

Effect of Polyethylene Glycol in Gas Sensing Behaviour of Composite Coating of Magnesium Oxide and Aluminium Oxide

R. Sakthivel¹, P. Mohamed Shameer²

¹Department of Mechanical Engineering, Government College of Technology-Coimbatore, Tamilnadu, India

Abstract: Gas detection instruments are increasingly needed for industrial health and safety, environmental monitoring, and process control. To meet this demand, considerable research into new sensors is underway, including efforts to enhance the performance of traditional devices, such as resistive metal oxide sensors, through nanoengineering. Metal oxide sensors have been utilized for several decades for low-cost detection of combustible and toxic gases. However, issues with sensitivity, selectivity, and stability have limited their use, often in favor of more expensive approaches. Recent advances in nanomaterials provide the opportunity to dramatically increase the response of these materials, as their performance is directly related to exposed surface volume. The recent availability of various metal oxide materials in high-surface-area nanopowder form, as well as implementation of newly developed nanofabrication techniques, offer tremendous opportunities for sensor manufacturers.

Keywords: Sensor, Metal Oxide, Toxic gases, Nanomaterials, Nanoengineering, Nanopowder, Nanofabrication.

1. Introduction

Nanotechnology is one of the most important and developing fields at present scenario. Nanotechnology can be clearly defined as "The design, characterization, production, and application of structures, devices, and systems by controlled manipulation of size and shape at the nanometer scale (atomic, molecular, and macromolecular scale) that produces structures, devices, and systems with at least one novel/superior characteristic or property". Much of nanoscience and many nanotechnologies are concerned with producing new or enhanced Sensors. Numerous materials have been reported to be usable as metal oxide sensors including both single (e.g., ZnO, SnO₂, WO₃, TiO₂ and Fe₂O₃) and multi-component oxides like Magnesium Aluminate. The mechanism for gas detection in these materials is based on reactions that occur at the sensor surface, resulting in a change in the concentration of adsorbed oxygen. Oxygen ions adsorb onto the material's surface, removing electrons from the bulk and creating a potential barrier that limits electron movement and conductivity. When reactive gases combine with this oxygen, the height of the barrier is reduced, increasing conductivity. This change in conductivity is directly related to the amount of a specific gas present in the environment, resulting in a quantitative determination of gas presence and concentration.

Several recent research reports have confirmed the benefits of "Nano-engineering" on sensor performance. For example, Rella, et al. [2] demonstrated good response to NO₂ and CO when the SnO₂ grain size was controlled below 10 nm. Ferroni, et al. [3] demonstrated good response to NO₂ for solid solutions of TiO₂ and WO₃ when grain size was held at near 60 nm. Chung, et al. [4] demonstrated that increasing the firing temperature (which increases grain size) significantly reduces the response of WO₃ sensors to NO_x. Chiorino, et al. [5] also demonstrated that firing temperature

plays a key role in the response of SnO₂ sensors, with films treated to 650°C showing nearly twice the response to NO₂ as films treated at 850°C.

2. Literature Survey

In 2008, Anton Kock [2], Et al., report on a new approach for the fabrication of ultra-long single crystalline SnO₂-nanowires for gas sensing applications based on a combined spray pyrolysis and annealing process. The SnO₂-nanowires are grown on SiO₂-coated Si-substrates and exhibit diameters of 30–400 nm and lengths up to several 100 μm. The experimental results suggest a competing evaporation and condensation process, which converts the nanocrystalline SnO₂ films into single crystalline SnO₂-nanowires directly on the chip. For the realization of gas sensors the SnO₂-nanowires are transferred to another SiO₂-coated Si-substrate. It was believed that the fabrication procedure might be the technology of choice for the controlled fabrication of SnO₂-nanowires as highly sensitive gas sensing elements on a wafer scale.

In 2003, S.Shukla [5], Et al., have done a paper on Synthesis and characterization of sol-gel derived nano-crystalline tin oxide thin film as hydrogen sensor. Tin oxide (SnO_x) semiconductor thin film is coated on Pyrex glass (silica) substrates using the sol-gel dip-coating technique utilizing alkoxide precursor. The thin film is extensively characterized for its surface morphology, chemistry, thickness, and nanocrystallite size using different analytical techniques such as scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and high-resolution transmission electron microscopy (HRTEM). Under the given processing conditions, SnO_x semiconductor thin film having thickness 100–150 nm and nanocrystallite size 6–8 nm is obtained. Sensitivity value as high as 394% is observed at room temperature for 4 vol % H₂, which is an explosive limit at

room temperature for the space-based applications as set by NASA.

In 2005, Kwang Soo Yoo [3], Et al., submit a paper in which nano-grained indium tin oxide (ITO) thin films catalyzed 0.5 wt.% Pd were deposited on the alumina substrate at ambient temperature or 300 °C by using a magnetron sputtering system and then annealed at 650 °C for 1 or 4 h in air. The crystallinity and microstructure of the annealed films were analyzed. The effects of their microstructure (nano-grain) and ITO composition on H₂ gas-sensing properties were systematically investigated. As the results of XRD and Field Emission Scanning Electron Microscope (FESEM) analysis, polycrystalline thin films with 10–35 nm in grain size were obtained. The ITO (In₂O₃:SnO₂ = 20:80) sensors showed high H₂ sensitivity, $R_{gas}/R_{air} = 0.008$ at 1000 ppm.

In 1998, R.G. Dhere, Et al. [6], have presented a paper on Characterization of SnO₂ films prepared using Tin Tetrachloride and Tetra Methyl Tin Precursors. In this the investigation in the effect of deposition conditions of SnO₂ films were done, deposited by chemical vapor deposition using tin tetrachloride and tetra methyl tin precursors, on the film properties. The type of precursor and the deposition temperature affect the morphology of the films. The structure of the films is determined by the deposition temperature: films deposited at low temperatures show a mixed SnO and SnO₂ phase. The processing temperature and type of substrate determine the impurity content in the films. Electrical properties (e.g. the carrier mobility) and optical properties of the films are affected by the structure and the impurity content in these layers.

In 2008, Hao-Jie Song and Zhao-Zhu Zhang [1] produce a paper about Study on the tribological behaviors of the phenolic composite coating filled with modified nano-TiO₂. In order to overcome the disadvantages generated by the loosened nanoparticle agglomerates dispersed in polymer composite coatings, nano-TiO₂ particles are modified using trifluoroacetic acid. Owing to the effective improvement of their dispersibility in the phenolic coating, compared with the cases of untreated nano-TiO₂, the employment of modified nano-TiO₂ provided the phenolic coating with much better tribological performance. Worn surfaces of the untreated nano-TiO₂ or modified nano-TiO₂ filled phenolic coating and transfer films formed on the surface of the counterpart ring sliding against the composite coating were respectively investigated by SEM and optical microscope (OM), from which it is assumed that the optimal content of TiO₂ or TF-TiO₂ is able to enhance the adhesion of the transfer films to the surface of counterpart ring. As a result, the wear resistance of the phenolic composite coating filled with modified nano-TiO₂ was significantly enhanced, especially at extreme wear conditions, i.e. high contact pressures.

In 2004, Y.Kousar, Et al. [4], did the paper Deposition of nanocrystalline diamond & titanium oxide coatings onto pyrolytic carbon using CVD & sol-gel techniques. In this paper, they report the deposition of freestanding nanocrystalline diamond (NCD) films and dense

nanocrystalline titanium oxide (nc-TiO₂) coatings onto pyrolytic carbon (PyC) using advanced chemical vapour deposition (CVD) and sol-gel techniques, respectively. The micro-structural properties, such as surface morphology and crystallinity, of PyC, NCD and nc-TiO₂ were characterised using XRD, Raman spectroscopy and SEM analysis. Freestanding NCD films were prepared using our newly introduced time-modulated CVD (TMCVD) process. Furthermore, conventional sol-gel technique was used to uniformly coat PyC with dense nc-TiO₂ coatings. The as-grown nc-TiO₂ coatings were found to display smooth surface profiles and the average crystallite size was in the range approximately 30–50 nm.

3. Description of Components

3.1 Magnetic Stirrer



Figure 1: Magnetic Stirrer

The magnetic stirrer is used in many biological labs, including microbiology labs also. A magnetic stirrer, as shown in figure 1, is a laboratory device consisting of either a rotating magnet or stationary electromagnets creating a rotating magnetic field. This device is used to cause a stir bar immersed in a liquid to spin very quickly, agitating or mixing the liquid. A magnetic stirrer often includes a provision for heating the liquid. Stirrers are often used in laboratories, especially in the field of biology and microbiology. They are preferred over gear-driven motorized stirrers because they are quieter, more efficient, and have no moving external parts to break or wear out.

Due to its small size, a stirring bar is more easily cleaned and sterilized than other stirring devices. Magnetic stirrers avoid two major problems with motorized stirrers. Firstly, motorized stirrers use lubricants, which can contaminate the reaction vessel and the product. Secondly, in motorized stirrers, the sealing of the connection between the rotating shaft of the stirrer and the vessel can be problematic, especially if a closed system is needed.

Magnetic stirrers also have drawbacks. For example, the limited size of the stirring bar means it can only be used for relatively small (under 4 liters) experiments. In addition, viscous liquids or thick suspensions are extremely difficult to

mix using this method, although there are some stirrers with special magnets to overcome this problem. The chamber of the solar air heater is made up of cast iron. The chamber is of rectangular in shape.

3.2 Scanning Electron Microscope

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

3.2.1 Principle

The types of signals produced by a SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown to the right.

A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter, which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher-energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

3.3 Four Probe Experiment

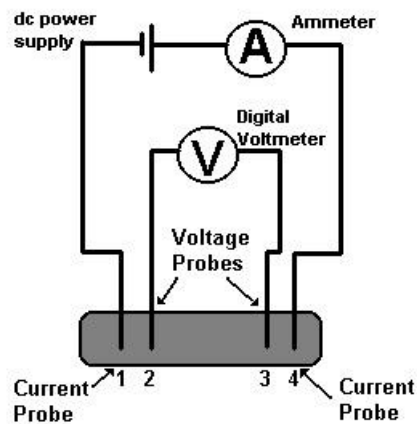


Figure 2: Schematic of Four Probe

The four point electrical probe is a very versatile device used widely in physics for the investigation of electrical phenomena. Colorado Superconductor Inc. has especially designed two four point superconducting devices from the $\text{YBa}_2\text{Cu}_3\text{O}_7$ and the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ materials for such investigations.

When a simple measurement of the electrical resistance of a test sample is performed by attaching two wires to it, one inadvertently also measures the resistance of the contact point of the wires to the sample. Typically the resistance of the point of contact (called contact resistance) is far smaller than the resistance of the sample, and can thus be ignored. However, when one is measuring a very small sample resistance, especially under variable temperature conditions, the contact resistance can dominate and completely obscure changes in the resistance of the sample itself. This is the situation that exists for superconductors.

The effects of contact resistance can be eliminated with the use of a four point probe. A schematic of a four point probe is shown in figure 2 above. In this diagram, four wires (or probes) have been attached to the test sample. A constant current is made to flow the length of the sample through probes labeled 1 and 4 in the figure. This can be done using a current source or a power supply as shown. Many power supplies have a current output readout built into them. If not, an ammeter in series with this circuit can be used to obtain the value of the current. A 5 Watt power supply capable of producing up to 0.5 Amp is required for the experiments described for our superconducting devices.

If the sample has any resistance to the flow of electrical current, then there will be a drop of potential (or voltage) as the current flows along the sample, for example between the two wires (or probes) labeled 2 and 3 in the figure. The voltage drop between probes 2 and 3 can be measured by a digital voltmeter. The resistance of the sample between probes 2 and 3 is the ratio of the voltage registering on the digital voltmeter to the value of the output current of the power supply. The high impedance of the digital voltmeter minimizes the current flow through the portion of the circuit comprising the voltmeter. Thus, since there is no potential drop across the contact resistance associated with probes 2

and 3, only the resistance associated with the superconductor between probes 2 and 3 is measured.

The four point probe devices in the complete exploration kit and the super exploration kit are both encapsulated in rugged brass casings. On one side of the casing, the superconductor disk is visible. An aluminum end cap has been inserted on the back side of the brass casing to seal and to protect the probe connections with the superconductor. Please do not attempt to remove the end cap. A matched thermocouple has also been attached to the superconductor in this casing. This thermocouple is a type 'T'.

The illustration in figure 3 below shows the salient features of the four point probe devices. The pair of black wires is current leads for the input of current from the power supply, and has been labeled probes 1 and 4 in figure 2. The pair of yellow wires is the voltage measurement probes for measuring the voltage drop across the superconductor with the help of a digital voltmeter, and has been labeled probes 2 and 3 in figure 2. The red and blue wires are leads for the thermocouple.

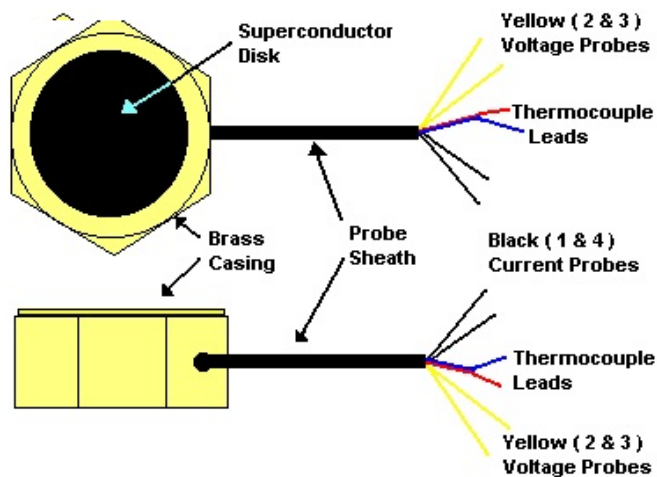


Figure 3: Super Conducting Four Probe

4. Experiment and Analysis

4.1 Preparation of MgO and Al₂O₃ Solutions

In the present work the precursor solutions of MgO and Al₂O₃ is prepared by the continuous stirring process with help of a magnetic stirrer. First of all the mass of the powder required to prepare the solution for given normality is calculated. It is given by a simple formula $MVS/1000$, Where M is Molecular weight, V is Volume to be prepared and S is solubility. Here 0.1N solution of MgO and Al₂O₃ is prepared where as PEG 6000(Poly Ethylene Glycol) solution is prepared at 0.01N.

The necessary values are substituted in the formula and the required mass is calculated as,

- Magnesium Oxide=0.403 g
- Aluminium Oxide= 1.0196 g
- Polyethylene glycol= 25 g

Before making the solutions, the apparatus and beakers are cleaned with Ethanol to remove water. The above calculated amount of powders are taken in separate beakers and added with De-ionized water. Then the solution is stirred at 40⁰C for 3 hours and 60⁰c for 4 hours. After continuous stirring, the solutions are separated into two halves.50ml of MgO and 50ml of Al₂O₃ is mixed together in a separate beaker and stirred for 3 hours at 60⁰C (It will be denoted as solution I hereafter). Another 100ml of the solution is added with 25ml of PEG 6000 and stirred for 3 hours at 60⁰C (It will be denoted as solution II hereafter).



Figure 4: Mixture of MgO and Al₂O₃ with and without PEG 6000

After this, the glass substrates are made ready for coating. Glass substrates are cleaned with water and it is immersed into ethanol for removing the water on the surface. Then the glass substrates are immersed into the solution I and solution II. In each solution, two glass substrates are immersed for 6 hours and 12 hours respectively.

After immersing the substrates are dried in the oven at 200⁰C for half an hour. This will allow the substrate to lose the water molecules on the surface and binds the molecules over the glass surface. PEG forms the polymeric linkage between MgO and Al₂O₃.

4.2 Characterization

4.2.1 Observation of Microstructure

The microstructure of the prepared samples are observed using the scanning electron microscopy .In order to take SEM image, powder preparation should be done. The prepared solutions (I&II) are allowed to settle for an hour. Then the unwanted water with ions is separated from the solutions. The precipitate is dried at 200⁰c for 3 hours to obtain fine powder. After 3 hours of heating, powder is deposited at walls of the beaker. It is collected to another clean beaker and it is set in order to get fine particles which are sent for SEM imaging.

SEM image was taken at P.S.G college of Technology, Coimbatore, Tamilnadu, India. Three sets of reading was taken at different magnifications as given below

4.2.2 With PEG 6000

The SEM image shows clearly that the molecules are bound closely and the PEG forms a polymeric linkage between the

two compounds. The gap between two adjacent molecules is very close so that the conductivity increases greatly.

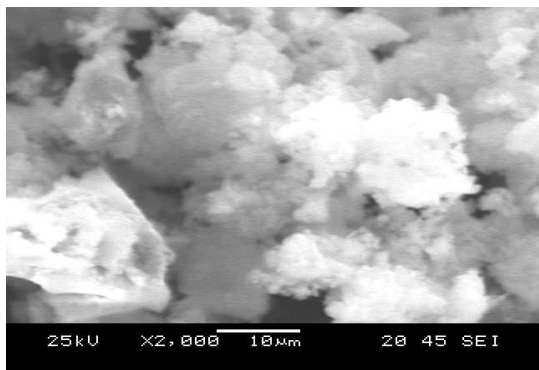


Figure 5: SEM Image with PEG (X2000)

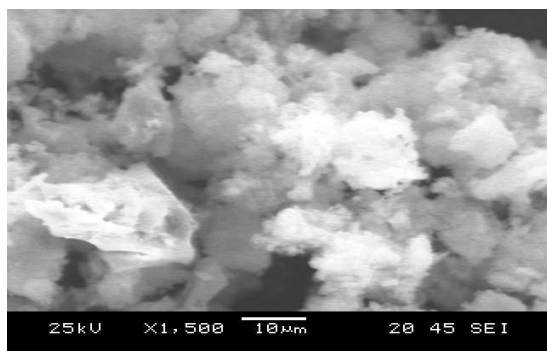


Figure 6: SEM Image with PEG (X1500)

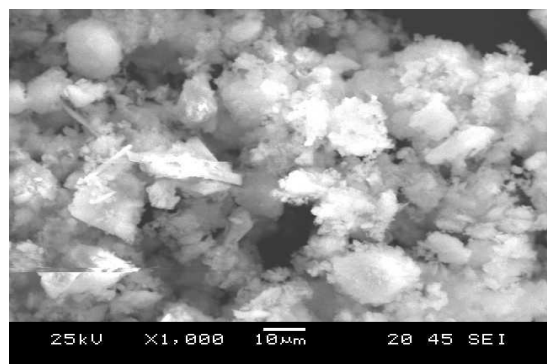


Figure 7: SEM Image with PEG (X1000)

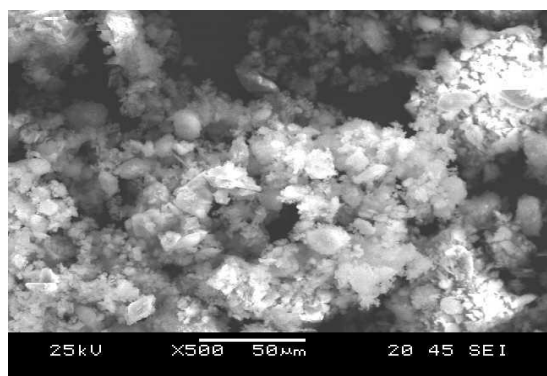


Figure 8: SEM Image with PEG (X500)

4.2.3 Without PEG 6000

Powder prepared without PEG 6000 exhibits different structure when comparing to that of previous one. The smaller particles are adsorbed on the larger molecules by bonding or by Vanderwaals force. Molecules are tightly

packed but the polymeric bonding is absent due to absence of PEG 6000.

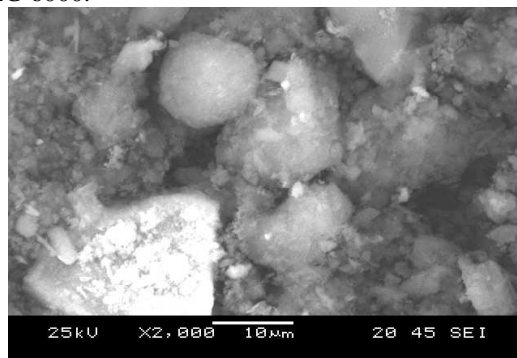


Figure 9: SEM Image without PEG (X2000)

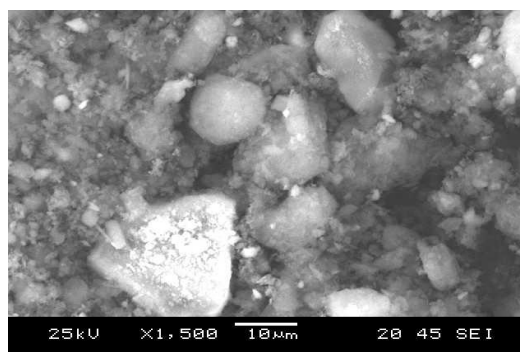


Figure 10: SEM Image without PEG (X1500)

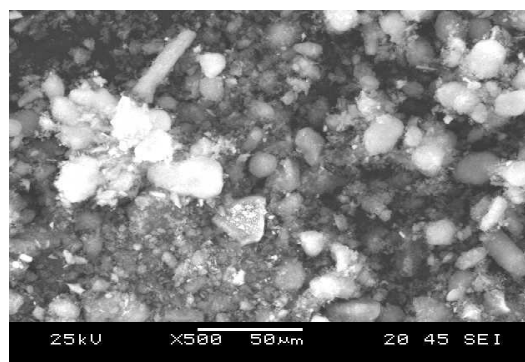


Figure 11: SEM Image without PEG (X500)

4.2.4 Current Conducting Behaviour

The conductivity test was done by Four Probe method. It shows the variation in electrical resistance for different coating done by using different solutions. At first the electrical resistance is calculated for glass reference substrate and then the coatings are compared. The results for various samples are given below,

X axis - Voltage (mV)

Y axis – Resistivity (Ωcm)

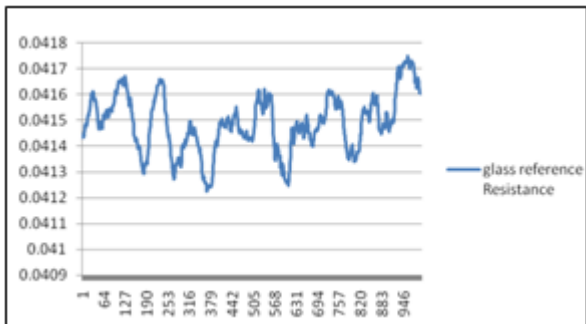


Figure 12: Glass Reference Resistance

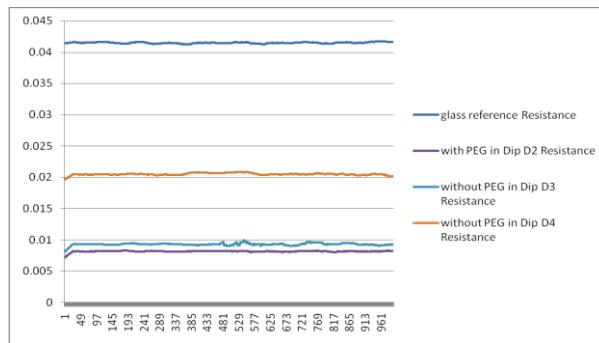


Figure 17: Glass reference with PEG in Dip D2 and without PEG in Dip 3 and Dip 4

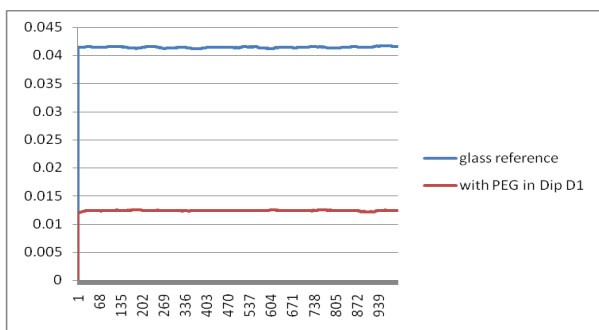


Figure 13: Glass reference with PEG in Dip D1

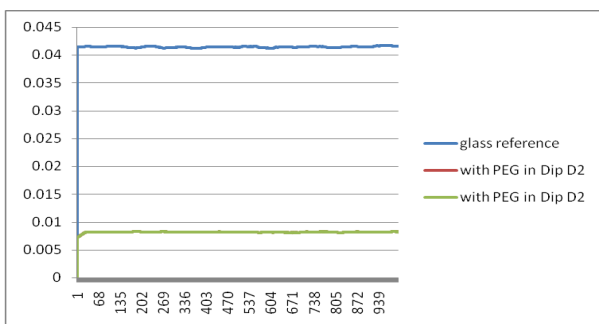


Figure 14: Glass reference with PEG in Dip D1 and D2

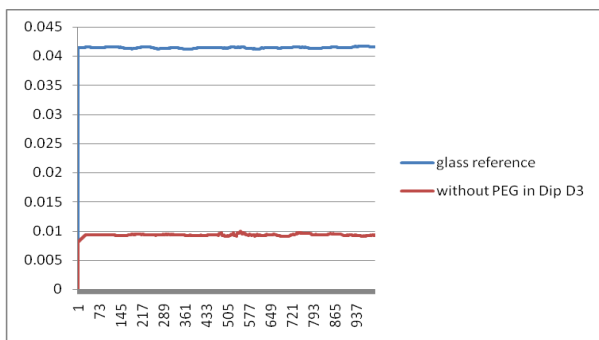


Figure 15: Glass reference without PEG in Dip D3

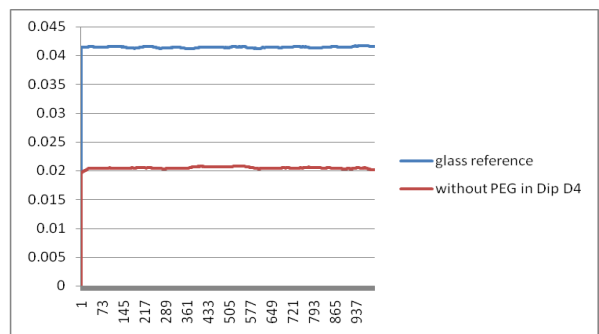


Figure 16: Glass reference without PEG in Dip D4

These results clearly show that the glass reference has highest resistivity when comparing to the other coated substrates. Here the discussion is made on 2 samples prepared by Spin Coating and 4 samples prepared by Chemical Bath Method.

Based on the observations, Glass reference shows the highest resistance of 0.0417. The resistance dropped suddenly on going through various coated samples. On taking the Spin Coated sample without PEG, it shows the apparent resistivity nearly 0.029 and sample with PEG at Spin Coating shows a variable resistance.

On the other hand the dip coated specimen also shows greater results in resistance. Here the substrates D1 & D4 are immersed in the solution for 6 hours and D2&D3 are for 12 hours. When comparing the characteristics of sample with PEG, the Substrate D1 (0.012) shows higher resistivity than D2 (0.008). When comparing the characteristics of sample without PEG, the Substrate D4 (0.02) shows higher resistivity than D3 (0.009).

4.3 Gas Sensing Test

After taking the four probe test, it is confirmed that the substrate possess conductivity. Next step to that is to perform the gas sensing test in order to ensure the response of coating towards gas exposure. Here hydrogen gas is used to check the sensitivity of the substrate. First the substrate is provided with initial voltage supply and the output voltage is noted during the exposure of hydrogen gas. The values are noted and tabulated.

Table 1: Gas Sensing Result

Input Voltage (V)	Output Voltage (with PEG) (mV)	Output Voltage (without PEG) (mV)
12	-0.5	-1.2
18	-0.3	-0.8
24	-0.2	-0.4

Negative values persist because in hydrogen, an H⁺ ion conducts. So instead of electron, positron conducts the electricity. Due to it the negative values results as output.

5. Results and Discussions

The mixture of Magnesium oxide and Aluminium Oxide is coated on a glass substrate by Chemical Bath Deposition

technique. In the above study four coatings were made in which two coatings were coating by the Magnesium oxide and Aluminium Oxide mixture with addition of Polyethylene glycol (PEG). Other two coatings were made without the addition of PEG. Also the films were deposited at two different dip timing. Figure 8 displays the SEM images, showing the molecular structure of the film with PEG. The polymer chain can be clearly seen in the figure. Figure 11 shows the SEM image of the sample without PEG in which MgO molecules are adhered over Al₂O₃ molecules. This effect may be attributed to the addition of PEG. Figure 17 shows the four probe test results of the samples. It can infer that the coating with PEG shows good conductivity results. Also the coatings dipped for 12 hours shows great deviations in conductivity when compared to the coatings which are dipped for 6 hours in the same solution. Table 1 shows the gas sensing test results of the prepared samples. In this test it can be inferred that samples without PEG shows better output voltage for the same input voltage than that of the sample with PEG.

6. Conclusion

From the above discussions it can be inferred that the samples with different compositions and different coating time shows extremely different results. In the analysis side, four probe test result shows the conductivity variation for samples with PEG and without PEG. Also the samples coated for 6 and 12 hours shows variations in change in conductivity. Scanning Electron Microscopy results shows that the polymer chain is formed due addition of PEG and sample without PEG shows even grain structure. The Magnesium Oxide molecules are adhered over Aluminium Oxide molecules. Finally Gas sensing test shows the change in conductivity for exposure of hydrogen gas.

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Author Profile



R. Sakthivel received the B.E in Mechatronics Engineering from Kongu Engineering College, Erode, Tamil Nadu, India in 2012 and he is pursuing M.E in Thermal Engineering in Government College of Technology, Coimbatore, Tamil Nadu, India.



P. Mohamed Shameer received the B.E in Mechanical Engineering from National College of Engineering, Kovilpatti, Tamil Nadu, India in 2013 and he is pursuing M.E in Thermal Engineering in Government College of Technology, Coimbatore, Tamil Nadu, India.

India.