Translated from *Uspekhi Khimii*, 52 922-935 (1983) U.D.C. 537.311.33 + 541.183

Kinetics and Mechanism of the Dissolution and Oxidation of Semiconductors

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A generalised kinetic approach to the description of the dissolution of semiconductors (including the thermal oxidation of silicon and germanium) is based on a statistical thermodynamic analysis of the adsorption steps, and on an analysis of the structure of the activated complex and of the effects of solvation of the intermediate and the final products (calculated from model descriptions). 66 references.

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I. INTRODUCTION

Academician Ioffe once wrote: "The most important property of semiconductors, which determines their behaviour and their suitability for various applications, is the nature of their chemical bond"[1]. The interaction between nearest neighbours has been used as a basis for classifying electronic, optical, and kinetic processes in semiconductors as well as in various vitreous solids[2,3]. This justifies the present attempt to analyse data on the kinetics of chemical dissolution reactions and of oxidation processes on semiconductor surfaces, aimed at identifying the main features of the elementary steps which play an important role in the transfer of an atom from the semiconductor to the adjacent gaseous or condensed phase as a result of chemical interaction[4-8]. We shall show that in spite of differences in the detailed chemistry of these phenomena the elementary acts which control the dissolution and oxidation processes are basically similar.

Once the basic characteristics of the elementary steps are known, a kinetic model of the overall multi-step process can be constructed, allowing for the special features of the reacting system: for example, a model for analysing the kinetics of semiconductor oxidation processes. A large amount of experimental information on the properties of the silicon–silica interface is now available. However, since these studies describe the system *a posteriori*, they do not allow the processes taking place at the semiconductor–dielectric interface during the oxidation to be reconstructed unambiguously. The approach suggested here offers entirely new possibilities for studying and controlling the properties of this interface.

II. DEFINITION AND CLASSIFICATION OF DISSOLUTION REACTIONS

In general, the term dissolution reaction describes a process at a phase boundary which results in the transfer of atoms or structural units from a crystal (or other solid) to the surrounding medium as a consequence of their chemical interaction with the active components of the neighbouring phase[9]. The chemical interaction can be treated in as much detail as in the molecular theory of solutions[10-12]. The dissolution reactions can be described as solvating, oxidising, or oxidising–solvating. The solvating type includes the reactions which cause the dissolution of ionic crystals in polar solvents, and also the dissolution of solids in melts. All other dissolution processes are either oxidising–solvating or oxidising.

Dissolution reactions can be classified (according to the type of phases in contact) as dissolution into a gas, a liquid, or a solid phase. Of course, reactions leading to dissolution into a gas phase are an example of oxidative dissolution. Reactions leading to dissolution into a condensed phase are the most complex type of oxidative–solvating interaction.

III. KINETIC MODEL

Like all heterogeneous reactions, the dissolution reaction is the result of a succession of elementary steps: adsorption of the active reactant, chemical conversion in the adsorption layer, and desorption of the product (with a corresponding reorganisation of the element of volume of the condensed phase in the interfacial region)[13-15]. This sequence of elementary acts can be described by the series of steps

$$A_2^{(II)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A_2^{(s)} \qquad (1)$$

$$A_2^{(s)} \underset{k_{-1}'}{\overset{k_1'}{\rightleftarrows}} 2A^{(s)} \qquad (1')$$

$$A^{(s)} + U^{(I)} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} UA^{(s)} \qquad (2)$$

$$UA^{(s)} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} UA^{(II)} \qquad (3)$$

Eqns.(1) and (1') describe the adsorption on the crystal surface (phase I) of the molecule A_2 in the surrounding phase II. In general, adsorption is a two-step process in which k_1 is the rate constant for the adsorption of the intermediate molecular form and k_1' is the rate constant for the dissociative adsorption step. In most cases the adsorption process is accompanied by a structural rearrangement of the near-surface region of the crystal. Eqn.(2) defines the step (chemical reaction in the adsorption layer) in which the

adsorbed particle $A^{(s)}$ reacts with an atom or with a structural unit of the crystal ($U^{(I)}$) to form an adsorbed particle of the reaction product $UA^{(s)}$. The last step corresponds to desorption of this particle and formation of the final reaction product in the near-surface region of phase II: $UA^{(II)}$.

The kinetic analysis of this sequence of steps is not difficult. We shall confine our discussion to reactions in systems far from thermodynamic equilibrium and ignore the reversibility of step (2), i.e. we shall put $k_{-2} \cong 0$. This condition cannot apply at the boundary between a crystal and its melt, or to the dissolution of a semiconductor in the gas phase at high temperature, when crystal growth and crystal dissolution processes take place at comparable rates.

In our model the rate of the dissolution process (w_2) can be written

$$w_2 = k_2 \frac{k_1}{k_{-1}} [A_2^{(II)}] / \left(1 + \frac{k_1}{k_{-1}} [A_2^{(II)}] + \frac{k_2}{k_{-1}}\right) . \quad (4)$$

Two important special cases can be defined. In the first, the adsorption rate constant for the irreversible chemisorption of the reactant A_2 is much smaller than the rate constant of reaction (2): $k_2 > k_1 \gg k_1$, and therefore

$$w_2 = k_2 \alpha [A_2^{(II)}] / (1 + \alpha [A_2^{(II)}]) , \quad (5)$$

where $\alpha = k_1/k_2$. In the second case the adsorption step is reversible, i.e. $k_{-1} \gg k_2$, and

$$w_2 = k_2 a [A_2^{(II)}] / (1 + a [A_2^{(II)}]) , \quad (6)$$

where $a = k_1/k_{-1}$.

The equations describing these two cases are formally identical, but the physical significance of the parameters is entirely different in the two cases. The case described by Eqn.(5) is typical of oxidative dissolution only. On the other hand Eqn.(6) corresponds to kinetics of the Langmuir type, and it applies both to oxidative and to oxidative–solvating dissolution.

These two possible alternatives of our kinetic model of the dissolution process lead to the following conclusions. In the region of low concentrations of the reactant A_2 the reaction is always of the first order with respect to the active molecules. However, in the first variant [Eqn.(5)] the reaction rate is determined by the rate of the adsorption step. We should stress that the experimental value of the activation energy corresponds to the activation energy for adsorption, and the pre-exponential factor is $C_T = k_{01}$. The parameter k_{01} can be calculated from model considerations of the adsorption complex[13–15]. In the second variant [Eqn.(6)] the activation energy found experimentally in the region of first-order kinetics is $E_{exper} = H_2^{\neq} - \Delta H_{ads}$ (where $H_2^{\neq}$ is the activation energy of step (2), and ΔH_{ads} is the heat of adsorption), and the pre-exponential factor is $C_T = a_0 k_{02}$. Usually $k_{02} = n_S \nu$, where n_S is the density of surface atoms (or structural units), and ν is the frequency of their thermal vibrations. Statistical mechanical calculations gave values of a_0 in the range of 10^{-14}–10^{-13} for the immobile adsorption state and 10^{-8}–10^{-4} Torr^{-1} for mobile adsorption.

At high concentrations of the reactant A_2 the reaction is kinetically of zero order. In both variants the experimental activation energy corresponds to the parameter $H_2^{\neq}$, and the pre-exponential factor is usually $C_T = n_S \nu$. By analysing the experimental kinetic and thermodynamic data for the oxidative dissolution of semiconductors we conclude that the main exothermic effect of the reaction is contributed by the chemisorptive interaction between the active molecule and the crystal surface. Often the heat of chemisorption is greater than 20 kcal mole^{-1}, and the energy released in the adsorption interaction step makes possible the rearrangement of the short-range order region surrounding the given surface atom. Under these conditions the kinetics of the dissolution reaction are no longer affected by the crystallographic orientation, as has been demonstrated for the interaction of germanium with H_2S, S_2, and Br_2,[13–15] with O_2,[16] and for the interaction of silicon with O_2.[17]

When the heat of adsorption is a few kcal mole^{-1}, as in the interaction of silicon and germanium with their tetra-halogen derivatives[15,18], the dissolution usually takes place in the region of low surface coverage and is kinetically of the first order with respect to the reactant. This usually implies a dependence of the heat of adsorption, and therefore also of the activation energy of the dissolution reaction, on the orientation of the crystal.

IV. SPECIAL FEATURES OF SEMICONDUCTOR DISSOLUTION REACTIONS IN A CONDENSED MEDIUM

Adsorption processes associated with dissolution reactions have a number of special features. If the heat of dissolution of the A_2 active molecules in the condensed phase is $\Delta H_{diss}^{(II)}$, their heat of adsorption on the semiconductor surface is

$$\Delta H_{ads}^{K} = \Delta H_{ads} - \Delta H_{diss}^{(II)} . \quad (7)$$

The special case of $\Delta H_{ads} = \Delta H_{diss}$ can occur. In this case there is no surface excess of component A_2, and the reaction takes place by simple collisions between the A_2 particles and the surface. There is an analogous case in the kinetics of catalytic reactions (the Eley–Rideal mechanism). This type of dissolution reaction was originally proposed by Myuller[19]. We conclude that in oxidative–solvating dissolution reactions the contribution from adsorption interactions to the observed activation energy is small (or even zero) as compared with gas-phase reactions.

The coefficient a_0^K which appears in the expression for the pre-exponential factor can be calculated by a model approach[20,21]. The simplest involves the assumption that the molecules of the active component A_2 occupy holes of linear dimension d in the condensed phase, and that when these molecules are transferred to a cell immediately adjacent to the crystal surface they lose one translational degree of freedcm and become adsorbed according to Eqn.(1). In this case

$$a_0^K = h/(2\pi MRT)^{1/2} d , \quad (8)$$

where h and R are Planck's and Boltzmann's constant (the gas constant here Ed. of Translation), and M is the molecular weight of the A_2 particle. A typical value of a_0^K is 1×10^{-2} cm^3 mole^{-1}.

Allowance for the adsorption of solvent molecules (as well as that of the A_2 molecules) is often needed when the dissolution medium is highly polar[8,22]. This means that the reaction rate is proportional to the product of the surface coverages by reactant molecules (θ_{A_2}) and by molecules of the polar solvent (θ_L):

$$w_2 = k_2 \theta_{A_2} \theta_L . \quad (9)$$

V. ATOMIC AND ELECTRON–ION SUBSYSTEMS IN THE DISSOLUTION PROCESS

The dissolution of a semiconductor is usually assumed to occur by two processes taking place in parallel (either independent, or conjugated): the delocalised interaction of the solid with the oxidiser and solvating agent particles (electrochemical mechanism) and the localised interaction of the

oxidiser with an active surface complex (chemical mechanism)[23–26]. We have shown[4,6,8] that in most cases the kinetics of the dissolution process are determined by the local aspects of the interaction between the oxidiser particles and the active surface complex. Though a strict calculation of the exchange currents for the electron–ion and atom–ion subsystems of the semiconductor has not yet been attempted, a qualitative comparison of semiconductors and metals can be based on experimental data.

The exchange currents for the electron–ion reactions Fe^{3+}/Fe^{2+} and $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ on a metallic electrode are known[26] to be 5×10^{-3} and 10 A cm^{-2} respectively. From the relationship between the exchange currents i_0^M and i_0^S for a metallic and semiconductor electrode (which are determined by the width of the forbidden energy gap E_g [27])

$$i_0^S = i_0^M \exp(-E_g/4RT) \qquad (10)$$

we find that for a typical semiconductor with a forbidden gap 0.75 eV wide the exchange currents of these electron–ion reactions are 10^{-6} and 10^{-2} A cm^{-2} respectively. Our study[28] of the temperature dependence of the anodic dissolution of germanium gave an exchange current of 10^{-10} A cm^{-2} (at 25 °C) for the exchange current of the atom–ion subsystem.

These numerical results confirm the conclusion that equilibrium in the electron–ion subsystem is established easily and rapidly at the semiconductor–electrolyte interface. In this sense the atom–ion subsystem is the slow system[29]. Thus we must examine the effects arising from two subsystems (electron–ion and atom–ion) in order to describe the dissolution of semiconductors in polar media. We have also shown[23] that the step in which the oxidiser particles interact with the crystal can be assumed to have reached equilibrium (including the injection of positive holes into the semiconductor as a result of electron transfer between the crystal and the oxidiser). It follows that the potential difference at the semiconductor–electrolyte interface ($\Delta\phi$) is determined by the constants of the adsorption equilibrium steps (1) and (1′).

If γ is the fraction of the potential drop $\Delta\phi$ corresponding to the Helmholtz layer, the activation energy of reaction (2) depends on the potential in the normal way[24]. The fraction of the potential $(1 - \gamma)$, associated with the space charge layer, affects the exchange current of the atom–ion subsystem (see Ref. 24). The establishment of thermodynamic equilibrium at the adsorption interaction step assists the electron transfer processes between the bands (valence, and conduction) of the semiconductor and the Red–Ox system of the solution (as was first pointed out by Gerischer[25]).

VI. STRUCTURE OF THE ACTIVATED COMPLEX

The structure and the characteristics of the activated complex can be determined strictly by calculating the profile of the potential surface for the system of interacting atoms. Recent advances in computational methods of quantum chemistry have made these calculations possible for some of the simpler systems. However, for the reactions being discussed here the calculations cannot be strict, but though the analysis is only qualitative it leads to some definite conclusions.

The special properties of the potential energy curves are identified by comparing the thermodynamic and the kinetic characteristics. The total enthalpy change of the reaction

$$\tfrac{1}{2}A_2 + U = UA(g) \qquad (11)$$

is

$$\Delta H = \tfrac{1}{2}(\Delta H_1 + \Delta H_{1'}) + \Delta H_2 + \Delta H_3 , \qquad (12)$$

where ΔH_1, $\Delta H_{1'}$, ΔH_2, and ΔH_3 are the enthalpies of steps (1), (1′), (2), and (3) respectively.

For exothermic reactions we have $\Delta H < 0$. It follows from published data[6,9,13,16,20] that for dissolution reactions giving rise to bivalent germanium and silicon products we can write

$$|\Delta H_2 + \Delta H_3| \simeq H_2^{\neq} , \qquad (13)$$

whereas for reactions in which quadrivalent compounds are formed

$$|\Delta H_2 + \Delta H_3| < H_2^{\neq} . \qquad (14)$$

From these expressions we note that reactions in which bivalent compounds are formed are barrierless, whereas reactions in which quadrivalent compounds are formed have an energy barrier (see Fig. 1). A barrierless reaction path indicates a smooth change in the structure of the activated complex from the state corresponding to the potential energy minimum to that of the final product. The presence of a barrier leads to the formation of a special type of complex which rearranges itself into the final product. Often the life-time of this complex is greater than 10^{-12} s, and in this case the formation of an intermediate product becomes possible.

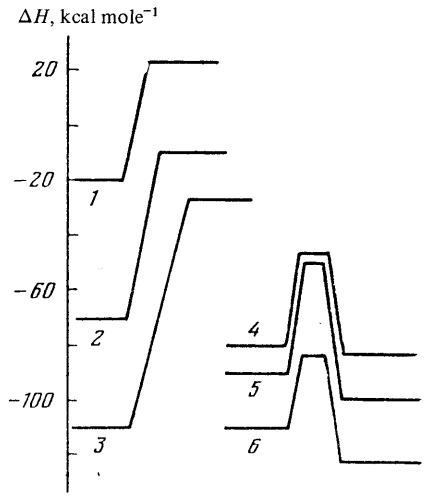
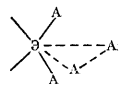


Figure 1. Examples of barrierless reactions [U + $1/2A_2$ = UA(g); U = Ge (*1, 2*) or Si (*3*), $A_2 = S_2$ (*1*) or O_2 (*2, 3*)] and of barrier reactions [U + $2X_2$ = UX_4(g); U = Ge (*4, 6*) or Si (*5*), $X_2 = Br_2$ (*4, 5*) or Cl_2 (*6*)].

We have previously studied[6] the nature of the activated complex for the formation of GeS by the interaction of Ge with H_2S and S, and we have shown that it has the Ge_2GeS structure, in which the germanium–sulphur bond is multiple but the two germanium–germanium bonds are weakened simultaneously as the GeS particle moves away from the surface. The displacement on activation amounts to 1.5–2.0 Å.

Dissolution reactions involving the formation of quadrivalent products take place by a barrier mechanism, and Eqn. (14) applies to these reactions. This conclusion was confirmed for the interaction of germanium and silicon with Cl_2 and Br_2.[15] In these reactions the activated complex has the structure



in which the A atoms are located at the corners of a distorted tetrahedron and the displacement of the semiconductor atom U on activation corresponds to the distortion of the bonds between the semiconductor atom and its nearest neighbours, and is therefore assisted by the insertion of the U atom into the centre of the tetrahedron.

The barrier mechanism is typical of dissolution reactions involving polar solvents. In these cases the donor–acceptor interaction of the adsorbed polar molecules of the solvent assists the formation of the tetrahedrally coordinated complex.

The kinetic characteristics of semiconductor gas-phase dissolution reactions are the simplest and the most accurately calculable. These can be treated as model reactions, and their kinetic parameters can often be used to establish the characteristics of reactions in which the semiconductor is dissolved into a liquid.

In the case of an inert solvent (which does not interact with the semiconductor) the activation energy of the dissolution reaction can be calculated from the linearity relationship

$$H_{\text{к}}^{\neq} = H_{\text{g}}^{\neq} - \alpha \Delta H_{solv} , \qquad (15)$$

where $H_{\text{K}}^{\neq}$ and $H_{\text{g}}^{\neq}$ are the activation energies of the reaction in the condensed and in the gas phase respectively, ΔH_{solv} is the enthalpy of solvation of the reaction product, and α is a fractional coefficient determined by the shapes of the potential surfaces. If the reaction product is chosen as the inert solvent the heat of solvation is equal to the heat of evaporation of the solvent. An example of this type of reaction is the interaction between germanium and a solution of bromine in $GeBr_4$.[20,21] In this case the activation energy of the reaction between germanium and bromine in a condensed phase is 25 kcal mole^{-1}, i.e. it is lower than the activation energy for the same reaction in the gas phase (33 kcal mole^{-1}) by an amount equal to the heat of evaporation of $GeBr_4$ (9 kcal mole^{-1}). It follows that $\alpha = 1$, and that the intermediate complex (in the case of an activated reaction) is relatively long-lived.

The value $\alpha = 1$ is typical of barrierless reactions[23], but since in this case the activation energy is high we cannot observe this behaviour experimentally in low-boiling liquids. However, suitable conditions may be met in the thermal oxidation of semiconductors, which we shall discuss below.

Clearly, in order to interpret the dissolution of semiconductors in polar liquids we need to know the composition of the reaction products and their heat of solvation. In many systems of great practical importance these characteristics are not known. In the absence of satisfactory methods of numerical estimation we must rely on expressions for the dependence of the kinetic characteristics of a reaction on the composition and properties of the solvent. This approach is discussed in detail in Ref.8.

VII. INITIAL STAGES OF OXIDATION

We shall use the considerations outlined above to discuss the special features of the thermal oxidation of semiconductors. At first sight the kinetics and mechanism of the reaction of silicon (say) with bromine and with oxygen have very little in common, since the former produces the volatile $SiBr_4$ whereas the latter produces a layer of SiO_2 whose thickness is determined by the rate at which oxygen can diffuse through it. We should immediately point out that when discussing the kinetics and mechanism of reactions at a phase boundary, i.e. of thermal oxidation processes, we are concerned with changes in instantaneous reaction rates, which can be determined experimentally by extrapolating to zero time the differential with respect to time of the thickness of the initial oxide layer. In this sense it is preferable to rely on experimental data obtained at moderately high temperatures or for relatively thin oxide layers.

The first step in our discussion is to examine the adsorption processes taking place during the initial stages of oxidation, and to establish the criteria which govern the transition from dissolution of the semiconductor in the gas phase (etching) to dissolution into an oxide phase (oxidation). We shall consider the steady-state reaction at constant temperature T and oxidiser pressure p in the gas phase. Using the symbol k_1 for the rate constant of the adsorption of the oxidiser on the atomically clean semiconductor surface we can express the rate of adsorption as

$$w_{\text{ads}} = k_1 p (1 - \theta) .$$

The coverage of the surface (θ) by particles of oxidiser is given by the sum $\theta_1 + \theta_2$, where the first term defines the fractional monolayer coverage of the surface by irreversibly chemisorbed oxidiser, while the second term describes the surface coverage by oxidiser species in the second and higher adsorption layers. In the latter case the adsorption is treated as reversible, and is characterised by the equilibrium constant a and by the relatively low heat of adsorption q_2. Under these conditions

$$\theta_2/\theta_1 = ap/(1 + ap) . \qquad (16)$$

The adsorption processes are accompanied by the transfer of semiconductor atoms to the gas phase with a rate constant $k_{2\text{g}}$ and to the oxide phase with a rate constant $k_{2\text{K}}$. The condition for the transition from dissolution into the gas phase to the formation of an oxide layer is the equality of the rates w_1 and w_2, i.e.

$$k_{2\text{g}} \theta_1 = k_{2\text{к}} \theta_2 , \qquad (17)$$

corresponding to

$$k_{2\text{g}} / k_{2\text{к}} = a p_{\text{кр}} / (1 + a p_{\text{кр}}) . \qquad (18)$$

We shall assume that for a barrierless surface reaction the activation energy of the reaction with rate constant $k_{2\text{K}}$ is lower by ΔH_{solv} than the activation energy of the reaction with rate constant $k_{2\text{g}}$ [Eqn.(15)]. Thus, since

$$\exp (\Delta H_{solv}/RT) \ll 1,$$

we have

$$p_{\text{кр}} = a_{02}^{-1} \exp \left(\frac{\Delta H_{solv} - q_2}{RT} \right) . \qquad (19)$$

It follows from this expression that the condition $p < p_{\text{Kp}}$ corresponds to the formation of a gaseous product (i.e. to etching of the semiconductor), whereas the condition $p > p_{\text{Kp}}$ corresponds to oxidation with formation of a layer of oxide phase. Evidently, by plotting $\lg p$ against $1/T$ we obtain a straight line which divides the pressure–temperature space into two regions corresponding to etching and to oxidation respectively. The slope of this straight line is determined by the quantity ($\Delta H_{\text{solv}} - q_2$). The parameter q_2 can be identified with the heat of dissolution of the oxidiser in the oxide phase. In many systems (for example, in the SiO_2 system) this parameter is of the order of 1 kcal mole^{-1},[7] and therefore it lies within the uncertainty limits of ΔH_{solv}, which thus plays the main role in determining the condition (19). The coefficient a_{02} can be estimated by model calculations, and is typically in the range 10^{-3}–10^{-4} Torr^{-1}.[14,15] Some values of ΔH_{solv} are calculated below, and used (see Table) to compare calculation with experiment for the oxidation of silicon[30,31] and the sulphidation of germanium[14]. Calculations by Eqn.(19) agree in order of magnitude with experimental data on the sulphidation of germanium at 461 °C. For the oxidation of silicon the limiting oxygen pressure (above which an oxide layer begins to be formed) is 1×10^{-2}

Torr at 1100 °C, as compared with an experimental value[31] of 4×10^{-2}–1×10^{-1} Torr. For higher oxidation temperatures the calculated values are an order of magnitude lower than the experimental values. However, we should note that the conditions used in those experiments[30,31] may have produced rate limitation by diffusion of the reactants in the gas phase.

Thermodynamic and kinetic characteristics of germanium and silicon oxidation reactions (kcal mole^{-1}).

U	A_2	Bond Strength			$\frac{1}{2}H_{ads}(A_2)$	ΔH^{form}_{298} (UA)	$H^{\neq}_{2g}$	ΔH_{solv}	$H^{\neq}_{2K}$
		U–U	U–A	U=A					
Ge	S_2	44.5 [65]	68 [3]	131 [61,65]	24 [6]	23.5 [61]	43.0 [14]	−7	36
Ge	O_2	44.5 [65]	85	156 [61,65]	70 [49]	−7.7 [61]	57 [16]	−14	41
Si	O_2	53.5 [65]	111 [34]	190 [65]	110 [49]	−26.7 [66]	83 [62]	−32	52

VIII. KINETIC CHARACTERISTICS OF REACTIONS AT THE SEMICONDUCTOR–OXIDE PHASE BOUNDARY

A large volume of experimental information on the thermal oxidation of silicon is now available. The following results are especially relevant to our discussion.

1. Beyond a certain thickness, the oxidation of silicon is controlled by the rate of diffusion of oxygen to the semiconductor–oxide interface. It has been shown that the oxygen diffuses as undissociated particles: O_2 molecules or O_2^- molecular ions[7,32–35]. The reaction rate is usually proportional to the oxygen pressure.

2. The presence of SiO_x structural units at the semiconductor–dielectric interface, where $x < 2$, has been confirmed by electron spectroscopy methods. At the Si–SiO_2 interface the thickness of the intermediate layer is 2–10 Å, but unusual properties are observed up to oxide thicknesses of 100–150 Å.[36–44]

The thermal oxidation reaction of germanium has been studied in detail for the germanium–sulphur system[14]. It was shown that the diffusion of sulphur through a layer of germanium disulphide up to 1 μm thick does not limit the rate of sulphidation. The intermediate layer is 100–200 Å thick and its thickness depends on the total thickness of the sulphide layer.

3. The layer of silicon dioxide is in a glassy state whose structure is described by two levels of ordering: short-range order, determined by the presence of tetrahedral $SiO_{4/2}$ structure units, and the ordering associated with various arrangements of the initial structure units to give ring and spiral structures which form microscopic pores and extensive channels along which the oxygen species can diffuse[45–48].

These observations allow us to describe the kinetic model of the thermal oxidation reaction of silicon at the semiconductor–dielectric interface as follows. The region close to the interface (Fig. 2) includes a layer of oxide (to the right of the geometric boundary) containing randomly distributed microscopic holes which are arbitrarily shown as spheres. Some of these holes are occupied by oxidised (A_2) molecules whose state can be defined as free gas-phase particles in a volume of linear dimension d. The transition of an A_2 particle from an occupied to an empty hole and back is described by the rate constants k_1 and k_{-1}. A special situation arises when the hole is directly adjacent to the geometric boundary. An A_2 particle entering such a hole can undergo a non-activated interaction with an atom of the semiconductor at the crystal surface (U), and the rate constant of the step leading to the formation of the intermediate compound $\geq$U=A is k_2. We shall assume that in this step the characteristics of the chemical interaction of the oxidiser particle with the atom from the crystal are the same for dissolution into the gas and for the formation of an oxide phase. The process is completed by the incorporation of the intermediate compound UA into the network of structure units of the oxide, characterised by the rate constants k_3 and k_{-3}. The energetics of this step (ΔH_{solv}) define the solvation of the UA species.

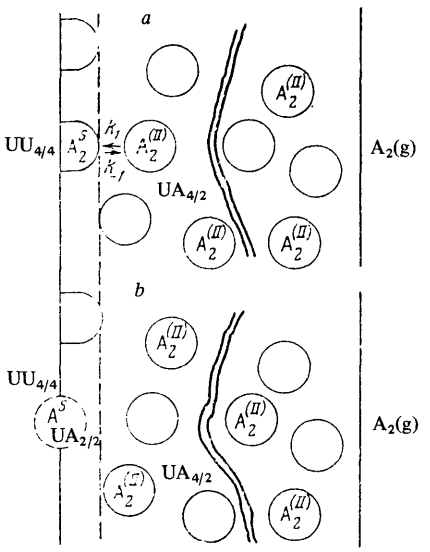


Figure 2. Schematic model of the thermal oxidation of a semiconductor U by interaction with A_2 to give a layer of $UA_{4/2}$: (*a*) adsorption of A_2 with rate constant k_1, (*b*) formation of the intermediate oxidation product $UA_{2/2}$ with rate constant k_2. Microscopic holes in the oxide layer are shown. The concentration of $A_2^{(II)}$ is constant throughout the thickness of the layer. The broken line indicates the intermediate (translational) layer at the U–UA_2 boundary.

The sequence of steps involved in the oxidation of silicon by oxygen can be described as follows[49–56]. The initial step is the chemisorption of oxygen molecules with formation of an adsorbed intermediate on a surface centre, which we assume to be a doubly coordinated silicon atom, $\geq$Si, corresponding (strictly speaking) to a (100) orientation of the crystal:

$$\geq Si + O_2 \rightarrow \geq Si \cdot O_2 \text{ (chemisor.)}$$

The second step leads to an oxidative form of adsorption:

$$\geq Si \cdot O_2 \text{ (chemisor.)} \rightarrow \geq Si{=}O + O \text{ (ads.)}$$

This results in the dissociation of an O_2 molecule in the adsorption layer, one of the oxygen atoms becoming incorporated in the surface centre by a double bond. The other oxygen atom is held by an adsorption bond whose form is not clearly understood. We should stress that in the case of the reaction at the silicon–silica interface the probability of finding two adjacent surface centres (each capable of forming an $\geq$Si=O structure) is very low. In this case the second oxygen atom probably forms a metastable adsorption bond with atoms of the glass network: for example, giving an

Si–O–O–Si peroxide group. The last step limits the rate of the overall process and controls the removal of silicon atoms from the crystal and their incorporation into the network of silicon dioxide:

$$\rangle \mathrm{Si{=}O} \rightarrow \mathrm{SiO_{2/2}} \ . \qquad (20)$$

The oxidation process is completed by the formation of an $SiO_4/_2$ structure unit:

$$\mathrm{SiO_{2/2}} + \mathrm{O\,(ads.)} \rightarrow \mathrm{SiO_{4/2}} \ . \qquad (21)$$

Thus our model is generally consistent with the sequence of steps (1)–(3) proposed above, and the general kinetic equation for the rate of the thermal oxidation process can be written in the form of Eqn.(4). Since the solubility of A_2 particles in the oxide is usually low, i.e. $(k_1/k_{-1})[A_2] \ll 1$, and in most cases $[A_2] = \kappa p_{A_2}$ (where κ is the Henry coefficient and p_{A_2} is the partial pressure of A_2 particles in the gas), we can write

$$w_2 = k_2 k_1 \kappa p_{A_2}/(k_2 + k_{-1}) \ . \qquad (22)$$

There are two important special cases. At relatively low temperatures, when $k_2 \ll k_{-1}$, Eqn.(22) simplifies to

$$w_2 = k_2 k_1 \kappa p_{A_2}/k_{-1} \ . \qquad (23)$$

On the other hand at high temperatures ($k_2 \gg k_{-1}$) we have

$$w_2 = k_1 \kappa p_{A_2} \ . \qquad (24)$$

These two cases correspond to rate limitation at the semiconductor–oxide interface [Eqn.(23)] and to slow supply of A_2 particles to the interface [Eqn.(24)] respectively. In the latter case p_{A_2} is the equilibrium pressure, determined by the concentration of oxidiser dissolved in the layer adjacent to the semiconductor–oxide interface.

IX. COMPARISON WITH EXPERIMENT

The main characteristics of the dissolution of O_2 in silicon dioxide have been discussed by various workers[24,57–59]. The heat of dissolution is found to be ~0.7 kcal mole^{-1}, and the Henry coefficient is $\kappa = 0.0017$ at 900 °C. It has also been shown[34,35,58] that the rates of oxidation of silicon (in the parabolic regime) and of penetration of O_2 through the SiO_2 are almost identical, so that in our symbols the rate constant can be expressed as

$$k_1, \mathrm{cm^2\ s^{-1}} = 2.8 \cdot 10^{-4} \exp\,(-27.6/RT) \ . \qquad (25)$$

In Eqn.(23) the ratio k_1/k_{-1} is the constant for the adsorption equilibrium

$$a^{\kappa} = \frac{k_1^0}{k_{-1}^0} \exp(q_2/RT).$$

We shall assume that the heat of adsorption of O_2 at the $Si–SiO_2$ interface is equal to the heat of adsorption of oxygen for coverages greater than a monolayer.

Then, using Eqn.(8) with $d = 4$ Å, we can calculate the pre-exponential factor C_T of Eqn.(23):

$$C_T = \frac{kT}{h} n_s a_{O\kappa} \ . \qquad (26)$$

In this expression k is Boltzmann's constant h is Planck's constant, T is the absolute temperature, n_S is the concentration of active sites on the silicon surface, corresponding to the average density of holes at the geometric boundary which are filled with oxygen molecules, and $a_{OK} \cong 10^{-2}$ cm^3 mole^{-1}. The solubility of O_2 in silicon dioxide is typically[34,36,37] 5×10^{16} cm^{-3}, or 1.5×10^{11} cm^{-2}, so that we obtain $C_T = 9 \times 10^{21}$ atoms cm^{-2} s^{-1} from Eqns.(23) and (26). This value is close to that obtained from van der Meulen's results[60] (7.6×10^{22} atoms cm^{-2} s^{-1}).

The activation energy for the case described by Eqn.(23) can be calculated by the expression

$$H_{2\kappa}^{\neq} = H_{2g}^{\neq} - \Delta H_{solv} - q_2 \ , \qquad (27)$$

where $H_{2g}^{\neq}$ is the activation energy for the formation of the gas-phase molecule (in this case SiO).

In contrast to the dissolution of semiconductors in electrolyte solutions or in molecular liquids, in the case of thermal oxidation the use of the solvation energy concept requires some clarification. By definition, the solvation energy is the energy evolved when a particle is transferred from a vacuum to the stated medium. If the dissolution product is chemically identical to the medium this quantity is equivalent to the heat of evaporation or sublimation. In many polar or molecular solutions the molecular relaxation time of the medium is so short that the activated complex (or intermediate compound) produced during the dissolution reaction can be assumed to be fully solvated, and the activation energy of the reaction can be calculated by using Eqn.(15). However, in the thermal oxidation of semiconductors the rate of structural relaxation is comparable to the rate of chemical reaction at the phase boundary, which formally implies that the intermediate product of the reaction is only partially solvated. This aspect of the reaction is accounted for by the scheme suggested above for the oxidation of silicon.

Whereas the silicon atoms in the bulk of the oxide have a four-fold coordination, the intermediate compound formed during the rate-limiting step has only two-fold coordination. This is a feature of all the thermal oxidation reaction of semiconductors. Since the nearest neighbour approximation is very accurate in covalently bonded systems, the solvation energy of the intermediates in these reactions can be calculated. It is easy to show that the parameter of interest (ΔH_{solv}) is given by

$$\Delta H_{solv} = H_{U=O} - 2H_{U-O}, \qquad (28)$$

where $H_{U=O}$ is the energy of the double bond in the U=O molecule (for example, SiO), and H_{U-O} is the energy of the U–O single bond (for example, Si–O). By using data for the germanium–sulphur[3,61], germanium–oxygen[3,61], and silicon–oxygen[34] systems we obtained the ΔH_{solv} values given in the Table. We note that the solvation energies are highest for the silicon–oxygen system. The qualitative conclusion from this observation is that in the silicon–oxygen system the semiconductor atoms can be most effectively incorporated into the network of the glassy dielectric layer. By combining these results with experimental values of the activation energy for the dissolution of semiconductors in the appropriate gases[14,16,17,62] we can calculate [by Eqn.(27)] the activation energies for the thermal oxidation ($H_2^{\neq}$) of the semiconductors, which are also given in the Table.

For the germanium–sulphur system comparison with experiment is possible by using the results of Ref.14. The comparison shows that the contribution from the entropy of activation is often important in interfacial reactions, and cannot be ignored. As we have shown[14], the entropic contribution to the activation of the surface complex includes cooperative effects in the layer of sulphide adjacent to the crystal. It is difficult to allow for these effects with adequate precision, but it can be shown that the free energy of activation of the sulphidation reaction corresponds (to within ±8 kcal mole^{-1}) to the activation energy for the dissolution of germanium in sulphur vapour. Since ΔH_{solv} for this system is 7 kcal mole^{-1}, the conclusion is confirmed.

For the germanium–oxygen system the tabulated value is a first estimate of the activation energy of the oxidation process, determined by the reaction at the phase boundary.

For the thermal oxidation of silicon the activation energy of the initial stages was found[60] to be 53.7 kcal mole^{-1}, and an activation energy of 60 kcal mole^{-1} was reported[63] for the region 750–900 °C. These experiments were carried out under conditions favouring rate limitation by the reaction at the interface. The published values of the activation energy are not inconsistent with our estimate of 52 kcal mole^{-1}.

The solvation of the reaction product can be discussed by using a model of the reactive centre consisting of one structure unit of the crystal and one structure unit of the dielectric. This model is obviously valid at temperatures below the glass transition temperature T_g. Above T_g the kinetic processes associated with the switching of valence bonds are strongly hindered, and the activation volume often includes several dozen structural units[64]. As a result, heats of solvation calculated by Eqn.(28) can be expected to be inaccurate.

However, at temperatures above T_g the reactions may take place not through the formation of the intermediate complex $UO_{2/2}$ but directly by the breaking of a U–U bond in the activated complex $U_{2/4}UO$, giving a $UO_{4/2}$ structure unit. This means that the heat of solvation increases almost two-fold, and the activation energy of the reaction at the phase boundary is correspondingly reduced. This effect may explain the decrease in the activation energy of the oxidation from 60 kcal mole^{-1} (at 750–950 °C) to 26.8 kcal mole^{-1} (above 950 °C).[63] Unfortunately the glass transition temperature is not always accurately known. For quartz glass $T_g \cong$ 1157 °C,[34] but there are reasons to believe that very thin layers may soften at a lower temperature. We should re-state the need to allow for the entropic contribution to the activation of the surface complex when the oxidation reaction takes place under conditions compatible with viscous flow of the glassy oxide[9,13,14].

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Our analysis of experimental data on the kinetics of the dissolution and of the thermal oxidation of semiconductors has shown that these two reactions have the same elementary step whose nature is determined by the activated displacement of a surface atom. This allows us to calculate the kinetic characteristics of the process at the semiconductor–oxide interface during thermal oxidation if the characteristics of the dissolution of the semiconductor into the gas phase and of the solvation of the intermediate by the oxide layer are known. In covalent systems the heats of solvation can be calculated by the two-fold coordination model of the semiconductor atom in the nearest neighbour approximation. The structure-chemical theory of reaction kinetics on a semiconductor surface and of relaxation processes in glass oxides offers a unified approach to the semiconductor oxidation reactions. As a result, an atomic–molecular theory of semiconductor–dielectric systems can be developed and used to synthesise materials having prescribed properties.

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