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Hydrogen permeability in thermally grown films of SiO_2 on silicon substrates

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We describe a technique for measuring the room-temperature permeability of molecular hydrogen through thin films of thermally grown SiO_2 on Si substrates. We have used this technique to determine the H_2 permeability in oxide films ranging from 161 to 1082 Å in thickness. We find that the permeability decreases as the film thickness decreases. Even for the thickest films studied, the permeability is only about 8% of the value characteristic of bulk SiO_2. We attribute the permeability differences to a gradient in the density of the thermal oxide.

There have been many studies of the diffusivity of various gases through bulk SiO_2.[1–3] But because standard techniques of determining bulk diffusivities cannot be applied to thin films on substrates, there have been very few studies of gas diffusivity in films of thermally grown SiO_2 on Si substrates. The diffusivities of oxygen and water in thermal SiO_2 at high temperatures have been estimated from the oxide growth rates in dry O_2 and in steam, respectively.[4] In thick films, the diffusivity values obtained in this way are in reasonable agreement with values characteristic of bulk SiO_2. For thin oxides grown in dry O_2, however, the growth rate is found to be anomalously fast. Some models[5] have attributed this to a gradient in the O_2 diffusivity near the Si/SiO_2 interface brought about by stress.

At least two previous measurements of hydrogen diffusivity in thermal SiO_2 films have been made.[6,7] In both studies the passivation of interface traps in metal-oxide-silicon (MOS) capacitors was studied as hydrogen diffused laterally across the oxide. Schols and Maes[6] observed the spatial variation of the number of interface traps (N_{it}) after annealing in H_2 at temperatures from 700 to 1000 °C. They observed an abrupt transition between a low-N_{it} region and a high-N_{it} region. The velocity of the front was used to calculate the H_2 diffusivity D. No attempt, however, was made to take into consideration the effect of H_2 consumption at the interface on the velocity of the front.

Fishbein, Watt, and Plummer[7] made a similar study, but measured the average N_{it}, rather than the spatial distribution of N_{it}. They developed a model for the chemistry of interface trap passivation, and, by fitting this model to their experimental data, determined D in the range of 400–500 °C. Their values of D are within a factor of 2 of those implied by an extrapolation of the results of Schols and Maes to this lower temperature range. The results for D obtained from these two thin film studies, however, are almost two orders of magnitude smaller than the value of D which had earlier been measured in bulk SiO_2.[1–3]

In this paper we describe a technique for the measurement of the room-temperature H_2 permeability K ($K \equiv SD$, where S is the hydrogen solubility), in thermal SiO_2 films on silicon substrates. We have used this technique to determine K for SiO_2 films of various thicknesses, and have found that the permeability depends on the oxide thickness. The technique is based on an earlier observation[8] that when the oxide of a previously irradiated MOS field-effect transistor (MOSFET) is exposed to hydrogen at room temperature, the number of interface traps increases. The increase was attributed[9,10] to the production of hydrogen ions (H^+) by radiation-induced cracking sites in the bulk of the oxide. Once formed the H^+ drift to the interface and create interface traps in a process similar to that by which interface traps are created during irradiation.[11]

A side view of the MOSFET's used in this work is shown in Fig. 1. The gate oxides are pyrogenic oxides grown at 900 °C on Si (100) substrates. Gate oxides with thickness from 161 to 1082 Å were used. As shown in Fig. 1, the MOSFET's have no encapsulating layer; hydrogen was therefore able to enter the gate oxide through both of the 140-μm-wide sides of the MOSFET. Each chip contains several MOSFET's which are identical except for their gate lengths L_g which varied from 3 to 25 μm.

The MOSFET's were irradiated with x rays to a dose of 2 Mrad. During irradiation and until the completion

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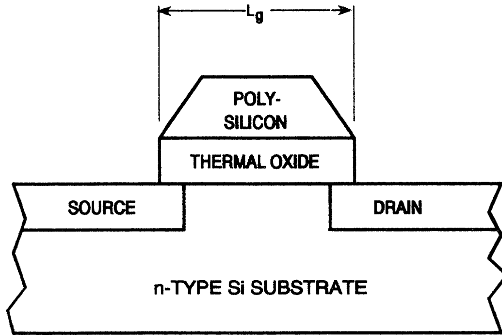

FIG. 1. Side view of MOSFET's. Sides of gate oxides are exposed to ambient to allow H_2 to enter the oxide.

of the measurements the gate electrode was positively biased to maintain a field of +1 MV/cm in the oxide. After irradiation the devices were exposed to forming gas (10.0% H_2 and 90.0% N_2). The increase in N_{it} was monitored using standard charge pumping techniques[12] such that interface traps in the central 0.5 eV of the band gap were counted.

Our determination of the hydrogen permeability involves measuring the time dependence of the increase in N_{it} which occurs when the gate oxide of the irradiated MOSFET is exposed to H_2. As stated above, the increase in N_{it} results from the production of H^+ by the cracking of H_2 at radiation-induced defects in the bulk of the gate oxide. Therefore, consumption of H_2 must be included when modeling the diffusion of the H_2 into the oxide. We assume that the H_2 is consumed only by reaction with the radiation-induced defects, and not by other mechanisms, such as absorption into either the silicon substrate or the polysilicon gate electrode. Evidence that this is an extremely good approximation has been obtained by measuring the relationship between the rate at which N_{it} increases and the H_2 partial pressure. These results will be presented in a future publication.

For the case in which the reaction rate is very fast compared to the diffusion rate, the H_2 diffusion can be described by the tarnishing model used by Shelby.[13,14] According to this model, at an elapsed time t the concentration profile of the cracking sites has a sharp boundary at each side of the oxide: the cracking sites have their original concentration C_x in the center of the oxide, and have zero concentration in the outer regions of the oxide which have been penetrated by the hydrogen. Each boundary is a distance X from the edge of the oxide, where X is given by

$$X=\sqrt{2fKPt/C_x}=\sqrt{2fSDPt/C_x}\ . \tag{1}$$

Here P is the H_2 partial pressure in the ambient atmosphere. Booth describes f, a function of SP/C_x, in Ref. 15. The model used to derive Eq. (1) assumed that C_x is uniform throughout the oxide. As discussed in Refs. 9 and 10, however, C_x may vary with distance from the Si substrate. But because the lateral diffusion distance (3–25 μm) is much larger than the H_2 hopping distance (a few Å) and oxide thickness (161–1082 Å), Eq. (1) is valid even for this type of nonuniformity in the concentration of the cracking sites if the average value of C_x is used.

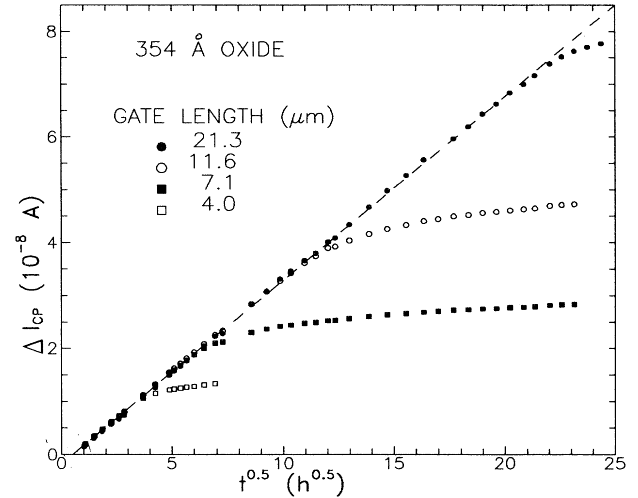

FIG. 2. Change in charge pumping current as a function of the square root of time (in hours) after exposure to forming gas. Data for four MOSFET's on the same chip are shown. The MOSFET's had gate oxides 354 Å thick, and were identical except for their gate lengths.

The number of cracking sites which have been removed at time t is therefore given by $2XWTC_x$, where W and T are the width and thickness of the oxide. The elimination of each cracking site produces one H^+ ion, which quickly moves to the interface where it forms one interface trap.[8] The number of interface traps formed during the hydrogen exposure is therefore

$$\Delta N_{it}^* = \sqrt{8fSDPC_x t}\, WT\ . \tag{2}$$

This relationship holds until the two moving boundaries meet at the center of the oxide.

Experimental data for the increase in the charge pumping current I_{cp}, measured for four MOSFET's on a single chip are shown in Fig. 2. Each MOSFET has the same gate oxide thickness (354 Å), but a different gate length. N_{it}, the number of interface traps measured by the charge pumping technique, is obtained from I_{cp} through the relation $N_{it}=(1/\omega q)I_{cp}$, where ω is the frequency of the charge pumping pulse (62.5 kHz), and q is the electronic charge. N_{it}^* shown in Eq. (2) is the total number of interface traps across the entire band gap, whereas N_{it} is the number measured in the middle 0.5 eV of the band gap. In Ref. 8 it was estimated that $N_{it}^* \approx 1.4 N_{it}$. The linearity of the increase in I_{cp} when plotted as a function of the square root of time, as in Fig. 2, is an indication of the validity of Eq. (2).

From Eq. (2) the H_2 permeability can be expressed as

$$K \equiv SD = (1/8fPC_x W^2T^2)(\delta \Delta N_{it}^* / \delta\sqrt{t}\,)^2\ , \tag{3}$$

where the term in the second set of parentheses is the slope of the ΔN_{it}^* versus $\sqrt{t}$ curve before saturation. C_x

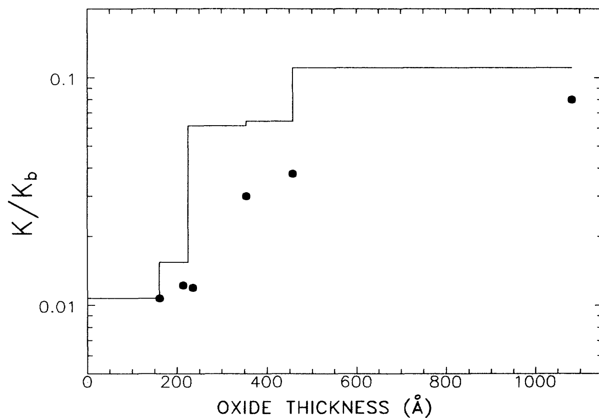

FIG. 3. Permeability of SiO_2 films (normalized to the bulk permeability, K_b) as a function of the oxide thickness. Solid circles are experimentally determined values of the permeability for oxides of shown thickness. Lines indicate deconvoluted values of the average permeability over various thickness ranges.

in Eq. (3) can be determined by dividing the saturation value of N_{it}^* by the volume of the MOSFET gate oxide, $L_g WT$. We are not able to use the experimental data to determine both S and D independently. Since f depends (weakly) on S, we can therefore only estimate K from Eq. (3). We have calculated K using two different assumptions: (1) S in the film is the same as in bulk SiO_2, 1×10^{18} $cm^{-3}\,atm^{-1}$,[2] and (2) D in the film is the same as in the bulk, 1.4×10^{-11} $cm^2\,s^{-1}$.[2] Results based on assumption (1) are shown in Fig. 3. We find that assumption (2) leads to values of S which are between 1% and 6% of the bulk value, and values of K which are 20–30 % smaller than those calculated from using assumption (1). We point out that it is possible to determine both S and D independently, and therefore determine K more accurately, by making measurements at two hydrogen partial pressures and/or radiation doses so as to change the ratio P/C_x. Results of such a study will be presented in a future publication.

These calculated permeabilities are averages over the entire oxide thickness, and may be expressed as

$$K = (1/T) \int_0^T K'(x)dx \ , \qquad (4)$$

where $K'(x)$ is the permeability at a distance x from the Si/SiO_2 interface. If we consider the thicker oxides to be composed of thinner oxides (with the average permeabilities shown in Fig. 3) and an overlayer, then we can use Eq. (4) to determine the average permeability of the overlayer. The results of using this procedure are shown as solid lines in Fig. 3. (Because of their nearly identical thicknesses, results for the 214- and 236-Å oxides have been averaged and treated as a single 225-Å oxide.)

Figure 3 shows that the hydrogen permeability increases rapidly with distance from the interface for distances less than 300 Å, and much less rapidly at larger distances. Even at very large distances from the interface the thermal oxide has a significantly lower H_2 permeability than bulk oxides. We suggest that the decreased permeability results from an increased density of the films, and that the variation in the permeability is evidence of a density gradient. Previous spectroscopic ellipsometry studies[16] support the hypothesis that thermally grown SiO_2 has a larger density than bulk SiO_2. We grew an oxide under conditions identical to those used to grow the 1082-Å pyrogenic oxide studied here, but without the further processing required for MOSFET fabrication. Our spectroscopic ellipsometry measurements indicate that this oxide has a density 3.3% greater than that of bulk SiO_2.

Shelby[17] has studied the effect of density of the permeability of helium in vitreous B_2O_3. His work indicates that at 100 °C a 3.3% decrease in the molar volume (i.e., increase in density) results in a decrease of the diffusivity by a factor of about 3.5 and a similar decrease in the solubility. The total decrease in the permeability is therefore a factor of about 12, fortuitously close to the factor of 12 decrease shown in Fig. 3 for the 1082-Å thermal oxide. Compaction of the oxide would be expected to decrease the permeability by increasing the activation energy E_a. Previous studies[6,7] have suggested that E_a for hydrogen diffusion is, in fact, larger in thermal oxides than in bulk SiO_2.

If an enhanced oxide density of the thermal oxide is, in fact, responsible for the decreased H_2 permeability, then other gases which diffuse noninteractively in SiO_2 should also be expected to have decreased permeabilities. Our results, then, would seem to lend some support to models[5] which invoke a decreased oxygen permeability near the interface to explain the "fast growth" regime of dry oxides. We note that Deal and Grove[4] reported that E_a for oxygen diffusivity is somewhat larger in (thick) thermal oxides than in bulk SiO_2 (1.24 compared to 1.17 eV), similar to the case for hydrogen diffusion mentioned above.

In summary, we have used a technique to determine the H_2 permeability in thermally grown oxides on silicon substrates. Application of this technique to oxides of various thicknesses suggests that the H_2 permeability decreases as the interface is approached. The decline is especially pronounced beginning at a distance of several hundred angstroms from the Si/SiO_2 interface. We suggest that this is an indication of a similar gradient in the density of the thermal oxide. Such a structural change near the interface could have important implications for Si-based semiconductor devices, which require thinner oxides as lateral dimensions are decreased. In particular, since the radiation sensitivity of bulk oxides is greatly enhanced by densification,[18] a density gradient in thin thermal oxides might also play a role in their radiation hardness.

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