УДК 539.25/88

A. Glot, E. Di. Bartolomeo[1], E. Traversa[1]

Dependence of ZnO/ZnO contact impedance on frequency and air humidity

Dep. of Radioelectronics, Dniepropetrovsk National University,
49050 Dniepropetrovsk, Ukraine,
E-mail: alexglot@mail.ru
[1] Dip. di Scienze e Tecnologie Chimiche,Università di Roma "Tor Vergata",
Via della Ricerca Scientifica, 00133 Roma, Italy

Relative humidity sensitivity of the impedance of ZnO/ZnO contacts between sintered bodies in the range 10^{-2}-10^{2} Hz was measured and a theoretical approach for the explanation of the experimental results is developed. The contact is modelled by a "double Schottky barrier" and a linear resistor connected in series. The calculated frequency dependence of electrical parameters gives a qualitative description of the experimental data.

Ключові слова: поверхні розділу, імпеданс, оксид цинку, сенсори відносної вологості.

Стаття поступила до редакції 19.08.2002; прийнята до друку 23.09.2002

I. Introduction

In the last decade many kinds of humidity and gas sensors based on heterocontacts between p and n type semiconducting oxides have been studied [1-12]. Heterocontacts obtained by mechanically pressing of two oxide sintered bodies exhibit an open interface to the environmental atmosphere that can be sensitive to humidity and/or gas with novel sensing mechanisms [13]. Many of the investigated sensors are made using a ZnO pellet as the n-type semiconducting component.

Zinc oxide based ceramics with certain additives have a varistor-like structure and are often used for voltage stabilizer or other electric devices. They have been widely studied [14-16] and have shown non-linear current-voltage characteristics which are derived from the so called "double Schottky barrier".

Recently it has been reported that ZnO/ZnO homojuction can be sensitive to humidity changes [17]. Nonlinear current-voltage characteristics 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. A recent paper reports a theoretical model of ceramic-ceramic interfaces between p and n type semiconducting oxides [19].

In this paper, a theoretical explanation of the frequency and humidity dependence of real and imaginary parts of impedance of ZnO/ZnO contact is developed, in comparison with experimental measurements.

II. Experimental

To obtain zinc oxide pellets, high-purity ZnO powder (99.99%) was pressed at 60 MPa into disks and then sintered at 1270 K for 1 hour. Sintered disks were grinded and polished using abrasive paper to get parallel and flat surfaces. After a cleaning treatment in acetone, Al paste was applied as electrode on one side of each pellet and then heat-treated at 850 K. ZnO/ZnO junctions were contacted by mechanical pressure using a spring.

Electrochemical impedance spectroscopy measurements were performed on ZnO/ZnO heterocontacts in the frequency range 10^{-2}-10^{2} Hz using a Solartron 1255 Frequency Response Analyzer (FRA) coupled with an impedance adaptor to increase the input impedance up to 10^{12} Ohm. All the measurements were performed at the controlled temperature of 40°C and at various relative humidity (RH) values, from 4% to 90%. Humidity was controlled by mixing controlled dry and wet air streams and measured by a Multisens. Inc. (mod. FG80J) hygrometric probe, which gave results accurate to within ≤ 2%.

Additional examination showes that observed changes of electrical parameters of ZnO/ZnO heterocontact at RH value variation are higher than that ones for each ZnO pellet with two Al electrodes. Besides that electrical parameters of ZnO/ZnO heterocontact are changed very weakly if thickness of each ZnO pellet is varied. Therefore the impedance of studied ZnO/ZnO heterocontact is due mainly to the contact region of ZnO pellets but not to the grain boundaries inside each ZnO pellets. This circumstance is in agreement to the high density of sintered ZnO according to scanning electron microscopy observation [17].

III. Experimental results

Figure 1 shows the frequency dependence of the real part of impedance, z', for ZnO/ZnO heterocontact at different values of RH. At low frequencies ($f < 1$ Hz), $z' = z'_{LF}$ is independent on f. At higher frequencies, a decrease in $z'(f)$ takes place. Plotting $\log z'$ as a function of log f, one can observe that the mentioned drop of z' took place up to about $3\ 10^5$ Ohm and the last value is further independent on frequency. Therefore, a relaxation process can take place at frequencies 1-100 Hz.

Figure 2 shows the frequency dependence of the negative imaginary part of impedance, $-z''(f)$, for ZnO/ZnO heterocontact at different values of RH, which supports this assumption. The maximums of $-z''(f)$ dependences in Fig. 2 are at frequencies $f = f_0 \approx 10$ Hz, thus in the same range where the decrease in $z'(f)$ was found (Fig.1). Therefore, the relaxation process is observed in the ZnO/ZnO heterocontact.

Increasing RH causes a decrease in the low frequency value, z'_{LF} (Fig. 1), a shift of f_0 to higher frequency values, and a decrease in the maximum value of $-z''(f_0)$ (Fig. 2). The observed relaxation process is occurred even in dry atmosphere (RH = 3%) and the intensity of this process (values of z'_{LF} and $-z''(f_0)$) is increased with RH decreasing. Therefore such relaxation process is originated from the nature of heterocontact and it is under the influence of humid atmosphere.

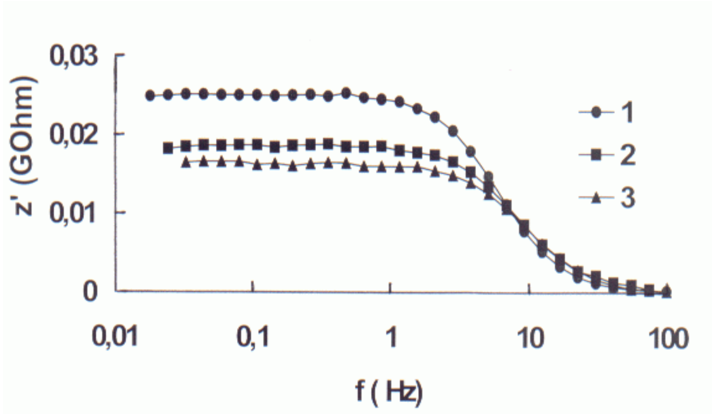

Fig.1. Frequency dependence of the real part of impedance for ZnO/ZnO heterocontact recorded at different relative humidity values: 1 – 3%, 2 – 40%, 3 – 69%.

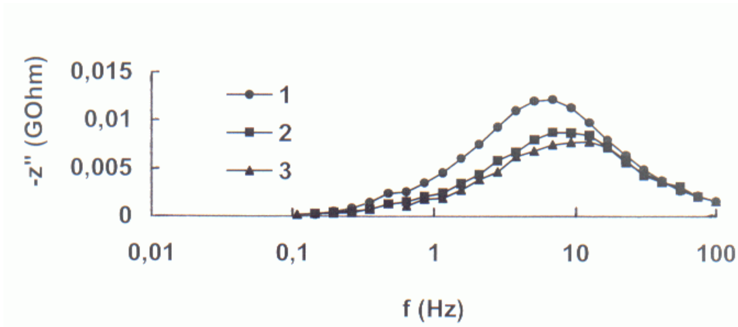

Fig.2. Frequency dependence of the negative imaginary part of impedance for ZnO/ZnO heterocontact recorded at different relative humidity values: 1 – 3%, 2 – 40%, 3 – 69%

IV. Discussion

To understand the obtained frequency dependence of real and imaginary parts of ZnO/ZnO heterocontact impedance it is necessary to calculate the impedance of the studied structure as a function of frequency. Keeping in mind the non-Ohmic properties of ZnO/ZnO heterocontact [17] and the widely accepted model of double Schottky barrier for the description of non-Ohmic behaviour of zinc oxide varistors [15], it is possible to consider such a model for the studied heterocontact.

Suppose that studied heterocontact can be modelled by the double Schottky barrier (DSB) with zero thickness of an intermediate dielectric layer between Schottky barriers having height φ and by linear resistor with resistance R_0 connected in series. This resistor in a first approximation reflects the existence of an intermediate thin dielectric layer between Schottky barriers and bulk resistance of two ZnO pellets.

It is assumed first that low d.c. voltage U_b is applied to DSB with unit cross-section. Current I through the contact can be presented as the difference between currents I_1 and I_2:

$$I = I_1 - I_2, \quad (1)$$

where I_1 is the electron current from the ZnO pellet with negative potential to the ZnO pellet with positive potential, and I_2 is the opposite current. Considering the thermionic emission mechanism of electron transport through the barrier as the single effective mechanism, the value of current I_1 can be written as

$$I_1 = A(T)\exp(-\varphi / kT),$$

where $A(T)$ is a coefficient with relatively weak dependence on absolute temperature T, φ is the barrier height, i.e., the difference between conduction band edges at the surface and at the quasineutral region in the ZnO bulk, k is Boltzmann constant. Almost the whole voltage U_b is applied to the reverse-biased Schottky barrier and the potential barrier for electron transition from the ZnO pellet with positive potential to the ZnO pellet with negative potential is $\varphi + qU_b$. Therefore, one can obtain:

$$I = A(T)\exp(-\varphi / kT)[1 - \exp(-qU_b / kT)]. \quad (2)$$

For low voltage values $(qU_b << kT)$ current I becomes Ohmic:

$$I = GU_b, \quad (3)$$

where barrier conductance G is:

$$G = (A(T)q / kT)\exp(-\varphi / kT). \quad (4)$$

To write the expression for small signal a.c. current it is necessary to take additionally into account the displacement current dQ/dt, where Q is the charge, for example, of the reverse-biased part of DSB. To obtain such expression we neglect the capture of electrons at the DSB interface and consider therefore simply that the barrier height φ is independent on time $(\varphi = \text{const})$. If it is assumed that donors with concentration N_D are shallow and fully ionized in the depletion layer, then $Q = qN_D L$, where L is the depletion layer thickness. The relationship between L and the reverse biased barrier height $\varphi + qU_b$ can be derived from the Poisson's equation $d^2\varphi / dx^2 = q^2 N_D / \varepsilon\varepsilon_0$ and presented in the form:

$$\varphi + qU_b = (q^2 N_D / 2\varepsilon\varepsilon_0)L^2, \quad (5)$$

where ε is relative dielectric permittivity and ε_0 is electric constant. For small voltages $(qU_b << \varphi)$ we have then

$$Q = (2\varepsilon\varepsilon_0 N_D \varphi)^{1/2}[1 + (1/2)(qU_b / \varphi)]. \quad (6)$$

To calculate a.c.current, it is possible to consider the voltage U_b as $\dot{U}_b \exp(j\omega t)$, where $\dot{U}_b$ is the complex amplitude of voltage (thus, $\dot{U}_b = U_b \exp(j\theta_U)$, where U_b is the amplitude of a.c. voltage, and θ_U is the initial phase of voltage), $j = (-1)^{1/2}$ is the imaginary unit, ω is the angular frequency, and t is time.

Then total a.c. current across DSB (in the complex form) can be presented as a sum of active current and reactive current:

$$\dot{I} = G\dot{U}_b + j\omega C\dot{U}_b. \quad (7)$$

The active conductance G of barrier is written above (see expression (4)) and capacitance C of DSB is:

$$C = (\varepsilon\varepsilon_0 q^2 N_D / 2\varphi)^{1/2}. \quad (8)$$

Substitute the voltage drop $\dot{U}_b$ at the DSB by the expression:

$$\dot{U}_b = \dot{U} - \dot{I}R_0, \quad (9)$$

where $\dot{U}$ is complex amplitude of voltage drop at the whole heterocontact. Then real z' and imaginary z'' components of heterocontact impedance

$$z = \dot{U} / \dot{I} = z' + jz'' \quad (10)$$

can be presented (using equation (7)) in the form:

$$z' = R_0 + G^{-1} / (1 + (\omega\tau)^2), \quad (11)$$

$$-z'' = G^{-1}\omega t / (1 + (\omega t)^2), \quad (12)$$

where:

$$\tau = G^{-1}C \quad (13)$$

is the relaxation time. This parameter is dependent on temperature and barrier height, as it can be seen using expressions (4) and (8):

$$\tau = (\varepsilon\varepsilon_0 N_D / 2\varphi)^{1/2}(kT / A(T))\exp(\varphi / kT). \quad (14)$$

For relatively high barrier heights $(\varphi >> kT)$, the relaxation time τ is increased with the barrier height and decreased with temperature.

From equations (11) and (12) it is seen that in the range of frequency around $\omega = \tau^{-1}$ a relaxation process is occured. The real part of impedance is decreased with frequency, according to (11). The negative imaginary part of impedance (see equation (12)) passes through a maximum because $-z'' \approx G^{-1}\omega\tau$ at low frequencies $(\omega\tau << 1)$ and $-z'' \approx G^{-1}(\omega\tau)^{-1}$ at high frequencies $(\omega\tau >> 1)$. It is obvious that the maximum of $-z''(\omega)$ takes place at $\omega_0 = \tau^{-1}$ and the maximum value of $-z''(\omega)$ is:

$$-z''(\tau^{-1}) = (2G)^{-1} = (kT/2A(T)q)\exp(\varphi/kT). \quad (15)$$

The obtained expressions for $z'(\omega)$ and $-z''(\omega)$ can be compared with the experimental data shown in Fig.1 and Fig.2.

Consider first the frequency dependence. At low frequencies $(\omega\tau << 1)$ the real part of impedance (11) is nearly independent on frequency: $z'_{LF} \approx R_0 + G^{-!}$. At RH = 3% and at frequencies $f <$ 1 Hz, z'_{LF} = 2.5 10^7 Ohm (Fig. 1). At higher frequencies $\omega\tau > 1$, z' is decreased with frequency approaching to $z'_{LF} \approx R_0$ = 3 10^5 Ohm. Therefore, the DSB resistance G^{-1} ≈ 2,5 10^7 Ohm is much higher than the resistance R_0: $G^{-1} >> R_0$. This conclusion is in accordance to the assumption that DSB gives the main contribution to the impedance of the heterocontact.

The maximum of $-z''(\omega)$ at RH=3% takes place at frequency $f_0 \approx$ 6 Hz

(Fig. 2). Then, from equation (13) one can obtain for the DSB capacitance $C = G(2\pi f_0)^{-1} \approx 1$ nF. The observed relaxation process is fairly slow. The reason for that is high resistance of the DSB due to the complicated structure of the contact points amongst ZnO ceramics surfaces.

From the maximum value of $-z''(f)$ (Fig. 2), the independent estimation of G^{-1} can be obtained using equation (15): $G^{-1} \approx$ 2,44 10^7 Ohm, which is in good agreement with the value of G^{-1} obtained from Fig. 1.

To realize better the nature of the observed relaxation process, one can present the expressions for z' and $-z''$ in slightly different form. The total current can be written as (see equation (7)):

$$\dot{I} = I_a + jI_r. \quad (16)$$

and then (assuming that initial phase of voltage $\dot{U}$ is zero):

$$z' = UI_a/(I_a^2 + I_r^2), \quad (17)$$

$$-z'' = UI_r/(I_a^2 + I_r^2). \quad (18)$$

Here I_a is the active (in-phase) component of current and I_r is the reactive (capacitive or $\pi/2-$ shifted) component of current.

At low frequencies a half of the period of applied voltage is enough for electron transitions through the barrier, and active (in-phase) component of current I_a is nearly independent on frequency. The reactive component of current I_r at low frequencies is fairly low due to a slow change of space charge with time. At higher frequencies the in-phase component of current I_a becomes smaller as far as electrons have not enough time to jump over the barrier during a half of voltage period. However, the $\pi/2-$ shifted current component I_r at higher frequencies becomes larger because it is not directly correlated with hopping of electrons over the barrier but to the oscillation of space charge near the DSB interface. Then, at higher frequencies, the numerator in equation (17) is decreased and the denominator rather is increased. Therefore z' drops with frequency, according to the experimental observation (Fig. 1).

The frequency dependence of $-z''$ at low frequencies is determined mainly by the numerator in equation (18) and $-z''(\omega)$ is increased with increasing of frequency till the active and reactive components of current become of the same order of magnitude. For $I_r >> I_a$ (at higher frequencies) the value $-z'' \propto I_r^{-1}$ and $-z''$ is decreased with increasing frequency. Therefore, $-z''(\omega)$ passes through a maximum due to a decrease in the active component of current I_a and an increase in the reactive component of current I_r with frequency.

Consider now the relative humidity dependence of z' and $-z''$. An increase in RH may cause a decrease in the potential barrier height φ. The mechanism of such behaviour is quite complicated [1-4]. Therefore, conductance G of a DSB should become larger according to equation (4). Then, from equation (11), z' should become smaller, in agreement with Fig. 1.

The decrease in the potential barrier height φ with increasing RH causes the lowering of the relaxation time τ according to equation (14) (at the condition that $\varphi >> kT$ exponential function in equation (14) gives a stronger dependence than $\varphi^{-1/2}$). Therefore, the frequency at which the maximum of $-z''(\omega)$ takes place ($\omega_0 = \tau^{-1}$) becomes larger as it is shown at Fig.2.

The increase in G with increasing RH leads to a decrease in the maximum value of $-z''(\omega)$, according to equation (15), and explains the experimentally observed decrease in its maximum (Fig. 2). Therefore, the experimental data shown in Fig. 1 and Fig. 2 support the performed calculations.

V. Conclusions

Heterocontacts made of two pellets of sintered zinc oxide and mechanically pressed together are sensitive to relative humidity. The real part $z'(\omega)$ of impedance $z(j\omega)$ is independent on ω at low frequencies and decreases with ω in the frequency range 1 – 100 Hz. The negative imaginary part $-z''(\omega)$ of the impedance $z(j\omega)$ shows a maximum as a function of frequency. The increase in relative humidity causes the decrease in the low frequency part of z', the decrease in the maximum value of $-z''(\omega)$ and the shift of this maximum to higher frequencies. All these effects are explained on the basis of a developed model of a.c. carrier transport through the double Schottky barrier, with height decreasing with increasing of relative humidity.

VI. Acknowledgements

A.G. would like to thank Professor Gualtiero Gusmano and his colleagues for the hospitality and useful discussions during his stay in Rome as Visiting Professor at the University of Rome “Tor Vergata”.

A. Glot *– Professor-Investigador Instituto de Electronica y Computacion, Universidad Tecnologica de la Mixteca;*
E.Di. Bartolomeo *– Professor Dept. of Chemical Science and Technology University of Rome "Tor Vergata";*
E. Traversa *– Professor of Materials Science and Technology University of Rome "Tor Vergata".*

[1] H. Yagi, H. Yanagida. Humidity sensor using ceramic heterocontact // *Jpn. Sens. Newsletter,* **53**, pp.23-31 (1991).
[2] Y. Ushio, M. Miyayama, H. Yanagida. Fabrication of thin film CuO/ZnO heterojunction and its humidity-sensing properties // *Sensors and Actuators,* **12**, pp.135-139 (1993).
[3] E. Traversa, A. Bearzotti, M. Miyayama, H. Yanagida. The electrical properties of La_2CuO_4/ZnO heterocontacts at different relative humidities // *J. Mater. Res.,* **10**, pp.2286-2294 (1995).
[4] D.Y. Yoon, S.J. Park. Electrolysis of water in CuO/ZnO heterocontact humidity sensor // *J. Electrochem. Soc.,* **143**, pp.L89-L91 (1996).
[5] Y. Nakamura, H. Yoshioka, M. Miyayama, H. Yanagida, T. Tsurutani,Y. Nakamura. Selective CO gas sensing mechanism with CuO/ZnO heterocontact // *J. Electrochem. Soc.,* **137**, pp.940-943 (1990).
[6] E. Traversa, M. Miyayama, H. Yanagida. Gas sensitivity of ZnO/La_2CuO_4 heterocontacts // *Sensors and Actuators.,* **17**, pp.257-261 (1994).
[7] K. Hikita, M. Miyayama, H. Yanagida. CO gas identification by use of complex impedance of pn heterocontact comprising of Na added CuO and ZnO // *J. Ceram. Soc. Japan*., **102**, pp. 810-817 (1994).
[8] G.S. Devi, S. Manorama, V.J. Rao. Gas sensitivity of SnO_2/CuO heterocontacts // *J. Electrochem. Soc*. **142**, pp. 2754-2756 (1995).
[9] M. Miyayama, K. Hikita, G. Uozumi, H. Yanagida. A.c. impedance analysis of gas-sensing property in CuO/ZnO heterocontacts // *Sensors and Actuators,* **24-25**, pp. 383-387 (1995).
[10] S.J. Jung, Y. Nakamura, A. Kishimoto, H. Yanagida. Modified CuO surface appropriate for selective CO gas sensing at CuO/ZnO heterocontact // *J. Ceram. Soc. Japan*, **104**, pp.415-421 (1996).
[11] Y. Nakamura, H. Zhuang, A. Kishimoto, O. Okada, H. Yanagida. Enhanced CO and CO_2 gas sensitivity of the CuO/ZnO heterocontact made by quenched CuO ceramics // *J. Electrochem. Soc*. **145**, pp.632-637 (1998).
[12] E.Traversa. Intelligent ceramic materials for chemical sensors // *J. Intelligent Mater. Systems and Structures*. **6**, pp. 860-869 (1995).
[13] E. Traversa. Design of ceramic materials for chemical sensors with novel properties // *J. Am. Ceram. Soc.* **78**, pp. 2625-2632 (1995).
[14] A.B.Glot, C.A.Hogarth. Highly non-linear voltage-current characteristic of the contact to a $ZnO-$based ceramic material // *Int. J. Electronics*. **58**, pp.117-121 (1985).
[15] A.B. Glot, R. Bulpett, A.I. Ivon, C.A. Hogarth. Zinc oxide non-Ohmic ceramics: large-scale inhomogeneous grain boundary controlled material // in *Fourth Euro-Ceramics*, **5**, Eds. G. Gusmano & E. Traversa, pp. 475-482, Gruppo Editoriale Faenza Editrice, Faenza (Italy), (1995).
[16] A.B. Glot, S.V. Mazurik. Nonohmic $ZnO-PbO-Co_3O_4-B_2O_3-TiO_2$ ceramics // *Inorg. Materials*. **34**, pp.189-191 (1998).
[17] A. Glot, E.Di Bartolomeo, E.Traversa. Humidity sensitive electrical properties of a novel ceramic heterocontact structure $ZnO/BaPb_{0.8}Bi_{0.2}O_3$ // *J. Eur. Ceram. Soc.* 19, pp.715-719 (1999).

[18] Y.Nakamura, T.Harada, H.Kuribara, A.Kishimoto, N.Motohira, H.Yanagida. Nonlinear current-voltage characteristics with negative resistance observed at $ZnO-ZnO$ single-contacts // *J. Am. Ceram. Soc.* **82**, pp.3069-3074 (1999).
[19] Y. Nakamura, Y. Ariga, A. Kishimoto, M. Miyayama, O. Okada, H. Yanagida. Electric control of the chemical reaction in ceramic-ceramic contact interface - modeling of the reaction scheme // *J. Electroceram*. **4**, pp. 105-112 (1999).

О. Глот, Е. Ді Бартоломео, Е. Траверса

Залежність імпедансу контакту ZnO/ZnO від частоти та вологості повітря

Дніпропетровський національний університет, факультет радіоелектроніки,
Дніпропетровськ, 49050, Україна,
E-mail: alexglot@mail.ru
[1]*Факультет науки і хімічної технології Римського університету "Tor Vergata",*
Roma, 00133, Italy

Виявлено чутливість до відносної вологості повітря імпедансу контакту ZnO/ZnO між спеченими пластинами оксиду цинку, який виміряно в діапазоні 10^{-2}-10^{2} Гц, і розвинуто теоретичний підхід до пояснення експериментальних результатів. Контакт моделюється здвоєним бар'єром Шотткі та послідовно включеним лінійним резистором. Розрахована частотна залежність електричних параметрів дає якісний опис експериментальних даних.