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Measurement of The Depth of Depletion Layer in Oxidation of C_2H_4 on ZnO

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A depletion layer may develop in adsorption processes when an electron moves to adsorbate from a semiconductor. Physically, the depletion layer in semiconductor has a low concentration of carriers compared to the bulk and it can be considered as a capacitor when two crystal semiconductors are contacted with each other. In recent, the variation of the depletion layer during the adsorption of oxygen and oxidation of carbon monoxide on zinc oxide was observed by monitoring the capacitance of two contacting ZnO ($10\bar{1}0$) faces.[1,2] In this note we report the variation of the depletion layer of ZnO ($10\bar{1}0$) during the adsorption and oxidation of C_2H_4.

Experimental

Oxygen (99.99%, H_2O 15 ppm, CH_4 12 ppm) and ethylene (99.99%, C_2H_6 90 ppm) were supplied from Korea Standard Research Institute and Kumho Monsanto Co., respectively. Polished single crystal ZnO ($10\bar{1}0$) ($4 \times 3 \times 1$ mm^3) was obtained from Atomergic Chemetals Co. A thin film of gold was deposited on one side of the crystal. Two faces of ZnO ($10\bar{1}0$) were contacted with four screws in a sample assembly and attached to a 10 pin-feedthrough. The sample was heated with nichrome wire embedded in alumina rods that were physically connected to the sample assembly. In adsorption experiments, we evacuated the sample assambly for 1 hour at 773 K as previously reported[1,2] and introduced C_2H_4 to the system at adsorption temperatures. A series of experiments was executed with the sample assembly without detaching the crystal faces. The capacitance between two contacted crystals was measured using a modified bridge composed of a function generator, a lockin amplifier and an AT type personal computer having DAC and ADC interfaces as previously reported.[2]

Results and Discussion

When ZnO was exposed to C_2H_4 at 298 K, there was little change in the depth of depletion layer, but the depth increased reversibly at 373 K. (Figure 1) At the temperatures
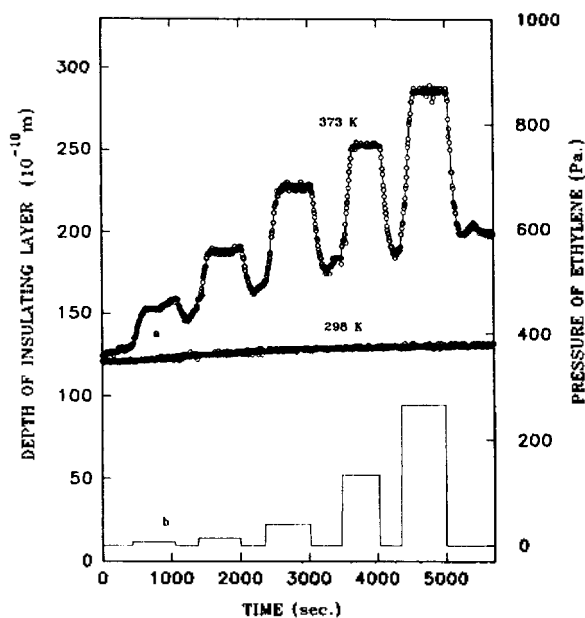
Figure 1. Variation of the apparent depth of the insulating layer (a) of ZnO ($10\bar{1}0$) depend on the pressure of C_2H_4 (b) at 298 K and 373 K.
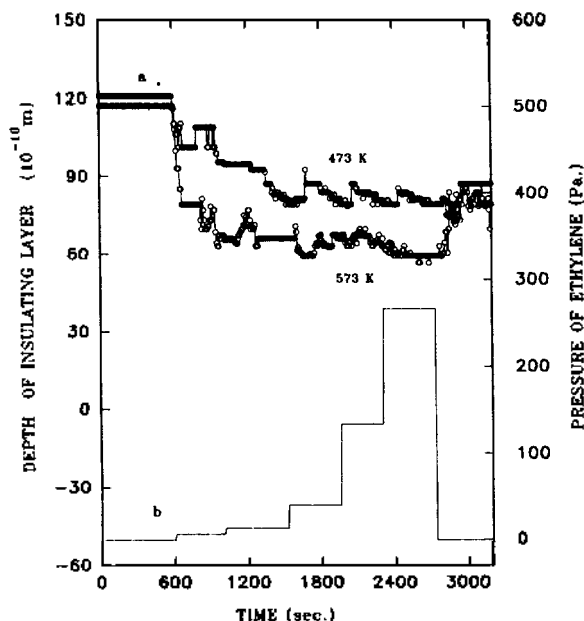

Figure 2. Variation of the apparent depth of the insulating layer (a) of ZnO ($10\bar{1}0$) depend on the pressure of C_2H_4 (b) at 473 K and 573 K.

above 473 K, the depth decreased with increasing the pressure of C_2H_4. (Figure 2) The fact suggests that C_2H_4 is adsorbed as a weak electron acceptor on ZnO at 298 K and 373 K, while C_2H_4 reacts with the lattice oxygen of ZnO and return electrons to ZnO above 473 K. The minimum apparent depth corresponds to the (harmonic) mean distance between

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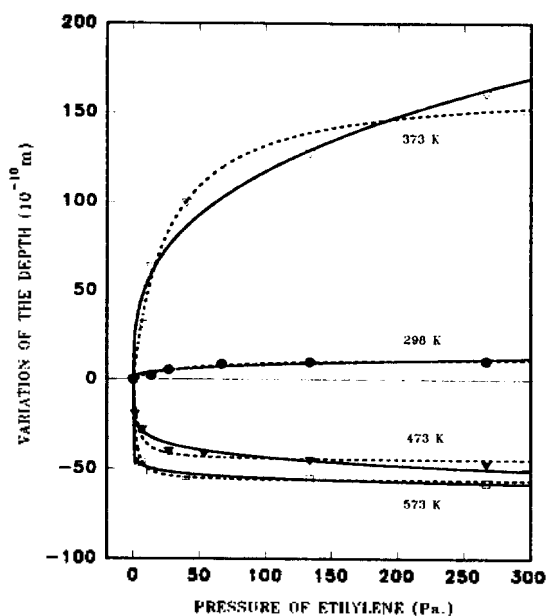
Figure 3. Effect of ethylene pressure on the depth of an insulating layer of ZnO at various tempertures. The dashed line and solid line represent the least squre estimated Langmuir and Freundlich type isotherms, respectively.

Table 1. A list of the parameters from the fits based on Langmuir and Freundlich type isotherms for the relation between the variation of the depth of the insulating layer (depletion layer) of ZnO (10$\bar{1}$0) face, d, and in the C_2H_4 pressure range of 1.3 Pa-266.6 Pa at various temperatures

Isotherm	Langmuir[1]			Freundlich[2]		
Parameters	a	b	cd	k	m	cd
298 K	0.35	0.028	0.98	1.9	0.32	0.92
373 K	6.4	0.039	0.98	26.4	0.32	0.97
473 K	−17.5	0.039	0.97	−22.4	0.15	0.98
573 K	−37.2	0.065	0.99	−43.6	0.05	0.99

[1]$d = a^*P/(1 + b^*P)$. Units of d and P are 10^{-10} m and Pa, respectively. [2]$d = k^*P^m$. Units of d and P are 10^{-10} m and Pa, respectively. [3]10^{-10} m of the depletion layer corresponds to 4.3×10^{13}, 4.8×10^{13}, 5.3×10^{13} and 5.7×10^{13} charged states m^{-2} for the sample at 298 K, 373 K, 473 K and 573 K, respectively.

two crystals.

Figure 3 and Table 1 show the variation of the depth of the depletion layer, Δd, measured after exposure of the sample to C_2H_4 at several temperatures and best fit parameters based on Langmuir and Freundlich isotherms. The values of the coefficient of determination (c.d.) suggest that the system fits well to the Langmuir isotherm. From the parameters of the Langmuir isotherm, the surface coverages of the chemisorbed C_2H_4 at $P = \infty$ are estimated to be 5.4×10^{-5} and 7.9×10^{-4} monolayers at 298 K and 373 K, respectively. The Weisz limit[5] controlling the adsorption of oxygen does not play an important role in the case of C_2H_4 adsorption.

Figure 4 shows the variation of the depth during admis-
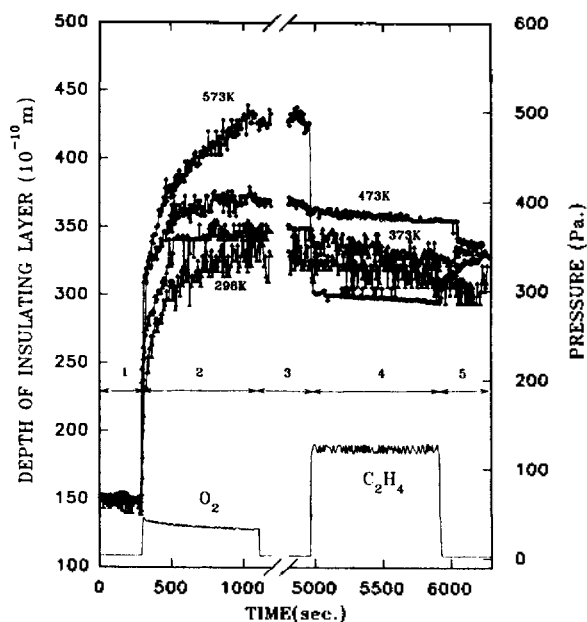
Figure 4. Effect of admission of O_2 and C_2H_4 on the depth of insulating layer of ZnO (10$\bar{1}$0) at 298 K, 373 K, 473 K and 573 K. 1: Sample previously evacuated at 773 K. 2: Exposure of 1 to 13.3 Pa O_2 for 20 min., 3: Evacuation of 2 for 60 min., 4: Exposure of 3 to 200 Pa C_2H_4 for 20 min., 5. Evacuation of 4.

sion of C_2H_4 on ZnO pretreated with oxygen. At 298 K and 373 K, there is no change in the depth. The fact suggests that adsorbed oxygen species[3] at those temperatures, $O_2^-{}_{(ads)}$, does not react with C_2H_4 or reaction intermediates do not release electrons to ZnO. Temperature programmed desorption (TPD) experiments of the single crystal assembly did not show any indication of the interaction between C_2H_4 and O_2 at 298-373 K in our experimental conditions. EPR measurement showed that C_2H_4 reacted with $O_2^-{}_{(ads)}$ ($g = 2.050$, 2.008, 2.002) at 373 K on powder ZnO (99.999%, New Jersey Zinc Co)[4]. When the ZnO powder treated with oxygen at 373 K was contacted with C_2H_4 (10^7 L) at the same temperature, an EPR signal with $g = 2.000$, 4.4 G_{pp} appeared as soon as the EPR signal of $O_2^-{}_{(ads)}$ decreased. The EPR signal ($g = 2.000$) disappeared during an evacuation of the sample at 473 K whereas the EPR signal of an electron ($g = 1.960$) enhanced[6]. TPD of a pelletized ZnO (purity : 99.999%, size : 1 cm$\times$3 cm$\times$0.2 cm, compacting pressure : 1.3×10^8 Pa, sintering temperature : 1070 K) formerly adsorbed oxygen (10^6 L) and exposed to C_2H_4 (10^7 L) at 373 K resulted in the evolution of C_2H_4 and oxygen in the range of 373-473 K, CO_2 and H_2O above 573 K, CO and H_2 in the range of 423-700 K, and a trace of CH_4 above 670 K. A prolonged exposure of the same sample to C_2H_4 yielded an increase in CO and H_2 with a decrease of O_2 in the thermal desorption. When C_2H_4 was exposed to the oxygen-adsorbed sample at 298 K, there was no evolution of CO and H_2 up to 623 K. It suggests that an acceptor like adduct is formed from the reaction of C_2H_4 with $O_2^-{}_{(ads)}$ at 373 K on ZnO and the intermediate decomposes to CO and H_2 at higher temperatures. It was reported that perepoxide was formed from a peroxy type $O_2^-{}_{(ads)}$ and decomposed to ethylene oxide on silver catalysts.[7] On the other hand, the O_2^- adsorbed on ZnO lies

parallel to the surface[8] and it is expected to produce a dioxetane stabilized by the electron from O_2^- (ads). The evolution of CO and H_2 can be explained in terms of the scission of the dioxygen bridge and the C-C bond of dioxetane; the decomposition of the fragments above 423 K.

The decrease in the depth of the insulating layer at 473 K and 573 K can be explained as follows; the adsorbed atomic oxygen O^- (ads), reacts with C_2H_4 at those temperatures and the electron trappped at O^- moves to ZnO. These results are consistent with EPR measurements of the powder ZnO.[4] Mass spectrometric analysis showed the formation of CO_2 and H_2O at 473 K and 573 K.

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8. EPR spectrum of $^{17}O^{16}O^-$ shows one set of hyperfine splitting with $a_{yy} = 80$ G.

High Performance Liquid Chromatographic Determination of Residual Sulfonamide Antibacterials in Meat using Alumina Cartridge

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Sulfonamide antibacterials (SAs), a kind of the synthetic antibacterials that have been used since the early part of the 1900's, are widely used for the treatment and prevention of disease of livestock and cultured fish, and the increase of feed efficiency[1]. Residues of these drugs in food derived from treated animals could pose a health threat to consumers, and the constant exposure of some microorganisms to these drugs may manifest itself in the development of drug-resistant strains. Also recent evidence has implicated some SAs as a possible carcinogen.[2]

When considered to increase the consumption of the livestock products day by day, a simple, rapid and reliable method for multiresidue analysis of SAs is urgently required. But national official method of USA[3], Japan[4], etc., including Korea[5] are not suitable for routine analysis because of the long analysis time, especially complicated clean-up procedure and being the individual determination method with respect to each SA.

Today, the various determination methods of SAs[2,6,7] has been developed and utilized as the development of the analytical instruments, but a simple and rapid clean-up procedure is a key point of routine analysis.

In order to simplify the clean-up procedure, prepacked cartridges have been utilized[8-11], among which the reversed phase type are the most frequently used. However, the normal phase and ion exchange types are more suitable than the reverse phase type because reverse phase cartridges need some time-consuming pretreatments such as evaporation of the organic solvents and elimination of fat from the extracts for clean-up of extracted SAs, whereas normal phase type cartridges do not require such pretreatments.[11]

Therefore, in this paper, we tried to establish a clean-up procedure using the normal phase type Alumina cartridge that not reported until now, and applied to meat for multiresidue ananlysis as the main target of five SAs established the tolerence limits in the Korean Code of Food Standards.[5]

Experimental

Apparatus. A HPLC system (Waters, Millipore Corp., Millford, MA, USA) eqipped with a constant flow pump (510 Solvent Delivery System) was used with a UV detector (486 Tunable Absorbance Detector) operated at 270 nm. The operating condition was described in Table 1. Alumina (Part No. 20500) and Florisil (Part No. 20525) cartridges were purchased from Waters (Millipore Corp., Millford, MA, USA).

Chemicals. Sulfadiazine (SDZ), sulfamerazine (SMRZ), sulfamethazine (SMTZ), sulfamonomethoxine (SMMX), sulfadimethoxine (SDMX) and sulfaquinoxaline (SQX) were ob-
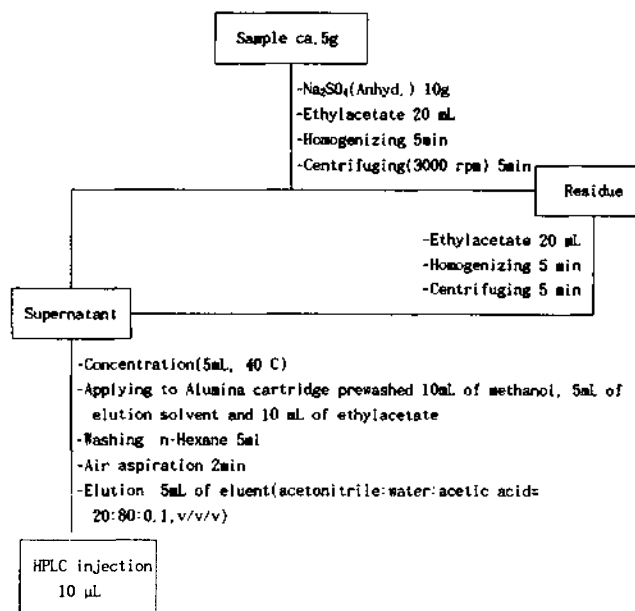
Scheme 1. Flow chart of extraction and clean-up procedure for SAs.