

An isotopic labeling study of the growth of thin oxide films on Si(100)

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(Received 4 May 1995; accepted for publication 13 July 1995)

The mechanism of thin (<8 nm) oxide growth on Si(100) has been studied by high-resolution medium energy ion scattering in combination with oxygen isotope substitution in the $T=800\text{--}900\text{ }^\circ\text{C}$ and 0.1–1 Torr oxygen pressure regime. Isotopic labeling experiments demonstrate that the Deal–Grove model breaks down for these films. In addition to the traditional oxidation reaction at the Si/SiO₂ interface, two other spatially specific reactions take place during thermal oxidation: an exchange reaction at the oxide surface and an oxidation reaction in the near-interfacial region. © 1995 American Institute of Physics.

The growth of thin oxide films during the thermal oxidation of silicon is still not well-understood.^{1–6} Oxidation kinetics for thick (>20 nm) films is described by the Deal–Grove model, in which oxide growth proceeds via molecular oxygen diffusion to the Si–SiO₂ interface and reaction with silicon at the interface.⁷ However, early studies^{4,8} demonstrated that the oxidation kinetics for ultrathin (<10 nm) oxides could not be explained by this model.

Recently, we have used sequential exposures of oxygen isotopes in combination with medium energy ion scattering (MEIS) to elucidate the growth mechanism of 2–5 nm oxide films.^{9,10} This technique¹¹ provides a determination of the isotope depth distributions with an accuracy ($\sim 0.4\text{--}0.5\text{ nm}$), significantly better than NRA⁵ and SIMS¹² which have previously been used to study the growth of thicker oxides. In particular, we showed that ¹⁸O₂ followed by ¹⁶O₂ oxidation results in overlapping depth profiles of the isotopes for 2–3 nm films (isotopic mixing), a behavior not expected from the traditional Deal–Grove model. We also observed ¹⁸O loss after ¹⁶O₂ exposures, the result of an oxygen exchange reaction near oxide surface. A new “interfacial+near-interfacial+surface exchange reaction” model was proposed to account for these results.¹⁰

Neither the near-interfacial nor the surface exchange reactions were directly resolved in our previous experiments. In this letter, we present results of an MEIS study of thicker ($\sim 6\text{ nm}$) Si ¹⁶O₂ films reoxidized in ¹⁸O₂ to final thicknesses up to $\sim 8\text{ nm}$. Since the thickness of the initial oxide is now greater than the thickness of the two reaction regions (which have a width on the order of 2 nm), two well-separated ¹⁸O peaks are observed in the MEIS spectra after the reoxidation; one corresponds to an ¹⁸O oxide near the surface, the other to ¹⁸O atoms at or near the interface. These results strongly support our “interfacial+near-interfacial+surface exchange reaction” model.

Samples were cut from a 5 in. *n*-type Si(100) wafer with a thin ($\sim 6\text{ nm}$) oxide film grown in ¹⁶O₂ at 800 °C at an IBM Fab-Facility. They were then reoxidized in an UHV

chamber (base pressure 10^{-10} Torr) in ¹⁸O₂ (isotopic enrichment 98%, water concentration less than 2 ppm). Although the samples were transferred in air from the IBM Fab to our UHV chamber, no carbon or other contaminants were observed in the spectra after a flash to $\sim 300\text{ }^\circ\text{C}$.

The energy of ions backscattered from a certain isotope is determined by target masses, the incident energy and the scattering angle. In addition, since protons lose energy while traveling in the film ($\sim 130\text{ eV/nm}$ in Si, and $\sim 140\text{ eV/nm}$ in SiO₂ for $\sim 80\text{--}90\text{ keV}$ protons¹⁰), one can (with our energy resolution) separate the contributions from atoms near the interface with those near the surface. The former are shifted to the lower energies with respect to the surface oxygen. Further information about sample preparation, data evaluation, and other technical details can be found elsewhere.¹⁰

Spectra for the samples before and after reoxidation are shown in Fig. 1. The spectrum for the initial oxide shows one broad peak from ¹⁶O atoms. In the reoxidized samples, both ¹⁶O and ¹⁸O atoms are seen. Moreover, there are two ¹⁸O peaks; one, at higher backscattering energies, corresponds to oxygen near the oxide surface, the other to oxygen located near the interface. Concurrent with the development of the surface ¹⁸O peak, the high energy part of the ¹⁶O peak becomes depleted. This observation shows that the higher energy ¹⁸O peak is not due to oxygen dissolution in the oxide (the Deal–Grove model includes very little oxygen dissolved in the oxide) but rather due to exchange reaction(s), i.e., ¹⁶O leaves the surface and ¹⁸O incorporates into the oxide. Although the area of the ¹⁶O decreases, the low-energy part of the peak becomes broader. This indicates that the thickness of the ¹⁶O-containing oxide increases. This kind of behavior holds for the two temperatures studied (Fig. 1), however, the absolute rates of both the surface exchange and the (near) interfacial reactions are higher at higher temperature. The observation of the two ¹⁸O peaks and the change of the shape of the ¹⁶O peak definitely show that the Deal–Grove model breaks down for thin oxide films. If this model had been valid, the ¹⁶O peak would have remained unchanged and only one ¹⁸O peak would have appeared at the interface.

More quantitative information about isotope distribu-

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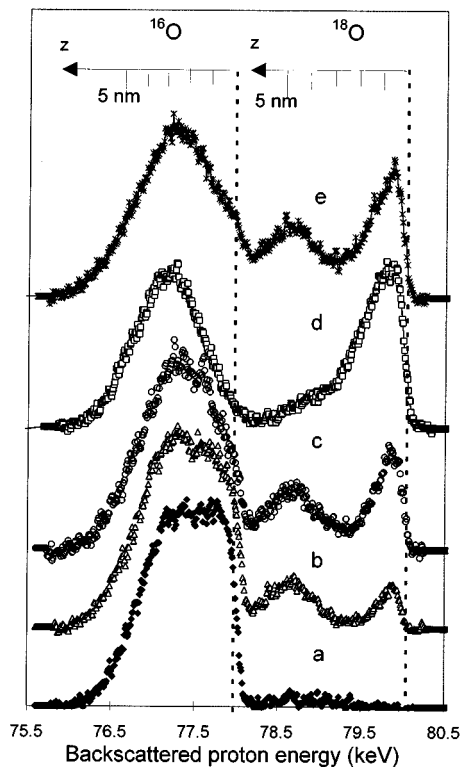


FIG. 1. MEIS spectra in the oxygen region for: (a) the initial Si^{16}O_2 film, and samples reoxidized in $^{18}\text{O}_2$: (b) at 800°C at 1 Torr for 21.5 h, 800°C , (c) 1 Torr, 40 h, (d) 900°C , 0.1 Torr, 5 h, (e) and 900°C , 1 Torr, 5 h. The spectra were taken in a channeling geometry (along the [001] direction) at a scattering angle of 138.5° . The proton energy in the incident beam was 97.2 keV. A depth (z) scale (converted from the energy scale with help of the known value of the stopping power) is also shown for both isotopes as a guide. The dashed vertical lines show where the peak position should be for oxygen atoms on the oxide surface.

tions in the films can be obtained by energy spectra modeling.¹⁰ Resulting depth profiles are shown in Figs. 2(a)–2(c), respectively. The ^{16}O distribution in the original oxide is also shown for comparison. The thickness of this oxide is ~ 6 nm; this includes ~ 4.5 nm of the SiO_2 [stoichiometry is preserved after reoxidation, see Figs. 2(c) and 3(c)] and a transition region (~ 1.5 nm) where the oxygen density is lower than in the “bulk” oxide. Among other contributions, the transition region is formed by incompletely oxidized silicon atoms (e.g., suboxides, silicon interstitials, silicon clusters, etc.). This is an important point in understanding the near-interfacial reaction. The nature of this region is discussed in more detail elsewhere.¹⁰

The distribution of ^{18}O has two regions where the concentration is high; one is near the surface, the other closer to the interface [Fig. 2(a)]. An increase of the ^{18}O concentration near the surface is accompanied by a decrease in the ^{16}O concentration [Fig. 2(b)] so that the total amount of oxygen in this oxide region remains constant [Fig. 2(c)]. This is evidence of a surface exchange reaction. The ^{18}O region near the interface [Fig. 2(a)] overlaps with the ^{16}O distribution in the oxide [Fig. 2(b)], indicating an isotopic mixture near the interface. Furthermore, both isotopes propagate deeper as the oxidation proceeds. The thickness of the ^{16}O -oxide layer increases, which cannot be explained within the Deal–Grove

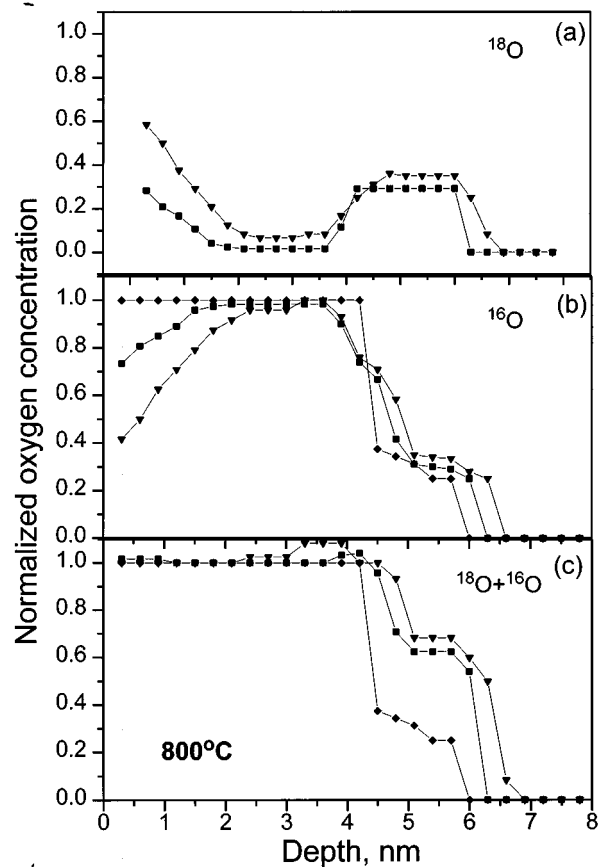


FIG. 2. Depth profiles of: (a) ^{18}O , (b) ^{16}O , and (c) their sum ($^{16}\text{O}+^{18}\text{O}$) after reoxidation at 800°C for: 21.5 h (squares) and 40 h (triangles). The oxygen distribution in the original Si^{16}O_2 film is shown by diamonds. Oxygen concentrations are normalized with respect to the bulk oxide value.

model in which the new Si^{18}O_2 oxide should buildup right at the interface leaving the initial Si^{16}O_2 layer unchanged on the top. Our results show that the reaction also occurs in the near-interfacial oxide, probably throughout the transition region, resulting in the isotopic mixture near the interface. This emphasizes the role of the near-interfacial transition region in the oxidation, consistent to some extent with the idea of a reactive layer.^{1,3,13} However, according to the reactive layer model, the growth reaction takes place only on top of a 1.5–2 nm reactive layer; this should result in isotope distributions different from the ones observed.

At the higher temperature, the ^{18}O regions near the surface and the interface are broader and reaction rates are higher (Fig. 3). The relative ratio of the surface exchange reaction and the (near) interface reaction depends on the oxidation conditions. In particular, under some conditions (when the reoxidation time is short or the temperature/oxygen pressure is low), only the exchange reaction can be observed. For the same oxidation temperature and time, a decrease in oxygen pressure from 1 to 0.1 Torr results in less interfacial growth and more surface exchange [Figs. 1(d) and 1(e)].

Our results clearly demonstrate that the traditional viewpoint of silicon oxidation⁷ as merely a reaction at the interface is too simplistic to fully describe the growth of sub-10 nm films. Deviations from Deal–Grove kinetics for thin ox-

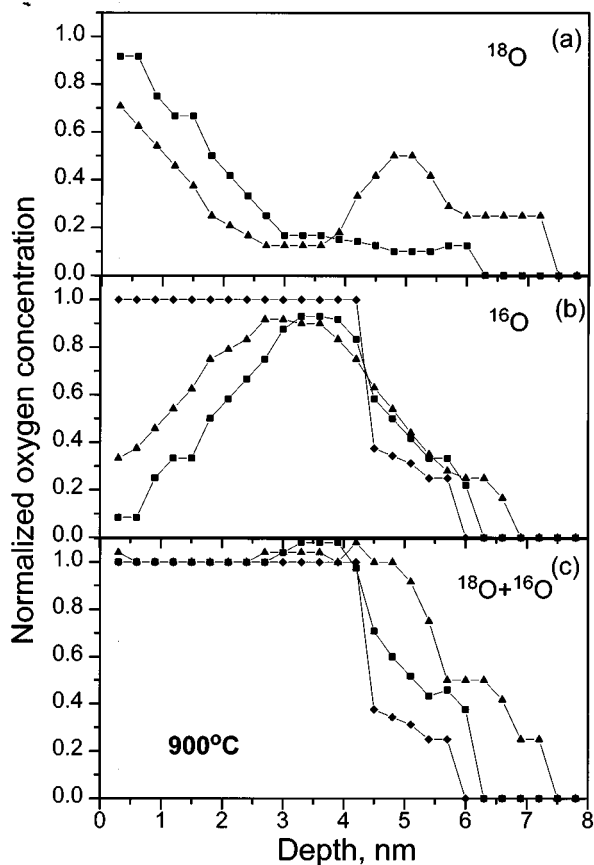


FIG. 3. Depth profiles of: (a) ^{18}O , (b) ^{16}O , and (c) the total amount ($^{16}\text{O} + ^{18}\text{O}$) after reoxidation at 900°C for 5 h at 0.1 Torr (squares), and 1 Torr (triangles).

oxide films have been observed previously.^{3,4,6,8} These experiments were generally not sufficient to rule out the Deal–Grove model. Instead, either the parameters relevant to oxygen transport to the interface or the reaction at the interface in the original Deal–Grove construct were modified to accommodate these results, in particular the faster oxidation kinetics.^{3,4,6} We have shown, however, that, in addition to the traditional interface reaction, there are two other reactions occurring: a near-interfacial reaction throughout the transition region and a surface exchange reaction. The near-interfacial reaction is an additional channel of the growth. Its importance could be a reason for the faster oxidation kinetics observed in the ultrathin regime. In contrast, the exchange reaction at the surface does not seem to affect the growth behavior for films thicker than $\sim 3\text{--}4$ nm. It results in an exchange of surface and gas phase oxygen but the overall

oxygen concentration near the surface is preserved [Figs. 2(c) and 3(c)].

According to our model,¹⁰ the near-interfacial reaction is due to reoxidation of incompletely oxidized silicon. In the interfacial reaction, the oxide is formed by the reaction of oxygen with silicon at the interface. This reaction also supplies the near-interfacial oxide region with incompletely oxidized silicon.

The concentration of incompletely oxidized silicon depends on a number of factors, such as the rate of its generation and removal. The relative rates of these processes vary with thickness, oxygen partial pressure, temperature, and reaction time, and may result in variations of the thickness and composition of the nonstoichiometric transition region with processing parameters. One more factor that may affect the relative reaction rates is the water and/or hydrogen content in oxygen and oxide.^{5,14} This issue is also of particular importance because hydrogen is known to accumulate near the interface and cause device (hot electron) degradation.^{15,16}

We would like to thank Dr. D. Buchanan for providing a wafer with a high quality initial oxide, and Dr. L. C. Feldman and Dr. M. L. Green for useful discussions. This work is supported by NSF (DMR-9408578) and PRF (28788-AC5) Grants.

¹N. F. Mott, S. Rigo, F. Rochet, and A. M. Stoneham, *Philos. Mag. B* **60**, 189 (1989).

²C. R. Helms and E. H. Poindexter, *Rep. Prog. Phys.* **57**, 791 (1994).

³C. J. Sofield and A. M. Stoneham, *Semicond. Sci. Technol.* **10**, 215 (1995).

⁴E. Irene, *Crit. Rev. Solid State Mater. Sci.* **14**, 175 (1988).

⁵F. Rochet, S. Rigo, M. Froment, C. d'Anterrosches, C. Maillot, H. Roulet, and G. Dufour, *Adv. Phys.* **35**, 237 (1986).

⁶J. M. Delarios, C. R. Helms, D. B. Kao, and B. E. Deal, *Appl. Surf. Sci.* **39**, 89 (1989).

⁷B. E. Deal and A. S. Grove, *J. Appl. Phys.* **36**, 3770 (1965).

⁸H. Z. Massoud, J. D. Plummer, and E. A. Irene, *J. Electrochem. Soc.* **132**, 2693 (1985).

⁹E. P. Gusev, H. C. Lu, T. Gustafsson, and E. Garfunkel, in *Interface Control of Electrical, Chemical, and Mechanical Properties*, edited by S. P. Murarka, K. Rose, T. Ohmi, and T. Seidel (Materials Research Society, Pittsburgh, 1994), p. 69.

¹⁰E. P. Gusev, H. C. Lu, T. Gustafsson, and E. Garfunkel, *Phys. Rev. B* **52**, 1759 (1995).

¹¹J. F. van der Veen, *Surf. Sci. Rep.* **5**, 199 (1985).

¹²C. J. Han and C. R. Helms, *J. Electrochem. Soc.* **135**, 1824 (1988).

¹³A. M. Stoneham, C. R. M. Grovenor, and A. Cerezo, *Philos. Mag. B* **55**, 201 (1987).

¹⁴R. Pfeffer and M. Ohring, *J. Appl. Phys.* **52**, 777 (1981).

¹⁵R. Gale, H. Chew, F. J. Feigl, and C. W. Magee, in *The Physics and Chemistry of SiO_2 and the Si-SiO_2 Interface*, edited by C. R. Helms and D. E. Deal (Plenum, New York, 1988), p. 177.

¹⁶E. Cartier, D. A. Buchanan, and G. J. Dunn, *Appl. Phys. Lett.* **64**, 901 (1994).