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Relaxation of Photogenerated Carriers under He, H₂, CO₂ and O₂ on ZnO

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The relaxation process of photogenerated carriers was investigated using conductivity measurement on ZnO under He, H$_2$, CO$_2$ and O$_2$. The process was well explained with the rate constant of reaction or recombination of hole and electron, k_h and k_e ($k_h > k_e$), respectively. Generally, k_h increased with the pressure of the gases. The slope of k_h with respect to the pressure increased in the order of H$_2 \leq$ He < CO$_2$, while k_h of O$_2$ was sensitive to the history of the sample. The relaxation process on ZnO which was exposed to oxygen at 298 K and 573 K was observed during the illumination at 298 K and it was found that the rate constant of hole decreased with illumination time. From the result, it was suggested that the rate constant of photogenerated excess carriers was affected by the surface barrier of the semiconductor.

Introduction

Photocatalysis on solid surface is an important field in environmental science and surface photochemistry, and it involves absorption of photon by solid and admolecules accompanying a change of the population of electron in the energy levels of solid and admolecules, and electron transfer between them. When the solid is a semiconductor, the absorption of photon induces an excitation of electron from valence band to conduction band of the semiconductor and increases the number of electron and hole in the valence and the conduction bands, respectively. Then, the photogenerated excess carriers react with chemical species or recombination centers to release the photon energy. In the photocatalytic process, the reaction of minority carrier in the relaxation process is more important than that of majority carrier since the majority carrier can react with the chemical species even in the absence of photon. For example, photodecomposition of organic molecule on TiO$_2$ (n-type) is initiated by the reaction of photogenerated hole (minority carrier) with the molecule or with water molecule forming hydroxyl radical,[1,2] while electron (majority carrier) does not contribute to the reaction pathway of the photo-

catalytic reaction. Therefore it is necessary to understand the (reaction) rate constant of the minority carrier to improve the yield of photocatalytic reactions. In this paper, the rate constant of photogenerated hole was studied by means of the relaxation of photoconductivity on ZnO (n-type semiconductor) under several gases. The relations of the rate constant with the height of surface barrier, surface state concentration and cross-section of the adsorbed species were discussed.

Basic Concept

When we illuminate a semiconductor with photons having the energy greater than the band gap energy, electrons in valence band excite to conduction band and there is a deviation from the thermal equilibrium in the concentration of carriers. After blocking of the light, the photogenerated holes and electrons recombine with specific rates. We can trace the relaxation process from the decay of conductivity of semiconductor.

For the case of direct recombination of photocarriers, the photoconductivity, $\Delta\sigma$, can be written as

$$\Delta\sigma = Ae^{-kt} \tag{1}$$

If photogenerated carriers react with different chemical species or trap centers, the conductivity can be expressed with different rate constants for the carriers as

$$\Delta\sigma = A \cdot \exp^{-k_e t} + B \cdot \exp^{-k_h t} \qquad (2)$$

where A and B are the conductivity of excess electron and hole at $t=0$ while k_e and k_h are the rate constants of electron and hole, respectively. When there are many reaction or trap centers, the rate constant k in Eq. (2) becomes

$$k_i = \sum_j k_{ij} \cdot n_j \qquad (3)$$

where k_{ij} is the capturing cross section for the carrier i to combine with j-th center and n_j is the number of the j-th center. Actually, the decrease of photogenerated carriers on the surface can be analyzed as migration of the carriers to surface and the reaction of the carrier with surface states. The movement of the carrier from bulk to surface is usually controlled by the energy barrier near the surface for the carrier. For example, the migration of hole is enhanced when the surface barrier of depletion layer increases while that of electron reduced. When we use Eq. (2) to trace relaxation processes, the k's may include the effect of the surface barrier.

Experimental

The conductivity measurement was carried out using ZnO pellet (10 mm × 30 mm × 1 mm, 99.999%, New Jersey Zinc Co.) which was pressed under 4 ton/cm² and sintered at 1000 K. Gold was evaporated to the corners of the sintered pellet for electric leads. Gold wires were welded to the evaporated gold surface on the sample and connected to a feedthrough. To observe the effect of gases, we used He (99.999% Matheson), H₂ (99.99%, Korea Standard Institute), CO₂ (99.999%, Matheson), and O₂ (99.999% Matheson). A 150 W Xe-lamp was used as a light source and irradiated to the sample through a sapphire window. The number of photogenerated carriers was 1×10^{10}/sec · cm². In all of the measurements, the sample was treated under 1.0×10^{-7} torr for 5 minutes at 673 K before exposures to gases. All conductivity measurements with respect to illumination time were carried out at 298 K. The experimental setup for conductivity measurement was constructed with a DC voltage source, I-V converter (Keithley Co.), 12 bit ADC (Axiom Co.) and an AT-type personal computer. The light was pulsed with a modified camera shutter. The rate of relaxation constant of electron (k_e) and hole (k_h) was calculated from the conductivity data and the model equation.

All of EPR measurements were performed with ZnO powder (99.999%, New Jersey Zinc Co.) at 77 K. The g-values and relative intensities were calculated by comparing the g-value and integrated area of the DPPH signal. The EPR sample tube was connected by Teflon to a conventional vacuum apparatus. In the photoeffect experiments, the EPR sample tube was made flat to 0.5 mm. The increase of photogenerated carriers on the sample in EPR tube was about 2×10^{13}/sec · cm² at 77 K.

Results and Discussion

Figure 1 shows the variation of EPR spectra of ZnO de-

pending on illumination at 77 K under 1.0×10^{-7} torr. When ZnO was evacuated at 773 K for 40 min, a nearly symmetric signal with g=1.960 (signal A) and a signal g=2.0032 (signal B) were observed as shown in Figure 1-1. Signal A has been assigned to conduction electrons, unionized Zn⁺ donors, and F centers.[3,4] It was reported that signal B (g= 2.0032) originated from the electron in highly dispersed Zn atoms or zinc clusters produced by the reduction of ZnO or the removal of lattice oxygen similar to Ru on ZnO.[5] When the sample was illuminated under vacuum at 77 K, there was an increase in the signal of electron (signal A), together with appearance of a new signal with g=2.014 (signal C) as well as a new asymmetric signal with g=2.020, 2.002, 2.001 (signal D) as shown in Figure 1-2. It was also reported that signal C and signal D originated from trapped hole in symmetric and asymmetric sites, respectively.[6] Cutting off the light at the same condition, signals C and D were slightly decreased but there was almost no change in the signal of electron. When the sample was heated to 298 K for 10 min and cooled to 77 K, signals C and D disappeared completely while signal A was larger than that of preilluminated state as shown in Figure 1-3. These facts indicate that the photogenerated hole disappeared faster than that of the electron.

Figure 2 shows the response of conductivity under illumination. After the light was shut off, the change of the conductivity can be resolved to the sum of two exponential decays with different rate constants. The rate constant of the excess carrier is the sum of the products of concentration and capturing efficiency of reactant or trap centers. If all kinds of species at the surface of the sample are desorbed by the thermal pretreatment, the calculated rate constants can be regarded as the rate constants originating from the
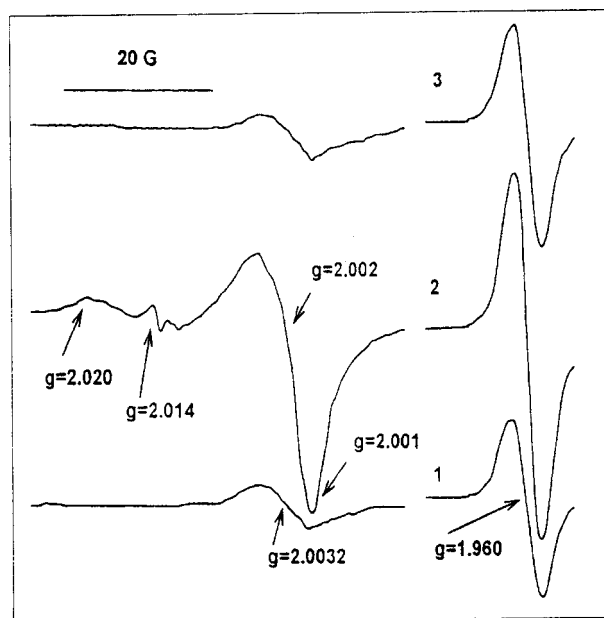

Figure 1. The variation of EPR spectra of ZnO depending on illumination at 77 K. Spectrum 1 was observed from ZnO after an evacuation (base pressure: 10^{-7} torr) at 773 K for 40 min. Spectrum 2 was observed after an illumination on ZnO with spectrum 1. Spectrum 3 was obtained at 77 K after heating the sample with spectrum 2 to 298 K for 10 min.
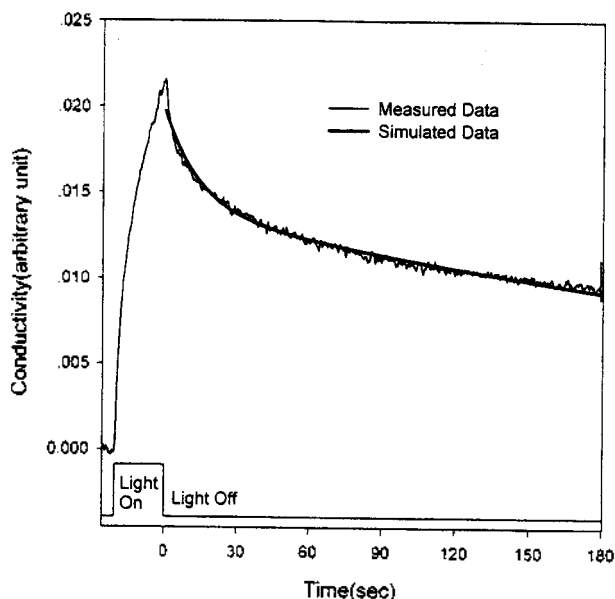
Figure 2. The variation of photoconductivity on ZnO depending on illumination at 298 K. The model equation is $0.014e^{-0.0024t}+0.0054e^{-0.0741t}$.

photogenerated holes and electrons in the bulk of ZnO. Taking into account the results of EPR, the rate constant with greater value corresponds to that of hole. For the case of Figure 2, k_h and k_e were 0.074 and 0.0024 sec^{-1}, respectively.

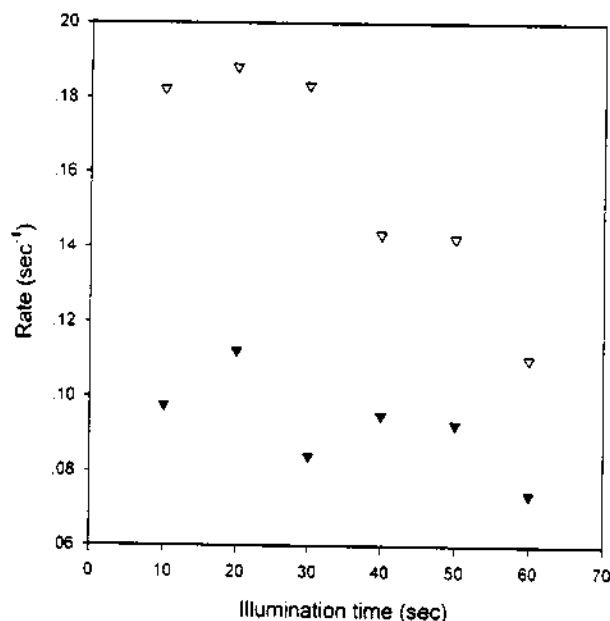Figure 3 shows the variation of k_h depending on the pressure of oxygen at 298 K. Comparing to He, H_2 and CO_2, k_h under oxygen was greater than other gases. The reason for the high value of k_h in oxygen can be found from a high value of the product of concentration and cross section of adsorbed oxygen species and/or the effect of surface barrier. In the previous study, the quantity of the adsorbed amount
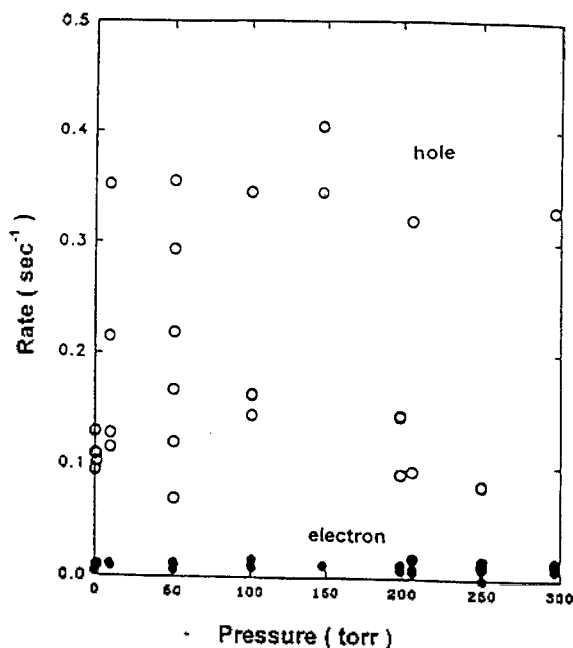
of oxygen on ZnO was measured by means of capacitance and the coverages of the negatively charged species were less than 10^{-3} and 10^{-4} monolayers at 298 K and 573 K, respectively.[7] Thus we can exclude the high value of the product of concentration and cross section from the reason. On the other hand, it was proved that oxygen adsorbs on ZnO as acceptors (O_2^- and O^-) and develops a depletion layer on the surface.[7-9] Since hole can migrate easily to surface in the depletion layer originated from the adsorption of oxygen, the overall value of k_h increases compared to other gases. We tried to find a relation between oxygen pressure and k_h but the result was too historically sensitive to write quantitatively.

Figure 4 shows the effect of illumination on the rate constant of hole for the sample treated at 298 K and 573 K in oxygen. After 10 sec irradiation, k_h of oxygen treated sample at 573 K was 0.18 sec^{-1} while that of 298 K was 0.098 sec^{-1}. The fact can be explained as the amount of adsorbed oxygen at 573 K is greater than that of 298 K and the surface barrier is lower for hole in the relaxation process. It agrees to the measured coverage of the oxygen on ZnO crystal[7,10] or sintered pellets.[11] When the sample treated at 573 K was irradiated at 298 K under 500 mtorr O_2, k_h decreases gradually to k_h of 298 K as shown in Figure 4. The decrease in k_h means the surface barrier for the hole migration is reduced by the reaction of photo-generated hole with the anionic oxygen species accompanied a decrease in the depletion layer. In the previous study, it was confirmed that the adsorption of oxygen on ZnO is primarily depend on the migration of electron from the bulk to surface.[12] Thus the photogenerated electron at 298 K cannot overcome the barrier generated in O_2 adsorption at 573 K while the movement of photogenerated hole is not affected by the barrier. As the barrier is lowered by the reaction of the photogenerated hole and oxygen species, the movement of electron and the reac-
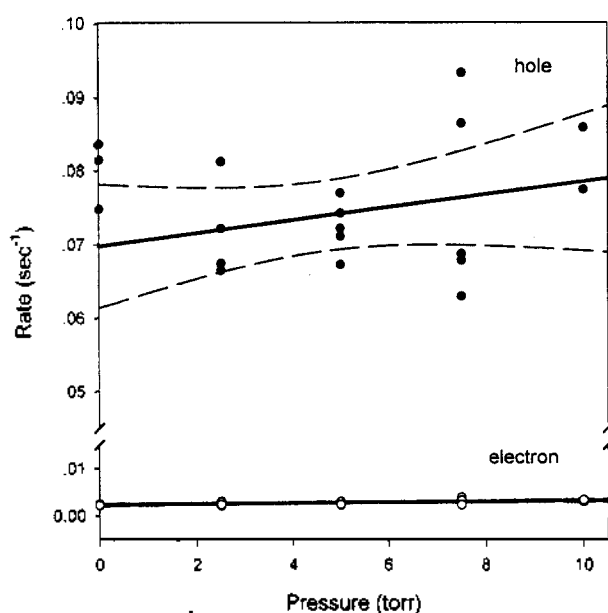

Figure 3. The rate constants of relaxation of photogenerated carriers depending on the pressure of oxygen at 298 K.

Figure 4. The rate constants of relaxation of photogenerated hole with illumination time at 298 K. The sample was treated with oxygen at 298 K (▼) and 573 K (▽), respectively.
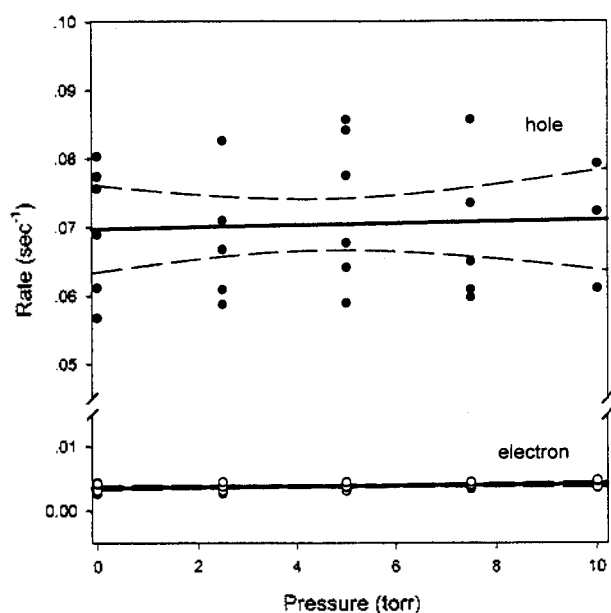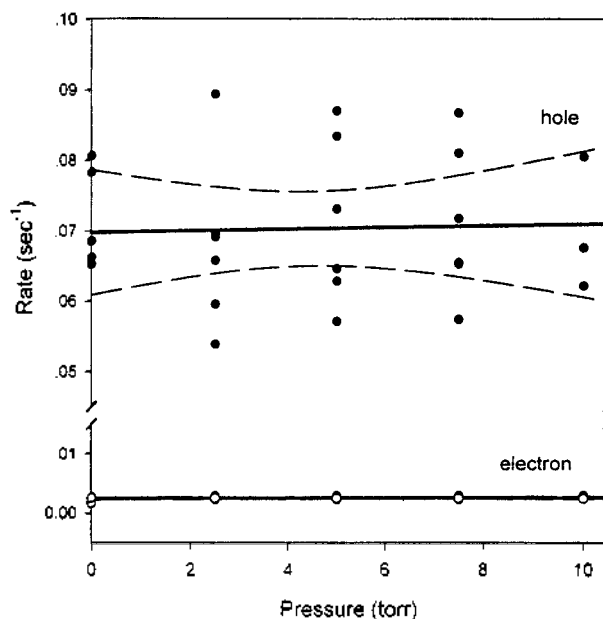
Figure 5. The rate constants of relaxation of photogenerated carriers on ZnO depending on the pressure of helium at 298 K. The lines were satisfied with 95% confidence.

tion of electron with oxygen enhanced and the barrier approaches to that of the treatment at 298 K. By the way, there is only small change in k_h for the case of the oxygen treatment and irradiation at 298 K as shown in Figure 4.

In order to compare the reaction efficiency of photogenerated holes depending on gases, k_h was measured under He, H_2, and CO_2, respectively. The slope of k_h with respect to the gas pressure increases in the order of $H_2 \leq He < CO_2$ at the same condition. Figure 5 shows the rate constant of hole under helium atmosphere at 298 K. The estimated equation of the plot is as follows: k_h (sec^{-1})=0.0697+1.29×

Figure 6. The rate constants of relaxation of photogenerated carriers on ZnO depending on the pressure of hydrogen at 298 K. The lines were satisfied with 95% confidence.

Figure 7. The rate constant of relaxation of photogenerated carriers on ZnO depending on the pressure of carbon dioxide at 298 K. The lines were satisfied with 95% confidence.

$10^{-4} \times P_{He}$, where P_{He} is the pressure of He in torr. The value is nearly similar with the case of vacuum state. Since helium is not adsorbed on the sample, a small increase in the rate can be explained in terms of the reaction of photogenerated carriers with the gaseous helium near the surface.

Figure 6 shows the rate constants of hole under hydrogen atmosphere. The estimated equation of the plot is k_h (sec^{-1})= $0.0697+1.17 \times 10^{-4} \times P_{H_2}$, where P_{H_2} is the pressure of H_2 in torr. The value of the rate constant is lower than that of He. This fact can be explained as H_2 induces a restriction on the relaxation process of hole from the change of the surface barrier and/or the decrease in product of the amount and the cross section of the reaction or trap centers compared to He. In previous studies, it was reported that H_2 adsorbed as a donor on ZnO and the amount of adsorption is near to monolayer at 298 K.[13] Thus we can suggest the decrease of k_h in H_2 atmosphere may originated from a development of an accumulation layer and diminution of the migration of hole to surface.

Figure 7 shows the plot of the rate constant for the photogenerated holes under CO_2 atmosphere. The estimated equation of the plot is k_h (sec^{-1})=$0.0697+8.69 \times 10^{-4} \times P_{CO_2}$, where P_{CO_2} is the pressure of CO_2 in torr. A large slope in Figure 7 compared to other gases indicates a high capturing efficiency of the adsorbed CO_2 for the hole. Photodesorption of CO_2 from ZnO surface was interpreted in terms of the capture of a photogenerated hole by an adsorbed CO_2^- ion to produce neutral CO_2 and thermal desorption of neutral CO_2 from the surface.[14]

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Synthesis of New Biodegradable Crosslinked Polyesters for Biomedical Applications and Their *In-Vitro* Degradation

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Two kinds of new aliphatic diols were synthesized by the ring-opening reaction of lactide and glycolide with 1, 4-butanediol, a difunctional initiator, in the presence of stannous octoate. The resulting aliphatic diols were melt-polymerized with D-tartaric acid at 150 °C to produce new crosslinkable polyesters. They were reacted with hexamethylene diisocyanate in THF at 65 °C in a teflon mold for 24 h to prepare sequentially ordered crosslinked polyesters (BD/LT/GL/D-tartarate). Degradation of the prepared yellow crosslinked films was carried out in a buffer solution in order to examine the effect of time, pH, temperature and crosslinking degree on their degradation rate and mechanism. The rate of degradation increased with an increase in pH and temperature, but it decreased with increasing degree of crosslinkage incorporated into the crosslinked polyesters. We also found that the crosslinked polymers were converted into the acidic compounds such as lactic, glycolic, and D-tartaric acids during the degradation.

Introduction

Aliphatic polyesters from cyclic lactones such as lactide, glycolide, ε-caprolactone and so on have attracted much attention in biomedical applications as medical sutures, drug delivery systems, and internal bone fixation, because these polymers have excellent biodegradability and biocompatibility.[1-3] Although metallic devices such as plates, screws, and rods' have been widely used in osteoplasty for internal fixation of bone fractures, basically they have two serious problems: one is osteoporosis due to stress protection atrophy and the other is that these nondegradable devices require a second surgical operation for their removal after the bone is healed.[4,5] To overcome these problems, therefore, it has been investigated many studies on biodegradable and bioabsorbable polymeric composites in replacement of metallic devices.[6-8] Especially, biocompatible polyesters from lactide and glycolide have been mainly studied as degradable matrix resins of biomedical composites.[9,10] These thermoplastics, however, also have inherent difficulty in interfacial wetting with reinforcing fibers, which limits optimum stress transfer between fiber and matrix.[7] This seriouly affects hydrolytic stability.[6]

In order to overcome these disadvantages, S. J. Huang *et al.* have examined the possibility of application of crosslinked polymers as matrix materials for composite bone plates.[11] They have focused either on the introduction of crosslinkable unsaturated double bonds into aliphatic polyesters derived from α-hydroxy acids or on their thermal crosslinking that causes morphological change.[12,13]

In this work we report synthesis of new sequentially ordered crosslinked polyesters and their *in-vitro* degradation in a buffer solution. We will also describe the effect of the structural factors on the degradation mechanism.

Experimental

Materials. D,L-Lactide and glycolide from Polyscience were sublimed at 100 °C and 90 °C, respectively, under vacuum prior to use. 1,4-Butanediol was distilled over calcium hydride to remove water. 1,6-Hexamethylene diisocyanate (HMDI) and all the solvents were purified in the usual manner. Stannous octoate (tin(II)-2-ethyl hexanoate), p-toluenesulfonic acid, D-tartaric acid were used without further purification. Buffer solutions were used as received from Micro Essential Laboratory.