RESEARCH NOTE

ELECTROPHORETIC FORMATION OF ZINC OXIDE BASED NTC RESISTORS

F. Hosseinbabaei and F. Taghibakhsh

Elec. Eng. Dept., K. N. Toosi University of Technology
Tehran, Iran, babaei@eetd.kntu.ac.ir
and far_ahead@yahoo.com

(Received: May 28, 1998 - Accepted in Final Form: May 30, 2000)

Abstract Fine zinc oxide particles were electrophoretically deposited on alumino-ferro-chrome substrates. The deposition was carried out in a cylindrical ZnO/acetone electrophoresis cell. The deposits were dried and sintered at 1030³C in air. The process resulted a porous polycrystalline ZnO cladding over the alloy core. Comb shaped silver electrodes were formed and fired at 350³C. The variation of device resistance vs. temperature was studied in air in the range of 100 - 250³C. The NTC of resistivity at 100³C and the activation energy of carrier generation was found to be 4.0% K^{-1} and 1.1eV respectively.

Key Words Electrophoresis, Electrophoretic Deposition, Zinc Oxide, Thick Film Resistors, NTC Resistors

p@åÚÍA s Ìå[n? Ø?ÑÙ@0måÛn ØÎl ?l ØÎl iÚåt½? oåÛl P?lj ÙÐÚSlÏµÎmRåÐ!? ÙÍ@åxÍ ÑÙÝ n? Ðh@´Ru? @K **æié³_** ÑÙÝ -iy Æ@Z!? ËRu?,ØÎl iÚt½? Ø?Ñ!?ÏRu? č ÚSlÏµÎmRÐ!? ÂÏÄu č Ú lh ÙÍ@xÍ ÑÙÝ -ÇÚÍ@xÍ ÆÎm½+Îmµ+ÏÌÚÉÏÍA Â@R tÚm½ÙÅ0 ÑÙÝ č Ú l@½ÑZÚRÍ -ÇÚhm½ v ÏZ´S hªmÀÚRÍ@u Ñ[lh /Ă1Ă Ø@Éh lh s Nu Î č xg ?iR!? ?l Ðiy ÃÚÐxS iÚåt½? ÑÙÝ ØÎl Ðm¸Í mÚÈg n? Ðh@´Ru? @K ÃĎy Ø?Ñ!Í@y hÎmRÐ!? Îh -hÏK ÑÙ@0mÛn ÑK ÐiÚJt_ ØÎl iÚt½? ÃfÅfRÉ @S /ĂĂ ÙÙ@Éh ÐhÎibÉ lh@Éh mÚÚ°S ÑK QJtÍ lÞµ? QÉÎ@¸É mÚÚ°S -iÙhmÁ QÚJVS Ñ[lh 13Ă Ø@Éh lh Î Ðiy ÑRg@u Î ËÚÏÅå½ Ñå[lh mK $2,Ă mKmK Ñ[lh /ĂĂ Ø@Éh lh QÉÎ@¸É mÚÚ°S Ù´ÌÉ I Ûm¡ -iy ÑC!@¤É hªmÀÚRÍ@u Ñ[lh 03Ă -iÉA QuiK Q!Î ÊÎmRÐ!? /,/ l@K Ø@ÒÀÉ@c iÚ!ÏS ÊÏÚu?ÏÚR½? ØpmÍ?

1. INTRODUCTION

Many fine particles acquire electric charge while suspended in a liquid medium. The charged particles could be driven by an external electric field and deposited on cathode or anode [1]. The process of electrophoretic deposition (EPD) and its wide applications have been reviewed by Sarkar & Nicholson [2]. These applications particularly include the techniques used for deposition of superconducting ceramics on metal substrates [3,4]. This method has also been recently used for fabrication of field emission display devices by deposition of ZnO based phosphorus [5].

The aim of the present work was to use the EPD technique for the fabrication of porous polycrystalline ZnO bodies for microelectronic applications. Our starting point was the optimum condition for EPD of ZnO in acetone medium reported previously [6]. In this article we have reported the negative temperature coefficient (NTC) of resistivity of electrophoretically formed ZnO bodies for the first time.

2. THE EXPERIMENT

Starting Materials The ZnO powder used was prepared by controlled oxidation of Zinc vapor in air. The evaporation was carried out in an

TABLE 1. The Concentration of Common Zinc Impurities Detected in Zinc Oxide Powder Using ICP Test.

Impurity	Concentration (ppm)
Pb	1500 ppm
Ca	180 ppm
Al	180 ppm
Ti	< 10 ppm
Si	< 10 ppm
Mg	not detected
Cd	not detected
Ag	not detected
Cu	not detected

alumina tank at 800³C. The oxide powder was collected in a borosilicate vessel. The average particle size of the powder was less than 0.5mm (see bellow). The powder was also analyzed for impurities by ICP. Results are presented in Table 1, indicating the major impurity to be Pb with a concentration of 1500 ppm.

Pure acetone obtained from Merck (Art. #13) was used for suspensions. Care was taken to avoid extensive exposure of the liquid to open air. The cylindrical substrate was made of alumino-ferro-chrome obtained from Kanthal AB, Sweden, with a nominal composition stated as 5wt% aluminum, 25wt% chromium and the rest iron.

Deposition Ten grams of ZnO powder was added to 100cc of acetone and stirred well. After a settling time of about 2 minutes, large particles were sedimented and the weight percentage of fine ZnO particles in the liquid was measured to be about 0.03 wt%. This suspension was then added to the deposition cell.

The deposition cell consisted of two electrodes placed in a Pyrex beaker. The inner electrode was the substrate and the outer was a foil of aluminum. The structure of the cell and its circuitry is depicted in Figure 1.

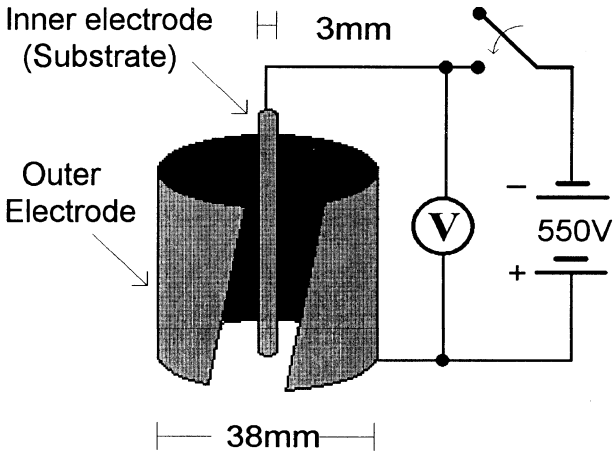


Figure 1. Schematic drawing and geometry of the electrophoresis cell.

The electrochemical potential of ZnO in acetone measured by a x meter is reported to be about 55 mV [7]. This value has been confirmed by electrophoretic migration measurements [6]. According to our experiments, zinc oxide deposition is constantly cathodic and the adherence of the deposits to the cathode is acceptable. Our qualitative observations confirmed the positive effect of 1000 ppm HCl in suspension [8] on the adherence of deposits to the substrate. At the presence of the HCl doping mentioned, the adherence of particles was high enough to resist a mild rubbing with a soft tissue.

We applied 550 V DC to the cell for 2min., which was long enough to sweep nearly all of the particles out of the liquid.

Sample preparation The deposit was left in open air at room temperature for 30 minutes for drying. Then it was placed in an electric furnace (Exciton-1500) and fired according to the profile given in Figure 2. The atmosphere of the sintering chamber in all of firings was air. At

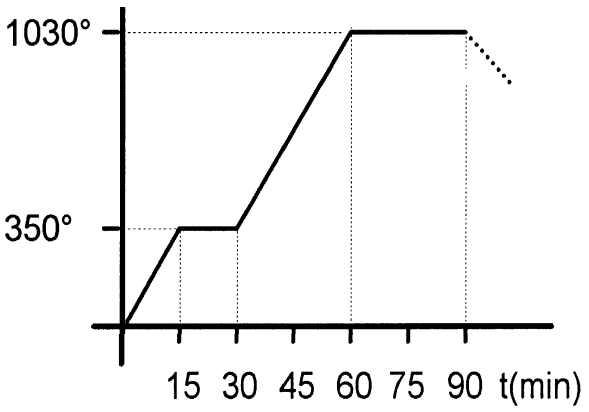


Figure 2. Sintering temperature profile.

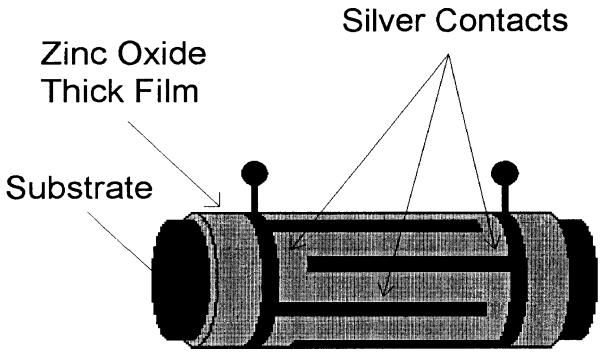


Figure 3. The schematic figure of the sample prepared.

the sintering temperature zinc oxide is sensitive to oxygen deficiency and care was taken to use mainly alumina based furnace furniture and sample holders.

Silver electrodes were deposited by paste painting followed by 30 minutes drying at room temperature and backing at 350³C in an electric oven. The electrodes were comb shaped ; the configuration of which determines the final resistance of the sample. These contacts were tested to be ohmic. The device fabricated is schematically illustrated in Figure 3.

Resistance Measurement The alumino-ferro-chrome alloy used acquires a native alumina layer at elevated temperatures in air [9]. The occurrence of the said layer during

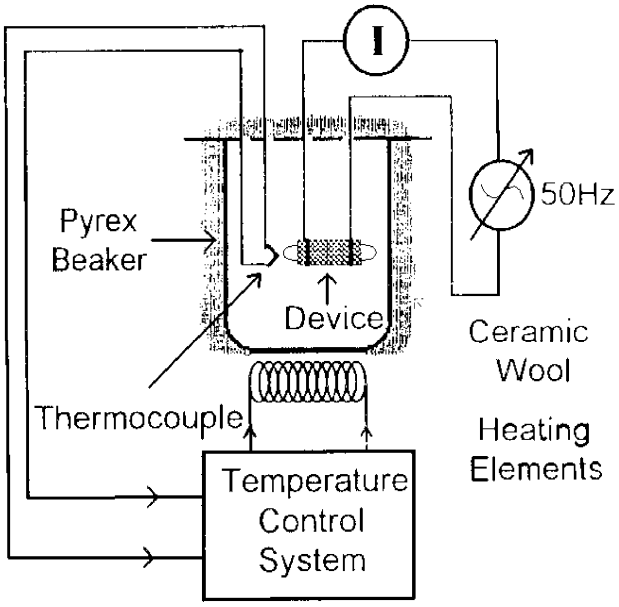
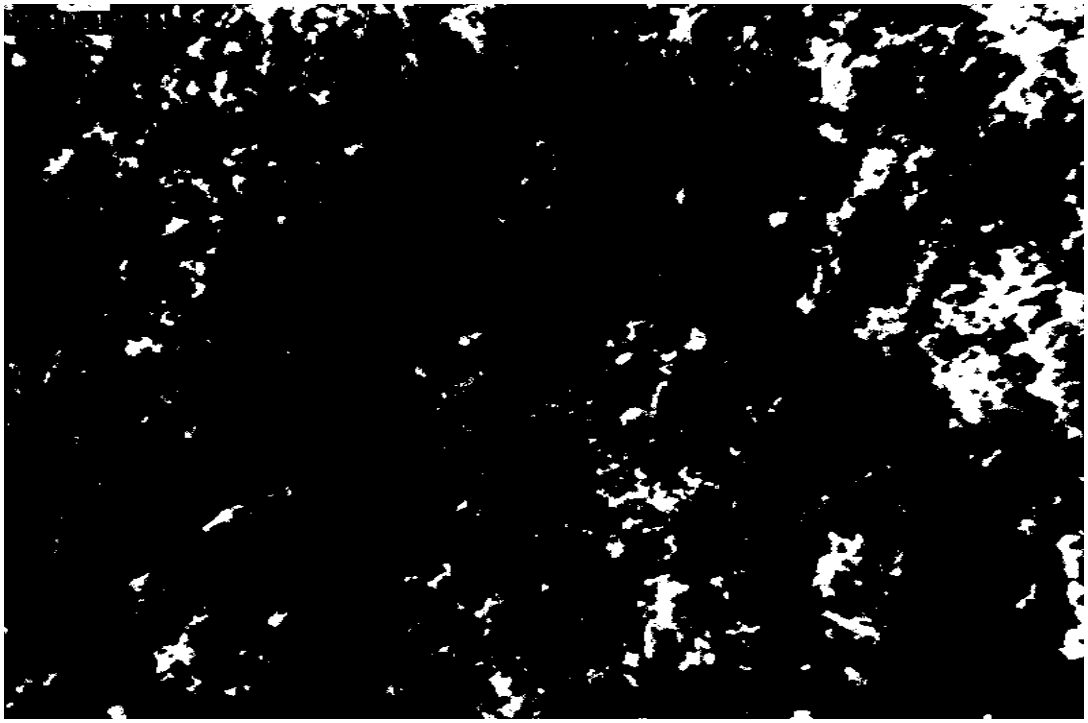


Figure 4. The schematic drawing of the measurement system.

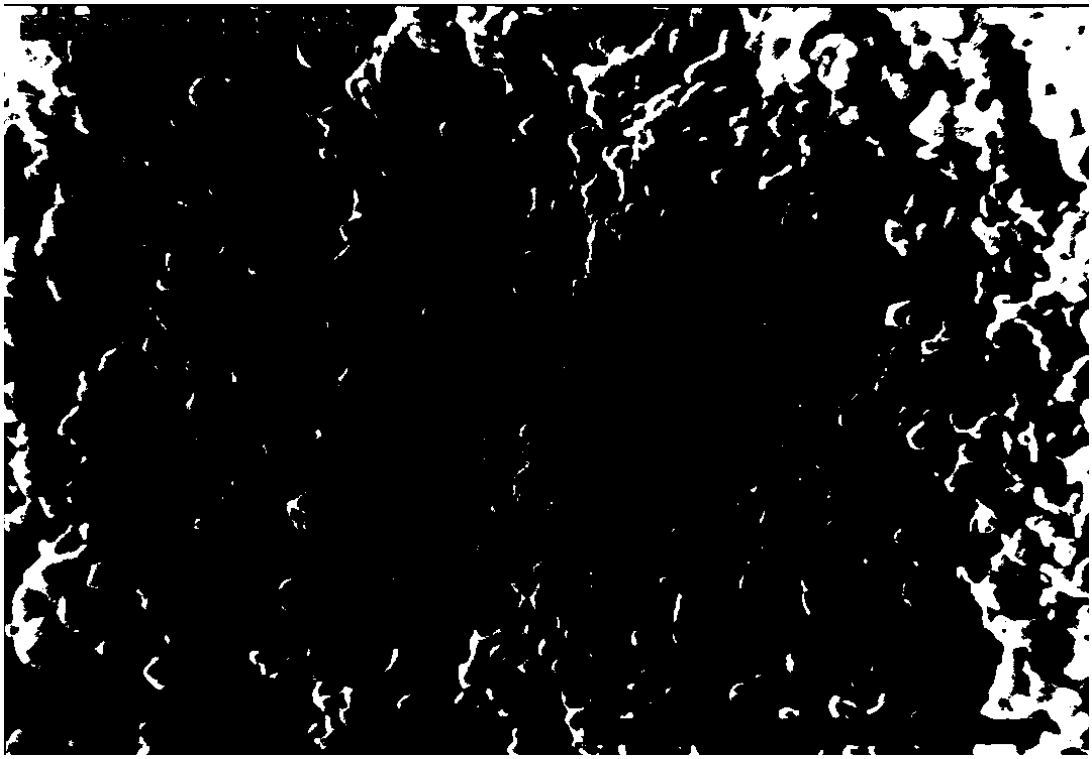
the sintering process, creates an electrical insulation between the alloy substrate and the zinc oxide thick film deposited. The effectiveness of the said insulation was tested by applying a DC voltage of 50V between each of the electrodes and the substrate. The leakage current was bellow 0.1mA. Then the resistance between the two contacts was measured using voltage and current measurement at 70 Hz at various temperatures. The device temperature was measured using a chromel-alumel thermocouple connected directly to the substrate. The schematic of the measurement system is shown in Figure 4.

3. RESULTS AND DISCUSSION

The optimum sintering temperature was found to be 1000 - 1050³C. Lower temperatures rendered mechanically weak structure and temperatures above 1050³C resulted cracking of the ZnO cladding due to the excessive shrinkage. The zinc oxide body sintered at the



(a)



(b)

Figure 5. SEM photographs of the surface of the ZnO thick film before (a), and after sintering (b).

optimum temperature was porous. The porosity was estimated to be about 70%. The SEM micrographs of a ZnO thick film before and after sintering are presented in Figs. 5a and 5b respectively. The average particle size of the powder, estimated by line averaging carried out on the SEM micrographs, was less than 0.5mm. A similar measurement on the micrographs of the sintered film confirmed the grain growth during the sintering and the average grain size of the sintered film was estimated to be 1mm. Figure 5b also clearly illustrates the open structure of the resulted thick film. This demonstrates the potentials of the technique described in the fields where such structures are required, e.g., gas sensor fabrication.

The experimental relationship of R vs. T is presented in Figure 6. It shows that the electrical resistance decreases exponentially with increasing temperature. The NTC factor obtained from Figure 6 is about 4.0% K^{-1} at

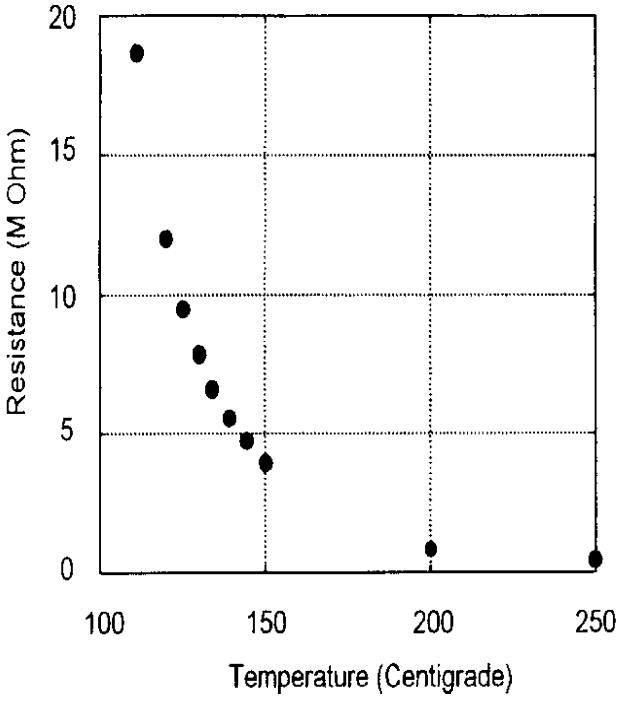


Figure 6. Variation of the device resistance vs. temperature.

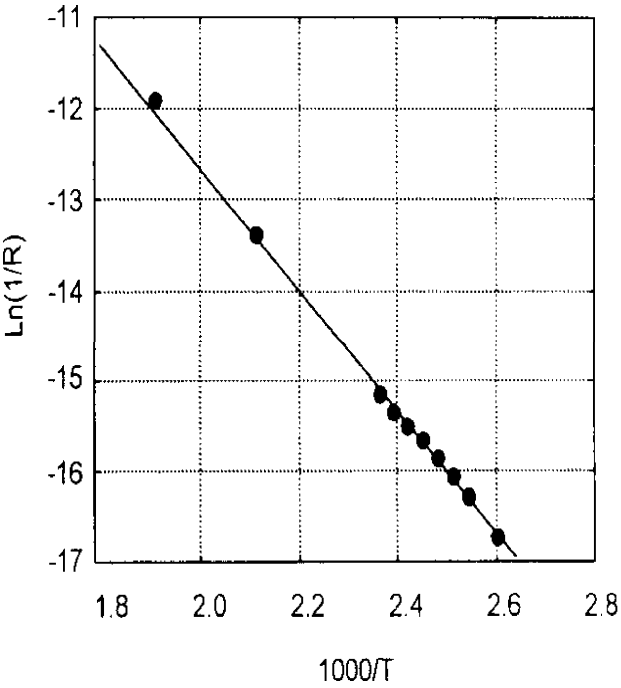


Figure 7. Electrical conductance of the device vs. 1000/T.

100³C. This value is in the range of the NTCs in commercially available devices [10].

The activation energy of carrier generation process could be found from the slope of ln(1/R) vs. 1000/T. This graph, presented in Figure 7, is linear and the activation energy was found to be 1.1 eV.

The stability of the device was tested by checking the resistance at various temperatures in several stages, each as long as 24 hours. The difference between each stage measurements was negligible.

4. CONCLUSIONS

ç Zinc oxide thick film was successfully formed on alumino-ferro-chrome substrate by EPD in acetone medium for the first time.

ç It was shown that the native alumina layer grown on alumino-ferro-chrome substrate effectively insulates electrically the thick film deposited from the alloy substrate.

ç It was confirmed that doping the

electrophoretic cell with HCl enhances the adherence of the film to the substrate.

ç Optimum sintering temperature was found to be 1030³C. Temperatures bellow 1000³C cause mechanical weakness, and those above 1050³C render cracked samples.

ç The NTC factor of the device resistance was -4.0% K^{-1} at 100³C and the activation energy of carrier generation process, extracted from the experimental data, was equal to 1.1 eV.

REFERENCES

1. Hennicke, J. and Hennicke, H. W., "Electrophoresis", in Ceramic Monographs, Handbook of Ceramics, 1.4.3, Verlag Schmid GmbH Freiburg, Germany, (1982), 1-7.
2. Sarkar, P., Nicholson, P., "Electrophoretic Deposition, Mechanisms, Kinetics, and Application to Ceramics", ***J. Am. Soc. Vol.***, 79, No. 8, (1996), 1987.
3. Chu, C. T. and Dunn, B., "Fabrication of $Yba_2Cu_3O_{7-y}$ Superconducting Coating by Electrophoretic Deposition", ***Appl. Phys. Lett.***, 55, 5, (1989), 492-494.
4. Kao, C. H., Tang, H. Y., Shiue, Y. S., Sheen, S. R. and Wu, M. K., "Fabrication of $Bi_{1.7}Pb_{0.4}Sr_{1.6}Ca_{2.4}Cu_{3.6}O_y$ Superconducting Films on Silver Substrates by the Electrophoretic Deposition Technique", ***J. Mat. Sci. Lett.***, 12, (1993), 1793-1794.
5. Jeon, B., Yoo, J. S. and Lee, J. D., "Electrophoretic Deposition of ZnO:Zn Phosphor for Field Emmition Display Applications", ***J. Electrochem. Soc.***, Vol. 12, p. 143, (1996).
6. Raissidehkordi, B. and Hosseinbabaei, F., "Electrophoretic Deposition of ZnO Powder in Non Aques Media", ***Proceedings of The Third Iranian Congress of Ceramics***, Isfahan, pp. 260-266, (April 27-29, 1998).
7. Koura, N., Tsukamoto, T., Shoji, H. and Hotta, T., "Preparation of Various Oxide Films by an Electrophoretic Deposition Method: A Study of Mechanism", ***Jpn. J. Appl. Phys.***, Part 1, 34, 3, (1995), 1643-1647.
8. Hosseinbabaei, F. and Raissidehkordi, B., "Impurity Dependence of Electrophoretic Mobility in MgO/Aceton Cell", ***The nineth CIMTEC***, Florance, Vol. 20, (1998), 65.
9. "Resistance Heating Alloys and Elements Handbook for Industrial Furnaces", Kanthal AB, Hallstahammar, Sweden, p. 10, (1990).
10. Buchanan, R. C., "Ceramic Material for Electronics", Marcel Decker, New York, p. 154, (1986).