Isotopic substitution of Si during thermal growth of ultrathin silicon-oxide films on Si(111) in O_2

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The transport of Si atoms during thermal growth of silicon-oxide films on silicon in dry O_2 was investigated by isotopic substitution of Si. The experiment consisted of depositing a 7.6-nm-thick epitaxial layer of ^{29}Si on a Si(111) substrate and determining the ^{29}Si profiles, with subnanometric depth resolution, before and after oxidation in 50 mbar of dry O_2 at 1000 °C for 60 min. The results constitute an experimental confirmation of a widely held belief that Si does not diffuse through the growing oxide to react with oxygen at the gas/oxide interface, leaving O_2 as the only mobile species. [S0163-1829(99)10127-9]

There is a renewed and increasing interest in modeling the initial stages of thermal growth of silicon oxide films on Si in dry O_2,[1] the most common material used as a gate dielectric in Si-based metal-oxide-semiconductor (MOS) structures. As microelectronic device dimensions shrink below 0.25 μm, these oxide films are forced to scale down to thicknesses of 5 nm and less. Reliability of highly integrated Si devices is critically dependent on the characteristics of the gate oxide film, such as thickness uniformity, defect density, dielectric strength, etc. as well as on those of the oxide/Si interface, such as roughness, electronic states density, etc.[2–4] The electronic structure and properties of ultrathin films of silicon oxide thermally grown on Si, and of the oxide/Si interface have been intensively studied, in strict synergism with the development of the semiconductor industry.[5] The knowledge of film growth kinetics, however, has not made any significant scientific progress since the early model of Deal and Grove,[6] which assumes that growth is promoted by interstitial diffusion of the oxidant species, the O_2 molecule, in steady-state regime, and reaction with Si at an abrupt oxide/Si interface. This model, and more specifically the resulting linear-parabolic growth law, is known to agree with the observed growth kinetics in dry O_2 only for films thicker than 20 nm,[6–8] well above the range of interest for present and future microelectronics applications.

Improvements on modeling oxide growth below 20 nm are therefore highly desirable. A wealth of O isotopic substitution experiments[9–11] performed in oxides with thicknesses well below 20 nm support the ''reactive layer'' model.[12,13] This layer, formed at the oxide/Si interface in the initial stages of growth, contains mostly non-fully oxidized Si (suboxides). The model proposes that the SiO_2 film grows by reaction between in-diffusing oxygen molecules and out-diffusing silicon atoms at the outer edge of the reactive oxide (boundary between amorphous silica and reactive layer). The weak point of the reactive layer model is the assumption of diffusion of Si atoms from the substrate, which so far has not been confirmed by direct observation. Besides the reactive layer model, recent molecular dynamics simulations[1] performed to investigate atomic scale mechanisms that govern the initial stages of the oxidation process indicated that Si interstitials are injected from the substrate into the growing oxide, a fact which demands experimental confirmation. On the other hand, we are currently modeling the thermal growth kinetics of silicon-oxide films on Si, aiming to describe the whole oxide thickness interval, based solely on the assumptions that (i) it is a diffusion-reaction phenomenon, (ii) the diffusing species is O_2,[9–12,14,15] and (iii) Si does not diffuse during the oxidation process. Thus, the thorough understanding of the initial stages of thermal growth of silicon-oxide films on single-crystalline Si (c-Si) requires a clarification of the Si mobility issue.

The only methodology capable of providing direct experimental evidence on the mobility of Si atoms during thermal oxidation is isotopic substitution of Si. To the best of our knowledge there is only one previous experiment[16] of this kind, performed in thick oxides grown in H_2O vapor and with a poor depth resolution (approximately 50 nm), which indicated the immobility of Si during thermal growth of Si oxide on Si(100). An indirect investigation,[17] using O isotopic substitution, led to the same conclusion. We report here on an experimental investigation of the situation of present practical interest using (i) isotopic substitution of Si in association with nuclear resonance profiling with subnanometric resolution, aiming to provide direct and high depth resolution evidence of the transport of Si, and (ii) thermal oxide growth on c-Si in dry O_2.

Si isotopic substitution was accessed by depositing approximately 7-nm-thick ^{29}Si-enriched silicon films on the surface of Si(111) wafers, by implantation of ^{29}Si ions at an energy of 30 eV, using a beam from a high mass resolution ion implanter. Although the semiconductor material of wide interest for gate dielectric in Si-based MOS structures is Si(001) and not Si(111), there are neither reasons nor experimental evidences that atomic transport phenomena would be different for different surface orientations, and thus the re-

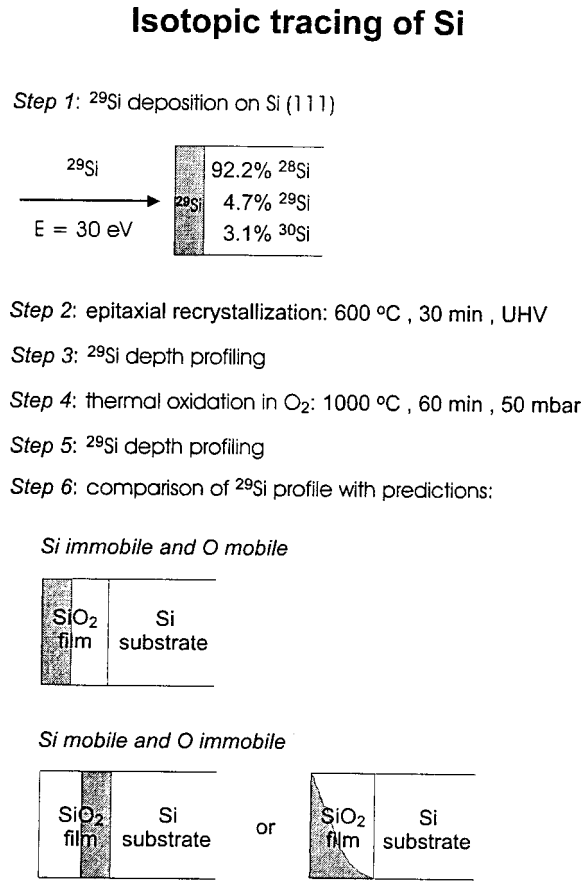

FIG. 1. Principles of isotopic substitution as applied to the case of ^{29}Si in the thermal growth of silicon-oxide films on Si in dry O_2.

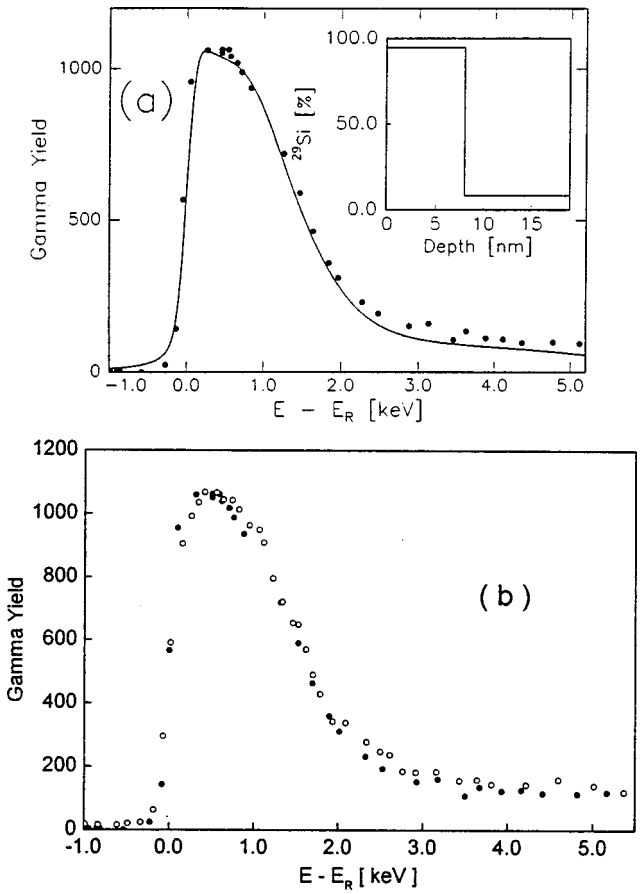

FIG. 2. (a) Excitation curve (solid circles) of the ^{29}Si(p,γ) ^{30}P nuclear reaction around the resonance at 417 keV for the as ^{29}Si-deposited Si(111) substrate, its simulation (solid line), and the correspondent ^{29}Si concentration profile in the inset. (b) Excitation curves for ^{29}Si/Si(111) samples as-deposited (solid circles) and after annealing in ultrahigh vacuum at 600 °C for 30 min (empty circles).

sults here obtained for Si(111) oxidation could be readily transferred to Si(001) oxidation. Following ion extraction from a sputter ion source (typically at 25 kV) and beam focusing with an Einzel lens, a 90° deflection magnet selected the desired ion species. A mass resolution of $M/\Delta M > 300$ allowed the separation of isotopes. Using natural silicon sputter cathodes, the ion currents of the different stable Si isotopes (^{28}Si, ^{29}Si, ^{30}Si) measured with a Faraday cup agreed reasonably well with their natural isotopic abundances, proving the absence of unwanted molecular beams, such as ^{28}Si ^{1}H^{+}, for instance. An electrostatic quadrupole triplet was used to focus the ion beam on the sample. Lateral uniformity of the deposition was achieved by means of a deflection unit which scanned the beam across the sample surface. Deceleration of the beam from the initial 25 keV to an energy of 30 eV was performed using a single gap electrode configuration at a distance of 23 mm from the sample. For the present work, Si(111) wafers 25 mm in diameter were used as substrates. Thickness fluctuations of the deposited ^{29}Si layer were smaller than $\pm 3\%$ across the wafer. Before introduction into the vacuum system, the wafers were cleaned using a 4%-diluted HF solution (60 s) followed by a rinse in pure deionized water (60 s) and drying in Ar flow. An annealing in an ultrahigh vacuum at 600 °C for 30 min was performed *in situ* after deposition in order to crystallize the deposited ^{29}Si layer epitaxially with the Si(111) substrate, which was checked by low-energy electron diffraction (LEED). Subsequently, a silicon-oxide film, approximately 19 nm thick, was grown in 50 mbar of 97% ^{18}O-enriched O_2, at 1000 °C for 60 min. The profiles of ^{29}Si before and after thermal oxidation, and of ^{18}O were determined by nuclear resonance profiling,[18–20] using the narrow, isolated resonances in the ^{29}Si$(p,\gamma)^{30}$P nuclear reaction cross section curve at 417 keV, and in the ^{18}O$(p,\alpha)^{15}$N nuclear reaction, at 151 keV, respectively. The depth resolution achieved by this technique is approximately 0.7 nm near the sample surface.

The principles of ^{29}Si isotopic tracing as applied to the situation of interest in the present work are summarized in Fig. 1. The ^{29}Si profiles in the oxides represent only the limit cases, namely either Si immobile and O mobile, or Si mobile and O immobile. The case in which the two species are mobile would give ^{29}Si profiles intermediate between those sketched in Fig. 1. Figure 2(a) shows the excitation curve of the ^{29}Si$(p,\gamma)^{30}$P nuclear reaction around 417 keV for the as ^{29}Si-deposited sample, and the correspondent ^{29}Si concentration profile assumed to simulate the excitation curve with the program SPACES,[19] which is based on stochastic processes of energy loss of ions in matter. This profile indicates the deposition of a homogeneous 7.6-nm-thick Si film on the Si(111) substrate, having a concentration of ^{29}Si of approximately 92%. The smaller, constant ^{29}Si concentration at depths beyond 7.6 nm is due to ^{29}Si existing in the c-Si substrate, in

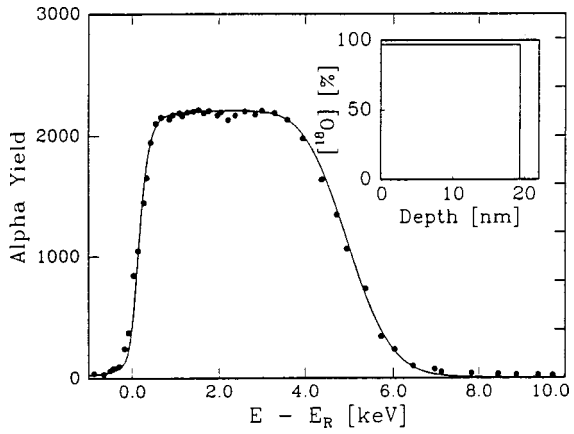

FIG. 3. Excitation curve of the $^{18}O(p,\alpha)\,^{15}N$ nuclear reaction around the resonance at 151 keV (solid circles), its simulation (solid line), and ^{18}O profile in the inset, for the epitaxial $^{29}Si/Si(111)$ sample oxidized in 50 mbar of 97% ^{18}O-enriched O_2, at 1000 °C for 60 min.

which its natural abundance is 4.7%. After annealing, the measured ^{29}Si excitation curve is very similar to the as-deposited one as shown in Fig. 2(b), indicating that there is no redistribution or loss of ^{29}Si during this annealing step. Annealing of the $^{29}Si/Si(111)$ structure leads to epitaxy of the ^{29}Si-deposited layer on the Si(111) substrate as confirmed by Rutherford backscattering in channeling geometries[18] and by LEED imaging of the sample surface after annealing, which evidenced a 7×7 reconstructed Si(111) surface.

The epitaxial $^{29}Si/Si(111)$ wafer was oxidized under the conditions specified above, giving the ^{18}O excitation curve and profile shown in Fig. 3. A homogeneous, 19-nm-thick oxide film was grown on the Si(111) wafer, containing ^{18}O in a concentration corresponding to the isotopic labeling of the gas. This means that the oxide growth consumed the entire ^{29}Si epitaxial layer plus a slight portion of the natural Si from the Si(111) wafer near the $^{29}Si/Si(111)$ interface.

The ^{29}Si excitation curve and profile in the oxidized sample are shown in Fig. 4(a), while Fig. 4(b) shows the excitation curves for the pre-oxidation [solid circles, ^{29}Si epitaxial on Si(111)] and post-oxidation [empty circles, ^{29}Si in $SiO_2/Si(111)$] samples. The arrows in Fig. 4(b) indicate the energy positions of the half maxima in the leading edges of the ^{29}Si excitation curves for the pre-oxidation (arrow pointing downwards) and post-oxidation (arrow pointing upwards) samples, which are the best indications available of the positions in energy of the outermost ^{29}Si atoms in each sample. Thus the thermally grown silicon-oxide film sample has a ^{29}Si distribution starting at its outermost surface. The areas of the two excitation curves in the regions corresponding to the ^{29}Si-enriched layer are equal within 5%. The different maxima yields and widths result from the different concentrations and lengths of the ^{29}Si distributions in the two samples, as well as from the differences in stopping power of 417-keV protons in Si and SiO_2. Apart from these differences, the excitation curves for the two samples coincide indicating that the profile of ^{29}Si atoms remained abrupt, starting at the sample surface, after thermal growth of the oxide film. According to the principles of isotopic substitution stated in Fig. 1, this means that Si is immobile during

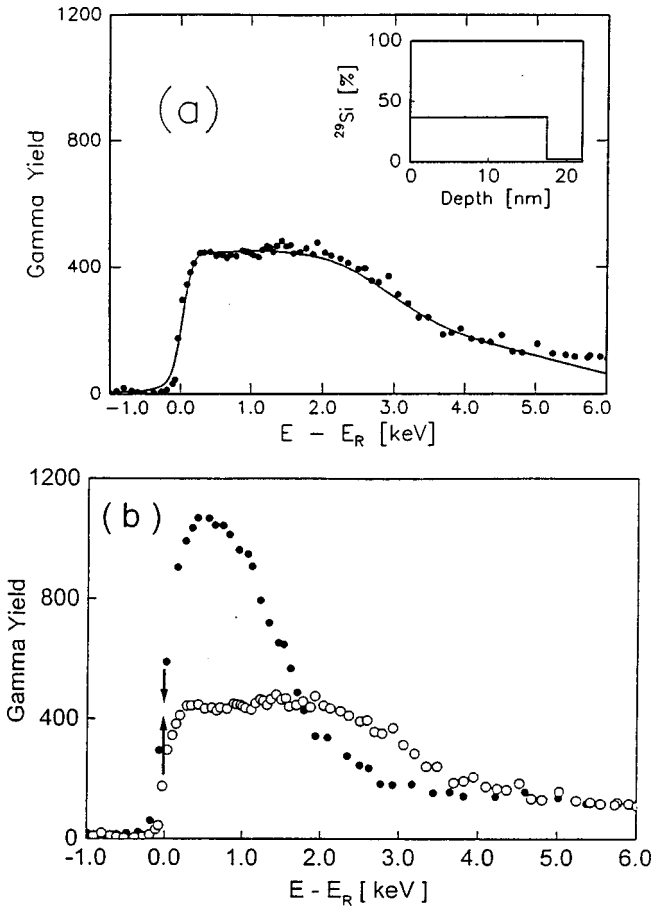

FIG. 4. (a) ^{29}Si excitation curve (solid circles), its simulation (solid line), and ^{29}Si profile in the inset for the oxidized sample. (b) ^{29}Si excitation curves in the pre-oxidation [solid circles, ^{29}Si epitaxial on Si(111)] and post-oxidation [empty circles, ^{29}Si in $SiO_2/Si(111)$] samples. The arrows indicate the energy positions of the half maxima in the leading edges for the pre-oxidation (arrow pointing downwards) and post-oxidation (arrow pointing upwards) samples.

oxide growth in the sense that it does not diffuse across the growing oxide to react with dry O_2 at the gas/oxide interface.

The present results cannot exclude short range Si transport from the substrate into the near oxide/Si(111) interface as predicted by the reactive layer model.[12,13] Indeed, if oxidation occurred following the reactive layer mechanism, the resulting ^{29}Si depth profiles would look similar to those presented here, since the model predicts that Si atoms from the substrate diffuse (or are injected) through only very short distances, typically 1 to 2 nm. After converting the whole ^{29}Si layer into $^{29}SiO_2$, a new oxide (mostly $^{28}SiO_2$) would build up underneath the thick $^{29}SiO_2$ layer and Si diffusion (injection) would cause some possible ^{28}Si–^{29}Si intermixing within 1–2 nm near the $^{29}SiO_2/^{28}SiO_2$ interface. However, observation of ^{28}Si–^{29}Si intermixing phenomenon at a depth around 19 nm below the oxide surface is beyond the capabilities of the present experimental methods, because the depth resolution of nuclear resonance profiling degrades with depth. The degradation in depth resolution is caused by loss of definition in the energy of the incident protons (straggling).[19,20] After the 417-keV protons have crossed 19

nm of silicon oxide one can estimate that the depth resolution increases from its near-surface value (0.7 nm) to approximately 1.5 nm. Furthermore, as mentioned above, natural Si has approximately 4.7% ^{29}Si, and the lack of depth resolution at the position of an eventually nonsharp $^{29}SiO_2/^{28}SiO_2$ interface would also degrade the sensitivity to distinguish between small concentrations of ^{29}Si atoms coming from the natural Si substrate and distributed within 1 to 2 nm from the interface, from those coming from the $^{29}SiO_2$ or $^{28}SiO_2$ layers.

In conclusion, one can say that, within the depth resolution of the present Si isotopic substitution experiment, which is of the order of 0.7 nm near the surface, the results confirm the immobility of Si during thermal growth of silicon-oxide films on Si(111) in dry O_2, in the sense that Si atoms do not diffuse across the growing oxide to react with O_2 at the gas/oxide interface. Therefore, the assumption that O_2 is the only mobile species in this process is justified. However, shallow diffusion of Si atoms from the substrate across an incompletely oxidized reactive layer[12] to react with O_2 at the oxide/reactive layer interface, or, alternatively, Si interstitial injection at the very initial stages of oxidation[1] cannot be excluded on the basis of the present findings. Further developments in the experimental methods here described are necessary to clarify this last aspect and work is now being undertaken in this direction.

[1] A. Pasquarello, M. S. Hybertsen, and R. Car, Nature (London) **396**, 58 (1998).

[2] L. C. Feldman, E. P. Gusev, and E. Garfunkel, in *Fundamental Aspects of Ultrathin Dielectrics on Si-based Devices*, edited by E. Garfunkel, A. Gusev, and A. Vul (Kluwer Academic Publishers, Dordrecht, 1998), p. 1.

[3] J. D. Plummer, in *The Physics and Chemistry of SiO_2 and the Si-SiO_2 Interface*, edited by H. Z. Massoud, E. H. Poindexter, and C. R. Helms (The Electrochemical Society, Pennington, 1996), p. 129.

[4] D. A. Buchanan and S. H. Lo, in *The Physics and Chemistry of SiO_2 and the Si-SiO_2 Interface* (Ref. 3), p. 3.

[5] K. F. Schuegraf and C. Hu, Semicond. Sci. Technol. **9**, 989 (1994).

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

[7] H. Z. Massoud, J. D. Plummer, and E. A. Irene, J. Electrochem. Soc. **132**, 2685 (1985).

[8] C.-J. Han and C. R. Helms, J. Electrochem. Soc. **134**, 1297 (1987).

[9] F. Rochet, S. Rigo, M. Froment, C. D'Anterroches, C. Maillot, H. Roulet, and G. Dufour, Adv. Phys. **35**, 237 (1986).

[10] F. C. Stedile, I. J. R. Baumvol, J.-J. Ganem, S. Rigo, I. Trimaille, G. Battistig, W. H. Schulte, and H. W. Becker, Nucl. Instrum. Methods Phys. Res. B **85**, 248 (1994).

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

[12] A. M. Stoneham, C. R. M. Grovenor, and A. Cerezo, Philos. Mag. B **55**, 201 (1986).

[13] N. F. Mott, S. Rigo, F. Rochet, and A. M. Stoneham, Philos. Mag. B **60**, 189 (1988).

[14] C.-J. Han and C. R. Helms, J. Electrochem. Soc. **135**, 1824 (1988).

[15] I. Trimaille, F. C. Stedile, J.-J. Ganem, I. J. R. Baumvol, and S. Rigo, in *The Physics and Chemistry of SiO_2 and the Si-SiO_2 Interface* (Ref. 3), p. 59.

[16] R. Pretorius, W. Strydom, J. W. Mayer, and C. Comrie, Phys. Rev. B **22**, 1885 (1980).

[17] M. P. Murrel, C. J. Sofield, and S. Sugden, Philos. Mag. B **63**, 1277 (1991).

[18] I. J. R. Baumvol, L. Borucki, J. Chaumont, J.-J. Ganem, O. Kaytasov, N. Piel, S. Rigo, W. H. Schulte, F. C. Stedile, and I. Trimaille, Nucl. Instrum. Methods Phys. Res. B **118**, 499 (1996).

[19] I. Vickridge and G. Amsel, Nucl. Instrum. Methods Phys. Res. B **45**, 6 (1990).

[20] I. J. R. Baumvol, F. C. Stedile, J.-J. Ganem, S. Rigo, and I. Trimaille, J. Electrochem. Soc. **142**, 1205 (1995).