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Electron Spin Resonance (ESR) Studies on the Interaction of Oxygen with Semiconductors under Photoirradiation[1]

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The paper describes an electron spin resonance (ESR) study on the interaction of oxygen with ZnO, TiO_2 and ZrO_2 during photoirradiation. Photoadsorption and photodesorption of oxygen were investigated on these oxides with simultaneous measurements of the ESR spectra due to adsorbed oxygen and of the residual oxygen pressure. Significance of the role of neutral oxygen present on the surface for the photoresponses was emphasized.

Photoadsorptive property of inorganic semiconductors has been recognized for long years. Recently the phenomenon has attracted the attention of many people in connection with the experimental and theoretical aspects of the photocatalytic and photoconductive properties of semiconductors. Little knowledge is available however about the behavior of the adsorbed gases. In the present paper, the authors will report the ESR studies concerning the interaction of oxygen with ZnO, TiO_2 and ZrO_2 during photoirradiation. Special attention will be given to the character of the adsorbed layer with which photoadsorption or photodesorption of oxygen is concerned.

Experimental

A quartz adsorption tube of 4 mm internal diameter, containing 0.1—0.4 g semiconductor sample, was connected by means of a flexible joint to a high vacuum line so that it could be situated in the ESR cavity without disconnecting the tube from the vacuum line. A Pirani gauge was used to measure changes of oxygen pressures at low values. A 500 W high pressure mercury lamp (Ushio Electric Co.) was employed as a light source combined with a $CuSO_4$ solution or a glass filter (Toshiba Co.).

The ESR measurement was carried out by JEOL-P-10 (100 kc, X band) spectrometer with semiconductor samples kept usually at room temperature, and was combined with a simultaneous measurement of the amount of oxygen adsorbed or desorbed by a Pirani gauge attached near the adsorption tube.

Absolute spin density calibrations were carried out by Mn^{2+}-MgO directly inserted in the sample tube and by DPPH in benzene. Oxygen gas was prepared by decomposing potassium permanganate. The source of the semiconductors investigated was as follows.

ZnO: New Jersey Zinc Co. S. P. 500. TiO_2: A sample was prepared by hydrolyzing $TiCl_4$ supplied by Koso Chemical Co. with ammonia and then by drying at 130°. The sample was then calcined at 500° in a stream of oxygen, and white sample of anatase type was obtained in this way. ZrO_2: Merck Co. These samples were outgassed usually at 500° before adding oxygen at room temperature.

Results and Discussion

1. ZnO-O_2

As reported previously,[3-7] the ESR spectrum of ZnO adsorbed by oxygen (designated as ZnO-O_2) consisted of a $g=1.96$ signal due to an electron in the bulk and an anisotropic $g=2.002$,

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[1] Introduced by T. Kwan before the Pre-congress Symposium (Magnetic Resonance) of the 7th International Congress of Biochemistry, Tokyo, 1967.

[2] Location: *Hongo, Tokyo.*

[3] Y. Fujita and T. Kwan, *Shokubai*, **5**, 206 (1963).

[4] M. Setaka and T. Kwan, *Shokubai*, **7**, 335 (1965).

[5] M. Setaka and T. Kwan, *Bull. Chem. Soc. Japan*, **38**, 1414 (1965).

[6] K.M. Sancier, *J. Catalysis*, **5**, 314 (1966).

[7] K.M. Sancier and T. Freund, *J. Catalysis*, **3**, 293 (1964).

2.008 and 2.049 signal due to an adsorbed oxygen species. As the intensity of the $g=1.96$ signal was found to decrease with increase of oxygen coverage while the triplet signal was increased, it may be presumed that electron transfer occurs from the bulk to the adsorbed oxygen species. We assume that the triplet signal is due to O_2^-. When the ZnO was irradiated with wavelengths (350—450 mμ) corresponding to the forbidden gap, changes in the ESR spectra took place accompanied by a pressure change in the tube. In other words, photoadsorption or photodesorption of oxygen was recognized. The phenomena will be described in more detail.

Photoeffect under High Oxygen Pressure

Photoirradiation was made on the ZnO–O_2 sample under 20 Torr oxygen pressure. For the sake of convenience, the change in the crystal current (ΔCC) was measured sometimes instead of investigating the $g=1.96$ intensity ($I_{1.96}$).[8] The result is shown in Fig. 1. It should be remembered that the pressure change due to photoirradiation is not detectable at high oxygen pressures and that the intensity of $g=2.0$ can be determined only by removing the residual oxygen. The spin density of $g=2.0$, determined in this way, will be denoted as $I_{2.0}$.

As shown in Fig. 1, both ΔCC and $I_{2.0}$ increased upon photoirradiation, and the increase in $I_{2..0}$ (1.3×10^{15} spins) is much greater than that of $I_{1.96}$ or ΔCC. Nevertheless, the result indicates qualitatively that photoadsorption of oxygen takes place or that electrons produced by the injection of photons react with neutral oxygen molecules present on the surface.

Photoeffect under Low Oxygen Pressure

In this case, the oxygen pressure was 10^{-5}—10^{-4} Torr and it was possible to follow the pressure change due to illumination. It was found by this technique that photodesorption of oxygen took place. Furthermore, the photodesorption was accompanied by a decrease in $I_{2.0}$ and by an increase in ΔCC. The results are shown in Fig. 2, where the amount of oxygen desorbed was smaller (3×10^{14} molecules) than the decrease in $I_{2.0}$ (8×10^{14} spins). The discrepancy is more than the experimental accuracy.

Let us discuss briefly the results obtained. We have observed photoadsorption at high oxygen pressure, and photodesorption at low oxygen pressure. However it has been already demonstrated[9] that photoadsorption of oxygen takes place on an oxidized ZnO sample while photodesorption of oxygen on a reduced sample. The ZnO sample in the present case was heated in vacuum at 500° before the experiment and so it may be expected to be in a reduced state. The fact that photoadsorption of oxygen does occur under the high oxygen pressure suggests that the presence of neutral oxygen molecule on the surface is an important factor in photoadsorption for this pretreatment. An attempt was made to oxidize the ZnO sample at 200°, for a short period, and then to subject the sample to photoirradiation at a low oxygen pressure where neutral oxygen molecules are less abundant on the surface. As expectedly, photoadsorption of oxygen took place in contrast with the case of the unoxidized ZnO sample. From the pressure decrease the amount of oxygen photoadsorbed was calculated to be 3×10^{14} molecules. On the other hand, $I_{2.0}$ remained almost unchanged. The result may be explained if reactions such as

$$O_2 + \ominus \longrightarrow O_2^-, \qquad O_2^- + \ominus \longrightarrow 2O^-$$

take place simultaneously or consecutively on the surface.

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[8] It was demonstrated preliminarily that the intensity of the $g=1.96$ signal is linearly proportional to the "crystal current." ZnO of high conductivity reduces the cavity Q resulting in the increase of the crystal current of the ESR apparatus; oxygen sorption increases the cavity Q and decreases the crystal current.

[9] Y. Fujita and T. Kwan, *Bull. Chem. Soc. Japan*, 31, 830 (1958).

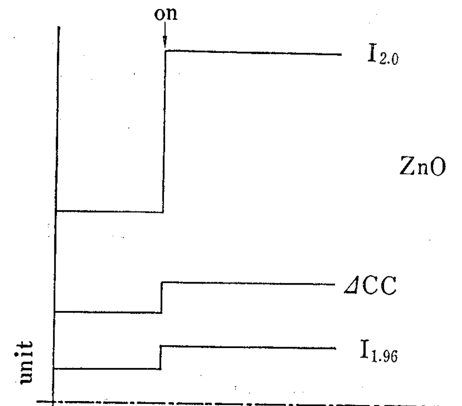

Fig. 1. Changes in the Spin Density, $I_{2.0}$ and $I_{1.96}$, of the $g=2.0$ Triplet Signal and the $g=1.96$ Signal and of the Crystal Current due to Photoirradiation. Residual O_2 Pressure: 20 Torr

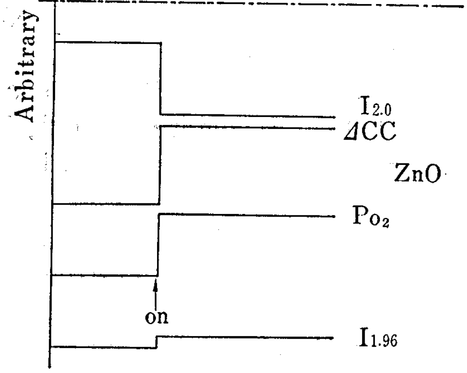

Fig. 2. Changes in the Spin Density, $I_{2.0}$ and $I_{1.96}$, of the $g=2.0$ Triplet Signal and the $g=1.96$ Signal, the Crystal Current, Δ CC, and the Residual Oxygen Pressure, P_{O_2}. Residual O_2 Pressure: 10^{-4}—10^{-5} Torr

2. TiO_2-O_2

Only photoadsorption of oxygen has been reported on TiO_2.[10] We have found that photodesorption of oxygen also occurs on TiO_2 at room temperature if the sample was well outgassed above 500° just as the case of ZnO. The result will be reported in a separate paper. Here, we shall confine ourselves to the photodynamic property of the $g=1.984$, 2.004 and 2.023 signal of the sample in an oxygen atmosphere. The triplet signal is illustrated in Fig. 3. It was possible to measure the ESR spectra in the presence of residual oxygen because the signal originated in the bulk where pressure broadening effect of oxygen were not active. Again, the photoeffects will be investigated at high and low oxygen pressures.

Photoeffect under High Oxygen Pressure

When the TiO_2 sample, kept under 40 Torr oxygen, was irradiated with wavelengths in the range of 300—410 $m\mu$, the triplet signal was found to increase; upon turning the light off the signal decreased gradually. Such a process is shown in Fig. 3. The origin of the triplet signal is not clear, but it appears to be due to a bulk defect, ionized thermally or by light, with the electron transferred to the surface. For example, it may be noted that the intensity of this signal became largest when the TiO_2 sample was calcined at 500° under oxygen pressures ranging from 0.1 to 10 Torr. Also, the triplet was found to grow upon adsorbing SO_2, an electron acceptor.

If it is assumed that the triplet intensity increases because an electron is donated during photoexcitation to neutral oxygen molecules, the data of Fig. 3 indicates photosorption of oxygen.

Photoeffect under Low Oxygen Pressure

An increase in the oxygen pressure was detected when the TiO_2 sample was illuminated in residua loxygen pressures as low as 10^{-4}—10^{-5} Torr, showing that photodesorption took place. The intensity of the triplet signal was found to decrease in contrast with the case of high

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10) D. Kennedy, M. Ritchie and J. Mackenzie, *Trans. Faraday Soc.*, **54**, 119 (1958).

oxygen pressure (40 Torr). The photodesorption of oxygen may be interpreted in terms of an electron transfer from the negatively charged oxygen species on the surface to the defect in the bulk. The result is shown in Fig. 4.

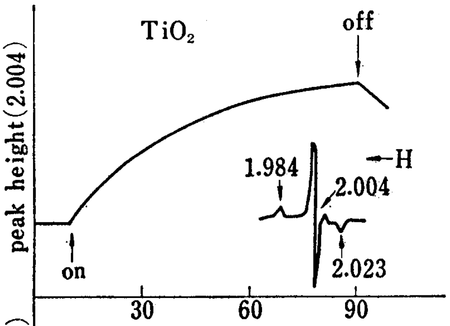

Fig. 3. Changes in the Spin Density of the g=1.984, 2.004, 2.023 Signal due to Photoirradiation. Residual O_2 Pressure: 40 Torr

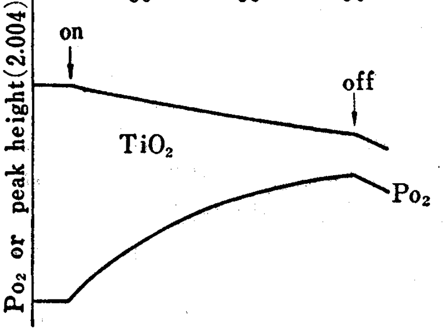

Fig. 4. Changes in the Spin Density of the g=1.984, 2.004, 2.023 Signal and the Residual Oxygen Pressure due to Photoirradiation. Residual O_2 Pressure: 10^{-4}—10^{-5} Torr

3. ZrO_2-O_2

Semiconducting properties of ZrO_2 are little known. The ESR spectrum for oxygen adsorbed on ZrO_2 was essentially the same as that on ZnO or on TiO_2; the ESR signals due to adsorbed oxygen on these oxides are compared in Fig. 5. A triplet signal at g=2.003, 2.008 and 2.027 was developed when oxygen was introduced to the ZrO_2 sample at room temperature. The growth of the triplet was rather slow, but when wavelengths of 250—380 mμ were used for illumination, the triplet increased much faster. Thus, it may be assumed that photoadsorption of oxygen occurred.

It was supposed that photodesorption may occur on a highly outgassed sample just as the case of ZnO. However we were unable to demonstrate this experimentally; the ZrO_2 sample, kept under a very low oxygen pressure, gave rise to only a faint photoadsorption. The heat of formation of ZrO_2 is much greater than that of ZnO or TiO_2. The absence of photodesorption of oxygen would probably be due to the difficulty in reaching a reduced state.

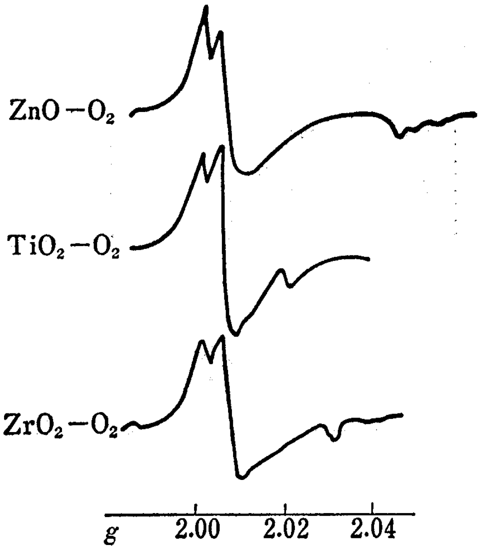

Fig. 5. The Triplet ESR Signals due to Adsorbed Oxygen Species on ZnO (g=2.002, 2.008, 2.049), TiO_2 (g=2.003, 2.009, 2.019) and ZrO_2 (2.003, 2.008, 2.027).

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