Kinetic Studies of Oxygen Chemisorption on the Rutile Single-crystal Surface by Means of Electrical Conductivity

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(Received October 30, 1974)

The reaction of oxygen with the surface of a rutile single crystal was studied in the temperature range from 212 to 362 °C and in the pressure range from 10^{-1} to 10^2 Torr. The process of the surface oxidation was examined by monitoring the electrical conductance change due to oxygen chemisorption. Two types of chemisorption kinetics were found for the rutile which had been reduced to different extents *in vacuo* before the introduction of oxygen. For the low-reduced rutile, the kinetics obeyed the parabolic rate law; this was interpreted by the diffusion-controlled reaction theory. On the other hand, it was found for the high-reduced rutile that the kinetics obeyed the Elovich equation; this could be explained by the boundary layer theory. The apparent activation energy for the former was 14.2 kcal/mol. For the latter, it was 4 kcal/mol and increased with an increase in the chemisorbed surface-charge density. In addition, the rate of oxygen chemisorption in the latter case was proportional to the pressure at a constant density of the chemisorbed surface charge.

It is well known that the electrical properties of semiconductor surfaces are influenced by the change in the ambient atmosphere. The adsorbed active molecules can drastically change the density of charge carriers in the solid and the work function. Since oxygen generally acts as an acceptor-type adsorbate, it is expected that the electrical conductivity of an n-type or p-type semiconductor will decrease or increase, respectively, when oxygen gas is introduced. These phenomena have been extensively studied for many kinds of semiconductor materials by means of the conductivity method.1—9) It has been reported that the kinetics of oxygen chemisorption on the surfaces of Ge,10) CdSe,2,7) CdS,3) SnO_2,5) and ZnO11) follows the Elovich equation and can be explained according to the "boundary layer" theory.3,12) However, no detailed examinations of the pressure dependence of the chemisorption and the activation energy have been made, and little is known about the oxidation kinetics on the surface of titanium dioxide.13)

When titanium dioxide is evacuated at a high temperature or treated in a reducing gas, such as hydrogen or carbon monoxide, oxygen atoms tend to be removed from the surface and also from the bulk through the surface region.14) A reduced rutile exhibits the characteristics of an n-type semiconductor, for the crystal lattice develops defects which act as donors with a low ionization energy.15) For a reduced rutile, the electrical,16,17) photoelectric,18) and dielectric properties19) have been investigated in order to clarify the electronic structure. On the other hand, the photovoltaic effect has been found for a once-reduced and then reoxidized rutile20) which has a barrier layer of the Schottky-Mott type in the surface region.21) It is of interest to examine the surface oxidation, which has much influence on the electrical properties of a reduced rutile. Further, the oxidation process may be expected to be affected by the degree of reduction.

In this paper, the kinetics of oxygen chemisorption was investigated for a single crystal surface of rutile by measuring the electrical conductivity in the temperature range from 212 to 362 °C and in the oxygen pressure range from 10^{-1} to 10^2 Torr. As a result, it was revealed that the reaction of oxygen with the rutile became remarkable above 200 °C, depending on the temperature and the oxygen pressure, and that the rate of chemisorption followed two types of rate equations because of a difference in the degree of reduction of the rutile.

Experimental

Material. A rutile single crystal grown by the Nakazumi Crystal Co. by means of the Verneuil method was used in this study. A spectroscopic analysis indicated that its purity was above 99.99% and that the main impurity was sodium, the amount of which was less than 0.005%.22) The crystal was cut into a rectangular wafer $10 \times 10 \times 0.18$ mm³ so as to make large the ratio of the surface to the bulk; the largest face, the (110) plane, was polished mechanically. The sample was then treated with a chromic acid mixture, washed thoroughly with distilled water, and dried at 100 °C. Evaporated gold was used for the electrodes. The distance between the electrodes was 6 mm. The electric contact between the rutile and gold was probably ohmic.17)

The sample connected with electrodes was mounted on a sample holder, using an insulating spacer of mica so as to facilitate the contact between both (110) planes and the introduced oxygen gas.

Treatment. A rutile single crystal mounted on the sample holder was placed in the apparatus, as is shown in Fig. 1. The measurements of the chemisorption were carried out for the rutile which had been treated by the following two different procedures:

(1) The sample was heated in an atmosphere of oxygen at 450 °C for 10 hr and then evacuated at the same temperature for 5 hr.

(2) The sample was evacuated at 450 °C for 20 hr.

After the measurement of the oxygen chemisorption, the oxidized surface was returned to the initial state by evacuating at 450 °C for 5—8 hr, the residual pressure being about 10^{-6} Torr. The two electrodes were grounded except when the conductivity was checked during the thermal treatment. It was very difficult, however, to get a constant conductivity after the treatment. As a result, the rutile sample had a conductivity varying between 10^{-5} and 10^{-4} mho·cm^{-1} at temperatures between 212 and 362 °C. In order to prevent

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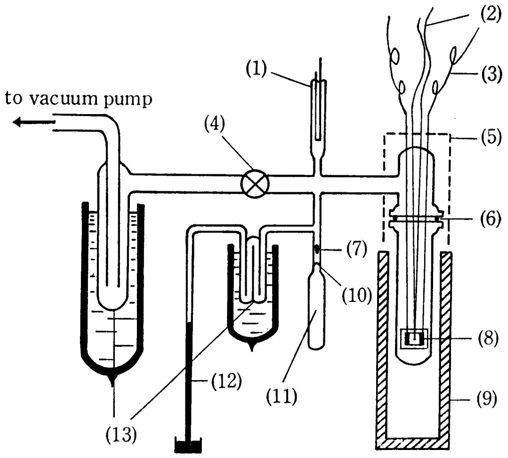

Fig. 1. Experimental apparatus for studying the oxygen chemisorption. (1) Pirani gauge, (2) thermocouple, (3) lead, (4) gleaseless stop-cock, (5) sealed box, (6) O-ring, (7) glass-covered iron core, (8) sample, (9) heater, (10) breakable seal, (11) oxygen gas, (12) Hg manometer, and (13) liquid-nitrogen trap.

any effect of organic contaminants and mercury vapor, liquid-nitrogen traps, an O-ring joint, and a greaseless stopcock were used, as is illustrated in Fig. 1.

Measurements. The kinetics of the oxygen chemisorption was examined at temperatures between 212 and 362 °C for the rutile treated as has been described above. The sample, an equilibrium state *in vacuo*, was brought into contact with dry oxygen by breaking the glass seal which separated the sample from the oxygen reservoir. Subsequent chemisorption was followed by monitoring the change in the electrical conductivity of the rutile. Electrical conductance measurements were made in the dark by detecting the current between two electrodes, to which a voltage of about 1.2 V was applied by means of a dry battery. The current was measured by means of a Takeda Riken-TR-8651 electrometer connected with a recorder (with a response less than 0.5 s). The pressure of oxygen was measured by means of a mercury manometer at high pressures and a Pirani gauge at low pressures.

Results and Discussion

Oxygen Chemisorption on Low Reduced Rutile. The oxygen-chemisorption measurements were carried out for a sample which had been treated by Procedure (1) and which had a free electron density of about 10^{15}/cm^3 at the measurement temperature. The conductivity decreased when oxygen gas was introduced at temperatures ranging from 212 to 362 °C. Figure 2 shows some representative results of conductance changes with the time. There was a difference in the initial conductance prior to the introduction of oxygen gas; this was a result of a difference in the temperature or the treatment. However, these results revealed that the conductance change increased with a rise in the temperature of the sample. It was found that the current change was proportional to n powers of time. This current change may be ascribed to a change in the number of free electrons, because the electrons are captured by the oxygen adsorbed on the surface. Therefore, the density of trapped electrons on the surface, that is, the chemisorbed surface-charge density, $N_c(t)$, can be estimated from the following equation:[4]

$$N_c(t) = (V/S)n_0(\Delta I/I) \qquad (1)$$

where V is the volume of the sample; S, its area in contact with oxygen; n_0, the initial free electron density; I, the initial current at $t=0$, and ΔI, the current change at $t=t$. This equation is obtained by assuming that the electron mobility remains unchanged throughout the run. Since the mobility of the electron in rutile was found to be proportional to $T^{-5/2}$ at temperatures between −196 and 27 °C,[17] the mobility in this study was estimated by extrapolating the relationship in the low-temperature range to 362 °C. By the use of the mobility value thus obtained, the free electron density, n_0, was determined to be about 10^{15}/cm^3, as has been described above.

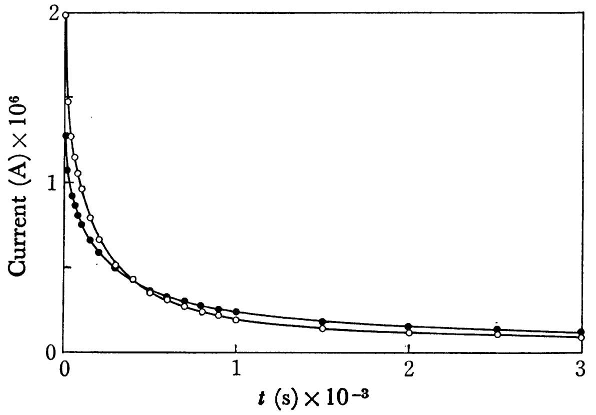

Fig. 2. Conductance change of low reduced rutile with time after the introduction of oxygen at 40 Torr and 212 ° (●) and 262 °C (○).

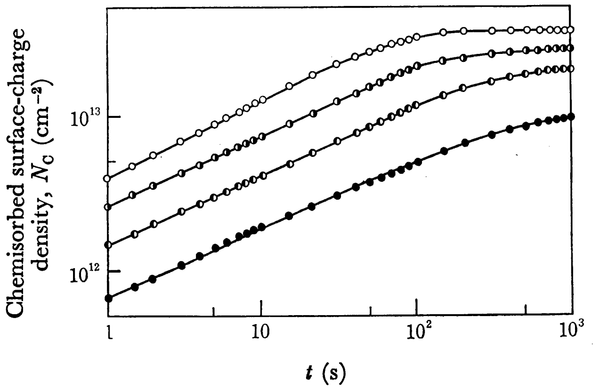

Fig. 3. Surface charge density of low reduced rutile as a function of time on log-log scale after the introduction of oxygen at 40 Torr and 362° (○), 316° (◑), 262° (◐), and 212 °C (●).

The chemisorbed surface-charge density was plotted as a function of the time on the log-log scale, as is shown in Fig. 3. These plots gave approximately straight lines, indicating that the following relationship holds:

$$N_c(t) = Bt^n \qquad (2)$$

where B is a constant at a given temperature; n, a constant independent of the temperature and nearly equal to 1/2, and t, the time after the admission of oxygen. This parabolic rate law has been explained in terms of the diffusion-controlled reaction;[23] the reaction occurs at the gas-solid boundary, forming oxygen ions, and the rate is controlled by the rate of migration of the oxygen ion on the surface. Such phenomena are conceivable, since the surface region of the sample is reduced rather than the bulk. It was estimated from the results of conductivity measurements that more than 95% of the free electrons were trapped by chemisorbed oxygen after 10^3 s. From the ESR studies of oxygen adsorbed on the TiO_2 surface, it has been considered that the chemisorbed oxygen exists in the form of the O^- ion in the temperature range of 140—450 °C.[24] It may be considered, therefore, that the oxygen ion diffuses into the surface region in the form of the O^- ion, resulting in the formation of the O^{2-} ion in the final state.

Activation Energy. It is evident from Fig. 3 that the chemisorption of oxygen requires an activation energy. Murty *et al.* have discussed the estimation of the activation energy, E_a, for a type of kinetic equation such as Eq. (2).[25] Often the B constant in Eq. (2) has an exponential temperature dependence as follows:

$$B = B_0 \exp(-Q/RT) \qquad (3)$$

where B_0 is the constant; Q, the term in connection with the activation energy; R, the gas constant, and T, the absolute temperature. From Eq. (2), the rate equation is given by:

$$\mathrm{d}N_c/\mathrm{d}t = nBt^{n-1} = nN_c/t \qquad (4)$$

From Eqs. (2) and (4),

$$nBt^{n-1} = nB^{1/n}N_c^{1-1/n} \qquad (5)$$

Thus,

$$\ln(\mathrm{d}N_c/\mathrm{d}t) = \ln n + 1/n \ln B_0 - Q/nRT + (1-1/n)\ln N_c \qquad (6)$$

On the other hand, the Arrhenius equation can be rewritten as:

$$\ln(\text{rate}) = \ln A - E_a/RT \qquad (7)$$

By a comparison of Eq. (6) with Eq. (7), we obtain:

$$E_a = Q/n \qquad (8)$$

Therefore, the activation energy can be obtained from the plots of ln(rate) *vs.* $1/T$ for a given N_c. From Eqs. (4) and (5), we obtain:

$$N_c/t = B^{1/n}N_c^{1-1/n} \qquad (9)$$

The plots of $\ln(N_c/t)$ *vs.* $\ln N_c$ yield a family of parallel lines with the intercepts of $1/n \ln B$ for various temperatures, while the slope of the $1/n \ln B$ *vs.* $1/T$ plots gives the apparent activation energy. Thus, the apparent activation energy was determined to be 14.2 kcal/mol.

Oxygen Chemisorption on High Reduced Rutile. The sample which was treated by Procedure (2) had a free electron density of about $10^{16}/\mathrm{cm}^3$ at the measurement temperatures, as estimated in the manner described previously. The changes in the currents after the introduction of oxygen gas are shown in Fig. 4. The kinetics of oxygen chemisorption exhibited the temperature and pressure dependences. However, there was a difference in the kinetics between the low reduced rutile and the high reduced one; the kinetics for the latter did not obey the parabolic rate law. The plots of ΔI *vs.* $\log t$ gave a family of straight lines until about 200 s, except for the results of chemisorption at 362 °C; these lines for various pressures at a given temperature were nearly parallel to one another. Consequently, these semi-logarithmic plots are in accordance with the Elovich equation:

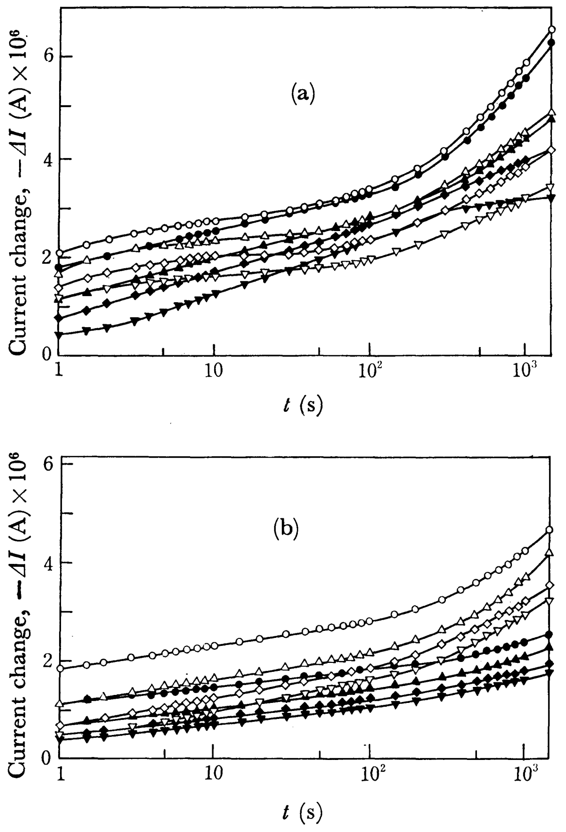

Fig. 4. Current change of high reduced rutile with time after the introduction of oxygen;
(a), at 362 °C and 140 Torr (○), 18.5 Torr (△), 1.6 Torr (◇), and 0.25 Torr (▽) and at 316 °C and 133 Torr (●), 16.0 Torr (▲), 2.0 Torr (◆), and 0.34 Torr (▼).
(b), at 262 °C and 134 Torr (○), 16.5 Torr (△), 2.4 Torr (◇), and 0.52 Torr (▽) and at 212 °C and 148 Torr (●), 17.5 Torr (▲), 2.0 Torr (◆), and 0.44 Torr (▼).

$$-\Delta I = b \log t + c \qquad (10)$$

where b and c are the constants at a given temperature and pressure. This expression can be derived from the boundary layer theory,[12] as will be described below.

Oxygen molecules once physisorbed on the surface are then chemisorbed by combining with free electrons and become negative ions. The charges in the negative ions are compensated for by the positive space-charge region caused by ionized donors near the surface. Thus, the potential-energy barrier, the so-called Schottky barrier, appears in the space-charge region. The chemisorption rate is limited by the arrival rate of electrons to the surface across the barrier, the height of which increases with an increase in the quantity of negative ions on the surface. Therefore, the rate of increase in the surface-charge density due to the chemisorbed ions is given by:[3,12]

$$dN_c/dt = N_p Cvn \exp(-eV_s/kT) \qquad (11)$$

where N_p is the density of the physisorbed oxygen molecules; C, the capture cross section of the physisorbed oxygen molecule for an electron; v, the thermal velocity of the electron; n, the density of the conduction electrons; e, the electronic charge; V_s, the Schottky barrier height, and k, the Boltzmann constant. The height of the Schottky barrier can be expressed as:[12]

$$V_s = (eN_c^2)/(2\varepsilon N_d^+) \qquad (12)$$

where ε is the dielectric constant, and N_d^+, the density of the immobile, ionized donors. Assuming that the density of the physisorbed molecules is proportional to $1/m$ power of the pressure with a form such as the Freundlich isotherm,[12] the rate equation is given by:

$$dN_c/dt = P_{O_2}^{1/m} K \exp(-\alpha N_c^2) \qquad (13)$$

where P_{O_2} is the oxygen pressure; m, the constant that depends on T, $K=Cvn$, and $\alpha=e^2/(2\varepsilon N_d^+)$. This equation cannot be integrated directly. It should be noted that the current decreases abruptly, followed by a gradual decrease when oxygen is introduced, as is shown in Fig. 4. Thus, the surface density of the trapped electrons increases suddenly to a certain value, $N_c°$, resulting in a build-up of the potential barrier, V_s, in the surface region. Therefore, the surface-charge density, N, must be increased gradually by the transfer of electrons from the bulk to the chemisorbed surface layer over the potential barrier. Since $N_c° \gg N$, Eq. (13) can be integrated in the region from $N_c=N_c°$ at time $t=t_0$ to $N_c=N_c°+N$ at time $t=t$:

$$P_{O_2}^{1/m} K \Delta t = \exp\{\alpha(N_c°)^2\} \times \{\exp(2\alpha N N_c°)-1\}/(2\alpha N_c°) \qquad (14)$$

After rearrangement, this expression becomes:

$$N_c = \{1/(2\alpha N_c°)\} \ln[2\alpha N_c° P_{O_2}^{1/m} K \Delta t \times \exp\{-\alpha(N_c°)^2\}+1] \qquad (15)$$

When $2\alpha N_c° P_{O_2}^{1/m} K \Delta t \exp\{-\alpha(N_c°)^2\} \gg 1$,

$$N_c = b \ln \Delta t + d + b/m \ln P_{O_2} \qquad (16)$$

where $b=1/(2\alpha N_c°)$ and $d=\ln(2\alpha K N_c°)[\exp\{-\alpha \times (N_c°)^2\}]/(2\alpha N_c°)$. If P_{O_2} is constant, this equation can be expressed as Eq. (10).

The deviations from the Elovich equation at 362 °C and above about 200 s may be explained as follows. When oxygen is introduced at 362 °C, the oxygen reacts abruptly with the surface of the rutile, trapping a great number of the free electrons near the surface. As a result, a high potential barrier is formed in the surface region. Any subsequent reaction may be much limited by the barrier. On the other hand, when the reaction time is long, the assumption that $N_c° \gg N$ can not hold, or oxygen ions on the surface may diffuse into the surface region or the bulk in the form of O^{2-} ions.

Activation Energy. The chemisorbed surface-charge density obtained exhibited the temperature dependence shown in Fig. 5. All the terms in Eq. (11) depend on the temperature. By combining Eq. (13) with the Arrhenius equation, the apparent activation energy, E_a, can be determined at a given chemisorbed surface-charge density and pressure. Instead of Eq. (13), however, the equation obtained by differentiating Eq. (16) by t can be used when the chemisorption kinetics obeys the Elovich equation.[26] The expression for the rate, r, at time t is given by:

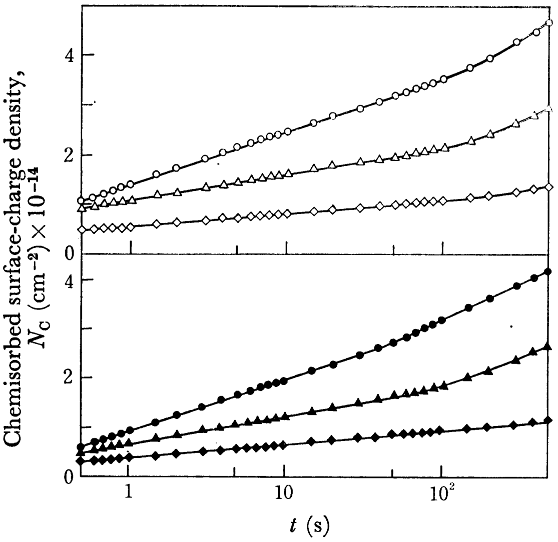

Fig. 5. Surface-charge density of high reduced rutile as a function of time after the introduction of oxygen at 17 Torr and 316 ° (○), 262 ° (△), and 212 °C (◇) and at 2 Torr and 316 ° (●), 262 ° (▲), and 212 °C (◆).

$$r = dN_c/dt = b/t \qquad (17)$$

where the value of b is determined from the slope of the N_c *vs.* $\ln t$ plots in Fig. 5. Thus the following relationship is obtained:

$$b/t = A \exp(-E_a/RT) \qquad (18)$$

The slope of the $\ln b/t$ *vs.* $1/T$ plots for a constant value of N_c is equal to E_a/R, which makes possible the evaluation of the activation energy.

The apparent activation energy in the temperature range of 212—316 °C was obtained in the above manner at various values of the chemisorbed surface-charge density and at the pressures of about 2 Torr and about 17 Torr. Figure 6 shows the apparent activation energy as a function of N_c. It seems that the difference in

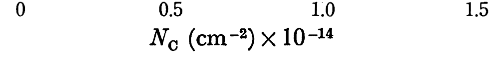

Fig. 6. Apparent activation energy for high reduced rutile as a function of N_C at 2 Torr (○) and 17 Torr (●).

oxygen pressure has scarcely any influence on the activation energy. In this chemisorption, the activation energy can be expressed by:

$$E_a = (25\pm1)\times10^{-14}N_c + 4\,\text{kcal/mol} \qquad (19)$$

Pressure Dependence. The straight lines of the N_c *vs.* ln t plots for various pressures at a given temperature were nearly parallel to one another, as can be seen in Fig. 5. By dividing both sides of Eq. (16) by b, the following equation is obtained:

$$N_c/b = \ln t + d/b + 1/m \ln P_{O_2} \qquad (20)$$

Plots of N_c/b *vs.* ln P_{O_2} at a given temperature and time give a straight line whose slope is equal to $1/m$. Plots of this type at t=10 s for three temperatures are shown in Fig. 7. From these slopes, the value of m was determined to be approximately unity, regardless of the temperature. This suggests that some of the oxygen molecules which strike the surface are physically adsorbed in the manner represented by the Henry law. From Eq. (13), therefore, the rate of oxygen chemisorption is proportional to the pressure at a constant density of the chemisorbed surface charge.

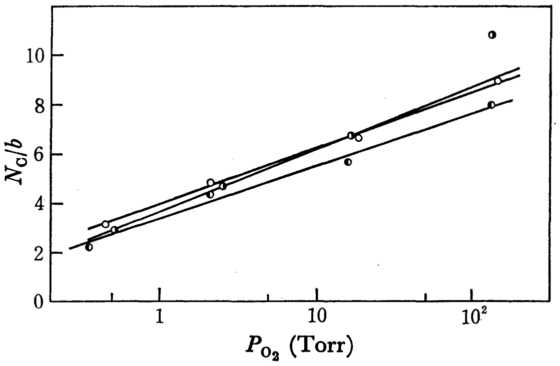

Fig. 7. Plots of N_C/b as a function of the pressure of oxygen at 212 ° (○), 262 ° (◑), and 316 °C (◐).

Conclusions. Two types of chemisorption kinetics were found for reduced rutile. This may be explained as follows: When a well-oxidized rutile is treated at a high temperature *in vacuo* for a relatively short time, only the surface region is reduced by the removal of the oxygen atoms, leaving electrons in the oxygen vacancies or at titanium ions in the neighborhood of the oxygen vacancies. These electrons are not restricted to the surface defects, but are raised to the conduction band at a moderate temperature. As a result, the surface is positively charged and the energy band for the electron bends downwards; the accumulation layer then appears in the surface region. In this case, the free electron density in the bulk is low because the bulk is almost unreduced. When the surface is exposed to oxygen gas in such a state, the oxygen takes free electrons from the accumulation layer and adsorbs chemically on the surface, thus compensating for the positive charge on it. Further, the oxygen ion thus produced tends to migrate toward the oxygen vacancy in the surface region. As a result, the chemical constitution and physical properties of the surface region approach those of the bulk. When most of the surface charges are neutralized by chemisorbed oxygen ions, scarcely any free electrons exist in this solid. Therefore, no potential-energy barrier appears in the surface region, or its height may be low even if one does exist. In such a case, the oxygen chemisorption belongs to the diffusion-controlled reaction and its kinetics obeys the parabolic rate law.

On the other hand, when a rutile is evacuated at a high temperature for a long time, not only the surface region but also the bulk is reduced, and the free electron density is fairly high, even in the bulk. The accumulation layer may also exist. In this case, the chemisorption of oxygen can continue even after the potential barrier appears in the surface region because of the large free electron density in the bulk. However, the reaction is limited by the height of the barrier. The chemisorption kinetics of such a type follows the Elovich equation.

The apparent activation energies were obtained as 14.2 kcal/mol and $(25\pm1)\times10^{-14}$ N_c+4 kcal/mol for the former type and the latter type respectively.

In addition, it was found that, in the latter type, the reaction rate of oxygen with the rutile surface was proportional to the pressure at a constant density of the chemisorbed surface charge.

The author wishes to express his cordial gratitude to Professor Masaji Miura for his continuous guidance and encouragement throughout this work. Thanks are also due to Dr. Toru Iwaki for his stimulating and informative discussions.

References

1) S. R. Morrison, *J. Phys. Chem.*, **57**, 860 (1953).
2) G. A. Somorjai, *J. Phys. Chem. Solids*, **24**, 175 (1963).
3) P. Mark, *ibid.*, **26**, 959 (1965).
4) C. Sébenne and M. Balkanski, *Surface Sci.*, **5**, 410 (1966).
5) H. E. Matthews and E. E. Kohnke, *J. Phys. Chem. Solids*, **29**, 653 (1968).
6) E. Arijs, F. Cardon, and W. Maenhout-Van der Vorst, *Surface Sci.*, **17**, 387 (1969).
7) K. Tanaka and Z. Huruhata, *J. Electrochem. Soc. Jap.*, **37**, 133 (1969).
8) J. P. Legré and S. Martinuzzi, *Phys. Status Solidi, A*, **1**, 689 (1970).
9) L. Surnev and G. Bliznakov, *ibid.*, **7**, 75 (1971).
10) M. Green, J. A. Kafalas, and P. H. Robinson, "Semiconductor Surface Physics," ed. by R. H. Kingston, Univ. of Pennsylvania Press, Philadelphia, N. J. (1957), p. 349.
11) T. I. Barry and F. S. Stone, *Proc. Roy. Soc., Ser. A.* **255**, 124 (1960).
12) P. B. Weisz, *J. Chem. Phys.*, **21**, 1531 (1953); G. A. Somorjai, "Principles of Surface Chemistry," Prentice-Hall, Englewood Cliffs, N. J. (1972).
13) S. Bourasseau, J. R. Martin, F. Juillet, and S. J, Teichner, *J. Chim. Phys.*, **71**, 122 (1974).
14) F. A. Grant, *Rev. Modern Phys.*, **31**, 646 (1959).
15) D. C. Cronemeyer, *Phys. Rev.*, **113**, 1222 (1959); J. B. Wachtman and L. R. Doyle, *ibid.*, **135**, 276 (1964).
16) H. B. Whitehurst, J. J. Morrison, F. L. English, B. M. Warmkessel, and C. J. Kevane, *J. Phys. Chem. Solids*, **28**, 861 (1967); J. Maserjian and C. A. Mead, *ibid.*, **28**, 1971 (1967); T. Goto and T. Okada, *J. Phys. Soc. Jap.*, **25**, 289 (1968).
17) T. Iwaki, This Bulletin, **46**, 1631 (1973).

18) O. W. Johnson, W. O. Ohlsen, and P. I. Kingsbury, Jr., *Phys. Rev.*, **175**, 1102 (1968); A. K. Ghosh, F. G. Wakim, and R. R. Addiss, Jr., *ibid.*, **136**, 284 (1964).

19) L. A. K. Dominik and R. K. McCrone, *ibid.*, **163**, 756 (1967).

20) R. Keezer, *J. Appl. Phys.*, **35**, 1866 (1964); T. Iwaki, M. Komuro, T. Kondo, and M. Miura, *Chem. Lett.*, **1974**, 1185.

21) K. Hauffe and H. Pfeiffer, *Z. Elektrochem.*, **56**, 390 (1952).

22) Y. Nakazumi, *Seramikkusu*, **3**, 731 (1968).

23) T. B. Grimley, "Chemistry of the Solid State," ed. by W. E. Garner, Academic Press, New York (1955), Chap. 14; F. H. Dorer, *J. Catal.*, **13**, 65 (1969).

24) T. Hatsushika, K. Iida, Y. Sashida, and H. Hasebe, *Nippon Kagaku Zasshi*, **89**, 1025 (1968).

25) H. N. Murty, D. L. Biederman, and E. A. Heintz, *J. Phys. Chem.*, **72**, 746 (1968).

26) M. J. D. Low, *Chem. Rev.*, **60**, 267 (1960).