Experimental Analysis of Electrical Conductivity of the 3D Printed Graphene

R.Hushein, V.Hima Deepthi

Abstract: To develop a 3D printed material system for extracting the electrical conductivity of the piezoelectric material, to fabricate the integrated piezoelectric prototype and it's always have a good availability with the more number of variety of materials for making with special characteristics. This paper introduces with direct ink writing method for printing the piezoelectric material by using multi materials such as terphinal, ethyl cellulose, methanol and graphene. The materials and processing steps for the manufacturing the 3D printed piezoelectric component, the individual material characteristics and the equivalent circuit is provided. Electrical Conductivity analysis on the 3D printed piezoelectric done with the above mentioned material and the result has been discussed by using the four point probe method.

Keywords : 3D Printing technology in Electronics, Piezoelectric material, Direct ink writing method, Four point probe method.

I. INTRODUCTION

3D printed electronics introduces the new ways to find the boundless opportunities in product design. On the other way, it also brings the challenges regarding massive aspects in the design of prototypes and manufacturing the processing steps of the products. 3D printing and electronics may still remain in unique way to manipulate the technology is used to bringing the huge changes to the industry sector. Meanwhile the technology is still giving more priority to use prototyping tool is the major one which can give the benefits of 3D printing in faster in time maintained to reach the market, freedom of designing a prototype with complex structure and provide more possible way to do the customization and it can be easily handled by the electronics manufacturing industry sector. 3D printing of Electronics also have the same processing steps of normal 3d printing such as 1.Prototype making, 2.Faster time-to-market, 3.Design flexibility, 4.Customisation and 5.Simplified Post process. More number of electronic devices are small miniature components which can have the minimal circuit element that are connected together in a specific area to influencing the flow of electrical current to make controlling the processing of data. This 3d printing method is applied to printing an integrated circuits has initiated the modern electronics manufacturing to make trend in worldwide. With this more number of possibility to manufacturing a modern electronics circuits, manufacturing of electronics components industry has been projected globally.

Additive manufacturing methods always likely to manipulate the technology to provide an easiest way to print an electronic circuits to maintain the more number of advantages to reach the greater degree.

A. Role of Electronics in 3D Printing

When the circuits or components being prepared with the backing of a more relevant material and required printer, the material has to maintain the more number of property without disturbing the main function of the particular component or circuit and the volume of the material dropping to the bed which is mainly fixed based on the size of the nozzles. Complex electronic circuits can be created more quickly than the normal traditional methods. There are some 3D printers available on the market where we can able to try with polymers having different properties and other multi material for creating more number of possible ways to provide a major printing strategies in the manufacturing sector.

Nowadays there’s a new technology available in the market named as Additive manufacturing technology with efficient manufacturing processes, which is creating an electronic circuits with more number of advantages compared with traditional manufacturing methods. It’s more reliable to considering the how additive manufacturing methods really different with traditional methods. One of the main reason to using with additive manufacturing processes rather than conventional engineering is the ability to reach the market from prototype design to 3d printed completed electronic circuits in very small spaces with stipulated time. Technology always play the major role to switch over the old manufacturing process to new manufacturing process but in recent years it has been set a new level in the manufacturing field through the 3D printing technology. Instead of using separate circuit boards, large number of wiring and hard-hitting connections is massively reduced the overall process under control to maintain the more reliable and user friendly manufacturing methods. This 3d printing technology not available to printing an electronic circuits alone, even it can able to print both active and passive electronic components and other electronic packaging devices to performing the complete manufacturing access in the electronic component manufacturing sector. Now, the technology has grown up to print antennas and sensors by using the various composite materials and printing methods.
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When 3d printing of electronics applied to any industries provides enormous technology for ability to printing directly onto the prototype and it’s creating a smoothest and more streamlined design. These designs will directly feed into the 3d printing machine. Experimental design parameters and the material properties with defined structure will make the final product in more comfort effect on the overall performance to achieve the required output [19].

B. Features of Electronics Manufacturing in 3D Printing Sector

Compared with other area when 3D Printing technology applied to electronics component manufacturing have more number of advantages, because of the wide variety of materials supported to print with the machine easily [15]. Other than the metal powder and binders, materials are categorized based on the conducting and non-conducting property. These specific inks are giving more number of possibility to print the electronic part [16].

In normal traditional manufacturing method, when manufacturing has started to make a prototype, it’s not easy to make the each and every parts of the prototype in single machine. Electronics circuits are having more number of miniature components as well as circuit connections. Each and every components are connecting or soldering with other component in conducting or non-conducting way. But in 3D printing technology once the circuit design has made based on the required structure, the final output will more accurate rather than the previous manufacturing methods [17].

Traditional manufacturing methods are always requires more number of human input, source material and time as well as economically it will spend more amount to make a complete prototype. When compared to the 3D printing techniques, there’s a huge benefit in the all the above categorized items and most importantly it’s economically fit one single printer with source material and one computer system enough for making the complete prototype. This method mainly saves money as well as the place also not required in that much level like the previous methods. Manufacturing defects and errors are also can able to identify easily at the same time it can able to overcome that errors also. The possibility for detecting and solve the issues in 3d printing is very easy. Generally the manufacturing process always requires less number of inputs and accurate output. It’s more easily defined in 3d printing technology and quickly carry more advantage in the market.

II. PROTOTYPE PREPARATION

A. Material

Graphene is the new type of 2D carbon nano material which is having a great physical, chemical and mechanical properties in a Room temperature. Graphene is also a one type of conductive material which is having the conductivity of 106 S/m and sheet resistance value will have 31 Ω/sq. Initially carbon atoms present in the sp2 level and releasing one more electron to the π bond under the room temperature its freely moving with diminutive interference, making the material as a high conductivity. so compared with silicon, mobility of the graphene almost 140 times higher and moreover mechanical strength and the thermal conductivity of the graphene are also very high [21]. PVA (Ployvinayl) solution will be prepared by using the PVA powder with De Ionized (DI) water added together (15% + 85%) and the resulting dispersion was centrifuged at 300 rpm for 45 min with 60 degree heat [23]. After this above flake will be removed and it’s just appearing a crystal clear transparent solution and then the final composites prepared by the combination of the all the material in concentration of the 7gm of graphene, 5gm of terphinal, 5gm of methanol and 3gm of ethyl cellulose and adding with prepared 20gm of final material. It will be filled in a flask and the flask was placed in a cool place during sonication in order to prevent temperature rising. After some time, the flask was taken out and it will be ready.

B. Printing Method

Direct Ink writing (DIW) 3D printing methods is also a one of the main printing methods for the additive manufacturing of composites. It is mainly used to printing the complex structure with advanced composite materials for various material property. These composite material filled in the syringe extruding with the help of pressure unit to deliver the 3D shape of the material(Fig 1). various types of needles are taken place based on the volume of the required output model which can have the free movement in all three dimensional directions. The extruder deliver the material layer by layer based on the given CAD model [23].

In this method, the, final composite material filled to the syringe and it’s attached with the 3d printer. The numerical model uploaded into the 3d printer then by varying the pressure value 0.5, 1 and 1.5 bar respectively with different needle size based on the required volume. The source material can be delivered through nozzle to the plot area, the pouring droplets from the needle make the alignment based on the given 3d CAD structure to form a continuous pattern which hardens with adequate strength to hold the consequent layers of printed materials.

The quality of the printed model defined by the viscosity of the material and deposition speed. This fast and effective method easily print the complex structure in flexible manner [24].

![Fig 1. Direct ink writing (DIW) method](image-url)
III. CHARACTERISTICS AND PROPERTIES

Characterization is mostly based on the thickness of the material. In graphene, thickness is in atomic scale, so horizontal dimension will extended sufficiently which occurs the proper mobility of the carbon atoms. Graphene is a light material which is having the planar density is 0.77 mg/m². Each carbon atom make a strong connecting bond with other carbon atom in adjacent position (Fig 2). Graphene is generally a hexagonal structure will have three σ bonds as mentioned earlier in each lattice to forming a stable hexagonal structure [25]. The π bond have located vertically in the lattice plane is the reason for electrical conductivity of the graphene.

![Fig 2. Carbon atom structure in graphene](image)

**A. Thermal Conductivity**

The coefficient of thermal expansion (CTE) for graphene is always negative only, here also this output showing the same results. Generally it is positive for most of the conductive silicon substrates due to the inner electron mobility.

When the sheet is appeared with the heat, both the graphene content and the below substrate taken place simultaneously with the same level. In cooling process also same thing happened but this time it occurs with the substrate contraction. So reverse phenomenon has taken place [26].

Here below mentioned graph (Fig 3) showing the coefficient of thermal expansion of graphene with temperature [35]. Initially it’s started in the negative region. When the temperature has slowly increases, the co-efficient value has been reached in the positive region.

![Fig 3. CTE of graphene vs temperature](image)

B. Sheet Resistance

Sheet Resistivity measured based on the resistance measurement results of four different places of graphene with aluminium ink mentioned as R1, R2, R3 and R4 [35]. Sheet resistivity were measured with the electrode in multi places (Table 1) noted the good variations in the output and the output value also has been derived as mean value of the sheet resistivity ± standard deviations.

\[
R_{sh} = R \times \frac{W}{L} \ldots \ldots (1)
\]

<table>
<thead>
<tr>
<th>Electrode’s</th>
<th>(R_{sh}(\Omega/\text{sq}))</th>
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<tbody>
<tr>
<td>R1</td>
<td>118.46 ± 3.7</td>
</tr>
<tr>
<td>R2</td>
<td>110.03 ± 8.1</td>
</tr>
<tr>
<td>R3</td>
<td>116.11 ± 2.2</td>
</tr>
<tr>
<td>R4</td>
<td>136.23 ± 4.4</td>
</tr>
</tbody>
</table>

Table 1. Sheet Resistance of Graphene Ink Measurements results

Resistivity of all the electrodes from the graphene sheet showing how the conductivity is happening as well as the average sheet resistance will be 120.20 (Ω/sq.). Due to the layer thickness, total volume of the material having the more number of free electrons which can make the more resistivity and the conductivity [27].

C. Raman Spectroscopy

To find out the presence of graphene content in the given composite material Raman Analysis were used and to check the two indicating point which is mentioned in peak level [28]. This peak point indicating (Fig 4) the carbon structure available in the sp² layer of graphene as well as make more effect in the characteristics. Due to this symmetry property, the graphene composites indicating the two peaks with the same height ratio [29][35].

![Fig 4. RAMAN Spectroscopy](image)

D. Young Modulus

The intrinsic thermal vibration in graphene which is “observed” by molecular dynamics is defined the Young’s modulus and also increases the size with threshold value. Mechanical property of the material theoretically it can be sustained up to 25% through tensile elastic strain but experimentally...
it’s having 20% measured at room temperature $^{[30][15]}$. Here by using the Raman analysis, the peak strain is measured from the graphene membranes (Fig 5), then compared this strain from the numerical simulation, and the calculated Young’s modulus was 1.4±0.04 TPa. The completed 3D Printed prototype has taken for the testing and 4 node point were selected randomly (Fig 7) with 3 selected regions for connecting the Power supply, ammeter and voltmeter. When the DC Power supply has applied in a regular interval (2V, 4V and 6V), the voltage and current variations are noted in the voltmeter and ammeter respectively (Table 2). From this variations as said earlier the resistivity and conductivity of the material has been found. By using the below mentioned formula (2), the conductivity has been calculated (Fig 8).

$$\sigma = \frac{1}{\rho} \quad \ldots \quad (2)$$

The graphene dispersions with the other material make the more effects on the physical and electrical properties of the composites and it will improve the printing ability for getting the quality product. Scanning electron microscopy (SEM) images captured from the final composite material caught from polymer matrix with diverse contrast and in depth morphologies in a surface and cross sectional areas $^{[31]}$. When a peak indicates in the images, its shows the electrical conductivity based on the graphene composites which can be defined based on the percolation threshold and so far graphene-based polymer. Generally the graphene composites was reported the percolation threshold around 0.1 vol% only. But in our samples the percolation threshold value has calculated from the 15 in wt% was 0.9 vol% only.

![Fig 5. Young Modulus](image)

E. Electrical Property of the graphene

A composite material consists of different properties compared with the original materials. It’s having versatile property variations due to their extensive range of process ability and also there are many other factors which can make impact on the electrical performance of the material but that factors varying based on the graphene production methods and post-production routines process. Each and every factors play the major role to achieve the ultimate performance $^{[32][33]}$.

This graphene material mainly used for the purpose of Piezo electric energy harvesting. When the electrical conductivity is happening in the material then only electrical energy harvesting will take place so need to find out how the conductivity is happening, based on that only will come to know, how the electrical energy conversion will done. Here is to find out the electrical characteristics of the material by using the four point probe method. It will measures the current with the voltage. Resistivity calculated from this measured values. Conductivity is always inverse proportional with resistivity. So the final value has been intended through experimental calculation.

![Fig 6. Scanning Electron Microscopy (SEM) images of the graphene composite specimen](image)

![Fig 7. Four point probe method](image)

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Volt(V)</th>
<th>Res $(\Omega m)$</th>
<th>Conductivity $(1/(\Omega m)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2V</td>
<td>5.56</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>4V</td>
<td>4</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>4V</td>
<td>3.33</td>
<td>0.3</td>
</tr>
<tr>
<td>4</td>
<td>2.63</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6V</td>
<td>2.22</td>
<td>0.45</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>0.5</td>
<td></td>
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![Fig 8. Resistivity and Conductivity of the material](image)

![Table 2. Resulted value from the material varying with desired input voltage (V)](table)

![Table 2](table)
The electrical conductivity of the composite material not based on the single factor of the material, more number of factors contributing to achieve the conductivity. The electrical conductivity achieved from sample is $0.35 \pm 1 \text{mS} \cdot \text{cm}^{-1}$. The output value has been varied the wide properties of graphene with the other composite material. This property have the ability to create a conductive network which can easily make the good conductivity in the material [34].

IV. CONCLUSION

These entire process just make clearly how these technologies will be adopted by the electronics packaging industry. Direct Ink writing method has been used to printing the filament with desired level as mentioned in the predefined structure. When the graphene make composite with the others materials it’s just easily extracting the real piezoelectric characteristics. In Four point probe method, when graphene content added more, resistivity will decrease meanwhile the conductivity increased. The conductivity of the composite material has proved that will always inverse proportional to the resistivity.

REFERENCE


