity
F_{d,O_2}	diffusion flux of O_2
$F_{s,O}$	oxygen flux consumed at the growing interface
f_{O_2}	O_2 flow rate in the reactor
f_{Total}	total gas flow in the reactor
h_g	mass-transport coefficient
h_{g,O_2}	mass-transport coefficient for oxygen
G	growth rate of an epitaxial film
G_{Si}	growth rate of a silicon epitaxial film
K_{eq}	equilibrium rate constant
k_s	surface reaction rate constant
$[O]_s$	oxygen concentration in the solid
p_{H_2}	H_2 pressure
p_{Total}	total reactor pressure
p_{O_2}	partial pressure of O_2 in the reactor
R	oxygen incorporation flux
S_{CVD}	sticking coefficient for oxygen during CVD
S_{eff}	effective sticking coefficient for oxygen on silicon
T_{gas}	gas temperature
v_{th}	thermal velocity of gas molecules

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