

## Invited

# Silicon Oxidation Kinetics: The Formation of Thin Silicon Dioxide Films

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Modern silicon device requirements of speed, size and device density on a chip have required the use of gate oxides less than several tens of nm in thickness. This review will consider recent studies of thin  $\text{SiO}_2$  film formation kinetics in the following areas: silicon orientation, silicon cleaning, impurities, photons, and the thermionic emission of electrons from Si into  $\text{SiO}_2$ .

The linear-parabolic, LP, Si oxidation model<sup>1</sup> as originally derived considers the processes of oxidant transport through the growing  $\text{SiO}_2$  film and reaction of oxidant and Si at the Si- $\text{SiO}_2$  interface to be in a steady state. Often for simplicity only very thick or very thin limits of the LP model are used. However, upon careful consideration of the steady state condition<sup>2</sup>, and through the use of flux diagrams, it was found that both processes can affect the oxidation process, even for thin and thick  $\text{SiO}_2$  films. This means that diffusion can affect the kinetics in the thin  $\text{SiO}_2$  film regime and the interface reaction can effect thick film growth kinetics. The concept of the kinetic dominance of one process or another in the steady state is discussed, since this idea is oftentimes misused in the literature on Si oxidation.

A wide variety of silicon oxidation studies has recently been reviewed<sup>3</sup> and from this review it is clear that kinetic and electronic differences in thin  $\text{SiO}_2$  films exist and seem to be related to the

specific details of the oxidation process. Recent studies of the Si oxidation process in the very initial regime have revealed that the LP model alone is insufficient for describing the kinetics and does not yield significant insight into the origin of the electrical properties of the Si- $\text{SiO}_2$  interface. To this end recent selected studies of the very thin film  $\text{SiO}_2$  growth regime are reviewed; the studies lead to a more coherent understanding of the very initial Si oxidation regime.

In-situ ellipsometric studies of thermal oxidation of five Si orientations has revealed important information about the Si surface reaction<sup>4,5</sup>. It was found that in the earliest stage the Si oxidation rate order, R is as follows:

$$R(110) > R(111) > R(311) > R(511) > R(100)$$

which corresponds to the areal density of Si atoms on the surfaces. However, the agreement is not quantitative and the oxidation rate order between the (110) and (111) Si orientations switches as the  $\text{SiO}_2$

film grows beyond about 20 nm. Not only do these facts strongly suggest that the surface atom density is very important, but also that other factors are important. Intrinsic film stress may be implicated<sup>6</sup>. The anomalously low compressive intrinsic stress found for SiO<sub>2</sub> grown on Si (111) relative to the stress measured for the other orientations may result in correspondingly higher oxidant diffusion fluxes for the SiO<sub>2</sub> grown on the (111) Si orientation, and hence cause a crossover in oxidation rate as the SiO<sub>2</sub> film thickens, i.e. as the resultant compressive forces become more significant.

It is now well established that standard Si cleaning procedures alter the Si oxidation rates<sup>7-9</sup> with HF treatments resulting in the highest oxidation rates and with NH<sub>4</sub>OH the lowest. Using in-situ contact angle and ellipsometry measurements<sup>10,11</sup> it was found that HF treatment leaves a hydrophobic surface film on Si while NH<sub>4</sub>OH forms bare Si. Thus it was concluded that the hydrophobic surface film increases the Si oxidation rate. A wide variety of studies<sup>12-16</sup> demonstrate that most impurities cause increases in the Si surface oxidation rate. Often the metallicity (density of electron states at the Fermi level) and/or the electron barriers are altered by the impurities. It is concluded that virtually all impurities enhance the Si oxidation rate by a metallicity and /or barrier lowering effect except in cases where barrier films are formed via the impurities.

Interestingly, photonic effects on Si oxidation<sup>17-19</sup> reveal similar enhancement effects related to both the electron concentrations and electron barriers. One study found that the photon stimulated decomposition of O<sub>2</sub> also enhances the Si

oxidation rate<sup>19</sup>. Based on similar mechanisms proposed for photonic oxidation, a thermionic Si oxidation model was proposed for the very initial oxidation regime<sup>20</sup>. This model was tested against experimental oxidation data for the very initial oxidation regime and was found to yield approximately the correct Si-SiO<sub>2</sub> barrier height. Using only the barrier height model it seems difficult to explain the virtually instantaneous formation of native oxide on Si even at room temperature. However, when the surface electronic states on Si are considered, there could be sufficient electrons available in these states to produce about 1 nm of oxide without the thermionic emission of electrons over the Si-SiO<sub>2</sub> barrier.

From these studies of Si oxidation, possible causes for the Si-SiO<sub>2</sub> fixed oxide charge, Q<sub>f</sub>, and interface electronic states, Q<sub>it</sub>, are proposed and relationships to the processing of thin SiO<sub>2</sub> films are drawn. These relationships are the subject of ongoing research, and progress with this work will be updated.

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