3D Printed Wearable Electronic Sensors with Microfluidics

by

BRIAN ANDREW ZELLERS

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3D Printed Wearable Electronic Sensors with Microfluidics

Brian Andrew Zellers, B.S.E.E.

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Abstract

Additive Manufacturing (AM) has made possible the creation of objects not possible with traditional manufacturing techniques. Additive Manufacturing creates a higher degree of design freedom; geometries and features impossible to create with a CNC mill or robotic arm can now be created with ease. Three dimensional electronics is one such field that is now possible due to the realization of Additive Manufacturing. Wearable electronics necessitate compact size and adaptive design; no two human bodies are the same, yet many electronics intended to be worn come in few to no variants in fitment. Wearable electronics are a hot topic in the current market. Through AM technologies the development of such items can be accelerated and made more cost efficient.

In this thesis all 7 types of AM technologies are highlighted, with Stereolithography being the main focus, and being primary technology used for this research. The technologies used to create electrical connections in AM electronic devices, will be analyzed and explained. The following research takes a traditional, two-dimensional, approach to additive manufacturing electronics, such techniques can be adapted for three-dimensional manufacturing. Such circuits will incorporate functionalized Carbon Nanotubes for use in the detection of airborne substances. Micro-Fluidics will be explored as a method for channeling airborne substances to the Carbon Nanotubes. Over-Molding will be demonstrated as a method for embedding electronics into Additive Manufactured devices. Herein the process of developing conceptual wearable electronics, the advantages of Additive technologies offer on described structures and the successful fabrication of a wearable electronic device are explored.

Table of Contents

Table of Figures

Table of Tables

Chapter 1: Additive Manufactured Electronics

1.1 Introduction

The evolution of technology demands smaller, more robust, devices; consequently, components have reduced in size and increase in complexity through nano packaging and multilayer designs. The one component in these systems that has experienced few technological advances, is the substrate which integrated circuits and passive components are mounted on, the Printed Circuit Board (PCB). PCBs are strictly two-dimensional, with the exception being two-sided PCBs and PCBs that are layered through bulky interconnects. Devices that conform to non-planar shapes typically require at least one planar face for the PCB, but Additive Manufacturing and conductive inks, opens the door to circuitry that can conform to complex shapes, including the human body. The one limiting factor to this, relatively, free range of design complexity, is the physical size of the necessary components. Otherwise, one can design a device that can conform to the most complex shapes imaginable. These design freedoms allow for optimized shapes that minimize bulk and material usage, subsequently reducing weight and interference.

Additive Manufacturing has few design limitations other than the limitations due to physics and gravity. The support needed for certain features can add immense complexity. Features that have a large overhang often require support that can be detrimental to features that may be present below the overhang, and features that are interior to the part can require support that may be impossible to remove. Creative methods of design, like splitting a part into sections that can be assembled after printing, make these features attainable even on the most complex scale. Through these methods electronics can be formed in three dimensions with cavities for both components and traces. These cavities allow for press fit components and traces to be protected from damage due to contact. Circuits designed for AM can be tamper proof in terms of modifications and replication. Tamper proof circuits are the goal of the grant for which this research was conducted, though the specifics of how circuitry can be made tamper proof are beyond the scope of this paper.

The substrate for which devices can be made is broad, many materials used in AM have great dielectric properties. The physical abilities of these materials ranges from extremely flexibility to heat and flame resistance to translucence. The SLA photopolymers used herein will be discussed in Section 3.2.

When used properly, AM can reduce cost and reduced production time of devices. One off design can be made in days rather than months and design changes can be made and tested with minimal down time due to retooling. Limited production runs can be costly due to the amortization of tooling cost, when considering traditional manufacturing techniques, while AM requires little to no tooling. Components can be made on a per unit basis, where each component has its own set of characteristics that differentiate it from other units in the production run. The design of such components is largely done in CAD software. CAD software makes the validation of fitment simple and allows for the use of advanced tools such as topology optimization.

The research described herein looks to accomplish the goals of the detection of chemicals with functionalized Carbon Nanotubes, a sleek design that can be worn for everyday use, and the integration of advanced design and manufacturing techniques such as Micro-Fluidics and Over-Molding.

1.2 Research Objectives

The goal of this research work described is the fabrication of a wearable sensor that detects the presence of NO2 gas. NO2 gas is a common byproduct in the fabrication of explosives and explosive material, but the detection of such gas in low concentrations can be difficult. The wearable will combine a microcontroller with the necessary circuitry to properly measure changes in the Carbon Nanotube (CNT) sensor, used for detecting such gases. The use of multiple AM techniques and technologies is a goal of the research, namely Stereolithography (SLA), Micro-Fluidics, and Over-Molding. Additionally, the fitment and practicality of the wearable are a priority for the final product.

The main challenges of these goals are the reliability and usability of the sensor in day to day activity. This includes testing that the device can be used repeatedly, and that the device is not a hindrance to wear. The electrical contacts need to withstand repeated use cycles and the conductive materials need to endure the stresses exerted by the constant motion of the human body. The structure of the device needs to be conformed to the individual user in the form of a bracelet that can be worn containing the sensor. The device will need to be flexible such that it conforms to the body, yet rigid in sections containing the circuitry. Figure 1-1 shows a device that satisfies such requirements, the black portion is flexible, but the clear portion has the rigidity needed for the circuitry.

Figure 1-1: Wearable 3D Printed Device

The focus of this research is on the application of the 3D technologies. The process of designing the circuitry and wearable will be discussed, in addition to the results after usage.

1.3 Trust Project

The Trust Project is a collaborative research grant between the United States Department of Defense (DOD) and academia. There have been many phases of projects that focus on the topic of electronics which can be labeled as “Trust”. These projects typically focus on using advanced techniques to create electronics which cannot be duplicated or have a method of verifying whether the component has originality. The current grant that this research is being conducted under, is being conducted by The Ohio State University (OSU), The University of Akron (UAK), and Youngstown State University (YSU). Each university is working on a separate method of accomplishing the task of creating an electronic device that can’t be duplicated. YSU is focusing on using Additive Manufacturing to create such devices.

Due to the sensitive nature of research conducted on behalf of the DOD, the specifics to how Trust devices can be manufactured using AM, for the purpose of validation, will not be discussed in this work. The research, which is made possible by the wealth of AM knowledge and equipment available at YSU, will.

1.5 Thesis Outline

This thesis is organized to provide a thorough source for the information in relation to the design techniques, manufacturing processes, and a conclusion. To begin, the past accomplishments, with relevance to this research, are examined. (CHAPTER 2: LITERATURE REVIEW). This leads to an outline of the process of design and fabrication for each process. (CHAPTER 3: EXPERIMENT SET-UP). Followed by a detailed description of the device and its use cases (CHAPTER 4: WEARABLE ELECTRONICS). Concluding with observations and future research opportunities and possible improvements for the manufacturing process (CHAPTER 5: CONCLUSIONS AND FUTURE WORK).

Chapter 2: Literature Review

Despite the recent advancements in Additive Manufacturing, the technology has existed since the first patent was filed in August of 1984, by Charles Hull [16]. At that time the technology was referred to as Rapid Prototyping, as the technology was portrayed as a quick way of creating prototypes of a design. A Stereolithography Apparatus (SLA) was used for the prototyping process and is the first process developed for AM.

Material selection and printing accuracy makes SLA among the most popular choices for manufacturing circuitry using AM. One of the first research cases was conducted by Medina [11], where a Direct-Write (DW) system was integrated into an SLA printer. This system was capable of printing traces on a layer by layer basis, but no electrical components were added. Lopes [7] improved upon this method by placing components on the top layer of the device. The circuit created could vary the frequency that an LED light blinked proportionally to the temperatures sensed by a thermistor. Figure 2-1 shows the final product of Lopes' research.

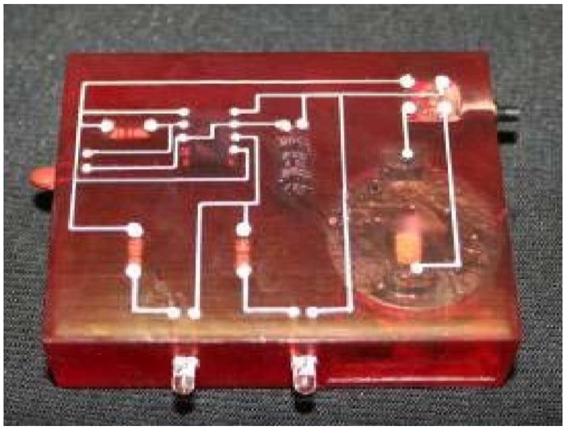


Figure 2-1: Hybrid SLA/DW AM device for displaying temperature [7]

As described by Navarette [12], this process can be further improved through optimizations in volume usage and channeling to form traces. Volume optimization was accomplished by placing components on multiple layers of the device, this reduced the footprint of the device. The use of channels for the placement of the conductive ink traces improved the accuracy of the ink laying process and allowed for tighter trace placement. DeNava [3] and Olivas [13] continued this trend and explored the use of off-axis component placement. A magnetometer circuit was used as an example and four generation of this circuit are described. The first generation made use of opposing faces placing components on these faces and connecting the faces through traces on a perpendicular face, like the use of two-sided PCBs. A second generation improved on the circuit layout and resulted in a smaller device overall. Generation three placed components on all faces, this subsequently reduced the size of the device further. These three generations vary greatly in size, Figure 2-2 illustrates this comparison well. The last generation, found in Figure 2-3, increased the design complexity and proved that components could be placed on a curved face.

Figure 2-2: Volumetric optimization of a magnetometer over three generations [13]

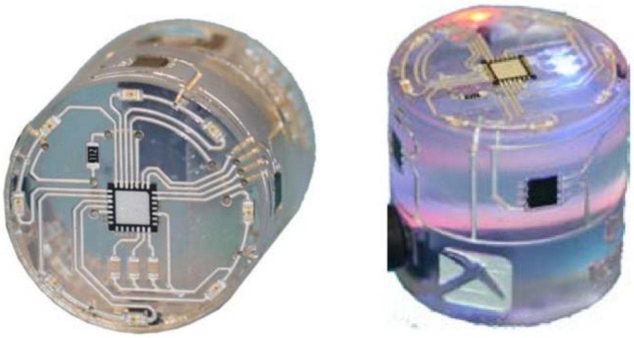


Figure 2-3: Magnetometer final generation with conformal electronic on all faces [13]

The devices discussed so far have used obscure shapes that didn’t conform to any shape or usage scenario. Olivas [13] changed that with a device that conformed to the shape of a helmet and included an antenna capable of transmitting data on a radio frequency. The device monitored movement and force using a magnetometer and transmitted this data to a receiver using a radio frequency. The shape was created using a silicone mold of the inside of the helmet, where the sensor would be placed. The silicone mold was then scanned using a laser scanner and the scan was used in Solidworks to create a plate with the same arc as the mold. The doubly curved surface, found in Figure 2-4, serves as the basis for the circuitry to conform to.

Figure 2-4: Doubly curved conformal helmet inserts demonstrating conformal electronics [13]

All this previous research conducted has been conducted using a form of Direct Write technology, referred to as Aerosol Jetting, a process that consists of layering silver ink for forming the conductive traces of the circuits. King [5] demonstrates the use Aerosol Jetting to produce traces as small as 10 microns wide and 100nm thick. These traces can be laid across non-planar surfaces and adhere to many surfaces found in the AM electronics field, this means traces can connect directly to components without the need of soldering. Additionally, non-conductive materials can be Aerosol Jetted, making it possible to create interlacing between traces without creating an electrical short.

Further research has been conducted by Roberson [15] on conductive inks, showing the effects of curing inks at high temperatures. Roberson's research explains that when silver ink is cured at a temperature higher than half the melting point of the conductive material, the conductivity of the traces is greatly improved. Ink made with microparticles rather than nanoparticles performed better after the curing process due to the larger grain size. Layer height and layer count can affect the results of the traces, with thicker traces creating reduced conductivity, as the internal structures of the ink never fully cures.

In order to create true AM electronic devices, the creation of devices that have components not only on the outside, but internally is also desired. Lopes [8] created a device that stacked components on multiple layers of an SLA printed device. The research compares two designs, one that is described as 2D, which had all components placed on one plane. The other design consisted of a true three-dimensional component placement. Here, the design incorporates two layers of components and three layers of traces and interconnects. The manufacturing process involved printing the device to a point where the component cavities were complete, followed by placing the components in the exposed cavities. After placing components, traces were created using Aerosol Jetting, and then cured with a laser. This process of printing then placing components and laying traces was repeated until the part is complete. The final part was placed in an oven to cure the resin and to ensure the ink traces are fully cure. The final devices, described in Figure 2-5, demonstrates that AM can create parts that use height to maximize on the device footprint.

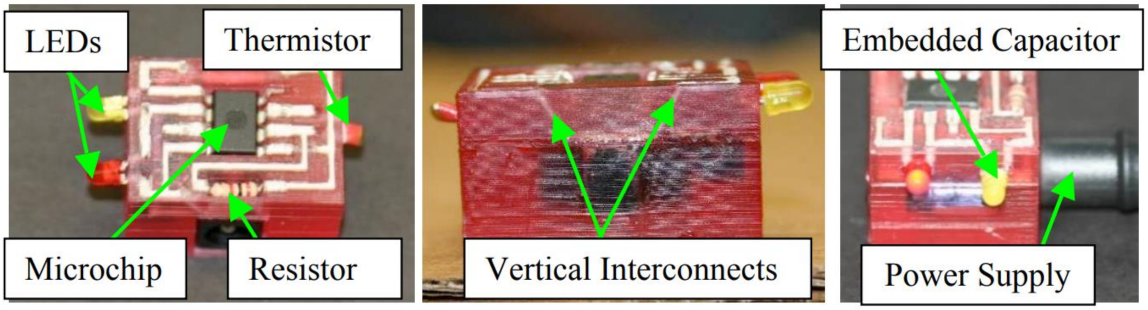


Figure 2-5: Multilayer AM 555 timer circuit with vertical interconnects [8]

The prior research conducted uses Direct Write (DW) and Aerosol Jetting has been acknowledged but not discussed. Perez [14] outlines that there are 3 types of Direct Write technologies for creating conductive traces in AM. These three types are Inkjet, Aerosol Jet, and Extrusion. Inkjet technology uses similar principles to an inkjet paper printer, a low viscosity solution containing conductive materials is laid on the print substrate. This technology can create detailed structures and is extremely versatile in the placement of the application apparatus. The use of this technology is limited due to the conductivity and viscosity of the inks. As the amount of conductive material increases, the viscosity increases also.

Aerosol Jetting works in a way similar to spray paint and aerosol spray technology. A venturi system inks are atomized in a jet of air, then dispensed through a nozzle onto the substrate. A high concentration of conductive material can be achieved, and a finer resolution is possible. Extrusion based DW technology can use either a syringe or pump system to force high viscosity inks through a dispensing nozzle. The concentration of conductive material can be extremely high and high speed printing can be achieved. A limiting factor of extrusion is that the resolution falls behind Inkjet and Aerosol Jet technologies.

Conductive metallic inks are a topic of much research and advancement, but much of this research is focused on traditional manufacturing techniques. Ahn [1] focused on the use of silver inks in Aerosol Jetting and shows promise for applications in AM. The research shows how the wetting behavior of silver inks can be tuned to fit varying applications and methods. Wetting refers to the ability for liquids to adhere to surfaces. Different levels of wetting are desired based on the substrate and method of application. Additionally, the ability to apply inks to flexible surfaces, such as Kapton are demonstrated in Figure 2-6. With the help of flexible AM materials, electronic devices with flexible traces are possible, this adds complexity to the devices that can be created with AM.

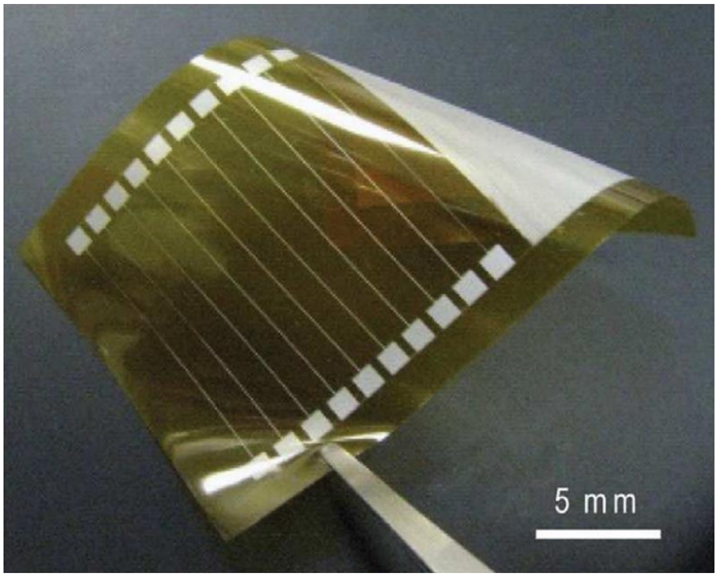


Figure 2-6: Flexible aerosol jet printed traces on Kapton [1]

The use of flexible electronics has application not only in AM but traditional manufacturing too. MacDonald [9] describes the transition of an electronic dice from an AM prototype to a device that could be manufactured using traditional techniques. The prototype device was created using SLA printing and silver ink traces and demonstrates a working design and proof of concept. The final part was constructed using an injection-molded plastic case and the circuit was placed on a flexible PCB. The final device holds much resemblance to the prototype but with the advantages of speed and cost provided by traditional manufacturing for high volume production. The prototyping phase could be assisted by the previously discussed work by Ahn, and a flexible circuit could have been created using AM, increasing the similarities to the final product.

The embedding of solid copper wire in AM parts presents an alternative way of manufacturing electronic devices. Espalin [4] elaborates on the topic, showing that copper wire can be embedded in devices printed in ULTEM 9085. Figure 2-7 demonstrates embedding wire, using an ultrasonic horn, to create an antenna design. The use of solid copper wire decreases the resistivity and increases the current carrying capabilities of AM electronic devices. This approach is achieved by using laser welding, an example of the result of laser welding can be found in Figure 2-8. In the case of the ultrasonic horn, this creates friction during the application process and can deform the surrounding location allowing the wire to be embedded into the substrate. As with the comparison of SLA to Material Extrusion, the comparison of Aerosol Jetting to solid wire embedding, comes down to speed and cleanliness. Solid wire embedding presents the opportunities for the technology to be integrated into existing machines and reduces the need for liquid materials which pose handling difficulties.

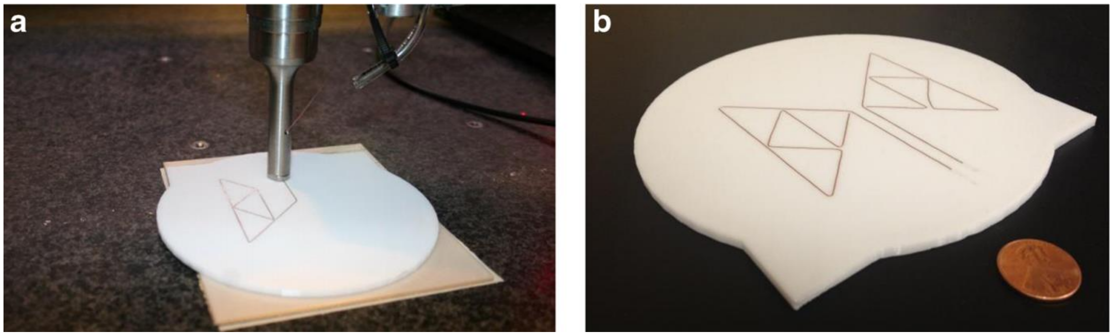


Figure 2-7: Ultrasonic Embedding of copper wire for antenna design [4]

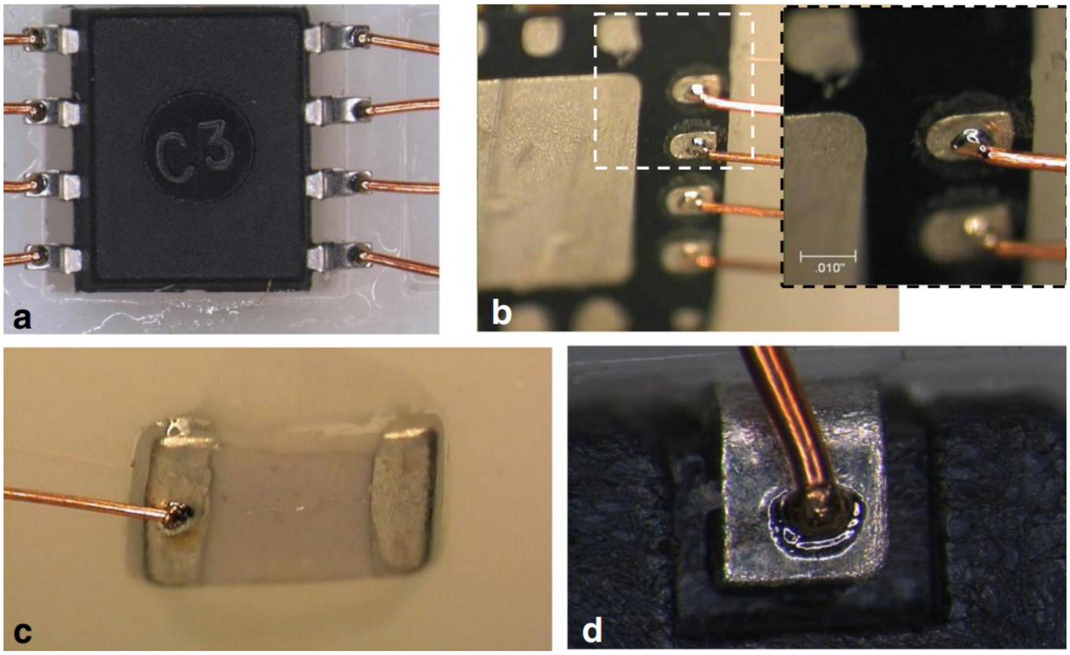


Figure 2-8: Laser-welded interconnects used in ultrasonic wire embedding [4]

The processes for creating AM electronics, discussed thus far, all share one key similarity, complexity. This complexity is due to the different machinery required to create such devices. The Aerosol Jetting processes discussed use SLA printers with a secondary gantry system or an entirely separate handling system.

The time required to setup and transfer devices between systems reduces the effectiveness of these processes. MacDonald [10] discusses a solution to improve the efficiency of these systems, using a six-axis robotic arm. This robot can transfer components between 3D-printers and auxiliary systems without the need for human interaction. These auxiliary systems can be pick and place systems, Aerosol Jetting systems, copper wire embedding systems, and many other CNC or robotic processing systems. MacDonald coins these systems “Robotic Multiprocess Additive Manufacturing” (RMAM) and demonstrates such a system, Figure 2-9, comprised of 2 Material Extrusion printers and a CNC gantry system with milling, pick and place, and silver ink dispensing capabilities. A RMAM can run 24 hours and day 7 days a week manufacturing parts without the need for human interaction, making AM a viable option for the manufacturing of complex and prototype electronics efficiently.

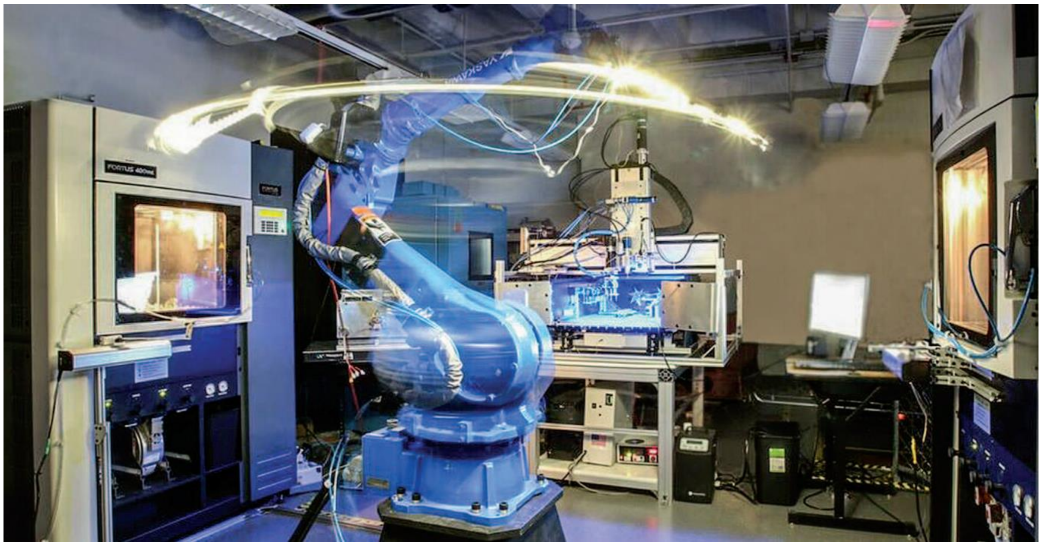


Figure 2-9: Robotic Multiprocess Additive Manufacturing [10]

A separate example of a RMAM is the system described by Lehmhus [6], which takes the system described by MacDonald [10] to the next level. This system places the six-axis robotic arm on a linear rail so it can access a hallway on 3D-printers and auxiliary systems. The system incorporates auxiliary equipment for DW of conductive inks, 3D scanning, and post processing, like thermal cure systems. Each piece of equipment makes the goal of creating prosthetics and medical equipment with integrated sensors and RFID tags possible. RFID tags make it possible to detect counterfeit devices and serve as a tracking system for the devices created using this system. When compared to traditional identification methods, that can be removed or damaged, embedded RFID tags presents a robust alternative.

The integrated sensors described by Lehmhus [6] provide ways of tracking strain and usage of a device. Strain tracking of a device provides opportunities to track the stresses that a device is exposed to, and intervene as needed, whether by replacing the device or improving upon the design to account for such stresses. Likewise, the ability to track usage of a device creates opportunities to track wear versus usage and unwanted usage of the device.

Chapter 3: Experimental Set-Up

3.1 CAD Process

Computer-Aided Design (CAD) software is a key tool when creating designs for Additive Manufacturing. The CAD software has many different applications, as such many different types of CAD software are available. CAD software used for 3D design is best suited for the AM design process. Two commonly used examples of such software are Dassault Systemes SolidWorks and Autodesk Fusion 360, both share similar core design tools but differ in their advanced features. The following will provide a brief overview of CAD modeling software.

The first step of any CAD process is choosing a unit system, it is generally recommended to choose a unit system that the designer is familiar with, herein the metric system will be used for design and all distance measurements will be in millimeters. The overall design shape and dimensions must be evaluated once a unit of measure is established. The overall shape of the part can be manipulated through cuts and extrusions to create desired features and details.

When the final design is properly manipulated to satisfy the objectives of the model, the circuitry can be planned. The method for which electrical interconnects will be created determines the following steps, certain processes require channels to be cut into the device for the placement of conductive material and pockets for component placement. Other processes only require a 2D layout of the interconnects and pockets cut for components. The creation of a 2D layout of the circuitry is a good first step no matter the method used to create interconnects. At the time of writing this paper there are no software packages that are capable of automatically rerouting circuitry and placing components in three dimensions. Software like the Proteus PCB Design Package exist, for auto-routing circuitry in a planner format. Such software can assist in design but are not used for the design of this circuit.

The placement of circuitry without the help of software requires careful planning to minimize circuit complexity but maximize the usage of space. With a component layout created the press fit cavities that the components will reside in can be created. These cavities need to have tolerance to allow the component to press into the device, minimizing the need for adhesives. The tolerance used varies based on the 3D Printer and AM process being used. If the process used in the creation of interconnects does not require trenches, the design process may be finished here. Processes that require channels, require a final step of cutting channels into the device for traces. Based on the process used, channel width can be sketched on the device and the ideal depth can be cut into the model. Figure 3-1 presents an early design of the circuit described herein.

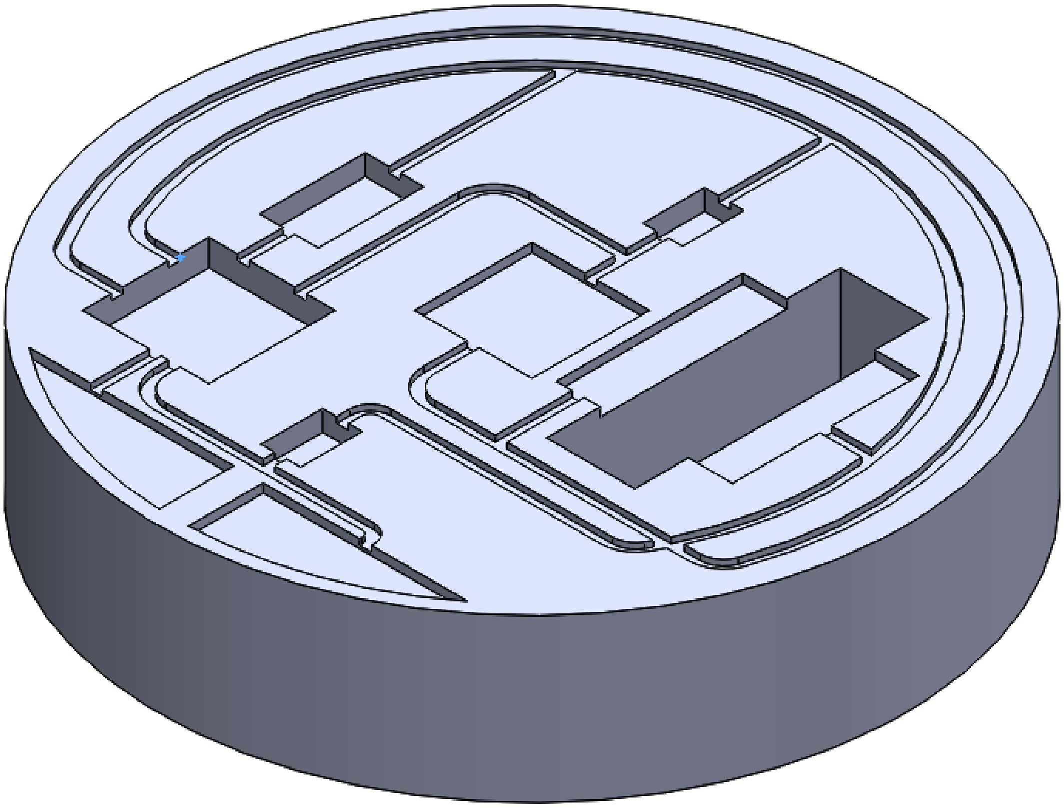


Figure 3-1: First circuit design

This process can be repeated as needed, if the device has multiple pieces. The completed rendering of the part must now be saved in a file format that AM software can use. Such files are STLs and OBJs, there are other file formats, but these are currently (November 2019) the most common. An STL is a rendering of a 3D design that converts the surfaces into triangular surfaces made up of vectors in a X-Y-Z coordinate system. When saving a component as an STL, many software packages allow the resolution of the rendering to be adjusted. If a resolution is selected that is too coarse, the resulting part will have artifacting on the surface, but with finer resolution come large file sizes. Large files may slow down the software used by the AM machine but will result in overall better print quality.

Object files or OBJs are essentially the same as STLs but incorporate the ability to apply surface mapping whether in the form of an image or coloring. With recent advancements in AM technologies this means parts can be created with many colors without the need for complicated post processing software.

3.2 Preparation Process

Prior to the start of the building process several preparations need to be completed, without properly completing these tasks a build may fail or create undesirable results. The STL or OBJ file must be validated for inaccuracies such as gaps or incomplete features. Many software packages conduct this step automatically and alert of any potential issues, but certain issues may get missed by the software, so a visual check of the rendering is recommended. Next, the physical features of the part must be analyzed, again, some software conducts such practices automatically. For those that lack this functionality, features such as overhangs, curves and fine details must be analyzed to ensure that the software recognizes the feature correctly and can create such a feature. Additional features, such as support may be needed to assist in the creation of certain features. Support serves the same purpose supporting features that otherwise may be too difficult or impossible to create due to gravity. Support can be thought of as scaffolding in the construction of homes and buildings, to support features that cannot or are not supported by the part itself during the print process. An example of a part that is being aided by support is described in Figure 3-2. Additionally, features that are to fine may not be properly recreated during the print due to resolution limitations in the AM process and may require modification to produce the desired result.

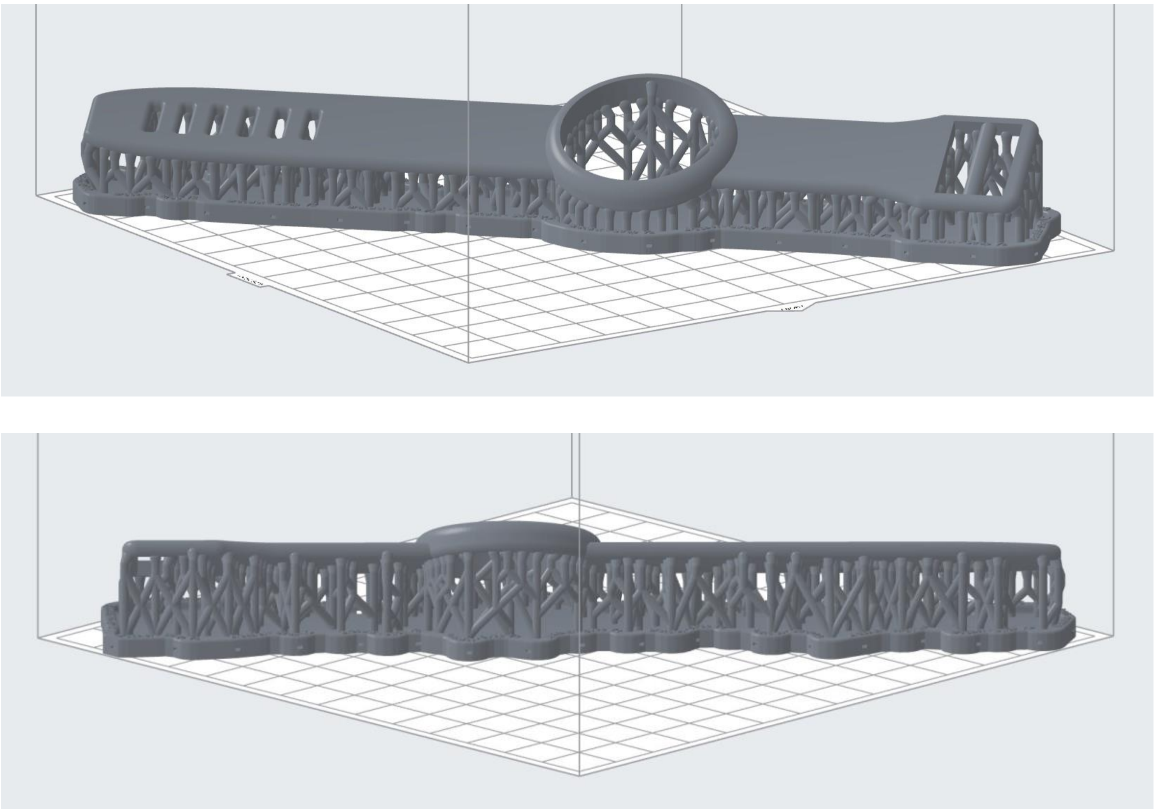


Figure 3-2: Preform part support example

With the rendering evaluated and features checked the structure can be sliced into the layers that will represent the vertical resolution of the part. Typically process parameters such as speed and resolution are outlined during the slicing process. The sliced part is then saved in a digital form for which the AM machine will create the part. This file format varies based on AM process and even between different machines.

3.3 Building Process

For the devices created in this thesis, a Formlabs Form 2 was used. The Form 2 utilizes SLA technology to create structures with high resolution details, up to 25 microns in the Z axis. The process described herein will focus on the Form 2, but there are many similarities between each machine and AM technology.

To begin the build process, the source file is uploaded to the printer from the host software and computer. Before the build can start, the printer runs through safety checks and material preparations. First, the build plate, which the part will be temporarily attached to during the print to control the vertical movement of the build process. As the resin level is being checked and adjusted, the resin is heated to a predefined temperature. When the material level is correct and is heated to the proper temperature, the machine checks the resin tank for obstructions using the material wiper and the printing process begins.

Photopolymer, or polymer that can be cured using light, is used in the SLA process. An ultraviolet (UV) laser is used to cure the polymer in a layer-by-layer process. For this reason, SLA can be thought of as 2D printing layer-upon-layer. The laser traces the outline of the part and raster the interior areas to cure a thin layer of resin. To create a new layer the current cured layer must be lifted off the bottom of the resin tank and positioned so that a gap, the thickness of a single layer, is created between the previously cured layer and the bottom of the resin tank. A single layer can range from 25 to 300 microns on the Form 2, this range varies based on the resin being used and the users printing parameters. With a gap, created the process can be repeated, doing so attaches a new layer to the previously cured layer. The outline and infill of the part will be adjusted as needed to gradually create the details of the part. This process is repeated until the part is finished.

The post processing can begin once the build has finished. To begin the part must be washed in an Isopropyl Alcohol (IPA) bath for a predetermined length of time, based on the resin being used, to remove any excess resin. With the part cleaned, the excess IPA must be removed using compressed air. Next the part must go through a final cure process, to do so, the part is placed in a UV oven and heated to a predefined temperature for a predefined time while UV light is shined on the part. Once the final curing process is finished, the support can be removed, and a surface polishing can take place if desired.

3.4 Process Hardware

The creation of the devices described herein was handled by Formlabs Form 2 printers. These systems utilize an inverted SLA technique and can be broken down into four main components: the software, the resin handling system, the motion system, and the laser system. A graphical rendering of these systems is present in Figure 3-3. In the previous section, 3.2 Preparation Process, the tasks conducted by the Formlabs Preform software are outlined and many are conducted automatically.

Figure 3-3: Formlabs Form 2 hardware overview

The resin handling system stores the resin, used to create devices, then conveys it to the building area, where the resin is consumed during the printing process. The resin cartridges, that store material, can contain 500ml or 1L of resin and include a sensor to monitor the level of the material. A dispensing nozzle on the bottom of the resin cartridge dispenses material into the resin tank, using an actuator that depresses a nozzle on the resin cartridge. The resin tank and cartridge both contain an electronic tag that identifies the resin that is in the cartridge and has been assigned to that tank. The bottom of the tank has an optical window, that the laser system shines through, and a layer of PDMS (Polydimethylsiloxane). PDMS is a material from the silicone family and provides the surface for resin is temporarily cured on but can be easily removed. Behind the resin tank is a material level sensor, used for monitoring the resin level, and below the tank is a heater used to control the temperature of the resin.

The motion system controls the Z-axis build process, mixes material, and removes the adhesion between the part and PDMS layer. The Z-axis moves the build platform in the vertical direction and is responsible for the layer thickness of the print. Before and during a build the resin is mixed and the PDMS layer is wiped of any unintentionally cured resin. A wiper arm that moves in the X-axis handles this operation, additionally if a print were to fail due to a part falling off the build platform, the wiper arm would detect the obstruction and pause the print. Additionally, the resin tank can move in the X-axis after each layer to remove the part from the PDMS layer.

The final system is the laser that cures the resin. The laser reflects light off two small mirrors attached to galvanometers and then a larger mirror that is aimed at the bottom of the resin tank. The 2 small mirrors attached to galvanometers shine the laser in the X/Y-axes and the galvanometers are small precision motors that control these motions. The large X-Y Scanning Mirror provides a surface for the 2 smaller mirrors to reflect off onto the bottom of the resin tank and the part.

3.5 Additive Manufacturing Materials

This research focuses on creating wearable devices that are both functional and aesthetically pleasing. In the world of AM, there is an ever-growing selection of material and researchers have many options in choosing a material to satisfy the needs of the research. To accomplish the goals of this research two materials are needed, one that is flexible and another that is translucent.

Materials that satisfy such needs are the RS-F2-GPCL-04 Clear resin and RS-F2-FLGR-02 Flexible resin from Formlabs. Photopolymers are not known for strength properties but the 25-micron layer resolution of the Formlabs resins makes creating visually pleasing AM devices possible. The clarity that a post processed part can achieve is presented in Figure 3-4.

Figure 3-4: Demonstrating RS-F2-GPCL-04 clarity

3.6 Conductive Ink

Using traditional manufacturing techniques, electrical interconnects are created using copper embedded in a substrate, the most common being FR4. Conductive inks placed using micro-dispensing or through manual application techniques present the opportunity to create circuitry that can conform to almost any surface. Micro-dispensing can create arbitrary traces in a quick clean manner but requires additional programming and machinery. For the research described herein, traces were created using hand laid silver infused paint.

MG Chemicals’ 842AR Silver Conductive Print is an acrylic lacquer pigment infused with conductive silver particles. Such material can be laid with a fine-tipped solvent-resistant brush and once cured has a described restivity of 0.0001 Ω/cm. The curing process can be completed at room temperature without the need for additional heat. Channels are an essential component to this style of application, as the channels prevent the paint from dispersing and allows the researcher to apply uniform traces with ease. Figure 3-5 demonstrates a test sample used to test conductivity of traces created with the 842AR material. Test results, described in Table 3-1, demonstrate consistent results when trace length is limited, but as trace length increases the reliability of trace conductivity decreases.

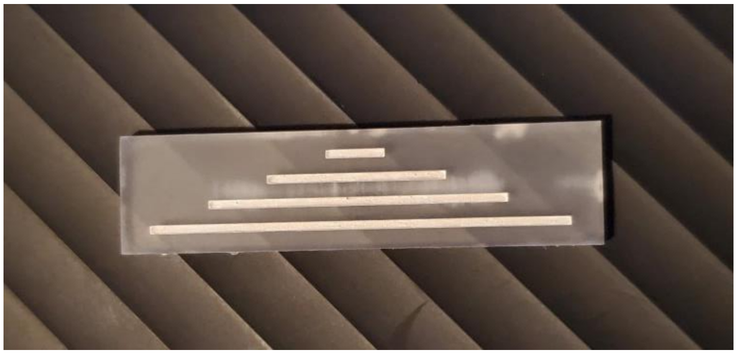
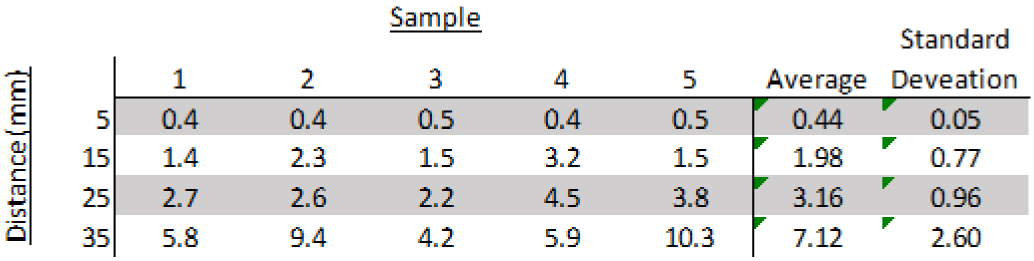


Figure 3-5: Conductivity test example



Distance (mm)	Sample						Standard
	1	2	3	4	5	Average	Deveation
5	0.4	0.4	0.5	0.4	0.5	0.44	0.05
15	1.4	2.3	1.5	3.2	1.5	1.98	0.77
25	2.7	2.6	2.2	4.5	3.8	3.16	0.96
35	5.8	9.4	4.2	5.9	10.3	7.12	2.60

Table 3-1: Conductivity test results in Ohms

Chapter 4: Wearable Electronics

At the time that this research was completed wearable electronics have become a new and trending topic in media. Wearables present many opportunities for research; the topics herein are a few examples of the opportunities AM is creating in the wearable industry.

With a style of device chosen, an application was necessary. Carbon Nanotubes presented the opportunity to research applications that can help those that help protect innocent civilians. When functionalized CNTs can detect a multitude of different compounds present in the air. Nitrogen Dioxide, or NO2 gas, is such a compound and is used in the process of producing rocket fuels and explosives. A wearable device for those that are responsible for checking for explosive devices at large events and at airport terminals is a topic that is not only unique but carries real-world applications.

4.1 Wearable Sensor Project

The following section will discuss the steps taken to realize a wearable device capable of detecting the presence of NO2 gas, and others if the correct functionalization process is used. The project was executed with the help of a team at YSU and completed based on the requirements of the Trust Project. The procedures of laying out a circuit for use in a 3D printed device (Section 4.2) and in a proof of concept PCB (Section 4.3), the functionalization of CNTs for the detection of NO2 gas (Section 4.4), the CAD design process of creating a wearable electronic device (Section 4.5), the software design for the monitoring of the CNTs (Section 4.6), the conductive inks used to create AM electronic devices (Section 4.7) and the testing completed to demonstrate the effectiveness of such a device (Section 4.8) will be discussed in the following sections.

4.2 Circuit Design

The circuit used to monitor the detection of NO2 gas, needs to monitor the resistance across the CNTs using a voltage divider circuit. A MSP430 microcontroller would be used to measure the voltage at the voltage divider reference point and create an alert signal when the presence of NO2 gas is detected. The alert signal in this case is a flashing LED.

A voltage divider provides a simple and reliable way to measure an unknown resistance of a device, using a known reference resistance. For this circuit the CNTs act as the unknown resistance and a 1,000 Ohm (1k Ohm) resistor is used as the known resistance. Generally, the known resistance should be a similar value to that of the unknown resistance being measured. After some testing, it was established that when functionalized the CNTs had a typical resistance in the 800-1.2k Ohm range. Making a 1k Ohm known resistance an optimal choice, because during the detection process the resistance across the CNTs falls to 600-800 Ohm.

The MSP430 Microcontroller, from Texas Instruments, serves as a low power, flexible MCU, capable of measuring the voltage at the reference point in the voltage divider and flashing the LED upon detection of NO2 gas. The MSP430 platform is easily programmed in C++ using the Code Composer Studio software, also provided by Texas Instruments. The microcontroller used was the MSP430G2452, which features a 16QFN package and 8kb of flash storage. The 16QFN surface mount package provides the ideal mixture of compact size and a pin pitch that is capable of being connected to through hand laid conductive ink traces. Figure 4-1 provides a circuit schematic to the layout of the circuit used in this project.

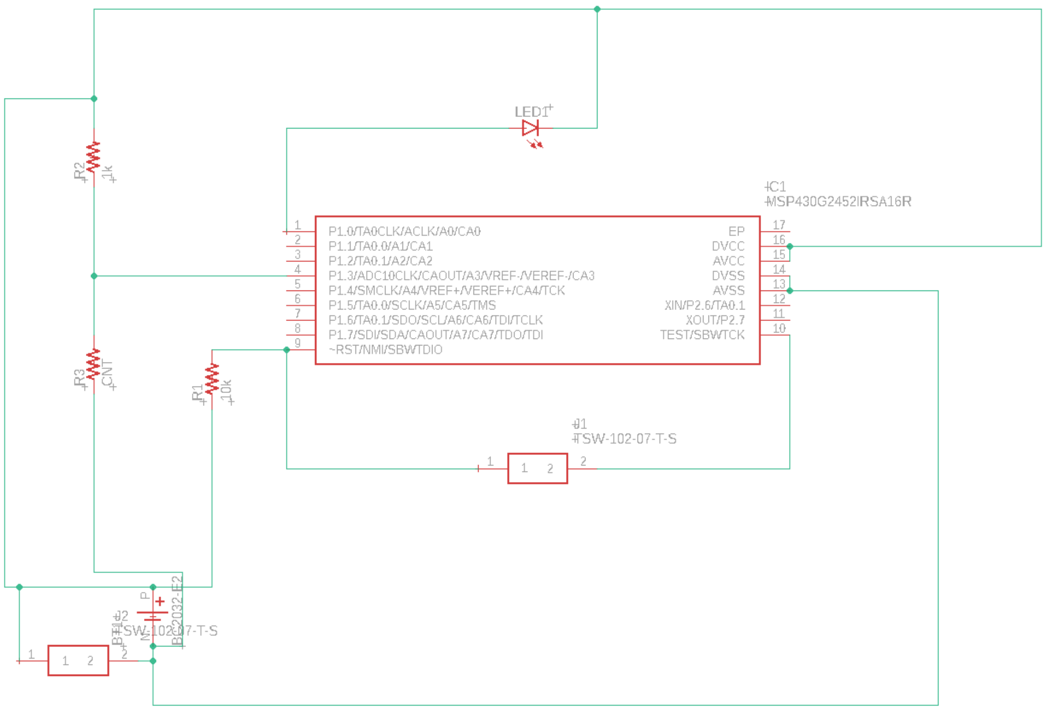


Figure 4-1: PCB circuit schematic

4.3 PCB Design

As a proof of concept, a PCB was designed, by a YSU team member, for the testing of the circuit and to assist with the calibration of the code used by the MSP430. For the design process AutoCAD Eagle was used to create the necessary Gerber files that were sent off for production.

The first step of creating the PCB design is laying out the circuit schematic in Eagle. Many components can be found in the libraries built into Eagle, but less common components like the MSP430 microcontroller must be created. The circuit schematic in Figure 4.1, outlines the circuit that will be used in the wearable explosive sensor. Note that a resistor is used to represent the CNTs in the circuit diagram.

With a circuit layout created, the PCB layout can be created. First the components must be placed in a way that both flows in terms of circuit layout and doesn't result in a large overall footprint. With components placed, the traces can be created. If the circuit is laid out in a manner that flows well this process is straight forward, but as the circuit complexity increases, this process can get difficult as many traces may require routing on different layers to create the proper interconnects. The final PCB design can be found in Figure 4-2.

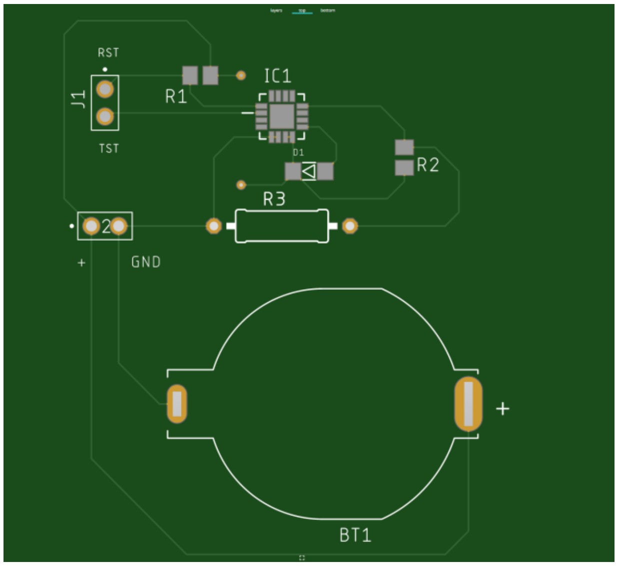


Figure 4-2: PCB Layout of CNT Sensor

4.4 CNT Testing

In order to write the code that will be used to measure the resistance, across the Carbon Nanotubes, multiple samples of the CNTs were created. These samples were measured to establish a base resistance, and then, using a voltage divider circuit, the resistance was measured and recorded while the CNT sensor was exposed to NO2 gas. With this data, an average baseline resistance and reaction curve could be created, Figure 4-3, illustrating what the code should look for when scanning for any changes in the resistance of the CNTs.

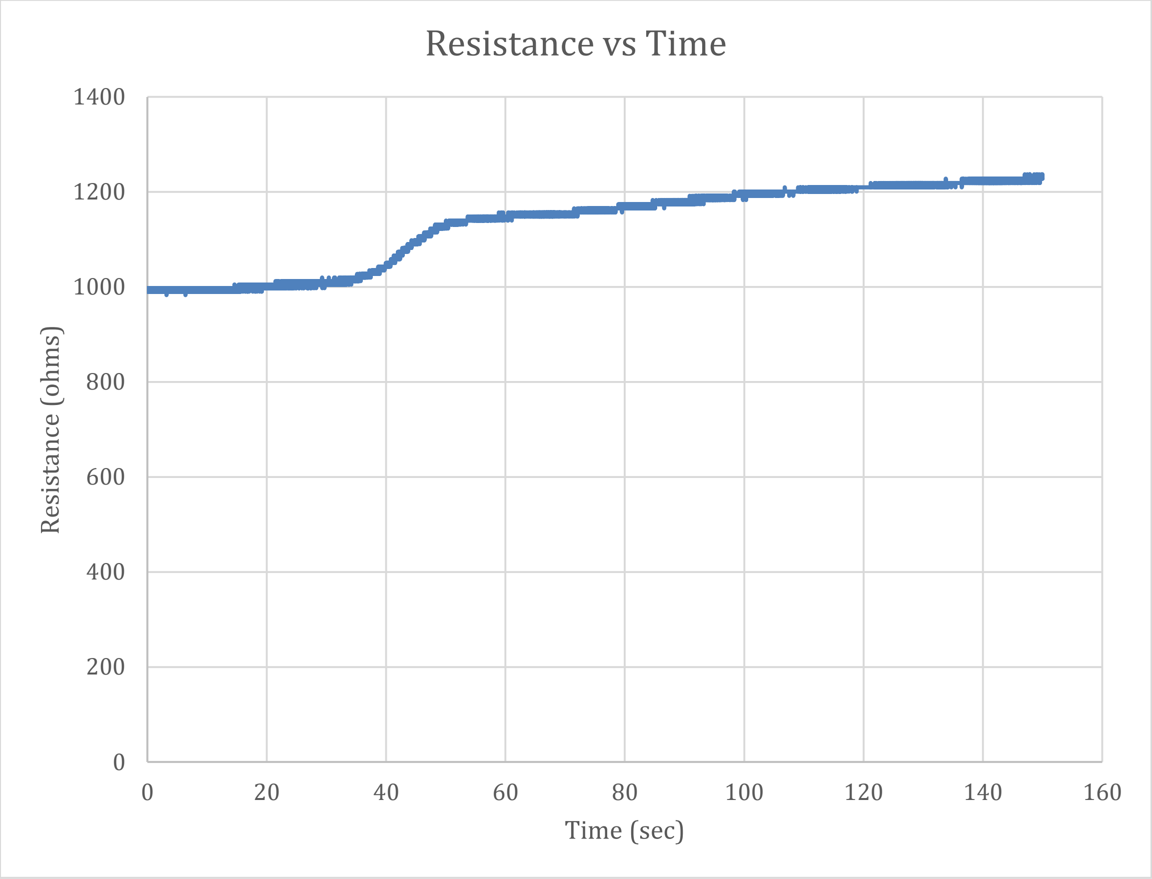


Figure 4-3: Resistance curve of CNTs during NO2 gas exposure

Once the code was written, further samples were created and connected to the PCB created in Section 4.3. An explanation of this code will follow in Section 4.5. The experiment involved, again, exposing the CNTs to NO2 gas and observing the LED. The LED would appear solid when no change was detected but as the concentration of NO2 gas increased, the detection of NO2 gas increased and the LED begins blinging. The blinking would transition from a fast rate to a much slower pace as the resistance changed further.

4.5 CAD Design

The CNT Sensor demonstrates the capabilities presented AM for the wearable electronic industry. The device herein showcases two possible use cases for AM in the wearable industry, rapid prototyping and mass customization. Two wearable designs are demonstrated, a clip-on device and a device worn as a bracelet. The possibilities don’t stop here, and different designs can be printed concurrently or consecutively without the need for tooling changes.

The design process begins with the creation of the basic shape of the device This shape will serve as a substrate for which the cuts and extrudes that will form the circuitry, will take place. This substrate takes the form of a cylinder with a diameter of 30mm and height of 6mm. This size provides the necessary space that the circuitry will need and is a similar size to a typical woman's watch or smartwatch.

With the basis of the device created, the placement of components can be explored. The circuit used in this device is rather simple, so software was not used to aid in the circuit layout process. Creating a sketch with all component’s cutouts on a single sketch, allows one to drag the components into position and experiment with circuit layout. This sketch will later contain the traces paths and serve as a template for making the extruded cuts that will contain the circuitry. Figure 4-4 illustrates this concept and includes the traces layouts discussed later in this section.

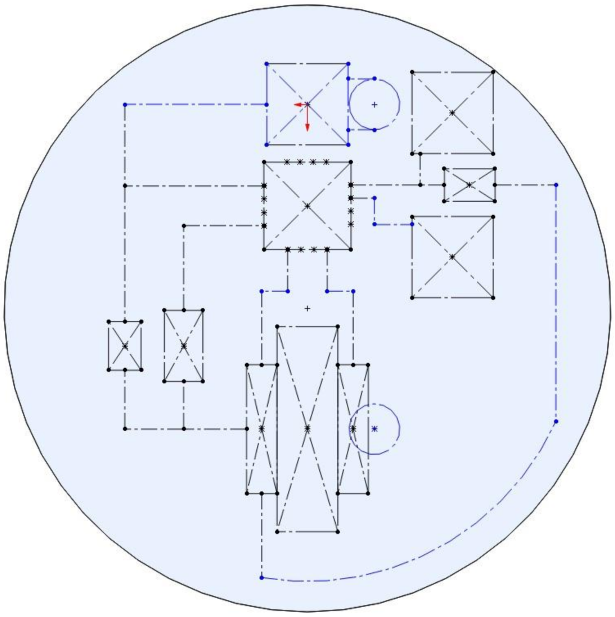


Figure 4-4: Component and circuitry layout

The microcontroller possesses the largest amount of connections, so the MSP430 was located at the center of the device, providing adequate room for circuitry placement. The battery was placed on the edge of the MSP430 that contains VCC and VSS, so the connections for power to the chip were as short as possible. After multiple design revisions, designs that limit the distance, between VCC and VSS to the battery, resulted in the best reliability of the device. This conclusion is likely due to the power losses in the silver ink traces. The TEST and RESET pins of the MSP430, also perform best when trace length is kept at a minimum. TEST and RESET are responsible for the programmability of the MSP430, so placement is quite flexible. The pull-up resistor attached to the RESET pin, is less of a concern due to the use of a 10k Ohm resistor, the extra resistance introduced by the silver ink traces stays below the 50k Ohm maximum.

The LED, used for indication of the CNT sensor status, was placed between the Pin P1.0 of the MSP430 and the positive terminal of the battery. Pin P1.4 was connected to the Vout position of the voltage divider circuit containing the CNT sensor and a 1k Ohm known resistance. The CNT sensor is then connected to ground and the 1k Ohm resistor to the positive battery terminal. A visual aid to this layout is provided in Figure 4-5.

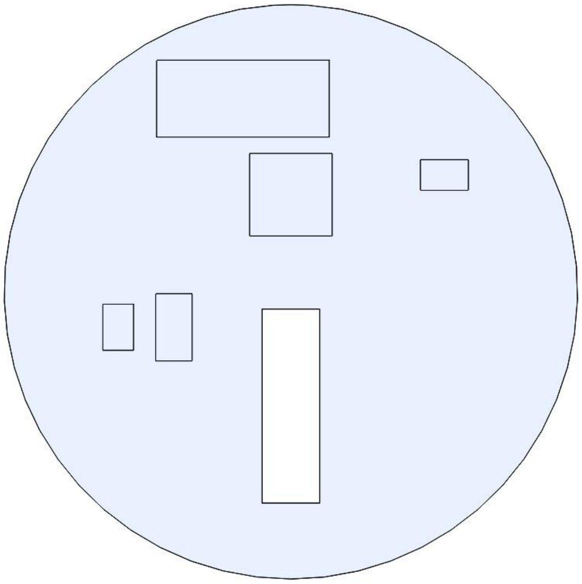


Figure 4-5: Component layout

With component placement finalized, the traces can be laid out. The use of construction lines in the same sketch, as the one used for component placement, can make the process easier, as many connections are made to the center of component, and many CAD software will snap to the middle of a line. Alternatively, placing sketch points in the locations of pins on a component, can simplify trace placement on more complex devices. Using the template sketch, described above, the trace paths can be laid out, such that traces lengths and points where two different traces cross are kept at a minimum. The result of trace placement is provided in Figure 4-6, note that the figure includes that cuts described in the following paragraph.

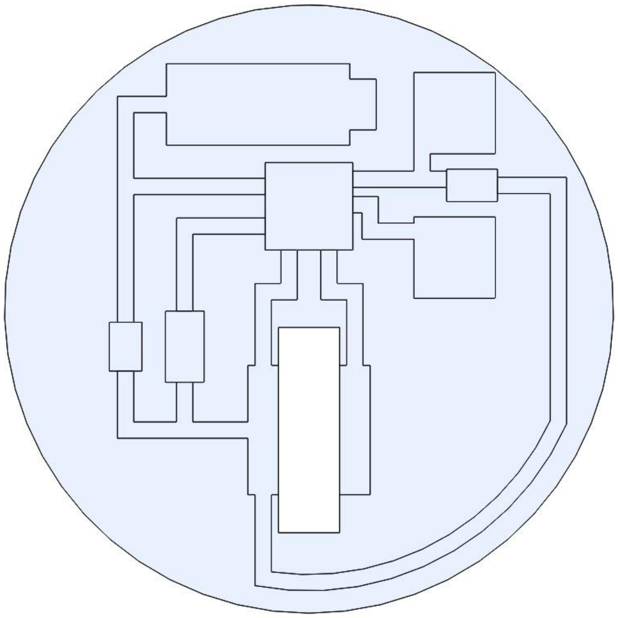


Figure 4-6: Trace layout

The next step, in the CAD design process, is making a cut where each component will be placed, the cut depth must place the contacts, of the component, at the same level as the sketch plane. Each component may have a different cut depth needed to properly seat the component, so this step can get repetitive. Traces are then cut using the Offset Entities tool, in Solidworks 2019. Offset entities allows the construction lines used previously to be defined with a width and capped ends, in either a square or circular pattern. Traces are cut to a total width of 0.8mm, or 0.4mm in both directions as defined by the offset entities tool, and a depth of 0.3mm. The Swept Cut feature in Solidworks 2019, is used to create what would be vias in a PCB, allowing traces to cross without a short being created. An example of a resulting via is presented in Figure 4-7.

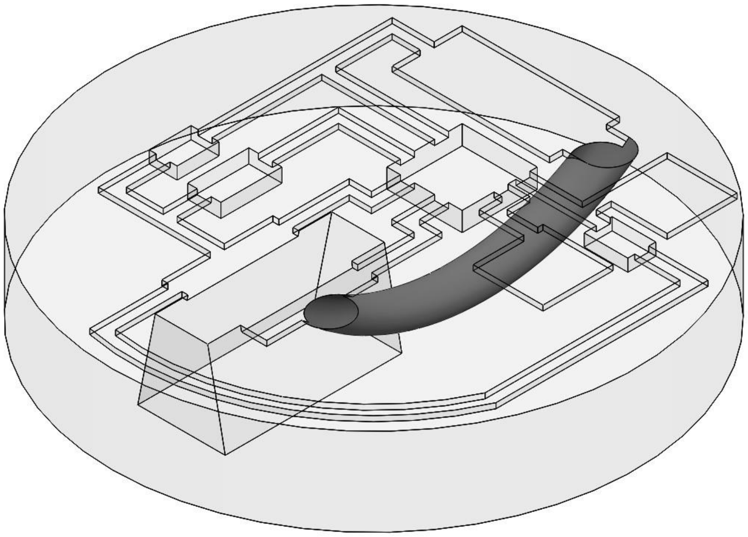


Figure 4-7: Via creation example

This concludes the design portion of the main body of the device. Auxiliary features such as a wristband, microfluidic cover, and shirt clip are designed using similar techniques described here, but the design process is withheld to prevent recurrent information. However, the final wristband design is presented in Figure 4-8.

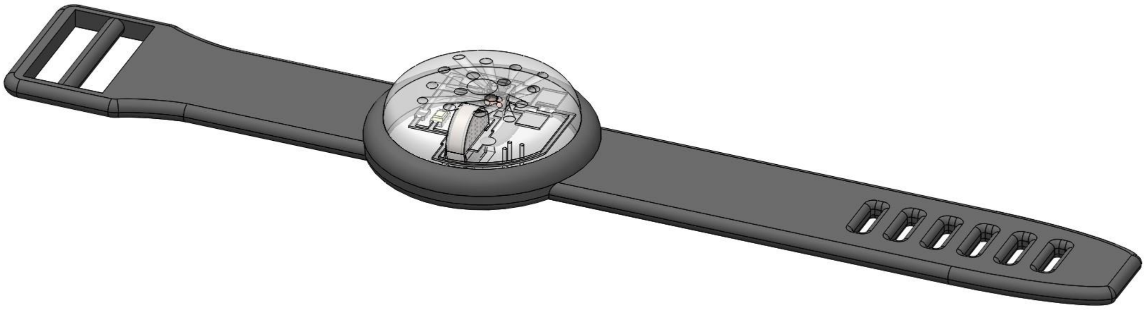


Figure 4-8: Wristband assembly

4.6 Software

The MSP430 microcontroller is available in many different configurations compatible with many sensing and measuring devices using integrated digital and analog peripherals. A MSP430 from the G2xx series was chosen for this project. The G2xx series provides the necessary I/O needed for controlling an LED and measuring the resistance of the CNTs.

The code used to create the explosives sensor was created. The first revision of the code, created by a fellow YSU team member, measured the voltage at the reference point of the voltage divider created with the CNTs and 1k resistor. This voltage is converted from an analog voltage to a digital value using the ADC (Analog to Digital Converter) function of the MSP430. The analog voltage ranging from 0-3.3V is converted to a binary 10 bit number ranging from 0-1023, where 0b0 is 0V and 0b1111111111 (1023 in base 10) is 3.3V. Due to the CNTs initial resistance being approximately 1k Ohms and the reference resistor of the voltage divider also being 1k Ohms, the voltage the MSP430 would measure when no NO2 is present is 1.65V or 0b0111111111. When N02 is present, the resistance of the CNTs will drop by at least 100 Ohms, on average. The code looks for this drop, which equates to nearly a .1V drop in voltage. When the voltage goes below 1.56V the LED begins blinking.

The first revision of the code was limited due to the assumption that the CNTs would always be 1k Ohms, but this was not the case, as the CNTs have a typical variance of 200 Ohms. This made the code unreliable during testing. A revision was made that measures the resistance of the CNTs when the MSP430 is powered up and stores this value as the initial resistance of the CNTs rather than assuming that the CNTs would always be 1k Ohms. After the initial reading is stored, the code checks for a change of 100 Ohms, or more, in the CNTs. Once this change is measured the LED will begin blinking. The rate that LED blinks is tied to the difference between the initial resistance and current, as the difference increases the delay between blinks increases.

4.7 Conductive Ink Traces

The traces of the circuit were created using a conductive coating, by MG Chemicals, called 842AR - Super Shield. This coating is like an acrylic paint and uses silver particles to create conductivity. During the design and build process, trenches were created in the positions that traces would be present, these trenches are used both as a guide for the applications process and to protect the traces during handling. The application process is done using a fine tip paint brush, with a small amount of 842AR at the tip of the brush, the coating in the applied to the tranches. A steady hand and precision are required during this process, as bridging between the contacts of a component can be difficult to remove.

Once a first application of conductive coating is applied to the tranches, the coating is given time to cure. At room temperature, 15 minutes is ample time before proceeding to the next step. The next step involves wet sanding the top layer of the circuit, this step removes any excess coating that is applied to the device face. A comparison of the result of wet sanding the top layer of the circuit is provided in Figure 4-9. With the top layer of the circuit sanded, the traces can be inspected for any cracks or voids, if any are present, touch-ups are made with the fine tipped paintbrush. The part is then left to cure at room temperature for 24 hours, this allows the coating to reach a fully cured state, where the conductivity is best. Finally, the circuit can be tested, if any problems arise, the circuit must be checked again both visually and with a multimeter for conductivity to identify problem areas. Further touch-ups and corrections may be needed to address problem areas. Once the circuit is tested for proper operation, final assembly can commence.

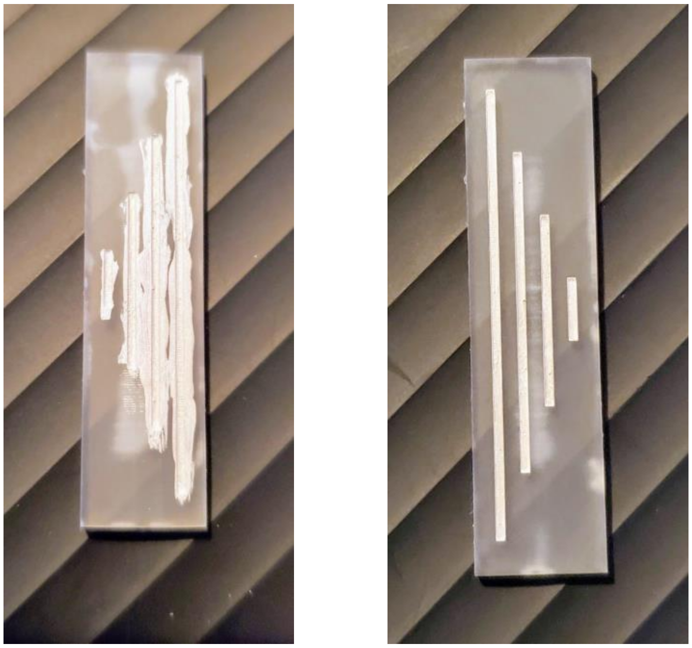


Figure 4-9: First coat of conductive coating before and after wet sanding

4.8 Over-Molding

The term Over-Molding has been coined to describe the process of assembling AM components, printed using SLA technology, by which the faces of the components are adhered using resin from which the components are printed. For this project, Over-Molding is used to combine the Explosive Sensor with the bracelet and microfluidic cover.

The process for Over-Molding process allows devices to be designed in multiple sections and circuitry or electronic devices placed in the mating faces of the device. Additionally, Over-Molding allows components made with different resins to bond, creating devices that are both rigid and flexible. The Explosive Sensor in this project is

Over-Molded to both the wrist band and microfluidics cover. The process involves placing a small amount of resin on the mating surfaces of the components, RS-F2-GPCL-04 Clear resin is used for the bonding described herein. With both surfaces prepared, the components are matted and placed in the Form Cure oven, that is used to cure the Formlabs parts. The device is left to cure at 60C for 30 minutes, but the temperature and duration vary based on the resin used for the Over-Molding process. Temperature and duration of the cure process are chosen to match those described in the "Form Cure time and temperature settings" page of the Formlabs website. A test sample, of the Over-Molding process, is presented in Figure 4-10

Figure 4-10: Over-Molding Example

4.9 Final Testing for the Explosive Sensor

Final testing of the Explosive Sensor is conducted by exposing the device to NO2 gas in a controlled environment and observing the behavior of the device. In the testing, when a reaction is created, generating Nitrogen Dioxide, the device should begin blinking. The reaction takes a few seconds to complete so a gradual shift from a fast pace blinking, with an interval of 0.1 second to a much slower blink, with an interval of 1.0 second, should occur.

The setup for testing involves placing a 50mm by 100mm sheet of copper in the bottom of a large container. A 50ml beaker turned upside-down as a pedestal for which the Explosive Sensor is placed, so the NO2 gas, produced by the copper, flows over the CNT sensor. To begin the test, the Explosive Sensor is turned on and a 20 uL drop of Nitric Acid is placed on the copper sheet. Figure 4-11 explains the reaction between copper and Nitric Acid producing Nitrogen Dioxide A lid is placed on the large container, to prevent the air flow of the fume hood from affecting the dispersion of the NO2 gas.

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

Figure 4-11: Reaction to produce NO2 gas

Testing done prior to this thesis has resulted in the sensor going directly from an untriggered state, where the LED is steady and not flashing, to a saturated state, with the LED blinking once every second. The testing demonstrates that the device behaves as expected, but it is believed that the amount of gas generated for testing is too large. If the amount of Nitric Acid used is reduced, the amount of gas and rate the gas is produced can be reduced. With a reduced reaction, the detection will occur at a slower rate and the transition from fast to slow, regarding the LED’s flashing rate, will occur more gradually.

Chapter 5: Conclusions and Future Work

5.1 Conclusions

Additive Manufacturing innovation is increasing at an exponential rate, especially in the field of electronic devices embedded in AM substrates. The device created in this thesis outlines the successful creation of an electronic device built using SLA technology. The methods and design practices described resulted in a device capable of being worn for the purpose of sensing NO2 gas.

Initial testing has shown that these sensors can detect NO2 gas. The design freedoms AM creates makes transferring the design described into many form factors to satisfy the needs of any possible scenario. Also, CNTs can be functionalized to detect a wide range of airborne substances.

5.2 Future Work

The wearable described herein will be fully built in December of this year (2019). At which point the functionality of the device can be evaluated. Revisions to the latching mechanism on the bracelet may be needed for proper functionality. The Microfluidics cover for the circuit has yet to be tested and revisions or further post processing may be needed to get the NO2 gas to properly reach the CNT sensor.

Testing of the Explosive Sensor with varying levels of NO2 gas will show at what level the sensor begins to detect NO2 gas. The testing described in Section 4.9, demonstrates a sharp transition from an undetectable amount of Nitrogen Dioxide to an amount that saturates the devices ability to display a detection level. Additionally, further tuning to the code may be needed to maximize the different levels of detection the device can display.

The CNTs have functioned well for NO2 testing thus far, but the detections of other chemicals are possible and may require minor modifications to the circuit, in terms of the voltage divider, if the new functionalized CNTs do not have a 1k Ohm resistance.

In addition to the detection of other gases, the ability to create other form factors of the device is a limitless pursuit. As an example, a sphere possessing the circuitry described in this thesis, but including an audible alert system in addition to the visual alert the LED creates, presents the opportunity to create a device that can be deployed into a room prior to entry to check for harmful chemicals.

Early testing has shown that the CNTs possess capacitance when exposed to NO2 gas. Further testing is currently (as of November 2019) being conducted to explore the data that measuring the capacitance of the CNTs may provide. The method for detecting conductance through the CNTs is currently done using a sine wave and comparing the wave before and after the CNTs to look for a phase shift and reduction in the peak to peak voltage. Measuring the phase shift and peak to peak voltage will show both the real and imaginary components of the impedance of the CNT sensor.

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