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GROWTH AND STRUCTURE OF NONCRYSTALLINE SiO₂ FILMS ON SILICON

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Résumé - L'épaisseur de la couche d'oxyde et la vitesse d'oxydation par traitement thermique du silicium sont interprétées sur la base d'un mécanisme où la diffusion de l'oxygène à travers l'oxyde non cristallisé est dû à la superposition de deux effets dont l'un ne dépend pas de l'épaisseur de la couche oxydée. Cet effet est attribué à l'existence de canaux structuraux.

Abstract - Oxide thickness and oxidation time data related to thermal oxidation of silicon are interpreted by a model in which the oxygen transport through the noncrystalline oxide has two components: one is the usual random-walk diffusion dependent on thickness and the other one is independent of thickness. The latter one is attributed to transport through structural channels.

I - INTRODUCTION

Thermal oxidation of silicon results in a noncrystalline (nc) SiO₂ film on silicon that plays an essential role in silicon device and integrated circuit technology. In many respects this SiO₂ film is very similar to silica glass but there are some important differences, especially when the film is prepared in a very dry O₂ ambient. These differences are particularly revealed by those aspects of the kinetics of oxide growth which are due to the characteristics of oxygen diffusion.

II - EXPERIMENTAL OBSERVATION

By analyzing extensive data sets of oxidation time, t, and oxide thickness, x, we have found earlier /1/ that the oxide growth in dry O₂ does not proceed with a linear-parabolic rate as has usually been assumed. Thus, the generally used relationship

\[
\left( \frac{dx}{dt} \right) = \left( \frac{1}{K_L} + \frac{2x}{K_P} \right)^{-1}
\]

(1)

corresponding to

\[
t = t_0 + \frac{x}{K_L} + \frac{x^2}{K_P}
\]

(2)

where \( K_L \) and \( K_P \) are the linear and parabolic rate constants, is replaced by

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where $C_1$, $C_2$, and $a$ are constants. The curvature of the $\frac{dt}{dx}$ vs $x$ plots, i.e., the deviation from the linear-parabolic rate, was expressed by "a" whose values vary from zero (linear growth) to one (true linear-parabolic growth) and depend on temperature, oxygen pressure, water content of O$_2$, and, very significantly, on the crystallographic orientation of the Si substrate.

The observation that for oxidation in dry O$_2$ $a\ll 1$ indicates that the linear-parabolic rate law is not generally valid. However, a physical interpretation of this phenomenological model is not quite straightforward. Therefore, we now propose a model which results in an equally good fit to the experimental data point as the integral form of Eq. (3) but has a simple physical interpretation. According to this model

$$\frac{dt}{dx} = \frac{C_2}{F} = C_0 \left( \frac{1}{F_S} + \frac{1}{F_T} \right)$$

(4)

where $F_S$ is the flux controlled by the surface reaction O$_2$+Si+SiO$_2$, and $C_0=2\times10^{22}$ O$_2$/cm$^3$ SiO$_2$ (corresponding to $4\times10^{22}$ network oxygen atoms per cm$^3$ SiO$_2$). The

![Fig. 1 - Oxygen flux as a function of oxide thickness at 870°C and 1 atm O$_2$ pressure. Notation is explained in the text.](image-url)
oxygen transport through the oxide film, $F_T$, is considered as having two components

$$F_T = C_0 \left( K_T + K_0 \right) = F_{T1} + F_{T2}$$

(5)

where $K_T$ is the transport parameter (comprising $O_2$ solubility and diffusivity) corresponding to the usual random-walk type diffusion, and $K_0$ represents a thickness-independent transport of $O_2$ molecules through structural channels. It is assumed in this approximative model that these channels extend throughout the whole oxide film and their density is constant. We find that the rate equation determined by integrating Eq. (4) represents an excellent fit to the experimental data sets as the correlation coefficients are about 0.9999 and the standard error ranges from -10 to -250 s out of total growth times of $-2 \times 10^4$ s.

The transport-controlled oxygen flux, $F_T$ for oxide growth at 870°C and its two components, are shown in Fig. 1. For $x < X_{C1}$ the usual, random-walk type, transport predominates, but for $x$ larger than $X_{C1}$, $F_{T2} > F_{T1}$. Notice that for $x$ larger than $X_{C2}$, $F_P > P$ where $P$ is the flux corresponding to $O_2$ permeation at 1 atm $O_2$ in vitreous (v)-SiO$_2$ /2/.

We have also found that $F_{T1}$ is linearly proportional to the $O_2$ pressure, $p$, as $O_2$ permeation in v-SiO$_2$ but $F_{T2} = \text{const.}$ $p^{0.6}$. From the temperature dependence of $K_T$ and $K_0$ in the range of 780-1000°C we estimate their activation energies as -2.6 and -0.4 eV, respectively.

### III - DISCUSSION

It has previously been suggested that structural channels of -2.5 nm length play a role in $O_2$ permeation in v-SiO$_2$ /3/. Since as we have observed here, $F_T$ exceeds $P$ for $x > X_{C2}$, these channels apparently play an even more important role in nc-SiO$_2$ films on silicon. The low activation energy of $K_0$ suggests that the transport of $O_2$ molecules in structural channels proceeds without significant interaction between the $O_2$ molecules and the SiO$_2$ network. Our observed -0.4 eV activation energy for $K_0$ is similar to the -0.3–0.45 eV range characteristic of the inert mode of $H_2$ diffusion in v-SiO$_2$ /4/. The higher activation energy, -2.6 eV, observed for $K_T$ suggests that the thickness dependent transport, $F_{T1}$, involves interaction between $O_2$ molecules and SiO$_2$. For $H_2$ diffusion in v-SiO$_2$ the activation energy of the interactive mode, involving the formation of SiOH groups, is 0.7 eV /5/. It is obvious that the exchange of $O_2$ molecules and network oxygen atoms has a higher activation energy than the formation of SiOH groups. Our idea about the interactive component of the oxygen flux is also supported by the observation that the extent of the oxygen exchange increases with decreasing oxide thickness /6/.

Because of the random distribution of channels in v-SiO$_2$, the decomposition of $O_2$ permeation into two components is impossible; nevertheless, its activation energy, 1.2 eV, indicates that it is intermediate between the interactive (-2.6 eV) and inert (-0.4 eV) modes of transport we have observed for nc-SiO$_2$ on Si. Additionally, the activation energy of the total transport component of oxide growth has been reported to decrease from 2.1 eV for 780°C to 1000°C to 1.3 eV for 980°C to 1150°C /7/. For the lower temperature range most of the data were obtained for oxides thinner than $X_{C1}$, whereas, for the higher temperature range more data were obtained for oxides thicker than $X_{C1}$ and even $X_{C2}$. Accordingly, the interactive component plays a more important role in the oxides formed at lower temperatures and this is reflected in the higher activation energy.

The formation of structural channels results from the great flexibility of the Si-O-Si bridging bonds and from the directional character of the oxygen flow during oxide growth. The bond flexibility, in turn, arises from the small variation in bond energy (-0.09 eV) within the range of the Si-O-Si bond angles in nc-SiO$_2$ (-120°–180°) /8/. In addition, the solubility sites that the $O_2$
molecules occupy in nc-SiO$_2$ are apparently not rigidly determined. Rather, the O$_2$ molecule occupying such a site may affect the local structure (conformation) within a radius of -1.5 nm. Thus, the motion of an O$_2$ molecule from one solubility site to another provides a possible mechanism for the development of a correlated percolation path consisting of adjacent six-member Si-O rings with an internal diameter of -0.3 nm which is comparable to the diameter of an O$_2$ molecule /3/. Such a path is thus somewhat similar to the "structural channel" along the C-axis in tridymite and quartz crystals.

IV - CONCLUSIONS

The growth of nc-SiO$_2$ films on silicon in dry O$_2$ is associated with an interactive and inert transport of O$_2$ molecules through the oxide. The inert flux results from transport in structural channels formed during oxide growth. The interactive flux results from random-walk type diffusion of O$_2$ molecules; this process is associated with interaction between O$_2$ molecules occupying some solubility sites and the SiO$_2$ network, therefore, its activation energy is higher than that for the inert transport. In fused v-SiO$_2$ the channels are randomly distributed and the probability of formation of fully extended percolation paths is reduced with respect to grown nc-SiO$_2$ films on silicon. Therefore, O$_2$ permeation in v-SiO$_2$ cannot be decomposed into its two components but its activation energy indicates that it involves both.

According to these considerations, the structures of thermally grown nc-SiO$_2$ films on silicon and fused v-SiO$_2$ are different on a subtle level which is not discernible by diffraction techniques. However, the difference is revealed by the transport of O$_2$ molecules during oxide growth. Hence, this process can be considered as a structural probe for this noncrystalline solid.

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