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Oxidation of Silicon

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Work on the oxidation of silicon in various gaseous media has been reviewed. Particular attention has been paid to the mechanism of formation and the kinetics of the growth of oxide films on silicon during high-temperature oxidation. Published data on the composition and structure of the resulting film of reaction products, the dependence of the rate of oxidation on the pressure of the oxidising medium, and the possible participation of silicon ions in the growth of the oxide film have been discussed. The bibliography contains 120 references.

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1. INTRODUCTION

The interest in oxide films on silicon is due to the development of semiconductor electronics with the use of these films to protect the surfaces of semiconductor devices and also as active and passive elements in solid silicon functional circuits.

The many methods for preparing these films have been for the most part the result of empirical research. In addition to methods involving the thermal[1-23] and anodic[24-30] oxidation of silicon, methods involving the deposition of silicon dioxide films from the gaseous phase have been developed. Methods of this kind which have found application include those involving the volatilisation of oxides of silicon in a vacuum[31-37], cathodic sputtering and sputtering in a high-frequency discharge[30,36-39], the pyrolytic decomposition of organosilicon compounds[30,41-43], and the chemical transport and hydrolysis of silicon halides[30,44-56].

When oxide layers are used as masks in processes of diffusion alloy-formation or the surface protection of a semiconducting device, the purity and continuity of the oxide are important, whereas when silicon dioxide is used as an active element, for example in MOS-structures (metal–oxide–semiconductor), the electrical properties of the film itself and more particularly of the interface between it and the semiconductor acquire considerable importance.

Such properties of the oxide film as the electrical conductivity and charge density in the bulk of the film and at the interface between it and the semiconductor, which determine the parameters of the device and their stability, depend chiefly on the conditions of formation of the oxide. It is the physicochemical conditions of the process (temperature, pressure, the oxidising medium, etc.), and hence of the formation of the oxide film, and the interface between it and the semiconductor, which determine its degree of stoichiometric and structural perfection and the related electrical properties of the MOS-structures.

Thus the detailed study of the mechanism and kinetics of the growth of oxide films, particularly in the initial stages of their formation, is of considerable importance for the production of films with required properties.

The present review deals with problems of the kinetics and mechanism of the thermal oxidation of silicon, which provides one of the basic methods for obtaining silicon dioxide films.

2. KINETICS OF THE GROWTH OF OXIDE FILMS ON SILICON

The initial stage of the reaction of silicon with oxygen when the silicon surface has been effectively cleaned should involve the adsorption of the gas on the surface. Subsequently, the oxygen may dissolve to some extent in the silicon, after which the production of oxide in the form of individual nuclei or a continuous film will take place.

In all the work dealt with in this review, the observation of the course of the high-temperature oxidation process was begun not with an atomically-clean silicon surface but with a surface carrying a thin oxide film, formed during the preliminary treatment of the specimens studied.

These films may have different thicknesses. The subsequent growth of the primary oxide film formed may obey different relationships, depending on its thickness, structure, and composition, and also on the actual conditions of oxidation.

The large number of studies of the kinetics and mechanism of the oxidation of various metals have been reviewed in a number of monographs[57-60], and they show that low-temperature oxidation in most instances is characterised by logarithmic or inverse-logarithmic relationships, whereas high-temperature oxidation most frequently shows a time dependence of parabolic type, deviations from which are observed in a number of instances in the initial stage of the oxidation. The parabolic law for high-temperature oxidation generally means that the rate of oxidation is limited by the rate of diffusion of the reacting components through the oxide film. A theoretical basis for this mechanism was proposed by Wagner[61,62]. His theory is based on the concept of conductivity in ionic crystals and semiconductors. The movement of ions through the oxide film is due to the cation concentration gradient which always exists as a consequence of the constant enrichment of the surface of the oxide layer in oxygen and of the internal interface in cations. Wagner's theory does not deal with the initial stages of the oxidation and is restricted to a consideration of the growth of oxide films after they have reached a definite thickness. The regular features of the initial stage of the oxidation have been interpreted in different ways by different authors. This problem will be discussed after an examination of published data on the kinetics of the high-temperature oxidation of silicon.

The kinetic features of the high-temperature oxidation of single crystals of silicon have been studied by various

methods by a number of authors over a wide range of temperatures and pressures.

Thus Atalla and coworkers[1] studied the stabilisation of the surface of silicon by oxide films grown at 1000° in an atmosphere of water vapour and oxygen.

McAdam and Geil[2] studied the growth of oxide films on silicon, using an optical method to measure the thickness of the oxide. They established that at temperatures in the range 500–950° the results can be described by the parabolic film-growth law:

$$\frac{dn}{dt} = \frac{k}{n} \quad (1)$$

where n is the number of molecules of oxygen reacting in time t, and k the oxidation rate constant.

Brodsky and Cubicciotti[3] studied the oxidation of silicon at p_{O_2} = 200 mmHg by recording the change in the oxygen pressure with time; they obtained at 950° and 1160° a parabolic relationship, and at 1015° and 1020° a logarithmic relationship of the form

$$W = k \lg(1 + at), \quad (2)$$

where W is the quantity of oxidant used in time t, and a and k constants.

The growth of the oxide according to a logarithmic relationship was attributed to the formation of a vitreous oxide of silicon, in which the concentration gradient of the diffusing particles changes not linearly but according to a relationship of the form $\partial c/\partial x = -c_0 \alpha e^{-\alpha x}$ (c_0 is the concentration of diffusing particles at a distance x from their starting point, and α a proportionality efficient). The estimated activation energy of oxidation is E = 26 kcal mole^{-1}.

Law[4] used a manometric method to study the kinetics of the oxidation of silicon at temperatures in the range 727–1027° at pressures of dry oxygen in the range 10^{-3}–5×10^{-2} mmHg. Under these conditions the rate of oxidation is described by a parabolic equation of the form

$$n = 2k\left(\frac{t}{n}\right) + c, \quad (3)$$

where n is the number of oxygen molecules which have reacted in time t, and c and k constants. According to Law's data, E = 36 kcal mole^{-1}.

Evans and Chatterji[5] studied the kinetics of the oxidation of silicon in dry oxygen by a gravimetric method and found that in the temperature range 1200–1400° the rate is given by a parabolic law (E = 43 kcal mole^{-1}). In their opinion, the straight lines shown in Fig. 1 do not, as might have been expected, pass through the origin of coordinates, because at all temperatures the rate of the process in the initial stage is greater than would be expected from a parabolic oxidation law.

Sah and coworkers[6] obtained a parabolic law for the oxidation of silicon in moist oxygen in the range 1200 to 1300° (E = 34 kcal mole^{-1}).

Ligenza and Spitzer[7] studied the oxidation of silicon by oxygen at p_{O_2} = 1 atm and 950°, and concluded that the kinetics of the oxidation can be described by the equation

$$x^2 = 8.4 \cdot 10^{10} \cdot p^{1/4}\left[\exp\left(-\frac{40000}{RT}\right)\right] \cdot t, \quad (4)$$

where x is the thickness of the oxide, Å; t the time, min; and p the pressure, atm.

Later, Ligenza[8] studied the oxidation of silicon in water vapour at a high pressure (25–500 atm) in the range 500–950°, and showed that the growth of the oxide film takes place linearly with time, and that its rate is directly proportional to the vapour pressure.

Yeh[9] used an optical method to determine the thickness of the growing oxide and established that the oxidation of silicon by water vapour at p_{H_2O} = 1 atm and 970° obeys a parabolic law.

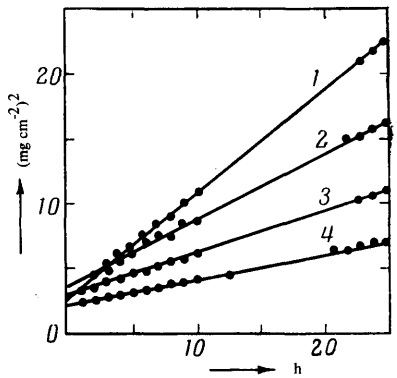


Figure 1. Oxidation of silicon[5]: *1*) 1360°; *2*) 1303°; *3*) 1255°; *4*) 1201°.

Claussen and Flower[10], using an ellipsometric method, found that the oxidation of silicon in dry moist oxygen or water vapour at 1200° also obeys a parabolic relationship.

A similar growth law for the oxide film on silicon in atmospheres of dry oxygen, moist oxygen, or water vapour in the range 1000–1200° was derived by Deal[11], who established that the rate of oxidation in water vapour is greater than that in moist or dry oxygen. The activation energy values obtained by Deal for the three oxidation conditions indicated are given in the Table.

Medium	Activation energy (kcal mole^{-1}) calculated from data	
	gravimetric	optical
Dry oxygen	28.4	30.2
Moist oxygen (95% H_2O)	21.4	20.8
Water vapour	20.0	19.9

Deal[11] noted that at ~1000° the growth of the film takes place according to the law

$$W^2 + k_1 W = k_2 t \quad (5)$$

where W is the quantity of oxide formed, t the duration of oxidation, and k_1 and k_2 constants.

The oxidation of silicon in dry oxygen and water vapour at elevated temperatures was studied by Edagawa and coworkers[12], who obtained the following experimental equations characterising the kinetics of the growth of the films: in an atmosphere of water vapour

$$x_0^2 = 3.35 \cdot 10^9 \cdot t \cdot \exp(-23000/RT) \quad (6)$$

and in an atmosphere of dry oxygen

$$x_0^2 = 4.84 \cdot 10^9 \cdot t \cdot \exp(-32200/RT) \quad (7)$$

where x_0 is the thickness of the oxide film, t the time, and R the gas constant.

Fuller and Streiter [13] studied the oxidation of silicon in an atmosphere of water vapour or dry oxygen in the range 700–1200°. To determine the thickness of the oxide layer they used an ellipsometer and a table of interference colours. In both media, for the reactions taking place below 1070°, they obtained a parabolic law of oxide growth with activation energy equal to 39 kcal mole^{-1}. The reactions taking place at higher temperatures are also characterised by a parabolic oxidation law, but with a lower activation energy.

Revesz and Zaininger [14] found that the oxidation of silicon in an atmosphere of water vapour obeys a parabolic relationship if the thickness of the film formed is greater than 3000 Å. A film of smaller thickness, in the opinion of the authors cited, grows according to a linear law.

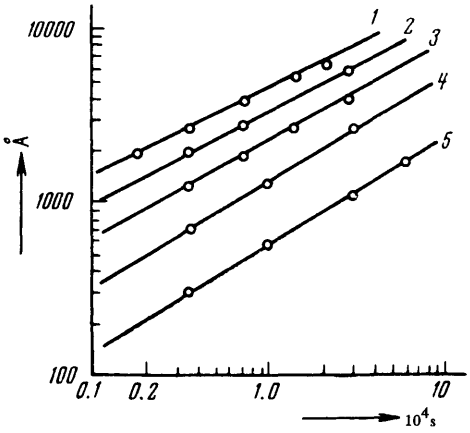


Figure 2. Oxidation of silicon [16]:
1) 1300°, *2*) 1200°, *3*) 1100°, *4*) 1000°, *5*) 900°.

Sladkova [15] used a polarimetric method to study the oxidation of silicon in air. In the range 300–560°, oxide could not be detected. In the range 560–950° the oxidation obeyed the linear law

$$d_1 = k_1\tau + d_0 \quad (8)$$

where d_1 is the thickness of the film, d_0 the initial thickness of the film, τ the time, and k_1 a constant. The value of k_1 depended on temperature: $k_1 = at^2 + b$, where t is the temperature, and a and b constants. In Sladkova's opinion, the oxidation of silicon in the range 950–1000° is described by the parabolic law

$$d_2^2 = k_2\tau + d_0^2 \quad (9)$$

where d_2 is the thickness of the film, d_0 the thickness of the original film, and k_2 a constant.

Evitts and coworkers [16], using an optical method, found the following relationships describing the rate of growth of oxides at temperatures equal to or greater than 1100° and a pressure equal to 1 atm:
for water vapour

$$x^2 = 1.21 \cdot 10^9 \cdot t \cdot \exp(-18400/RT) \quad (10)$$

and for dry oxygen

$$x^2 = 3.53 \cdot 10^9 \cdot t \cdot \exp(-30590/RT) \quad (11)$$

where x is the thickness of the oxide, Å, and t the time, s. The results [16] for the oxidation of silicon in dry oxygen are given in Fig. 2.

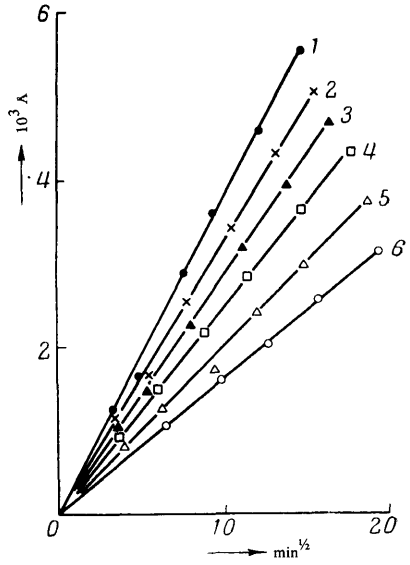


Figure 3. Oxidation of silicon [17]:
1) 1300°, *2*) 1247°, *3*) 1205°, *4*) 1150°, *5*) 1100°, *6*) 1050°.

Lukes and Schmidt [17] used an optical method to study the oxidation of single crystals of silicon in an atmosphere of dry oxygen at 1050° and 1300° and obtained a parabolic law for the oxide film growth (Fig. 3):

$$d^2 = kt, \quad (12)$$

where d is the thickness of the oxide film, t the duration of oxidation, and k a constant. They found that the temperature dependence of the parabolic rate constant k in Eqn. (12) was not exponential, but satisfied the relationship

$$k = A(T - T_0)^2 \quad (13)$$

where A is a constant, and $T_0 = 860°$ (from the experimental data).

The data of Deal and Grove [18] on the oxidation of silicon in dry oxygen, obtained by determining the thickness of the oxide by an optical method, are given on logarithmic coordinates in Fig. 4. The slope of the lines on the graph corresponds to the exponent n in the equation

$$x_0^n = kt \quad (14)$$

where x_0 is the thickness of the oxide film, t is the time, and k a constant.

It can be seen from Fig. 4 that the value of n at 1200° is close to 2, whereas at lower temperatures and smaller oxide thicknesses the value of n at first decreases to 1.5 and then increases again. Thus the data obtained by these authors cannot be described by a simple power law. The difference in the kinetics of the oxidation of silicon in dry

and moist oxygen is demonstrated in Fig. 5. The curve characterising the kinetics of the oxidation in dry oxygen intersects the axis of ordinates at $x_0 = 250$ Å. The authors conclude that this course of the curve is due either to the presence of an oxide film of definite thickness on the silicon surface before the start of the measurements or to the manifestation of a different oxidation mechanism in the first stage of the process. Since in the oxidation of silicon in moist oxygen a primary oxide film was not observed, the authors used the second alternative to explain the results obtained on oxidation in an atmosphere of dry oxygen. The rate of oxidation was higher at the start of the process in dry oxygen at 700° (Fig. 6).

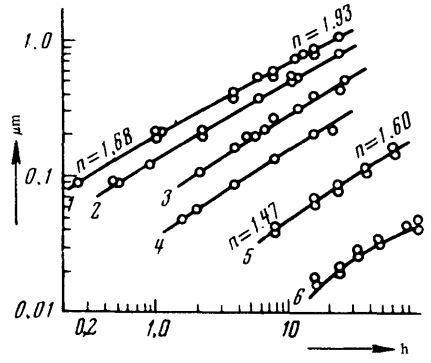


Figure 4. Oxidation of silicon in dry oxygen[18]: *1*) 1200°, *2*) 1100°, *3*) 1000°, *4*) 920°, *5*) 800°, *6*) 700°.

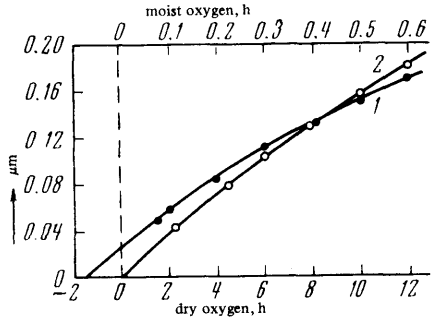


Figure 5. Oxidation of silicon in dry and moist oxygen[18]:
1) dry, *2*) moist.

Deal and Grove[18] consider that the kinetics of oxidation of silicon over a wide range of temperature and pressure by the action of oxygen or water vapour obeys a relationship of the form

$$x_0^2 + Ax_0 = B(t + \tau) \qquad (15)$$

where x_0 is the thickness of the oxide film, t the time, and A, B, and τ are constants for the oxidation.

According to Pliskin[19], the oxidation of silicon in an atmosphere of water vapour also obeys a linear–parabolic law.

Nakayama and Collins[20] studied the kinetics of the growth of films of SiO_2 on silicon in a mixture of water vapour and oxygen or argon in the range 850–1217° and partial pressures of water in the range 4.6–355 mmHg. In this temperature range the authors observed a mixed linear–parabolic oxidation law of the form

$$Ax + Bx^2 = t \qquad (16)$$

where x is the thickness of the oxide, t the time, and A and B constants. Hikaru and Dzenti[21] give data on the influence of the treatment of the surface of the specimen, the moisture content of the oxidising medium, and the crystallographic characteristics of the crystal plane studied, on the rate of oxidation of silicon. They did not observe any differences in the rates of oxidation of specimens subjected to mechanical and chemical polishing. The rate of oxidation increased with increase in the moisture content. In the range 995–1050° the rate of oxidation depended on the orientation of the crystal plane studied, as follows: $v_{[111]} = v_{[110]} > v_{[100]}$. It was found that the activation energy of oxidation changes on going to the temperature range below 1100°. The authors cited conclude that at low temperatures the mechanism of oxidation is different, and the growth of the oxide film does not follow a quadratic law.

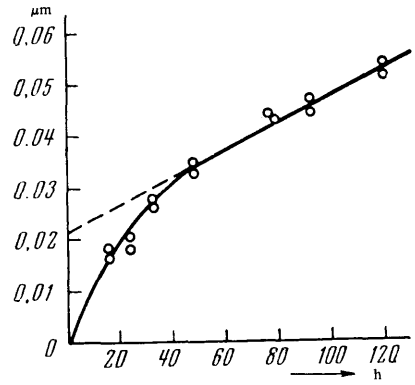


Figure 6. Oxidation of silicon in dry oxygen at 700°.[18]

According to the data of Mai[22], the growth of the oxide film in the successive oxidation of silicon in dry oxygen, moist oxygen, and water vapour at 1150° obeys a parabolic relationship, the rates of the corresponding processes decreasing in the order: $v_{\text{water vapour}} > v_{\text{m.o.}} > v_{\text{d.o.}}$

Burkhardt and Gregor[23] determined the volume of oxygen used in the oxidation from the position of a mercury seal in a measuring tube; adopting the interpretation of the oxidation put forward by Deal and Grove[18], they obtained a linear–parabolic relationship for the growth of oxide films as far as thickness of 5000–6000 Å.

3. MECHANISM OF FORMATION OF OXIDE FILMS

Analysis of published data on the thermal oxidation of silicon shows that at high temperatures the growth of the oxide film follows a parabolic time dependence, deviations from which have been observed by a number of authors[5,11,13,18,23] in the initial stages of oxidation.

Many authors try to explain the formation of the primary oxide films on silicon on the basis of the mechanism of formation of thin oxide films put forward by Cabrera and Mott[63]. This mechanism assumes that in the film of oxide formed on chemisorption, the electrons of the metal, moving independently of the ions, pass through the thin layer of oxide, either by a tunnel effect or as a result of thermionic emission, and react with oxygen on the outer surface of the film, that is at the oxide–gas interface, forming oxygen anions. Metal cations are formed correspondingly at the metal–oxide interface. As a result, in the opinion of the authors cited, a strong electric field, which facilitates the transfer of positive ions to the oxide–gas interface, is created inside the oxide film. The rate of ion transfer should show an exponential dependence on the field intensity, and the oxidation is described by a corresponding inverse logarithmic equation.

In a recent paper, Mott and Fehlner[64], taking into account the ideas of Eley and Wilkinson[65], dealt with the role of the structural factor in oxidation for the example where the growth of the oxide film involves the migration of oxygen through the oxide film.

Other authors[4,13] attribute the deviation from the parabolic law in the initial stage of the oxidation to the production of a space charge, in accordance with the ideas of Engell and Hauffe[66–68]. According to these ideas, exchange of charge carriers between the gas molecule being adsorbed and the semiconductor takes place on chemisorption, so that this stage leads to charging of the surface. As a result, a space charge is produced in the layer of the semiconductor next to the surface, leading to the manifestation of a diffusion potential, resulting from the difference in the mobilities of the electronic and ionic defects in the thickness of the oxide. In the opinion of this group of authors, a parabolic oxidation law should not be observed so long as the thickness of the growing layer is comparable with the region of the space charge influencing the ion diffusion responsible for the growth of the film.

Deal and Grove[18], using the model of oxidation proposed by Evans[57,69], suggest that for "short" times, the duration of which is determined by the specific conditions of the oxidation, a linear law of oxide growth should operate. Evans, however, in the interpretation of the equation which he derived, of the form

$$k_1 y^2 + k_2 y = k_3 t + k_4 \qquad (17)$$

where y is the thickness of the oxide film, t the time, and k_1, k_2, k_3, and k_4 constants, considered that for small values of t and y, Eqn. (17) becomes a simple parabolic equation, and at high values of t and y it may approach a linear equation.

Growth of the oxide film according to a linear law is possible if the oxide splits with the passage of time, as a consequence of a difference in the volumes of the oxide and the metal. In this instance, oxygen has free access to the metal surface, and the stage determining the rate of oxidation will be the reaction at the oxide–gas interface. It should be noted that a linear oxide growth law is also possible at very low oxygen pressures, when the oxygen being supplied is unable to compensate the loss of oxygen during its reaction with the cations passing through the oxide film, as observed, for example, by Gulbransen and coworkers[70], who made a gravimetric study of the oxidation of silicon at oxygen pressures equal to 9×10^{-3}, 4×10^{-2}, and 1×10^{-1} mmHg and temperatures of 1100, 1200, and 1300°. The authors cited put forward four equations to describe the reactions involved in the oxidation of silicon

$$Si_{(s)} + {}^1/_2 O_{2(g)} \rightleftarrows SiO_{(g)}, \qquad (18)$$

$$Si_{(s)} + O_{2(g)} \rightleftarrows SiO_{2(s)}, \qquad (19)$$

$${}^1/_2 Si_{(s)} + {}^1/_2 SiO_{2(s)} \rightleftarrows SiO_{(g)}, \qquad (20)$$

$$SiO_{2(s)} \rightleftarrows SiO_{(g)} + {}^1/_2 O_{2(g)}. \qquad (21)$$

A small increase in weight, indicating the formation of a layer of oxide on the surface according to Eqn. (19), was observed only at $p_{O_2} = 1 \times 10^{-1}$ and a temperature of 1100°. Under all other conditions, a decrease in weight as a result of the formation of the volatile monoxide according to Eqn. (18) was observed. Gulbransen and coworkers[70] established that the rate of oxidation is linearly dependent on the rate of flow and pressure of oxygen. They concluded that the rate of oxidation at low oxygen pressures is a function of chiefly the pressure and velocity of the gas stream, and is almost independent of temperature. In this case the rate of the process is determined by the transfer of gas to the surface of the specimen.

An analysis of the primary stage of the oxidation would be incomplete without consideration of the importance of the active sites on the metal surface, the role of which may be extremely significant, particularly in the examination of the influence of the pressure of the oxidising medium on the oxidation.

Arslambekov[71] has examined the kinetics of the formation and growth of the primary oxide film from the viewpoint of kinetic theory. The rate of the process in this instance can be represented by the equation

$$\frac{\partial n}{\partial t} = (N_0 + N_{\text{diff}} - n) \cdot \sigma \cdot Z \cdot e^{-E/RT} \qquad (22)$$

where N_0 is the initial number of active metal atoms on the surface, N_{diff} the number of active metal atoms coming out on the surface as a result of diffusion, n the number of metal atoms reacting, δ the effective cross-section of the metal atom–gas molecule reaction, Z the number of oxygen molecule collisions taking place on 1 cm² of the surface, and t the time.

The solution of this equation for low temperatures and low pressures, that is for the conditions under which the formation of thin oxide films can be followed, has the form

$$n = N_0(1 - e^{-kt}) \qquad (23)$$

where $k = 6 \times 10^6 \frac{p}{\sqrt{T}} \cdot e^{-E/RT}$ is the rate constant; p the pressure, mmHg; E the activation energy; and T the temperature, °K.

On the basis of the theoretical considerations developed in Refs. 71–73, Arslambekov put forward a mechanism for the formation of the oxide film, describing the interaction between oxygen and an atomically-clean metal surface, with allowance for local superheating.

In the elementary stage of the interaction of a gas molecule with a metal surface, all the heat of reaction is liberated in a negligibly small volume, and this leads to a local increase in temperature. The next gas molecule entering the local superheating zone undergoes reaction with a greater probability than that for the cold regions. This leads to additional liberation of heat and an increase in the temperature of the surface. The latter will increase until a steady state, in which the quantity of heat supplied by the reaction is equal to the quantity of heat removed by the thermal conductivity of the metal, is established.

At low oxygen pressures, the frequency of collisions against the surface is low, so that in the time interval

between two successive collisions of oxygen molecules in the same zone the heat from each elementary stage of the interaction is able to undergo complete scattering. Each new molecule of oxygen then reacts with a cold surface, so that the formation of the oxide film should take place relatively slowly, and the thickness of the layer formed may be very small (only several monolayers).

It should be noted that in all the above theories of formation of the primary oxide films, attention was not paid to the role of the crystal lattice type of the metal being oxidised and the oxide, or the crystal-chemical relationships between them. Allowance for the crystal-chemical correspondence between the structures of the metal and the oxide, however, reveals significant features of the actual mechanism of formation of oxide layers on metals.

According to Dankov's crystal-chemical theory of oxidation [74,75], the establishment of a stoichiometric relationship between the components takes place as soon as a monomolecular layer of oxide is formed. The characteristic feature of the primary stage of the oxidation is that in this stage there is direct contact between the oxygen molecules and the chemically non-combined metal atoms, whereas in the subsequent stages the O_2 molecules encounter the chemical compound M_xO_y on the surface.

A characteristic feature of the oxidation, observed when the reaction takes place at room temperature, is the attainment of a limiting oxide film thickness; this limit lies in the range of submicroscopic thicknesses. In the mechanism proposed by Dankov for the formation of oxide films of limiting thickness, it is assumed that the growth of the oxide film at moderate temperatures, in which diffusion of the components through the oxide is required, is made possible by the penetration of defect sites in the oxide lattice. The latter results from the non-coordinated growth of a large number of oxide blocks consisting of stoichiometric saturated formations.

On the basis of the theory that there is a gradual decrease in the concentration of the defects which are responsible for the diffusion and hence which determine the rate of formation of the oxide, Dankov derived an equation which characterises the change in the thickness of the oxide with time and which indicates the existence of an oxidation limit:

$$y^2 = \frac{2k''}{k}(1 - e^{-kt}), \qquad (24)$$

where y is the thickness of the oxide, k'' and k constants, and t the time.

A development of Dankov's principle of orientational and dimensional correspondence as applied to solid-phase chemical reactions was provided by the scheme proposed by Arkharov [76] for the nucleation of the primary crystal of a chemical compound. According to Arkharov, the reaction of a metal with a gas involves the formation of a supersaturated solid solution, in the volume of which the primary nucleus of the oxide phase is formed.

The reasons and conditions for the formation of nuclei of the oxide phase on a metal surface in its reaction with an oxidising medium have been examined by a number of authors [58,77,78].

The following scheme for the growth of oxide films on silicon in dry oxygen was proposed by Ono and coworkers [79]. In the initial moment of oxidation, isolated oxide units are formed around the defects in the silicon surface (impurity atoms, dislocations, lattice defects, etc.). Subsequently, each isolated unit expands, and its surface acquires a planar form. The upper layers of these regions consist of SiO_2, and the inner layers consist of a series of lower oxides of silicon. The secondary projections produced between the isolated oxide units on subsequent oxidation expand and join up with one another, and when the process lasts for a sufficiently long time they cover the Si surface completely.

Arslambekov and coworkers [80] give experimental data on the kinetics of the oxidation of silicon at temperatures in the range 700–1180° and oxygen pressures in the range 10–320 mmHg, obtained by continuous weighing on an automatic vacuum micro-balance. They also give a theoretical analysis of the kinetics of the growth of oxide films on silicon with allowance for the defects produced in the oxide film in the primary stage of the oxidation, and also with allowance for the possible counter-diffusion of oxygen and metal through the oxide. The experimental data are effectively described by the derived kinetic equation, which takes account of a number of possible stages in the high-temperature oxidation:

$$(Q + Q_0)^2 = 2kt + 2A\tau_a(1 - e^{-t/\tau_a}) + 2B\tau_b(1 - e^{-t/\tau_b}) + Q_0^2 \qquad (25)$$

where Q is the quantity of oxygen absorbed in the oxidation, Q_0 the quantity of oxygen absorbed in the primary stage of the oxidation, k the parabolic oxidation rate constant, t the time, A and B coefficients making allowance for the influence of the concentration of defects in excess on the diffusion of the components (oxygen and silicon respectively), and τ_a and τ_b the non-equilibrium defect relaxation time constants for oxygen and silicon respectively.

The accelerated growth of the oxide film at small thicknesses ($t < 3\tau$)—compared with the parabolic—which follows from the relationship derived by the authors cited, is due to the presence of an excess of structural defects produced in the primary stage of the reaction between silicon and oxygen. When the concentration of defects reaches the equilibrium value for the given temperature, when $t > 10\tau$, the exponential terms become much less than unity, and the growth of the oxide film will be described by a parabolic equation of the form

$$Q^2 + 2QQ_0 = 2kt + c \qquad (26)$$

where

$$c = 2A\tau_a + 2B\tau_b + Q_0^2 . \qquad (27)$$

4. COMPOSITION AND STRUCTURE OF OXIDE FILMS ON SILICON

The reliable determination of the mechanism of oxidation requires continuous measurement of the change in the weight of the specimen over a fairly prolonged period, and comparison with the composition and structure of the reaction products. The detailed analysis of the nature of the oxide films on silicon is made difficult by their amorphous structure, established by a number of authors [81–86] by X-ray and electron diffraction.

Pavlov and Shitova [87] made an electron diffraction study of films on silicon, produced by oxidation in water vapour under pressure (p_{H_2O} = 0.25 atm, temperature 650°) and in a high-frequency discharge plasma with tetramethoxysilane as starting material. Depending on temperature and pressure, crystalline silicon dioxide can exist in various structural modifications: quartz (α, β), tridymite (α, β, γ), and cristobalite (α, β) [88], which have been shown by X-ray diffraction [89] to be based on SiO_4 tetrahedra which are joined at their apices and are

arranged in space according to a definite law. In the cristobalite structure, closed cavities are formed, whereas in the tridymite structure, channels penetrating the entire framework are left. It has been shown[87] that irrespective of the method of production, all the films have an amorphous structure, in which the short-range order is identical to that in the structures of β-cristobalite and β-tridymite. Experiments on the diffusion of boron and phosphorus at 1200° gave very low values for the diffusion coefficients (10^{-15} cm^2 s^{-1}) for all types of film[90], and it was concluded that the cristobalite structure is the most probable from the energetic viewpoint.

Revesz[84] studied the structure of films obtained by different methods: thermal oxidation in moist or dry oxygen, anodic oxidation, and pyrolytic decomposition of tetraethoxysilane. In all instances the diffraction patterns contained only a diffuse ring or "halo" indicating that the oxide has an amorphous structure. Revesz considers that the small crystallites which may be formed in the initial stage of the growth of the oxide when the silicon surface carries projections and cracks facilitating the formation of nuclei of the crystalline phase are subsequently "displaced" to the oxide surface and no longer serve as crystallisation centres. He points out that the refractive indices and absorption of the films in the infrared range of the spectrum are very similar to those for vitreous silica, the structure of which is similar to that of cristobalite. In Revesz's opinion, the "vitreous" oxide formed is a non-crystalline chemically homogeneous material characterised by short-range order and the presence of Si—O bonds.

Thus according to modern theories[30,91], amorphous silica consists of a disordered three-dimensional network of silicon—oxygen tetrahedra, which are connected only through their apices, and not via edges or faces. The tetrahedra in quartz glass are similar to those in crystalline quartz, but in the glass they form a disordered network, and in crystalline quartz they form a regular lattice; even in quartz glass, however, many of the tetrahedra are grouped to form the hexagonal rings characteristic of crystalline quartz. According to modern theories of the vitreous state, the arrangement of the tetrahedra is not completely random[92]; the short-range order in the network of tetrahedra may be characterised by regions of crystallinity with dimensions from 10 Å to 100 Å. Thus the terms "quartz lattice", "vacancy", "interstitial atoms", etc. are used to describe the structure of the glasses.

In an examination of the problem of the phase composition of the oxide films formed on silicon, it must be borne in mind that since the free energy of the silicon—oxygen interface is different from that for the bulk of the material, there is a probability that compounds which are unstable in the volume of the material may be formed in this region. Thus the thermo-dynamic characteristics of the films formed on the surface may differ significantly from those of the same material in compact form.

The existence of the following oxides of silicon has now been established: SiO, Si_2O_3, SiO_2, and Si_3O_4[93].

Published data on the nature of solid silicon monoxide are contradictory. Most authors, on the basis of X-ray diffraction studies, regard it as an amorphous material[94-97]. Some workers consider that it is a fine mixture of silicon and silica (indistinguishable by X-ray diffraction[98-100], but direct proof for this hypothesis has not been given. Only two papers[101,102] describe SiO specimens with a cubic lattice with constant $a = 5.16$ Å.

Valuable information on the properties of silicon monoxide can be obtained by optical methods, particularly in the infrared range[103-106]. It has been noted[104-106] that the optical properties of a condensed film of silicon monoxide differ significantly from the properties of films of elementary silicon and of silicon dioxide. York[107] considers that data on the absorption spectra of silicon oxide films in the ultraviolet, visible, and infrared ranges can be used to establish quantitatively the proportions of the phases SiO, Si_2O_3, and SiO_2 in films obtained by condensation in a vacuum. According to Nishimura and coworkers[108], analysis of the infrared absorption spectrum indicates that the oxide films deposited in a high vacuum with a source at an elevated temperature contain SiO, whereas the films obtained in a low vacuum and with a source at a low temperature contain Si_2O_3. Litvinova and coworkers[93] report that it is possible that the phases Si_2O_3, Si_3O_2, and Si_3O_4 exist in the compact state in addition to the phase SiO. The materials studied were specimens of silicon oxides obtained by the condensation of SiO vapour in a vacuum. Films of oxides richer in oxygen than SiO were obtained under conditions in which small quantities of air were supplied to the vacuum chamber of the furnace. The compositions of the phases were established by high-precision chemical analysis and X-ray micro-analysis, and verified by carrying out the oxidation with continuous weighing. The authors cited concluded that the gaseous monoxide SiO, on condensation, can pass directly into the solid state, but that in order to prevent its disproportionation it is necessary to ensure a sufficiently high rate of cooling of the SiO vapour. In their opinion, the oxides SiO, Si_3O_4, and Si_2O_3 are stable only at high temperatures, have a high vapour pressure, and can exist indefinitely in solid form. albeit in a metastable state.

The explanation given by Sladkova[15] for the increase in the refractive index of oxide films on silicon from 1.48 to 1.55 is that in some instances the films formed on the silicon surface contain an SiO phase.

An attempt has been made[109,110] to establish the phase composition of the oxide films formed in the thermal oxidation of silicon in dry oxygen, by the analysis of data characterising the volatilisation of these films. Silicon itself, and some of its oxides, have an appreciable volatility. If the heats of evaporation of the individual phases differ significantly, it is sometimes possible, by carrying out studies over a wide range of temperatures, to reveal regions in which the kinetics of the overall process are determined by the volatilisation of one of these phases. In this instance, if the oxide film consists of several phases with different heats of volatilisation, inflections should be observed on the graphs giving the temperature dependence of the volatilisation rate constants on coordinates $\lg k$ against $10^4/T$. In both of the works cited, the analysis of the temperature dependence of the rate of volatilisation did in fact reveal three regions corresponding to volatilisation in the temperature ranges 810—1010, 1010—1082, and 1082—1150° (Fig. 7). The values of the heats of volatilisation calculated from the experimental data for these regions were found to be ~60, ~145, and ~117 kcal $mole^{-1}$ respectively. Microscopic analysis of the silicon surface after oxidation[110] showed that the oxide film had a marked defect structure, probably due to the change in the temperature conditions during oxidation and the long duration of the experiments. The presence of micropores and cracks in the oxide film probably also explains the fact that at about 950° the specimen showed a decrease in weight, due to the volatilisation of silicon monoxide present under a layer of silicon dioxide. This suggestion may also explain the difference in the data on the course

of the volatilisation of oxide films from a silicon surface in its initial stages [109,110].

Thus the oxide film on silicon, as on most metals, consists of several oxides: the outer layer consists of the dioxide, and the inner layer consists of silicon monoxide.

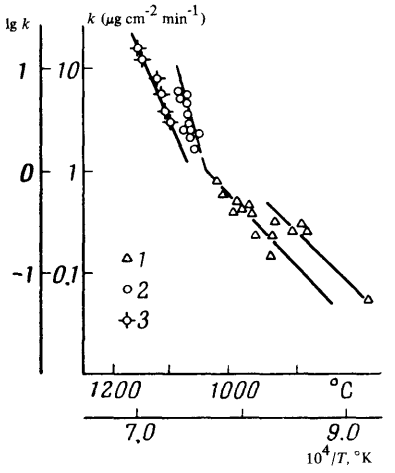


Figure 7. Volatilisation of silicon oxide films obtained by oxidation in dry oxygen at p_{O_2} = 40 mmHg in the range 816–916° for 44 h [110]:
1) volatilisation of SiO, *2*) volatilisation of SiO_2, *3*) volatilisation of Si.

5. DEPENDENCE OF THE RATE OF GROWTH OF OXIDE FILMS ON SILICON ON THE PRESSURE OF THE OXIDISING MEDIUM

A detailed understanding of the high-temperature oxidation of silicon requires a knowledge of the dependence of the reaction rate on the pressure of the oxidising medium.

If the rate of oxidation is limited by adsorption, the reaction usually depends markedly on the oxygen pressure. Under limiting conditions at very low oxygen pressures, the rate of oxidation is proportional to the rate of collision between oxygen and the surface, and hence to the oxygen pressure. At higher oxygen pressures the rate of oxidation is often proportional to $(p_{O_2})^{1/2}$. This is observed, in particular, in oxidations obeying the linear relationship, when the reaction rate is determined by processes beyond the limits of the phases.

Law [4] considers that the parabolic oxidation rate constant for thin oxide layers (100–1000 Å) is described by an equation of the form:

$$k = k_0 \ln p_{O_2} + \text{const} \qquad (28)$$

where k is the oxidation rate constant, and p_{O_2} the oxygen pressure.

A more marked dependence of the rate of oxidation of silicon on the pressure of oxygen, reflected by the empirical equation (29), was established by Arslambekov [109]:

$$x^2 = 1.1 \cdot 10^6 \cdot t \cdot p^{1/3} \cdot e^{-40000/RT} \qquad (29)$$

where x is the thickness of the oxide film, Å; p the pressure of oxygen, mmHg; and t the time, min.

6. NATURE OF THE DIFFUSING PARTICLES IN THE OXIDATION OF SILICON IN VARIOUS GASEOUS MEDIA

A number of papers [7,8,30,83,111–113] have been devoted to the investigation of the nature of the diffusing particles in the oxidation of silicon in various gaseous media.

Some authors [30] suggest that in the oxidation of silicon by water vapour, the first layers of oxide are formed by the chemisorption of water. Since these layers prevent further contact between water and silicon, the reaction takes place either between surface silicon atoms, combined in the crystal lattice, and water molecules, present in the interstices of the oxide, or between an intermediate silicon hydroxide group and silicon.

In the first instance the oxide is formed in the reaction

$$H_2O + Si{-}Si \rightarrow Si{-}O{-}Si + H_2 . \qquad (30)$$

In the second instance the following reactions take place: close to the gas–oxide interface

$$H_2O + Si{-}O{-}Si \rightarrow 2\,(Si{-}OH) , \qquad (31)$$

at the oxide–silicon interface

$$2\,(Si{-}OH) + Si{-}Si \rightarrow 2\,(Si{-}O{-}Si) + H_2 . \qquad (32)$$

In both reactions of oxide formation, described by Eqns. (30) and (32), the hydroxyl groups reacting with silicon must diffuse through the oxide layer in order to reach the oxide–silicon interface. It is assumed that the hydrogen, the rate of diffusion of which is fairly high ($D_{(H_2)_{1050°}} = 2.2 \times 10^{-6}$ cm² s⁻¹), diffuses through the oxide layer to the oxide–gas interface.

If a loose oxide layer is formed in the oxidation of silicon in an atmosphere of water vapour, the diffusion of hydroxyl groups or water molecules is facilitated. In this instance the process retarding the oxidation may be the reaction of the diffusing particles with silicon. Confirmation that the reaction rate is the factor limiting the oxidation can be provided, in the opinion of the authors cited, by the dependence of the rate of oxidation on the crystallographic characteristics of the surface being oxidised; this dependence is shown particularly clearly at high vapour pressures and low temperatures. It is found that $v_{[110]} > v_{[311]} > v_{[111]}$, where v represents the rates of oxidation of the corresponding faces.

The presence of impurities on the surface and in the volume of the semiconductor may lead to the production of pores of molecular dimensions, micro-cracks, dislocations, and other defects and inhomogeneities in the oxide. The pores and cracks make the oxide layer permeable to gases [115–118], and this must influence the regular features of the growth of the oxide.

In oxidation by water vapour, the presence of impurities in the volume of the silicon may influence both the rate of the surface oxidation and the diffusion coefficient of the reacting particles. For example, phosphorus influences chiefly the rate of the surface reaction: the surface containing a high concentration of the element is oxidised more rapidly than a surface containing a low concentration [118]. On silicon containing boron, the growing oxide "extracts" a large quantity of boron from the volume of the silicon [119]. The increasing defect nature of the oxide lattice leads to an increase in the rate of diffusion of the components of the reaction through the oxide.

Under conditions of prolonged oxidation at pressures of ~100 atm, dissolution of the oxide in water vapour is possible [8]. At even higher pressures, the silicon surface is etched as a result of the increased intensity of this process.

Study of the oxidation of silicon in a mixture of water vapour, oxygen, and argon[20] established that the concentration of water in the gas stream is the most important variable determining the rate of growth of the oxide at a given temperature. Change in the ratio of the partial pressures of water and oxygen may lead to a significant change in the kinetics of oxidation. Thus the activation energy of oxidation in moist oxygen decreases with increase in the concentration of water vapour. The process takes place much more rapidly in water vapour than in moist or dry oxygen, and the rate of oxidation in moist oxygen is greater than that in dry oxygen.

The nature of the diffusing particles in the oxide in the reaction of silicon with oxygen has been studied by various methods[83,112,113]. Thus Karube and coworkers[112] deposited the radio-active tracer ^{32}P on the oxidised surface of a specimen. The oxidation was then repeated under the same conditions (in a stream of oxygen at 1250°). The distribution of the diffusing particles was determined from the radio-activity values obtained by successively etching away layers of the oxide. The study was based on the following considerations: if silicon diffuses in the repeated oxidation, it will react at the gas interface, and the surface containing the radio-active tracer will again be covered by the growing oxide. If the process takes place as a result of the diffusion of oxygen, the chemical reaction will take place on the $Si-SiO_2$ interface, and the surface of the oxide obtained in the first oxidation will remain the gas–oxide interface. The results of the experiment confirmed the second mechanism, according to which the oxidation takes place with the transfer of oxygen through the oxide lattice.

Jorgensen[113] used a combination of methods involving the deposition of a Pt tracer on the surface and the application of an electric field. A layer of platinum with thickness 1 μm was deposited on the surface of a silicon crystal with a specific resistance of 1000 Ω.cm. A layer of silicon monoxide was deposited on the platinum and then oxidised to the dioxide. The position of the tracer was determined by measuring the resistance. If the resistance between the tracer and the silicon had remained unchanged on oxidation, this would have indicated that the platinum remains at the metal–oxide interface and that the oxidation product is formed under the platinum. The experiment showed that the resistance was equal to 4000 Ω before oxidation, and 6000 Ω after oxidation. On the basis of these results the author cited concluded that during the oxidation, the oxygen diffuses through the deposited layer of SiO, the platinum, and the layer of SiO_2 formed in the process, and then reacts at the oxide–silicon interface. To determine whether the oxygen diffuses in the oxide in the form of atoms or ions, Jorgensen carried out experiments, the results of which showed that the rate of oxidation is influenced by an electric field applied at right angles to the silicon surface. This increases the rate of oxidation when the silicon at the $Si-SiO_2$ interface is at a higher positive potential than that at the SiO_2-O_2 interface, indicating that oxygen diffuses in the form of negatively changed ions. Laverty and Ryan[120], however, carried out analogous studies at different oxygen pressures and concluded that in addition to the ionic component, neutral oxygen in molecular form takes part in the diffusion responsible for the growth of the oxide film.

Balk and coworkers[83] used electron microscopy to study the structure of a silicon surface subjected to thermal oxidation in dry oxygen and in water vapour, and established that the relief of the original silicon surface in the first stages is preserved in the outer layers of oxide, whereas the internal surface after removal of the oxide is smoothed. The explanation put forward by the authors cited for this phenomenon is that both with dry oxygen and with water vapour, the oxidation takes place at the silicon–oxide interface, so that the diffusing particles responsible for the growth of the oxide are oxygen particles.

In all the above work on the investigation of the nature of the particles diffusing through the oxide, the reaction of silicon with oxygen was carried out with gas at atmospheric pressure. While stating that the growth of the oxide films takes place under these conditions chiefly as a result of the diffusion of oxygen, the authors cited do not exclude the possibility of diffusion of silicon.

Arslambekov and coworkers[80], in an investigation of the influence of pressure on the kinetics of the oxidation of silicon, found that with decrease in pressure the activation energy of oxidation increases. The experimental results can be explained on the basis of the following considerations. At increased oxygen pressures the rate of oxidation of silicon is determined chiefly by the diffusion of oxygen through the oxide film. With change in the oxygen pressure there is a change in its concentration in the surface layer of oxide, and this leads to a change in the difference in the concentrations of oxygen at the gas–oxide and oxide–silicon interfaces. This should lead to a change in the overall diffusion stream, and hence to a change in the oxidation rate constant k. The difference in the concentrations of silicon at the interfaces, and the chemical potential gradient, are almost independent of the oxygen pressure. With marked decrease in the oxygen pressure in the system, the ratio of the diffusing atoms of silicon and oxygen taking part in the formation of the oxide film changes considerably. There are grounds for assuming that at a certain critical oxygen pressure in the system the quantity of oxygen diffusing in unit time may become commensurate with the quantity of silicon diffusing in unit time. Further decrease in the oxygen pressure may lead to a situation in which the process will be determined chiefly by the diffusion of silicon atoms. Since the activation energies for the diffusion of oxygen and silicon are different, we should also expect a change in the effective activation energy of the oxidation as a whole, as observed experimentally[80].

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The variety of complex phenomena observed in the oxidation of silicon explains the observed differences in the properties of the oxide films obtained under different conditions, and indicates the possibility of directed control of a number of these properties. This follows primarily from the dependence of the diffusion stream of silicon and oxygen on the conditions under which the process is carried out. In accordance with this, the zone which moves should be that in which the characteristic chemical reaction corresponding to the kinetic measurements takes place with the greatest probability. The distribution of heat in the oxide layer takes place accordingly.

Displacement of the regions in which the reaction takes place and heat is liberated should naturally influence the nature of the distribution of the stresses in the oxide and also the structural defects responsible for the electrical properties of the system.

The properties of oxide layers may also be influenced significantly by the conditions of the primary reaction of oxygen and silicon, the mechanism of which is also examined in this review.

REFERENCES

1. M. M. Atalla, E. Tannenbaum and E. J. Scheibner, Bell System Techn. J., 38, 749 (1959).
2. D. J. McAdam, Jr. and G. W. Geil, J. Research Natl. Bureau Standart, 28, 593 (1942).
3. M. B. Brodsky and D. D. Cubicciotti, J. Am. Chem. Soc., 73, 3997 (1951).
4. J. T. Law, J. Phys. Chem., 61, 1200 (1957).
5. J. W. Evans and S. K. Chatterji, J. Phys. Chem., 62, 9, 1064 (1958).
6. C. T. Sah, H. Sello, and D. A. Tremere, J. Phys. Chem. Solids, 11, 288 (1959).
7. J. R. Ligenza and W. G. Spitzer, J. Phys. Chem. Solids, 14, 131 (1960).
8. J. R. Ligenza, J. Electrochem. Soc., 109, 73 (1962).
9. T. H. Yeh, J. Appl. Phys., 33, 2849 (1962).
10. B. H. Claussen and M. Flower, J. Electrochem. Soc., 110, 983 (1963).
11. B. E. Deal, J. Electrochem. Soc., 110, 527 (1963).
12. H. Edagawa, Y. Morita, and S. Maekawa, J. Appl. Phys. (Japan), 2, 765 (1963).
13. C. Fuller and F. Streiter, "Paper presented at the Spring Meeting of the Electrochem. Soc. Abstract", Toronto, 1963, p. 3.
14. A. Revesz and K. H. Zaininger, J. Physique, 25, 66 (1964).
15. J. Sladkova, Czechos. J. Phys., cip. B, 13, 452 (1963).
16. H. C. Evitts, H. W. Cooper, and S. S. Flaschen, J. Electrochem. Soc., 111, 688 (1964).
17. F. Lukes and E. Schmidt, J. Phys. Chem. Solids, 26, 1353 (1965).
18. B. E. Deal and A. S. Grove, J. Appl. Phys., 36, 3770 (1965).
19. W. A. Pliskin, J. Electrochem. Soc. (abstract), 112, 259c (1965).
20. T. Nakayama and F. C. Collins, J. Electrochem. Soc., 113, 706 (1966).
21. A. Hikaru and S. Dzenti, Electr. Commn. Lab. Techn. J., 15, 4, 657 (1966).
22. C. C. Mai, Semicond. Prod. and Solid State Technol., 9, 1 (1966).
23. P. J. Burkhardt and L. V. Gregor, Transactions of the Metallurgical Soc. of AIME, 236, 299 (1966).
24. P. F. Schmidt and W. Michel, J. Electrochem. Soc., 104, 230 (1957).
25. E. F. Duffek, E. A. Benjamini, and C. Mylroie, Electrochem. Techn., 3, 75 (1965).
26. E. A. Efimov and I. G. Erusalimchik, "Elektrokhimiya Germaniya i Kremniya" (The Electrochemistry of Germanium and Silicon), Goskhimizdat, Moscow, 1963.
27. L. Young, "Anodic Oxide Films" (Translated into Russian), Izd. Energiya, Leningrad, 1967.
28. J. R. Ligenza, "Extended Abstracts of Electronics Division", 13, 1, 178 (ESM, Toronto, May 3–7, 1964).
29. J. L. Miles and P. H. Smith, J. Electrochem. Soc., 110, 1240 (1963).
30. "Osnovy Tekhnologii Kremnievykh Integral'nykh Skhem" (Principles of the Technology of Silicon Integral Circuits) Izd. Mir, Moscow, 1969, p. 62.
31. D. B. York, J. Electrochem. Soc., 110, 271 (1963).
32. F. Nesh, Rev. Sci. Instr., 34, 1475 (1963).
33. J. R. Priest, H. L. Caswell, and Y. Budo, J. Appl. Phys., 34, 347 (1963).
34. L. Holland, "Vacuum Deposition of Thin Films", New York., J. Wiley, 1, (1960).
35. B. Lewis, Microelectronics and Reliability, 3, 109 (1964).
36. Collected papers "Fizika Tonkikh Plenok" (Collected Papers on the Physics of Thin Films), Vol. 3, Izd. Mir, Moscow, 1968.
37. Collected papers "Fizika Tonkikh Plenok" (Collected Papers on the Physics of Thin Films), Vol. 4, Izd. Mir, Moscow, 1970.
38. C. R. Fuller and S. S. Baird, "Extended Abstracts Volume of Joint Symposium" (all divisions), Apr. 15–18, 1963, p. 17 (ESM, Pittsburg, Apr. 1963).
39. J. R. Ligenza, J. Appl. Phys., 36, 2703 (1965).
40. E. Jordan, J. Electrochem. Soc., 108, 478 (1961).
41. J. Klerer, J. Electrochem. Soc., 108, 1070 (1961).
42. J. Klerer, J. Electrochem. Soc., 112, 503 (1965).
43. V. N. Dyagilev, V. V. Matveev, and I. I. Petruchuk, Zhur. Fiz. Khim., 40, 2544 (1966) [Russ. J. Phys. Chem., No. 10 (1966)].
44. R. J. Myron and A. Z. Ashworth, J. Electrochem. Soc., 113, 48 (1966).
45. C. R. Bames and C. B. Geeser, J. Electrochem. Soc., 110, 361 (1953).
46. W. Steinmaier and J. Bloem, J. Electrochem. Soc., 11, 206 (1964).
47. S. K. Tung and R. E. Caffrey, Trans. Met. Soc. AIME, 233, 572 (1965).
48. Sylvania Semiconductor Division Development of Epitaxial Technology for Microelectronics and Large Area Device Application, Quarterly Report No. 8, Contract N, Nobstr-Woburn, Mass, 1 Feb–30 Apr. 1964 (U) AD 601 343.
49. C. H. Li, J. Electrochem. Soc., 109, 952 (1962).
50. M. Kuisi and W. Langheinrich, Ztschr. angew. Phys., 22, 201 (1967).
51. I. V. Grebenshchikov, G. Ya. Podvigalkina, and G. I. Khalezova, Pribory i Tekh. Eksper., No. 2, 206 (1969).
52. T. L. Chu, J. R. Gavaler, G. A. Gruber, and Y. C. Kao, J. Electrochem. Soc., 111, 1433 (1964).
53. T. L. Chu and G. A. Gruber, Transactions Met. Soc. AIME, 233, 568 (1965).
54. T. L. Chu and G. A. Gruber, Electrochem. Technol., 5, 43 (1967).
55. V. A. Arslambekov, K. M. Gorbunova, and V. I. Karateeva, Izv. Akad. Nauk SSSR, Neorg. Materialy, 6, 1625 (1970).
56. Y. Haneta and S. Nakanuma, J. Electrochem. Soc., 114, 6 (1967).
57. U. R. Evans, "The Corrosion and Oxidation of Metals" (Translated into Russian), Izd. Mashin. Lit., Moscow, 1962, p. 745.
58. J. Benard, in "The Oxidation of Metals" (Translated into Russian), Izd. Metallurgiya, 1967, p. 7.
59. O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys" (Translated into Russian), Izd. Metallurgiya, Moscow, 1965, p. 100.
60. P. Kofstad, "The High-Temperature Oxidation of Metals" (Translated into Russian), Izd. Mir, Moscow, 1969, p. 111.
61. C. Wagner, Ztschr. Phys. Chem., 21, 25, 42 (1933).
62. C. Wagner, "Diffusion and High Temperature Oxidation of Metals in Atom Movements", Ohio, 1951.
63. N. Cabrera and N. F. Mott, Rept. Progr. Phys., 12, 163 (1948).
64. F. P. Fehlner and N. F. Mott, Oxidation of metals, 2, 1, 59 (1970).
65. D. D. Eley and P. R. Wilkinson, Proc. Roy. Soc. (London), Ser. A, 254, 327 (1960).

66. H. J. Engell and K. Hauffe, Ztschr. Electrochem., 56, 366 (1952).
67. H. J. Engell and K. Hauffe, Ztschr. Electrochem., 58, 249 (1954).
68. K. Hauffe, Adv. in Catalysis, 7, 243 (1955).
69. U. R. Evans, Trans. Electrochem. Soc., 46, 247 (1942).
70. E. A. Gulbransen, K. F. Andrew, and F. A. Brassart, J. Electrochem. Soc., 113, 834 (1966).
71. V. A. Arslambekov, Zhur. Fiz. Khim., 32, 170 (1958).
72. V. A. Arslambekov, in "Mekhanizm Vzaimodeistviya Metallov s Gazami" (The Mechanism of the Reaction of Metals with Gases), 1964, p. 68.
73. V. A. Arslambekov and G. V. Smirnov, Izv. Akad. Nauk SSSR, Neorg. Materialy, 2, 220 (1966).
74. P. D. Dankov, Dokl. Akad. Nauk SSSR, 51, 449 (1946).
75. P. D. Dankov, D. V. Ignatov, and N. A. Shishakov, "Elektronograficheskie Issledovaniya Okisnykh i Gidrookisnykh Plenok na Metallakh" (Electron Diffraction Studies of Oxide and Hydroxide Films on Metals), Izd. Akad. Nauk SSSR, Moscow, 1953, p. 162.
76. V. I. Arkharov, in "Mekhanizm Vzaimodeistviya Metallov s Gazami" (Mechanism of the Reaction of Metals with Gases), Izd. Nauka, Moscow, 1964, p. 93.
77. F. Groenlund, J. Chem. Phys., 53, 660 (1956).
78. F. W. Young, Jr., Acta Met., 8, 117 (1960).
79. K. Ono, T. Yashiro, and S. Yagi, Rev. Electr. Commen Lab., 17, 70 (1969).
80. V. A. Arslambekov, I. D. Kazarinova, and K. M. Gorbunova, Ref. Zhur. Khim., 9, 9B937 (1969, deposited).
81. R. Stickler and J. W. Faust, Jr., Electrochem. Techn., 2, 289 (1964).
82. A. N. Knopp and R. Stickler, Electrochem. Techn., 5, 37 (1967).
83. P. Balk, C. F. Aliotta, and L. V. Gregor, Transactions of the Metallurgical Soc. of AIME, 233, 563 (1965).
84. A. G. Revesz, Phys. Status Sol., 24, 115 (1967).
85. R. J. Archer, J. Electrochem. Soc., 104, 619 (1957).
86. R. H. Doremus, J. Electrochem. Soc., 115, 181 (1968).
87. P. A. Pavlov and E. V. Shitova, Kristallokhimiya, 12, 119 (1967).
88. A. Shishakov, "Voprosy Struktury Silikatnykh Stekol" (Problems of the Structure of Silicate Glasses), Izd. Akad. Nauk SSSR, Moscow, 1954, p. 39.
89. D. Fortnum and J. O. Edwards, J. Inorg. Nuclear Chem., 2, 264 (1956).
90. A. S. Berezhnoi, "Kremnii i ego Binarnye Sistemy" (Silicon and Its Binary Systems), Izd. Akad. Nauk Ukrain. SSSR, Kiev, 1958, p. 99.
91. W. H. Zachariasen, J. Am. Chem. Soc., 54, 3841 (1932).
92. J. M. Stevels, Philips Techn. Rev., 22, 300 (1960–1961).
93. T. I. Litvinova, V. A. Kravchenko, V. P. Barzakovskii, and T. F. Raichenko, Izv. Akad. Nauk SSSR, Neorg. Materialy, 4, 1071 (1968).
94. N. A. Toropov and V. P. Barzakovskii, "Vysokotemperaturnaya Khimiya Silikatnykh i Drugikh Okisnykh Sistem" (The High-Temperature Chemistry of Silicate and Other Oxide Systems), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1963, p. 136.
95. P. V. Gel'd and O. A. Esin, "Protsessy Vysokotemperaturnogo Vosstanovleniya" (High-temperature Reduction Processes), Metallurgizdat, Sverdlovsk, 1957, p. 346.
96. P. V. Gel'd, "Vysokotemperaturnye Protsessy Vosstanovleniya" (High-temperature Reduction Processes), Metallurgizdat, Sverdlovsk, 1951, p. 10.
97. P. V. Gel'd and S. I. Popel', Zhur. Prikl. Khim., 5, 466 (1952).
98. M. V. Coleman and D. J. D. Thomas, Phys. Status Solidi, 22, 593 (1967).
99. G. P. Fadeeva and Z. P. Pasheva, Dokl. Akad. Nauk SSSR, 165, 1329 (1965).
100. G. W. Brady, J. Phys. Chem., 63, 1119 (1959).
101. M. S. Beletskii and M. B. Rapoport, Dokl. Akad. Nauk SSSR, 22, 465 (1950).
102. N. A. Vasyutinskii, V. I. Mil'ko, and Yu. I. Rysaeva, Izv. Akad. Nauk SSSR, Neorg. Materialy, 1, 835 (1956).
103. G. Hass and C. D. Salzberg, J. Opt. Soc. Amer., 44, 181 (1954).
104. L. E. Howarth and W. G. Spitzer, J. Amer. Ceramic Soc., 44, 28 (1961).
105. G. M. Kurdyumov, V. A. Molochko, and A. V. Chekunov, Izv. Akad. Nauk SSSR, Neorg. Materialy, 2, 1786 (1966).
106. B. A. Sakharov, K. G. Marin, V. K. Lyubimov, D. L. Fedorova, I. D. Kulagin, and L. M. Sorokin, Izv. Akad. Nauk SSSR, Neorg. Materialy, 4, 2035 (1968).
107. D. B. York, J. Electrochem. Soc., 110, 271 (1963).
108. Y. Nishimura, T. Inagaki, and H. Sasaki, Fujitsu Scient and Techn., 2, 87 (1966).
109. V. A. Arslambekov, in Ref. 72, p. 167.
110. I. D. Kazarinova, V. A. Arslambekov, and K. M. Gorbunova, Izv. Akad. Nauk SSSR, Neorg. Materialy, 5, 1126 (1969).
111. W. A. Pliskin and R. P. Gnall, J. Electrochem. Soc., 111, 872 (1964).
112. N. Karube, K. Yamamoto, and M. Kamiyama, Vide, 18, 162 (1963).
113. P. J. Jorgensen, J. Chem. Phys., 37, 874 (1962).
114. J. R. Ligenza, J. Phys. Chem., 62, 2011 (1961).
115. F. J. Norton, Nature, 171, 701 (1966).
116. S. W. Ing, Jr., R. E. Morrison, and J. E. Sandor, J. Electrochem. Soc., 109, 221 (1962).
117. A. J. Moulson and J. P. Roberts, Trans. Faraday Soc., 57, 1208 (1961).
118. R. P. Donovan and M. N. Hobgood, J. Electrochem. Soc., 112, 49c (1965).
119. B. E. Deal, A. S. Grove, E. H. Snow, and C. T. Sah, Transactions of the Metallurgical Soc. of AIME, 233, 3 (1965).
120. S. J. Laverty and W. D. Ryan, Internat. J. Electronics, 26, 519 (1969).

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