In situ measurements of ultrathin silicon oxide dissolution rates

Dinesh Chopra, Ian Ivar Suni

Department of Chemical Engineering, Clarkson University, P.O. Box 5705, Potsdam, NY 13699-5705, USA

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Abstract

An in situ optical probe of ultrathin silicon oxide dissolution has been developed based on changes in the concentration of chelated Cu$^{2+}$ near the surface of a silicon wafer during diffusion-limited deposition of Cu. A laser is reflected from the surface of a silicon wafer at glancing incidence, which allows the diffusion layer to be sampled over about 7% of the laser path, while the laser intensity is monitored for changes in the optical absorption of chelated Cu$^{2+}$. This method has been employed to measure the average dissolution rate of ultrathin silicon oxides into dilute HF solutions of various strengths. The silicon oxide layers were approximately 8.6 Å thick, as measured by spectroscopic ellipsometry, and were formed by aqueous cleaning. The dissolution rates were on average 24% lower than those measured previously for thick thermally grown oxides into HF solutions. The reduction in the dissolution rate is consistent with the known densification of silicon oxide near the Si/SiO$_2$ interface.

Keywords: Silicon oxide; Dissolution rate; HF solutions

1. Introduction

The nature of the protective SiO$_2$ layer on Si surfaces has recently been the subject of tremendous inquiry. This heightened interest is driven to a large extent by increasing device integration and decreasing device dimensions in the microelectronics industry, with gate oxides now expected to eventually reach dimensions of 30–50 Å. At such thicknesses, the composition, morphology and interfacial microroughness of the gate oxide are considered to be critical to obtaining satisfactory device performance [1–5]. In order to obtain greater interfacial control, attempts have been made to replace thermally grown oxides with oxides deposited by chemical vapor deposition [6]. However, forming a device-quality Si/SiO$_2$ interface without annealing above 900°C has proven difficult, and such annealing often proves detrimental to overall device performance. Rather complex deposition schemes have therefore been developed to circumvent this problem [6]. Despite the importance of the SiO$_2$ layer, neither its formation nor its dissolution mechanism is well understood for thin films [7,8]. The growth kinetics of thick (> 100 Å) SiO$_2$ layers are known to follow the Deal–Grove model [9], with an initial linear growth rate followed by a parabolic curve. However, the growth kinetics of ultrathin films have been shown to occur more rapidly than the expected linear behavior, leading to the development of several phenomenological models to describe oxidation kinetics [7]. In addition, controversial questions have also been raised about the possibility of islanding [10,11]. Regarding the interfacial composition, general agreement exists for a densified SiO$_2$ transition region between crystalline Si and a-SiO$_2$, but the thickness reported varies widely from 5–30 Å [7]. A number of researchers claim evidence from X-ray photoelectron spectroscopy and other techniques for lower Si oxidation states of Si$^{+}$, Si$^{3+}$, and Si$^{5+}$ in the interfacial region [12–14]. An additional complication is that the thickness of the Si/SiO$_2$ interfacial region has been seen to vary during oxide growth [15–17].

For gate oxide thicknesses in the range 30–50 Å, the chemical oxide, which is usually between 7–20 Å thick, formed by various aqueous cleaning procedures would be a significant fraction of the total gate oxide thickness. In addition, the composition at the interface and the surface microroughness have been shown to be sensitive to the aqueous cleaning procedure employed prior to device fabrication [2,18–20]. Thus, the initial development of thermal oxides, chemical oxides grown during aqueous cleaning, and CVD oxides is important for both fundamental and practical reasons. Although the growth and dissolution of chemical oxides during aqueous cleaning have been less...
well studied than the growth and dissolution of thermal oxides, many of the same difficulties arise in understanding the interface. Ellipsometric measurements have yielded an oxide thickness of 7–9 Å following an HF etch and water rinse [21,22]. Subsequent cleaning in SC-1 (NH₄OH:H₂O₂:H₂O) solution has been reported to produce a thicker chemical oxide [22,23] whereas SC-2 (HCl:H₂O₂:H₂O) solutions have been reported to have no measurable effect on the oxide layer [22,23]. Recent infrared studies suggest that SC-1 solutions will chemically replace any existing oxide layer [23]. These spectra show differences in both the intensity and peak position of the Si–H and Si–O absorption for oxides treated in SC-1, SC-2, SPM (H₂SO₄:H₂O₂) and HNO₃, suggesting chemical variations between oxides formed by different means. The spectrum of the SPM-formed chemical oxide most closely resembles that obtained for a thermally grown oxide [23].

This report describes an in situ method for probing the dissolution of ultrathin thermal, chemical or CVD oxides using absorption spectroscopy in aqueous solutions deliberately contaminated with a CuEDTA²⁻ spectroscopic probe. After the completion of oxide dissolution, CuEDTA²⁻ starts to deplete from the diffusion layer, increasing the transmission of a probe laser. This technique can probe the dissolution rate of thin silicon oxide films and can be employed to indirectly study the chemical stability of the oxide. Dissolution into aqueous HF has already been employed as a probe of the density of silicon oxide [24,25], and this methodology can now be extended in situ to dissolution of ultrathin silicon oxides.

2. Experimental details

The experimental setup, shown in Fig. 1, has been described elsewhere and will be described here only briefly [26]. The sample cell is mounted on manipulators capable of both angular and Cartesian adjustments, and, to prevent corrosion by HF, the materials of construction have been carefully chosen and include a virgin Teflon cell body and piston, Chemraz o-rings and sapphire optical windows. These materials have been soaked in both concentrated and dilute aqueous HF for 24 h without visible deterioration. The silicon substrates are highly polished n-type two-inch Si(111) wafers from Valley Design. The silicon sample is epoxied to the Teflon piston in the main cell body using TorrSeal, a highly chemically inert epoxy. ULSI grade reagents are used exclusively. Prior to each experiment, the sample was cleaned by immersion in SC-1, HF, and SC-2 solutions. Wafers were replaced after several experiments.

The intensity stabilized Melles–Griot model 05-STR-901 HeNe laser strikes the silicon surface at 3.5° incidence so that about 7% of the laser path traverses the expected diffusion layer. The achromatic lens expands the laser beam by approximately 15 × in order to use the entire detector, a 1024-element (2.5 mm × 25 μ) Princeton Instruments model RY-1024 photodiode array (PDA), which is employed for absorption measurements. The laser mirror in front of the Teflon cell rejects 99.9% of the HeNe laser, limiting the photon flux reaching the detector while minimizing the possibility of thermal lensing. The background light is minimized by performing experiments in the dark, as well as placing laser line filter in front of the PDA. On the experimental time scale there is no detectable background light. All experiments were performed at room temperature.

3. Results and discussion

Oxide dissolution is studied indirectly by detection of the onset of Cu deposition from aqueous HF solutions containing a CuEDTA²⁻ spectroscopic probe. At that point, CuEDTA²⁻ begins to deplete from the diffusion layer, decreasing absorption of the laser. This technique depends on the inability of Cu to deposit onto SiO₂ and on the assumption that diffusion and not surface reaction is rate-limiting for Cu deposition onto bare Si [27]. These assumptions are verified by the current results. HF etch solutions of 0.10, 0.15, 0.25 and 0.40 vol.% were tested, each of which also contained 3.5 ppm Cu²⁺ and 10⁻³ M Na₄EDTA. The complexing agent EDTA increases the molar absorptivity at 632.8 nm from about 2 M⁻¹·cm⁻¹ for Cu(H₂O)⁶²⁺ to 36.7 M⁻¹·cm⁻¹ for CuEDTA²⁻. Control experiments indicate that the background F⁻ and SiF₆²⁻ anions are noncomplexing and have no effect on absorption. During HF etching the following dissolution reaction occurs,

\[
\text{SiO}_2 + 6\text{HF} \rightarrow \text{SiF}_6^{2-} + 2\text{H}_2\text{O} + 2\text{H}^+ \tag{1}
\]

until the SiO₂ has completely dissolved. Silicon suboxides would dissolve by a similar mechanism. Following the dissolution of the SiO₂ layer, Cu deposition can occur according to the following pair of half-reactions:

\[
\text{Si}^0 + 6\text{F}^- \rightarrow \text{SiF}_6^{2-} + 4\text{e}^- \tag{2}
\]

and

\[
\text{CuEDTA}^{2-} + 2\text{e}^- \rightarrow \text{Cu}^0 + \text{EDTA}^{4-} \tag{3}
\]
Bare silicon is a strong reducing agent with a standard reduction potential of $-1.2 \text{ V}$ [28]. Prior to SiO$_2$ dissolution, HF etch solutions do not contain strong enough reducing agents to induce Cu deposition.

Figs. 2 and 3 show the evolution of the total integrated intensity reaching the PDA as a function of time for 0.10 and 0.40 vol.% HF concentrations. The eventual drop in transmittance seen in Figs. 2 and 3 probably represents saturation of the surface with Cu and may not always be observed [26]. Before and after Cu deposition, the standard deviation of consecutive data in Figs. 2 and 3 is approximately 0.01% of the total signal and is due to fluctuations in the laser intensity. This noise level is below the 0.02% short-term and 0.10% long-term stability claimed by the laser manufacturer. However, the integration time of 1 s will invariably reduce intensity fluctuations somewhat. Theoretically, a dual beam experiment could compensate for source fluctuations and reduce the detection limit down to the 0.001% shot noise limit expected for a photon count of about $10^{10}$ per scan. The ultimate sensitivity of an optimized system should be better than 100 ppb [26]. For the current study, the most important result from Figs. 2 and 3 is the induction time for SiO$_2$ dissolution. This is observed as the time at which the total transmitted intensity increases, reflecting a decrease in the absorbance as a result of CuEDTA$^{2-}$ depletion from the diffusion layer. This occurs at the times given in Table 1 for each HF concentration.

The oxide thickness after the cleaning sequence has been obtained by spectroscopic ellipsometry, which is difficult for a variety of practical and theoretical reasons. Even for a flat, homogeneous film, the results can be quite sensitive to both the precise angle of incidence and the optical constants of the materials [30]. In addition, the interfacial roughness may influence thickness determinations [30,31]. Perhaps the most difficult problem for ultrathin SiO$_2$ is the densification and subsequent increase in the refractive index of SiO$_2$ near the Si/SiO$_2$ interface. Numerous authors have fit ellipsometric measurements by proposing an interfacial layer from 6–12 Å thick with a refractive index in the range 2.5–3.0, compared to 1.46 for bulk SiO$_2$ [32–35]. However, other ellipsometric studies have instead used a broader transition region with a lower refractive index [36–38]. Spectroscopic ellipsometry allows detailed analysis of the best approach to modeling this interfacial region. Recent studies have suggested that the best fit to spectroscopic ellipsometric data is provided by modeling the interfacial layer as being composed of a mixture of SiO$_2$ and amorphous Si [39,40]. The dielectric function ($\varepsilon$) of this mixture layer can be obtained from the Bruggeman effective medium approximation [37],

$$
0 = \frac{f_2(\varepsilon_1 - \varepsilon)}{(\varepsilon_1 + 2\varepsilon)} + \frac{(1 - f_2)(\varepsilon_2 - \varepsilon)}{(\varepsilon_2 + 2\varepsilon)}
$$

where $(1 - f_2)$ and $f_2$ are the fractions of SiO$_2$ and a-Si, respectively, and $\varepsilon_1$ and $\varepsilon_2$ are similarly their dielectric functions. This analysis, which is described in more detail elsewhere [41], yields an oxide thickness for the wafers following SC-2 cleaning of approximately 8.6 Å. This is close to the oxide thickness that has been obtained by ellipsometry measurements after an HF etch [21].

The etch rates of the various HF solutions based on this film thickness are given in Table 1. The etch rates of thick thermally grown SiO$_2$ in dilute HF/H$_2$O have been measured previously by Ohmi et al. [29] and are given in Table 1 for comparison. The etch rates reported here are on average 24% lower than those previously reported for a

Table 1

<table>
<thead>
<tr>
<th>HF (vol.%)</th>
<th>$\tau_{min}$ (s)</th>
<th>Etch rate$^a$ (Å/min)</th>
<th>Etch rate$^b$ (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>275</td>
<td>1.9</td>
<td>2.5</td>
</tr>
<tr>
<td>0.15</td>
<td>125</td>
<td>4.1</td>
<td>5.5</td>
</tr>
<tr>
<td>0.25</td>
<td>75</td>
<td>6.9</td>
<td>10</td>
</tr>
<tr>
<td>0.40</td>
<td>30</td>
<td>17</td>
<td>20</td>
</tr>
</tbody>
</table>

$^a$Current results.

$^b$Thick thermal oxide etch rate from Ref. [29].
thick thermally grown oxide. These results are in agreement with measurements demonstrating that the HF etch rate declines for thermally grown oxides even as far as 1000 Å from the Si/SiO₂ interface [42]. These and other HF etch rate measurements on densified buried oxides are consistent with a decline in HF etch rate as the silicon oxide density rises [42,43]. This is in agreement with basic chemical intuition. It should be noted that if the oxide layer has thickness inhomogeneities, the present measurements will detect the minimum thickness, in which case the true etch rate may be underestimated. Any possible effects of the spectroscopic probe on the dissolution kinetics can be easily dismissed. All Cu²⁺ species will be chelated as CuEDTA²⁻ due to the high formation constant and the excess of EDTA²⁻. Adsorption measurements have shown that chelation with EDTA⁻ completely suppresses the adsorption of Cu²⁺ [44]. Although EDTA can dissolve oxides composed of transition metals which complex readily [45], EDTA has been shown to be completely inert towards silica dissolution [46].

This optical method for measuring dissolution rate is particularly suitable for ultrathin silicon oxide films. One advantage of the present method is that its in situ nature makes it highly flexible in its application. For example, one could simultaneously monitor oxide films grown on different regions of the same silicon wafer by different processes. The thickness variation of the dissolution rate is also accessible if one grows a series of ultrathin silicon oxide films of increasing thickness by the same process, then measures their dissolution rates.

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References