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CHANGE IN THE THERMIONIC WORK FUNCTION OF SEMICONDUCTOR POWDERS EXPOSED TO ELECTROMAGNETIC RADIATION

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Translation of "Variation du travail d'extraction thermoélectronique de semiconducteurs pulvérulents soumis a l'action d'un rayonnement électromagnétique," Journal de Chimie Physique, 1974, No. 7-8, pp. 1017-1024

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16. Abstract

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NO. 157. - CHANGE IN THE THERMIONIC WORK FUNCTION OF SEMICONDUCTOR POWDERS EXPOSED TO ELECTROMAGNETIC RADIATION

IV. - Photoadsorption and Photodesorption of Oxygen on Titanium Dioxide.

By: S. Bourasseau, J. R. Martin, F. Juilet
and S. J. Teichner.

SUMMARY

The variations of the thermoelectronic work function of titanium dioxide (mainly anatase), submitted to an ultraviolet or visible and infrared radiation, in the presence of oxygen, are studied by the vibrating condenser method. It is shown that during the ultraviolet irradiation, a desorption of a first species of oxygen simultaneously occurs with the adsorption of a second species of oxygen and that this phenomemon is found for any structure of TiO_2 (anatase or rutile) any texture, oxygen pressure, radiation intensity and nature of introduced dopes.

INTRODUCTION.

The study of the properties of the surface of titanium dioxide exposed to ultraviolet radiation, carried out using the vibrating condenser method, and the topic of earlier articles [1,2,3] is aimed at specifying the catalytic photo-oxidation mechanism of isobutane [4].

In the initial work [2], on the one hand, we have shown the photodesorption of oxygen under vacuum through the effect of holes on oxygen atoms adsorbed on the surface of anatase and, on the other hand,

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*Numbers in margin refer to foreign pagination.

the possibility of obtaining by means of photodesorption a reference state for TiO_2 (called "standard state") corresponding to the minimum work function of this solid under the expected experimental conditions.

In the second work [3], it has been shown that oxygen should adsorb on the surface of TiO_2 in the absence of irradiation in two charged forms, called O_I and O_{II}, such that electrons captured by the adsorbed oxygen come from two sets of shallow donor levels.

The third stage, which is the subject of this publication, concerns the study of changes in the thermionic work function W in TiO_2 (or of its thermionic potential ϕ such that $W = e\phi$, where e is the charge of the electron), in the presence of radiation (mainly ultraviolet) and of oxygen. The experimental apparatus and the operating technique have already been described in detail [1].

I. ULTRAVIOLET IRRADIATION OF TITANIUM DIOXIDE IN THE PRESENCE OF OXYGEN.

1. Experiment.

The powdered sample of anatase (nonporous TiO_2, specific area: $67 m^2/g$) undergoes prior standardization treatment, by thermo- and photo-desorption, and is placed in a vacuum of 10^{-6} torr, in the absence of irradiation at ambient temperature. The potential ϕ has its minimum value ϕm. The changes in ϕ as a function of times are measured from ϕm (for $\phi = \phi m$, $\Delta\phi = 0$) taken as the reference state in a series of four successive sequences (Fig. 1).

In the first one, an oxygen pressure of 2 torrs is established /1018
in the measurement cell. ϕ increases by $\Delta\phi_1$ (400 mV) within one hour and stabilizes.

In the second sequence, the sample was irradiated, still in the presence of oxygen, by means of an Osram lamp XBO 250 across a Corning ultraviolet filter 7.54 + 0.54 (see transmission curve, Fig. 2). After the application of the radiation, ϕ decreases rapidly by $\Delta\phi_2$ (150 mV) and reaches a minimum value (however, greater than ϕm) in about two minutes, then increases slowly for 32 hours and reaches a constant value. The value of $\Delta\phi$ obtained ($\Delta\phi_3 - \Delta\phi_2 + \Delta\phi_1$) is 750mV, with respect to the standard state.

At the end of sequence 3, irradiation is terminated. This is followed by another increase $\Delta\phi_4$ (180mV) and the thermionic potential stabilizes in about one hour.

In the fourth sequence, the sample is first exposed to another irradiation. ϕ decreases rapidly down to the value previously obtained at the end of sequence 2, and keeps this value regardless of the duration of irradiation. Then, having turned the radiation off, ϕ increases just like during sequence 3 (the two curves coincide). The same final value of ϕ is obtained. The phenomena observed in sequence 4 are thus perfectly reproducible.

2. Discussion.

The kinetics observed during sequence 1 has already been studied in detail [3]. It enabled us to propose an energy diagram for TiO_2, where we show the two forms of oxygen adsorbed on the surface, O_I and O_{II} (Fig. 3a) and two sets of shallow donor levels, D_1 and D_2. The

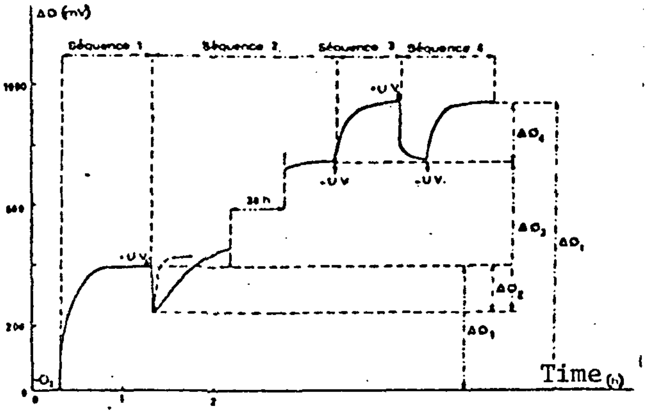

Fig. 1. Change in the work function of titanium dioxide in the presence of oxygen (p_{O2}=2 torr) in the presence or absence of UV irradiation.

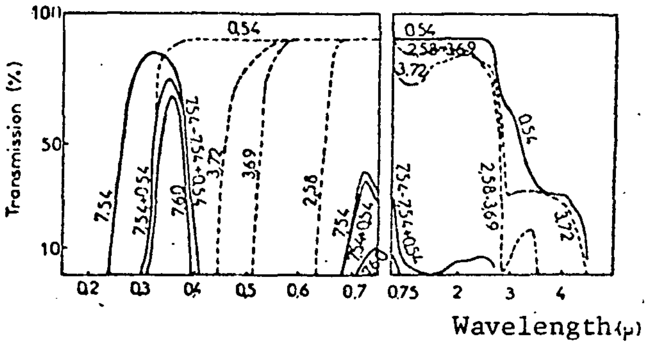

Fig. 2. Transmission curves of the Corning optical filters.

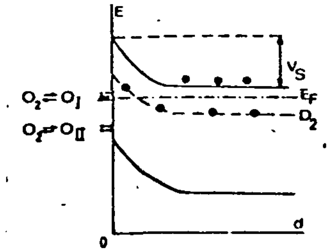

FIGURE 3a

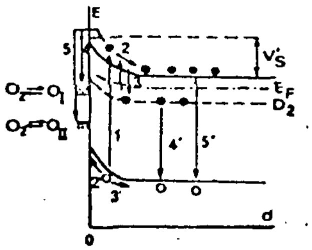

FIGURE 3b

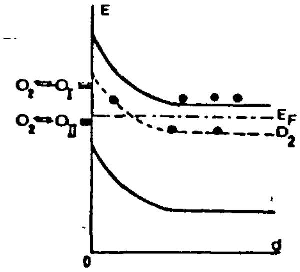

FIGURE 3c

Fig. 3a. TiO_2 (anatase energy band after adsorption of oxygen without irradiation.

Fig. 3b. TiO_2 (anatase) energy bands in the presence of oxygen after a few minutes of UV irradiation (dark circle = electron; open circle = hole).

Fig. 3c. TiO_2 (anatase) energy bands after photoadsorption of oxygen in the absence of UV irradiation.

set D_1, since it is not involved any further, is not shown in Fig. 3, for the purpose of clarity. Since the solid is at thermal equilibrium, the Fermi level E_f is horizontal. The surface energy states due to oxygen, which are not occupied by electrons, are located above the Fermi level (they are shown by dotted lines).

At the end of sequence 2, the application of radiation (of energy 3.7eV greater than the band gap of TiO_2) on the sample leads to electron transitions at the surface and in the bulk, of which the major ones are shown in Fig. 3b.

In the solid, close to the surface and at the oxygen anatase interface, transitions 1, 2, 3, 4, 5, 2' and 3' occur:

1) The photons absorbed by anatase create additional anatase free holes in the valence band and excess free electrons in the conduction band (transition 1). The latter can proceed according to

transitions 2, 3, 4 or 5.

2) Under the effect of an electric field, due to the surface potential, electrons migrate to the interior of the solid close to the bottom of the conduction band. On the other hand, the diffusion current of the free electrons created by irradiation from the surface to the interior of the solid is probably zero or negligible since in TiO_2, an n type semiconductor, the density of free electrons far from the surface should be greater than that in the space charge region (it is assumed that the number of electrons trapped on the adsorbed oxygen is low, and that the adsorption of oxygen does not affect the bulk properties of TiO_2).

3) Some of the free electrons are in thermal equilibrium with the partially ionized D_2 levels. The D_1 levels, totally ionized at ambient temperature, are not involved.

4) and 5) Electrons freed by radiation in the conduction band overcome the surface potential barrier, and react with the oxygen adsorbed physically, leading to the formation of additional O_I or O_{II} species which have gone from the chemisorbed to the physisorbed state due to the effect of the holes (transition 2').

The holes can behave in two different ways (2' and 3').

2') Part of the holes created in the space charge region migrate to the surface under the influence of the electric field. They react /1019 with electrons trapped on the adsorbed oxygen. Since we have assumed that the O_{II} species is more highly charged than the O_I^- species, and that its concentration is higher, the holes are trapped practically only by the O_{II} form, at least at the start of irradiation. The result is that a certain concentration of this species goes from the chemisorbed to the physisorbed form, in equilibrium with the gas phase. Therefore, desorption takes place due to deionization by holes.

3') The concentration of holes created at the surface by irradiation is greater than the concentration of holes within the solid, which are the minority carriers, since TiO_2 is an n type semiconductor. Consequently, part of the holes diffuse from the surface to the interior.

Let us now consider the effect of radiation within the solid.

Transition 1 takes place. However, the number of free carriers created by this mechanism is small far from the surface (the adsorption coefficient of anatase is high). It follows that the thermal equilibrium between the D_2 levels and the conduction band is barely changed.

Finally, the electrons and the holes could recombine, either directly band to band (transition 5') or through a defect level such as D_2 (transition 4'). However, transition 5' has a low probability physically.

The recombination processes 4' and 5' are also possible in the solid close to the surface.

At the start of irradiating the sample in the presence of oxygen, the excess electron and hole densities (relative to thermal equilibrium) close to the surface are essentially the same, if we assume that the number of carriers drifting toward the interior of the solid (transitions 2 and 3') is negligible. Under these conditions, the number of holes trapped by the adsorbed species at the surface (O_{II}) is much higher than the number of electrons trapped by oxygen in the form of O_I since the holes react without an activation energy in contrast with the electrons, which should overcome the surface potential. The rate of desorption of the O_{II} ions is much higher than the rate of adsorption of O_I ions, so that a decrease in charge at the surface is produced, that is, a decrease in the potential barrier V_s which takes a new value V_s' less than the value of V_s in Fig. 3a.

This explains the decrease in the work function of TiO_2 at the start of sequence 2.

However, after irradiation for two minutes, ϕ levels off then increases again slowly (Fig. 1) for two reasons.

On the one hand, the desorption of the O_{II} species by deionization through transition 2' is limited by the inverse reaction due to transition 5: an equilibrium is established between these two reactions, 2' and 5, leading to the onset of a steady concentration for O_{II}.

On the other hand, the O_I species continues to be adsorbed (transition 4). The overall effect is therefore an increase in the surface charge, and consequently in ϕ. This explains why the electron flux arriving to the surface is greater than the number of holes which reach it and go into reaction there. In other words, the number of holes diffusing into the interior of the solid, subsequently to recombine, is greater than the number of free electrons which return into the bulk of this solid.

The additional adsorption of oxygen can thus be explained by considering the Fermi level of the solid.

Prior to irradiation (Fig. 3a), when the adsorption is at thermal equilibrium, the Fermi level is horizontal and represents the theoretical adsorption limit above which electrons cannot be trapped by adsorbed oxygen.

By irradiating the solid, a quasi-Fermi level is created for the electrons, localized at the surface, and different from the Fermi level at the interior of the semiconductor, which remains the same (Fig. 3b). This quasi-Fermi level creates a new theoretical adsorption limit, on the condition that a part of the holes created simultaneously will be trapped or will recombine within the solid.

It is possible that this limit would not be reached, but that photoadsorption stops for the following reasons:

-- The spontaneous desorption of a part of the adsorbed species is no longer negligible when the rate of photoadsorption becomes low;

-- Since the concentration of the O_1 species has become considerable, some of the holes are trapped by this species. Then an absorption - desorption equilibrium is produced, as for the O_{II} species.

The O_I species has been identified by electron paramagnetic resonance [4, 5]. It consists of the O_2- form.

The adsorption then the desorption phenomena observed during sequence 2 (change in the trend of ϕ) has also been observed by mass spectroscopy [6] but only in the pressure range of 10^{-7} to 10^{-5} torr, confirming the conclusions reached from the contact potential method (simultaneous photoadsorption and photodesorption).

At the end of sequence 3 (Fig. 1) turning the radiation off leads to the disappearance of the quasi-Fermi level at the surface. The excess electrons reoccupy the states freed by the departure of part of the O_{II} species, which are readsorbed, which is reflected by another increase $\Delta\phi_4$ (180mV).

A mass spectroscopy study [6] in the pressure range of 10^{-7} to 10^{-5} torr shows that the adsorption of oxygen takes place in the dissociated form. The O_{II} species therefore would be O^- or O^{--}.

The identification of this species has been attempted in this laboratory using EPR since O- is paramagnetic, as opposed to O--. Although there was no signal observed corresponding to O-, it is not possible to conclude that O-- is present. In effect, as this has been emphasized by Kazanskii, et al. [7], the O- form is observable by EPR only in limiting cases, which are rarely achieved. Measurements of the isotropic photoexchange rate of oxygen also show that the adsorbed species in the absence of radiation is not O-- [8].

The O_{II} form can therefore be attributed to O-; however, this symbol designates a dissociated species having approximately a single negative charge. In other words, the bond between O- and the solid could be partially covalent.

Sequence 4 (Fig. 1) shows that by again irradiating the sample, we first produce photodesorption (confirmed by mass spectroscopy [7]) /1020 which leads to the equilibrium state that the sample had at the end of sequence 2. Then termination of irradiation enables the O- species that had been desorbed to be readsorbed. The energy diagram of TiO_2 after irradiation is shut off is therefore as shown in Fig. 3c (the Fermi level is again horizontal).

3. Analysis of the Kinetic Curves.

a) Photoadsorption.

The analysis of the photoadsorption curve (Fig. 1) $\Delta\phi_3 = f(t)$ shows that it obeys a formula of a Roguinskii-Zeldovitch-Elovitch type (Fig. 4) of the form

$$\Delta\varphi_3 = 4{,}4 \times 2{,}3 \frac{kT}{e} [\log(t + t_0) - \log t_0] \qquad (1)$$

indicating that the adsorption of O_2- is activated.

The constant t_0 which depends on the oxygen pressure and the initial state of the sample, is determined by successive approximations (for $p_{O2} = 2$ torr, $t_0 = 10$ minutes). In general, points corresponding to $t+t_0 < 10$ min have not been shown (if $t_0 < 10$ min for $p_{O2} = 2$ torr) given the uncertainty in the choice of the initial moment for photoadsorption. Furthermore, this uncertainty is increased by the fact that the constant t_0 is not known at the start.

In order to explain equation 1, verified manometrically with respect to the quantity of O_2 fixed in another work [9], it is assumed on the one hand, that only the O_2- species contributes to the increase in ϕ, and, on the other hand, that the desorption is negligible (this hypothesis is obviously not valid at the end of adsorption).

To react with the O_2 molecules adsorbed physically, excess electrons created by ultraviolet irradiation should overcome the potential barrier $\Delta V(d) + \chi/e$ (χ: = electron affinity of TiO_2) where the probability of reaction is proportional to

$$\exp\left[-\frac{eV(d)+\chi}{kT}\right]$$

and χ changes only by a proportionality constant. Hence, only the term V(d) will be called the potential barrier. At a given instant t, electrons created at various points in the solid in the space charge region, do not have the same potential barrier to overcome. Thus, for $d \simeq 0, \Delta V(0) \simeq 0$, while for d = to ℓ (ℓ = width of the space charge region, $\Delta V(\ell) \simeq \Delta V_s$. Since the distribution of the free electrons in the solid in the space charge region is not known, it is assumed that these electrons behave as if each of them overcame the same average potential barrier $\overline{\Delta V}$ (an"equivalent" surface potential independent of D). Since different values of $\Delta V(d)$ are less than or equal to ΔV_s (that is, $\Delta\phi$) $\overline{\Delta V}$ is less than $\Delta\phi$. We therefore put $\Delta V = \Delta\phi/n$, with $n > 1$.

Furthermore, it is assumed [2] that $\Delta\phi$ varies linearly with the coverage by the O_2- ions (Mott barrier) given that additional free electrons created by the irradiation are in thermal equilibrium with the partially ionized D_2 levels. Thus we get

$$\frac{d(\Delta\varphi)}{dt} = A \exp\left[-\frac{e\Delta\varphi}{nkT}\right] \qquad (2)$$

where A is a constant depending on the oxygen pressure and the initial state of the sample.

Integration of equation 2 gives:

$$\Delta\varphi = 2{,}3 \times \frac{nkT}{e}\left[\log(t+t_0) - \log t_0\right] \qquad (3)$$

Comparison of equations 1 and 3 shows that the equivalent potential barrier is equal to about a fifth of the maximum barrier that the electrons created by irradiation should overcome at a given instant.

b) Adsorption of Oxygen in the Absence of Radiation after Photoadsorption.

After shutting of irradiation at the end of sequence 2 (Fig. 1)

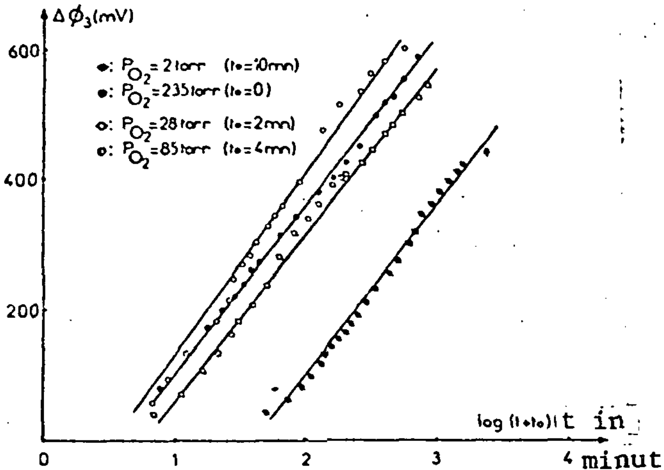

Fig. 4. Photoadsorption of oxygen on TiO_2 (anatase, $67m^2/g$) under UV irradiation.

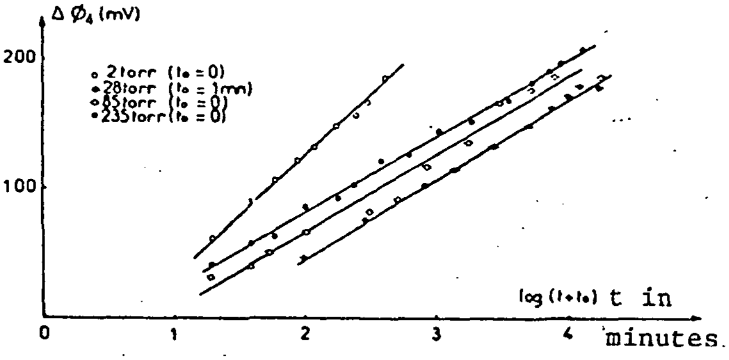

Fig. 5. Adsorption of oxygen on TiO_2 (anatase $67m^2/g$) in darkness,

oxygen is adsorbed per a formula of the Roguinskii-Zeldovitch-Elovitch type [3] with a slope of about 90mV or 1.5 X $2.3\frac{kT}{e}$ (Fig. 5, P_{o2} = 2 torr). Since the quasi-Fermi level at the surface is eliminated, the kinetics observed at the end of adsorption reappear in the absence of irradiation, on photodesorbed (slope≈70mV) or thermodesorbed (slope≈80mV) [3].

4. Effects of Different Parameters of the Photoadsorption of Oxygen.

According to equation 3 the only factor likely to change when the characteristics of the TiO_2 sample are modified is t_0 which depends on the oxygen pressure, the concentration of free electrons in the anatase at the moment or at the start of photoadsorption on the intensity of irradiation and also, a priori, on the structure of TiO_2. However, equation 3 can be changed only "quantitatively" from one sample to another, since the slope of the curve $\Delta\varphi = f[\log(t + t_0)]$ should remain the same if the starting hypotheses are correct.

In the following experiments it has not been possible to find a correlation between t_0 and the various parameters characterizing the sample, since the value of t_0 was too imprecise. On the other hand, equation 3 is always verified with a value of n essentially constant. /1021

Thus, when p_{O2} changes from 2 torr to 235 torr (Fig. 4) the value of n changes from 4.4 to 5. Given the large dispersion in the experimental points, n can be considered constant (a difference of 10% between the extreme values); similarly, equation 3 is not uniquely valid for anatase. A sample of rutile with a specific area equal to $10m^2/g$ (prepared by heating anatase of specific area = $67m^2/g$ to 1000°C in air) undergoes photoadsorption of oxygen in the presence of UV radiation (Fig. 6). In this case, the mass of the sample is 400mg instead of 40mg as with anatase, in order that it could fill all the gaps in the sample holder, and thus be irradiated under the same conditions as anatase. Figure 6 shows that equation 3 is still valid with n=4, for a maximum difference of 20% from the value obtained in the case of anatase.

The effect of the specific area of TiO_2 on photoadsorption has been studied by using samples of anatase of 13, 35, and $98m^2$ per gram, prepared in an oxyhydrogen flame, with an oxygen pressure of 50 torr. The results obtained are shown in Fig. 7. Equation 3 is still verified with n varying between 4 and 5.5.

The amplitude of photoadsorption increases with specific area, but not much since $\Delta\phi_3$ increases by 30% while the specific area is

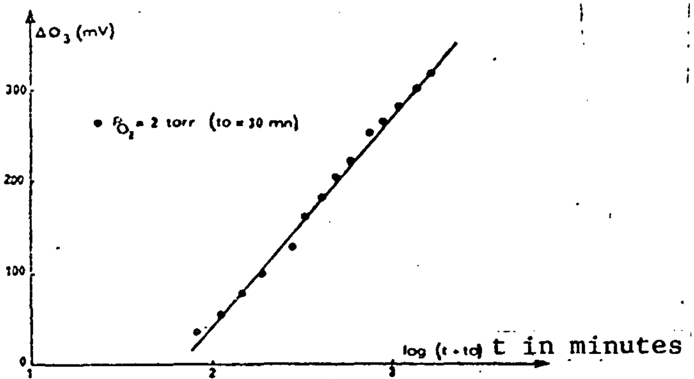

Fig. 6. Photoadsorption of oxygen (rutile $10m^2/g$) under UV irradiation.

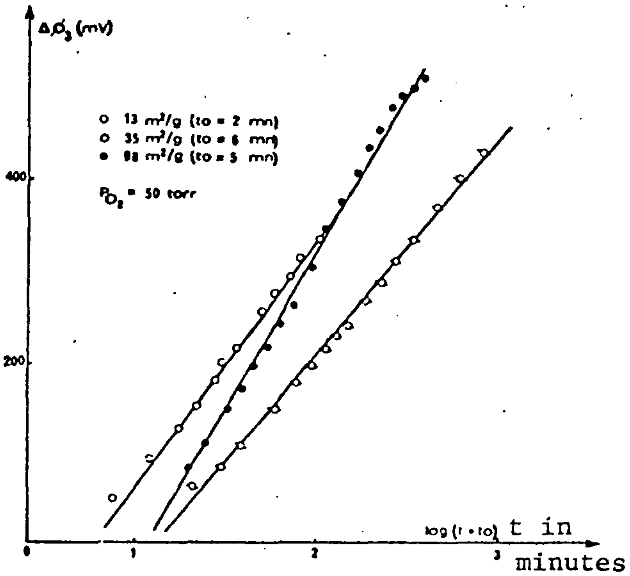

Fig. 7. Photoadsorption of oxygen on different samples of TiO_2 (anatase 13; 35; and $98m^2/g$).

multiplied by 7.5. Since the standard state (before adsorption and photoadsorption of oxygen) is the same for the three samples, in principle the same value of ϕ should be obtained in all three cases after photoadsorption, since the coverage rate by oxygen is the same. We therefore have to assume that the coverage rate by oxygen increases with the "division state" of the solid, which makes ϕ increase or even that the irradiated surface area is not exactly proportional to the specific area. These two effects could also be involved simultaneously.

The study of the effect of the irradiation intensity on the photoadsorption of oxygen has been carried out for p_{O2} = 235 torr by means of two grids in the role of an attenuator, letting only 52 and 20% of the incident photons through (photon flux without attenuation = I_0). After the first photoadsorption on TiO_2 (67m^2/g anatase) for $I=I_0$ the irradiation is turned off. ϕ increases and reaches a constant value at the adsorption equilibrium in darkness. Vacuum is then established (10^{-5} torr) and the sample is again degassed for 15 hours at 150°C. After cooling to ambient temperature, it is exposed to ultraviolet irradiation for 40 min under vacuum of 10^{-6} torr. In this way the standard state is again obtained but only within 7% (the value of the Au-TiO_2 contact potential is 650mV instead of 750mV for the /1022
customary initial standardization). From this second reference state, very close to the first, TiO_2 again undergoes the complete sequence represented in Fig. 1, but with $I=0.52I_0$. Finally, after the second photoadsorption, a third reference state is again obtained like before, but only within 14% (the value of the Au-TiO_2 contact potential is no more than 600mV). This sequence in Fig. 1 is restarted a third time, with $I=0.20I_o$. Thus, Fig. 8 shows that the total change $\Delta\phi_3$ is the same in the three cases and that in the three experiments we obtain a straight line by plotting $\Delta\phi_3$ as a function of $\log(t+t_0)$. The value of n is equal to 4.7, again verifying equation 3, regardless of the intensity of irradiation.

The study of the effect of doping on the photoadsorption of oxygen under 235 torr has been carried with samples of anatase of an area essentially equal to 80m^2/g containing Niobium, Gallium or

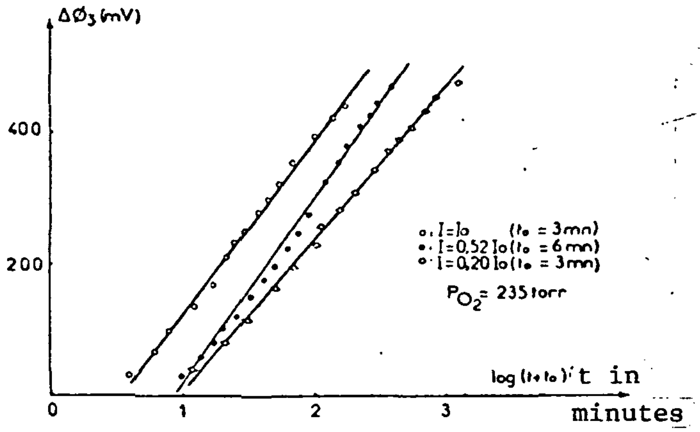

Fig. 8. Photoadsorption of oxygen on TiO_2 (anatase $67m^2/g$) under UV irradiation of various intensities.

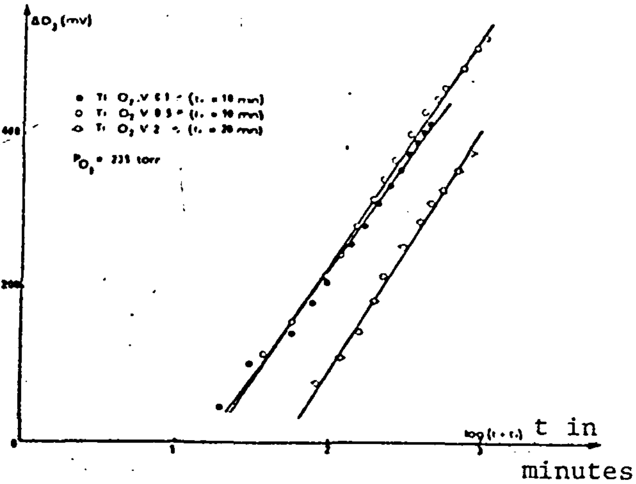

Fig. 9. Photoadsorption of oxication of TiO_2 (anatase $80m^2/g$) doped with Gallium or Lithium.

Vanadium. A comparison of a sample of TiO_2 doped with Niobium at 0.2 atom % (n type doping) and a sample of TiO_2 doped with Gallium at 0.3 atom % (p type doping) shows that the amplitude of the photoadsorption is greater for TiO_2-Nb, than for TiO_2-Ga; that is, it increases with the number of free electrons present at the initial moment (Fig. 9). However, equation 3 is still verified with n=5. For samples doped with Vanadium (Fig. 10) the amplitude of photoadsorption increase with the percentage of Vanadium for low concentrations (0.1 to 0.5%) then decreases for higher concentrations (2%). However, equation 3 is always verified such that n changes between 4.7 and 5.2.

5. Adsorption of Oxygen on TiO_2 in Darkness Following Photoadsorption Under UV.

After having studied the influence of various parameters on the photoadsorption of oxygen on TiO_2 by ultraviolet irradiation, we have analyzed, by varying the same parameters, the kinetics of the adsorption of oxygen in the absence of irradiation, which follows photoadsorption (Fig. 1, sequence 3).

In Fig. 5 we plot the values of $\Delta\phi_4$ as a function of $\log(t+t_0)$

for various oxygen pressures (anatase sample with 67m^2/g). The straight lines obtained have slopes of 2.3kT/e except that corresponding to p_{o2} = 2 torr, which has a slope of 1.5 x 2.3kT/e. The amplitude of the change is close to 180mV, or 30mV than the amplitude of the photodesorption peak ($\Delta\phi_2$) in Fig. 1. However, for the two minutes between the start of sequence 2 ("+UV") in Fig. 1 and the instant where $\Delta\phi$ passes through a minimum (amplitude change = $\Delta\phi_2$) oxygen is adsorbed in the form O_2- [11] which has reduced slightly the height of the $\Delta\phi_2$ peak. The magnitude of this decrease can be evaluated by turning the irradiation off at the moment when $\Delta\phi$ passes through this minimum, which leads to another increase $\Delta\phi$ (dotted curve in Fig. 1). In this case, the new $\Delta\phi$ value obtained at equilibrium in darkness is greater by 30 mV than that which has been obtained before, at the end of sequence 1. Therefore, by adding 30mV to the value of $\Delta\phi_2$ (150mV) we obtain the value of $\Delta\phi_4$ (180mV), which agrees well with the readsorption in darkness of the 0- species desorbed previously.

Figure 11 shows the readsorption on samples of anatase with different specific areas for p_{o2} = 235 torr. The slope of the straight lines obtained fall between 0.9 x 2.3kT/e and 1.1 x 2.3kT/e. The amplitude of the changes ranges from 150 to 250mV. /1023

In the case of doped samples, Fig. 12 shows that $\Delta\phi_4$ is still a linear function of $\log(t+t_0)$. The slope of the straight lines obtained for TiO_2-Nb and TiO_2-Ga is equal to 1.1 x 2.3kT/e while that

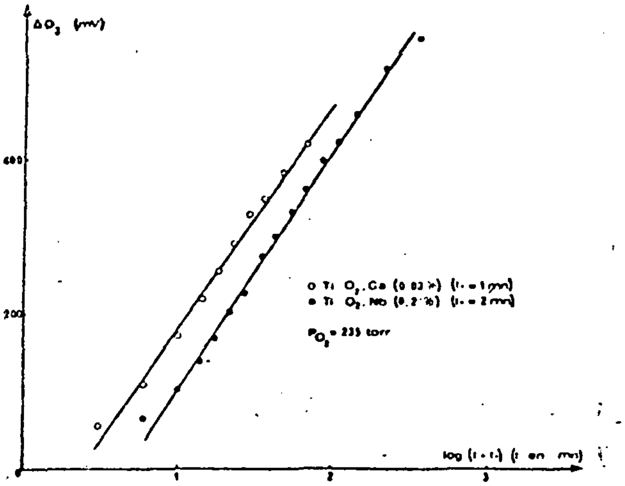

Fig. 10. Photoadsorption of oxygen on TiO_2 (anatase 80m^2/g) doped with vanadium.

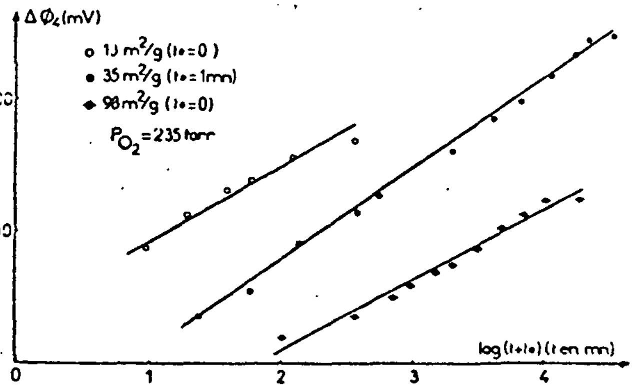

Fig. 11. Adsorption of oxygen on TiO_2 (anatase 13, 35, and 98m^2/g) in darkness following photoadsorption.

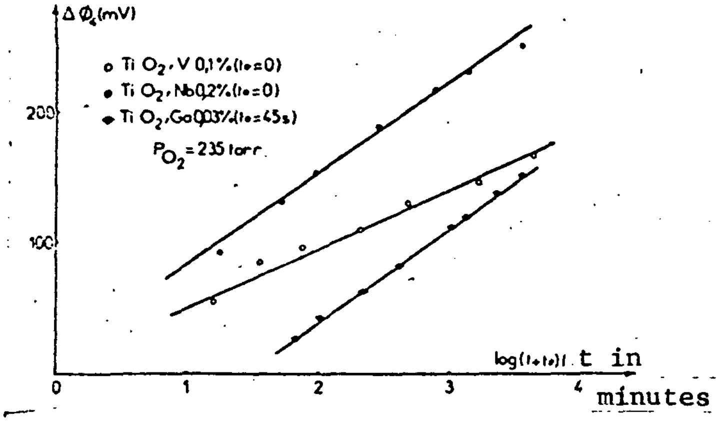

Fig. 12. Adsorption of oxygen on TiO_2 (anatase $80m^2/g$ doped with vanadium, niobium, or gallium).

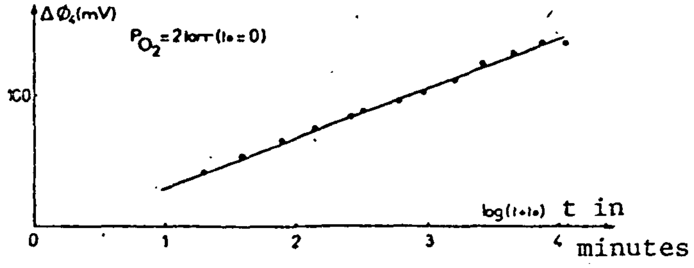

Fig. 13. Adsorption of oxygen on TiO_2 (rutile $10m^2/g$) in darkness following photoadsorption.

of the line corresponding to TiO_2-V is equal to 0.8 x 2.3kT/e. The amplitude of the adsorption falls between 180 and 250mV.

Finally, for rutile (Fig. 13) a line with slope 0.7 x 2.3kT/e is obtained even under an oxygen pressure of 2 torr.

In sum, whatever the structure or the texture of TiO_2, or the nature of the dopant, or the pressure of the oxygen, the adsorption of oxygen in darkness following photoadsorption under UV always obeys the same Roguinskii-Zeldovitch-Elovitch formula with a slope of the order of 2.3kT/e. Moreover, it has been found that the amplitude of this adsorption is approximately equal to that of the photodesorption of the same sample. This agrees well with the conclusions found before, regarding the readsorption of oxygen that has been photodesorbed for all the samples.

II. VISIBLE AND INFRARED IRRADIATION OF TITANIUM DIOXIDE IN THE PRESENCE OF OXYGEN.

After having studied the changes in ϕ_{TiO_2} under ultraviolet irradiation, the behavior of TiO_2 in the presence of visible and infrared radiation (that is, energized less than the band gap of TiO_2) is examined.

To this end, three Corning filters, 2.58, 3.69 and 3.72, whose transmission curves are given in Fig. 2, have served to select a range of wavelengths.

The samples of anatase (67m^2/g) is "standardized" then put under 235 torr of oxygen in darkness. After ϕ stabilizes, TiO_2 is illuminated and the changes in its work function is measured as a function of time. For each filter we have used a different sample of anatase.

Figure 14 shows the results obtained. From the beginning of irradiation, ϕ increases by 10 to 20 mV in a few seconds, then decreases slightly within the same time, then increases for several hours and finally stabilizes. Although the small changes in contact potential observed at the start of irradiation are of the order of the reference electrode fluctuations, these variations cannot be attributed to the latter but to TiO_2. In effect, the variations in the thermionic potential of gold take place in several minutes, while the changes in the Au-TiO_2 contact potential observed have taken place in a few seconds. Furthermore, the temperature of the samples rises a few degrees during the illumination of anatase.

The interpretation of these phenomena is difficult. It is likely that three effects are involved simultaneously from the beginning of irradiation with different magnitudes and rates: /1024

1. A slight thermal effect decreasing the adsorbing capacity (therefore ϕ);
2. The excitation of electrons from several impurity levels located in the band gap of TiO_2. Part of the electrons freed is trapped in the intrinsic surface states of the solid, thus increasing ϕ;
3. Part of the electrons freed by irradiation is trapped on the adsorbed oxygen.

Effect 2 could explain the increase in ϕ at the initial moment, and effect 1 the subsequent slight decrease in ϕ . However, effect 3 is more important since it leads to a very clear adsorption of a form

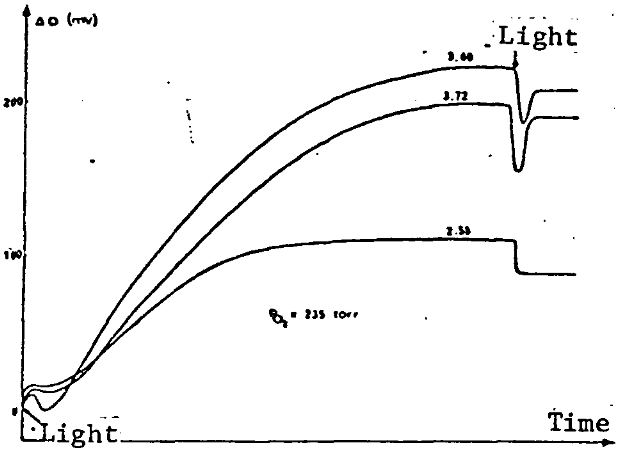

Fig. 14. Photoadsorption of oxygen on TiO_2 (anatase $67m^2/g$) under visible or infrared radiation (abscissa not to scale)

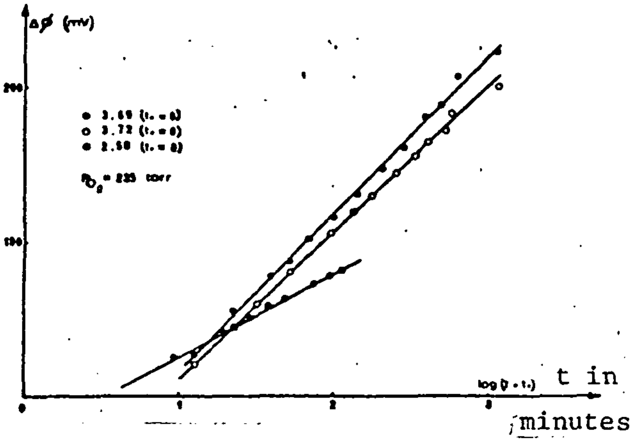

Fig. 15. Photoadsorption of oxygen on TiO_2 (anatase $67m^2/g$) under visible or infrared radiation.

of oxygen, identified by EPR as the O_2- form [10]. It also seems like the longer the wavelengths used, the smaller the quantity adsorbed. This result is in agreement with that of reference 10. We also note that the quantities of photosorbed oxygen are much less than under ultraviolet irradiation.

Finally, when the light is shut off, the three effects mentioned before disappear at various rates, which roughly give (except for the 2.58 filter) changes that are inverse of those observed at the initial moment.

On Fig. 15 we plotted the changes in $\Delta\phi$ (due to photoadsorption of oxygen) as a function of $\log(t+t_0)$ for the different filters. The values of $\Delta\phi$ are calculated from the second extremum, located after the indication "+ light" (see Fig. 14). The slope of the lines obtained depends on the range of the wavelengths used. Thus, for the 2.58 filter, the slope is equal to 2.3kT/e while for the 3.69 and 3.72 filters is close to 1.8 x 2.3kT/e.

It is possible to conclude from this that the adsorption of oxygen is still being activated as in the experiments affected under

UV. However, a more precise interpretation is difficult since the electrons freed by the radiation are no longer in thermal equilibrium with the impurity levels affected by the radiation, and, in addition, the density and the distribution of these levels in terms of energy is not known.

CONCLUSION

The effect of ultraviolet radiation on the thermionic work function of TiO_2 in the presence of oxygen has been compared to the effect produced under the same conditions by visible and infrared radiation.

The results obtained show that in some cases additional adsorption of oxygen takes place in the form of O_2^- even though the electrons trapped do not have the same origin (valence band for one, and impurity levels for the other).

But the important difference resides in the fact that at the same time that photoadsorption takes place, we also have photodesorption -- preceded by deionization by the holes -- of the O^- form of oxygen during ultraviolet radiation, while this effect does not exist during illumination by visible and infrared radiation. This difference therefore allows us to assume that holes play a fundamental role in the catalytic photo-oxidation of isobutane in the presence of anatase under the influence of ultraviolet irradiation [4].

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