Oxygen Adsorption Process on ZnO Single Crystal

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which isotope is enriched and how it behaves with time in a baby.

Conclusion

In conclusion, Ca isotope ratios could be measured precisely by removing water related isobaric interferences. Liquid Ar cryogenic condenser was used in addition to a conventional condenser and membrane desolvator. Drift was corrected with frequent calibration of standards. The technique was applied to feces from a baby dosed with ^{44}Ca enriched milk. For biological samples, it was found that Na could give an erroneous Ca isotope ratio, and that matrix separation was beneficial for more precise determination of isotopic ratios. Currently, RSD is 0.5-1.0% for the ratio of ^{42}Ca/^{44}Ca in 10 minutes of total measurement time. However, it can be improved easily if just two isotopes are monitored with a longer observation time.

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Oxygen Adsorption Process on ZnO Single Crystal

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The adsorption of oxygen on ZnO was monitored by measuring the capacitance of two contacting crystals which have depletion layers originated from the interaction between oxygen and ZnO at 298 K-473 K. An admission of oxygen to the sample induced an irreversible increase in the depth and the amount of adsorbed oxygen was less than 0.001 monolayer in the experimental condition. The relation between pressure of oxygen and variation of the depth was tested from the view point of Langmuir or Freundlich isotherm. Using Hall effect measurement and kinetic experiment, a model equation on the adsorption process was proposed. From the results, it was suggested that oxygen adsorption depended on the rate of electron transfer from ZnO to oxygen while the amount of adsorbed oxygen was kinetically restricted by the height of surface potential barrier.

Introduction

The electron transfer between gas species and semiconductor surface induces a surface layer such as a depletion layer or an accumulation layer depending on their mutual energy levels.[1] The layer characterizes not only chemical and electrical properties of the surface but also catalytic processes. The surface layer theory is often tested on ZnO powder and single crystal because the electron configurations of zinc ion is d^{10} and they have negligible activity compared to the other transition element ions. The properties of the layer which was developed in adsorption process were characterized by potential barrier and carrier density near the surface.[2-6] In general, oxygen was adsorbed on anion vacancy or surface defect by capturing the conduction electron of ZnO.[7] In 1950, Weisz first pointed out the fact that, no matter how impure the sample, the surface coverage is limited to about 10^{-3}-10^{-2} monolayer of equilibrium adsorption when a depletion layer is present.[8] Unfortunately, there is no direct quantitative evidence of the theory until now.

Since the depletion layer has very low concentration of

carriers compared to the bulk, a capacitance will be observed when two crystals are placed in facing each other and the surfaces have depletion layers. Thus the depth of the layer can be measured from the capacitance of the system. From this physical suggestion, we have previously developed an experimental method to measure the depth of depletion layer quantitatively by measuring the capacitance of two contacting faces of $ZnO(10\bar{1}0)$.[9-11] In the present study a kinetic model has been proposed on the adsorption process of oxygen on ZnO by pursuing the capacitance of two contacting $ZnO(10\bar{1}0)$ faces.

Experimental Section

When electrons transfer from a n-type semiconductor to gas molecules, the electron density of the semiconductor surface becomes lower than the bulk and two contacted crystals can be considered as a parallel capacitor. In principle, the total capacity C_t of the sample system (lead-semiconductor-space-semiconductor-lead) can be expressed as

$$\frac{1}{C_t} = \frac{1}{C_{s_1}} + \frac{1}{C_g} + \frac{1}{C_{s_2}} \tag{1}$$

where C_{s_1} and C_{s_2} are the capacitance originated from the space charge regions, the depletion layers of the crystals 1 and 2 and C_g is the capacitance depending on dielectric constants of the space and the mean distance between the two crystals. The depth of the layer of crystal i, d_i can be calculated from C_{si} using the simple relation,

$$C_{si} = \frac{\kappa \varepsilon_o A}{d_i} \tag{2}$$

where κ, ε_o and A are the dielectric constant of ZnO, 8, the permittivity of free space, 8.854×10^{-12} $C^2m^{-1}J^{-1}$, and the area of the faces, respectively. The distance between two contacting crystals estimated from the maximum value of C_t was less than 100 Å. Since the $1/C_t$ is greatly influenced by smaller value of any C, i.e. C_{si} or C_g, and d_i spans to several thousand Å in the experiment, we can include $1/C_g$ to $1/C_s$'s in the Equation 1. Now the apparent depth of the depletion layer, d, is monitored with the relation

$$C_t = \frac{\kappa \varepsilon_o A}{2d} \tag{3}$$

The change of the number of charges per unit area on the surface, ΔN_s, during an adsorption process can be calculated from the variation of the depth of depletion layer, Δd, as

$$\Delta N_s \cong N_D \cdot \Delta d \tag{4}$$

where N_D is the density of ionized donor levels of the crystals or the concentration of free carrier of the bulk at the given temperature. The value of N_D is measured from Hall effect measurement while the apparent depth of the depletion layer is estimated from the capacitance.

The capacitance between two contacted crystals is measured using a modified bridge consisting of a function generator, a lockin amplifier, and an AT type personal computer having ADC and DAC interfaces as shown in Figure 1. The personal computer scanned the amplitude of Vc and Vr through DAC's and the capacitance of the sample was
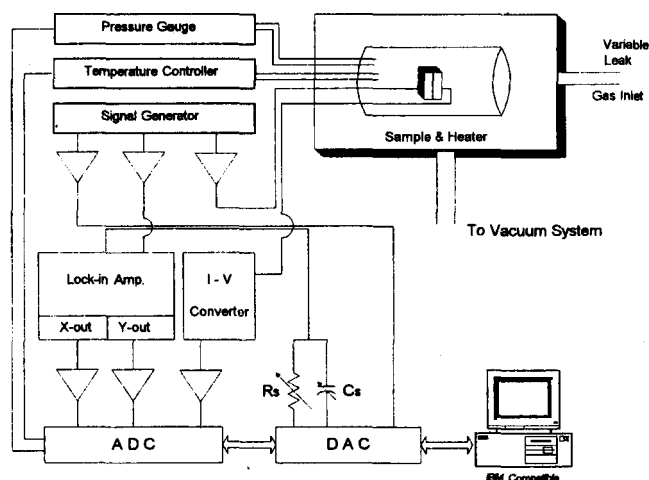

Figure 1. Schematic diagram of experimental setup to measure the capacitance between two contacting ZnO crystals.

calculated from Vc, Vr, Vs, and Cs when the output of the lockin amplifier became zero. Where Vc, Vr are the applied voltage to standard capacitor and standard resistor from DAC, Vs is the applied voltage to the sample and Cs, Rs are the standard capacitor and resistor, respectively. The system is programmed to obtain a value within 2-3 seconds. The 400 Hz, 0.5 Vpp sine wave is used but there is no significant change in capacitance up to 5 Vpp.

The purity of oxygen was 99.95%. Polished single crystals of $ZnO(10\bar{1}0)$ are obtained from Atomergic Chemetals Co. and the size is $4 \times 3 \times 1$ mm^3. For an electrical lead, a thin film of gold is deposited on one face of the crystal. Two faces of $ZnO(10\bar{1}0)$ are contacted with four screws in a sample assembly and the electrical leads connected to a feedthrough. The base pressure of the system is below 10^{-5} N/m^2. Gases are introduced through a variable leak valve and a series of experimental procedure are performed without moving to eliminate any change in contacted position of the sample. The sample has been heated with nichrome wire embedded in alumina rods that are physically connected to the sample assembly. The temperature of the sample is measured with a K type thermocouple welded to a rod supporting the crystals. The temperature is controlled with a custom-made temperature controller based on a personal computer.

Results and Discussion

Pretreatment of ZnO. The concentration and the mobility of electrons of the single crystal at 298 K-473 K are obtained using Hall effect measurement (Table 1).

To estimate pretreatment condition for the adsorption experiments, total capacitance between two contacting crystals is measured during evacuation of the system at 773 K under base pressure of 1.3×10^{-5} N/m^2. The apparent depth of a depletion layer decreases drastically during the first 10 minutes and approaches to the range of 40 Å and 100 Å after 1 hour. It seems that the variation is originated from surface irregularities, matching characteristics of two contacting faces, and the original depth after the pretreatment. Therefore it is considered that this range of the depth is

Table 1. The results of Hall effect measurements*

Temp.	Electron density (m^{-3})	Mobility $(m^2V^{-1}sec^{-1})$
298 K	5.65×10^{21}	175×10^{-4}
373 K	6.32×10^{21}	132×10^{-4}
473 K	6.90×10^{21}	96×10^{-4}

*Hall effect is measured using van der Pauw method (four point method).

derived from C_g. The experimental setup is checked by repeated exposures of the sample assembly to oxygen at 573 K and evacuation at 773 K as shown in Figure 2. The variation of the depth after the exposure-evacuation process is very small compared to the total variation in the process. The evacuation of the crystal at 773 K for 1 hour eliminated the most part of the adsorbed oxygen species and the increase in the depth during the oxygen adsorption indicated the formation or increase of a depletion layer. In the adsorption experiments, the sample assembly is evacuated for 1 hour at 773 K and admitted oxygen to the system at adsorption temperatures.

Adsorption. Figure 3 shows the variation of the apparent depth of depletion layer depending on the pressure of oxygen at 298 K, 373 K and 473 K, respectively. To observe the variation of the depth depending on the pressure of oxygen, the pressure was maintained to indicated value for 20 minutes and then degassed to base pressure $(<10^{-5}$ $N/m^2)$ as shown in Figure 3. The alternative gas pressure increment gave us a direct evidence that the adsorbed oxygen did not readily desorb at the temperature. As shown in Figure 2-2, 2-4, 2-6, the depth varied drastically within ten minutes after admission of oxygen. Thus the interaction may be reached to an equilibrium or a limitation state after
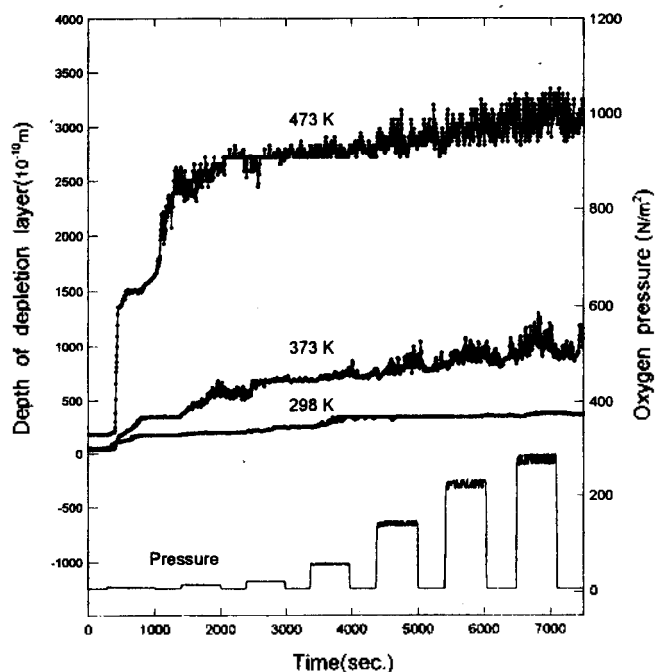

Figure 3. Variation of the depth of depletion layer of $ZnO(10\overline{1}0)$ depending on the oxygen pressure at 298 K, 373 K, and 473 K, respectively.

twenty minutes from the admission of oxygen at experimental conditions. In these experiments, the types of oxygen species are not identified but Chon et al.[2] had been verified the species and reported previously. It is well known that oxygen consumes electrons of ZnO in the adsorption process and the depletion layer is formed.[1,7] The variation
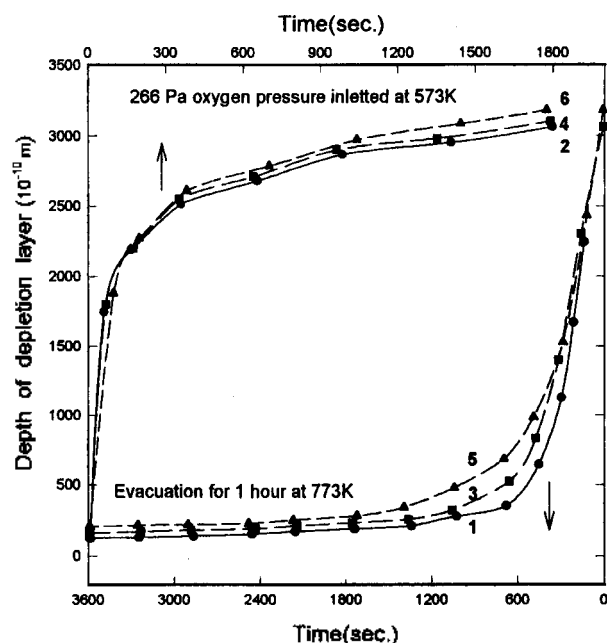

Figure 2. Variation of the depth of depletion layer of $ZnO(10\overline{1}0)$ during the evacuation of the sample at 773 K and exposure of the sample to oxygen at 573 K. Numbers indicate the treatment sequence.
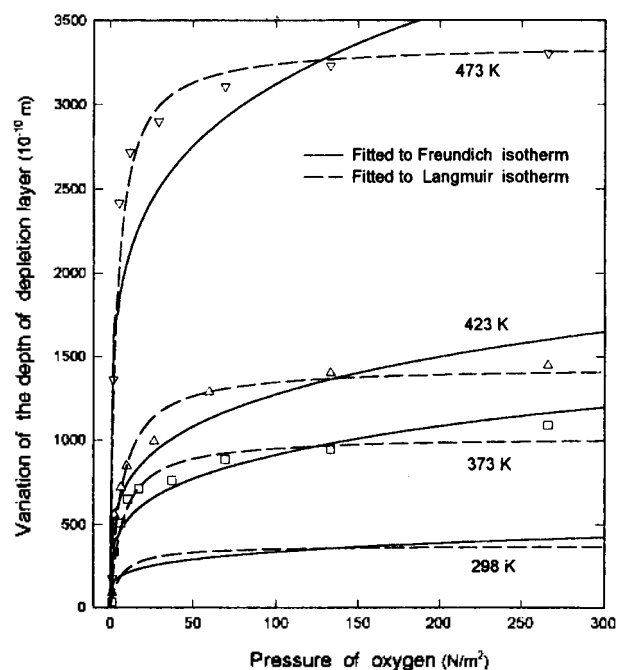

Figure 4. Effect of the oxygen pressure on the depth of depletion layer of $ZnO(10\overline{1}0)$ at various temperatures. The dashed and solid lines represent the least square estimated Langmuir and Freundlich type isotherms, respectively.

Table 2. Variation of the amounts of charges depending on O_2(266 N/m^2) adsorption and the parameters from the fits based on Langmuir and Freundlich type isotherms at each temperature

Temp.	Layer depth $(10^{-10}$ m)	N_s^a $-(N_d$-$N_o)\cdot\Delta d$ (m^{-2})	Monolayer[b]	Langmuir type[c]			Freundlich type[d]		
				a	b	cd[e]	k	m	cd
298 K	3.70×10^2	2.09×10^{14}	1.04×10^{-5}	58	0.16	0.95	128	0.21	0.81
373 K	1.09×10^3	6.89×10^{14}	3.45×10^{-5}	139	0.13	0.89	299	0.24	0.65
473 K	3.30×10^3	2.28×10^{15}	1.14×10^{-4}	938	0.28	0.91	1360	0.18	0.68

[a] Negative sign means that the charges are exhausted from the surface depends on the adsorption. [b] There are the order of 2×10^{19} surface atoms/m^2 on a typical crystallographic plane. [c] $d=aP/(1+bP)$, units of d and P are 10^{-10} m and N/m^2, respectively. [d] $d=kP^m$, units of d and P are 10^{-10} m and N/m^2, respectively. [e] cd (coefficient of determination)=1-(SSE/SST), where SSE is the error sum of square and SST is the total sum of square.

of the depth is regarded as the amount of adsorbed oxygen. Figure 4 and Table 2 show the variation of the depth Δd, amount of the charges involved in the adsorption process and the best fit parameters based on Langmuir and Freundlich isotherms. The values of the depth are adapted after exposure of the sample to oxygen for 20 minutes. The type of oxygen adsorption on ZnO single crystal might be more close to Langmuir type isotherm than Freundlich one. However it is not perfectly coincide with that type of isotherm.

Adsorption process. Figure 5 shows the variation of the depth with time at 298 K, 373 K, and 473 K when 6.7 N/m^2 of oxygen is admitted to the sample previously evacuated at 773 K for 1 hour. The depth of the layer increases with time while the rate of the increment decreases as the depth becomes large. The adsorption process can be analyzed in terms of the transfer of electron from bulk to surface and reaction of the electron with oxygen molecule while the desorption process depends on detachment of electron from adsorbed species and movement of the electron to bulk.

The rate of adsorption is proportional to number of the bare sites N_o, the gas pressure P, and the Boltzmann factor

Figure 5. Variation of the depth of depletion layer of ZnO($10\overline{1}0$) with time at several temperatures when the 6.7 N/m^2 of oxygen pressure is admitted to the system.

originating from the surface barrier V_s ($e\cdot ND\cdot\Delta d^2/2\kappa\varepsilon_o$), or equal to k_a P N_o $\exp(-eV_s/kT)$. The rate of desorption is taken to be proportional to number of occupied sites N or equal to k_d (N_t-N_o) where N_t is the total number of adsorption site on the surface. The rate of adsorption can be written as

$$\frac{dN_s}{dt} = k_a P (N_t - N_s) \exp(\frac{-e V_s}{RT}) - k_d N_s \qquad (5)$$

The coverage of the charged state on ZnO is usually less than 1% and the Equation 5 will be

$$\frac{dN_s}{dt} = A \cdot P \exp[-B \cdot N_s^2] - C \cdot N_s \qquad (5)'$$

where A, B and C are k_a N_t, $\dfrac{-e^2}{2\kappa\varepsilon_o N_D RT}$, and k_d, respectively.

The fitted parameters of Equation (5)' calculated from Figure 5 and the result of the statistical test based on the model are listed in Table 3. The values of coefficient of determination are near 1.00 and it means that the kinetic model is acceptable in the system. The results supports the Weisz's suggestion[8] that ionosorption on semiconductor is a kinetically controlled system and the coverage of the surface is restricted by the surface potential barrier. The increase in A with temperature means that k_a includes a term of activation energy of the reaction between oxygen and electron.

Lagowski *et al.*[3] measured contact potential during oxygen exposure and they suggested that oxygen and electron penetrated the surface barrier must overcome the activation energy of adsorption. The term, $\exp[-B\cdot N^2]$ represents the effect of number of surface states on the probability to overcome the surface barrier energy and it is expected that the value of B decreases with temperature. The concentration of charged states of oxygen is able to be estimated when the surface barrier is equal to kT from B values. In the present experiment, the concentration at 298 K, 373 K and 473 K
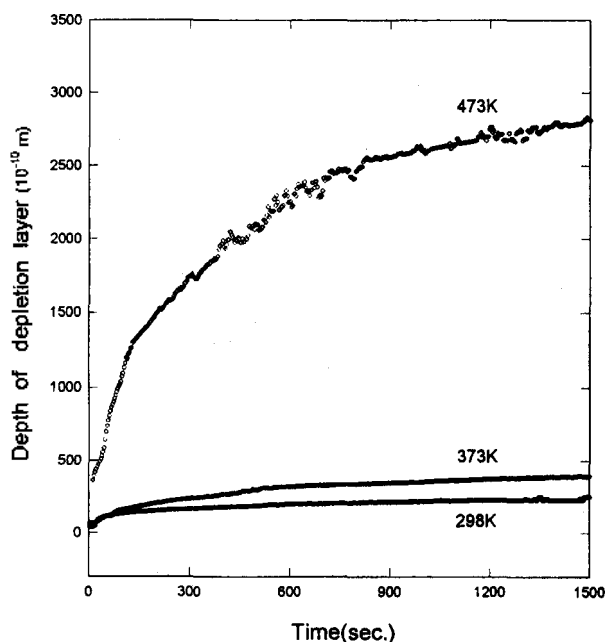
Table 3. A list of the parameters of the kinetic model[a] for Figure 4

Temp.	A^b	B^c	C^c	cd
298 K	8.91×10^{10}	3.78×10^{-28}	5.32×10^2	0.93
373 K	1.07×10^{11}	6.81×10^{-29}	5.32×10^2	0.98
473 K	1.11×10^{12}	1.01×10^{-30}	5.32×10^3	0.98

[a] $dN_s/dt=A\cdot P$ $\exp$ $[-B\cdot N_s^2] - C\cdot N_s$ (see text). [b] Unit in [states/(N·sec)]. [c] Unit in [m^4/(states)^2]. [d] Unit in [1/(m^2·sec)].

are 5.1×10^{13}, 1.2×10^{14} and 1.0×10^{15} states/m², respectively. If it assumes that one monolayer corresponds to 10^{19} states/m², 1.0×10^{15} states/ma² does to 10^{-4} monolayer when the height of surface barrier is comparable to kT at 473 K. Therefore the adsorption of oxygen on ZnO is controlled by the surface barrier even very low coverage of oxygen species. The rate constant of desorption C is very small compared to that of adsorption A and the adsorption process can be believed as an irreversible one.

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Mechanism for the Reaction of Substituted Phenacyl Arenesulfonates with Substituted Pyridines under High Pressures

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The rates for the reaction of (Z)-phenacyl (X)-benzenesulfonates with (Y)-pyridines in acetone were measured by an electrical conductivity method at 1-2000 bars and 45 °C. The magnitudes of the Hammett reaction constants, ρ_X, ρ_Y and ρ_Z, represent the degree of Nu-C bond formation and that of C-L bond breaking. The magnitude of correlation interaction term ρ_{ij} can be used to determine the structure of the transition state (TS) for the S_N reaction. As the pressure is increased, the Hammett reaction constants, ρ_X, $|\rho_Y|$ and ρ_Z are increased, but correlation interaction coefficient, $|\rho_{XZ}|$ and ρ_{YZ}, are decreased. The results indicate that the reaction of (Z)-phenacyl (X)-benzenesulfonates with (Y)-pyridines probably moves from an associative S_N2 to late-type S_N2 mechanism by increasing pressure.

Introduction

Menschutkin reactions of alkyl halides with tertiary amine forming quarternary ammonium salts have been widely investigated under various pressures.[1-5] The study of substituent and pressure effect provides one of the most powerful tools for probing the structure of transition state. The reaction mechanism for the nucleophilic substitution reaction of substituted phenacyl benzenesulfonates with substituted pyridines in acetonitrile has been investigated through multiple Hammett correlation under atmospheric condition.[6] In this connection, we have studied the reaction of (Z)-phenacyl (X)-benzenesulfonates with (Y)-pyridines in acetone in order to investigate the substituent and pressure effect. This yielded detailed information on the transition state. One of the linear free energy relationships (LFER), the notable Hammett equation has been used as an empirical means of characterizing transition-state (TS) structures.[7-9] The Hammett coefficient ρ is first derivative of log

k as shown in equation (1) and reflects TS structures involved in a series of reactions with structural changes affecting the reaction center.

$$\rho = \partial \log k / \sigma \qquad (1)$$

The magnitudes of the ρ values in the nucleophile and leaving group can measure the degree of bond formation and bond breaking. However, it has occasionally been suggested that the ρ value cannot be used as a measure of TS structure, since the efficiency of charge transmission for different reactions series may differ.[10,11]

In previous work,[12] we proposed that the TS structure in nucleophilic substitution (S_N) reactions can be predicted by the sign and absolute values of ρ_Z and comparison of the relative value of the correlation interaction coefficient, ρ_{XZ} with ρ_{YZ}. We report our results on the substituent and pressure effect for the reaction of substituted phenacyl benzenesulfonates with pyridines as shown in equation (2), respectively.