The Effect of Oxygen Adsorption on the Depth of Space Charge Region on ZnO (10$\bar{1}$0)

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The apparent depth of space charge region on the ZnO (10$\bar{1}$0) surface in chemisorption of oxygen has been estimated from the capacitance of two contacting faces. When the sample (donor concentration: 2.4×10^{22} m^{-3}) was evacuated at 773 K for 1 hr. the depth reached to 40-100 Å depending on sample assembly. Admission of oxygen to the sample resulted in an increase of the depth to 3600 Å where the increment was greater at higher oxygen pressure between 6.6-1600 N/m^2. Admission of CO to the sample previously exposed to oxygen yields a decrease in the depth. The results of the measurement support that oxygen is adsorbed as an acceptor on ZnO (10$\bar{1}$0).

Introduction

Observations[1] suggest that the chemical adsorption of oxygen removes electrons from the conduction band of ZnO and a space charge region with a depletion layer is formed depending on the adsorption temperature. Several attempts to investigate this region have been reported, based on the change of carrier density,[2,3] contact potential difference upon the irradiation of the light with the band gap energy, 3.2 eV,[4] photoresponse of semiconductor,[5] work function[6] or catalytic activity of thin film of semiconductor deposited on metal.[7] However a direct measurement of the depth of the region was not reported yet. Physically, the space charge region in ZnO has very low concentration of electron and it can be considered as an insulating region. Thus two crystal faces with the space charge regions are contacted, a measurable capacitance, originated from the depth of the region, between the other sides of crystals will be observed. In this paper, we present an experimental result on the variation of the space charge region during the adsorption of oxygen on ZnO by monitoring the capacitance of two contacting ZnO (1010) faces.

Experimental

The oxygen used was Matheson's ultra high pure and CO was of high purity grade. Single crystal ZnO (1010) was obtained from Atomergic Chemetals Co. and the size was $4\times3\times1$ mm^3. The crystal faces were etched with phosphoric acid and washed with distilled water. A thin film of gold was deposited on one side of single crystal under a vacuum of 1.3×10^{-4} N/m^2. Two faces of ZnO (1010) 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 which were physically contacted to the sample assembly. Temperature of the sample was measured with K type thermocouple welded to a rod supporting the crystals. Temperature of the sample was controlled with a custom-made temperature controller based on an 8 bit personal computer.[8] The capacitance between them was measured using a capacitance bridge with 10 kHz, 10 Vpp sine wave source. The change in capacitance is not significant up to 20 Vpp. In principle, the total capacity C_t of the contacted crystals can be expressed as

$$1/C_t = 1/C_{s1} + 1/C_g + 1/C_{s2} \qquad (1)$$

where C_{s1} and C_{s2} are the capacitance originated from the space charge regions of the crystals, 1 and 2, respectively, and C_g is the capacitance of two crystal surfaces, *i.e.*, the capacitance for the flat band limit. The depth of the space charge region of crystal i, d_i, can be calculated from C_{si} using the simple relation, $C_{si} = \kappa\varepsilon_o A/d_i$ where κ, ε_o and A are the dielectric constant of ZnO, 8, the permittivity of free space, 8.854×10^{-12} F/m and the area of the faces, 12×10^{-6} m^2, respectively. The distance between two contacting crystals estimated from the capacitance for the case of flat band limit was less than 100 Å and we neglected $1/C_g$ in the equation 1, since d_i spans to several thousand Å. We monitored the mean of the apparent depth of the space charge region, d, with the relation,

$$C_t = \kappa\varepsilon_o A/2d \qquad (2)$$

The number of charges per unit area on the surface, N_s, arising from electrons withdrawn from the depth d to the surface is given by

$$N_s \sim -N_D d \qquad (3)$$

where N_D is the density of ionized donor levels of the crystal at the given temperature.

Results and Discussion

From the variation of conductivity of the single crystal sample with temperature, it was calculated that the total concentration of donor level was 2.4×10^{22} m^{-3} assuming electron mobility of 150×10^{-4} $m^2V^{-1}s^{-1}$.[9] To estimate pretreatment condition for the adsorption experiments, total capacitance between two contacting crystals, was measured during evacuation of the system at 773 K under base pressure of 1.3×10^{-5} N/m^2. Figure 1 showed the variation of apparent depth of the space charge region with evacuation time. It was observed that the depth decreased drastically during 10 min. and approached to the range of 40 Å and 100 Å after 1 hr depending on the sample assembly. It seems that the variation is originated from surface irregularities and

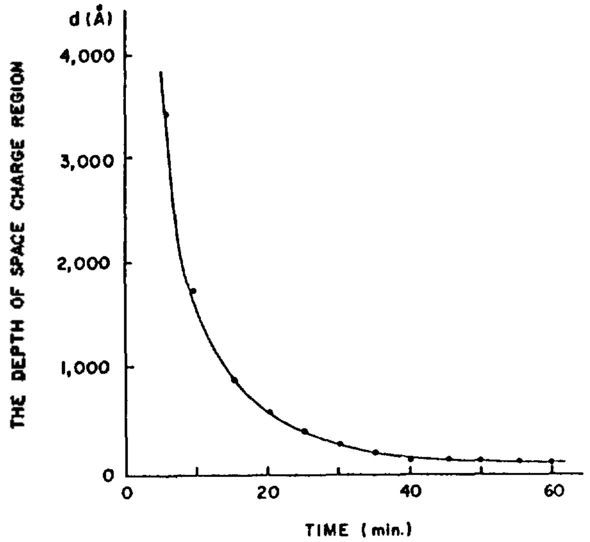

Figure 1. Variation of the apparent depth of space charge region of ZnO (10$\bar{1}$0) depend on evacuation time at 773 K.

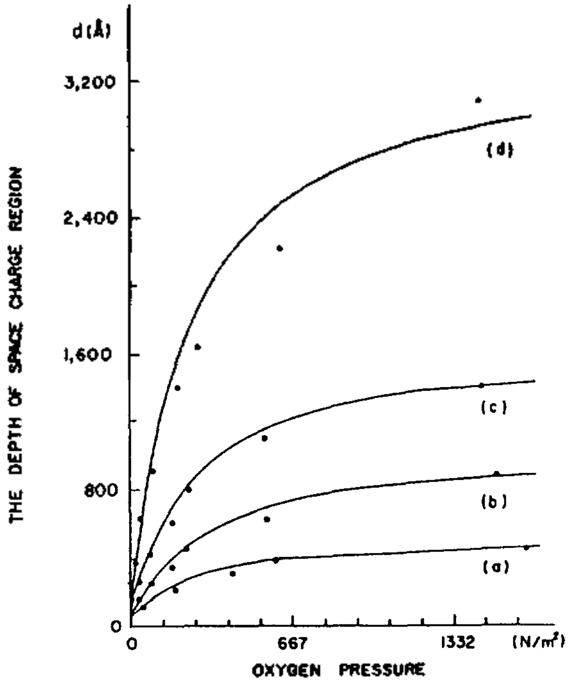

Figure 2. Effect of oxygen pressure on the depth of space charge region of ZnO (10$\bar{1}$0) at 298 K (a), 373 K (b), 473 K (c) and 573 K (d). The solid lines represent the least square estimated Langmuir isotherms.

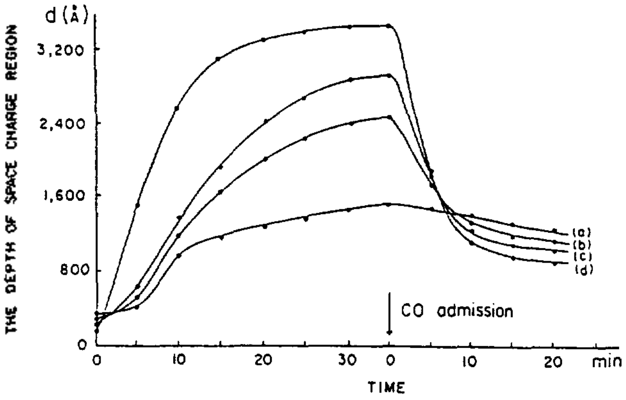

Figure 3. Effect of admission of oxygen (400 N/m^2) and carbon monoxide (2660 N/m^2) on the apparent depth of space charge region of ZnO (10$\bar{1}$0) at 373 K (a), 473 K (b), 573 K (c) and 673 K (d).

matching characteristics of two contacting faces. The experimental setup was checked by a cycle of adsorption of oxygen at 573 K and evacuation at 773 K. Every adsorption-evacuation treatment induced a slight increase in the depth but the increment, under 10 Å, was very small compared to the total variation. From the results, we can assume that the evacuation of the crystal at 773 K for 1 hr. eliminates the most part of the ionosorbed oxygen species. In the adsorption experiments, we evacuated the contacted crystal sample in the sample assembly for 1 hr. at 773 K and admitted oxygen to the system at adsorption temperature. Usually, a constant and reproducible value of capacitance of the sample assembly was obtained after 30 min. of gas exposure. A series of experiment was executed with a sample assembly without detaching the crystal faces.

Figure 2 shows the effect of pressure of oxygen and temperature of adsorption on the depth of the space charge region, *d*. The best fit Langmuir type isotherms were sketched to show the dependence of the depth profile with oxygen pressure. The depth increases with the temperature of adsorption and the value reaches to 3000 Å at 573 K. These facts can be explained as due to adsorbed oxygen withdrawing electrons near the ZnO surface, developing an space charge region with carrier depletion, and the amount of adsorbed oxygen increases with the temperature of adsorption. In the present work, the amount of adsorbed oxygen was not measured directly, but the depth of an insulating region of 1000 Å corresponds to a density of charged surface states of 4×10^{14} m^{-2} at 573 K, i.e., about 4×10^{-5} monolayer. This low coverage of ionosorbed oxygen species on ZnO is well consistent with Weisz's limit based on the double-layer theory of semiconductor surface.[10]

When CO was admitted to the sample previously treated with oxygen at 373 K, 473 K, 573 K and 673 K, the depth of the space charge region decreases as shown in Figure 3. As the treatment temperature is increased, the variation of the depth becomes greater. The decrease in the depth may originate from the reaction of adsorbed oxygen species with carbon monoxide and transfer of electrons from the oxygen species to the conduction band of the semiconductor.[11] These facts support that the space charge region is originated from the adsorption of oxygen.

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Theoretical Studies on the Gas-Phase Pyrolysis of 2-Alkoxypyrimidines, 2-Alkoxypyrazines, 4-Ethoxypyrimidine and 3-Ethoxypyridazine[1]

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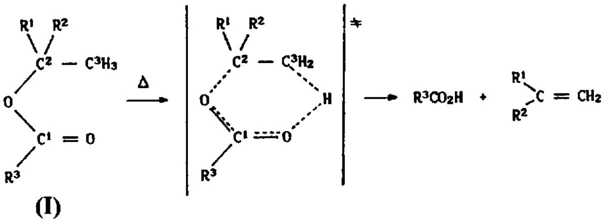
The gas-phase pyrolysis reactions of 2-alkoxypyrimidines(II), 2-alkoxypyrazines(III), 4-ethoxypyrimidine(IV) and 3-ethoxypyridazine(V) are investigated theoretically using the AM1 MO method. These compounds pyrolyze in a concerted retro-ene process with a six-membered cyclic transition state (TS). The relative order of reactivity is (IV)>(II)>(III)>(V), which can be rationalized by the two effects arising from electron-withdrawing power of the aza-substituent: (i) Electron withdrawal from the C-O bond accelerates the rate and (ii) electron withdrawal from the N^1-atom, that is participating in the six-membered TS, deactivates the reaction. We are unable to explain the experimental result of the greatest reactivity for pyridazine, (V), with our AM1 results. The reactivity increase accompanied by successive methylation of the ethoxy group, ethoxy<*iso*-propoxy>*tert*-butoxy, is due to a release of steric crowding in the activation process.

Introduction

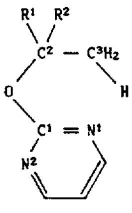
Thermal decomposition of esters, (I), has been extensively studied experimentally[2] and theoretically[3], and it is believed to proceed by a concerted retro-ene type reaction with a six membered cyclic TS, Eq. (1). On the other hand, little work has been reported on the thermal decomposition of the nitrogen analogues of esters, imines and amides.



(1)

(I)

In a previous work[4], we examined theoretically the pyrolysis mechanism of 2-alkoxypyridines, and as part of a continuing effort to understand the pyrolysis mechanism we have carried out the AM1 studies of the pyrolysis reactivities of the aza-substituted pyridines, (II)~(V). The reactivity of these compounds has some interesting aspects: the aza-substituent exerts differing strength of inductive and resonance (or mesomeric) electron withdrawing effects (−I and −M) on the C^2-O bond and the N-atom participating in the six-membered cyclic TS (hereafter denoted as N^1) depending on the site in the ring. The effect of the aza-substitutent on the reactivity of thermal decomposition can be examined by comparing relative rates between these compounds, (II)-(V), and by relating the rates to that of the unsubstituted 2-alkoxypyridine.



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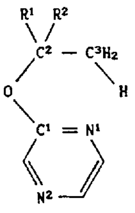

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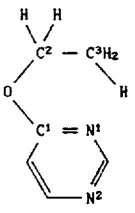
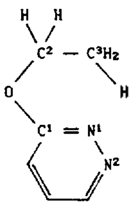


(IV)



(V)

The gas-phase experimental results of Al-Awadi *et al.*,[5] have shown an increase in the rate of decomposition due to methyl group substituted in the aromatic ring of 2-ethoxypyridine. The methyl group has dual effects: (i) Electron supply to the C^2-O bond hinders its cleavage and so decreases the reaction rate. (ii) Electron supply to the C=N bond raises the nucleophilicity of the nitrogen atom, thereby increasing the reaction rate. Of the two opposing effects, the latter is found to prevail experimentally. Moreover, the effect of a methyl group at the ortho- or para-position was greater than that at the meta-position. An aza-substituent, being an inductive electron-withdrawer, is expected to have exactly the opposite trend in the dual effects on the C^2-O and C=N bonds. However, the effect of the aza-substituent is more complex since the aza-substituent can also exert resonance (mesomeric) effect.