Diffusion-reaction in thermal growth of silicon oxide films on Si

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The thermal growth of silicon oxide films on Si in dry O₂ is modelled as a dynamical system, assuming that it is basically a diffusion-reaction phenomenon. Relevant findings of the last decade are incorporated, as structure and composition of the oxide/Si interface and O₂ transport and reaction at initial stages of growth. The present model departs from the well established Deal and Grove framework (Deal, B.E. and Grove, A. S. General Relationship for the Thermal Oxidation of Silicon J. Appl. Phys. 36, 3770-3778 (1965)) indicating that its basic assumptions, steady-state regime and reaction between O₂ and Si at a sharp oxide/Si interface are only attained asymptotically. Experimental growth kinetics by various authors, obtained for a wide range of growth parameters are shown to collapse into one single curve when the scaling properties of this model equations are explored.

Silicon oxide films thermally grown on single-crystalline Si (c-Si) wafers in dry O₂ are still the most common materials used as gate dielectrics in Si-based metal-oxide-semiconductor (MOS) structures. As device dimensions shrink below 0.25 μm, the 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 vitreous oxide film, like thickness uniformity, defect density, dielectric strength, and others, as well as on those of the oxide/Si interface, like roughness, electronic states density and others.

The dielectric performance of ultrathin films of silicon oxide thermally grown on Si and the structural and electronic properties of the oxide/Si interface have been intensively studied experimentally, theoretically, and computationally in synergism with the development of the semiconductor industry. The understanding of film growth kinetics, however, did not make any significant progress since the early model of Deal and Grove, which subsisted as the only fundamental approach. The Deal and Grove model, and more specifically the resulting linear-parabolic law, agrees with the observed growth kinetics in dry O₂ only above a certain thickness, which is not required. Therefore, the model is expected to describe the whole oxide thickness interval. Diffusion-reaction equations have been used to describe different systems but, to our knowledge, this is the first time they are applied to silicon oxide growth kinetics. The diffusing species is taken to be O₂, to model what has been largely demonstrated by isotopic substitution experiments. Growth is promoted by reaction of O₂ with Si, not necessarily at the oxide/Si interface, but wherever the two species meet. The growth kinetics can then be obtained at any temperature by specifying the diffusivity of the O₂ molecule in the silica network, D, the reaction rate between O₂ and
Si, $k$, and the O$_2$ pressure in the gas phase. Growth in one dimension is considered, which is the most common experimental situation, meaning that as a face of c-Si is exposed to O$_2$, the silica film grows in the direction perpendicular to this face. The proposed description for the growth kinetics is contained in the following coupled partial differential equations:

$$\frac{\partial \rho_{O_2}}{\partial t} = D \frac{\partial^2 \rho_{O_2}}{\partial x^2} - k \rho_{O_2} \rho_{Si}$$

$$\frac{\partial \rho_{Si}}{\partial t} = -k \rho_{O_2} \rho_{Si}$$

(1)

where $\rho_i = c_i / c_{Si}^{bulk}$ is the concentration of the i-species ($i = Si, O_2$) in the solid phase, in units of number of atoms per unit volume, $c_i$, normalised by the concentration of Si in c-Si, $c_{Si}^{bulk}$. Thus, the state of any species at any time is characterised by a density function $\rho(x, t)$, where $x$ is the coordinate in the direction of growth, $x = 0$ indicating the surface of the sample, and $t$ is the elapsed growth time. The first equation describes the O$_2$ concentration rate and it is essentially a balance equation. At a given position the concentration of oxygen may vary due to the net flux of O$_2$ through fully (SiO$_2$ in oxide bulk) or partially (SiO$_x$, $x < 2$, near the interface oxidised Si, modelled by the diffusion term with a diffusion constant $D$, or due to reaction to produce silicon oxide, characterised by a reaction rate constant $k$. The second equation describes the Si concentration rate, which is only due to reaction with O$_2$, implying that Si is an immobile species. The silicon oxide concentration, $\rho_{oxide}$, does not explicitly appear in these equations, but it is in direct connection with $\rho_{Si}$ through the expression

$$\rho_{oxide}(x, t) = 1 - \rho_{Si}(x, t)$$

(2)

reflecting conservation of Si species in the Si + O$_2$ → SiO$_2$ reaction. It is assumed that the O$_2$ diffusivity at a certain temperature does not change during oxidation, and therefore $D$ is constant throughout the whole growth process. Furthermore, based on the fact that oxygen diffuses mainly through oxide, one neglects volume changes due to the above chemical reaction. In order to complete the description in terms of equations (1), it is necessary to provide the initial and boundary conditions. They are

$$\rho_{Si}(x, 0) = 1 \quad \forall x \geq 0$$

$$\rho_{O_2}(0, t) = \frac{c_{gas} f_v}{c_{Si}^{bulk}} \quad \forall t \geq 0$$

(3)

where $c_{gas}$ is the O$_2$ concentration in the gas phase and $f_v$ is the ratio between the accessible free volume for O$_2$ in the silica network and the unit volume of the solid. Initially there is a pure, c-Si substrate from $x = 0$ to $\infty$, whose surface is exposed to a gaseous medium, O$_2$, with a relative concentration at this surface represented in the second condition by $\frac{c_{gas} f_v}{c_{Si}^{bulk}}$. Reaction of these two species produces silicon oxide, not necessarily stoichiometric, as the solid-phase reaction Si + O$_2$ → SiO$_2$ may occur in several steps. As time proceeds, O$_2$ diffuses through the oxide network, reaches Si, reacts producing more oxide, and consequently pushes the oxide/Si interface further in the positive $x$ region. Different values of $D$, $k$ and $c_{gas}$ imply different kinetics. However, the values of $D$ and $k$ may be used to define “natural” units for the system, resulting in a set of adimensional equations with the only one parameter, namely $c_{gas}$ [23]. Under the following transformations:

$$\tau = tk$$

$$u = x \sqrt{\frac{k}{D}}$$

$$\phi_i(u, \tau) = \rho_i(x, t) \quad \text{for } i = Si, O_2, oxide$$

(4)

the resulting adimensional set of differential equations and initial and boundary conditions are

$$\frac{\partial \phi_{O_2}}{\partial \tau} = \frac{\partial^2 \phi_{O_2}}{\partial u^2} - \phi_{O_2} \phi_{Si}$$

$$\frac{\partial \phi_{Si}}{\partial \tau} = -\phi_{O_2} \phi_{Si}$$

$$\phi_{Si}(u, 0) = 1 \quad \forall u \geq 0$$

$$\phi_{O_2}(0, \tau) = \frac{c_{gas} f_v}{c_{Si}^{bulk}} \quad \forall \tau \geq 0$$

(5)

leaving $c_{gas}$ as the only parameter. This is a powerful statement. It predicts that in all experiments performed at the same gas pressure, oxide growth kinetics and O$_2$ and Si concentrations versus depth curves (profiles) at different temperatures collapse to the same curves, provided that appropriate units are used: $1/k$ for time and $\sqrt{D/k}$ for thickness.

In order to obtain profiles and growth kinetics, eqs. (3) must be solved. Those are partial, nonlinear, coupled differential equations and cannot be analytically solved at all times. On the other hand, they can be easily solved by finite differences methods, iterating for as long as it takes to reproduce the growth time of interest. The calculation gives then the profiles $\phi_i(u, \tau)$ of all species and the kinetics. Typical profiles at different growth times for a given value of $c_{gas}$ are shown in Figure 1. The O$_2$ profiles are not straight lines as they are assumed to be in the steady-state regime [4]. Strictly speaking, steady-state is never attained as long as the oxide/Si interface moves deeper into the c-Si substrate. Furthermore, this interface is not sharp, in accordance with a wealth of experimental evidences [20,23,24]. Still in strict accordance with theoretical predictions [4,7,15] and experimental observations [4,9,20,27], a finite width region formed by Si in various lower oxidation states (+1, +2, +3, sub-oxides or Si-excess) early develops between the stoichiometric SiO$_2$ film and the c-Si substrate. In this way, O$_2$-Si reaction can take place in the whole region where non-fully oxidised Si is available.
therefore is determined by a unique parameter \( \phi \) by applying the oxide growth kinetics, with \( O_2 \) concentration of \( \chi(\alpha) \), whose evolution is ruled by eqs. (5) and (7) extending from 0.1 to 1000 min, and from 1 to 80 nm. For these curves the pressure scaling predicted by eqs. (7) is not perfect at long growth times, probably due to an increase in diffusivity. They were then collapsed one by one into the theoretical curve using eqs. (8) first, and then eqs. (9). The same procedure was used to collapse the kinetics from references [27,29] into the theoretical curve.

These predictions were tested with kinetic curves taken from references [27,29] corresponding to oxidations in Joule-effect heated and rapid thermal processing furnaces in a variety of growth parameters (temperature, \( O_2 \) pressure, and time) leading to oxide thicknesses ranging from 1 to 100 nm. In Fig. 2 we show the collapse of the experimental kinetics (symbols, colours) into the theoretical curve (line, black). For the kinetics curves from reference [28], with five points in each curve, we first used the scaling predicted by eqs. (8), obtaining four different curves, one for each temperature. We then scaled these curves using natural units for \( x \) and \( t \) according to eqs. (9) until they overlapped the theoretical curve. The curves from reference [6] contained much more experimental points, extending from 0.1 to 1000 min, and from 1 to 80 nm. For these curves the pressure scaling predicted by eqs. (7) is not perfect at long growth times, probably due to an increase in diffusivity. They were then collapsed one by one into the theoretical curve using eqs. (8) first, and then eqs. (9). The same procedure was used to collapse the kinetics from references [27,29] into the theoretical curve.

**Fig. 2.** Calculated growth kinetics (solid line, black) and experimental growth kinetics from the indicated references (symbols, colours) collapsed into the calculated curve.

The asymptotic depart from the theoretical curve is an expected result, since the present model assumes a constant diffusivity throughout the whole growth process, despite many evidences that this is not the case: i) transport of the diffusing species through the O-excess region near the surface [14,25,26], through the Si-excess region near the oxide/Si interface [12,14,16,30], and through the stoichiometric SiO\(_2\) in the bulk of the
growing oxide film have different diffusivities; ii) the growth of the defective, near-surface and near-interface regions saturate within a few nm [12,18,25,30], while the bulk, stoichiometric oxide grows continuously. So, interstitial diffusion of O2 through the bulk of the growing oxide gives a relative contribution that increases as the width of this region becomes dominant; iii) oxidizing oxide gives a relative contribution that increases as $\chi(\tau)\sqrt{Dk},$ and defining $\rho_{\nu} = \rho_{O2}(0, t) = \frac{c_{\text{gas}}k}{c_{\text{Si}}},$ the asymptotic solution to eqs. predicts the inverse growth rate $\frac{dt}{dX} = \frac{1}{\rho_{\nu}} X,$ with $D$ constant, which is very similar to the asymptotic approximation of the Deal and Grove model [5] $\frac{dt}{dX} = \frac{1}{\rho_{\nu}} X.$ In Fig. 3 the inverse growth rate is plotted as a function of oxide film thickness for different experimental kinetics [6].

A deviation from a straight line in the thick film range is apparent, corresponding to a variable, increasing diffusivity, contrary to the theoretical prediction shown in the inset.

Thus, the thermal growth of silicon oxide films on c-Si in dry O2 is promoted by diffusion of O2 through the growing oxide with variable diffusivity. Similar physical arguments could support a variable diffusion rate. Nevertheless, even using constant, effective values for the diffusivity and reaction rate, modelling the growth as a diffusion-reaction process where conditions such as initial thickness, steady-state regime, and reaction solely at an abrupt interface are abandoned allows to reproduce the observed kinetics, especially in the lower thickness (ultra-thin film) regime which is the one of present and future practical interest. Realistic model evaluations of variable diffusivity and reaction rate stay beyond the scope of the present work, although this seems to be the only route to a quantitative description of the complete growth kinetics.

The present approach opens the possibility of incorporating new and determinant facts on O2 transport at initial stages of thermal oxide growth and on structure of the oxide/Si interface, that were discovered after the proposal of Deal and Grove [5] and not yet integrated into growth kinetics models. Some were discussed here, like the graded, Si-excess nature of the oxide/Si interface and the incorporation of freshly arriving O2 into different regions of the growing oxide, while several others may also be included in a diffusion-reaction approach, such as the role played by oxygen excess centers [26] in the near-surface region on oxygen transport which has been recently investigated [27].

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