THIN FILMS SCIENCE AND TECHNOLOGY

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THIN FILMS SCIENCE AND TECHNOLOGY, 4

Passivity of Metals and Semiconductors

Proceedings of the Fifth International Symposium on Passivity, Bombannes, France, May 30-June 3, 1983, Organized by the Société de Chimie Physique

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F O R E W O R D

Passivity is the situation in which a metal is prevented from corroding by
a thin film, despite thermodynamic conditions which foresee an instability of
this metal towards the aggressive environment. Such films are very important
because they frequently provide an efficient protection for highly reactive
metals.

Nevertheless, the loss of passivity by metals or alloys gives rise to corro-
sion damage of either a general or localized form. Localized breakdown pro-
cesses involved in crevice corrosion, pitting, stress corrosion, cracking ...
are of considerable theoretical and practical interest.

This volume is composed of invited lectures and communications presented
during the Fifth International Symposium on Passivity, held in Bombannes
(France), from 30 May to 3 June 1983.

The previous symposia were essentially devoted to the passivity of metals
such as iron, nickel, aluminium, titanium and their alloys, with special atten-
tion to stainless steels. Localized corrosion and film breakdown too were dealt
with in a large number of conferences and communications. Undoubtedly, both
topics, passivity of metallic materials and localized corrosion, remain of
basic importance and have been treated in several sessions. Experimental tech-
niques were also given full attention. In addition to classical approaches such
as optical techniques and electron spectroscopy, EXAFS and Raman Spectroscopy
now appear as new tools promising for in-situ characterization of passivity
phenomenon ; these aspects have been developed in a full day session.

Moreover, the Organizing Board has estimated that basic and practical pro-
blems connected with the passivation of semiconductors are of growing impor-
tance. For instance, new advances in microelectronics devices and very large
scale integrated circuits are to a large extent dependent on our knowledge of
thin films on semiconductors such as silicon or gallium arsenide. It seems
detrimental to both fields of investigation that the development of techniques
and concepts is carried out separately. That is the reason why, by way of
experiment, we have introduced semiconductor passivity as a new theme in the
form of invited lectures. Recent advances in photoelectrochemical solar energy
conversion are highly promising, but the application on an industrial scale of
the more efficient junctions is restrained by their poor stability under illu-
mination. Therefore we decided to have a session devoted to photoelectrochemis-
try. From another point of view, studies of the passive film in metals in terms

of semiconducting material, although controversial, are certainly fruitful. For instance, theoretical descriptions of charge transfer at passive layers are likely to be improved by recent advances in photoelectrochemistry. Finally, spectrophotoelectrochemistry of passive layers can be regarded as an in-situ technique, easy to use and providing relevant data.

In view of the very large number of contributions, it was not possible to arrange an oral presentation for all contributors. Therefore the number of oral lectures was limited by the Organizing Committee and four Posters Sessions were organized. However, in order to allow thorough discussions and to enhance informal exchanges, each Poster Session was followed by a Round Table Discussion. These discussions were stimulated by the Chairman and the invited lecturers of the same session. Short transactions of these discussions have been included in this Proceedings Volume.

These transactions are in no way a precise recording of the poster discussions but only an attempt to report as far as possible the content of contributions, questions, answers and comments. The Organizing Committee apologizes for distortions with respect to an exact transcription.

The Organizing Committee would like to thank all those who contributed to the preparation of this Symposium. Special acknowledgments are due to the members of the Scientific Committee and to our colleagues approached during the elaboration of the programme and the referees of so many manuscripts. We are extremely grateful to invited lecturers and chairmen who were in charge of the animation of their session.

Undoubtedly, the many invited lectures and communications presented in Bombannes have established the advances achieved since the last Symposium held in Airlie (USA) in 1977, particularly with regard to the composition and some of the properties of the passive layers. However, as substantiated by the very active discussions which took place after the oral presentations and during the Round Tables, we are still far from understanding clearly the relationships between the physicochemical properties of the passive layers and their dynamic response to chemical attacks and mechanical stresses. The connection between mechanisms of formation and structure of the passive layers on metals such as iron or semiconductors such as silicon was scarcely dealt with in Bombannes and deserves further attention. I hope that further progress in these fields will be reported at the Sixth Symposium, to be held in Japan.

M. FROMENT

TRANSPORT OF OXYGEN AND WATER IN OXIDE LAYERS

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ABSTRACT

In this paper a discussion is given of the mechanisms by which the oxidising agent passes through the layer of oxide already formed, with special reference to silicon, and to other materials where the oxide is vitreous. In silicon in dry oxygen O_2 appears to diffuse through the layer of SiO_2 with little exchange of oxygen with the network already formed. For oxidation in H_2O, though the mechanism is similar, there is considerable exchange for a reason which will be explained; thus some small charge transport by network oxygen can occur. For thin films transparent to electrons and in anodic oxidation, on the other hand, ionic motion can predominate; various mechanisms are discussed.

If an oxide film is formed on a metal or other material such as silicon, we have to understand how the oxidising agent passes through the film; if the film is protective, growth must virtually stop at a certain thickness. In this lecture, I discuss films of network-forming oxides, in which the oxide is non-crystalline. Silicon and aluminium are examples. Silicon has been so extensively studied that I shall pay particular attention to this material, in the hope that the discussion will yield insights into other materials.

The high temperature oxidation of silicon is described by the Deal-Grove[1] equation

$$X^2 + AX = B(t + t_o) \qquad (1)$$

where X is the thickness after time t. The parabolic form $X^2 = Bt$ to which this tends for large thicknesses is governed by diffusion through the film; for the linear law at small thicknesses the reaction at the Si/SiO_2 interface determines the rate. It is known that in the parabolic regime the molecule O_2 is the diffusing species, the constant B being proportional to the pressure of O_2 (Doremus[2]; for discussions by the author see refs. [3,4]). Also for <u>dry</u> oxygen by the use of the isotope ^{18}O in O_2 Professor Amsel's group has shown that O_2 diffuses through the oxide without exchange with the oxygen already in the network, ^{18}O being deposited at the Si/SiO_2 interface[5].

The present author[3, 4] has pointed out that, to account for the solubility of O_2 and of rare gases in vitreous Si_2, it is necessary to assume the presence of a small number of sites to which the O_2 can be transferred from the gas with a small change on free energy. The potential energy should thus appear as in fig. 1
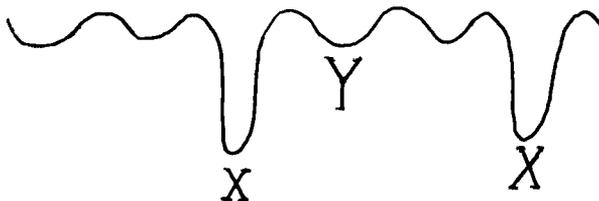

Fig. 1. Potential energy of O_2 in SiO_2

The nature and distance apart (26Å) of these deep sites is also discussed by Revesz and Schaeffer[6]. These deep sites, marked X in fig. 1, have no effect on the rate of oxidation; the constant B in equation (1) should contain the exponential $\exp\left\{-(W + U)/kT\right\}$, where W is the free energy required to bring an O_2 molecule from the gas to a site Y, and U is the activation energy to move it to a neighbouring site.

Schaeffer in earlier papers supposed that charge transport occurs also partly by diffusion of network oxygen, on the basis of results showing ^{18}O deposited throughout the film. In view however of these results from Professor Amsel's laboratory for dry oxygen, Revesz and Schaeffer[6] now believe that the earlier observations were due to traces of water vapour and that in its absence network diffusion now contributes to the oxygen transport one part in 300 or less.

We turn now to the effect of water vapour. As Deal and Grove[1] point out, the rate of oxidation is, as for O_2, proportional to the partial pressure of H_2O. As is well known, the presence of water vapour greatly increases the rate of oxidation, the main reason being that H_2O diffuses more rapidly than O_2; it is

thought that hydrogen is released at the Si/SiO_2 interface and diffuses out of the specimen. On the other hand, the solubility of H_2O in vitreous SiO_2 is proportional to the square root of the pressure. Various authors (e.g. Roberts and Roberts[7]) have pointed out that this is because H_2O goes into solution as two non-bridging Si-OH bonds. These must have much lower mobility than interstitial H_2O, but this does not mean that they are not mobile at all. If they move, there can therefore be some movement of network oxygen and some plastic flow which may greatly increase the ductility.

An extremely interesting result from Prof. Amsel's group[8] is that, if $H_2{}^{18}O$ is used, the ^{18}O is now deposited at the gas/SiO_2 interface. Rapid exchange of O with the network already formed is thus indicated. The present author has suggested that this is because H_2O can react with the SiO_2 network to form the two non-bridging Si-OH bonds; there is no corresponding reaction for O_2. The formation of non-bridging Si-OH can give a mechanism of rapid exchange of ^{18}O with the network. At the same time it does not look as if these defects have a high mobility, or contribute much to the passage of oxygen, since the rate of oxidation is proportional to p, the pressure of H_2O. Irene and Ghez[9] give evidence that network diffusion does give some contribution, since the pressure dependence of the rate of oxidation is rather less than linear.

Many measurements confirm the approximate validity of the linear-parabolic model, for instance Irene and Van der Meulen[10] and Hopper[11], though the latter work shows different constants for thick and thin films.

We next examine the linear regime of the Deal-Grove equation (1), in which diffusion has produced a nearly constant concentration of O_2 or of H_2O in the oxide layer and the rate of the reaction is determined by the rate of reaction at the interface, with an activation energy comparable with that for diffusion (1.5 eV compared with 2.3 eV)[10]. O_2 attacks a clean silicon surface without activation energy – though the initial sticking probability is low[12] ($\sim 6 \times 10^{-3}$). The difference when oxidation is by O_2 in interstitial positions in SiO_2 is, of course, that all silicon atoms at the surface (or nearly all) form strong Si-O bonds, so the O_2 must diffuse through the surface layer and react at a point where the much weaker Si-Si bond is broken, presumably by thermal activation. This must be a complicated process in which there is a rearrangement of the atoms locally, and for which it is hardly possible to make a mathematical model.

SiO_2 occupies considerably more volume than Si in crystalline silicon; the effect of this volume change, in setting up strains in the oxide, has been considered by several authors (e.g. [13, 14]). The present author has in several

papers suggested that the volume change is of little importance. The process is illustrated in fig. 2 ;the Si atom, <u>below</u> the Si layer bonded to oxygen, is thought to be at a kink site. Reaction with oxygen is impossible unless
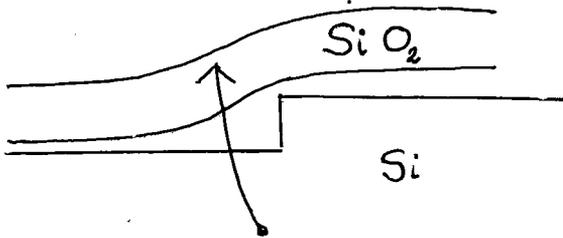
Fig. 2. Mechanism of film growth

considerable place-exchange occurs, allowing the SiO_2 to be incorporated into the network. If the latter is viscous, no strains will be set up, the extra volume being incorporated by a thickening of the oxide layer. But viscous flow may occur only under the very high stresses produced by the chemical reaction. If so, a small lateral strain may remain. We would expect this stress to decrease with increasing temperature. This seems in agreement with the observations of EerNisse[15, 16] who observes a (small) intrinsic stress as a result of oxidation at temperatures below $1000°C$; above $1000°C$. he supposes that viscous flow can occur (even for small stresses), as the oxide is formed. Irene et al find higher stress values with consequent higher density at lower temperatures (see also Irene et al[17], Taft[18]).

Irene and Dong[19] find a significant curvature in the Arrhenius plot of the linear rate constant, and ascribe this to the presence in the network at high temperatures of 0, the O_2 molecules being partly dissociated. It is supposed that the atomic 0 leads to a faster rate of reaction than O_2.

There is evidence[20] that the interface between Si and SiO_2 is sharp; there is no layer of SiO_x (x < 2) greater than $6Å$ in width.

We now turn to mechanisms of low temperature oxidation, both for silicon

and metals, mechanisms which characteristically lead to a logarithmic growth law and the formation of a protective film. Fehlner and Mott[21], in a review of mechanisms of low-temperature oxidation, proposed that the first few layers are produced by a mechanism of "place exchange", which can occur as a consequence of the very strong fields which must exist. The process is considered further by Fromhold[22] who calls the elementary excitations "hopons". Present models however are hard to compare with experiment.

Fromhold also suggests that place exchange may take place in anodic oxidation of metals. There is extensive experimental evidence that in the oxidation of aluminium the cation transport number is about 0.4 (see Skeldon et al[23]). Pringle's[24] work on Tantalum gives 0.24 for the cations. Fromhold points out that it is improbable that very different ions would have almost the same activation energy for movement, and a correlated mechanism is indicated. An alternative, however, if the activation energy for forming an interstitial ion at a surface is what matters, is to assume that - say - the cation, arriving at the oxide-electrolyte interface, excites on the average a given number of anions into the oxide through the heat released in the oxidation process.

For further growth, the logarithmic growth law and the formation of protective films, a theory was given in 1938 by Cabrera and Mott[25], subsequently developed by Fehlner and Mott[21]. This theory envisages oxidation by <u>charged</u> species, normally anions, the film being transparent to electrons. This could occur by electron tunnelling for films up to 20 - 30 Å thick or at high temperatures by excitation of electrons from the metal (or silicon) into the conduction band of the oxide. It is supposed that the energy W to form the charged species at the oxide/gas interface is such that $\exp(-W/kT)$ is negligable, so that normally the reaction will not take place; but if the film is transparent to electrons a potential V_o will be set up between surface states at the oxide/gas interface and the metal (or silicon). The rate at which the charged species are formed will then be of the form

$$C \exp \{ - (W - qaV_o/x)/ kT \} \tag{2}$$

where q is the charge on the ion, <u>a</u> the hopping distance and x the thickness of the film. Integration leads to a logarithmic or inverse logarithmic growth law.

The same model was applied to anodic oxidation by Verwey[26] in 1932, V_o being now the applied voltage.

If W is greater than the activation energy for parabolic growth according

to the Deal-Grove equation, then we would expect logarithmic growth always to be followed by a very slow parabolic growth. It is remarkable that this is found by Ponpon and Bourdon[27] in their work on the oxidation of hydrogenated amorphous silicon; logarithmic behaviour is shown for 10^5 seconds, followed by approximately parabolic growth. In crystalline silicon according to Lukes[28] logarithmic behaviour persists up to 10^7s. The smaller contribution from the logarithmic term in the amorphous material is to be expected if the crystal is n-type, because in the amorphous material, unless doped, the Fermi energy lies in mid-gap; therefore the potential V_o will be smaller.

Equation (2) would suggest an even smaller logarithmic term for crystalline p-type material; experiments in this regime would be of interest.

In the oxidation of silicon the work of Kamigaki and Itoh[29] is of interest; this was at 1000°C. While at high pressures parabolic growth was observed, at low pressures they claim to have observed logarithmic growth. Since according to the Cabrera-Mott model this will depend little on pressure (p), it should always take over at low enough values of p.

As regards the nature of the charged species, OH^-, O^- and O^{2-} are candidates. In anodic oxidation, the work of Schmidt and Ashner[30] and Croset and Dieumegard[31] show that water plays an overwhelming role, so OH^- is perhaps the most likely species. Defects, such as charged non-bridging oxygens, are also candidates; Raman spectra of steam-grown SiO_2 shows $\frac{1}{3}$% of OH (Galeener[32]). Here the work of Jorgensen[33], Mills and Kroger[34], and Barton[35] is relevant. Jorgensen showed that an applied electric field, using a permeable platinum electrode, can accelerate or retard the process. So if electrons are available from an open circuit, a process involving the movement of an anion is preferred. Also (at 800°C) a voltage of 1.78V blocks the process, while four times this is the energy, in electron volts per O_2 molecule, released in the reaction. Thus four electrons must flow around the circuit for each oxygen molecule, and this suggest that O^{2-} is formed through the reaction

$$O_2 + 4e \rightleftarrows 2O^{2-} \qquad\qquad (3)$$

If O^{2-} is the mobile species it is not clear why the reaction rate is, according to Jorgensen, still proportional to the oxygen pressure; one would expect $p^{1/2}$ (Barton[35]). The discrepancy can perhaps be resolved by supposing that, when electrons are freely available at the SiO_2/O_2 interface, charged silicon vacancies are formed there and are responsible for the diffusion. Since

one such vacancy is formed per O_2 molecule, the pressure-dependence is explained and if the vacancy carries four charges (one for each oxygen dangling bond) the blocking voltage is also as observed.

It must be emphasized that this model is applicable only if electrons are available, either from a platinum electrode or by tunnelling. To form the defect two Si-O bonds must be broken, and the large energy involved could come only from electrons falling from the Fermi level in the silicon into the oxygen orbitals.

In this model we need not suppose that neutral and charged species are in thermodynamical equilibrium, as postulated by Collins and Nakayama[36]; if electrons can get through the film, the charged defect is formed; if not, O_2 is the predominant mobile species.

Our hypothesis that a species carrying four charges is formed is certainly open to criticism; it should easily form a complex, for instance with hydrogen. We put it forward, however, as a very tentative explanation of Jorgensen's results.

Some new results do, however, shed some light on this process. Rochet[37] has found that, at $1000°C$ and in dry oxygen, a small amount of ^{18}O is deposited at the gas/oxide interface for thin films. The results are given in the table. Column I denotes the thickness of the oxide film before ^{18}O was substituted for ^{16}O; column II is, in equivalent thicknesses, the amount of deposition of ^{18}O at the gas/oxide interface, and column III is the deposition at the oxide/silicon interface (all thicknesses in Angstroms). The residual water concentration was 1 to 3 p.p.m., and was not thought to have any effect.

I	II	III
2600	9	72
1800	11.5	92.5
270	13	150
500	15.4	188

If, as Rochet suggests (private communication), this is associated with some small passage of electrons through the film, and if this allows the formation of a negatively charged silicon vacancy, then clearly the oxygen will be built into the SiO_2 network immediately at the interface. This would explain

these results.

Here again, we would have to assume that the large energy needed to break two silicon-oxygen bonds was provided by the electrons, with energies in defect states high in this energy gap of SiO_2, dropping to the defect. Since the width of the gap is perhaps 9 eV, much energy would be available.

Another model of interest is the proposal of Derrien and Commandre[38]; these authors also postulate for thin films the motion of an oxygen ion, which by "place exchange" produces a dipole layer increasing the work function (as observed for Al, Cr and Si), and which would hinder the motion of the ions and eventually bring oxidation to an end. These authors give calculations based on this model which give good agreement with experiment for oxidation at low pressures.

Finally we give a brief discussion of the formation of micropores (flaws) in oxidation. Gibson and Dong[39] give direct evidence for 1 nm micropores in dry thermal SiO_2 from high resolution transmission electron-microscopy, confirming earlier work by Irene (see this volume). Irene's hypothesis is that these form through misfit of "islands" formed initially. They are not observed in "wet" oxidation, and this could be due to the smaller viscosity of the oxide, for which   the hypothesis discussed earlier could account. In anodisation of metals similar "flaws" are observed[40]. They are thought to form on impurity segregates.

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Note added in proof :

In view of Professor Good's model for logarithmic oxidation discussed at this meeting, I suggest that the Cabrera-Mott model may apply principally to amorphous oxides, which are probably much less susceptible to doping than crystals.

Dr. Rochet suggest that trivalent Si is a charged defect, already known from its ESR spectrum, which can be responsible for oxygen transport in SiO_2.

AN OVERVIEW OF THE KINETICS OF OXIDATION OF SILICON: THE VERY
THIN SIO$_2$ FILM GROWTH REGIME

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INTRODUCTION

    Modern microelectronic devices such as bipolar and field
effect transitors are fabricated on silicon single crystal
surfaces using a planar technology. This kind of processing
utilizes primarily the surface of the semiconductor. The
individual devices operate based on the electrical properties of
the silicon surface. For reliable device operation, the surface
properties must be reproducible over large dimensions as compared
to the size of the devices, in order that large arrays of densely
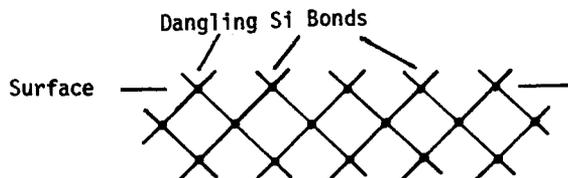packed devices can be produced.

Fig. 1. Si (100) Surface with Dangling Bonds

    It is intuitive that atoms on the surface of a solid are
environmentally different from atoms in the interior of the
material. Indeed, the earliest literature on semiconductor
physics reports this idea (1-3). Fig. 1 shows a cross-sectional
view of a Si crystal. It is seen that the surface contains atoms
with unsatisfied chemical bonds or so-called "dangling bonds". It
was predicted (1-3) that such dangling bonds would produce
electrically active states, ie. states in the Si band gap. This
prediction was confirmed. Such surface electronic states were
measured and the number of states was found to be in agreement
with the prediction. The dangling bond model for the surface