Journal of the European Ceramic Society 19 (1999) 715–719

PII: S0955-2219(98)00302-1
0955-2219/99/$ - see front matter

Humidity Sensitive Electrical Properties of a Novel Ceramic Heterocontact Structure $ZnO/BaPb_{0\cdot 8}Bi_{0\cdot 2}O_3$

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Abstract

The humidity dependence of the voltage-current characteristics of nonsymmetrical and symmetrical heterocontacts $ZnO/BaPb_{0\cdot 8}Bi_{0\cdot 2}O_3$, $ZnO/BaPb_{0\cdot 8}Bi_{0\cdot 2}O_3/ZnO$ and ZnO/ZnO have been studied at fixed temperature in air with different relative humidity values. Nonlinear characteristics have been observed for all the contacts at any humidity values. The increase in the nonlinearity coefficient for the $ZnO/BaPb_{0\cdot 8}Bi_{0\cdot 2}O_3/ZnO$ contact with respect to the ZnO/ZnO contact, and the voltage-current relationship at forward bias for $ZnO/BaPb_{0\cdot 8}Bi_{0\cdot 2}O_3$ heterocontacts are attributed to surface states. The increase in relative humidity causes the decrease in the Schottky potential barrier height, thereby resulting in a redistribution of the voltage drop at the heterocontact interface and in the current growth at lower voltages.

Keywords: interfaces, electrical conductivity, ZnO, sensors, heterocontacts

1 Introduction

At present, the commercial humidity sensors are based on polymeric films, in spite of the better properties of ceramics for this application.[1] This is due to the lower costs of the polymeric sensors and to the need for a heating treatment of the porous ceramic humidity sensors.[2] In fact, a drift in resistance of the ceramic sensors is observed for exposure to humid environments, due to the gradual formation of stable chemisorbed OH^- on the oxide surface.[3] The drift is strictly related to the protonic-type humidity sensing mechanism for porous oxides at room temperature.[4]

Therefore, for the search of perspective ceramic materials for humidity sensors with improved performance, the development of systems with novel humidity sensing mechanisms has been proposed.[5] Heterocontacts between two different oxides, made as simple mechanical contacts with interface open to environmental atmosphere, have shown novel sensing mechanisms both as humidity and gas sensors.[6,7] Humidity sensors using bulk heterocontacts between *p*- and *n*-type semiconducting oxides were first proposed by Yanagida in 1979,[8] and recently were studied with a view to the development of commercial devices.[9–11] Zinc oxide has been often used as one component of relative humidity (RH) sensitive heterocontacts due to its surface properties.[12–16] As the second component of a heterocontact, it is quite interesting to investigate materials with remarkable surface properties. We decided to focus our attention on the $BaPb_{0\cdot 8}Bi_{0\cdot 2}O_3$ (BPB) ceramics, due to the reported switching effect and other contact phenomena.[17] In this paper, we studied the voltage-current characteristics (VCC) of nonsymmetrical ZnO/BPB and symmetrical ZnO/BPB/ZnO and ZnO/ZnO heterocontacts taken in air with different relative humidities. Recently, nonlinear VCC have been reported for ZnO/ZnO single crystal contacts by Nakamura *et al.*[18] Different nonlinearity behaviour was observed depending on the orientation of the contacted single crystals.

2 Experimental Procedure

Zinc oxide ceramic samples from commercial ZnO powders (99·9% pure) were uniaxially pressed at 30 or 60 MPa into discs 10 mm in diameter and 2 mm

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in thickness. The pellets of ZnO were sintered in air at 1000 °C for 5 h, with a resulting relative density of about 98%. $BaPb_{0.8}Bi_{0.2}O_3$ (BPB) powders were prepared starting from commercial (99·9% pure) barium carbonate, lead oxide, and bismuth oxide. The appropriate amounts of these components were mixed in distilled water, dried, compacted at 120 MPa into discs 10 mm in diameter and 2 mm in thickness, and then sintered at 750 °C for 1 h in air. The sides of the pellets were polished in order to obtain parallel surfaces on both sides of each pellets, before the application of ohmic electrodes for the electrical measurements. Ag paste electrodes were used for the BPB pellets, and Al paste electrodes for the ZnO pellets.[19] After checking the ohmic behaviour on pellets with electrodes on both sides, one of the electrodes was removed by polishing with abrasive paper, always keeping parallel the sides of the pellets, in order to prepare the heterocontacts. The pellets were cleaned in acetone before contacting ZnO and BPB, 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. Electrical measurements were performed also on ZnO/ZnO contacts, made with pellets compacted at the same or at different pressures. Symmetrical ZnO/BPB/ZnO contacts were obtained by pressing a BPB pellet without electrodes between two ZnO pellets with one electrode each.

The electrical measurements were performed using a picoammeter/voltage source (Keithley, mod. 487) as d.c. source and amperometer, and a digital multimeter (Solartron Schlumberger, mod. 7150 plus) as external voltmeter. The dark voltage-current characteristics (VCC) were measured at various relative humidity (RH) values, from 4 to 90%, obtained by mixing, dry and wet air controlled streams. Monitoring of RH within the test chamber was performed using a Multisens Inc. (mod. FG80J) hygrometric probe, which gave results accurate to within ±2%. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 10^{-2} to 10^5 Hz, using a Solartron 1255 frequency response analyzer (FRA). In order to increase the input impedance of the apparatus up to 10^{12} Ω, the FRA was coupled with an impedance adaptor built by us. All the measurements were performed at the controlled temperature of 40 °C.

3 Results and Discussion

Figure 1 shows dark VCC of ZnO/BPB heterocontacts measured in forward bias (BPB^+/ZnO^-) at different RH values. One can observe that VCC of ZnO/BPB heterocontacts were nonlinear and RH-sensitive for voltage values higher than 1 V, with a current increase with increasing RH. A hysteresis in the current values was observed when the voltage was decreased, with an increase in current at a given voltage value. We estimated the nonlinearity coefficient (α), defined as equal to (U/I)(dI/dU) = d(logI)/d(logU), as the slope of VCC presented in double logarithmic scales. The VCC of ZnO/BPB heterocontacts (Fig. 1) measured at forward bias at 2% RH showed three regions with different nonlinearity coefficients, $\alpha_1 = 1$ (which means ohmic behaviour) at low voltages, $\alpha_2 = 4{\cdot}4$ at intermediate voltages, and $\alpha_3 = 2$ in the high voltage region. The nonlinearity coefficient α_2 showed the highest values, which also increased sharply with increasing RH, being 10 at 80% RH. However, the α_3 values remained nearly constant at any RH value tested, in the range 1·8–2·5.

Figure 2 shows dark VCC of ZnO/BPB heterocontacts measured in reverse bias (ZnO^+/BPB^-) at different RH values. In this case, the VCC slope increased monotonously with voltage, and current increased with RH in the whole voltage range. The comparison between VCC of ZnO/BPB contacts measured in forward and reverse bias demonstrated a nonsymmetrical behaviour. Moreover, in reverse bias the current values were lower when voltage was decreased (Fig. 2), while the opposite behaviour was observed for VCC in forward bias (Fig. 1).

The nonsymmetry of the VCC for the ZnO/BPB heterocontact can be explained under the assumption that a nonsymmetrical potential barrier exists at the ZnO/BPB interface. This barrier is mainly associated with the ZnO surface depletion layer. However, the presence of an interfacial layer with some additional localized interface states at the surface of BPB ceramics must be taken into account as well. The aforesaid localized states are responsible for the complicated shape of forward-

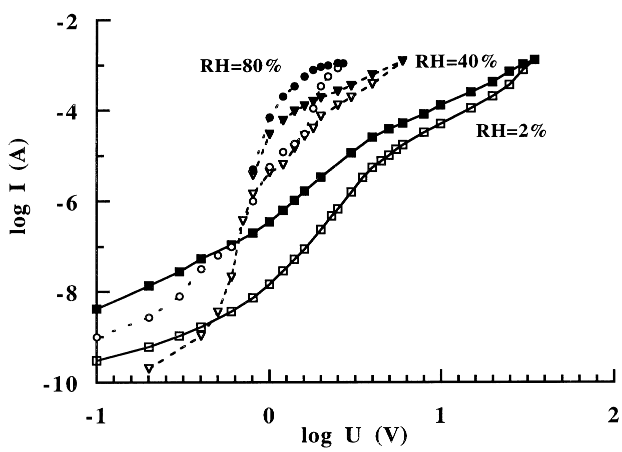

Fig. 1. Dark forward-biased VCC of a ZnO/BPB heterocontact measured at 40 °C increasing (open symbols) and decreasing (full symbols) the voltage at various RH values.

biased VCC, while they play a negligible role in the reverse-biased VCC.

The VCC of ZnO/BPB heterocontacts at forward bias can be explained by the simultaneous occurrence of electron transport through the forward-biased barrier and of a limited filling of interface states. The higher nonlinearity coefficient observed at intermediate voltages, α_2, at low RH is associated to the limited filling of such traps. At higher voltages, the nonlinearity coefficient became lower, assuming a value around 2, which is a value expected for bulk dielectrics with filled traps.[20] The increase in RH caused a lowering of the potential barrier and the redistribution of the voltage applied at the heterocontact. As a result, the process of interface states filling took place in a narrower voltage range, and the nonlinearity coefficient α_2 at higher RH became larger (Fig. 1).

The conduction of ZnO/BPB heterocontacts at reverse bias was controlled mainly by the reverse-biased ZnO surface barrier. The nonlinear increase in current with voltage at a given RH value can be attributed to the decrease in the reverse-biased Schottky potential barrier with the electric field (Schottky effect).[21] The increase in RH caused the reduction of the potential barrier height and the corresponding shift of the whole VCC towards higher current values (Fig. 2).

The observed hysteresis of VCC (Fig. 1 and Fig. 2) has a kinetic origin. At forward bias it can be related to a partial filling of the interface states, which remained filled even after the voltage was lowered. Therefore, the current for some time stayed at higher values. At reverse bias a temporary increase in the ZnO surface barrier height took place and thus the current became lower.

In order to better understand the behaviour of the ZnO/BPB contacts, we performed VCC on symmetrical ZnO/BPB/ZnO contacts at different RH values, as shown in Fig. 3 for one of the bias polarity. The data reported in Fig. 3 are for a contact made with ZnO pellets compacted at different pressures, with the following biasing: $ZnO(60)^+$/BPB/$ZnO(30)^-$. One can observe that also the VCC of ZnO/BPB/ZnO contacts was sensitive to RH, with a trend which was similar to the trend observed for the reverse-biased VCC of ZnO/BPB heterocontacts, although the hysteresis was similar to the forward biased VCC of ZnO/BPB contacts. Therefore, one can assume that conduction of ZnO/BPB/ZnO contacts is controlled by those of the two ZnO/BPB heterocontacts which is reversely biased. VCC for the opposite polarity were similar but not exactly the same, both in the case when we used ZnO pellets compacted at the same or different pressures; this was probably due to the difference of the Surface barriers for the ZnO pellets used. This observation gives an additional evidence for the interface origin of the voltage and humidity dependence of the current in a heterocontact. We evaluated the nonlinearity coefficient at high voltages for the various RH values, being 6 at 2% RH

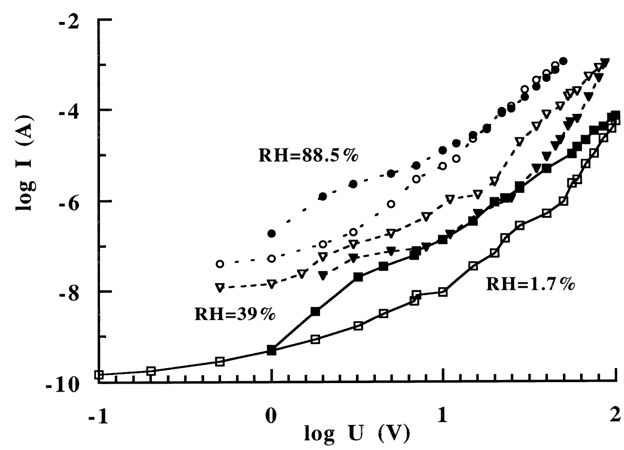

Fig. 3. Dark VCC of a symmetrical ZnO/BPB/ZnO contact measured at 40 °C increasing (open symbols) and decreasing (full symbols) the voltage at various RH values.

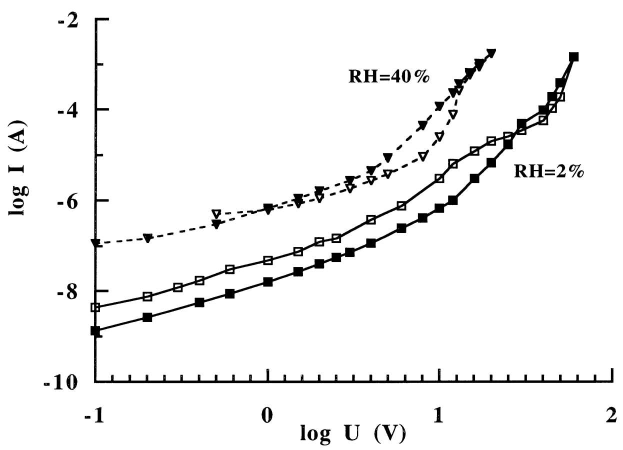

Fig. 2. Dark reverse-biased VCC of a ZnO/BPB heterocontact measured at 40 °C increasing (open symbols) and decreasing (full symbols) the voltage at various RH values.

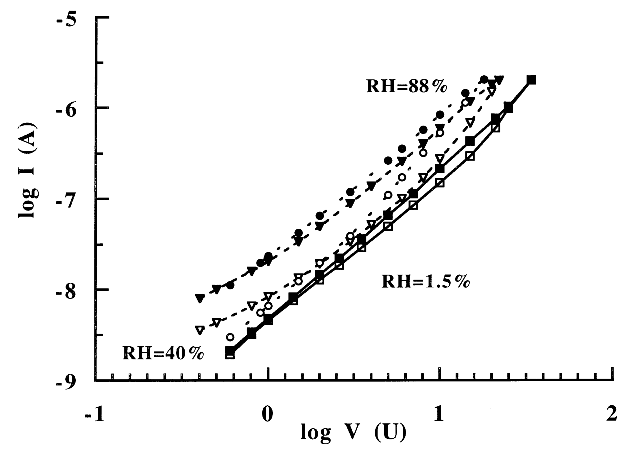

Fig. 4. Dark VCC of a ZnO(60)/ZnO(30) contact measured at 40 °C increasing (open symbols) and decreasing (full symbols) the voltage at various RH values.

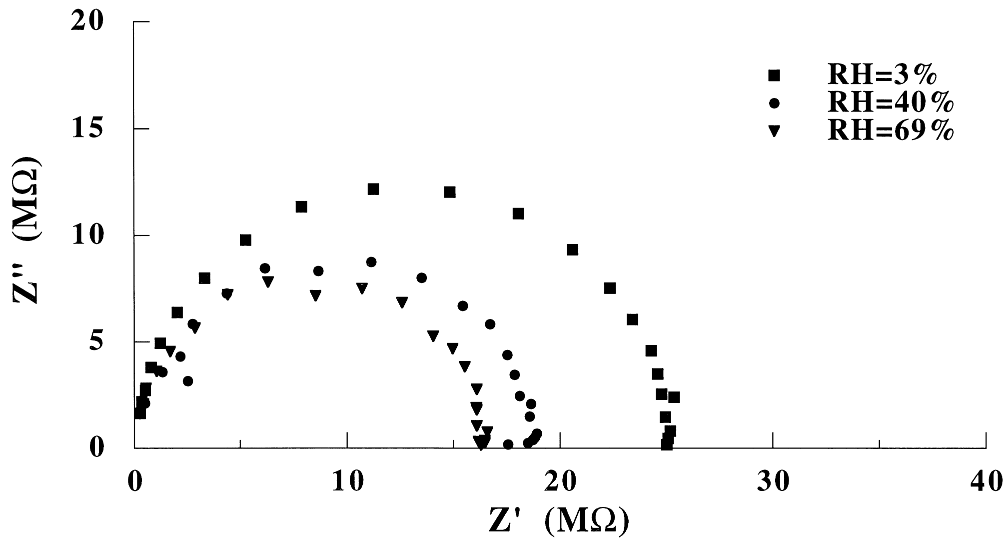

Fig. 5. Complex impedance spectra of a ZnO(60)/ZnO(30) contact measured at 40 °C at various RH values.

and 3·3 at 89% RH. In this case, the nonlinearity coefficient decreased with increasing RH.

We performed also VCC of ZnO/ZnO contacts, in order to study the role of BPB ceramics in the ZnO/BPB/ZnO contacts. Figure 4 shows VCC of ZnO/ZnO contact made with one ZnO pellet compacted at 60 MPa and the other at 30 MPa, the same ZnO pellets used for the data reported in Fig. 3. The curves are reported for the following biasing: $ZnO(60)^+/ZnO(30)^-$. One can observe that VCC were nonlinear, with α between 1·7 and 2·3, and showed a limited RH sensitivity. Clearer increase in current with increasing RH were observed at the highest voltages. The nonlinearity coefficient for ZnO/ ZnO contact was lower than α for the ZnO/BPB/ZnO contacts. This indicates that $BaPb_{0.8}Bi_{0.2}O_3$ gives a contribution to the increase in the nonlinearity coefficient for ZnO/BPB heterocontacts due to some modification of the ZnO/BPB interface electronic structure, although the main role in conduction was played by ZnO surface barrier for reverse bias polarity.

Also for the ZnO/ZnO contact made with two pellets pressed at 60 MPa VCC were nonlinear, with α comprised between 2·1 and 3·3, and showed limited RH sensitivity. In this case, the change in polarity caused only a slight change in VCC, much smaller than the change observed for VCC of the ZnO(60)/ZnO(30) contacts in reverse bias. SEM observations showed that both type of pellets were dense; the ZnO pellets pressed at 60 MPa showed well crystallized, polyhedra grains of about 10 μm, while the ZnO pellets pressed at 30 MPa showed rounded grains of about 1 μm in size. As reported by Nakamura *et al.*,[18] different nonlinear VCC have been reported for ZnO/ZnO single crystal contacts depending on the orientation of the contacted single crystals. The observed nonlinear behaviour for ZnO/ZnO contacts between pellets can be explained in terms of an averaging effect between the conduction at the interfaces of the various grains in the polycrystalline samples.

To support these observations. the EIS spectra of ZnO(60)/ZnO(30) contacts were recorded at different RH values, as shown in Fig. 5. A single distorted semicircle was observed at all the RH values tested. Thus, the equivalent circuit for the ZnO/ZnO contacts can be described as a parallel RC circuit. Resistance, evaluated from the intercepts of the semicircle with the real axis in the complex impedance plots, decreased with increasing RH.

4 Conclusions

$ZnO/BaPb_{0.8}Bi_{0.2}O_3$ heterocontacts showed nonlinear and nonsymmetrical voltage-current characteristics. With increasing relative humidity, an increase in current was observed at high voltage values. Such humidity-controlled behaviour takes place for both voltage polarities. The voltage-current characteristics of $ZnO/BaPb_{0.8}Bi_{0.2}O_3$ heterocontacts at different relative humidities are qualitatively explained by a model with ZnO surface Schottky barrier and an interfacial layer with interface states related to the $BaPb_{0.8}Bi_{0.2}O_3$ surface. Symmetrical $ZnO/BaPb_{0.8}Bi_{0.2}O_3/ZnO$ and ZnO/ ZnO contacts show also a humidity dependence of their voltage-current characteristics. Relative humidity dependence of the ZnO/ZnO contact resistance is supported by EIS measurements. Nonlinearity coefficient for $ZnO/BaPb_{0.8}Bi_{0.2}O_3/ZnO$ contacts were larger than that observed for ZnO/ZnO contacts. This is attributed to the existence of electronic states at the surface of $BaPb_{0.8}Bi_{0.2}O_3$.

Acknowledgements

This work was performed during a stay in Rome of Alexander Glot, supported by a grant as Visiting Professor of the University of Rome "Tor Vergata". This work was supported in part by the National Research Council of Italy (CNR), under the framework of the Targeted Project "Special Materials for Advanced Technologies II". The authors thank Professor Gualtiero Gusmano (University of Rome "Tor Vergata") for helpful discussions and criticisms.

References

1. Kulwicki, B. M., Humidity sensors. *J. Am. Ceram. Soc.*, 1991, **74**, 697–708.
2. Traversa, E., Intelligent ceramic materials for chemical sensors. *J. Intelligent Mater. Systems and Structures*, 1995, **6**, 860–869.
3. Fagan, J. G. and Amarakoon, V. R. W., Reliability and reproducibility of ceramic sensors: part III, humidity sensors. *Am. Ceram. Soc. Bull.*, 1993, **72**, 119–130.
4. Traversa, E., Ceramic sensors for humidity detection: the state-of-the-art and future developments. *Sens. Actuators B*, 1995, **23**, 135–156.
5. Traversa, E., Beyond the limits of chemical sensors: novel sensing mechanisms for ceramics. In *Progress in Ceramic Basic Science: Challenge Toward the 21st Century*, ed. T. Hirai, S. i. Hirano and Y. Takeda. The Basic Science Division, The Ceramic Society of Japan, Tokyo, 1996, pp. 145–158.
6. Yanagida, H., Intelligent materials—a new frontier. *Angew. Chem.*, 1988, **100**, 1443–1446.
7. Traversa, E., Design of ceramic materials for chemical sensors with novel properties. *J. Am. Ceram. Soc.*, 1995, **78**, 2625–2632.
8. Kawakami, K. and Yanagida, H., Effects of water vapor on the electrical conductivity of the interface of semiconductor ceramic–ceramic contacts. *J. Ceram. Soc. Jpn.*, 1979, **87**, 112–115.
9. Yagi, H. and Yanagida, H., Humidity sensor using ceramic hetero-contact. *Jpn. Sens. Newsletter*, 1991, **5**(3), 23–31.
10. Ushio, Y., Miyayama, M. and Yanagida, H., Fabrication of thin-film CuO/ZnO heterojunction and its humidity-sensing properties. *Sens. Actuators B*, 1993, **12**, 135–139.
11. Ichinose, N., R & D trends in chemical sensors. *Chem. Sensors*, 1993, **9**(Suppl. A), 41–44.
12. Toyoshima, Y., Miyayama, M., Yanagida, H. and Koumoto, K., Effect of relative humidity on current–voltage characteristics of Li-doped CuO/ZnO junction. *Jpn. J. Appl. Phys.*, 1983, **22**, 1933.
13. Nakamura, Y., Ikejiri, M., Miyayama, M., Koumoto, K. and Yanagida, H., The current–voltage characteristics of CuO/ZnO heterojunctions. *J. Chem. Soc. Jpn.*, 1985, 1154–1159.
14. Marra, R. A., Nakamura, Y., Fujitsu, S. and Yanagida, H., Humidity sensitive electrical conduction of ZnO–$Ni_{1-x}Li_xO$ heterocontacts. *J. Am. Ceram. Soc.*, 1986, **69**, C143–145.
15. Traversa, E., Bearzotti, A., Miyayama, M. and Yanagida, H., The electrical properties of La_2CuO_4/ZnO heterocontacts at different relative humidities. *J. Mater. Res.*, 1995, **10**, 2286–2294.
16. Yoo, D. J. and Park, S. J., Electrolysis of water in CuO/ZnO heterocontact humidity sensor. *J. Electrochem. Soc.*, 1996, **143**, L89–91.
17. Glot, A. B. and Vasheruk, A. V., Switching phenomenon in Ba–Pb–Bi–O ceramics based structures. In *Proceedings of Electroceramics V, Intern. Conf on Electronic Ceramics and Applications*, Vol. 2, ed. J. L. Baptista, J. A. Labrincha and P. M. Vilarinho. University of Aveiro, Portugal, 1996, pp. 561–564.
18. Nakamura, Y., Harada, T., Kuribara, H., Kishimoto, A., Motohira, N. and Yanagida, H., Nonlinear current–voltage characteristics with negative resistance observed at the ZnO–ZnO single-contact. *J. Am. Ceram. Soc.*, submitted, for publication.
19. Traversa, E., Bearzotti, A., Miyayama, M. and Yanagida, H., Influence of the electrode materials on the electrical response of ZnO-based contact sensors. *J. Eur. Ceram. Soc.*, 1998, **18**, 621–631.
20. Lampert, M. A. and Mark, P., *Current Injection in Solids*. Academic Press, New York and London, 1970.
21. Sze, S. M., *Physics of Semiconductor Devices*. J. Wiley, New York, 1981.