



Electric Control of the Chemical Reaction in Ceramic–Ceramic Contact Interface—Modeling of the Reaction Scheme

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Abstract. The CuO/ZnO heterocontact is made by stacking CuO and ZnO porous ceramics and its catalytic activity for CO oxidation reaction is evaluated as a function of applied bias. Its catalytic activity is strongly depend on the dc applied bias and when the reverse bias (CuO^- , ZnO^+) is applied to the heterocontact, the amount of the produced CO_2 from the catalytic interface rapidly increases, while it decreases when forward bias is applied. The magnitude of the enhancement of the catalytic activity by reverse applied bias is extremely large (30% for -2.0 V at 320°C), comparing with the results in the gradient composition CuO/ZnO heterocontact. The p-i-n structure is suggested as to the electronic structure of the CuO-ZnO contact interfaces and supposing p-i-n structure, the surface Fermi level position of CuO and ZnO are guessed to move as a function of applied bias. The catalytic reaction over CuO make a large contribute to the whole catalytic reaction at the CuO/ZnO heterocontact and it would be modified by the applied voltage dependent surface Fermi level position of CuO. The working mechanisms of such phenomena are qualitatively discussed by the electronic theory of catalyst proposed by Wolkenstein.

Keywords: heterocontact, CO oxidation, electric control, cupric oxide, zinc oxide

Introduction

The heterocontact of ceramics is one of the p-n junction diode which is made using two different ceramic sintered compacts in contact with each other by mechanically pressing [1]. The authors had investigated the electrical properties of the heterocontacts between cupric oxide (CuO) and zinc oxide (ZnO) [2,3], nickel oxide (NiO) and ZnO [1,4], silicon carbide (SiC) and ZnO [5,6] or other compositions. The electrical properties of these heterocontacts are changed by the introduction of water vapor, reducing gases, or oxidizing gases to their contact area and such phenomena can be applied to humidity sensor and chemical sensor materials [1–6]. In 1985, the authors

had found out that the CuO/ZnO heterocontact gas sensor showed selective CO gas sensing characteristics and tried to apply it to a CO gas sensor [3]. The working mechanism of the CuO/ZnO heterocontact gas sensor is suggested to be the consumption of ionized adsorbed oxygen (O^-) on the surface of n-type semiconductor material (ZnO), because the electric current passing through the CuO-ZnO interface increases by the introduction of reducing gases. Interestingly, the surface properties of ZnO are modified by the CuO surface in contact with ZnO and that would be the origin of the selective CO gas sensing characteristics of the CuO/ZnO heterocontact [7]. As for the gas sensing mechanisms of the CuO/ZnO heterocontact, several models are proposed,

however, valid and universal model has not been obtained yet, because the defect structures of CuO are easy to change during firing process and for this reason, control of defect structures or surface properties is difficult to be done.

The gas sensing properties of the CuO/ZnO heterocontact show interesting character owing to its non-linearity in voltage-current characteristics. That is, its gas sensitivity strongly depends on the applied bias [3]. The chemisorption of oxygen or other chemical species on CuO and/or ZnO surface is known to be accompanied by electron transfer from (to) the bulk to (from) the adsorbed species and the phenomena are guessed to be governed by their surface electronic properties. The electronic properties of both CuO and ZnO surface in the CuO/ZnO heterocontact will be controlled by the control of the applied bias and the electronic control of the catalytic reaction at the CuO-ZnO interface by an applied electric field would be possible. Since the 1950s, catalytic properties of semiconducting metal oxides has been investigated from the viewpoint of the electronic theory or the theory of semiconductors and the effect of the Fermi level position of the catalyst on its catalytic properties had been studied and discussed [8–10]. In the case of the CuO/ZnO heterocontact, applied electric field would affect the chemistry of the adsorbed species at the interface.

The surface of CuO shows high catalytic activity for CO oxidation reaction and the reaction over the CuO is greatly contributed to the total catalytic activity of the CuO/ZnO heterocontact. The author had fabricated a gradient composition CuO/ZnO heterocontact by stacking six layers of $x\text{CuO}-(1-x)\text{ZnO}$ porous ceramics of different composition and employed it as a catalyst for CO oxidation. From the result, it is found out that rate of the CO oxidation over CuO in contact with ZnO is modified by the applied bias to the CuO-ZnO contact interface. When the heterocontact is reverse biased, its catalytic activity is enhanced, while it is suppressed under forward bias and the electric control of the CO oxidative reaction is performed [11]. The working mechanism of the modified catalytic activity in the CuO/ZnO heterocontact is not precisely understood yet. The structure or texture of the gradient composition CuO/ZnO heterocontact is complicated and it is not suitable for the study on the working mechanism of the applied voltage dependence of the

CO oxidation at around the contact points of CuO and ZnO. For the discussion of the more detailed working mechanism, the CuO/ZnO heterocontacts with more simple styles are needed.

In the present study, the CuO/ZnO heterocontact is fabricated by stacking porous CuO and ZnO layers. The CO_2 uptake from the catalytic surface (catalytic activity) of the CuO/ZnO heterocontact is measured and the effect of applied bias on the reaction rate is studied and discussed. The applicability of the electronic theory to the heterogeneous reaction can be qualitatively adapted for explaining our experimental results.

Experimental Procedure

The CuO/ZnO heterocontact is fabricated by firing a powder compact with the stacking of the CuO and ZnO powder compact layers. High purity cupric oxide (CuO) and zinc oxide (ZnO) powder (Kojundo Chemical Co., Ltd., 99.9% in purity) are starting materials. A 0.5 g sample of CuO and ZnO powder are subsequently placed in a cylindrical mold and uniaxially pressed under 9.8 MPa. The pressed CuO/ZnO powder compact is again isostatically pressed under 30 MPa and sintered at 850°C for 3 h in air. We are apprehensive of fracturing of the specimen during firing, because CuO is easy to be sintered and well shrunk comparing with ZnO. To prevent the fracture of the specimen during firing, CuO powder is calcined at 850°C for 3 h before placing it into a mold. Obtained CuO/ZnO compacts are sufficiently porous and the apparent density of the specimens are 60.6% of theoretical for CuO part and 57.6% of theoretical for ZnO part. The scanning electron micrograph (SEM) view of the CuO-ZnO contact interface is shown in Fig. 1. From the SEM view, grain sizes of the CuO and ZnO part of the heterocontact specimen are 1 μm for CuO and 0.5 μm for ZnO, respectively. Owing to its porous structure shown in Fig. 1, introduced gas molecules can be easily transferred to the contact interface between CuO and ZnO particles.

Ohmic electrodes (silver for CuO and In-Ga alloy for ZnO) are applied on the both ends of the specimen and platinum wires covered with Pyrex tube are attached to the both electrodes. Electrodes and lead wires are covered with silica-alumina paste to avoid the exposure to the reacting gas stream. Schematic

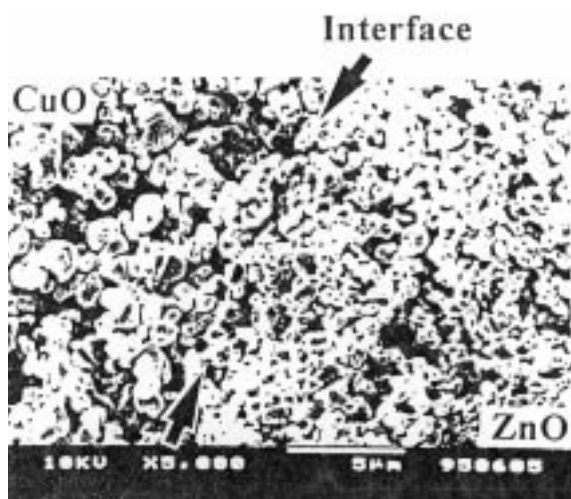


Fig. 1. The scanning electron micrograph (SEM) view of the CuO-ZnO contact interface.

view of the heterocontact specimen and experimental system are shown in Fig. 2. Dried air ($P_{O_2} = 0.2$ atm) with 4142 ppm of CO is the reacting gas and its volumetric flow rate is fixed at 10 ml/min (3.14×10^{-8} mol/min for CO), and the reactor is kept at 220–320°C. The composition of the outlet gas is analyzed using gas chromatography. The CO or

CO₂ gas concentration is determined using a calibration curve from the analysis of standard gases. dc bias is applied to the heterocontact specimen and its catalytic activity is evaluated as a function of applied bias.

Result and Discussion

Figure 3 shows the current-voltage (I - V) characteristics of the CuO/ZnO heterocontact at 320°C. The catalytic activity for CO oxidation (the CO₂ uptake) is simultaneously shown in the figure. It shows highly rectifying character even at 320°C. Because the structure or texture of the interface between CuO and ZnO particles are too complicated, the electronic structure of each CuO-ZnO contact interface is not uniform and we can not discuss its rectifying I - V characteristics by employing a simple model. In addition, cations (Cu^{2+} , Zn^{2+}) are interdiffused through the CuO-ZnO interface during the sintering process and formation of the abrupt junction such as p-n junction diode is not expected at the CuO-ZnO interface. Solution of Cu^{2+} in ZnO by 850°C firing is confirmed by the variation in the lattice parameters of ZnO phase and c -axis of ZnO increases by the incorporation of Cu^{2+} to Zn^{2+} sites. Copper ions

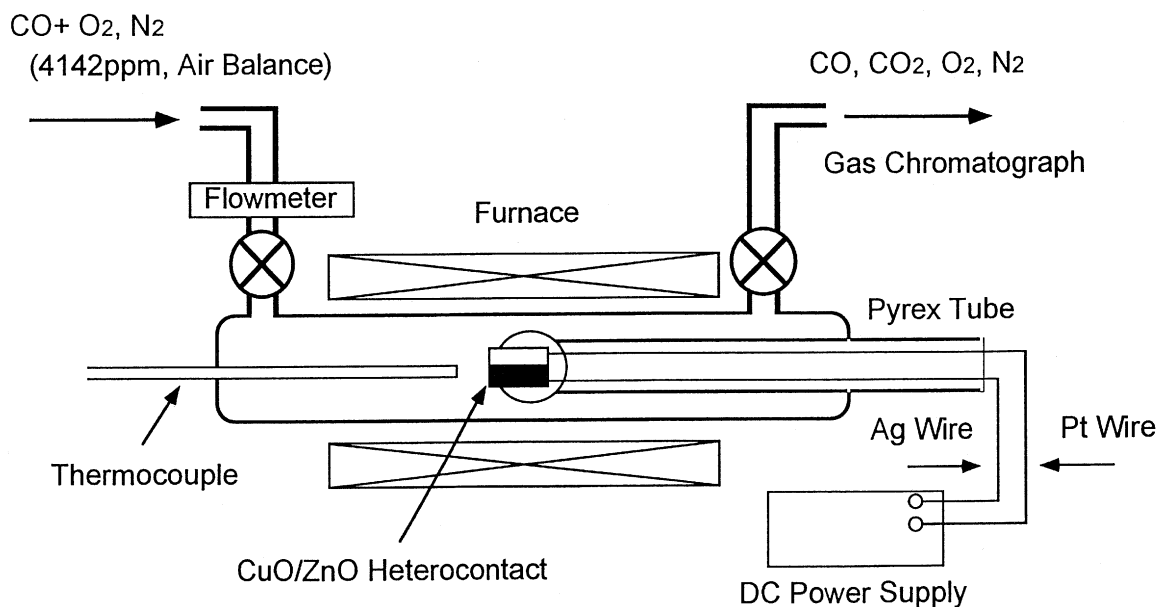


Fig. 2. Schematic view of the CuO/ZnO heterocontact specimen and experimental system for the evaluation of its catalytic activity. Electrodes and lead wires are covered with silica-alumina paste to avoid the exposure to the gas stream.

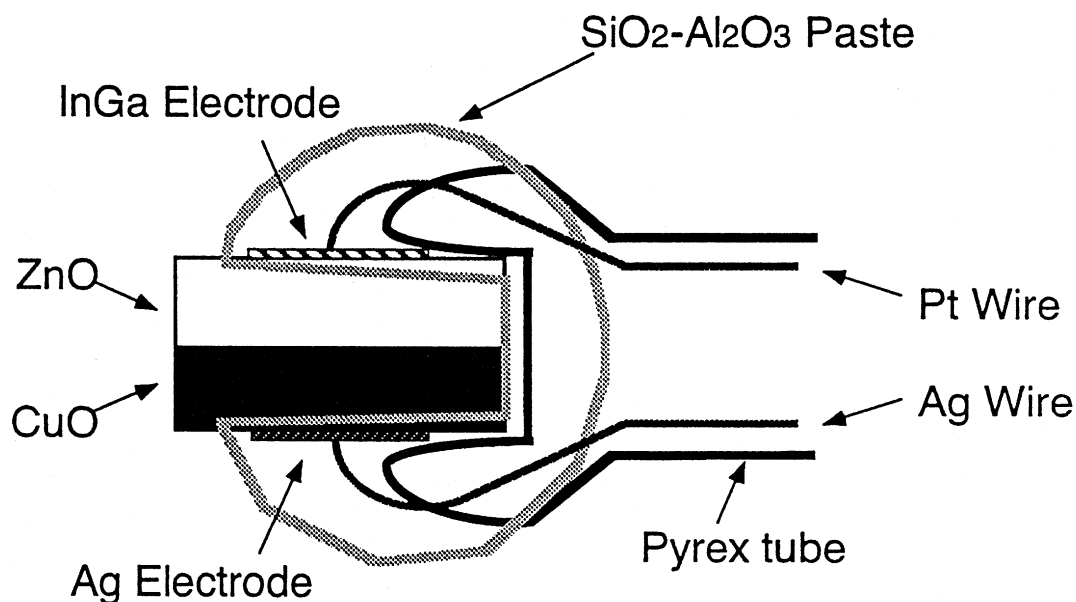


Fig. 2. (Continued)

(Cu²⁺) solvated in ZnO are known to work as an electron acceptor [12]. As a result, incorporated Cu²⁺ ions become Cu⁺, whose ionic radius (0.96 Å) is far larger than that of Zn²⁺ (0.74 Å) [13] and they increase the surface resistivity of ZnO. Interface resistance between CuO and ZnO particles would be increased by the interdiffusion of cations (Cu²⁺, Zn²⁺) through the interface and p-i-n structure would be formed at the boundary region.

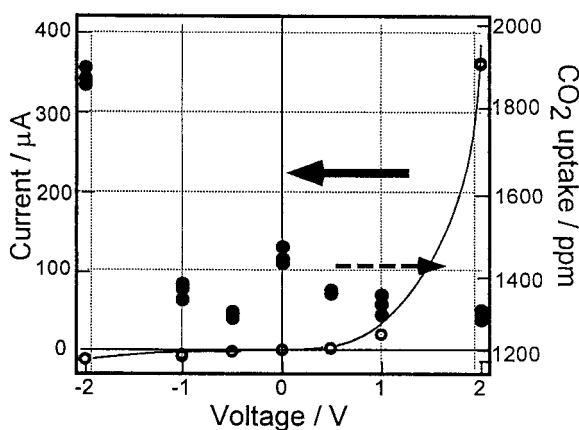


Fig. 3. The current-voltage (*I-V*) characteristics of the CuO/ZnO heterocontact in CO gas (4142 ppm) stream at 320°C. The catalytic activity for CO oxidation (CO₂ uptake) is simultaneously shown in the figure.

Similar to the results in the gradient composition CuO/ZnO heterocontact in our previous study [11], the catalytic activity of the CuO/ZnO heterocontact for CO oxidation varies as a function of applied bias. Figure 4 shows the relation between the amount of

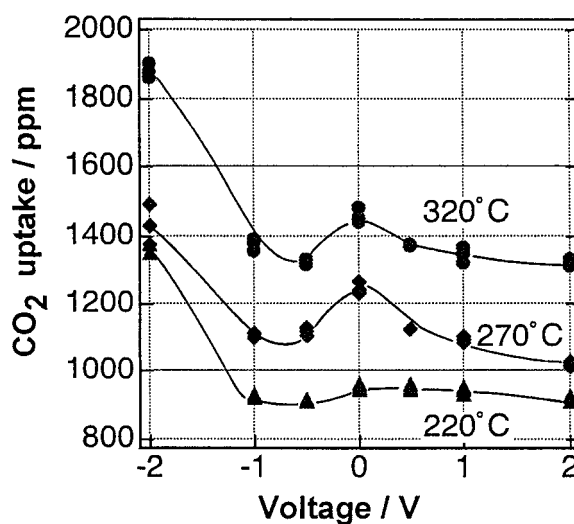


Fig. 4. The relation between the amount of CO₂ production (CO₂ uptake) and applied voltage at the CuO/ZnO heterocontact. The measurements are performed at 220, 270, and 320°C. The introduced CO gas concentration is 4142 ppm and its flow rate is 3.14×10^{-8} mol/min for CO.

CO₂ production and applied voltage at the CuO/ZnO heterocontact measured at 220-320°C. The amount of CO₂ produced varies as a function of applied bias, and when the reverse bias (CuO⁻, ZnO⁺) is applied, the CO₂ production increases with an increase in applied bias, therefore, it decreases with an increase in the forward applied bias. The magnitude of the increase in the catalytic activity by reverse applied bias (-2.0 V) is about 30% at 320°C. Similar results are obtained in the gradient composition CuO/ZnO heterocontact [11]. The enhancement of the catalytic activity of the CuO/ZnO heterocontact in the present study is far larger than that of the gradient composition CuO/ZnO heterocontact in our previous study.

The electric current passing through the contact interface increases with the introduction of CO gas into the reactor and its character is similar to the results in the CuO/ZnO heterocontact which is made using CuO and ZnO sintered compacts in contact with each other by mechanically pressing [3]. For confirming whether the phenomena are related to the carrier transport process through the interface or not, the current-time behavior and the CO₂ uptake (catalytic activity)-time behavior of the CuO/ZnO heterocontact are compared. Figure 5 shows the current-time behavior and the catalytic activity-time behavior by the reverse step bias (-1.0 V) applied to the CuO/ZnO heterocontact. When the reverse bias is applied to the heterocontact, the current rapidly increase then gradually decrease. The CO₂ uptake

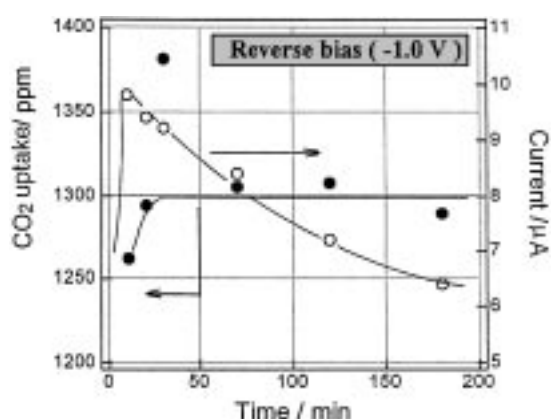


Fig. 5. The current-time behavior (---) and the CO₂ uptake-time behavior (---) by the step reverse bias (-1.0 V) applied to the CuO/ZnO heterocontact. Measuring temperature is 320°C. Introduced CO gas concentration is 4142 ppm.

(catalytic activity) does not follow the behavior similar to the current variation and it is rapidly enhanced then almost unchanged about 30 min after applying a potential step. The current-time behavior and the CO₂ uptake-time behavior by the step forward bias (+1.0 V) applied to the CuO/ZnO heterocontact are shown in Fig. 6. Contrary to the case with reverse bias application, the current gradually increases, while the catalytic activity is rapidly suppressed then almost unchanged also about 30 min after applying a forward potential step. Slow response of the catalytic activity to the voltage step is due to the small flow rate of the reactant gas introduction and the catalytic activity of the CO oxidation at the CuO/ZnO heterocontact is considered to depend on the applied voltage directly, but not depend on the current passing through the interface. From the results of Figs 5 and 6, it is also suggested that the contribution of generated Joule heat to the enhancement or suppression of the catalytic activity of the CuO/ZnO heterocontact are small and the enhancement of the CO₂ uptake under the reverse bias is not to be due to the local heating of the catalyst by the electric current flow. The CO₂ uptake and the conversion of CO to CO₂ by CuO, ZnO are summarized in Table 1. The catalytic oxidation reaction of CO over CuO is much higher than over ZnO and the produced CO₂ from ZnO surface is negligible even at 320°C, which is the working temperature of a ZnO gas sensor. The result indicates that most of the detected CO₂ are the product from

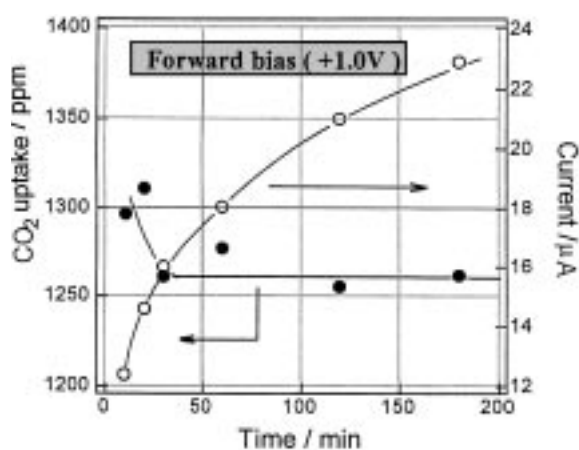


Fig. 6. The current-time behavior (---) and the CO₂ uptake-time behavior (---) by the step forward bias (+1.0 V) applied to the CuO/ZnO heterocontact. Measuring temperature is 320°C. Introduced CO gas concentration is 4142 ppm.

Table 1. Extent of conversion of CO to CO₂ for CuO and ZnO powder

Specimen	Temperature (°C)	CO ₂ uptake(ppm)	Conversion(%)
CuO*	320	1736	41.9
	30	82.2	1.98
ZnO**	320	53.8	1.30

Note: The power specimen (5.0g of CuO or ZnO) is mounted on a quartz plate and exposed to the reactant gas (Dried air + 4142ppm of CO). *Calcinated at 850°C for 3 hours: Specific surface area is 0.375m²/g **Calcinated at 850°C for 3 hours: Specific surface area is 1.11m²/g

CuO surface. A part of them are production from the CuO surface interfaced with ZnO and its production rate is regulated by the variation in the applied voltage.

Several authors had been trying to explain the catalytic activity of a semiconductor catalyst from the viewpoint of the electronic theory of catalysts [8–10]. Based on the electronic theory of catalysts, it is considered that the applied voltage dependence of the catalytic activity of the CuO/ZnO heterocontact is suggested to be due to the variation in the surface Fermi level position of CuO in contact with ZnO. A relation between the catalytic activity and the Fermi level position of the metal oxide catalysts had been discussed since 1950s. Schwab et al. had evaluate the NiO catalysts doped with several kind of altermvalent metal ions and explained the origin of the variation in their activation energy for the CO oxidation by considering the variation in Fermi level position by donors or acceptors doping [10]. However, their speculation had not been accepted widely, because their discussion had the disadvantage of the lack of the effect of lattice defects introduced by doping of the altermvalent ions [14]. The relation between the catalytic activity and Fermi level position of a catalyst is theoretically introduced by Wolkenstein [9]. In his theory, ‘‘strong adsorption’’ of chemical species are in accordance with charge transfer from/to the bulk to/from the adsorbed species and the occupancy of an electric charge on the adsorbed species on a catalyst is supposed to vary as a function of the Fermi level position of a catalyst. Considering an acceptor type adsorption, the occupancy of a negative charge on the adsorbed species (η_{O^-}) is expressed as [9]

$$\eta_{\text{O}^-} = \frac{\exp[(-\Delta u + \varepsilon_s^+ - u^+)/kT]}{1 + 2 \exp(-\Delta u/kT) \cosh[(\varepsilon_s^+ - u^+)/kT]} \quad (1)$$

where, ε_s^+ , Δu and u^+ are the surface Fermi level position, the potential between the adsorption state and conduction band, and the potential between the adsorption state and acceptor state of adsorbed species, respectively. The adsorption of oxygen shows acceptor type adsorption owe to its large electronegativity and the occupancy of charge on the adsorbed species would follow the Eq. (1). Supposing that oxidative reaction of CO over CuO proceeds by the Rideal mechanism, the reaction rate of CO oxidation is expressed as [9]

$$r = \alpha N_{\text{O}} \eta_{\text{O}^-} P_{\text{CO}} \quad \alpha; \text{ constant} \quad (2)$$

where N_{O} and P_{CO} is the total amount of adsorbed oxygen and CO partial pressure, respectively. The relation between ε_s^+ and η_{O^-} , which is supposed by the electronic theory of catalysts proposed by Wolkenstein, is illustrated in Fig. 7. When the surface Fermi level is risen up, the value of η_{O^-} increases and as a result, the reaction rate r increases.

Electronic structure of the CuO-ZnO contact interface is complicated, but the p-i-n structure is supposed as a model of the interface. Assuming the p-i-n structure, the surface Fermi level of the CuO of the CuO/ZnO heterocontact would be risen up by applying the reverse bias [15] and the amount of negatively ionized adsorbed oxygen (O^-) will be increased. As a result, the catalytic activity of the CuO

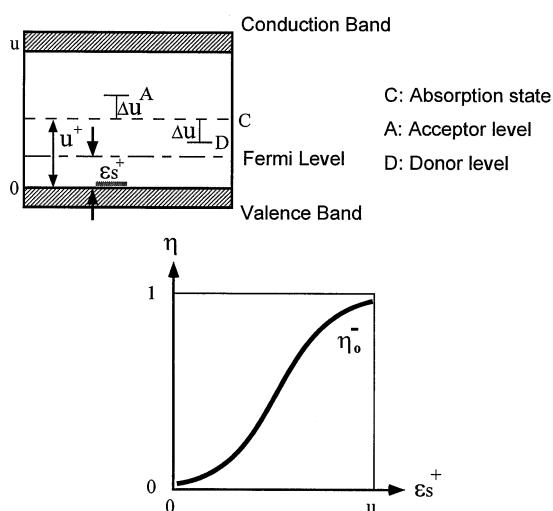


Fig. 7. The relation between the surface Fermi level position (ε_s^+) and the occupancy of a negative charge on chemical species (η_{O^-}), which is supposed by the electronic theory of catalysts proposed by Wolkenstein (ref. 9).

surface would be enhanced. Supposing the highly resistance layer between the CuO and ZnO particles, the enhancement of the catalytic activity of CO oxidation in the CuO/ZnO heterocontact by applying the reverse bias can be explained qualitatively. Increase (decrease) in electron concentration of the surface layer of CuO under reverse (forward) bias is qualitatively explained using a band model and our speculation is shown in Fig. 8. The enhanced catalytic activity for CO oxidation reaction under reverse bias is suggested to be due to the increase in the amount of oxygen ions on CuO, which are negatively ionized by excess electrons produced at the surface layers of CuO. The relation between the CO₂ uptake and applied voltage (Fig. 4) would reflect a part of the

calculated $\varepsilon_s^+ - \eta_O^-(r)$ curve proposed by Wolkenstein (illustrated in Fig. 7) [9].

In Fig. 4, the catalytic activity at zero bias is a little enhanced and a small peak of the CO₂ uptake–voltage relation is observed. The origin of the phenomena is not fully understood yet, however, if the absorbed CO⁺ on CuO is supposed, i.e., the Langmuir-Hinshelwood mechanism is supposed for the CO oxidation over CuO, the occupancy of a positive charge on the adsorbed CO(η_{CO^+}) must be considered and the reaction rate is also expressed as [9]

$$r = \alpha N_0 N_{CO} \eta_O^- \eta_{CO}^+ \quad \alpha; \text{ constant} \quad (3)$$

where N_{CO} is the total amount of the adsorbed CO. If

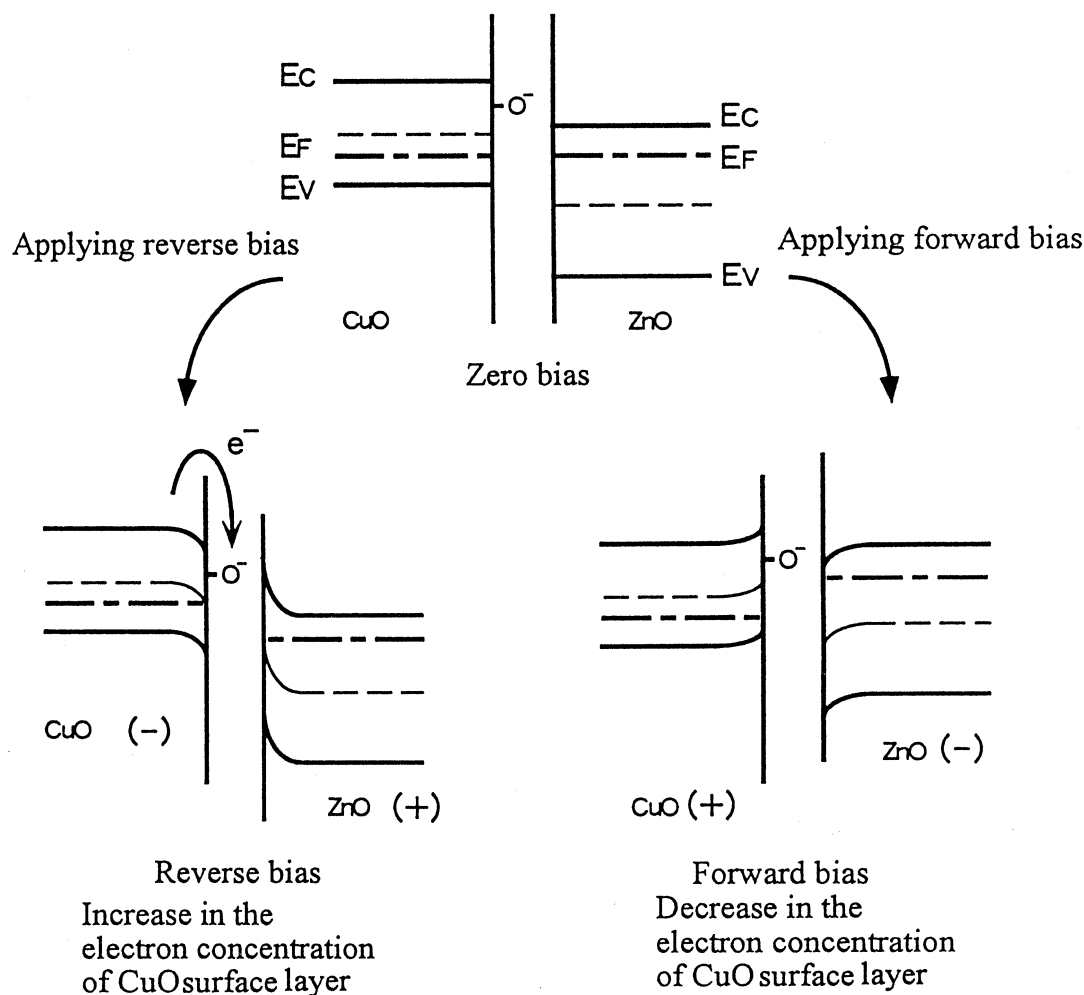


Fig. 8. A band model of the contact interface between CuO and ZnO under forward and reverse bias. Surface Fermi level position of CuO moves as a function of applied bias.

the rate of the CO oxidation at the CuO/ZnO heterocontact followed Eq. (3), the presence of a peak of the CO₂ uptake-voltage relation at around zero bias would be acceptable. However, the validity of Eq. (3) is questionable, because even the reaction mechanisms of CO oxidation over CuO is not fully understood yet and it easily changes by changing the experimental conditions such as CO/O₂ ratio [16]. The origin of the complicated shape of the relation between the CO₂ uptake and applied bias shown in Fig. 4 would be the complicated structure or texture of the CuO-ZnO interface.

The mechanisms of the modification of the catalytic activity for CO oxidation reaction at the CuO/ZnO heterocontact are able to be discussed only qualitatively because of its complicated structure and texture of the interfaces. The result in Fig. 4 would reflect the $\varepsilon_s^+ - \eta_0^-$ curve provided by the theory of Wolkenstein. However, we believe that the discussion of the present study provides the evidence for the validity of the application of electronic theory to the CO oxidation reaction over a semiconductor catalyst and possibly it can be applied to other chemical reaction system at semiconductor heterogeneous catalysts.

Conclusion

Modification of the catalytic activity by applied bias is confirmed at the CuO/ZnO heterocontact made by stacking porous CuO and ZnO sintered bodies. Comparing with the results of the gradient composition CuO/ZnO heterocontact presented in our previous paper, extremely large enhancement of the catalytic activity for CO oxidation reaction is obtained by applying large reverse bias (−2.0 V). The highly rectifying voltage-current characteristics of the CuO/ZnO heterocontact is obtained even at 320°C and the formation of p-i-n structure is suggested as to the electronic structure of the CuO-ZnO interface. The variation in the Fermi level position at the CuO-ZnO contact interface can be considered supposing the p-i-n structure and it plays an important role for the applied voltage dependent catalytic activity of the CuO/ZnO heterocontact. Variation in the surface

Fermi level position of CuO by the variation in applied bias may be a reasonable explanation of the applied voltage dependent catalytic activity of the CuO/ZnO heterocontact and the phenomenon can be explained qualitatively by the electronic theory of catalyst proposed by Wolkenstein.

Acknowledgment

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