Ba TiO_3 doped Polyaniline based Nanocomposites thick film senor for humidity sensing Application

T R Ingle[1], R M Agrawal[2], G T Lamdhade[3], R J Gajbe[4]
1,3Department of Physics, Vidya Bharati Mahavidyalaya, Camp, C. K. Naidu Road, Amravati(M.S.)
2Department of Physics Shri R.L.T.College of Science, Civil Lines Road, Akola,(M.S)
4Department of Electronics, Vidya Bharati Mahavidyalaya, Amravati M.S. India
Corresponding Authors:Email:ingletr@rediffmail.com,oumgajanan@gmail.com

Abstract

Polyaniline (PANI) and $BaTiO_3$-Pani composites were synthesized by chemical polymerization method using ammonium per sulphate (APS) as an oxidizing agent. This is a single step polymerization process to synthesize the conducting polymer. Thick films of PANI and BaTiO3-Pani were fabricated by Screen – Printing followed by firing at 70° c for 30 min. BaTiO3-Pani thick films resulted in humidity sensor. An exceptional sensitivity was found to the relative sensor at 80° c and no cross sensitivity was observed to other hazardous and polluting gases ever at higher concentration. . The effect of microstructure and dopant concentrations on the gas response,Hysteresis , sensitivity, of the sensor in the presence of humidity were studied and discussed.

Keywords: *Polyaniline , Barium Titanate,BaTiO3-Pani composites , Humidity sensor.*

1. Introduction

The use of sensors by human being has been day by day increasing at an astounding rate in the last few years and modern society depends heavily on the use of the sensors for variety of purposes. Over the last decades a variety of chemical sensors have been developed based upon semiconductors, which monitor different characteristic sensor properties such as conductivities for electronic conductivity sensors, impedance for capacitance sensors, potentials for field effect sensors or temperatures for calorimetric sensors. For the determination of gas components, many of these devices make use of the same molecular detection principle. Depending on the operation temperature, their signals are caused by changes in the concentration of free electrons, dielectric constants, electrical fields and heats of adsorption or reaction. These changes result from physisorption, chemisorption, catalytic reactions, and surface or bulk defect reaction with particles from the gas phase.

There is a continuing need for accurate, reliable, inexpensive sensing systems for measuring relative humidity (RH), not only for human comfort but also for a broad spectrum of applications in chemical industry, process control, atmospheric sciences, agriculture etc. Humidity is one of the most common constituents present in the environment and its measurement is indispensable when it comes to monitoring of various environmental parameters. For instance, detecting organic pollutants in indoor atmosphere, organic vapour monitoring, maintenance of Green houses, performance of air/ smoke filters, hydrocarbon sensing are all affected by relative humidity conditions. Therefore, sensing and controlling relative humidity is of great importance [1].

In the recent years there has been significant progress in the field of polymer based humidity sensors. According to their sensing mechanisms these can be either resistive type or capacitive type. In addition to the traditional quaternary ammonium and sulfonate compounds, polymers containing phosphonium have also been studied for humidity sensing. Copolymers, mutually reactive copolymers and conjugated polymers have also been reported for humidity sensing. Conjugated polymers especially conducting polymers like polypyrrole, polyethylene, polypropylene etc. have shown humidity sensing properties [2]. Besides these metal-polymer nanocomposites for instance iron oxide-polypyrrole have also been reported for relative humidity sensing sensor. The present study deals with the humidity sensing application such as relative humidity, stability humidity, selectivity etc. of selected inorganic materials.

Humidity control and monitoring are of great interest to a wide area; these include moisture sensitive products, fresh and pack-age food, drug storage and environmental control for valuable Antiques or paintings etc. [3,4]. Humidity sensors that are avail-able in the market include dew point, infrared, catalytic and tin oxide sensors, which may be expensive, or require high temperature operation and consume significant amount of power

and high cost ofmaintenance [5].Much research has been focused on the development of humidity sensitive material [6–8]. Among these are the investigation of using conducting polymers such as polyaniline, polypyrrole, and polythiophene for humidity and gas sensing [9–11]. Advantages with polymers as sensing materials are light weight, flexible, low cost and simple fabrication process [12]. Pure polymer, polymer blends and polymer–inorganic composites have also been studied for the purposes, resulting in different degree of advancements in this area [13–19].

2. Synthesis of Material :

A) Synthesis of Polyaniline (PANI): In general is synthesized using two major polymerization approaches : electronic and chemical polymerization. In the present work polyaniline is synthesized by chemical polymerization method in which 0.2 M aniline hydrochloride is used as monomer unit . the synthesis is done by oxidative polymerization with 0.25 M ammonia peroxysulphate inaqeous medium . both solution kept 1 hour at room temperature then mixed in beaker ,briefly stirred. And left at rest to polymerize, next day, the pani precipitate was collected on a filter , washed with three 100 ml portion of 0.2 M HCL and similarly with acetone . polyaniline hydrochloride powder was dried in air and then in vaccum at 60°c. Polyaniline prepared under these reaction and processing condition are further referred to as standard sample[63].

B)Synthesis of Barium titanate ($BaTiO_3$): In preparation of barium titanate ($BaTiO_3$) 0.25 M $Ba(NO_3)_2$ solution and 0.25 M $TiO(NO_3)_2$ solution were dissolved in 2 N nitric acid solution in a beaker. About 0.6 M tartaric acid solution was then added to under constant magnetic string. The solution heated under continuous string to its boiling point until all the liquid evaporated. About 7 gm of ammonium nitrate was added towards the ends to avoid slurry formation. Brown fumes evolution takes places and fluffy mass were settled at the base of the beaker. The product is then dried in vacuum oven at 96^oC for 2 hrs. So that moisture will removed from the final product and we will get dry product. Then this dry product was crushed into fine powder and finally this fine nanopowder of $BaTiO_3$ was calcinated at temperature 800^oC for 5 hrs. in the auto controlled muffle furnace to remove the impurity form the product will be completely removed and get a final product of $BaTiO_3$ nanoparticle.

3. Experimental methodology for humidity: -

The humidity chamber/ stability chamber has stainless steel body purchased from Gayatri Scientific, Mumbai . The working size of humidity chamber is 50×43×430cm (H×D×W). The chamber having two open side door window namely inner side door and outside door, inner side is full length inner plexi glass door which is transparent and outer side door was metal door with magnetic gasket and lock . inside the chamber it has two trays, which are made of stainless steel. it has PID digital display temperature indicators which is outside at the top of the chamber , indicating the current temperature of the chamber .indicating the current temperature of chamber. The power sources of 230 V having frequency of 50Hz required. the temp[rapture range is ambient to 80 C. The chamber has temperature accuracy of ± 1.0 C .

The range of humidity varying from 40% RH to 80% RH having the accuracy of ± 3% RH. To operate the chamber a program feed for the varying RH as well as different temperature. Which will sets the controlled the humidity of set temperature for given time. To measure the humidity characteristics , the sensor element was placed inside the humidity chamber by operating the program at different RH and temperature the humidity was varied . The sensor element was placed inside the humidity was measured by standard hygrometer which is already placed inside chamber . The electrical resistance of the file was measured by using Keithley source meter (2400). The humidity and temperature of the chamber camn be controlled by using Bull's Eye control UK-100, it is a program controller for humidity and temperature verses time even controller .The UK-100 can be program by varing RH, temperature , time parameters. The total number of programs are 99out of this are set program for set temperature 40 C by varying RH 1 steps NO. Of program 8, event 0001, are tabulated

4.Characterization :

The above synthesized PANI-$BaTiO_3$ composites are structurally and surface morphologically characterized by using different technique like X- ray diffraction (XRD), and scanning electron microscopy (SEM).the x-ray diffraction patterns of the prepared samples are obtained by Siemens D 5000 X-ray diffractometer using CuKα radition (λ =1.717 A°). The diffractograms are recorded in terms of 2ɷ in the range

40°-50° at ambient temperature with scanning rate of 2° per minute .The surface morphology of polyaniline and its composites are studied by using Leica's SEM (modal S 440) at 10kv.

X-Ray Diffaration

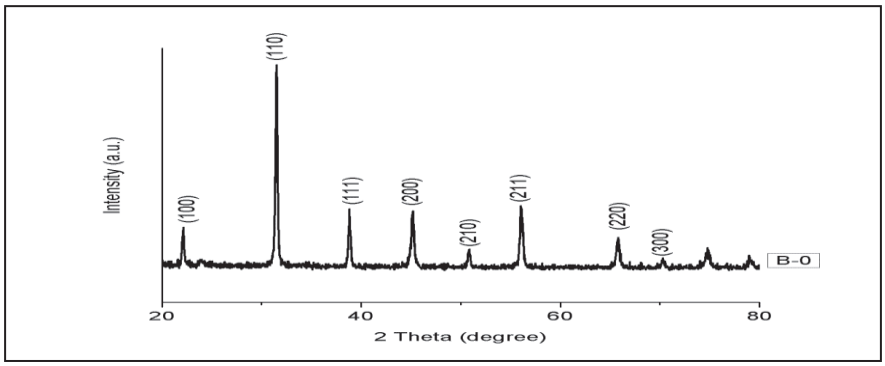

Figure: 1 XRD of ($BaTiO_3$) (B-0)

The XRD pattern of pristine Barium Titanate ($BaTiO_3$) nanostructure synthesized by liquid phase method via solid state method calcinated at 800ºC as shown in figure 1.The crystalline nature with 2θ peak lying at (100), (110), (111), (200), (210) and (220) planes. All the peaks match well the standard provskite type structure of Barium Titanate ($BaTiO_3$) with lattice constants a = 3.992 nm and c = 4.036 nm . All the peaks are perfectly match with pure $BaTiO_3$structure, which indicates the high purity of the obtained $BaTiO_3$nanoparticle. The average crystalline size was found to be 46.90 nm calculated by Deye-Scherrer formula.

Hysteresis plot :

Hysteresis plot shows the variation between resistances of sample with respect to the relative humidity in increasing and decreasing order from 30 to 90 % RH as shown in the figure. 2. A very small hysteresis present during forward and reverse cycle of relative humidity, where as a very significant average change observed in the value of resistance of sample, in the sample BP-1 (10$BaTiO_3$ – 90PANI) the change in value of resistance is from $10^{11}\Omega$ to $10^{3}\Omega$, these is a remarkable change in the value of resistance.

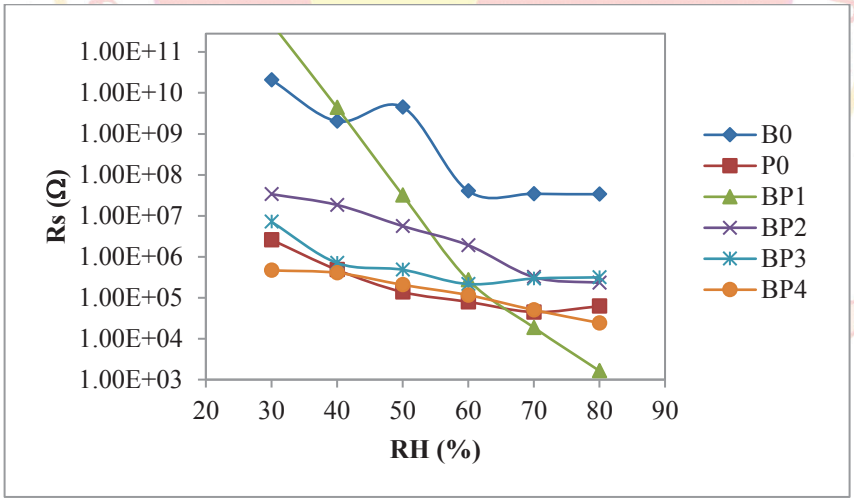

Figure: 2 Hysteresis plot

Sensitivity

In the above samples the sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant as shown in figure 3. For higher RH the sensitivity is found to be higher in case of all samples of thick films. The sensitivity of BP-1 (10 $BaTiO_3$ -90PANI) is more than BP-2, BP-3, and BP-4 samples and also from the pristine samples P-0 and B-0. The ($BaTiO_3$-PANI) composite sensors exhibits significantly higher sensitivity than sensor constructed specially from Barium Titanate nanoparticles and PANI itself due to the formation of heterogeneous interface between them and more adsorption site was created to absorbed more water vapours.

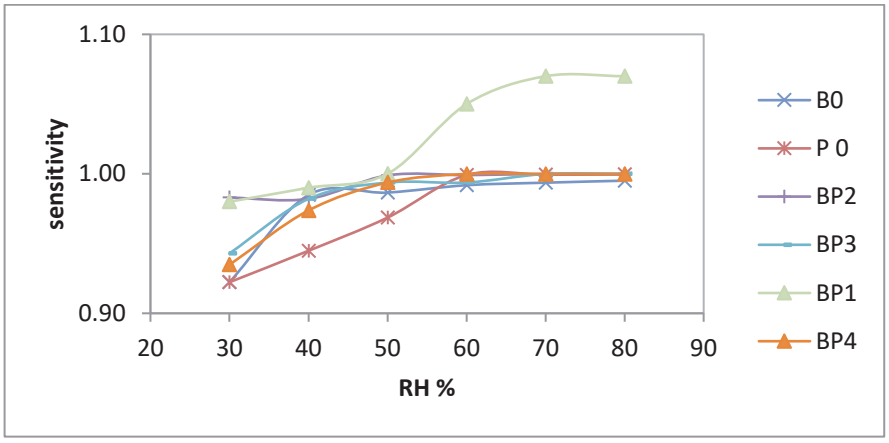

Figure: 3 Sensitivity curve

5. Conclusions

Nanostructured $BaTiO_3$ was successfully prepared via chemical precipitation method and PANI with IUPAC polymerization technique. Minimum crystallite size was found to be $BaTiO_3$ is 46..90 nm. The Hysteresis plot shows very significant average change in the value of the resistance from $10^{11}\Omega$ to $10^{3}\Omega$ during forward and reversed cycles of sample BP-1 (10 $BaTiO_3$ -90PANI)). The sensitivity is found to be increasing with the RH for all the samples of thick films and it is increasing up to some particular RH and then afterward it remains constant. Amongst all the prepared samples BP-1 is more sensitivity than other prepared composite samples.

References:

[1] TraversaE .Sens.Actuators B 23, (1995), 135-136.
[2] AnsbacherF.and Jason A. C., Nature 24, (1993), 177-178 .
[3] E. Bracken, Combating humidity the hidden enemy in manufacturing, Sens.Rev. 17 (1997) 291–298.
[4] C.Y. Lee, G.B. Lee, Humidity sensors: a review, Sens. Lett. 3 (2005) 1–15.
[5] D. Hodgins, The electronic nose using conducting polymer sensors, Sens. Rev.14 (4) (1994) 28–31.
[6] S.K. Khijwania, K.L. Srinivasan, J.P. Singh, An evanescent-wave optical fiber rel-ative humidity sensor with enhanced sensitivity, Sens. Actuators B 104 (2005)217–222.
[7] Z.M. Rittersma, Recent achievements in miniaturised humidity sensors are view of transduction techniques, Sens. Actuators A 96 (2002) 196–210.
[8] Z. Chen, C. Lu, Humidity sensors: a review of materials and mechanisms, Sens.Lett. 3 (2005) 274–295.
[9] N.Parvatikar,S.Jain,S.V.Bhoraskar,M.V.N.A.Prasad,Spectroscopic and electri- Cal properties of polyaniline /CeO_2 composites and their application as humidity sensor, J. Appl.Polym. Sci. 102 (2006) 5533–5537.
[10] T.Maddanimath,I.S.Mulla,S.R.Sainkar,K.Vijayamohanan,K.I.Shaikh,A.S.Patil, S.P. Vernekar, Humidity sensing properties of surface functionalisedpolyethy- lene and polypropylene films, Sens.Actuators B 81 (2002) 141–151.
[11] A.G. MacDiarmid, Polyaniline and polypyrrole: where are we headed? Synth.Met. 84 (1997) 27–34.
[12] G. HarsaÂnyi, Polymer films in sensor applications: a review of present uses and future possibilities, Sens. Rev. 20 (2000) 98–105.
[13] R. Nohria, R.K. Khillan, Y. Su, R. Dikshit, Y. Lvov, K. Varahramyan, Humidity Sensor based on ultrathinpolyaniline film deposited using layer-by-layer nano-assembly, Sens. Actuators B 114 (2006) 218–222.
[14] K. Ogura, T. Saino, M. Nakayama, H. Shiigi, The humidity dependence of theelectrical conductivity of a soluble polyaniline–poly(vinyl alcohol) compositefilm, J. Mater. Chem.7 (1997) 2363–2366.
[15] N. Parvatikar, S. Jain, C.M. Kanamadi, B.K. Chougule, S.V. Bhoraskar, M.V.N.A. Prasad, Humidity sensing and electrical properties of polyaniline /cobalt oxide composites J. Appl. Polym. Sci. 103 (2007) 653–658.
[16] S.T. McGovern, G.M. Spink, G.G. Wallace, Micro-humidity sensors based on a processable polyaniline blend, Sens. Actuators B 107 (2005) 657–665.
[17] M.L. Singla, S. Awasthi, A. Srivastava, Humidity sensing using polyaniline/Mn_3O_4 composite doped with organic/inorganic acids, Sens. Actuators B 127 (2007) 580–585.
[18] M. Wan, Z.X. Wei, Z.M. Zhang, L.J. Zhang, K. Huang, Y.S. Yang, Studies on nanostructures conducting polymers via self-assembly method, Synth. Met.135 (2003) 175–176.
[19] S. Jain, S. Chakane, A.B. Samui, V.N. Krishnamurthy, S.V. Bhoraskar, Humidity sensing with weak acid-doped polyaniline and its composites, Sens. Actuators B 96 (2003) 124–129.

Sol-gel Auto Combustion Synthesis and Characterizations of Cobalt Ferrite Nanoparticles

Amit M. Bagde[1],Avinash S. Dive[2],Jitendra S. Kounsalye[1*]
[1]Late R. B. Arts, Commerce and Smt. S. R. Bharti Science College, Arni, Dist. Yavatmal (M.S.), India.
[2]Department of Physics, R. G. Rathod Arts and Science College, Murtizapur, Dist. Akola(M.S.), India.

Abstract
Cobalt ferrite ($CoFe_2O_4$) nanoparticles were successfully synthesized by sol-gel auto combustion method. Pure phase formation of cobalt ferrite with cubic spinel structure was observed in X-ray diffraction pattern. The average crystallite size, lattice parameter and other structural parameters were calculated from XRD data and they were in reported range. The magnetic parameters were measured by M-H hysteresis loop technique at room temperature and saturation magnetization, remenant magnetization and coercivity was estimated.
Keywords: *Cobalt ferrite, Sol-gel auto combustion,XRD, Magnetization.*

1. Introduction:

In order to meet today's technologies requirement, the development of new synthes is technique to develop new materials is essential which produces nanosized materials with superiormagnetic performance compared to that of bulk materials is desired. Different wet chemical methods areavailableforthesynthesis of spinel ferrite nanoparticles, suchas, chemical co-precipitation,sol–gel, hydrothermal, solvothermal, thermaldecomposition and microwavecombustion methods[1, 2]. These wet chemical methods are economic, easy, requires less time and low temperature, produces particles of nanometer dimensions and therefore now a days commonly used in the synthesis of magnetic nanoparticles of spinel ferrite.

Amongst these wet chemical methods, thesol–gel auto-combustion technique is one of the most convenient and effective method, involving a low reaction temperature(80°C–100 °C) and a rapid turn-around time for powder synthesis[3]. In the variety of spinel ferrite materials, cobalt ferrite is the unique spinel ferrite with inverse spinel structure, in which Co^{2+}ions occupy an octahedral [B] site. The high saturation magnetization,high permeability,high electrical resistivity,high Curie temperature, high magneto-crystalline anisotropy etc are the notable properties of nanocrystalline cobaltferrite[4].These properties are useful in many applications including magnetic recording media, magnetic sensors, magnetic memories, magnetic fluids, magnetic composites and catalysis, antennarods, permanentmagnets etc[5].

Thus, the present work reports on synthesis of nano-crystalline spinel structured cobalt ferrite sample by sol-gel auto combustion method using citric acid as a fuel. The results on structural, morphological and magnetic properties are reported in this work.

2. Experimental

The nano-crystalline cubic spinel structured cobalt ferrite ($CoFe_2O_4$) sample was prepared by sol-gel auto combustion method using citric acid as a fuel. AR grade chemicals such as cobalt nitrate ($Co(NO_3)_26H_2O$), ferric nitrate ($Fe(NO_3)_39H_2O$) and citric acid ($C_6H_8O_7$) were used for the synthesis. The metal nitrates to fuel ratio calculated using propellant chemistry was taken as 1:3. Ammonia solution was added to maintain the pH of the solution at 7. The as-synthesized powder is sintered at 550°C for 4 h and then used for further investigations. The detailed procedure is reported in the literature[6].

The prepared sample was characterized by X-ray diffraction (XRD) technique by Regaku model. The XRD patterns were recorded at room temperature in the 2θ range of 20° to 80° using Cu-Kα radiation (λ = 1.54056 Å). The magnetic properties of the cobalt ferrite sample were measured using pulse field hysteresis loop technique at room temperature.

3. Results and Discussions

3.1 Structural characterizations

The room temperature X-ray diffractions patterns of un-irradiatedand irradiated $CoFe_2O_4$ ferrite nano-particles are shown in Fig. 1. All the reflection peaks in the XRD pattern were indexed by using Bragg's law. The presence of planes (220), (311), (222), (400), (422), (511) and (440) in the XRD pattern reveals the cubic spinel structure of all the samples.It is also evident that all the reflection peaks are intense and sharp. No impurity peaks were observed thus the samples are single phase in nature[7].