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Influence of the Electrode Materials on the Electrical Response of ZnO-based Contact Sensors

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Abstract

The sensitivity to CO and H_2 of heterocontacts between p-*type* La_2CuO_4 *and* n-*type ZnO semiconducting oxides, and the humidity sensitivity of Au/ZnO heterocontacts have been studied. Heterocontacts were prepared by mechanically pressing sintered pellets of the two oxides, or sintered pellets of ZnO and Au sheets. As ohmic electrodes, three different materials were applied on ZnO pellets (Zn-containing Ag, In- and Ga-containing Ag, and Al pastes). This paper reports the influence of the electrode materials used as ohmic contact for ZnO on the chemical sensitive electrical response of both systems. For ZnO pellets with two ohmic electrodes, different resistivities were observed using the various electrode materials. Current–voltage (I–V) characteristics for single ZnO pellets were linear, showing ohmic behaviour. Little chemical sensitivities were observed for ZnO pellets. I–V curves for heterocontacts showed a rectifying character, due to a* p–n *diode behaviour for* La_2CuO_4/ZnO *contacts, and to a Schottky barrier behaviour for Au/ZnO. For both systems, the rectifying character was enhanced in the presence of reducing gases (CO and* H_2*) or humidity, respectively. The chemical response of the heterocontacts, which was due to the* La_2CuO_4/ZnO *and Au/ZnO interfaces, was dependent on the electrode materials applied on ZnO pellets, with the same trend for both systems. The greater the resistivity of the ZnO pellets, the larger the sensitivity of the heterocontacts. Slight differences in the potential barrier heights are induced by the different resistivities of the three electrode materials. The larger the band-bending at ZnO/metal or ZnO/*p-*type semiconducting oxide interfaces, the larger the influence of adsorbates, resulting in increased sensitivity.* © *1998 Elsevier Science Limited. All rights reserved*

1 Introduction

In recent years, world awareness about environmental problems has continued to increase. The continuous release in the atmosphere of chemical pollutants, originating mainly from combustion processes, is the main cause of the deterioration of environmental quality. The development of new methods to monitor gaseous pollutants in air is of primary concern for the knowledge of the extension of the environmental deterioration. Measurements of gas concentrations in air are being carried out mostly by using analytical instruments, which are very precise, but also very costly, they often cannot be placed on-site, and need long periods for data acquisition; thus, they are not suitable for on-line gas monitoring.[1] Solid-state gas sensors, which are cheap, compact, resistant to be placed on-site, and fast for continuous monitoring, are therefore needed for the detection of hazardous gases at low concentrations. The use of semiconducting oxides for the detection of these gases has been proposed for more than 30 years.[2] However, important problems, such as insufficient gas selectivity, lack of systems able to detect very low gas concentrations, and changes in the sensing properties caused by

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surface contamination, are still to be solved for the use of this kind of sensor in outdoor environmental monitoring. In particular, the international standards require that the concentration of pollutant gases should be maintained in the ppb range. The development of gas sensors much more sensitive and selective than those available at the present time is needed. Nevertheless, it is really problematic to overcome the aforesaid limits of semiconducting oxide-based gas sensors because these problems are strictly correlated with their sensing mechanisms.[3]

Similar problems limit the present applications of ceramic humidity sensors.[4] Even though ceramics have superior properties for use in humidity sensors, given their chemical resistance and mechanical strength,[5] the currently available commercial humidity sensors are mainly based on polymeric films. The present success of the polymer-based humidity sensors is due not only to their lower costs, but also to the need for a heating treatment of the porous ceramic humidity sensors.[6] In fact, a progressive drift in resistance of the ceramic sensors occurs for prolonged exposure to humid environments, due to the gradual formation of stable chemisorbed OH^- on the oxide surface.[7] The drift is strictly related to the ionic-type humidity sensing mechanism for porous oxides at room temperature.[8]

It seems thus that the approach which may bring us closer to solving these problems is the investigation of materials showing novel principals of detection.[9] The most promising results have been reported for multiphase materials having intelligent properties.[10] Humidity sensors using bulk heterocontacts between *p*- and *n*-type semiconducting oxides were first proposed by Yanagida in 1979,[11] and recently were studied with a view to the development of commercial devices.[12–14] Since it is assumed that electrolysis of adsorbed water takes place at *p–n* junction sites,[15] *p–n* contacts can be considered as a different class of ceramic humidity sensors.[7] The interfaces between *p*- and *n*-type semiconductors have also shown to possess a gas-sensing mechanism different from that of the single oxide semiconductors.[16] Mechanically pressed heterocontacts between *p*- and *n*-type semiconducting oxides have been developed for detecting reducing or flammable gases,[17–26] chlorine,[27] NO_x,[28] and humidity.[29–33] In order to overcome the poor reliability of mechanical contacts, thin-film heterojunction devices have been produced for gas and humidity detection.[34,35] A few studies dealt with understanding electrical properties and sensing mechanisms of the heterocontacts.[36–38] Another type of multiphase materials which showed novel properties as chemical sensors are metal/semiconducting oxide interfaces.[39] Schottky-barrier sensors have been studied for the detection of gases[40–44] and for humidity sensing.[45–47]

In previous papers, we have reported the sensitivity to reducing gases (CO and H_2) of heterocontacts between *p*-type La_2CuO_4 and *n*-type ZnO,[48] and the sensitivity to humidity of contacts between dense ZnO pellets and Au sheets,[49] using different electrode materials applied on ZnO. In this paper, we compare and discuss the results obtained for both these contact systems, considering that the same ZnO pellets were used either to be pressed on La_2CuO_4 pellets or on Au sheets. It must be emphasized that in both cases the different electrode materials applied on the side of ZnO not in contact with the other material affected with the same trend the chemical sensitivity of the *p–n* and metal/oxide interfaces.

2 Experimental Procedure

2.1 Materials

La_2CuO_4 powder was prepared by solid-state reaction between La_2O_3 and CuO (both 99·9% pure, Ko-Jundo Kagaku Co., Ltd.): the two oxides were ball-milled with isopropanol for one day. After the isopropanol evaporation, the mixture was calcined at 900°C for 5 h and again ball-milled for one day. Standard X-ray diffraction (XRD) analysis showed the presence in the final product of La_2CuO_4 only. Both La_2CuO_4 and commercial ZnO (99·99% pure, Ko-Jundo Kagaku Co., Ltd.) powders were uniaxially pressed at 20 MPa into discs 10 mm in diameter and 2 mm in thickness. The pellets of ZnO were sintered in air at 1000°C for 5 h, with a resulting relative density of about 98%, while the pellets of La_2CuO_4 were sintered at 1100°C for 5 h and their relative density was about 75%.

For electrical measurements, Ag paste electrodes were used for the La_2CuO_4 pellets to have an ohmic contact. Three different kinds of electrode materials were applied to the ZnO pellets: Ag paste containing Zn, Ag paste containing In and Ga, and Al paste (all Demetron). The three electrode systems contain metals with a low work function, which, as is well known,[50] will produce an ohmic contact for *n*-type semiconductors, like ZnO. The pastes were printed on the sides of the pellets and then fired at different temperatures, following the recommendations of the supplier, i.e. 500, 580, and 640°C for the three pastes, respectively, in the order as cited above. The electrodes were applied on both sides of the pellets, or on one side only when measured in contact with La_2CuO_4 or Au.

2.2 Electrical measurements for La_2CuO_4/ZnO heterocontacts in gas atmosphere

Electrical measurements were repeatedly carried out on each pellet and on the heterocontact of the two oxides, obtained by mechanically pressing two pellets of the different oxides together with one electrode on each pellet, using a sample holder developed by us for this purpose. The electrical measurements were performed using a digital electrometer (Advantest, mod. TR8652) and a programmable d.c. source (Yokogawa mod. 7651), controlled by a NEC PC 9801F computer. The current–voltage (I–V) characteristics were measured at different temperatures (room temperature, 200, 300 and 400°C), in environments at different concentrations of CO and H_2 (up to 2000 ppm), obtained by controlling flow rates of dry air and of the gas tested. In order to evaluate their response time, a constant d.c. voltage was applied to the specimens and changes in current upon variation of the concentration of the gases were recorded.

2.3 Electrical measurements for Au/ZnO heterocontacts in humid atmosphere

Pellets with two or one ohmic contact, made using the three pastes, were tested. As a comparison, also pellets with no ohmic contact were tested. The electrical response of the pellets was analysed by taking d.c. measurements at different relative humidity (RH) values, using a test cell developed by us, where gold electrodes were mechanically pressed by springs on both sides of the pellets. With this experimental arrangement, fairly reproducible trends were obtained. Dark current–voltage (I–V) characteristics were recorded at room temperature using a digital multimeter (Hewlett Packard, mod. 3458A) and a programmable d.c. source (Keithley, mod. 230), controlled by a computer. The RH-dependence of d.c. was measured by recording the current upon application of a constant d.c. bias, varying RH continuously from 2 to 85%, at a constant rate of 1% min^{-1}. Stability and response time tests were performed by measuring the current for a constant d.c. voltage application, during RH cycling, using a Keithley quasistatic CV-meter 595. For these measurements, the volume of the test chamber was 150 cm^3 and the total flow was 200 cm^3 min^{-1}. In the following text we refer to conditions of 2% RH as dry environment, and 85% RH as wet environment.

3 Results

3.1 ZnO pellets with two ohmic electrodes

The I–V characteristics in dry air for the pellets of ZnO with the three different electrodes (paste of Ag+Zn, paste of Ag+In/Ga, and Al paste), applied on both sides of the pellets, were linear. The ohmic behaviour was observed at all the temperatures tested. At room temperature, the resistivities were evaluated at about 100 for ZnO with Ag+Zn electrodes, 200 for ZnO with Ag+In/Ga electrodes, and 400 Ω cm for ZnO with Al electrodes. The resistivity of ZnO increased up to about 300°C, and then decreased above 300°C. The temperature-dependence of the resistivity had the same trend for all the electrodes used. At 400°C, the resistivities were evaluated at about 400, 600, and 1200 Ω cm for ZnO with Ag containing Zn, Ag containing In and Ga, and Al electrodes, respectively. Ohmic behaviour was observed also for La_2CuO_4 pellets with two Ag electrodes at all the temperature tested. The resistivity of La_2CuO_4 decreased from 25°C (30 Ω cm) to 200°C, and above 200°C increased with increasing temperature, being 10 Ω cm at 400°C.

The ZnO pellets were insensitive to RH: in both dry and wet environments their I–V curves were more or less the same, whatever the electrode materials used.[49] A small sensitivity to RH was observed for La_2CuO_4 pellets, due to the presence of a rather large porosity in the sample.[33] The response to RH was small, however, because of the very low resistivity of this material.[8]

The gas (CO and H_2) response of the single pellets was investigated. The I–V curves for all the pellets continued to show a linear behaviour in the presence of the gases tested. For La_2CuO_4, a typical behaviour of *p*-type semiconductor was observed, with an increase in resistivity when in contact with reducing gases. La_2CuO_4 was slightly more sensitive to CO than to H_2. These results are reported in detail elsewhere.[21] The results for the ZnO pellets with Ag+Zn, Ag+In/Ga, and Al electrodes were in line with the generally accepted explanation of the sensing mechanism for ZnO, an *n*-type semiconductor, which is based on the decrease in resistivity caused by a decrease in adsorbed oxygen concentration due to the oxidation of reducing gases.[51]

The electrical response to the gases tested of the ZnO pellets was influenced by the electrode materials. At temperatures lower than 400°C, the pellets showed negligible sensitivity to gases. Except for the ZnO pellets with Ag+In/Ga electrodes, which showed a response (denoted as I/I_0, where I is the current flowing in gas atmosphere and I_0 the current flowing in air) of about 1·25, ZnO pellets were practically insensitive to CO. At 400°C, the best response to 2000 ppm of H_2 in air, about 2, was shown by ZnO with Ag+In/Ga electrodes, while ZnO with Al electrodes showed the worst response of about 1·15, and an intermediate

response (1·4) was obtained for ZnO with Ag + Zn electrodes. Figure 1 shows the I–V characteristics recorded at 400°C in air and at 2000 ppm H_2 for the ZnO pellets with Ag + Zn, Ag + In/Ga, and Al electrodes. These very low sensitivities can be ascribed to the very low porosity of the ZnO pellets.

The response time to hydrogen was rather low (several minutes), while the response time to CO was faster, but with unstable results. The higher the response of the pellet, the slower the response time, as it is possible to observe in Fig. 2, which shows a comparison of the response time to 200 ppm of CO or H_2 for the three ZnO pellets, at 400°C, with an applied d.c. potential of 0·01 V.

3.2 Gas sensitive La_2CuO_4/ZnO heterocontacts

The I–V characteristics measured in air for the La_2CuO_4/ZnO heterocontacts showed a typical *p–n* diode behaviour in the temperature range from 25 to 400°C. The rectifying current in the forward direction (La_2CuO_4 + /ZnO–) followed a different trend at the various temperatures, with a nearly linear behaviour at 400°C, and a reduced reverse current was observed, with a linear dependence on reverse bias.[21] The higher the temperature, the lower the voltage at which substantial reverse current was first found.

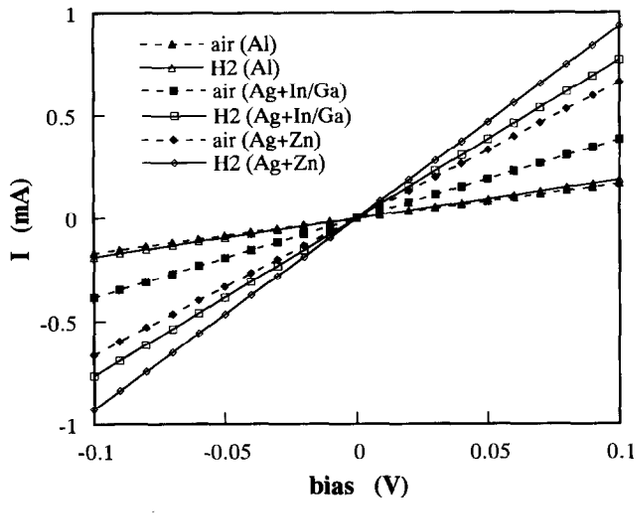

Fig. 1. Dark I–V characteristics of ZnO pellets with two ohmic electrodes at 400°C in air and 2000 ppm of H_2.

The gas response of the heterocontacts was due to the La_2CuO_4/ZnO interface. Nevertheless, their gas-sensitivity was dependent on the electrode materials applied as ohmic contact on ZnO pellets. Figures 3(a), 4(a) and 5(a) show the I–V curves, measured at 400°C in environments with different concentrations of gases, for the heterocontacts between La_2CuO_4 and ZnO with Ag + Zn, Ag + In/Ga, and Al electrodes, respectively. The I–V characteristics in the presence of reducing gases continued to show a *p–n* diode behaviour. However, for heterocontacts with ZnO having Ag + In/Ga electrodes, a substantial increase in the reverse current was observed upon contact with reducing gases at very low reverse bias. As a general trend, high response to hydrogen and lower response to CO was measured for the heterocontacts. The response (I/I_0) increased with increasing temperature: CO was detected only at 400°C, hydrogen at temperatures higher than 300°C.

Figures 3(b), 4(b) and 5(b) show the voltage-dependence of the gas response (I/I_0) calculated from the corresponding curves in Figs 3(a), 4(a) and 5(a). The voltage-dependence of the gas response hanged on the materials used as electrode. The gases affected mainly the forward current and slightly the reverse current, which increased with increasing gas concentration. The highest response was observed for contacts with Al electrode, which at 1 V of forward bias was above 10 for 2000 ppm of H_2, and about 3·5 at 2000 ppm of CO. Different trends for response with bias were observed in

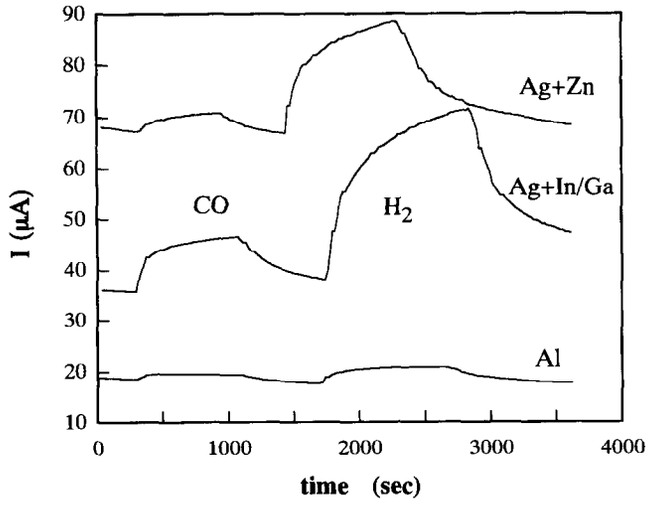

Fig. 2. The typical current response of ZnO pellets with different electrode materials (as stated in the figure) at 0·01 V and 400°C, in the presence of 2000 ppm of CO or H_2.

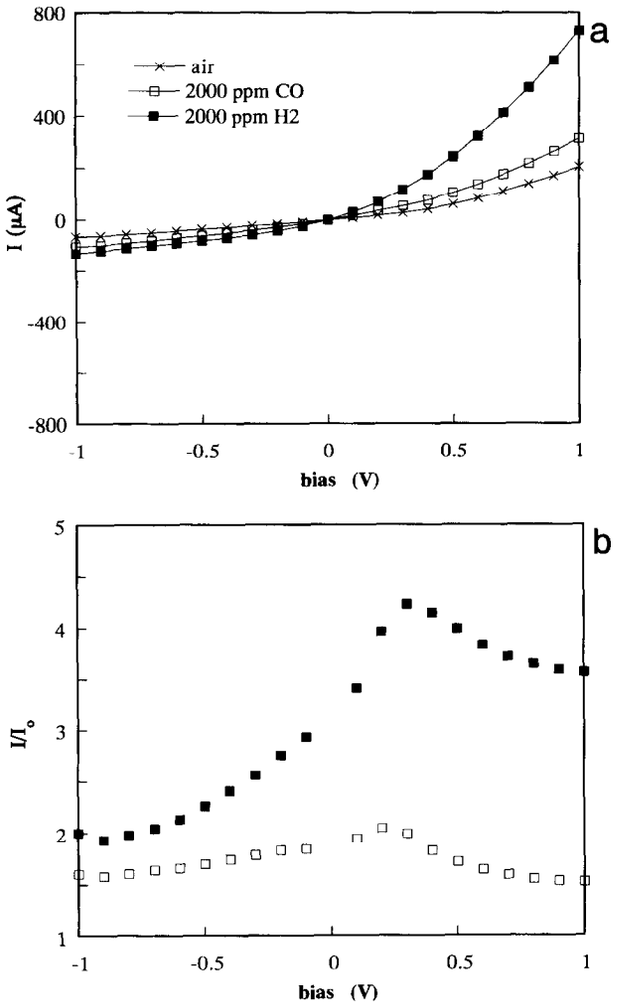

Fig. 3. (a) Dark I–V characteristics and (b) the derived voltage-dependence of the gas response of ZnO(Ag+Zn electrode)/La_2CuO_4 heterocontacts at 400°C in environments at different gas concentrations.

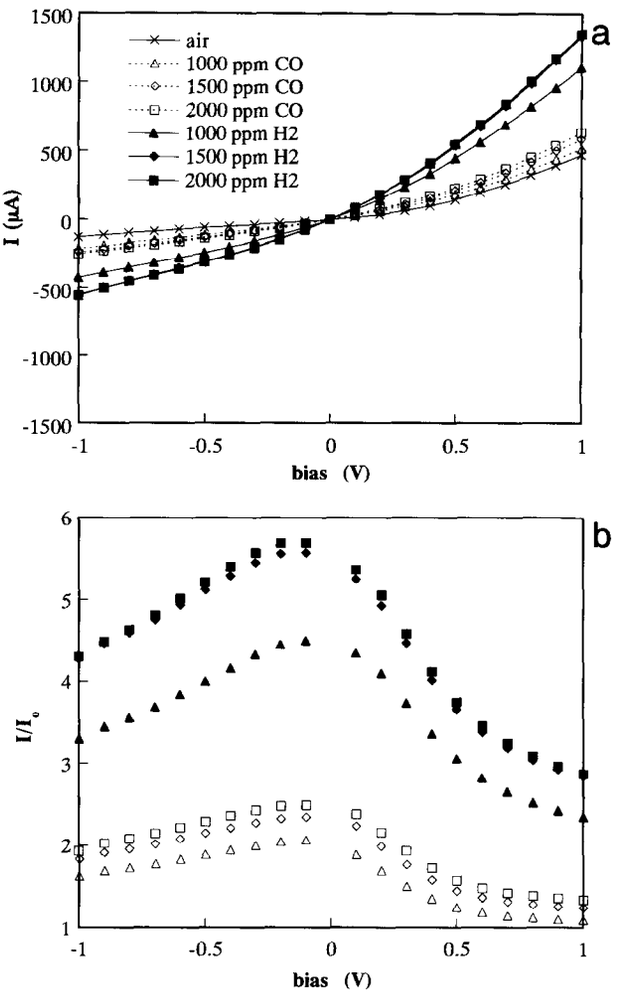

Fig. 4. (a) Dark I–V characteristics and (b) the derived voltage-dependence of the gas response of ZnO(Ag+In/Ga electrode)/La_2CuO_4 heterocontacts at 400°C in environments at different gas concentrations.

hydrogen and CO atmospheres. For the latter, a larger response at reverse bias was observed. The contact with Ag+Zn electrode showed a different trend of bias-dependence, with its maximum at 0·3 V of forward bias, and the lowest response (4·2 for 2000 ppm H_2 at 0·3 V forward). A peculiar behaviour was evidenced by contacts with Ag+In/Ga electrode: the maximum resistivity was observed in reverse bias. This fact may be related to the steeper increase of reverse current level upon contact with H_2 [Fig. 4(a)]. Moreover, poor resolution of the electrical response was observed for different H_2 concentrations. Figures 6, 7 and 8 show the d.c. response time upon applied voltage after exposure to 2000 ppm of CO or H_2 at 300 and 400°C for all the heterocontacts between La_2CuO_4 and ZnO with Ag+Zn, Ag+In/Ga, and Al electrodes, respectively. The response time to hydrogen was very fast (less than 1 min), while the response time to CO was much slower. Fast response time to hydrogen and the most stable results were obtained again by using in the contacts ZnO with an Al electrode. Contacts with Ag+In/Ga electrode showed faster response time to CO but unstable results.

3.3 Humidity sensitive Au/ZnO heterocontacts

When dense pellets with only one ohmic electrode were tested with the other side of the pellet in contact with Au, a diode behaviour was found. Figure 9 shows the I–V characteristics measured on Au/ZnO pellets with Al ohmic contact, in dry (about 2% RH) and wet (85% RH) environments, at room temperature (forward bias is for Au+/Al−). Au has a high work function, and a Schottky barrier may be formed at the chemically abrupt Au/ZnO interfaces, at contact points between the mechanically pressed ZnO pellet and the Au sheet. The Au/ZnO junction sites can be thus reached by the atmosphere. The rectifying character was enhanced in wet environments. The introduction of a non-ohmic contact made the pellets sensitive to humidity, due to the presence of Au/ZnO interfaces. The changes in I–V curves were reversible.

But also in this case the RH-sensitivity depended on the electrode materials used. The I–V curves for

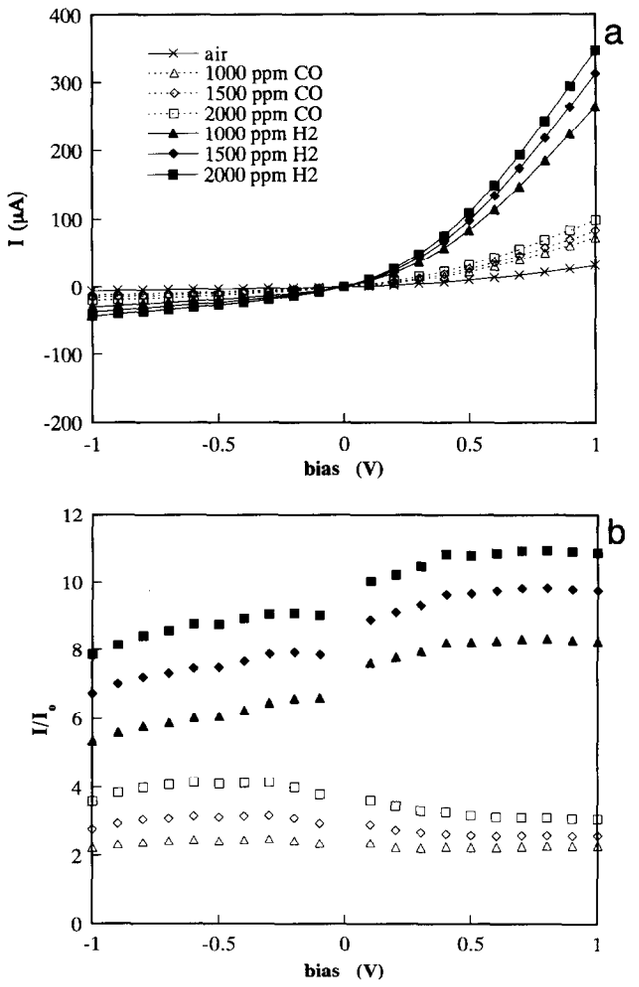

Fig. 5. (a) Dark I–V characteristics and (b) the derived voltage-dependence of the gas response of ZnO(Al electrode)/La_2CuO_4 heterocontacts at 400°C in environments at different gas concentrations.

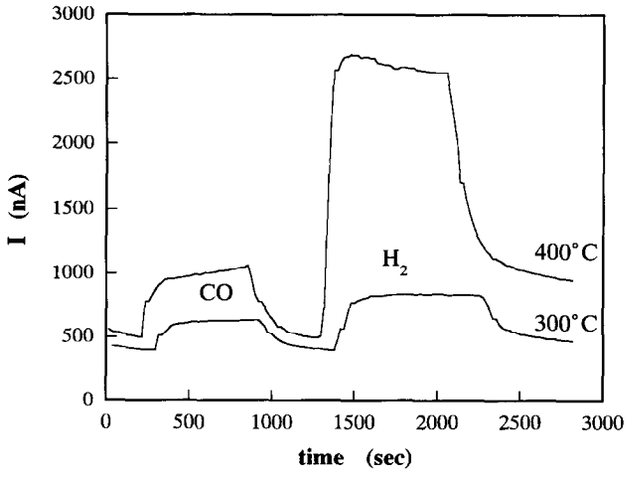

Fig. 6. The typical current response of ZnO(Ag+Zn electrode)/La_2CuO_4 heterocontacts at 0·01 V and different temperatures, in the presence of 2000 ppm of CO or H_2.

Au/ZnO pellets with Ag + Zn contact showed a very limited response to RH, but with the same trend observed for Au/ZnO/Al contacts. Figure 10 shows the I–V characteristics for Au/ZnO pellets with Ag + In/Ga contact in dry and wet environments. In

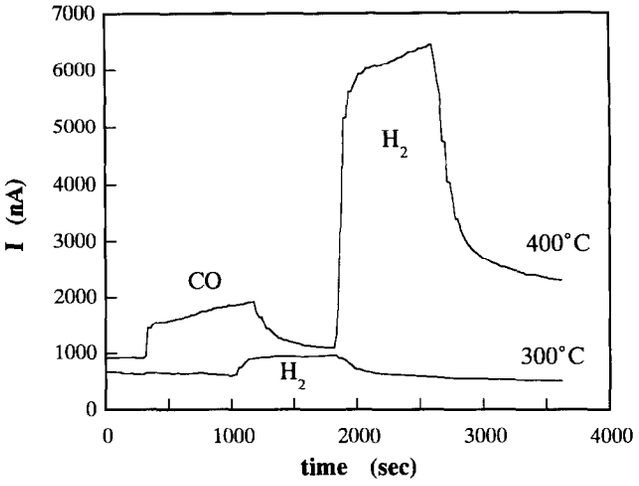

Fig. 7. The typical current response of ZnO(Ag+In/Ga electrode)/La_2CuO_4 heterocontacts at 0·01 V and different temperatures, in the presence of 2000 ppm of CO or H_2.

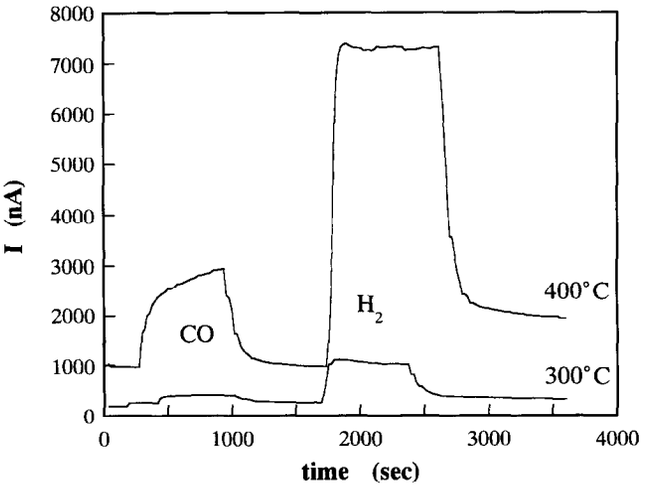

Fig. 8. The typical current response of ZnO(Al electrode)/La_2CuO_4 heterocontacts at 0·1 V and different temperatures, in the presence of 2000 ppm of CO or H_2.

this case, a different trend of the I–V curves in the reverse bias region is observed. For these specimens, the voltage at which substantial reverse currents were first found was about −7 V at 2% RH, and increased with increasing RH, being higher than the voltage observed for the other Au/ZnO contacts (about −10 V). As shown in Fig. 11, the response to RH was voltage-dependent. The Au/ZnO contacts with Al electrode responded to humidity in the forward bias region, with a maximum response (evaluated as the ratio I_{wet}/I_{dry}) of about 2·6 at a bias of 10 V. The same trend was observed for pellets with one Ag + Zn contact, but with a nearly negligible RH response (about 1·2 at 10 V). With reverse bias, these contacts showed no sensitivity. For the Au/ZnO contacts with Ag + In/Ga electrode, a maximum response of about 2·4 was observed with a forward bias of 8 V, but a response to humidity was measured also in the reverse bias region.

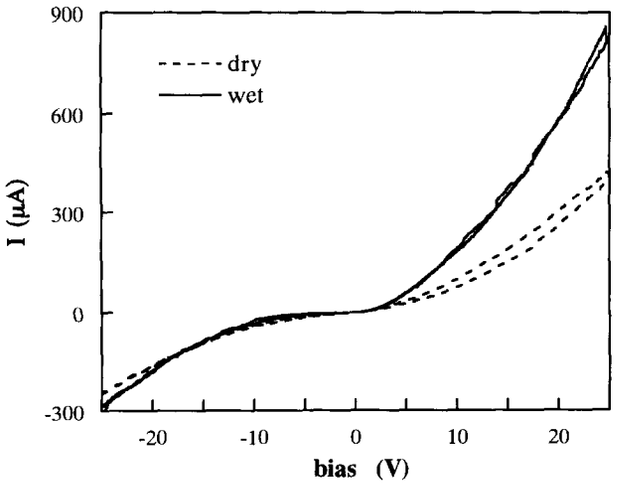

Fig. 9. Dark I–V characteristics of Au/ZnO(Al electrode) contacts, in dry and wet environments, at room temperature.

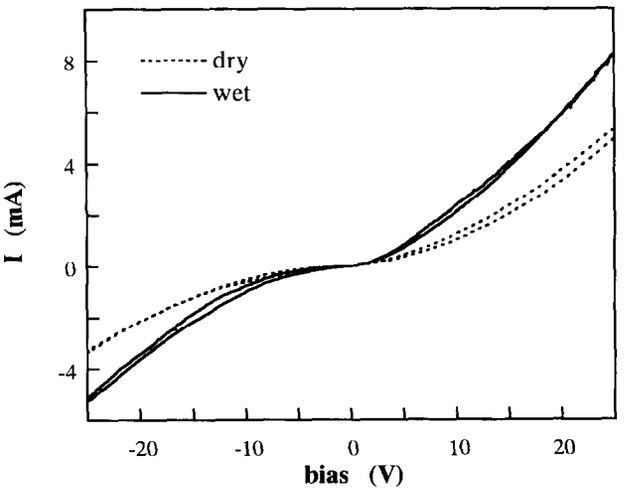

Fig. 10. Dark I–V characteristics of Au/ZnO(Ag+In/Ga electrode) contacts, in dry and wet environments, at room temperature.

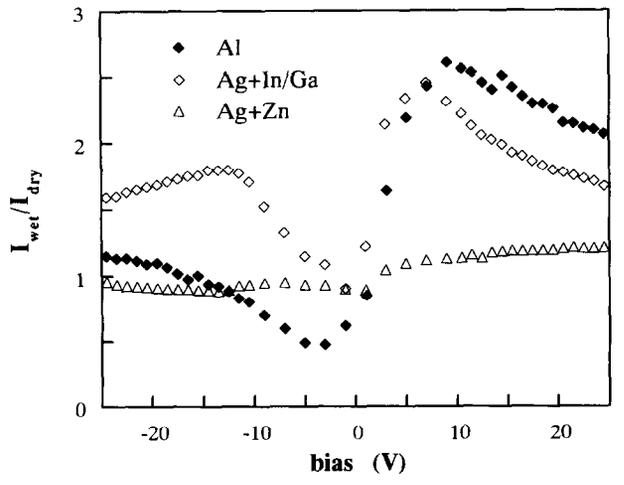

Fig. 11. The voltage-dependence of the RH response (I_{wet}/I_{dry}) of Au/ZnO contacts with various ohmic electrode materials, at room temperature, evaluated from the dark I–V curves in dry and wet environments.

The different electrode materials affected also the response time. As shown in Fig. 12, Au/ZnO contacts with Ag+In/Ga electrode showed the fastest response, particularly during water desorption. Under the experimental conditions, the response time was slower than that in general reported for ionic-type humidity sensors.[8]

4 Discussion

Given the numerous experimental results reported, we have schematically summarised in Table 1 the main results obtained, in order to help the reader in following the discussion.

4.1 ZnO pellets

For ZnO pellets, different ohmic resistivities were observed using different electrode materials. This was quite surprising, given also that the higher resistivity was observed for pellets with Al electrodes. In fact, for bulk ZnO, doping with trivalent elements, such as Al, Ga, and In, produces new donor levels.[52] The trivalent ions occupy normal Zn^{+2} sites, with conversion of a Zn^{+2} ion to a Zn+ ion to maintain electrical neutrality, resulting in increased electron concentration.[53] One thus would have expected that Al/ZnO/Al pellets had the lowest resistivity, which was not the case. In the present case, however, the firing temperatures of the electrodes were too low to expect doping of ZnO in bulk. In fact, energy dispersive spectroscopy (EDS) measurements on cross section of the ZnO pellets with the different electrodes showed the presence of Zn only.

Another possible reason for the different resistivity of ZnO is a different number of charge carriers, induced by a slight stoichiometry change due to the different firing temperatures. But also in this case a large number of charge carriers caused by oxygen deficiency should be expected at the highest temperature, that is for Al electrodes. In fact, we measured the resistivity of some ZnO pellets which were annealed in the same conditions of the electrode firing (500, 580, and 640°C), but without application of electrodes. In–Ga alloy electrodes were used as ohmic contacts. For these samples, resistivity slightly decreased with increasing annealing temperature.

In order to have ohmic contacts for *n*-type semiconductors with surface states, it is necessary that the metal, or an ingredient of the electrode system, has a high oxygen affinity for disrupting the surface layer.[54] The oxygen affinity undergoes the following order: Al > > Ga > Zn. Ag has a very little oxygen affinity. Once again the order of resistivity is the opposite to that expected. Given the firing temperatures of the different electrodes, one possible explanation may be a slight oxidation of the electrode materials which results in increasing

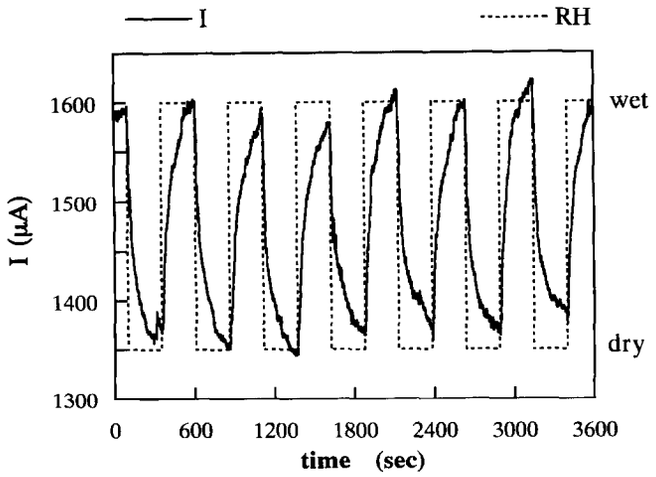

Fig. 12. Current response of Au/ZnO(Ag + In/Ga electrode) contacts to cyclic RH variations, at 10 V and room temperature.

Table 1. Schematic summary of the results obtained for the different systems studied, with the various combinations of electrode materials (Me). The current flowing in air (I_0) and the hydrogen (H_2 resp., measured at 400°C) or humidity [RH resp., measured at room temperature (RT)] responses are compared in terms of low (L), medium (M), and high (H) values for each electrode

	System		
Me	*Me/ZnO/Me*	*Au//ZnO/Me*	*Ag/La_2CuO_4//ZnO/Me*
Ag + Zn	I_0 (RT/400°C): H H_2 resp.: M	I_0 (RT): M RH resp.: L	I_0 (400°C): M H_2 resp.: L
Ag + In/Ga	I_0 (RT/400°C): M H_2 resp.: H	I_0 (RT): H RH resp.: M	I_0 (400°C): H H_2 resp.: M
Al	I_0 (RT/400°C): L H_2 resp.: L	I_0 (RT): L RH resp.: H	I_0 (400°C): L H_2 resp.: H

// mechanical (non-ohmic contacts); / paste (ohmic contacts).

resistivity, following the oxygen affinity order. An overlong firing may have caused the slight oxidation of the electrodes, after disruption of the surface layer. The influence of the electrodes is thus due to some phenomena occurring at the ZnO/electrode interface. However, it must be kept in mind that pastes were used for printing electrodes; the composition of the pastes was not precisely known and they may contain ingredients affecting the formation of the ohmic contacts.

The negligible RH-sensitivity of dense ZnO with two ohmic contacts can be explained by their very low porosity and specific surface area. It has been reported in the relevant literature that a large pore volume is necessary to obtain high RH sensitivity for sintered ceramics.[55] For this reason, the ionic-type mechanism does not occur, given also the low resistivity of the pellets measured in dry air. In fact, the choice of using a dense, pore-free ZnO material was made to reduce the influence of the humidity-sensitive ionic-type conduction mechanism. This allowed us to verify that Schottky barrier metal/semiconductor interfaces are sensitive to humidity.

The understanding of why ZnO pellets with different electrode materials showed different gas sensitivities is even more difficult. It seems likely that the different sensitivities of these pellets can be related to trapping. ZnO with Al electrodes may have an increased trap density, prevailing mutual compensation of donors and acceptors in the bulk, which allows high concentration of defects and low carrier concentration.[56] These defects or traps within the space-charge layer or at the surface can bind electrons and decrease the efficiency of electron injection or extraction at the surface.[57] The influence of the depletion layer (ZnO with Ag + In/Ga electrodes may have an increase band-bending because of adsorbed oxygen producing surface acceptors and binding electrons out of the bulk donors below the surface, thereby resulting in an increased sensitivity to reducing gases), or a different catalytic effect on the oxidation reactions of the metal in the electrodes, with a chemical sensitization occurring through a spill-over effect, may also be claimed for explaining these results. The chemical sensitivity of the ZnO pellets, though small, is without any doubt due to the direct contact between the ZnO surface and the atmosphere. Indeed, the results have shown that the gas response of ZnO pellets is affected also by the interface between the electrode and ZnO.

4.2 ZnO-based heterocontacts

The sensing mechanism of reducing gases is due to phenomena occurring at the *p–n* heterojunctions. Recent results obtained by some of the authors of

this paper showed the importance of the presence of interface states on the sensing properties of *p–n* heterojunctions.[35] It is assumed that the main part of interface barrier is not a physical diffusion barrier, but a chemical-like barrier. The distribution of charge at the interface is derived from chemical adsorbates.[58] The fact that for the heterocontacts the forward current increase is not as abrupt as that observed for conventional *p–n* heterojunctions[59,60] may support the hypothesis that also in this case interface states are mainly responsible for the barrier. The forward current is enhanced by the contact of reducing gases, which decrease the amount of acceptor-type chemisorbed oxygen by an oxidative reaction. The barrier height decreases, thereby resulting in an increase in the current transport across the *p–n* junction in the forward-bias region.

However, the gas response of the *p–n* heterocontacts followed a different trend with respect to the electrode materials from that observed for the single ZnO pellets, as shown in Table 1. The largest hydrogen response for the *p–n* heterocontacts was observed when Al electrode was used for the ZnO pellet, while ZnO pellets with Al electrodes showed the lowest hydrogen response. It is very interesting to point out that the same trend with the ohmic contact materials for ZnO was observed for the RH response of the Au/ZnO Schottky barriers. In this case, too, the largest RH response was observed for Au/ZnO/Al samples, and the lowest for Au/ZnO/Ag + Zn samples.

This is due to the fact that the RH sensing mechanism of Au/ZnO Schottky barriers is similar to the gas sensing mechanism of *p–n* heterocontacts. The I–V curves measured for pellets with Au/ZnO Schottky barrier revealed that their bias-dependent conductance is determined by the Au/ZnO interface, and the ZnO sub-surface depletion layer. The bias-dependent, RH-sensitive resistivity of Au/ZnO interfaces is determined by variations of Schottky-barrier height, with a mechanism similar to that shown by Schottky-barrier gas sensors.[44] Semiconducting oxides usually possess surface states associated with adsorbed oxygen or water-decomposed species.[61] At low RH, the barrier height is affected by the presence of extrinsic surface states which can be formed by water chemisorption. The shape of the I–V curves in the forward-bias region is due to the band bending at the ZnO surface. At high RH, layers of water molecules physisorb on the chemisorbed layer. Therefore, exposure to water vapour leads to the complete saturation of hydroxyl ions through hydrogen bonds, resulting in the neutralization of the charge due to the extrinsic surface states. The result is a further decrease in the Schottky barrier height at high RH, in turn resulting in an increase in the forward current.[47]

It is thus clear that, though in different materials systems and with different detectable species, the two sensing mechanisms are very similar. In both systems, the sensitivity is given by non-linear conduction phenomena. The presence of a Schottky barrier gives a rectifying character, which in the case of heterocontacts is given by *p–n* junctions. This rectifying character is responsible for the RH/gas sensitivity, which is related to the variation of the barrier height because of the presence of surface/interface states. The neutralization of these states by means of physisorbed water/gas oxidation causes the current enhancement with RH/gas in the forward-bias region.

It is possible to observe that the greater the resistivity of the ZnO pellets, the larger the gas response of the *p–n* heterocontacts and the larger the RH response for Au/ZnO Schottky barriers. The same influence on the two systems of the electrode materials used for ohmic contact on ZnO can be thus explained in terms of slight differences in the potential barrier heights induced by the different resistivities of the three ohmic contacts. The difference in resistivity acts in the same way for the Schottky barrier and the *p–n* junction. The larger the band-bending at ZnO/metal or ZnO/*p*-type semiconducting oxide interfaces, the larger the influence of adsorbates, resulting in increased sensitivity.

5 Conclusions

The sensitivity to reducing gases of La_2CuO_4/ZnO heterocontacts and the humidity sensitivity of Au/ZnO mechanical contacts were affected by the materials used as ohmic electrode for ZnO pellets. The electrode materials applied on ZnO pellets in the heterocontacts influenced their chemical sensitivity, probably by the resistivity of the ZnO pellets, which changed with the different materials. The higher the resistivity of the ZnO pellet, the higher the chemical sensitivity. The same influence on the two systems of the electrode materials used for ohmic contact on ZnO can be due to their similar chemical sensing mechanisms. In both systems, the sensitivity is given by non-linear conduction phenomena. The presence of a Schottky barrier gives a rectifying character, which in the case of heterocontacts is given by *p–n* junctions. In both systems, the chemical sensitivity is due to the variation of the barrier height because of the presence of surface/interface states. Thus, slight differences in the potential barrier heights may be induced by the different resistivities of the three

ohmic contacts. The difference in resistivity have the same influence on the Schottky barrier and the *p–n* junction. The larger the band-bending at ZnO/metal or ZnO/*p*-type semiconducting oxide interfaces, the larger the influence of adsorbates, resulting in increased sensitivity.

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