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The Influence of Surface Donor States on the Chemisorption Kinetics of Oxygen at the Surface of ZnO Single Crystals

I. Theoretical Model

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The kinetics of the conductivity changes, due to the adsorption of oxygen on partially compensated ZnO have been derived theoretically in the case where surface donors are present at the semiconductor surface.

The influence of the bulk donor density and the density of the surface donor states on the chemisorption kinetics have been investigated by means of a numerical treatment.

It is shown that in four cases the resistance is a linear function of time and that from this relationship the pressure dependence of the density of physisorbed oxygen can be deduced.

1. Introduction

The irradiation of ZnO with uv light results in a conductivity rise, which consists of a fast and a slow effect (*1*). The fast effect, corresponding to a rapid rise of the conductivity during and a rapid fall after illumination, turned out to be independent of the surrounding gas atmosphere and has been thoroughly studied by Heiland (*2*). However, the time dependence of the slow photoconductivity effect, as well as its rate of decay after irradiation, are largely influenced by the ambient oxygen pressure. The slow photoconductivity has therefore been attributed to the photodesorption of oxygen. Direct evidence for this assumption has been given by Medved (*3*). In order to explain the dark conductivity behavior of sintered ZnO layers as a function of ambient oxygen pressure, Morrison (*4*) proposed a model, in which the physisorbed oxygen transforms to chemisorbed oxygen, by capturing electrons from the conduction band. Subsequently Melnick (*5*) proposed that the holes, from the electron hole pairs produced under illumination with band-gap light, move to the surface, where they neutralize the chemisorbed oxygen. The model described above can be fitted into the frame work of the theories of chemisorption developed by Aigrain and Dugas (*6*), Hauffe and Engell (*7*) and Weisz (*8*). These theories are based on the electron exchange between the adsorbate and the solid, which give rise to a space charge layer near the surface. The adsorption of oxygen on ZnO results in a depletion layer, which can be approximated by a Schottky barrier (*5, 9*).

The kinetics of the conductivity changes, due to the readsorption of oxygen at photodesorbed ZnO sintered layers have been thoroughly studied by Melnick (*5*) and Medved (*9*). By assuming the rate limiting step of the process to be the capturing of an electron by the adsorbed species, they deduced an Elovich rate equation. Such a rate equation, however, is only valid if the conductivity changes due to the oxygen adsorption are small and if a depletion layer is formed at the surface. These results have been extended to single crystals by Van Hove and Luyckx (*10*)[1].

On the other hand it has been pointed out by Heiland (*17*) that the model proposed above

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[1] The oxygen adsorption and its influence on the electrical conductivity has also been studied to a great extent on CdS. Especially the kinetics of the chemisorption have received great attention in the work of Sébenne and Balkanski (*11*), Mark (*12–14*) and Weber (*15*). A summary of this work is reported in a recent article by Weber (*16*).

cannot explain the large conductivity changes of single crystals after illumination in vacuum. It was therefore suggested that the oxygen free surface would have an accumulation layer (*18*), which could be destroyed by the chemisorption of oxygen. The photoconductivity experiments of Collins and Thomas (*19*) indicated the existence of surface donor states, due to the excess Zn ions after illumination in vacuum. The experiments of Collins and Thomas were completed by the field effect measurements of Krusemeyer (*20*, *21*), which revealed the existence of fast surface states. These surface states were ascribed to the displacement of oxygen, removed from the lattice by photolysis.

The experiments of Collins and Thomas thus revealed that the illumination of ZnO in vacuum could result in an accumulation layer at the surface. This accumulation layer can be destroyed by the readsorption of oxygen. To the best of our knowledge no detailed study about the kinetics of the conductivity changes in this case are present. In an earlier work (*22*) we have reported some preliminary measurements, which must be accounted for by an accumulation layer theory.

A model in which we assumed the presence of surface donor states and the complete compensation of bulk donors has been put forward to explain our experiments on Li-doped ZnO single crystals. Some new experimental data, described in Part II of this series (*23*), could not be completely explained by this model, nor by one of the above described theories. It is felt that the influence of the bulk conductivity cannot be neglected. Therefore an extended model is presented which describes the conductivity changes in the case of an accumulation layer as well as in the case of a depletion layer being present at the surface. The validity of the model is discussed in (*23*) by comparing the theoretical derivations to the experimental results. It is shown that the agreement between the theory and the experiments is very satisfying.

2. Model and Outline of the Treatment

The model upon which the calculations are based is shown in Fig. 1. The basic assumptions are:

1. The crystal is considered as a plate with thickness W, limited by two parallel infinite planes perpendicular to the x-axis. The origin of the x-axis is chosen in the middle of the crystal.

2. In the bulk shallow donor levels are present, partly compensated by deep lying acceptor levels. All noncompensated bulk donors are always ionized. Therefore, if no other states were present, the conduction band electron density would equal the effective donor density n_0.

3. At both sides of the crystal surface donor states with a surface concentration N_s are present at an energy E_s below the conduction band. A possible origin of these surface states would be the photolysis of ZnO (*19*).

These states are considered to be in thermal equilibrium with the conduction band. Their occupation can therefore be described by Fermi statistics.

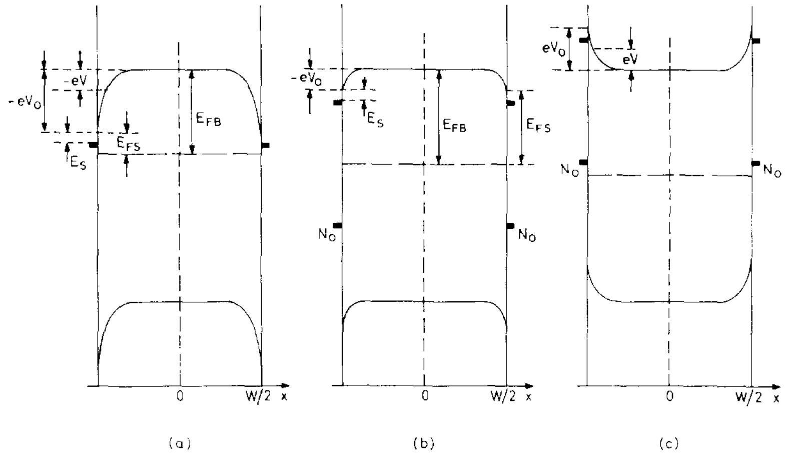

FIG. 1. Band scheme for a n-type semiconductor of finite thickness: (a) with surface donors; (b) with surface donors and surface acceptors giving an accumulation layer; (c) with surface donors and surface acceptors giving a depletion layer.

4. Trapping in the bulk will be neglected, as well as the mobility changes due to the presence of space charge layers in the crystal.

5. When the crystal is exposed to oxygen gas, the oxygen physisorbs at the crystal surface and gives rise to localized acceptor surface states with a surface concentration N_0. The physisorption step is in immediate equilibrium. Since one normally expects the number of sites where physisorption can take place to be much larger than the number of chemisorbed oxygen species, N_0 will be considered as constant during the chemisorption mechanism.

6. The rate of filling of the surface acceptors is determined by the capture probability of an electron in these states and not by the transport rate of electrons to the surface.

7. No interaction between the surface donors and the adsorbed oxygen is assumed. If one would ascribe the surface donors to the presence of excess Zn at the surface, such an interaction could be the direct oxydation of the excess Zn. It can be shown, however, that the experimentally observed kinetics described in Part II (*23*) can hardly be explained if such interactions dominate.

The list of notations used throughout the paper, is given in Sect. 7.

In order to derive the time dependence of the conductivity during gas adsorption, the chemisorption mechanism is pictured in the following way. No acceptor surface states are present before the crystal is exposed to oxygen. Part of the surface donors are ionized and give off their electrons to the conduction band. This gives rise to an accumulation layer at the surface (Fig. 1a). At $t = 0$ the crystal is exposed to oxygen; in this way the surface acceptors are created, part of which are filled in the course of time. As long as N_0^- is smaller than N_s^+, the space charge layer is of the accumulation layer type (Fig. 1b). However, at a certain time N_0^- exceeds N_s^+ and a depletion layer originates at the surface (Fig. 1c).

Under the above assumptions the conductivity is given by the following set of equations:

$$\sigma = \langle n \rangle \cdot e \cdot \mu, \tag{1}$$

$$\langle n \rangle = n_0 + \frac{2 \cdot N}{W}, \tag{2}$$

$$N = N_s^+ - N_0^-, \tag{3}$$

$$\frac{dN_0^-}{dt} = N_0 u \cdot S_n' \cdot n_s, \tag{4}$$

$$N_s^+ = N_s[1 + \exp(E_s - E_{fs})/kT]^{-1} = N_s\left[1 + \exp(E_s/kT) \cdot \frac{n_s}{N_c}\right]^{-1}. \tag{5}$$

In Eq. (4) an effective capture cross section S_n' has been used, in order to include the effect of a potential barrier which may exist near the surface.

Combining Eqs. (3), (4) and (5) we find

$$\frac{dN}{dt} + \frac{N_s \exp(E_s/kT)}{N_c[1 + n_s/N_c \exp(E_s/kT)]^2}\frac{dn_s}{dt} = -N_0 \; uS_n'n_s. \tag{6}$$

The problem thus can be reduced to the integration of Eq. (6). This integration can only be done if n_s is known as a function of N. This problem is treated in the following sections.

The time interval during which the chemisorption takes place will be split up in two regions, an accumulation layer controlled region and a depletion layer controlled one. Both cases are discussed separately.

3. Accumulation Layer Controlled Region

3.1. The Density of Conduction Band Electrons at the Surface

The band bending is given by the Poisson equation

$$\frac{d^2 V}{dx^2} = -\frac{4\pi}{\epsilon}\rho(x). \tag{7}$$

It will be supposed that the space charge originates from conduction band electrons and non compensated ionized donors.

Putting $V = 0$ at $x = W/2$ Eq. (7) may be written

$$\frac{d^2 V}{dx^2} = \frac{4\pi}{\epsilon} e \left[n_s \exp\left(\frac{eV}{kT}\right) - n_0\right], \tag{8}$$

in the case of nondegeneracy.

During oxygen adsorption we know, that, according to Gauss' theorem

$$\left(\frac{dV}{dx}\right)_{x=W/2} = \frac{4\pi}{\epsilon} e(N_s^+ - N_0^-). \tag{9}$$

Putting $dV/dx = 0$ at $x = 0$ and taking into account Eqs. (9) and (3), Eq. (8) can be easily integrated, which yields

$$\begin{cases} \left(\dfrac{dv}{dx}\right)^2 = \dfrac{8\pi e^2}{\epsilon kT}\{n_s[\exp(v) - \exp(v_0)] - \\ \quad - n_0(v - v_0)\}, & (10) \\ n_s = \left[\dfrac{2\pi e^2}{\epsilon kT} N^2 - n_0 v_0\right][1 - \exp(v_0)]^{-1}. & (11) \end{cases}$$

No further integration of Eqs. (10) and (11) is possible, unless by numerical methods. In principle it would be possible by means of Eqs. (8), (10) and (11) and by the use of a computer, to obtain the exact value of σ as a function of time. In such a procedure, however, it is very difficult to see the influence of the different physical parameters involved.

On the other hand an exact computer solution of n_s as a function of N can also be found by means of Eqs. (10) and (11). It is shown below that it is possible to find an analytical expression of n_s which is a good approximation for the exact computer solution of n_s. This expression will be used for the integration of Eq. (6).

The computer solution of n_s, for different values of the effective bulk donor density n_0, is given by the points in Fig. 2. These points have been calculated by means of Eq. (11) where v_0 has been obtained by an iterative method in such a way that v_0 is a solution of

$$W/2 = \left(\frac{\epsilon kT}{8\pi e^2}\right)^{1/2} \int_0^{v_0} \left\{\left[\frac{2\pi e^2}{\epsilon kT}\cdot N^2 - n_0 v_0\right] \times \left[\frac{\exp(v) - \exp(v_0)}{1 - \exp(v_0)}\right] - n_0(v - v_0)\right\}^{-1/2} dv.$$

A value of 0.1 cm has been chosen for W. Further numerical values are $T = 300°\mathrm{K}$ and $\epsilon = 8.5$ for ZnO (*9*).

In order to find the approximated expression for n_s, we will make use of the fact that Eqs. (10) and (11) can be integrated in two simple cases.

a. Very high effective bulk donor density. In this case Eqs. (10) and (11) can be replaced by

$$n_0 = n_s \exp(v_0), \qquad (12)$$

and

$$\frac{2\pi e^2}{\epsilon kT} N^2 = n_0[\exp(-v_0) + v_0 - 1]. \qquad (13)$$

Expanding $\exp(-v_0)$ for small band bending in Eq. (13) it follows that

$$n_s = \frac{2\pi e^2}{\epsilon kT} N^2 + n_0 + 2N/(\sqrt{2}L_D) \qquad (14)$$

This expression has been plotted in Fig. 2 (solid lines). It follows that although the expression (14) has been derived for small values of v_0, the fitting to the exact n_s values is very satisfying over the whole region of interest for $L_D < W$.

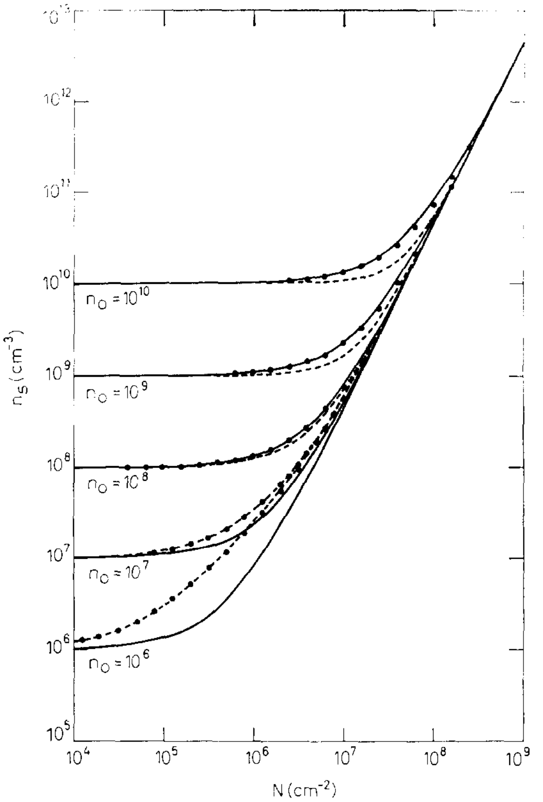

FIG. 2. Concentration of conduction band electrons as a function of the positive surface charge and free electron density at flat energy band, for a semiconductor of 0.1 cm.

b. Very small effective donor density. If $n_0 = 0$ Eqs. (10) and (11) reduce to

$$n_s = \frac{2\pi e^2}{\epsilon kT} N^2 [1 - \exp(v_0)]^{-1},$$

which, for considerable downward bending of the energy bands can be simplified to

$$n_s = \frac{2\pi e^2}{\epsilon kT} N^2.$$

For small band bending we may write

$$n_s = 2N/W.$$

Knowing however that in reality n_0 does not vanish, the function,

$$n_s = \frac{2\pi e^2}{\epsilon kT} N^2 + n_0 + 2N/W, \qquad (15)$$

has been plotted in Fig. 2 (broken lines). From this it can be seen that expression (15) is a good approximation for the exact solution of n_s if $W < L_D$.

According to Eqs. (14) and (15) the adsorption kinetics must be treated in two distinct cases namely $W > L_D$ and $W < L_D$.

3.2. Adsorption Kinetics for $W < L_D$

Defining the new variables n_1 and N_1 by

$$N_1 = N + \frac{\epsilon kT}{2\pi e^2}\frac{1}{W}, \tag{16}$$

$$n_1 = n_0 - \frac{\epsilon kT}{2\pi e^2}\frac{1}{W^2}, \tag{17}$$

the differential Eq. (6) reduces to

$$\frac{dN_1}{dt} + N_s\alpha\frac{dN_1^2/dt}{(\alpha N_1^2 + \delta_1)^2} = -(\beta N_1^2 + \gamma_1). \tag{18}$$

It must be emphasized that according to Eq. (17) and taking into account that $L_D > W$, n_1 is always negative, which implies a negative value of γ_1. Integration of Eq. (18) can be done by expansion in partial fractions, which yields

$$t = \varphi_1(N_{1B}) - \varphi_1(N_1), \tag{19}$$

where N_{1B} is the value of N_1 for $t = 0$ and φ_1 is defined by

$$\varphi_1(N_1) = \frac{\theta_1}{2}\ln\frac{N_1 - (-\gamma_1/\beta)^{1/2}}{N_1 + (-\gamma_1/\beta)^{1/2}} + \frac{N_s\alpha}{\beta}\left[\ln\frac{(\beta/\gamma_1)N_1^2 + 1}{(\beta/\gamma_1)N_1^2 + 1 + \eta_1} + \frac{\eta_1}{(\beta/\gamma_1)N_1^2 + 1 + \eta_1}\right] \tag{20}$$

3.3. Adsorption kinetics for $W > L_D$

In order to integrate Eq. (6) a set of new variables is defined by

$$N_2 = N + \frac{\epsilon kT}{2\pi e^2}\frac{n_0}{2}, \tag{21}$$

$$n_2 = n_0/2. \tag{22}$$

Equation (6) now reduces to

$$dN_2/dt + N_s\frac{\alpha dN_2^2/dt}{(\alpha N_2^2 + \delta_2)^2} = -(\beta N_2^2 + \gamma_2), \tag{23}$$

which after integration gives

$$t = \varphi_2(N_{2B}) - \varphi_2(N_2), \tag{24}$$

where $N_2 = N_{2B}$ at $t = 0$ and the function φ_2 is defined by

$$\varphi_2(N_2) = \theta_2 \arctan\left(\frac{\beta}{\gamma_2}\right)^{1/2} N_2 + \frac{N_s\alpha}{\beta}\left[\ln\frac{(\beta/\gamma_2)N_2^2 + 1}{(\beta/\gamma_2)N_2^2 + 1 + \eta_2} + \frac{\eta_2}{(\beta/\gamma_2)N_2^2 + 1 + \eta_2}\right]. \tag{25}$$

4. Depletion Layer Controlled Region

If the number of adsorbed oxygen ions equals the number of ionized surface donors the surface will become electrically neutral. This results in the flat band situation. If further chemisorption then takes place the surface will become negatively charged and the energy bands are bent upwards. The band bending can then be approximated by a Schottky barrier (*3*) the height of which is given by:

$$V_s = \frac{2\pi e}{\epsilon}n_0 L^2 = \frac{kT}{e}\left(\frac{L}{L_D}\right)^2, \tag{26}$$

the width of the Schottky barrier L being given by

$$L = \frac{N_0^- - N_s^+}{n_0} = \frac{N'}{n_0}. \tag{27}$$

Once the depletion layer is reached, it will be assumed that the surface donors are situated well above the Fermi-level so that they are all ionized. This implied $N_s^+ =$ constant. Equation (26) is only valid for $L_D < W$. If $L_D > W$ it follows that $L_D > L$ and the space charge layer can no longer be represented by a Schottky barrier. However in the latter case the band bending is unimportant and

$$n_s = n_0 - 2N'/W. \tag{28}$$

Again two distinct cases will be treated.

4.1. Adsorption Kinetics for $L_D > W$.

Using Eq. (28) the differential equation for chemisorption can be written as

$$\frac{d(n_0 W/2 - N')}{dt} = -(2uS_n' N_0/W)\cdot\left[\frac{n_0 W}{2} - N'\right],$$

which after integration gives

$$[n_0 \cdot W/2 - N'] = (n_0 \cdot W/2 - N_b')\exp\left(-\frac{t}{\tau}\right) \tag{29}$$

and

$$1/\tau = \frac{2}{W}uS_n' N_0 \tag{30}$$

4.2. *Adsorption Kinetics for $L_D < W$.*

In this case we can write for n_s

$$n_s = n_0 \exp\left(-\frac{eV_s}{kT}\right). \tag{31}$$

The differential equation for chemisorption now becomes

$$\frac{dN'}{dt} = \gamma_0 \exp\left(-\frac{eV_s}{k \cdot T}\right). \tag{32}$$

If V_s is replaced by a series expansion about some mean value the Elovich equation can be deduced. This rate equation, however, is only a good approximation if the changes of N' are small compared to N'. A rigorous treatment of Eq. (32) can be done as follows. By putting

$$y = \left(\frac{\beta}{\gamma_0}\right)^{1/2} N',$$

Eq. (32) can be written

$$\frac{dy}{dt} = (\beta\gamma_0)^{1/2} \exp(-y^2). \tag{33}$$

Integration of which gives

$$t = \frac{1}{(\beta\gamma_0)^{1/2}} \left\{ D\left[\left(\frac{\beta}{\gamma_0}\right)^{1/2} N'\right] - D\left[\left(\frac{\beta}{\gamma_0}\right)^{1/2} N_b'\right] \right\}, \tag{34}$$

where $D[(\beta/\gamma_0)^{1/2} N']$ is the Dawson integral of $(\beta/\gamma_0)^{1/2} N'$ and N_b' the value of N' for $t = 0$.

5. Discussion

To compare the model with the experimental data, the kinetics derived theoretically in the previous sections have been calculated numerically and are represented in Figs. 3 and 4. Instead of σ, $R_n - R_{nb}$ has been plotted versus t, where R_n is defined by

$$R_n = \frac{1}{e\mu W}\left[\frac{1}{n_0 + 2N/W}\right] \tag{35}$$

and R_{nb} is the value of R_n for $t = 0$.

The choice if $R_n - R_{nb}$ has already been explained in a previous paper (*22*) and will become clear during the discussion. Two separate cases $L_D > W$ and $L_D < W$ have been treated.

5.1. *The Debye Length is Larger than the Thickness of the Crystal*

With the aid of Eqs. (19), (20) and (35) $R_n - R_{nb}$ has been calculated as a function of time and is represented in Fig. 3 (solid lines) for different values of N_s. The physical constants used for ZnO are

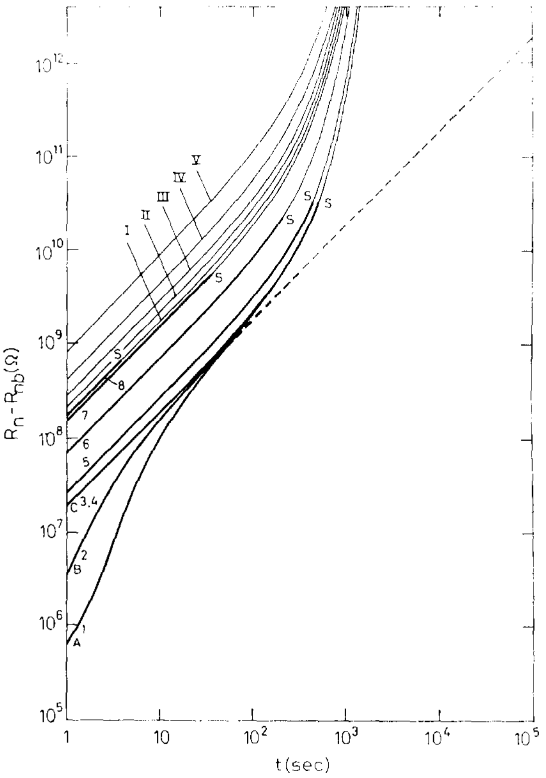

FIG. 3. $R_n - R_{nb}$ versus t, for different surface charges at $t = 0$ ($L_D > W$).

$$\mu = 180 \text{ cm}^2/\text{V sec and } N_c = 6 \times 10^{18} \text{ cm}^{-3}.$$

Furthermore the following parameters were chosen:

$$E_s = 3.844\, kT, \qquad W = 0.1 \text{ cm},$$
$$N_0 S_n' = 2.7 \times 10^{-11}, \qquad n_0 = 10^7 \text{ cm}^{-3}.$$

The calculations for curves 1 to 8 have been done in the assumption that $N_0^- = 0$ before oxygen admission. In this case we can write

$$R_{nb} = \frac{1}{e\mu W}\left[\frac{1}{n_0 + 2N_s^+/W}\right],$$

where N_s^+ is given by

$$N_s^+ = N_s\left[1 + \frac{n_s}{N_c}\exp\left(\frac{E_s}{kT}\right)\right]^{-1}$$

and

$$n_s = \frac{2\pi e^2}{\epsilon kT}(N_s^+)^2 + n_0 + \frac{2N_s^+}{W}.$$

Parameters of curves 1 to 8 are given in Table I.

TABLE I

KEY TO CURVES 1 TO 8 OF FIG. 3

Curve	N_s (cm^{-2})	N_s^+ (cm^{-2})	N_{1B} (cm^{-2})	R_{nb} (Ω)	t_0 (sec)
1	1.207×10^{13}	7×10^{11}	7×10^{11}	2.4801×10^{4}	491.8
2	4.643×10^{12}	5×10^{11}	5×10^{11}	3.4722×10^{4}	487
3	1.331×10^{11}	10^{11}	1×10^{11}	1.7361×10^{5}	484
4	10^{9}	10^{9}	1.002×10^{9}	1.7352×10^{7}	483
5	10^{7}	10^{7}	1.234×10^{7}	1.6534×10^{9}	413
6	10^{6}	10^{6}	3.348×10^{6}	1.157×10^{10}	195
7	10^{5}	10^{5}	2.448×10^{5}	2.893×10^{10}	33.7
8	10^{4}	10^{4}	2.358×10^{5}	3.404×10^{10}	3.66

The time t_0 corresponds to the moment at which R_n equals the normalized resistance R_{n0} at flat band (here 3.472×10^{10} Ω). This time is represented by the points S in Fig. 3. From these points on the kinetics have been obtained by means of Eq. (29).

The curves I to V have been calculated for a depletion layer already present at $t = 0$. Here the normalized resistance is given by

$$R_n = \frac{1}{e\mu W} \cdot \frac{1}{n_0 - 2N'/W}.$$

The parameters of these curves are shown in Table II.

The broken lines in Fig. 3 represent the kinetics which have been derived in a previous paper (*22*) and which are given by:

$$t = \frac{2e\mu}{\beta}(R_n - R_{nb}) + \frac{\alpha N_s}{\beta}\left\{2\ln\frac{R_n}{R_{nb}} - \ln\left[\frac{1+\alpha'/R_{nb}^2}{1+\alpha'/R_n{}^2}\right] + \frac{1}{1+\alpha'/R_{nb}^2} - \frac{1}{1+\alpha'/R_n{}^2}\right\}. \tag{36}$$

Curves A, B and C have been plotted for the same parameters as curves 1, 2 and 3, respectively.

TABLE II

KEY TO CURVES I TO V OF FIG. 3

Curve	N_B'(cm^{-2})	R_{nb}(Ω)
I	10^{4}	3.543×10^{10}
II	10^{5}	4.430×10^{10}
III	2×10^{5}	5.787×10^{10}
IV	3×10^{5}	8.681×10^{10}
V	4×10^{5}	1.736×10^{11}

As shown in Fig. 3 the kinetics described by Eqs. (19), (20) and (36) are in good agreement as long as the bulk conductivity at flat energy bands can be neglected with regard to the additional conductivity due to surface donor states. Furthermore it can be seen from curves 3 and 8 that, in the accumulation layer controlled region, $R_n - R_{nb}$ versus t can be represented by a linear relationship, if the density of the surface donors is such that most of them are ionized. This can be easily derived from Eqs. (19) and (20). Indeed if all surface donors are ionized Eqs. (19) and (20) reduce to

$$t = \frac{1}{2(-\gamma_1\beta)^{1/2}}\left\{\ln\frac{N_{1b} - (-\gamma_1/\beta)^{1/2}}{N_{1b} + (-\gamma_1/\beta)^{1/2}} - \ln\frac{N_1 - (-\gamma_1/\beta)^{1/2}}{N_1 + (-\gamma_1/\beta)^{1/2}}\right\} \tag{37}$$

For values of $N > (\epsilon kT/2\pi e^2)\cdot(1/W)$ this reduces to

$$t = \frac{1}{\beta}\left[\frac{1}{N_b} - \frac{1}{N}\right] = \frac{2e\mu}{\beta}[R_n - R_{nb}] \tag{38}$$

For values of $N_b < (\epsilon kT/2\pi e^2)(1/W) - (-\gamma_1/\beta)^{1/2}$ or

$$N_b < n_0 W/2, \tag{39}$$

Eq. (37) reduces to:

$$N = N_b - \beta n_0 \frac{\epsilon kT}{2\pi e^2}\cdot t = N_b - \gamma_0 t.$$

which with the aid of Eq. (35) and taking into account the inequality (39), can be written as

$$R_n - R_{nb} = 2e\mu R_{nb}^2 \gamma_0 t = 2e\mu R_{nb}^2(n_0 u S_n' N_0) t. \tag{40}$$

In the depletion layer controlled region the chemisorption kinetics are described by Eq. (29), which for $t < \tau$ becomes

$$R_n - R_{nb} = (2\cdot R_{nb}/W)\cdot u S_n' N_0 \cdot t. \tag{41}$$

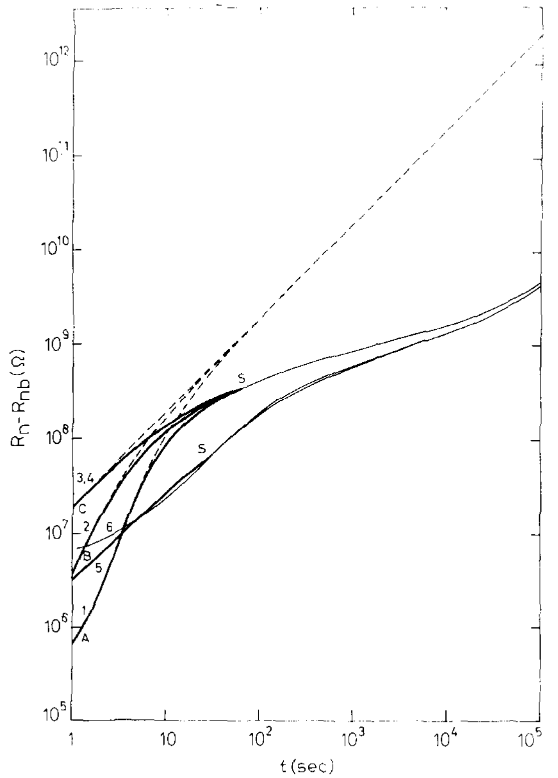

FIG. 4. $R_n - R_{nb}$ versus t, for different surface charges at $t = 0$ ($L_D < W$).

5.2. Debye Length Smaller than the Thickness of the Crystal

Using Eqs. (24), (25) and (35) the fully drawn lines of Fig. 4 have been plotted for the parameters of Table III. The effective donor density is given by $n_0 = 10^9$ cm^{-3}, corresponding to a value of $R_{n0} = 3.4722 \times 10^8$ Ω. Except for n_0 all other parameters have the same value as in Sect. 5.1.

Curve 6 represents the chemisorption kinetics in the depletion layer controlled region with $N_b' = 10^4$ and $R_{nb} = 3.4729 \times 10^8$ Ω.

The broken lines in Fig. 4 again represent the kinetics given by Eq. (36). As can be seen from the figure the agreement between the model described by Eq. (36) and by Eq. (24) and (25) is only satisfying in the first seconds. The reason for this is that the influence of the bulk donor density becomes more pronounced in Eq. (35). Two regions can again be found, where, in a small time interval, $R_n - R_{nb}$ versus t can be described by a linear relationship. If all surface donors are ionized Eq. (25) reduces to

$$t = \theta_2 \left[\arctan\left(\frac{\beta}{\gamma_2}\right)^{1/2} N_{2b} - \arctan\left(\frac{\beta}{\gamma_2}\right)^{1/2} N_2\right] \tag{42}$$

which for values of $N_{2b} \gg \left[\frac{\epsilon kT}{2\pi e^2}\frac{n_0}{2}\right]^{1/2}$ yields

$$t = \frac{1}{\beta}\left[\frac{1}{N_2} - \frac{1}{N_{2b}}\right] = \frac{2e\mu}{\beta}[R_n - R_{nb}]. \tag{43}$$

If $N_{2b} \ll [(\epsilon kT/2\pi e^2)\cdot(n_0/2)]^{1/2}$, Eq. (42) becomes

$$t = \theta_2\left(\frac{\beta}{\gamma_2}\right)^{1/2}(N_{2b} - N_2),$$

which can be written as

$$R_n - R_{nb} = e\mu R_{nb}^2 n_0 u S_n' N_0 \cdot t \tag{44}$$

6. Conclusions

From the discussion it becomes clear that the most interesting regions in the chemisorption kinetics are those, giving a linear relationship between $R_n - R_{nb}$ and t. If the influence of the bulk donor density is small, Eq. (38) can be used

TABLE III

KEY TO CURVES 1 TO 5 OF FIG. 4

Curve	N_s (cm^{-2})	N_s^+ (cm^{-2})	N_{1b} (cm^{-2})	R_{nb} (Ω)	t_0 (sec)
1	1.206×10^{13}	7×10^{11}	7.000×10^{11}	2.480×10^{4}	69.19
2	4.64×10^{12}	5×10^{11}	5.000×10^{11}	3.472×10^{4}	65.40
3	1.33×10^{11}	10^{11}	1.000×10^{11}	1.735×10^{5}	63.1
4	1.003×10^{10}	10^{10}	1.004×10^{10}	1.657×10^{6}	62
5	10^{7}	10^{7}	2.084×10^{7}	2.893×10^{8}	24.54

to derive the pressure dependence of the surface concentration of the physisorbed oxygen. In order, however, to interpret such results a knowledge of the bulk donor density is necessary, since not only Eq. (38) gives rise to a linear $R_n - R_{nb}$ versus t relationship, but also the Eqs. (40), (41) and (44).

The influence of increasing surface concentration of the surface donors can also be seen in the transition from the linear $R_n - R_{nb}$ versus t relation, to the curves of the type of 1 and 2 in Fig. 3.

7. List of Symbols and Definitions

n_0	density of free electrons at flat energy bands; density of noncompensated bulk donors.
n_s	density of free electrons at the surface.
$\langle n \rangle$	mean value of the density of free electrons.
N_c	effective density of states in the conduction band.
N_s	surface concentration of surface donor states.
N_s^+	surface concentration of ionized surface donors.
N_0	surface concentration of surface acceptor states.
N_0^-	surface concentration of chemisorbed oxygen.
μ	mobility of the electrons in the conduction band.
σ	specific conductivity.
u	thermal velocity of electrons in the conduction band.
S_n'	effective capture cross section of the surface acceptors for electrons from the conduction band.
E_s	energy difference between conduction band edge and surface donors.
E_{fb}	energy difference between conduction band edge in the bulk and fermi level.
E_{fs}	energy difference between conduction band edge at the surface and fermi level.
V	electrical potential in the crystal.
$v = eV/kT$	
v_0	value of v at $x = 0$
L_D	Debye length, defined by

$$L_D = \left[\frac{\epsilon kT}{2\pi e^2}\cdot\frac{1}{n_0}\right]^{1/2}$$

$$\alpha = \frac{2\pi e^2}{\epsilon kT}\cdot\frac{1}{N_c}\exp(E_s/kT)$$

$$\beta = \frac{2\pi e^2}{\epsilon kT}\cdot u S_n' N_0$$

$$\gamma_i = n_i \cdot u \cdot S_n' N_0 \qquad (i = 0, 1, 2)$$

$$\delta_i = 1 + n_i/N_c \exp(E_s/kT) \qquad (i = 1, 2)$$

$$\theta_1 = 1/(-\gamma_1 \beta)^{1/2}$$

$$\theta_2 = 1/(\gamma_2 \beta)^{1/2}$$

$$\eta_i = N_c/n_i \cdot \exp(-E_s/kT) \qquad (i = 1, 2)$$

$$\alpha' = \alpha/(2e\mu)^2$$

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