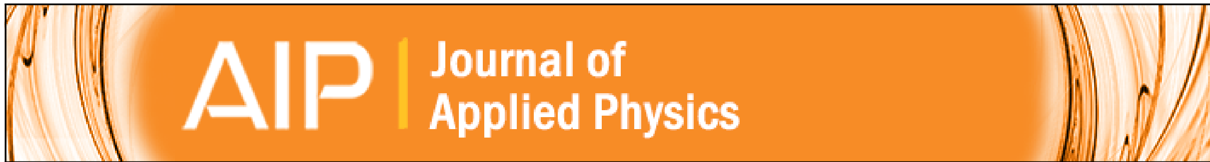

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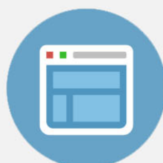

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COMMUNICATIONS

Diffusion of near surface defects during the thermal oxidation of silicon

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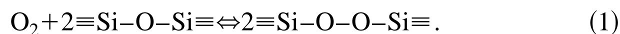
The diffusion of defects during the thermal growth of SiO_2 film on Si(100) in dry O_2 was investigated using sequential treatments in natural oxygen ($^{16}O_2$) and in heavy oxygen ($^{18}O_2$) in a Joule effect furnace. The ^{18}O depth profiles were measured with a depth resolution better than 1 nm, using the nuclear reaction narrow resonance $^{18}O(p,\alpha)^{15}N$ ($E_R = 151$ keV, $\Gamma_R = 100$ eV). From these profiles, we confirmed that just below the surface an exchange between the oxygen atoms from the gas phase and those from the silica occurs, even for silica films thicker than 20 nm. This fact is not predicted by the Deal and Grove model. A diffusion of oxygen related defects takes place in the near surface region, with an apparent diffusion coefficient $D^* = 4.33 \times 10^{-19}$ cm^2/s for an oxidation temperature of $T = 930$ °C and for an oxygen pressure of $P = 100$ mbar. © *1997 American Institute of Physics.* [S0021-8979(97)02212-3]

The Deal and Grove model[1] was the first one generally accepted for the description of the thermal growth of SiO_2 on silicon in dry O_2, for films thicker than 20 nm. Many studies have reported that deviations from this model occur at the initial stages, where the growth rate is higher than that expected from the model. Besides, Rochet *et al.*[2] and later Trimaille and Rigo[3] and Lu *et al.*[4] have demonstrated through isotopic tracing experiments that a parallel atomic transport mechanism takes place during the oxidation, due to silica network defects created during the growth. This parallel mechanism leads mostly to an exchange between the oxygen atoms from the gas phase and those from the silica network in the near-surface region. This phenomenon, which is not predicted by the Deal and Grove model, also occurs for films thicker than 20 nm. As the atomic exchange takes place in parallel with interfacial growth, and in a smaller scale, it cannot be extracted only from the oxide growth kinetics. The suggested defect responsible for the atomic exchange near the surface is the peroxyl bridge which diffuses interstitialcy in the silica network.[3] In this previous work, isotopic tracing experiments were carried out to investigate the near surface exchange mechanism. It has been established that the amount of this exchange supports a $P[O_2]^{1/4}$ law ($P[O_2]$ is the oxygen gas pressure). This favors, among the defects relevant to atomic diffusion,[5] the peroxyl bridge (O–O bond, equivalent to an interstitial oxygen atom) as the defect responsible for the step-by-step motion of oxygen atoms. It has been stated that the peroxyl bridge is formed through the reaction:



$$O_2 + 2{\equiv}Si{-}O{-}Si{\equiv} \Leftrightarrow 2{\equiv}Si{-}O{-}O{-}Si{\equiv}. \quad (1)$$

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Owing to the mass action law, for an oxygen transport by peroxyl bridges, the concentration of defects ($C_d = [{\equiv}Si{-}O{-}O{-}Si{\equiv}]$) is proportional to the square root of the O_2 pressure according to Eq. (1). As the surface exchange is proportional to the square root of C_d for a diffusion process, this exchange should be therefore proportional to $P[O_2]^{1/4}$. The presence of peroxyl bridges is also consistent with the observations of *EX* centers by Stesmans *et al.*,[6] which can also be interpreted in terms of oxygen excess. In this communication we report on a study based on isotopic tracing experiments, allowing an accurate measurement of the apparent diffusion coefficient D^* of the near surface defects during the thermal oxidation of Si in dry O_2.

Monocrystalline silicon wafers *n* type, lightly doped ($\rho = 3-6\ \Omega$ cm), and (100) oriented have been thermally oxidized in a Joule effect heated furnace in which the atmosphere can be well controlled. The gases used here were either ultradry natural oxygen, named $^{16}O_2$, or 99.7% ^{18}O labeled oxygen, named $^{18}O_2$. A liquid nitrogen trap was used to maintain the partial pressure of water vapor in the oxygen gases below 1 ppm. The thermal oxidations were performed under an oxygen pressure of $P[O_2] = 100$ mbar for both gases. Three different sequential processing steps were performed

(i) oxidation in $^{16}O_2$ at $T = 1000$ °C for 3 h [first step-sample (i)];
(ii) same as for sample (i), followed by an oxidation in $^{18}O_2$ at $T = 930$ °C for 5 h [second step-sample (ii)];
(iii) and same as for sample (ii) followed by an oxidation in $^{16}O_2$ at $T = 930$ °C for 2 h [third step-sample (iii)].

The first step was chosen to grow a silica film of about 20

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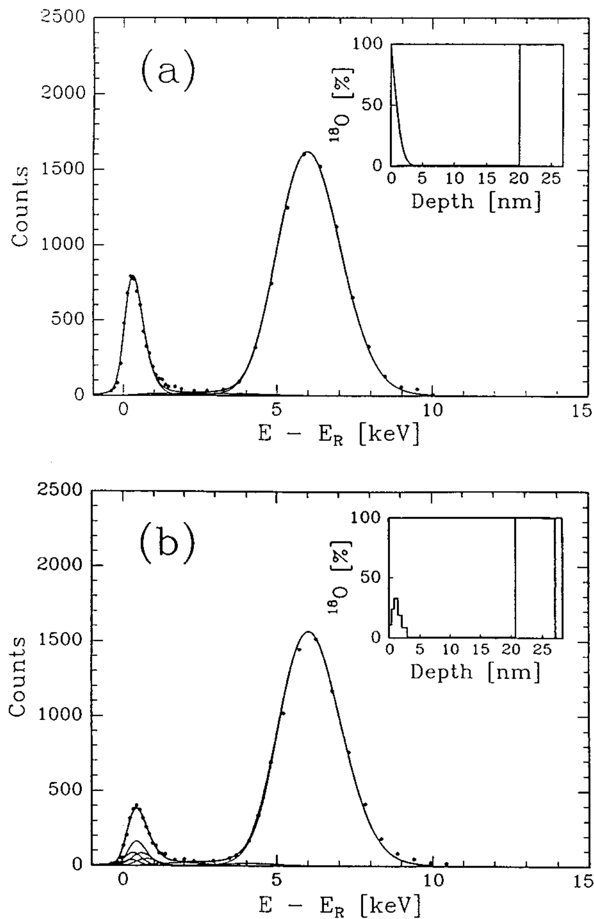

FIG. 1. Excitation curves of the nuclear reaction $^{18}O(p,\alpha)^{15}N$ around the energy of the resonance $E_R=151$ keV for a silicon wafer oxidized in: (a) $^{16}O_2$ for 3 h at 1000 °C, followed by $^{18}O_2$ at 930 °C for 5 h [sample (ii)], and (b) same as in (a), followed by oxidation in $^{16}O_2$ at 930 °C for 2 h [sample(iii)]. In insets are represented the related $[^{18}O]$ concentration profile obtained using the program SPACES.

nm. The total amount of ^{16}O and ^{18}O present in the films after each processing step was measured by nuclear reaction analysis (NRA) with a precision better than 3%. The depth profiles of ^{18}O present in the films after the second and third processing steps, were determined by nuclear reaction resonance profiling (NRP) using the very narrow resonance in the nuclear reaction $^{18}O(p,\alpha)^{15}N$ at $E_R=151$ keV ($\Gamma_R=100$ eV). This technique[7] consists in measuring the excitation curve, i.e., the yield of the α particles versus the proton energy, around the resonance energy E_R. The excitation curve can be converted into a concentration depth profile using the SPACES program.[8] In order to enhance the depth resolution, the samples were tilted at 65° with respect to the proton beam direction. In such experimental conditions, the NRP technique provides a depth resolution better than 1 nm near the sample surface. Due to the characteristics of this resonance, the excitation curves present a very low background to signal ratio (10^{-4}), rendering then the determination of the profiles accurate.

In Figs. 1(a) and 1(b) are represented the excitation curves measured by NRP on sample (ii) and on sample (iii). The insets show the concentration depth profiles of heavy oxygen atoms $[^{18}O]=[^{18}O/(^{18}O+^{16}O)]$ in the oxide film. In sample (ii) the ^{18}O atoms are found in two well separated regions. The high energy ^{18}O signal (well above E_R) is attributed to the interfacial growth according to the Deal and Grove model: the oxidizing species diffuse into interstitial positions in the silica network towards the SiO_2/Si interface where they react to form the new oxide. The low energy ^{18}O signal (close to E_R) corresponds to the ^{18}O atoms (4.6×10^{15} atoms/cm^2), encountered just below the sample surface, due to exchanges between the oxygen from the gas phase and those from the silica network.[3] Here the oxygen atoms diffuse via an interstitialcy mechanism by means of peroxyl bridges which are created near the surface. Simulations of the excitation curves with the program SPACES show that the profile of the ^{18}O atoms near the surface in sample (ii) is very close to an erfc function [Eq. (2a)] confirming that the transport of ^{18}O species is most probably driven by a diffusion mechanism. The surface peak can be expressed by:

$$C(x;t_0)=C_0\times\mathrm{erfc}\left(\frac{x}{2\sqrt{D^*t_0}}\right), \tag{2a}$$

$$Q_s^{18}=\int_0^\infty C(x;t_0)dx=2C_0\sqrt{\frac{D^*t_0}{\pi}}, \tag{2b}$$

where C_0 is the surface concentration of the ^{18}O atoms in the silica, and D^* represents the apparent diffusion coefficient of the mobile species in the silica. C_0 is found to be equal to the labeling of the gas $[(C_0/N_n=99.7\%)$, N_n is the number oxygen atoms needed to form a unit volume of silica] and $t_0=5$ h is the duration of the ^{18}O oxidation. Q_s^{18} is the total amount of ^{18}O atoms located in the surface peak. D^* can be expressed by:

$$D^*=D\times\frac{C_d}{N_n}, \tag{3}$$

where D is the diffusion coefficient of the mobile species, and C_d is the concentration of defects responsible for the oxygen transport in the silica and fixation of ^{18}O just below the surface.

After the third oxidation step in $^{16}O_2$ [sample(iii)], two distributions of ^{18}O remain in the sample as shown in Fig. 1(b). As in the previous case, the high energy one corresponds to atoms located near the SiO_2/Si interface. As expected, except for the ^{16}O rich layer at the interface, no significant change in the ^{18}O amount and distribution can be detected between sample (ii) and sample (iii) in this region as shown in the inset of Fig. 1(b). However, for the low energy distribution, i.e., for the ^{18}O atoms located near the sample surface, a significant loss of ^{18}O atoms has occurred during the third treatment step. The total loss of ^{18}O atoms measured by NRP gives 1.8×10^{15} atoms/cm^2, which corresponds to a decrease of ^{18}O of 42% in the surface region, and the ^{18}O depth distribution is no longer an erfc. The ^{18}O atoms diffuse in the silica film, and when they reach the sample surface they are replaced by ^{16}O atoms from the gas phase. Assuming that the defect concentration is constant or varies weakly in the first nanometers below the surface where the exchange takes place, and that the silica constitutes an infi-

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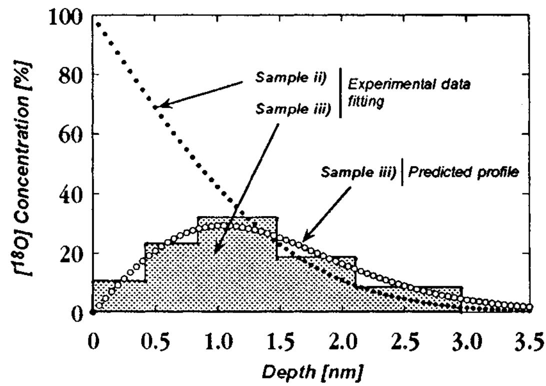

FIG. 2. Near surface [^{18}O] concentration profile in sample(ii), and in sample (iii) as extracted from the measured excitation curves via the SPACES program theoretical profile, and the predicted profile after the third treatment step, calculated using Eq. (5).

nite media, the diffusion process would lead ^{18}O to follow a Gaussian distribution for an initial plane distribution:

$$G(x;t)=\frac{1}{\sqrt{2\pi\sigma}}\times\exp\left(-\frac{x^2}{2\sigma^2}\right), \tag{4}$$

with $\sigma=\sqrt{2D^*t}$. Furthermore, assuming that the sample surface is permeable to the diffusing species, then after the third oxidation step in $^{16}O_2$ for $t=2$ h, the new profile of the ^{18}O atoms which were incorporated during the second oxidation step in $^{18}O_2$, can be calculated from the following convolution:

$$C(x;t_0+t)=G(x;t)^*C(x), \tag{5}$$

where $C(x)$ is the equivalent ^{18}O initial profile in a virtual infinite medium for diffusion in a semi-infinite medium with a permeable surface. $C(x)$ is then given by:

$$\begin{cases} C(x)=C(x;t_0)\rightarrow & \text{for } x\geqslant 0 \\ C(x)=-C(-x;t_0)\rightarrow & \text{for } x<0 \end{cases}. \tag{6}$$

In Fig. 2 the initial erfc depth profile of ^{18}O is represented after the second treatment step [sample(ii)], and the ^{18}O depth profile after the third treatment step [sample(iii)], as extracted from the measured excitation curves via the SPACES program, and the predicted profile after the third treatment step, calculated using Eq. (5). The calculations were made using the same value of D^* for the initial erfc-like and for the profile after the third oxidation step. One notices the good agreement between the profile obtained from the SPACES simulation of the experimental excitation curve and that calculated with Eq. (5), confirming the hypotheses:

(i) the defects can be thought as diffusing in a semi-infinite medium and
(ii) the gas/SiO_2 interface at $x=0$ constitutes a permeable surface.

This result strongly supports the idea of a diffusion of the oxidizing species via an interstitialcy mechanism. The calculated value of the apparent diffusion coefficient of the near surface mobile oxygen is $D^*\approx 4\times 10^{-19}$ cm^2/s. This value is more than six times lower than previously obtained results at 930°C,[9] probably due to the lower concentration of defects in the samples analyzed in the present study, since D^* is proportional to the defects concentration [see Eq. (3)]. The only difference in the sample preparation between this work and the one reported in Ref. 9 was the first oxidation step. In Ref. 9 this oxidizing step was carried out in a gas flow furnace in O_2 at atmospheric pressure, whereas in this work, the first oxidation step was performed in dry oxygen, at a static pressure below atmospheric pressure. Thus, the difference in the diffusion coefficients, intimately related to local defects, can be explained either by the existence of water vapor traces in the gas flow system which would produce more defects in the growing oxide, or by an oxygen pressure dependence of the concentration of defects in the film. We think that the presence of water vapor traces is more plausible to explain such a difference in the apparent diffusion coefficients.

Work is in progress to investigate the effects of thermal processing parameters (initial surface cleaning, treatment time, temperature, and gas pressure) on the near surface defects, hoping that this approach will contribute to optimizing the reliability of the future gate oxides.

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