CO Gas Identification by Use of Complex Impedance of pn Heterocontact Comprising of Na-Added CuO and ZnO

Kazuyasu HIKITA, Masaru MIYAYAMA and Hiroaki YANAGIDA*

Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153

*Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113

ナトリウムを添加した酸化銅及び酸化亜鉛よりなる pn ヘテロ接触の複素インピーダンス特性を用いた一酸化炭素ガスの識別

足田和康・宮山 勝・柳田博明*

東京大学先端科学技術研究センター, 153 東京都目黒区駒場 4-6-1

*東京大学工学部工業化学科, 113 東京都文京区本郷 7-3-1

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To improve the gas selectivity for carbon monoxide from hydrogen, the complex impedance characteristics under DC bias voltages were studied on a pn semiconductor heterocontact comprised of 1 mol% Na₂O-added CuO (as a p-type semiconductor) and ZnO (as an n-type), in the atmosphere of air-balanced CO or H₂ gas (concentration: 4000 ppm) at 250 and 400°C. In this heterocontact system, the capacitance component of the equivalent-circuit at the interface at 250°C was larger in the CO mixture, but smaller in the H₂ mixture than that in air. As the results of characteristic changes of the equivalent-circuit components to each ambient gas at 250°C, it was shown that CO gas was selectively distinguishable from H₂ gas by using a decrease in the absolute value of reactance at 10 kHz under the bias voltage of -1 V. Moreover, the identification of CO and H₂ gases was shown to be feasible by DC bias dependence of reactance at a fixed frequency and by frequency dependence of reactance at a fixed DC bias. The CO gas identification by use of Na-modified CuO/ZnO was found to be feasible at a lower temperature of 250°C than that for Na-free CuO/ZnO (at 400°C).

Key-words: Gas sensor, Identification, CO, Heterocontact, CuO, ZnO, Na, Complex impedance

1. Introduction

Recently, ceramic gas sensors have been used increasingly to monitor gases in such various fields under harsh conditions as industrial control, environmental control, security and others, because they have such excellent features as durability, stability and reliability compared with other types of sensors.¹⁾⁻³⁾ Among many kinds of objective gases, the sensing of carbon monoxide (CO) with high sensitivity and selectivity is demanded in view of ensuring a safe living environment in today's world. The ceramic-semiconductor gas sensors make use of changes in electrical conductivity based on the delivery and acceptance of electrical charges, that is a phenomenon caused mainly by the adsorption and

desorption of chemical species at the sensor surfaces.^{4),5)} The surface of semiconductor gas sensors is covered with chemisorbed oxygen in air and their amount dominates the conductivity of the sensor surface. Accordingly, it is difficult to distinguish among gases exhibiting similar adsorption behavior and/or similar reactivity with chemisorbed oxygen. The CO and H₂ gases are those having such similar characteristics, and hence additions of metal catalysts and precise control of temperature are required to distinguish CO from H₂.⁶⁾⁻⁸⁾

On the other hand, the sensing characteristics of heterocontact-types of gas sensors have been studied for a variety of gases such as water vapor, flammable gases (H₂, CO, C₃H₈), chlorine, nitrogen oxides and others.⁹⁾⁻¹⁴⁾ In those studies, the gas sensing was carried out by measuring changes of the DC current at a forward bias. It was reported on a heterocontact comprised of ZnO and CuO (prepared from basic copper carbonate) that sensitivities to CO and H₂ gases varied with the applied DC bias.^{10),11)} The best CO sensitivity was obtained when the DC bias of +0.5 V was applied to the heterocontact in the direction of a forward bias (CuO (+), ZnO (-)).¹⁰⁾ In addition, it was reported that the CO gas-sensitivity was improved by using a heterocontact comprised of ZnO and 1 mol% Na₂CO₃ added CuO.¹⁴⁾

The method for tuning sensitivity and selectivity by controlling the DC bias, available on the heterocontact, can not be applied to the usual ceramic-semiconductor types of gas sensors, because their sensitivities are changed little by applied voltage only.¹³⁾ Changes in the dielectric property and the impedance of semiconducting ceramics have so far been used as sensor outputs by several researchers,¹⁵⁾⁻¹⁷⁾ but no studies have dealt with distinguishing gas species by use of changes in the AC signal under a DC bias.

The advantage of using gas sensors with a pn heterocontact is that the different characteristics of gas adsorption on various semiconducting ceramic sur-

faces (p- and n-type) make it possible to distinguish gas species effectively. AC measurements of a CuO/ZnO heterocontact have revealed that the capacitance of the heterocontact was increased by CO adsorption and this chemical adsorption was a process with a long time constant.¹¹⁾ However, even in this system, the gas identification utilizing the AC signal under a DC bias has not been studied.

In the previous papers, we presented that the identification of CO gas from H₂ gas was feasible by use of the impedance of the CuO/ZnO heterocontact on which a DC bias was applied.^{18),19)} The gas was identified well under a minus bias voltage which had never been attracted because of its small DC current. It was also found to be important for the gas identification that the resistance and the capacitance at the interface had different values in each gas atmosphere. In the present study, the effect of Na addition to CuO on the improvement of CO gas identification was examined, by the use of the complex impedance of the Na₂O-added CuO/ZnO heterocontact under a DC bias.

2. Experimental procedure

2.1 Sample preparation

The starting powder materials of CuO (99.9% purity) and Na₂CO₃ (99% purity), for the p-type semiconductor, were mixed at the molar ratio of 1 mol% Na₂O, by a ball mill with zirconia balls in ethanol for 6h. After filtrating and drying, the mixed powder was calcined in an alumina crucible at 600°C for 3h. The calcined powder was milled again with zirconia balls in ethanol for 6h, and dried. The semiconducting materials of ZnO (n-type, 99.99% purity) and the 1 mol% Na₂O-added CuO were granulated with the addition of a PVA solution, and then pressed into disks 10 mm in diameter and about 1 mm thick. The ZnO and the Na₂O-added CuO disks were sintered for 3h at 1000°C and 800°C, respectively. The relative density of the ZnO was 98% of the theoretical value and that of the modified CuO 85%. After each ceramic disk had been polished (using #1000 emery paper), an ohmic silver electrode was printed onto one side of the disk surface, and the disk was fired at 550°C for 15 min.

2.2 Measurement

Figure 1(a) shows the structure of the Na₂O-added CuO/ZnO pn heterocontact and the sample holder made of stainless steel. The modified CuO and ZnO ceramic disks were clamped in the sample holder by a pair of platinum plates contacting the silver electrodes as to make a heterocontact at the polished surfaces.

Figure 1(b) shows a block diagram of the measurement system for DC current-voltage characteristics and complex impedance under controlled gas atmosphere and temperature.¹⁸⁾ The sample holder was set in the silica-glass tube. As testing gases, air, air-balanced CO (hereinafter, CO mixture) and air-

Fig. 1. The structure of the sample with a pn heterocontact and the block diagram of the measurement system.

(a) The structure of a pn heterocontact comprising semiconducting ceramic disks of 1 mol% Na₂O-added CuO and ZnO.

(b) The block diagram of the measurement system of DC current-voltage characteristics and complex impedance under controlled temperature and gas atmosphere.

balanced H₂ gases (hereinafter, H₂ mixture) of 4000 ppm were flowed at the rate of 200 ml/min. The complex impedance, Z , at the frequencies ranging from 10 Hz to 10 MHz under a DC bias voltage (-10 V– $+10$ V) were measured by applying AC signal (sine wave of 1 V) in the controlled gas atmosphere at 250 and 400°C.

3. Results and discussions

3.1 Electrical properties and influence of gases

Figure 2 shows the temperature dependence of the electrical conductivity (in a logarithmic scale) of the single samples in air. The conductivity of CuO increased, but the temperature dependence of it decreased, with the addition of Na₂O.

Figures 3(a) and (b) show current-voltage characteristics of an Na-added CuO/ZnO pn hetero-

contact in testing gas atmospheres at 250 and 400°C, respectively. The rectifying characteristics are observed in both figures. In our previous papers,^{18),19)} the system using a high-purity CuO ceramic disk gave larger current changes for H₂ gas mixture than

Fig. 2. Temperature dependence of electrical conductivity. Temperatures in parenthesis indicate sintering temperatures.

Fig. 3. Rectifying characteristics of the CuO (1 mol% Na₂O-added)/ZnO pn heterocontact in the testing gas atmospheres (air, CO (4000 ppm) and H₂ (4000 ppm)) at (a) 250°C and (b) 400°C.

Fig. 4. Complex impedance plots (Cole-Cole plots) for the pn heterocontact under DC bias in each testing gas ((a) air, (b) CO (4000 ppm) and (c) H₂ (4000 ppm)) at (A) 250°C and (B) 400°C.

that for CO gas mixture at both 250 and 400°C. In this system (using a 1 mol% Na₂O-added CuO ceramic disk), the CO gas mixture gave almost the same current changes under the forward bias as did an H₂ gas mixture at 250°C. In contrast, the current change by H₂ gas was larger than that by CO gas at 400°C. Therefore, although an improvement of CO sensitivity by the Na₂O addition was confirmed at 250°C, the identification of CO and H₂ gases was still difficult only by using the DC current-voltage characteristics of the pn heterocontact in the forward bias at 250°C.

Figure 4 shows the complex impedance plots in each testing gas at (A) 250°C and (B) 400°C under various DC bias voltages applied to the heterocontact. In Fig. 4, the reactance (X : an imaginary component of impedance) is plotted as a minus value, since it was measured as $Z=R+jX$ (where R is a real component). The data were scattered at very low frequencies, but showed semicircles converged into near the origin point in the high frequency range. In Fig. 4, the semicircle contracted at plus DC biases, but expanded at minus DC biases. The size of semicircles was varied with not only the DC bias applied but also the ambient gas atmosphere at both temperatures.

The basic equivalent circuit of the pn heterocontact is supposed to be the serial connection of the bulk resistance (R_s) and the impedance of the interface (Z_i), which is composed of the parallel connection of a resistance (R_i) and a capacitance (C_i) at the interface, as shown in Fig. 5(a). Then the impedance plot (X vs. R) for the equivalent circuit produces a semicircle, as shown in Fig. 5(b). Since the high frequency end of the Cole-Cole plot converged into the point of the origin as shown in Fig. 4, the resistance R_s of the bulk is found to be negligibly small compared with the resistance R_i at the interface ($R_s \ll R_i$). Therefore, the actual model of the equivalent circuit for a pn heterocontact is assumed to be a parallel connection of a resistance (R_i) and a capacitor (C_i), especially under a minus DC bias.

Fig. 5. An equivalent circuit model of the heterocontact (a), and the theoretical impedance diagram (Cole-Cole plot) for it (b).

In the CO mixture at 250°C, however, the impedance plots exhibited a scatter of data at very low frequencies. At 400°C, the impedance plots also exhibited the deformation of the semicircles at low frequencies in each gas atmosphere, and increases in the absolute value of reactance with increasing resistance were observed at low frequencies under the DC bias of -5 V. This phenomena was not observed in the complex impedance plot on the heterocontact with high-purity CuO and ZnO.¹⁹⁾ A process relating to a chemical reaction with a large time constant may occur in this system, as discussed in the previous papers,^{10),11)} but details are not clear.

3.2 Analysis of equivalent circuit components

The equivalent circuit components (R_i and C_i , shown in Fig. 5(a)) can be obtained by analysis of Cole-Cole plot. Figure 6(a) shows a plot of bias dependence of the resistance component, R_i , for each gas atmosphere at 250°C, and the difference of which is observed significantly in the bias range of minus. The resistance component was decreased in the reducing gas and was the minimum in the CO mixture. The resistance component had corresponded to the resistance of the barrier at the interface, as described in the previous paper.¹⁹⁾ As shown in Fig. 6(b), however, the resistance component (R_i) showed the minimum value in the H₂ mixture at 400°C. Accordingly, the best sensitivity for CO gas was given under the minus DC bias at 250°C.

Figures 7(a) and (b) show the bias dependence of the capacitance component, C_i , of the equivalent circuit at 250 and 400°C, respectively. An increase of

Fig. 6. DC bias dependence of the resistance component, R_i , composing the equivalent circuit of the pn heterocontact, in each testing gas (air, CO (4000 ppm) and H₂ (4000 ppm)) at (a) 250°C and (b) 400°C.

Fig. 7. DC bias dependence of the capacitance component, C_i , composing the equivalent circuit of the pn heterocontact, in each testing gas (air, CO (4000 ppm) and H₂ (4000 ppm)) at (a) 250°C and (b) 400°C.

capacitance by CO gas and a decrease of capacitance by the H₂ gas were observed under minus DC biases at 250°C. Such unique phenomena that the direction of changes in capacitance was different was not observed when the Na₂O-free CuO and ZnO were used to the heterocontact in the previous study.¹⁹⁾ It is considered that the Na addition affected the capacitance changes by atmospheric gas species. In other words, this suggests that the CO gas can be distinguished from the H₂ gas by only use of the changes of the capacitance value of the pn heterocontact under the DC minus bias.

The reactance (X) of the interface of parallel connection with C_i and R_i , as shown in Fig. 5, is written by use of those components and the angular velocity, ω , as below.

$$X = \frac{-\omega C_i R_i^2}{(1 + \omega^2 C_i^2 R_i^2)} \quad (1)$$

When the equivalent components (C_i and R_i) change depending on the ambient gas atmospheres, the frequency dependence of the reactance would also change. Figure 8 shows the dependence of reactance (X) on both the frequency and the DC bias voltage applied to the heterocontact, in each testing gas at 250°C. The curve shows a peak at the characteristic frequency that depends on the ambient gases and the bias voltage. The frequency at the reactance peak shifted to a lower value in each testing gas with an increase in the applied bias to the minus direction.

3.3 Identification of CO gas

Fig. 8. Dependence of reactance (X) on frequency and DC bias applying on the pn heterocontact in each testing gas ((a) air, (b) CO (4000 ppm) and (c) H₂ (4000 ppm)) at 250°C.

In this section, the method to distinguish the CO gas from the H₂ gas is discussed by use of the reactance shown in Fig. 8. Figure 9(a) shows the DC bias dependence of the reactance, measured at 10 kHz for each gas atmosphere at 250°C. The reactance in the H₂ mixture exhibited nearly the same value as that in air under the whole DC bias range applied. The reactance in the CO mixture, however, was different from that in air, and was about one eighth of that in the H₂ mixture under the DC biases between -1 and -5 V. Accordingly, it is considered that the CO gas is distinguishable selectively by a decrease in the absolute value of reactance under the above DC bias range. The decrease in reactance in the CO mixture under the DC bias range at 250°C is considered to derive from both of the decrease of resistance component R_i shown in Fig. 6 and the increase of capacitance component C_i shown in Fig. 7.

In Fig. 9(b), the reactance is normalized by the reactance measured under the DC bias of -1 V for each gas atmosphere, as the form of $X/X(-1V)$. In

Fig. 9. DC bias dependence of reactance (10 kHz) for each testing gas (air, CO (4000 ppm) and H_2 (4000 ppm)) at 250°C (a), and normalized by the reactance under the bias of -1 V in each testing gas (b).

the testing gas of CO mixture, the reactance ratio increased in the DC bias range between -3 and -5 V. On the other hand, increases of the reactance ratio in the H_2 mixture and in air were negligibly small in the same DC bias range. Accordingly, the CO gas is distinguishable from the H_2 gas because the CO gas exhibits a large increase in reactance ratio when the DC bias moves from 0 V to -3 or -5 V.

Figure 10 shows the AC frequency dependence of the reactance under the DC bias of -1 V in each gas atmosphere, normalized by the reactance measured at 1 kHz as the form of $X/X(1 \text{ kHz})$. The reactance ratio in the H_2 mixture decreased with an increase in frequency from 4.5 kHz to 28 kHz. On the contrary, the reactance ratio in the CO mixture increased with an increase in frequency in the same range. These two gases thus can be distinguished because the changing directions of their reactance between 4.5 kHz and 28 kHz are quite opposite.

From the above results, CO and H_2 gases were found to be identified at 250°C by measuring

(i) the reactance at a fixed frequency (10 kHz) and its DC bias dependence, or

(ii) the frequency dependence of the reactance at a fixed DC bias (at -1 V).

From the comparison with the results on a heterocontact of Na-free CuO and ZnO,^{18),19)} the Na_2O addition to CuO is found to be effective to improve the CO selectivity.

3.4 Mechanism of identification of gas

Figure 11 shows a proposed equivalent circuit for the interface of the pn contact. In this equivalent circuit,

Fig. 10. AC frequency dependence of the reactance ratio X/X (at 1 kHz), which is normalized by the reactance measured at 1 kHz under the DC bias of -1 V in each testing gas (air, CO (4000 ppm) and H_2 (4000 ppm)) at 250°C.

Fig. 11. The equivalent circuit of the heterocontact with additional circuit elements in a reducing gas atmosphere.

circuit, an additional resistance R_{ads} and a capacitance C_{ads} , derived from adsorption or reaction of gases, are included. The R_{ads} means an additional path for electrical conduction produced by gases. The R_{ads} and C_{ads} are considered to be connected in parallel to the original resistance (R_{io}) and capacitance (C_{io}) in air atmosphere. Here, R_{io} and C_{io} are treated to be constant. If the introduction of gases gives the specific resistance R_{ads} and capacitance C_{ads} , the resistance and capacitance at the interface, shown in Fig. 11, are written as below.

$$C_i = C_{io} + C_{ads} = aC_{io} \quad (2)$$

$$R_i = \frac{(R_{io} \cdot R_{ads})}{(R_{io} + R_{ads})} = bR_{io} \quad (3)$$

Here, a and b are given as, $a = 1 + (C_{ads}/C_{io})$, $b = (R_{ads})/(R_{io} + R_{ads})$.

Then, reactance, X_o (in air) and X (in reducing atmosphere), are written as follows.

$$X_o = \frac{-\omega_0 C_{io} R_{io}^2}{1 + \omega_0^2 C_{io}^2 R_{io}^2} \quad (4)$$

$$X = \frac{-\omega (ab^2) C_{io} R_{io}^2}{1 + \omega^2 (a^2 b^2) C_{io}^2 R_{io}^2} \quad (5)$$

The angular velocity at the peak of reactance in

reducing atmosphere is given by solving the equation of $dX/d\omega=0$, and expressed as follows.

$$\omega = \frac{1}{(C_i R_i)} = \frac{1}{(a C_{i0})(b R_{i0})} = \frac{\omega_0}{ab} \quad (6)$$

The frequency giving the minimum reactance in the testing gas is proportional to the reciprocal number of the product, $C_i R_i$, according to Eq. (6). If the ab changes depending on the gases and the applied bias, the frequency producing the minimum reactance should also change depending on the gases and the applied bias and then the gas identification would become feasible.¹⁹⁾

Figure 12 shows the DC bias dependence of the product of $C_i R_i$ in each testing gas at (a) 250°C and (b) 400°C. At 250°C, the product, $C_i R_i$, in the CO mixture had the smallest value under minus DC biases and the deviation from that in air was larger than that in the H_2 mixture. Such a decrease of $C_i R_i$ by CO gas would bring about a larger shift of the frequency giving the reactance peak to a high frequency, and a larger change of absolute value of the reactance at the peak position than those by H_2 gas. Such changes can be observed actually in Fig. 8.

On the contrary, the change of $C_i R_i$ by H_2 gas was larger than that by CO gas at 400°C as shown in Fig. 12(b). In this case, the changes of reactance by the H_2 gas is considered larger than that by CO gas. The absolute value of the reactance in the H_2 gas mixture were smaller than that in the CO mixture as shown in Fig. 4(B). From these results, it is found that the shift of frequency and the change of absolute value

of the reactance at the peak position reflect the changes in the resistance and capacitance components at the interface by gases and the applied bias. In addition, the heterocontact composed of Na_2O -added CuO and ZnO was suggested to have the properties (combination of C_i and R_i) suitable for the CO identification at 250°C. From another point of view, the sensitivity of the sensor can be tuned to the maximum for an objective gas by means of applying the minus DC bias at a constant frequency or of scanning AC frequency under a minus DC bias.

What was changed by the addition of Na to CuO? The effect of Na additive is discussed below. According to the previous study of Jung et al.,¹⁴⁾ the solubility limit of Na^+ into CuO was estimated about 1 at%, and high CO sensitivities were observed in the heterocontacts of ZnO and CuO added with Na^+ at concentrations above the solubility limit. From those results, the second phase containing Na^+ , precipitated at the surface or grain boundary of CuO, was supposed to work for stabilizing the CO adsorption on the CuO surface.¹⁴⁾ Since 1 mol% Na_2O addition would produce the second phase in the CuO ceramic body¹⁴⁾ in the present study, such a second phase with excess Na^+ could be considered to work for stabilizing the CO adsorption on the CuO surface and to support the CO selectivity of the heterocontact at 250°C. The increase of capacitance in the CO mixture under the minus DC bias, as shown in Figs. 7(a) and (b), may suggest that the amount of adsorbed CO is larger than that of adsorbed H_2 .

From the other view point of the lattice defect, the role of electronic holes should be taken into account for the specific gas selectivity. If Na^+ ions would dissolve substitutionally in CuO crystal, oxygen vacancies (V_O^{**}) and electron holes (h^*) are supposed to be formed through following equations;

The decrease in resistivity of CuO by an addition of Na_2O , as shown in Fig. 2, is considered due to an increase in electron hole density. The increase of the hole density may promote the chemical adsorption of reducing gas with positive charge on the surface of the CuO semiconductor, as follows.^{10),20)}

However, the contribution of the increased hole density to the promotion of CO adsorption is not clear at present.

The charge transfer at the interface of the heterocontact has been explained to occur through the interface states by adsorbed gases or an oxidation process of the adsorbed gas species with the adsorbed oxygen.^{10),12)} In both cases, an increase in the amount of adsorbed CO would promote the charge transfer, resulting in a decrease of resistance and

Fig. 12. DC bias dependence of $C_i R_i$ in each testing gas (air, CO (4000 ppm) and H_2 (4000 ppm)) at (a) 250°C and (b) 400°C.

reactance. In contrast, H_2 is assumed to be oxidized without the stable adsorbed states and other mechanisms should be considered.

The gas identification, especially for CO gas, was found to be possible by investigating the dependence of reactance on both bias and frequency of a sensor element with a pn heterocontact, in CO or H_2 gas. The function of identification was given by tuning the optimum sensing characteristics for the objective gas by selecting an AC frequency and a DC bias, as described in the previous paper.¹⁹⁾ Moreover, on the gas sensing by use of the impedance characteristics of the pn heterocontact comprised of ZnO (n-type) and Na-added CuO (p-type), the improvement of the gas selectivity for CO was demonstrated. Since it is important on the gas identification that the specific product of the resistance and the capacitance at the interface is different in each gas atmosphere, improvement in selectivity for CO gas would be brought about by the Na addition giving a large change in the product of C_i and R_i . Following the same way of thinking, it is expected that the gas selectivity of gas sensor can be improved by making a suitable combination of hetero-type of ceramic semiconducting materials, of which the resistance and the capacitance will change specifically to the objective gases adsorbed.

4. Conclusions

The DC current-voltage characteristics and the impedance characteristics of a pn heterocontact, comprised of ceramic disks of 1 mol% Na_2O -added CuO and ZnO, were investigated in the atmosphere of air-balanced gases of H_2 or CO (4000 ppm, respectively) at 250 and 400°C.

(1) CO gas exhibited smaller resistance under minus DC biases than that did in H_2 gas mixture at 250°C. The identification of CO gas, however, was difficult by the DC current-voltage characteristics only in this system.

(2) Na_2O -addition to CuO increased the capacitance component of the equivalent circuit at the interface in the CO mixture, but decreased the capacitance component in the H_2 mixture, compared with that in air at 250°C. The identification of CO gas was feasible only by measuring changes in the capacitance component under the minus DC bias.

(3) As the results of characteristic changes of the equivalent-circuit components in each ambient gas at 250°C, the absolute value of reactance at 10 kHz in the CO gas mixture decreased to about one eighth of that in H_2 gas mixture which was nearly the same with that in air, under the DC bias voltages be-

tween -1 and -5 V. Accordingly, it was shown that the CO gas was distinguishable selectively from the H_2 gas by a decrease in the magnitude of reactance under the above DC bias range. Moreover, the identification of CO and H_2 gases was shown to be feasible by the DC bias dependence of reactance at a fixed frequency and by the frequency dependence of reactance at a fixed DC bias. The CO gas identification by use of Na-modified CuO/ZnO was found to be feasible at 250°C lower than that for Na-free CuO/ZnO at 400°C.

(4) Na_2O -addition to CuO (of pn heterocontact with ZnO) made a different combination of equivalent-circuit components for each testing gas, and was effective to improve the selectivity for CO gas by use of complex-impedance characteristics of the pn heterocontact under minus DC biases at 250°C.

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