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SENSORS OF HUMIDITY ON THE BASIS OF ZnO-CERAMICS

Direct current in ZnO-Co₃O₄, ZnO-Co₃O₄-PbO, ZnO-Cr₂O₃, ZnO-MnO ceramics in humid air atmosphere as a function of time after an application of voltage is studied. Samples studied in this paper were obtained by conventional ceramic route. Air atmosphere with fixed relative humidity was created in closed chamber above the surface of saturated water solutions of appropriate salts. All measurements were performed at fixed relative humidity value. Maximum of current in time after a change of applied voltage polarity was observed. Nonmonotonous dependence of current vs. time is discussed on the basis of polarization phenomenon in proton conducting oxide surface. Hydroxyl ions OH⁻ take part in the formation of hydroxyl layer at the oxide surface. Therefore they do not take part in a conduction process. On the contrary protons can easily move at the surface under the influence of electric field. Therefore conduction of oxide ceramics in humid air atmosphere can be due mostly to migration of hydrogen ions (protons) in electric field.

Keywords: oxide ceramics, humidity sensors, time dependence of the current, polarization phenomenon, proton conductivity.

Досліджено часові залежності струму в зразках ZnO-Co₃O₄, ZnO-Co₃O₄-PbO, ZnO-Cr₂O₃, ZnO-MnO кераміки в повітряній атмосфері з підвищеною вологістю. Досліджувані зразки були отримані за стандартною для кераміки технологією. Повітряна атмосфера з постійною відносною вологістю створювалася в закритих посудинах над поверхнею насичених водних розчинів солей. Всі вимірювання виконувалися при постійному значенні відносної вологості. Після зміни полярності прикладеної до зразків кераміки постійної напруги на часових залежностях струму спостерігається максимум. Немонотонна залежність струму від часу обговорюється на основі поляризаційних явищ у кераміці та виникнення протонної провідності. Іони OH⁻ беруть участь в утворенні гідроксильного шару на поверхні оксидів. Вони не беруть участі в процесі провідності. Навпаки, протони можуть легко переміщатися поверхнею під впливом електричного поля. Тому провідність оксидної кераміки у вологій повітряній атмосфері може бути обумовлена в основному за рахунок міграції іонів водню (протонів) в електричному полі.

Ключові слова: оксидна кераміка, вологочутливість, часові залежності струму, поляризаційні явища, протонна провідність.

Исследованы временные зависимости тока в образцах ZnO-Co₃O₄, ZnO-Co₃O₄-PbO, ZnO-Cr₂O₃, ZnO-MnO керамики в воздушной атмосфере с повышенной влажностью. Исследуемые образцы были получены по стандартной для керамики технологии. Воздушная атмосфера с постоянной относительной влажностью создавалась в закрытых емкостях над поверхностью насыщенных водных растворов солей. Все измерения выполнялись при постоянном значении относительной влажности. После изменения полярности приложенного к образцам керамики постоянного напряжения на временных зависимостях тока наблюдается максимум. Немонотонная зависимость тока от времени обсуждается на основе поляризационных явлений в керамике и возникновения протонной проводимости. Ионы OH⁻ принимают участие в образовании гидроксильного слоя на поверхности оксидов. Они не участвуют в процессе проводимости. Напротив, протоны могут легко перемещаться по поверхности под воздействием электрического поля. Поэтому проводимость оксидной керамики во влажной воздушной атмосфере может быть обусловлена в основном миграцией ионов водорода (протонов) в электрическом поле.

Ключевые слова: оксидная керамика, влагочувствительность, временные зависимости тока, поляризационные явления, протонная проводимость.

1. Introduction

Oxide ceramic materials are used quite often for the development of humidity sensors [1, 2]. It was found that ceramics in a system ZnO-Co₃O₄ is a simple example of humidity sensitive resistive material [3, 4] which can be used as a model for studying electrical properties in humid air.

It is commonly accepted that change of electrical parameters of ceramics on relative humidity (RH) is due to the influence of protons H⁺ which exist at the surface as a result of decomposition of adsorbed water molecules: H₂O→H⁺+OH⁻. Hydroxyl ions OH⁻ take part in the formation of a hydroxyl layer at the oxide surface. Therefore they do not take part in a conduction process. On the contrary, protons can easily move at the surface under the influence of electric field. Therefore conduction of oxide ceramics in humid air atmosphere can be due mostly to migration of hydrogen ions (protons) in electric field. In this paper we report some features of direct current observed in ZnO-Co₃O₄ and some other ceramics.

2. Experimental details

Samples studied in this paper were obtained by conventional ceramic route. Starting oxides were weighted in the proportion (mol. %) 95% ZnO and 5% one of the oxides from Co₃O₄, Cr₂O₃ and MnO. Besides that, the composition of 96% ZnO, 1% Co₃O₄, 3% PbO. Oxides were mixed in distilled water, then dried and pressed at pressure 45 MPa. Sintering was performed in air by heating of a sample with the rate 400 K/hour, by exposition of a sample at highest fixed temperature (sintering temperature) T_s=1220 K and by cooling it to the room temperature with the rate 400 K/hour. To obtain electrodes flat surfaces of the samples were grinded and covered with silver paste followed by heat treatment with slow heating up to 970 K and subsequent slow cooling.

Air atmosphere with fixed relative humidity was created in closed chamber above the surface of saturated water solutions of appropriate salts. All measurements were performed at fixed relative humidity value.

Measurements of direct current as a function of time were made after d.c. voltage was applied to a sample or d.c. voltage was changed to the same value of opposite polarity or d.c. voltage was dropped to zero.

3. Results

Application of d. c. voltage to a sample causes current decay on time (Fig. 1, curve 1). It is due to gradual maintenance of polarization in a sample because protons migrate in the direction of external electric field creating internal electric field of opposite direction. If to switch voltage to zero, depolarization current of opposite polarity is observed (Fig.1, curve2) due to the migration of protons back to their balance positions. This migration causes current in external circuit. Such phenomenon is well known and usually takes place in dielectrics and low conducting semiconductors. Mechanism of such slow polarization can be related, for example, to hopping of protons at the surface of ceramics.

After voltage was applied to a sample and current was decreased (Fig. 2, curve 1), the change of voltage polarity only leads to a different behavior of current on time. Current increased, then decreased on time (Fig. 2, curve 2). Subsequent change of voltage polarity each time gives current on time dependence with maximum. Sometimes maximum is not well developed. But in any case such behavior is strongly different on I(t) curve recorded during the first polarization (Fig. 2, curve 1).

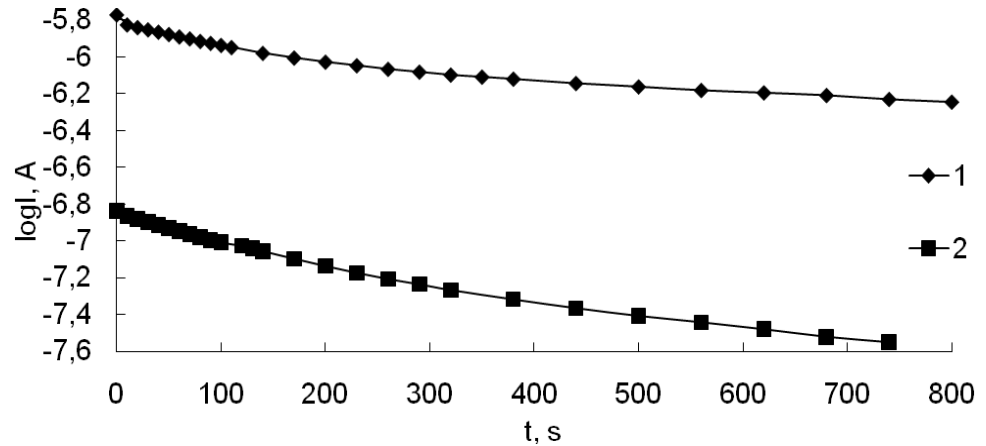


Fig. 1. Time dependence of current for ZnO-Co₃O₄ ceramics in the air with relative humidity 86% observed after application of voltage $U=3$ V (curve 1) and opposite polarity current at the same humidity after decrease of voltage to zero (curve 2).

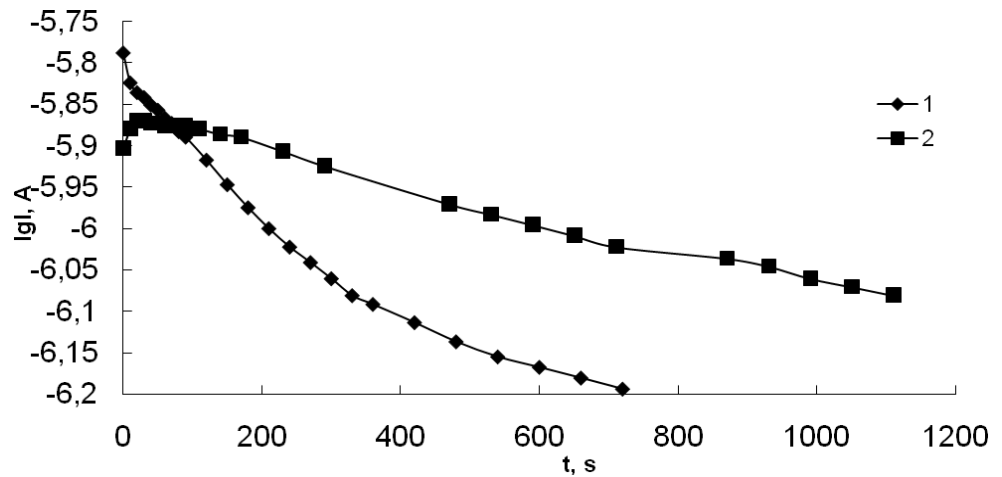


Fig.2. Dependence of current on time for ZnO-Co₃O₄ ceramics studied at relative humidity 86% at voltage $U=3$ V (curve 1) and just after that at voltage $U= - 3$ V (curve 2).

All observed processes can be reproduced after keeping of a sample without voltage at the same relative humidity at least during several hours. Short circuiting of sample's terminals can accelerate such process.

At higher relative humidity (RH=92%) sample has lower resistance but maximum of current after polarization at opposite voltage polarity takes place as well. In this case $I(t)$ curve obtained during polarization process is situated below all subsequent curves recorded after the change of polarity. Such phenomenon was observed as well for ceramics of different chemical composition, for example, ZnO-Cr₂O₃ (Fig. 3), ZnO-Co₃O₄-PbO (Fig. 4), ZnO-MnO.

4. Discussion

Electrical conductance of studied ceramics is strongly dependent on relative humidity. At high RH one can expect some contribution of protonic conduction over surface and neighboring regions of the ceramic sample. The observed features of current on time dependence (Figs. 2-4) can be caused possibly by the reaction of protons at the surface on the change of external electric field.

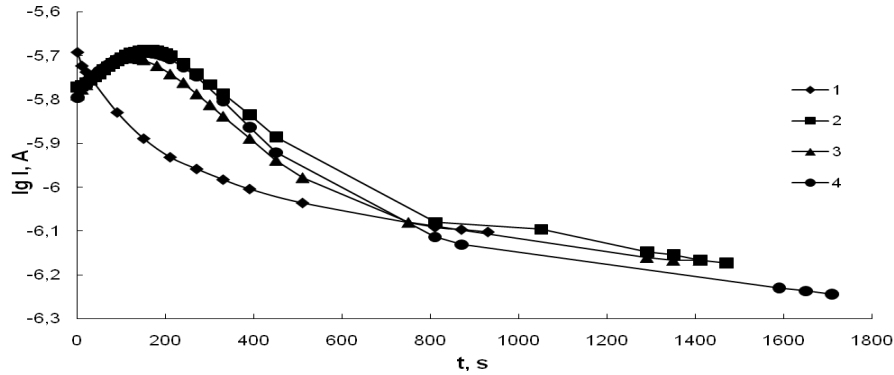


Fig.3. Current on time dependence for ceramics $\text{ZnO-Cr}_2\text{O}_3$ at relative humidity 86% measured in numbers order at voltage $U=3$ V (1, 3) and $U=-3$ V (2, 4).

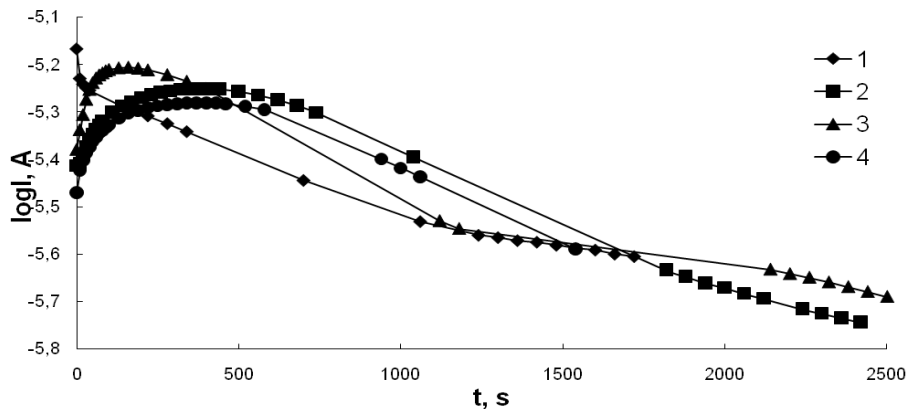


Fig.4. Current on time dependence for ceramics $\text{ZnO-Co}_3\text{O}_4\text{-PbO}$ at relative humidity 86% measured in numbers order at voltage $U=3$ V (1, 3) and $U=-3$ V (2, 4).

The existence of relatively large depolarization current I_{dep} after the application of voltage to a sample (Fig.1, curve 2) certifies that polarization process in a sample took place in electric field. Polarization means some shift of carriers (protons) from their balanced positions in the direction of electric field. Therefore some internal electric field appears with direction which is opposite to the direction of external electric field. Subsequent drop of external voltage to zero and short circuiting the sample lead to the appearance of the depolarization current I_{dep} which is monotonous. Sample approaches gradually to unpolarized state (Fig.1, curve 2).

On the contrary, sharp change of the applied voltage polarity (i.e. the direction of electric field) causes the maximum in the time dependence of current (Fig. 2 -4). Just after the change of voltage polarity current increased on time. Later current goes over

maximum. Observed maximum at $I(t)$ dependence can be related to features of polarization process. Consider possible mechanism of processes related to maximum at $I(t)$ dependence.

Suppose that conduction of studied material is attributed by protons at the surface of a sample. Protons are appeared as a result of adsorption of water molecules and their subsequent decomposition to mobile protons (H^+) and immobile OH^- -groups. Electric field causes migration of protons though OH^- -groups are practically immobile.

Observed gradual change of current (Fig. 1, curve 1) allow us to assume that it is due to a change of polarization $P(t)$:

$$j(t) = dP(t) / dt, \quad (1)$$

where $j(t)$ is density of direct current at a moment t after external constant electric field E was created in the sample, $P(t)$ is polarization (i.e. electric moment of the unit of a sample volume). It means that drift proton current is believed to be smaller comparatively to the displacement proton current (1). Actually protons can migrate for quite long distances, for example, by hopping mechanism. So, expression (1) should be accepted as a generalization of all possible types of proton motion.

From general principles the rate of polarization change dP/dt can be presented by two items. In the absence of electric field the process of polarization disappearance takes place with a rate which is proportional to the value of polarization $P(t)$. In electric field E the rate of polarization change dP/dt is proportional to the value of E . Therefore the behavior of polarization $P(t)$ on time can be found from differential equation

$$dP / dt = -(P / \tau) + gE, \quad (2)$$

where τ is relaxation time, g is proportionality constant. In the absence of electric field ($E=0$) equation (2) gives exponential decrease of polarization on time

$$P(t) = P(0) \exp(-t / \tau), \quad (3)$$

with characteristic time τ . If external electric field exists appears and initial polarization is zero ($P(t)=0$ at $t=0$), then polarization as a function of time can be found from equation (2) in the form

$$P(t) = g \tau E (1 - \exp(-t / \tau)). \quad (4)$$

Polarization in this case increases gradually with decreasing rate and at $t \rightarrow \infty$ it reaches value $P(\infty) = g \tau E$. It is necessary to stress that decrease of the rate of $P(t)$ change is caused by the system approaching to a steady state (it is due to the term $-P/\tau$ in equation (2)).

Consider now the situation which takes place just after the change of voltage polarity after the application of d.c. voltage to the sample during some time. In this case polarization cannot be changed immediately. System aspires to the balance state and electric field strengthens such tendency. Therefore we have the situation when protons at the beginning are shifted to anode and than start to move to cathode not only under the action of external electric field but under the action of internal electric field of polarization (or under the action of concentration gradient). In this case the rate of polarization change is not limited by the opposite process (returning to the balance state). On the contrary $dP(t)/dt$ should be proportional to P/τ . Therefore for time duration till polarization becomes zero the behavior of polarization obeys to the equation

$$dP(t) / dt = P / \tau + gE \quad (5)$$

with starting condition $t=0, P(0) = -P_0$. Then solution of equation (4) can be presented as

$$P(t) = (g\tau E - P_0) \exp(t/\tau) - g\tau E. \quad (6)$$

Equation (6) gives increase of $P(t)$ on time with increasing slope. This solution takes place during time when $P(t)$ is changed from $-P_0$ till zero. At this point equation (5) should be replaced by the equation (2) with gives decreasing slope $P(t)$. Therefore after the change of polarity of external voltage polarization changes from negative value $-P_0$ up to $P=0$ will be in according to equation (6) with increasing slope of $P(t)$. Then polarization increases from $P=0$ up to some value $P>0$ according to equation (4) with decreasing slope of $P(t)$.

Then current (1) can be found from equations (6) and (3) in the form

$$I = ((g\tau E - P_0)/\tau) \exp(t/\tau), \quad 0 \leq t < t_m \quad (7)$$

$$I = gE \exp(-t/\tau), \quad t \geq t_m \quad (8)$$

where t_m is time at which maximum of current is observed:

$$t_m = (\tau/2) \lg(g\tau E / (g\tau E - P_0)). \quad (9)$$

Expressions (7) and (8) give quite sharp maximum though in real situation this maximum becomes not so sharp. The reason for that may be due to the scattering of a distance of protons from their balance position in the state of previous polarization i.e. before the change of voltage polarity. Therefore after switching off the direction of electric field protons may cross their balance positions not exactly at the same time. This effect can decrease the rate of current increase on time. In any case current reaches its maximum at time value when the sign of polarization is changed, i.e. at zero polarization.

5. Conclusions

Monotonous direct current decay on time after the application of d.c. voltage to ceramic sample (discharged prior to this experiment) is recorded. Subsequent discharge of a sample by short circuiting gives depolarization current which is decreased on time slowly. However it is observed that after the keeping of a sample at certain voltage polarity the change of voltage polarity to opposite causes subsequent increase and then decrease of current on time. It means that current on time dependence goes over maximum. Such maximum of $I(t)$ dependence is observed for ceramics of different compositions $ZnO-Co_3O_4$, $ZnO-Co_3O_4-PbO$, $ZnO-Cr_2O_3$, $ZnO-MnO$. Simple semiquantitative model for the explanation of observed effect on the basis of polarization phenomenon at a surface with protons as dominant carriers is presented. Increase of current on time may be due to the migration of protons back to initial balance positions under the influence of external electric field as well as under the influence of internal field of polarization. Subsequent decrease of current on time takes place when protons move from balance positions to positions which correspond to new polarized state.

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