Nikolic, M.V., Lukovic, M.D., Vasiljevic, Z.Z., Vujancevic, J., 2018. Application of Nanocrystalline Pseudobrookite (Fe2TiO5) Thick Films for Humidity Sensing. Presented at the Proceedings of the International Spring Seminar on Electronics Technology, IEEE Computer Society. https://doi.org/10.1109/ISSE.2018.8443672

Application of Nanocrystalline Pseudobrookite (Fe_2TiO_5) Thick Films for Humidity Sensing

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***Abstract**: Pseudobrookite nanocrystalline thick films were screen printed on alumina substrate with small interdigitated PdAg electrodes (width 6mm, length 12 mm, electrode spacing 0.2 mm) and fired at 600°C for 30 minutes. Scanning electron microscopy (SEM) of the thick film surface confirmed the formation of a porous structure consisting of agglomerated nanocrystalline grains of pseudobrookite. Impedance response of pseudobrookite thick film samples was measured in a humidity chamber at operating temperatures of 25 and 50°C in the relative humidity (RH) range 40-90% and frequency range 42Hz-1MHz. At the lowest frequency of 42 Hz at 25°C the impedance reduced ~7 times (from 35.74MΩ for RH 40% to 4.91 MΩ for RH 90%) and at 50°C ~ 33 times (from 30.98 MΩ for RH 40% to 0.944 MΩ for RH 90%). Low hysteresis (1.82 and 3.65%) was obtained at 25 and 50°C, respectively. Complex impedance was analyzed using an equivalent circuit consisting of parallel impedance and constant phase (CPE) element showing the dominant influence of grain boundaries.*

1. INTRODUCTION

Many different metal oxide semiconductor materials have been used in humidity sensors [1]. The humidity sensing mechanism of metal oxides is simple and is based on water adsorption on the material surface. When exposed to different atmospheric humidity conditions and different gases the grains, grain boundaries and pores composing the structure of these materials directly influence and utilize changes in their physical and electrical properties. In the world of nanomaterials metal oxides are one of the most fascinating functional materials [2]. They have been widely investigated for a number of applications including photoelectrochemical water splitting, photocatalysts and gas sensors. We have previously investigated possible application of pseudobrookite thick films (Fe_2TiO_5) for NO gas sensing [3]. Initial work on analyzing the potential of pseudobrookite as a humidity sensing metal oxide was conducted on bulk samples [4]. In this work we have investigated the humidity sensing potential of screen printed nanocrystalline pseudobrookite thick films by analyzing the change in impedance in the relative humidity range of 40-90%.

2. MATERIALS

Pseudobrookite (Fe_2TiO_5) nanopowder was obtained by solid state synthesis of hematite and anatase nanopowders (weight ratio 55:45) as described in detail in [5]. X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM-Tescan MIRA3 XM FESEM) analysis (Fig. 1) confirmed the formation of nanocrystalline pseudobrookite with an orthorhombic crystal structure [5]. The crystallite size was estimated as 47 nm using the Scherrer equation.

Thick film paste was prepared by mixing the obtained powder with a binder, dispersant and adhesion agents as described in detail in [5, 6]. Five layers were printed on alumina substrate with interdigitated PdAg electrodes (Fig. 1). Each layer was dried for 15 minutes at 60°C. SEM (TESCAN Electron Microsope VEGA TS 5130MM) of the thick film surface confirmed the formation of a porous structure consisting of agglomerated nanocrystalline grains of pseudobrookite. The average film thickness was estimated to be 60 μm, as each layer was ~ 12 μm. The sensors were heat-treated in air in a furnace at 600°C for 30 minutes.

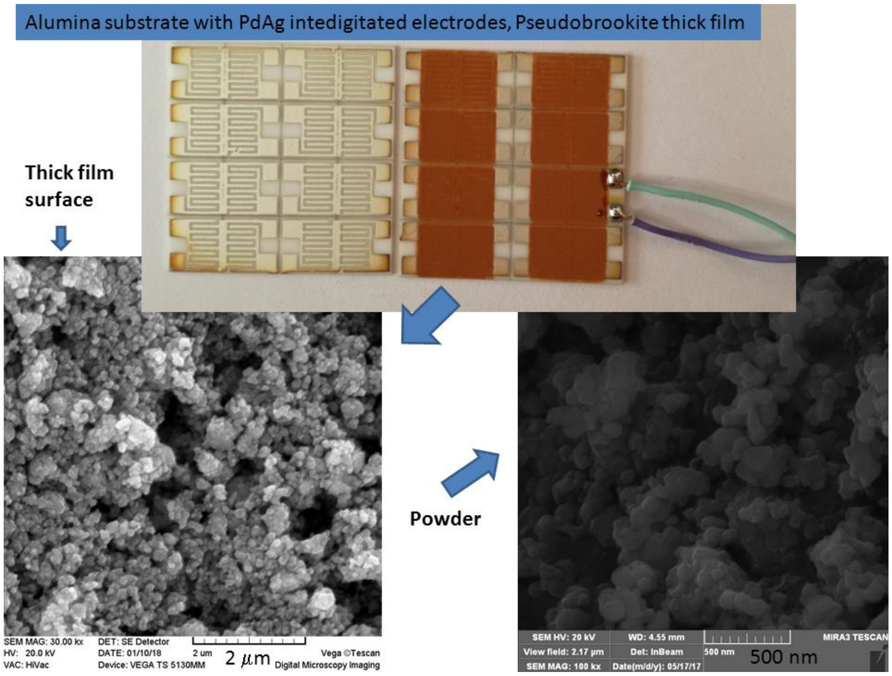

Fig. 1. Fabricated pseudobrookite (Fe_2TiO_5) thick film sample, FESEM image of pseudobrookite powder, SEM image of Fe_2TiO_5 thick film surface

3. HUMIDITY SENSING CHARACTERIZATION

The change in impedance of pseudobrookite thick film samples was measured in a JEIO TECH TH-KE-025 Temperature and humidity climatic chamber by measuring the change in impedance, resistance and capacitance in the frequency range 42 Hz - 1MHz on a HIOKI 3532-50 LCR HiTESTER device at two operating temperatures 25°C (room temperature) and 50°C (slightly elevated temperature) and in the relative humidity range 30-90%. The humidity at the start of measurement was estimated as 18%.

Fig. 2 shows that the measured impedance decreased with frequency for different relative humidity levels at 25 (a) and 50°C (b). Slightly lower values were obtained at 50°C. The measured impedance values decreased with increase in relative humidity and this change was most expressed at lower frequencies as shown for frequencies of 42 and 105 Hz in Fig. 3. Thus, at the lowest frequency of 42 Hz at 25°C the impedance reduced ~7 times (from 35.74MΩ for RH 40% to 4.91 MΩ for RH 90%) and at 50°C ~ 33 times (from 30.98 MΩ to 0.944 MΩ).

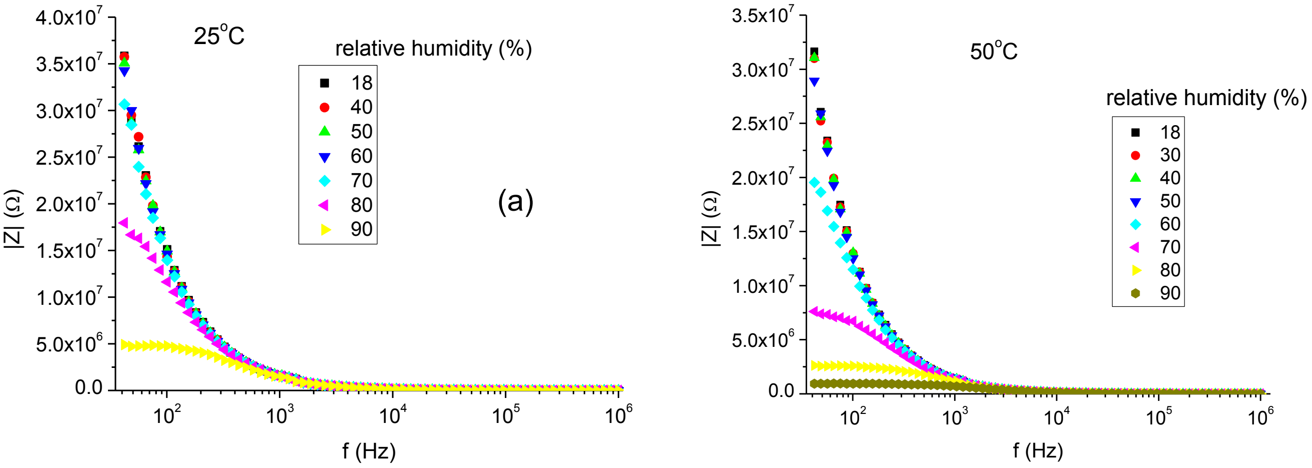

Fig. 2. Change of impedance of PSB thick film samples with frequency at 25 (a) and 50°C (b) with relative humidity.

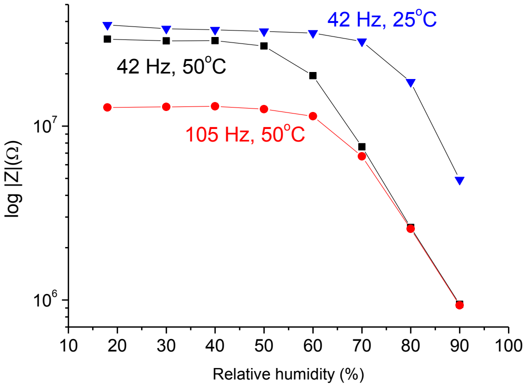

Fig. 3. Change of impedance with relative humidity at 42Hz (25 and 50°C) and 105Hz (50°C)

The humidity sensing mechanism of metal oxides that includes Fe_2TiO_5 has been previously explained in detail [5, 7, 8]. It represents adsorption of water molecules on the porous sample surface. It starts with chemisorption when water molecules are first absorbed onto available active sites when the sample is exposed to humidity. As humidity increases physisorption starts by physical adsorption of water molecules on the surface forming a double hydrogen bond. Further increase in humidity leads to the formation of multi physisorbed layers onto available oxygen sites by single hydrogen bonding that enables mobility of water molecules. At high relative humidity hopping of H^+ via H_2O in physisorbed water occurs. All these processes are reflected in the change of the impedance of pseudbrookite thick film samples with increase in humidity. The change in the water absorption mechanism is reflected in the change of the slope of the impedance decrease (Fig. 3). This change occurs at relative humidity values above 70% at 25°C and 60% at 50°C.

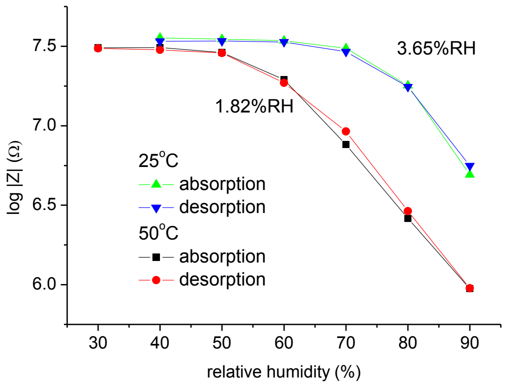

Fig. 4. Hysteresis curves for pseudobrookite thick films measured at 25 and 50°C

Hysteresis curves measured at 42Hz for pseudbrookite thick film samples measured at 25 and 50°C are shown in Fig. 4. They define the time delay between the absorption and desorption process that can be attributed to disordered mesoporous solids [9]. They were calculated as 3.65%RH and 1.82%RH at 25 and 50°C.

Fig. 5 shows the complex impedance plots for pseudobrookite thick film samples obtained at 25 °C (a) and 50°C (b). Similar curves were obtained in the form of part of a depressed semicircular arc. With increase in humidity the semicircular arc decreased in size (shrank) and showed more of the depressed semicircle that became a complete semicircle for relative humidity of 90%. These changes are linked with the humidity sensing mechanism.

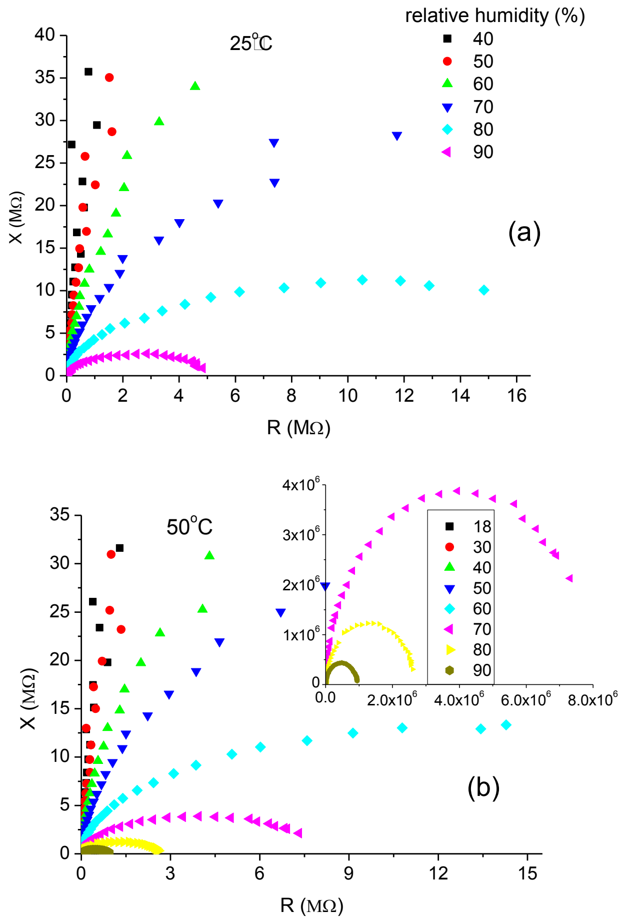

Fig. 5. Complex impedance diagrams for pseudobrookite thick films measured at 25 and 50°C

Measured impedance data was analyzed using an equivalent circuit with the EIS Spectrum Analyzer Software [9]. It consisted of parallel resistance and constant phase element (CPE) representing the dominant grain boundary component. The CPE element was used to replace the capacitance. The obtained grain boundary resistance (R_{gb}) decreased with increase in humidity as shown in Fig. 6a. The grain boundary relaxation frequency increased with increase in humidity as shown in Fig. 6b. The grain boundary capacitance C_{gb} did not change significantly with increase in relative humidity and was in the range 110-117 pF at 25°C and 126-135 pF at 50°C.

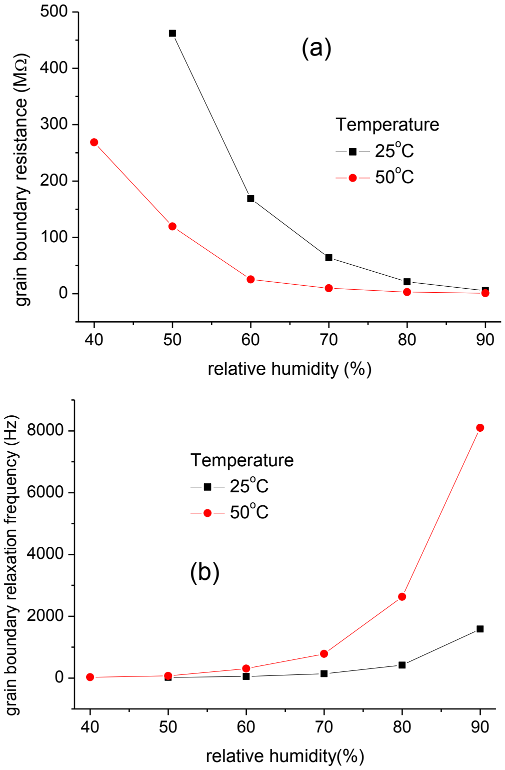

Fig. 6. Change of grain boundary resistance (a) and relaxation frequency with humidity

5. CONCLUSION

In this work we analyzed humidity sensing of nanocrystalline pseudobrookite thick films obtained by screen printing five layers of pseudobrookite paste on alumina substrate with small intedigitated PdAg electrodes. Change in relative humidity led to a decrease in impedance especially at low frequency (42 Hz) at both analyzed temperatures (25 and 50°). Low hysteresis values were also obtained showing that pseudobrookite thick films can be applied as humidity sensors, especially for higher humidity values. Complex impedance was analyzed using an equivalent circuit confirmed the dominant influence of grain boundaries.

Acknowledgement

This work was performed as part of projects III45007, TR32016 financed by the Ministry for Education, Science and Technological Development of the Republic of Serbia.

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