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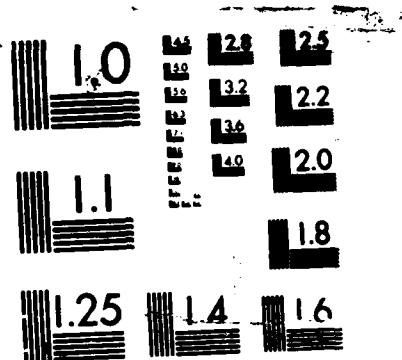
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Thermionic Emission Model for the Initial Regime of Silicon Oxidation

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Abstract

The very early stage of the thermal oxidation of single crystal Si has been the subject of continual study for the last two decades. In the light of very recent experimental oxidation data on the initial regime, we report that a simple thermionic electron flux from Si into SiO_2 closely agrees with the SiO_2 film growth rate. The importance of electrons for the oxidation kinetics has also been attested to in several recent experimental studies. Thus a consistent model is presented for the initial oxidation regime based on the electron flux as the rate limiting step.

The kinetics for the formation of SiO_2 films on Si has received considerable attention both from the technological and scientific viewpoint (see refs. 1-5 and refs. therein). Many models have been proposed (see refs. 1,4,5 and references therein) based on new phenomena incorporated into the Linear-Parabolic, L-P, model proposed in the 1960's(6-8). This latter model considers only the processes of transport of oxidant and reaction of oxidant and silicon in a steady state and as kinetically simple processes. However, a growing body of studies(1,4,5 and references therein) now show that the simple L-P model is inadequate and further elucidation of what was thought to be simple processes is necessary. Of particular relevance are a number of studies on the initial oxidation regime which have implicated the interface reaction as the dominating process(9-17) for SiO_2 films thinner than 100nm.

The purpose of this letter is to show that a key step in the interface reaction process is the emission of electrons from Si to SiO_2 . This idea was suggested in a number of earlier studies(14,17-20), but quantification has not been possible because the appropriate experimental oxidation data has only recently become available.

Calculations comparing the maximum diffusion flux of oxygen with oxidant flux obtained from the experimental oxidation rates have shown that transport is not rate limiting below at least 100nm(10,18-20). Random walk calculations and a consideration of the thermodynamic potentials for transport and the interface

reaction further support that the interface reaction must be considered in the Si oxidation process(18-20). A steady state between these two processes likely occurs with the interface reaction having the smaller maximum value. This steady state situation is complex and treated in more detail elsewhere(20).

Recently, there has been substantial experimental evidence supporting the kinetic importance of the interface reaction in the initial regime of oxidation. The very recent extensive oxidation data of Lewis et al.(10,12) using five Si orientations is concordant with previous studies(9,13) that show the oxidation rate order parallels the Si atom areal density for the initial oxidation regime. Perhaps more significant is the new finding that the rates of oxidation are orientation dependent even well beyond 100nm SiO₂ growth(10).

Two recent studies have strongly suggested the importance of the availability of electrons to the oxidation mechanism. The study of photon enhanced oxidation by Young and Tiller(14) shows that there are three regimes of photon energy that enhance the oxidation rate. Photon energies above 3eV show large enhancements of more than ten fold compared with lower energies. The 3eV and higher energy photons likely excite electrons over the Si-SiO₂ barrier. The 5eV and greater energy radiation decomposes O₂ to atomic oxygen with a resulting enhancement compared to the 3eV energies. The recent work by d'Heurle et al.(15) and Frampton et al.(16) shows that different metal silicides, that are oxidized under conditions which preserve the silicide film and form only

SiO₂, display oxidation rates in the order dictated by the availability of free electrons on the silicide surface. This finding supports previous studies by Cros(17) which strongly suggested that the higher density of electrons at the Fermi level was influential in determining the Si oxidation rate.

The control of the oxidation kinetics at the Si-SiO₂ interface, plus the requirement for electrons enables the following formulation of a new Si oxidation model based on thermionic emission of electrons from Si into SiO₂. Thermionic emission of electrons in terms of the electron flux, F_e, is governed by the Richardson-Dushman equation which may be written as:

$$F_e = AT^2 \exp(-\chi_0/kT) \quad (2)$$

where A is the Richardson constant, T is absolute temperature, and χ_0 is the barrier height which for metals extends from the Fermi energy to vacuum for thermionic emission to vacuum. For the case of emission from Si to SiO₂, we modify the situation by considering electron emission from levels in Si that have sufficient electrons for the oxidation reaction. From the band diagram in Figure 1, several options are seen for the promotion of an electron from Si to the SiO₂ conduction band. The emission from the densely populated Si valence band requires about 4.25eV, from the intrinsic Fermi level of Si about 3.70eV, and from the Si conduction band about 3.15eV is required.

The model assumes that the electron flux into SiO_2 is rate limiting and governed by the Richardson equation. We show first that this choice for the rate limiting flux is reasonable, and then the specific mechanism steps are presented. Depicted in Figure 2 are the fluxes now considered. It was previously shown(10,18-20) that the maximum diffusive flux of oxidant, $F(D)$, is larger than the experimental flux of O_2 , $F(\text{exp})$. Before we focus on the assumed rate limiting step, F_{ep} , the electron flux to the Si surface, F_e , must be considered. This flux can be estimated from the relationships:

$$F_e = D_e N_e / L_e \quad (3)$$

$$D_e = \mu_e (kT/e) \quad (4)$$

where D_e and N_e are the electron diffusivity and concentration, respectively, μ_e is the electron mobility, and L_e is the distance into the bulk Si away from the oxidized surface. Using literature values for μ_e and N_e , it is found that even at L_e values greater than 10^3 nm the electron flux is 10^4 times larger than the oxidation rate. Thus, with the three flux situation in Figure 2, only the electron flux over the barrier, F_{ep} , remains for evaluation.

In order to establish that F_{ep} is a possible rate limiting flux, the values of x_0 that yield values for F_{ep} which are identical to the experimental oxidation flux, $F(\text{exp})$ are

calculated. The χ_0 values required for the equivalency of F_0 with $F(\text{exp})$ are shown in Table 1 for several oxidation temperatures. Several points are made from this Table. First, and most important, is the finding that at all temperatures the calculated value for χ_0 corresponding to the very initial SiO_2 growth regime is within about 0.2eV of the barrier of 3.15eV from the bottom of the Si conduction band. While this result seems impressive, it should be remembered that a value of 0.2eV alters the electron flux, F_0 , by about 10^1 . The agreement could be physically significant, however, considering that the position of the SiO_2 band edge has at least tenths of an eV uncertainty at room temperature, and at the higher temperatures is more uncertain. Based on experiments on the Al- SiO_2 interface(22) in which it is observed that the barrier is apparently lowered at elevated temperatures, it is quite likely that the Si- SiO_2 barrier is also lowered at higher temperatures. However, it is also known that the Si band gap decreases at elevated temperatures(21), thereby populating higher levels in the Si conduction band. Thus the precise definition of the band edges is uncertain to at least several tenths of an eV. Next is the result that the (110) orientation, the fastest oxidizing Si surface in the initial regime consistently displays the lowest χ_0 . It is clear that this difference is forced by the requirement of the equivalence of the fluxes. An independent measurement of the barrier on different orientations would provide confirmation for the proposed model. There is the general result that for all

temperatures and orientations there is an apparent increase in χ for the larger film thicknesses. This is most noticeable for the higher oxidation temperatures where, due to experimental difficulties, there is no reliable data available for SiO_2 less than 5nm. This effect is also likely an artifact due to the growing importance of other kinetically significant processes such as transport of oxidant, film stress or the reduction of the oxidant concentration at the interface.

The question whether there are sufficient electrons in the Si conduction band to permit F_{ox} to control the rate is answered affirmatively for any temperature above room temperature. At room temperature there is near equivalence at about 10^{19} cm^{-3} for both the number of electrons required considering one per O_2 molecule and actually present. Another question arises from the observation that even at room temperature, a 1nm native oxide grows rapidly on the Si surface and then oxidation is slow up to 2nm where oxidation essentially stops unless impurities are present or the temperature is raised. The question is how does this oxide grow without sufficient electrons (or at least marginally sufficient) and then why does it stop? This problem is understood if we consider that a restricted number of electrons are available in defect states on the Si surface, ie. so called surface states. Such states are known to trap electrons(23), and thus provide a limited source of electrons other than by emission over the barrier (perhaps by a tunneling mechanism for example). In order to form 1nm of SiO_2 per cm^2

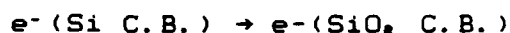
requires about 2×10^{15} electrons at one electron per SiO_2 molecule. This number is approximately equal to the experimentally determined number of surface states per cm^2 on a freshly cleaved Si surface(24). Thus an initial native oxide about 1nm thick would have sufficient electrons available to form rapidly and without high temperatures, as is observed. It follows that once the 1nm SiO_2 forms, the surface states are reduced to below the 10^{15} cm^{-2} level, the barrier is formed, and the emission process over the barrier is rate limiting.

With the flux of electrons as the rate limiting step, the oxidation mechanism is envisioned to have the following four main steps with step two being rate limiting:

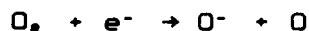
1. In the Si conduction band:



2. At the Si- SiO_2 barrier:



3. In SiO_2 :



4. The interfacial reaction:



Accordingly, both the formation and reaction of atomic O is important in this mechanism. The electron attachment reaction to O_2 is not only a favored thermodynamical process, but also the resulting molecular ion, O_2^{-} , has a lower dissociation energy thereby producing more atomic O species(25). The importance of the reaction of atomic oxygen with Si has been discussed by Ghez

and van der Meulen(26) to explain the pressure dependence of the oxidation rate, by Blanc(27) to explain the unusually fast initial oxidation regime and by Irene(28) to explain the curvature of Arrhenius plots of the initial regime rate constant.

With this thermionic model, several perplexing facts about Si oxidation in the very initial oxidation regime become obviated. The observed sensitivity of the oxidation kinetics to impurities and indeed to the cleaning process for the Si wafers(29,30) is understood in the context of recent studies that shows that changes in barrier heights of tenths of an eV are measured for nickel silicides on silicon when interfacial defects and common impurities such as C are present(31). The rapid formation of an initial oxide of about 1nm on Si with the subsequent decrease in rate to low values requiring high temperatures for oxidation to proceed measurably is also explained.

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Table 1. The barrier heights, χ_0 , yielding a thermionic electron flux, F_0 , equal to the experimental O_2 flux, $F(\text{exp})$. Data from references 9 and 10.

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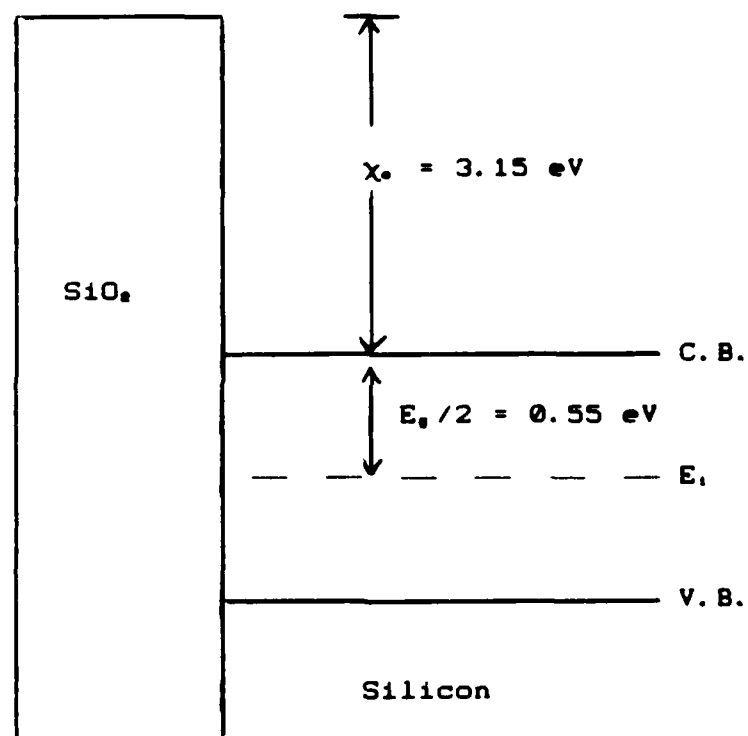
- Figure 1. Energy band diagram for Si-SiO₂.
- Figure 2. The fluxes for the thermionic emission model: $F(D)$, the diffusive flux; F_e , the electron flux; and F_{te} , the thermionic emission flux of electrons.

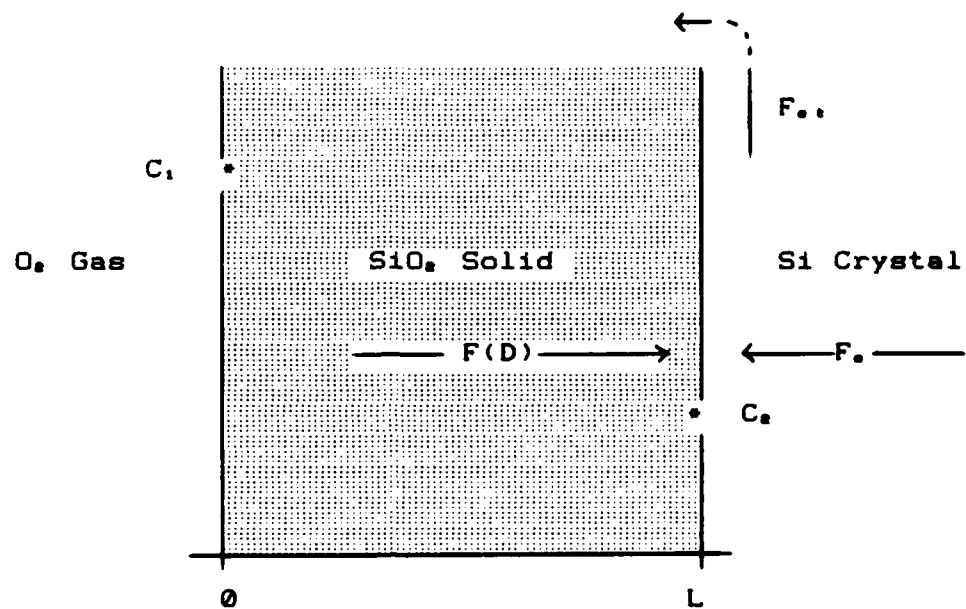
Table 1

Oxidation Temperature (°C)	Si Orientation	Oxidation Rate (nm/min)	SiO ₂ Thickness Range (nm)	χ (eV)
600	(100)	0.0004	2-3	2.87
	(110)	0.0012	2.5-6	2.79
650	(100)	0.014	2.5-7	2.95
	(110)	0.041	2.5-10	2.86
700	(100)	0.014	2.5	2.92
		0.0057	10	3.00
		0.0043	20	3.02
	(110)	0.033	2.5	2.85
		0.014	10	2.92
		0.0094	20	2.96
750	(100)	0.028	5	3.02
		0.024	10	3.03
		0.019	20	3.06
	(110)	0.057	5	2.96
		0.035	10	3.00
		0.024	20	3.04
1000	(100)	1.79	7	3.35
		0.9	20	3.43
		0.27	100	3.56
	(110)	3.45	9	3.28
		1.74	20	3.35
		0.4	100	3.52

Si-SiO₂ Band Diagram

Vacuum Level





$$F(D) = D(C_1 - C_2) / L(\text{SiO}_2)$$

$$F_0 = D_0 N_0 / L(\text{Si})$$

$$F_{01} = AT^2 \exp(-\chi_0 / kT)$$

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