Nonequilibrium water permeation in SiO₂ thin films

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Nuclear resonance profiling was used to measure the distributions of hydrogen incorporated into dry SiO₂ films by thermal treatments in steam. Thermal oxides were grown on silicon to a thickness of 260 nm in dry O₂ and were subsequently treated in steam at temperatures of 320 and 500 °C for periods lasting between 390 and 6 × 10⁶ s. The concentrations of hydrogen carried in by permeating water were then profiled with 6.4 MeV ¹⁵N ions using the resonant nuclear reaction H(¹⁵N, αγ)²⁰C. Water was seen to penetrate the films rapidly and to slowly react with the SiO₂ uniformly throughout the films. Two distinct stages were observed in the buildup of H, indicating that the water/SiO₂ reaction involves at least two concurrent processes rather than a single-stage process.

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Thermal oxidation of silicon to form high-quality insulating films of SiO₂ is an important process in modern electronic technology. The properties of the oxides formed by this process have been found to depend critically on the presence of water absorbed in the films during or in subsequent high temperature processing. An example of this is the recent observation of morphological differences between wet and dry ultra-thin metal-oxide-semiconductor (MOS) gate oxides: wet films were seen to be free of the micropores present in dry films and showed improved breakdown resistance. Physical models of the diffusion and incorporation of water in SiO₂ have received comparatively little experimental testing. In an early study of water diffusion in fused silica, Moulson and Roberts proposed that the transport involved mobile OH groups arising from the reaction

\[
\text{H}_2\text{O} + \text{Si-O-Si} \rightarrow 2\text{SiOH},
\]

at the outer surface. They modeled the process with Fick's second equation using a constant effective diffusion coefficient

\[
\frac{\partial [\text{OH}]}{\partial t} = D_{\text{eff}} \nabla^2 [\text{OH}],
\]

determining \( D_{\text{eff}} \) by observing the time behavior of the total OH content during the early stages of steam absorption and vacuum desorption. An alternative model, proposed by Doremus, was the transport of dissolved molecular water through "doorways" between cells or interstices in the network, with the SiOH groups produced by reaction (1) being immobile. He also assumed (a) that the reaction proceeded rapidly compared to diffusion, allowing the equilibrium concentrations of dissolving water and SiOH groups to be related by the law of detailed balance

\[
[H_2O] = [OH]^2/K,
\]

and (b) that the water concentration and its time derivative were negligible compared to those for SiOH. These assumptions led him to model the process with the concentration-dependent diffusion equation

\[
\frac{\partial [\text{OH}]}{\partial t} = (2D/K^2) \nabla^2 [\text{OH}],
\]

where \( D \) and \( D_{\text{eff}} \) are related by \( D_{\text{eff}} = 2D[H_2O]/[OH] \). This produced a much better match to the [OH] profiles measured by Roberts and Doremus in fused silica than is possible with a solution to Eq. (2). (A profile measured by Moulson and Roberts was insufficiently precise to distinguish the two models.) This model, unlike the earlier one, also implies a larger effective diffusivity for absorption than for desorption, consistent with the measurements of Moulson and Roberts. Doremus also used this model to treat the steady-state steam oxidation of silicon, relating the temperature and pressure dependence of the parabolic oxidation-rate constant to that of \( D_{\text{eff}} \).

Doremus' model applies to the regime where equilibrium has been established between \([H_2O]\) and [OH]. Our previous observations of tracer \(^{18}O\) exchange during water diffusion at relatively low temperatures were generally consistent with this model. However, we saw evidence of a systematic trend toward anomalously low exchange rates during the early stages of absorption in dry oxides. This suggested that the [OH] had not reached its saturation value, contrary to our expectation from Eq. (4) that it should have reached it on a time scale of \( x^2/D_{\text{eff}} \), where \( x \) is the film thickness. We therefore decided to investigate the early behavior of water absorption in dry oxides.

Samples were prepared by forming thermal oxide films in nominally dry \( O_2 \) at 1100 °C on \( 100 \) surfaces of \( 5 \Omega \) cm (nominal) \( n \)-type silicon to a thickness of 260 nm. The samples were subsequently treated in flowing steam at 1 atm according to the procedure described in Ref. 6. Formation of additional oxide during the steam treatments was negligible. The concentrations of hydrogen carried in by absorbed water were then profiled with 6.4 MeV \(^{15}N\) + ions by detecting the characteristic 4.4-MeV gamma rays from the resonant nuclear reaction \( H(^{15}N, \alpha\gamma)_{20}C \). The beam current was about 40 nA and the beam spot was about \( 3 \times 10 \) mm, producing negligible sample heating. Data collection lasted about 8 min at each beam energy. The integrated ion-beam current was 24 μC at each beam energy.

Detailed profiles of the near-surface regions showed
that a hydrogenous layer about 5 nm thick coated the surface of every sample, including an unoxidized Si sample which was profiled to determine instrumental background. This layer, which commonly forms on SiO₂ surfaces exposed to air, allowed us to determine the effects of beam spread, energy straggling, and resonance width on the depth resolution of the profile. A yield curve of gamma rays collected from the layer was matched to a theoretically obtained curve generated by assuming a Lorentzian resonance in the cross section. The best fit to its effective width was about 8 keV, corresponding to a depth resolution of about 5 nm near the surface; energy straggling approximately doubled this near the oxide-silicon interface. The [H] was therefore sampled only every 30 nm and no closer than 80 nm to the surface to avoid contributions from the hydrogenous outer layer.

Some difficulties have been reported by other investigators involving changes in H profiles induced by nuclear profiling; these have included hydrogen effusion⁴ from α-Si and room-temperature vacuum desorption of water from some soda-lime glasses.⁵ To check for these effects, data collection from points sampled early was repeated after completion of profiling. No statistically significant variations in [H] were observed, either in the interior or at the surface.

Our profiling results are listed in Table I, which shows the number of counts recorded from reactions occurring at various depths below the base of the hydrogenous layer (depths were calculated using a specific energy loss of 1.69 MeV/μm). The samples are in two groups, one whose treatments were at 300 C and the other at 320 C; also shown is an oxidized but untreated sample (number 309). An unoxidized silicon sample (not shown) was included for background determination; this yielded about 36 counts at every depth. After background subtraction, the counts were converted to H concentrations with calibration data obtained from previous measurements of samples containing known quantities of hydrogen.¹⁰ Some representative profiles are plotted in Fig. 1; the error bars indicate statistical uncertainty.

These results show that the [H] profiles are essentially uniform throughout the oxides, rather than taking the form of advancing fronts of diffusant. This is clearly contrary to the prediction of the Fickian OH-diffusion model, Eq. (2). In the context of the molecular H₂O diffusion/reaction model, it indicates that chemical equilibrium had not been achieved during the permeation process, invalidating Eq. (4) as well. This can be seen by inspection of Fig. 2, in which are plotted the profiles predicted by solving those equations. The relative flatness of the observed profiles is an indication that the diffusion through the oxides was rapid compared to the reaction, allowing the diffusant concentration to approach uniformity before any appreciable quantity of product had built up. The one exception observed was the oxidized but untreated sample, which shows a small but detectable accumulation of H near the surface; this may have entered the oxide immediately after its formation.

The relative uniformity of the distributions under the conditions of this experiment (i.e., thin films and moderate

### Table I. Observed yield of 4.43 gamma rays emitted from reactions occurring at indicated depths in 260-nm SiO₂ films: number of counts recorded per 24 μC of incident ¹⁵N ions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment temp. (C)</th>
<th>Time (s)</th>
<th>Counts at depths in films (nm)</th>
<th>80</th>
<th>140</th>
<th>199</th>
<th>229</th>
<th>255</th>
<th>288</th>
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<tr>
<td>201</td>
<td>500</td>
<td>96 030</td>
<td>329</td>
<td>280</td>
<td>283</td>
<td>256</td>
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<tr>
<td>202</td>
<td>500</td>
<td>29 150</td>
<td>256</td>
<td>211</td>
<td>231</td>
<td>219</td>
<td>208</td>
<td>43</td>
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<tr>
<td>203</td>
<td>500</td>
<td>14 510</td>
<td>250</td>
<td>201</td>
<td>206</td>
<td>211</td>
<td>215</td>
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<tr>
<td>204</td>
<td>500</td>
<td>4 350</td>
<td>241</td>
<td>172</td>
<td>202</td>
<td>159</td>
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<tr>
<td>205</td>
<td>500</td>
<td>1 860</td>
<td>209</td>
<td>193</td>
<td>139</td>
<td>114</td>
<td>43</td>
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<tr>
<td>301</td>
<td>320</td>
<td>601 320</td>
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<td>306</td>
<td>243</td>
<td>51</td>
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<tr>
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<td>320</td>
<td>57 000</td>
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<td>235</td>
<td>212</td>
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<td>147</td>
<td>43</td>
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<tr>
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<td>320</td>
<td>21 600</td>
<td>249</td>
<td>216</td>
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<tr>
<td>305</td>
<td>320</td>
<td>7 320</td>
<td>210</td>
<td>198</td>
<td>175</td>
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<tr>
<td>306</td>
<td>320</td>
<td>2 760</td>
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<td>1 020</td>
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<td>308</td>
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<td>390</td>
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<td></td>
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</tr>
<tr>
<td>309</td>
<td>Untreated</td>
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<td></td>
<td></td>
<td>32</td>
<td></td>
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</tr>
</tbody>
</table>

*At depth of 170 nm.

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![FIG. 1. Representative [H] profiles measured with 6.4-MeV ¹⁵N ions for some samples listed in Table I. All samples were 260-nm thick oxides which had been thermally grown in nominally dry O₂ at 1200 C and then treated in 320 C steam at 1 atm for the durations indicated.](image-url)
temperatures) enabled the hydration process to be singled out for study independently of diffusion. For this purpose, the measured data was summarized by averaging for each steam treatment the [H] in the interiors of the oxide films. Results of this procedure appear in Fig. 3, which may be regarded in this context as an example of a Powell-plot used for reaction-rate law determination. Note that a break clearly occurs in the curve of [H] vs t for either treatment temperature, implying that the hydration of SiO₂ involves at least a dual rather than a single reaction. One component reaction appears to approach completion before the other has contributed significantly; the value of [H] arising from the fast component appears to saturate at about $1.5 \times 10^{20}$ cm⁻³ at 320°C. This is well below our projection of $4.1 \times 10^{20}$ cm⁻³ for the equilibrium concentration at that temperature, which we obtained by extrapolating the plot of OH solubility versus temperature calculated by Shackelford and Masaryk. We are aware that other investigators have obtained different results. At 500°C the fast component appears to saturate at $2 \times 10^{20}$ cm⁻³, accounting for most of the projected equilibrium concentration of $2.5 \times 10^{20}$ cm⁻³. A rough estimate of the activation energies can be obtained from the buildup rates for the products of the component reactions at different temperatures. This procedure yielded respective activation energies of approximately 0-2 and 15-18 kcal/mol for the fast and slow components, respectively.

Although the details of the hydration process are not yet fully clear, the results of this and related experiments allow some inferences to be drawn. Our evidence for a multi-component reaction is consistent with the results of Walrafen and Samanta, who showed that the 3690-cm⁻¹ OH stretching contour which observed in the Raman and infrared absorption spectra of fused silica could be decomposed into as many as four distinct components. The low activation energy which we infer for our fast component is consistent with their suggestion that hydrogen bonding plays an important role in the reaction; its magnitude is typical of those associated with that type of bonding. The comparative rapidity of that component reaction and its limited extent suggest the possibility that it represents hydrogen bonding between network oxygen and molecular water. The higher activation energy of the slow component suggests its interpretation as the dissociation reaction which Mikkelsen recently observed to produce complete oxygen exchange between network SiO₂ and diffusing water, excluding the possibility of a limited number of fixed saturable sites for that reaction. Further clarification of the hydration mechanism awaits more detailed studies of reaction-product evolution. These are now in progress, as are model calculations of total H buildup and ¹⁸O exchange kinetics.

ACKNOWLEDGMENTS

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