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Barrier Height from V-I Characteristics of Semiconductor Contact: Reaction of Adsorbed Oxygen with Carbon Monoxide on ZnO (1010)

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Barrier height on the surface was monitored at 77 K by observing the inflection of V-I characteristics of ZnO (1010)-ZnO(1010) contact in the surface reaction of oxygen species with carbon monoxide. The contact showed inflections at 10-20 mV and 10-50 mV for the sample adsorbed oxygen at 298 K and 573 K, respectively. When the sample adsorbed oxygen at 573 K was exposed to carbon monoxide at 298 K and 573 K, inflections were observed at 10-40 mV and 10-30 mV, respectively. The results indicated that the adsorption of oxygen on ZnO increased the surface barrier height, and the reaction of carbon monoxide with the oxygen-preadsorbed (at 573 K) ZnO decreased the surface barrier height.

Introduction

Catalytic reactions on semiconductor surface are often controlled by the surface barrier of the semiconductor which was developed by reactants. A measurement of the barrier height during the reaction process is important to understand the detailed mechanism of the reactions. We found a method to estimate the variation of the surface barrier height using V-I characteristics of semiconductor-semiconductor contact.

When acceptor type molecules are adsorbed on the surface of an n-type semiconductor crystal with n_b or $N_D - N_A$ bulk electrons, the electrons in the semiconductor move to the molecules leaving a depletion layer with a depth, x_0 . The mathematical description of surface barrier height V_s^0 of the layer is obtained from Poisson relation.¹

$$V_s^0 = \frac{q_e(N_D - N_A)x_0^2}{2\kappa_s\epsilon_0} \quad (1)$$

where κ_s , ϵ_0 and q_e are the static dielectric constant of semiconductor (≈ 8 for ZnO), the permittivity of the vacuum ($8.854 \times 10^{-12} \text{ C}^2\text{m}^{-1}\text{J}^{-1}$) and the unit charge ($1.602 \times 10^{-19} \text{ C}$), respectively. If faces of two semiconductors with the same layer are contacted and a bias voltage is applied to them, the new surface barrier height of the negatively biased semiconductor, V_s^- becomes²

$$V_s^- = V_s^0 \left(1 - \frac{V}{4V_s^0} \right)^2 \quad (2)$$

and the surface barrier height of the positively biased semiconductor, V_s^+ becomes

$$V_s^+ = V_s^0 \left(1 + \frac{V}{4V_s^0} \right)^2 \quad (3)$$

Since the electron moves from the negatively biased semiconductor to the positively biased semiconductor through the contact zone, the electron current can be given by

$$I \approx C \cdot T \cdot n_e \cdot \mu_e \cdot q_e \cdot \frac{A}{2t} \cdot e^{-\frac{q_e V^-}{k_B T}} \cdot V \quad (V < 4V_s^0)$$

$$\approx C \cdot T \cdot n_e \cdot \mu_e \cdot q_e \cdot \frac{A}{2t} \cdot V \quad (V \geq 4V_s^0) \quad (4)$$

where c , T , n_e and μ_e are the fraction of contact of the crystals, the tunneling factor through the contact, the number of free electron per unit volume and the mobility of the electron, respectively. Eq. (4) implies that V-I characteristics shows inflection at the bias voltage, $4V_s^0$ for the depletion layer. In the most cases, V-I characteristics shows a simple straight line and it is difficult to decide the bias voltage showing the inflection. We represented V-I characteristics as I - kV vs. V plot to visualize the inflection where k is the mean conductance of the sample. In fact, the contact of two single crystals is a sum of many microscopic contacts having different heights of the surface barrier and there can be many inflections. In this paper, we reported observations on the variation of surface barrier height in the surface reaction of carbon monoxide with adsorbed oxygen on ZnO surface.

Experimental

Polished single crystal ZnO(1010) was obtained from A-

tomergic Chemetals Co. and the size was $4 \times 3 \times 1 \text{ mm}^3$. Carbon monoxide (99.95%) and oxygen (99.95%) were obtained from Korean Standard Research Institute. A thin film of gold was deposited on one side of the crystal by vacuum evaporation. Two faces of ZnO(1010) were contacted with four screws in a sample assembly and attached to a 10 pin feedthrough as previously reported.^{3,4} The sample assembly was positioned in a quartz tube which was connected to a gas handling system with a base pressure of $1.33 \times 10^{-5} \text{ Pa}$. The temperature of the sample was monitored with a K type thermocouple contacted to the sample assembly. V - I characteristics was measured between the gold films of the assembly in the range of the applied bias voltage 0-0.4096 V. Voltage sweep was performed by an AT type personal computer using a 12 bit digital to analog converter (DAC) and the current was measured by a current to voltage converter-ADC interface. To improve the signal to noise ratio of V - I characteristics, average of 1000 sweeps was used for data analyses. All measurements were carried out under liquid nitrogen temperature after evacuation.

Results and Discussion

Figure 1 showed I - kV vs. V plots of ZnO(1010)-ZnO(1010) contact during the surface reaction of carbon monoxide with oxygen adsorbed on ZnO at 298 K. Figure 1-a is the plot of the sample evacuated at 773 K for 10 min. It showed a minimum at 4.8 mV and a downward concave shape in the range of bias voltage 30-400 mV. Though it was hard to find the inflection for this case, we thought the inflection could be observed around the bias voltage 8 mV and the surface barrier height was about 2 meV. Figure 1-b showed I - kV vs. V plot of the contact after adsorption of oxygen at 298 K. Inflections were observed at bias voltage 10-

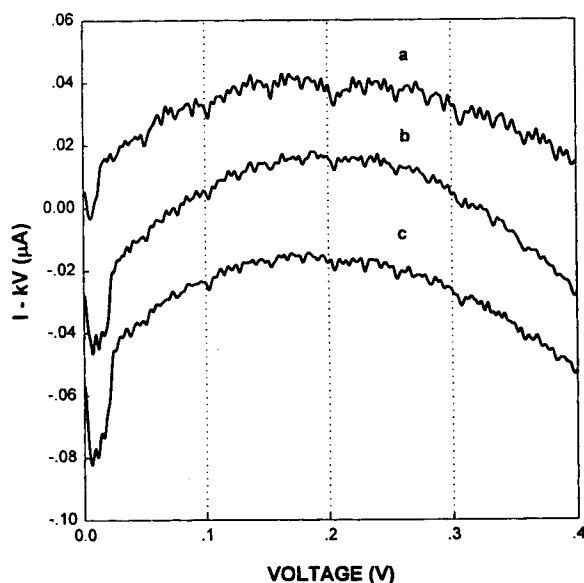


Figure 1. I - kV vs. V plots of ZnO(1010)-ZnO(1010) contact at 77 K. The sample assembly was evacuated at 773 K for 10 min. (a), exposed to 66.7 Pa oxygen for 30 min and evacuated at 298 K (b), and exposed to 66.7 Pa carbon monoxide for 30 min and evacuated at 298 K (c). The mean conductance k was $118.5 \mu\Omega^{-1}$, $71.4 \mu\Omega^{-1}$ and $71.0 \mu\Omega^{-1}$ for a, b and c, respectively.

20 mV and the mean conductivity was decreased. Figure 1-c was taken after an exposure of the oxygen-preadsorbed (at 298 K) ZnO to carbon monoxide at 298 K. There was no considerable change from Figure 1-b.

Figure 2-b showed V - I characteristics of ZnO(1010)-ZnO(1010) contact after adsorption of oxygen at 573 K. In this case, the mean conductivity was significantly decreased and inflections were observed in the range of bias voltage 10-50 mV. When the oxygen-preadsorbed ZnO at 573 K was exposed to carbon monoxide at 298 K, the mean conductivity slightly decreased and the inflections were observed in the bias voltage 10-40 mV as shown in Figure 2-c. An evacuation of the sample at 473 K showed an increase in the mean conductivity and a decrease in the bias voltage showing the inflections. When the oxygen-preadsorbed ZnO at 573 K was exposed to carbon monoxide at 573 K, the mean conductivity increased and the inflections were observed at the bias voltage 10-30 mV as shown in Figure 3-c.

When oxygen was adsorbed on ZnO at 298 K or 573 K, there was an increase in the bias voltage showing inflections in I - kV vs. V plot. The result can be explained in terms of an increase of surface barrier height and a development of a depletion layer. Since the depletion layer could be formed in the capturing of majority carrier by surface state, it was suggested that adsorbed oxygen became anions in the process. In the previous studies using EPR and Hall voltage measurements, it was reported that oxygen adsorbed on ZnO as O_2^- and O^- at 298 K and 573 K, respectively.⁵⁻⁷ Thus our observations are in good agreement with the previous reports though the detailed feature of the anion can not be identified from V - I characteristics.

No change in V - I characteristics of the contact was observed when oxygen-preadsorbed ZnO (at 298 K) was exposed to carbon monoxide at the same temperature. The

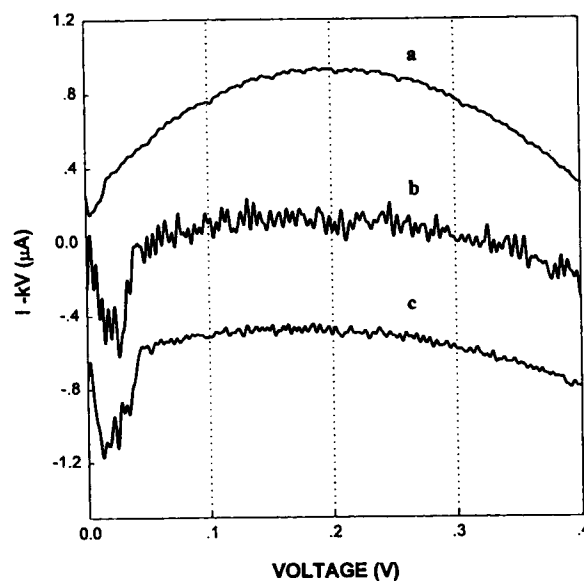


Figure 2. I - kV vs. V plots of ZnO(1010)-ZnO(1010) contact at 77 K. The sample assembly was evacuated at 773 K for 10 min. (a), exposed to 66.7 Pa oxygen for 30 min and evacuated at 573 K (b), and exposed to 66.7 Pa carbon monoxide for 30 min and evacuated at 298 K (c). The mean conductance k was $94.9 \mu\Omega^{-1}$, $45.9 \mu\Omega^{-1}$ and $41.1 \mu\Omega^{-1}$ for a, b and c, respectively.

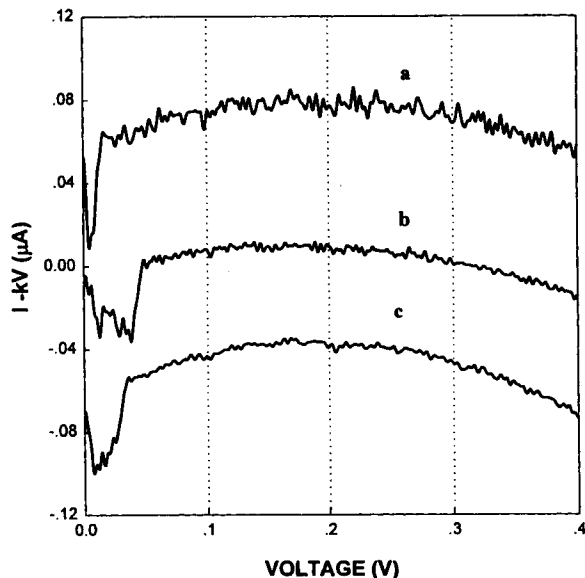


Figure 3. I - kV vs. V plots of $ZnO(10\bar{1}0)$ - $ZnO(10\bar{1}0)$ contact at 77 K. The sample assembly was evacuated at 773 K for 10 min. (a), exposed to 66.7 Pa oxygen for 30 min and evacuated at 573 K (b), and exposed to 66.7 Pa carbon monoxide for 30 min and evacuated at 573 K (c). The mean conductance k was $84.9 \mu\Omega^{-1}$, $37.6 \mu\Omega^{-1}$ and $52.2 \mu\Omega^{-1}$ for a, b and c, respectively.

result could be explained as the oxygen species at 298 K (O_2^-) did not interact with CO at 298 K. For the case of the oxygen species adsorbed at 573 K (O^-), the bias voltage showing the inflections decreased during the interaction with CO at 298 K, and the voltage decreased additionally during the evacuation at 473 K. Since the adsorbed oxygen species at 573 K (O^-) could not be desorb-

ed easily at 473 K, it could be suggested that the oxygen species, O^- reacted with CO at 298 K and a produced anion, probably CO_2^- , was completely desorbed at 473 K from the surface releasing electrons to ZnO. At the interaction at 573 K (Figure 3), it could be expected that O^- reacted with CO and the produced CO_2^- was directly desorbed at the temperature. This result is consistent with the previous investigations which described the reactivity of the oxygen species with CO on ZnO.⁸⁻¹¹

The shapes of V - I characteristics also varied with the temperature at which the measurement was taken. We are expecting that the shape gives the information on the adsorbed states and the surface itself in near future.

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Stereochemical Course of the Reductive Decyanation of Cyclic α -Phenylnitrile. Dependence on the Added Alcohol and Metal of the Decyanation of 4-*t*-Butyl-1-phenylcyclohexanecarbonitrile

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Stereochemical course of the reductive decyanation of two stereoisomeric 4-*t*-butyl-1-phenylcyclohexanecarbonitriles **3** and **4** using solvated electron has been studied. While sodium-mediated reactions of both **3** and **4** in the presence of alcohols give the same ratio, 1.5:1, in favor of the thermodynamically more stable product **5** over the other one **6**, the ratios obtained from the potassium-mediated process are found to be very sensitive to the kind of H-donors. When reactions are performed without H-donors, **5** is only obtained from the experiments with both stereoisomers irrespective of the metal species.

Introduction

The nitrile function¹ has been widely used in introducing various substituents² at its neighboring position in synthetic

organic chemistry. The maximum efficiency of the overall sequence involving the nitrile function usually requires the subsequent removal of the nitrile group in a convenient and facile manner. Many different methods³ have been de-