Development of a CTD system for environmental measurements using novel PCB MEMS fabrication techniques

Heather Allison Broadbent
University of South Florida

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Development of a CTD System for Environmental Measurements Using Novel PCB MEMS Fabrication Techniques

by

Heather Allison Broadbent

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science
College of Marine Science
University of South Florida

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Eric T. Steimle, Ph.D.

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Keywords: microsensors, salinity, conductivity, temperature, liquid crystal polymer, microfabrication

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To my father

for always being there
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Development of a CTD System for Environmental Measurements Using Novel PCB MEMS Fabrication Techniques

Heather Allison Broadbent

ABSTRACT

The development of environmental continuous monitoring of physicochemical parameters via portable small and inexpensive instrumentation is an active field of research as it presents distinct challenges. The development of a PCB MEMS-based inexpensive CTD system intended for the measurement of environmental parameters in natural waters, is presented in this work. Novel PCB MEMS fabrication techniques have also been developed to construct the conductivity and temperature transducers. The design and fabrication processes are based on PCB MEMS technology that combines Cu-clad liquid crystal polymer (LCP) thin-film material with a direct write photolithography tool, chemical etching and metallization of layers of electroless nickel, gold, and platinum. The basic principles of a planar four-electrode conductivity cell and the resistive temperature device are described here as well as the integration and the packaging of the microfabricated sensors for the underwater environment. Measurement results and successful field evaluation data show that the performance of the LCP thin-film microsensors can compete with that of conventional in-situ instruments.
CHAPTER I

INTRODUCTION

Background on CTD Instruments

Salinity is one of the primary measurements to be determined by oceanographers when analyzing a sample of seawater. By determining salinity, researchers can calculate numerous other important properties of seawater, such as density, conservative element concentrations, and solubility of gases (Pilson, 1998). Also, salinity affects functional and structural properties of organisms through changes in total osmotic concentration, relative proportions of solutes, coefficients of absorption and saturation of dissolved gases, density and viscosity (Kinne, 1964). Salinity measurements provide relevant information to all fundamental fields of oceanography including chemical, biological, physical and geological. For instance, in the biological arena, salinity has been correlated to the upstream distribution of species within estuaries (Wells, 1961). Also, salinity data have provided geologists with information about carbonate building organisms (Heckel, 1974). Since the 1960’s, oceanographers have determined salinity based on comparative measurements of electrical conductivity with instruments called salinometers in place of the earlier titrimetric determination of chlorinity (Farland, 1975). In the early 1970’s, these instruments evolved into reliable, accurate, field-deployable devices due to the advancement of microprocessor technology. They are currently able to measure
conductivity ratios with an accuracy of +/- 0.001 Siemens (Pilson, 1998). Because these
in-situ instruments not only measure conductivity, but also temperature and depth, they
are now referred to as CTD instruments. The three in-situ measurements are used in an
algorithm to calculate salinity based upon the Practical Salinity Scale 1978 (PSS 1978)
(Lewis, 1980). Many different CTD models are commercially available that range in size
and cost (Table 1).

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Conductivity Range [mS/cm]</th>
<th>Conductivity Accuracy [mS/cm]</th>
<th>Temperature Range [°C]</th>
<th>Temperature Accuracy [°C]</th>
<th>Size [Inches]</th>
<th>Cost [+]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Falmouth</td>
<td>0-70</td>
<td>+/- 0.005</td>
<td>-5 to 36</td>
<td>+/- 0.002</td>
<td>12 x 2</td>
<td>10,000+</td>
</tr>
<tr>
<td>Applied Microsystems</td>
<td>0-70</td>
<td>0.005</td>
<td>-2 to 32</td>
<td>+/- 0.002</td>
<td>20 x 2</td>
<td>6,900+</td>
</tr>
<tr>
<td>Ocean Sensors</td>
<td>0.5-65</td>
<td>0.02 (FS)</td>
<td>-2 to 32</td>
<td>0.01</td>
<td>28 x 2.5</td>
<td>7,000+</td>
</tr>
<tr>
<td>Sea-Bird</td>
<td>0-90</td>
<td>0.003</td>
<td>-5 to 35+</td>
<td>0.002</td>
<td>25 x 2.5</td>
<td>8,000+</td>
</tr>
<tr>
<td>InterOcean Systems</td>
<td>0.5-60</td>
<td>+/- 0.05</td>
<td>-5 to 45+</td>
<td>+/- 0.02</td>
<td>7 x 5</td>
<td>8,500+</td>
</tr>
<tr>
<td>RBR</td>
<td>0-70</td>
<td>+/- 0.003</td>
<td>-5 to 35</td>
<td>+/- 0.002</td>
<td>16 x 2.5</td>
<td>4,000+</td>
</tr>
</tbody>
</table>

Conductivity, temperature and depth measurements can be acquired using several
types of sensors or transducers. Inductive-style conductivity sensors usually consist of
two high-grade toroids or coils which are incorporated concentrically and adjacent to
each other. The coils form a current transformer. As the conductive liquid media flows
past the toroids, it forms a closed conductive field path. When voltage is applied to the primary coil it causes a current flow that is proportional to the conductivity of the sample medium. Another type of conductivity sensor is the electrode cell, which is typically constructed of platinum metal rings or bars with a known cell constant. When they are immersed within a conductive liquid medium and a known voltage is applied, the conductivity of the fluid is proportional to the measured current across the two electrodes. Inductive sensors have an advantage over those with electrodes, as electrodes are adversely affected by polarization and fouling (Dauphinee, 1981), although an appropriate surface conditioning treatment has been shown to improve the polarization characteristics of planar electrode cells (Jacobs et al., 1990).

Resistive temperature devices (RTD) are metallic sensors (platinum or copper) in which the metal’s resistance increases with increasing temperature in a known and repeatable manner. A thermocouple consists of two dissimilar metal wires welded together into a sensing junction with a reference junction at the other end of the signal wires. A thermoelectric potential proportional to the temperature difference between the two junctions is generated when the sensing junction is heated. This potential indicates the temperature at the sensing junction, when compensation is made for the known temperature of the reference junction. Of the two, RTD sensors have the advantage in environmental monitoring due to fact that they produce the best linearity and are extremely stable, whereas thermocouples are best suited for extreme conditions of high temperatures.

Depth is calculated from pressure, water compressibility, and latitude. The piezoelectric pressure sensor is one type of transducer used in oceanographic CTD
instruments. The sensor consists of a pressure-sensing diaphragm that transduces the force to a stack of discs made of piezoelectric ceramics or crystalline quartz. The electrical charges produced are proportional to the pressure. Another pressure sensor used to measure depth is the strain gauge. The strain gauge consists of a metal foil pattern that is distorted when force is applied, resulting in a change in the resistance. Piezoelectric pressure sensors have the advantage of inherent static accuracy and offer excellent long-term stability, whereas the strain gauge is moderately accurate and long-term stability is an issue (Matthews, 2005).

A major trend in CTD development is miniaturization, which not only impacts the instrument’s size and weight, but also its cost (Brown, 1991). Miniaturization of electrical components, microprocessors and memory chips by technological advances in microfabrication techniques and materials enables the development of very small oceanographic CTD systems capable of continuous monitoring that are rapid, reliable and cost effective (Madou, 1997). Miniaturization of the CTD will impact the oceanographic community greatly by (1) increasing the range of applications by allowing in situ measurements of dynamic physical, chemical, and biological properties over varying temporal and spatial scales, and (2) reducing the cost per unit thus allowing greater accessibility to researchers. Woods Hole Oceanographic Institute (WHOI) and ocean instrument manufacturer, Falmouth Scientific Instruments (Cataumet, MA.), have collaborated to develop very small (12 inches x 2 inches), low cost ($10,000), deployable CTD systems (Figure 1). Applied Microsystems (Sidney, BC, Canada) has introduced a Micro CTD instrument for measuring salinity, which is 20 inches long by 2 inches wide (Figure 2).
Figure 1. Excell 2” Micro CTD, Falmouth Scientific, Inc

Figure 2. Micro CTD, Applied Microsystems LTD
Other CTD research has focused on high performance coupled with low power for long-term deployment applications (Brown, 1994). CTD research has also been conducted on instruments that are capable of long-term deployments in biologically active ocean regions (Fougere, 2000). Some research has been conducted to develop a microcomputer-controlled, expendable CTD profiler that is launched from aircraft (Downing et al., 1992).

A miniature, low cost CTD provides scientists with a powerful analytical instrument that can be integrated into many types of research systems. For example, this sensor system can be coupled with autonomous underwater vehicles (AUV), remotely operated vehicles (ROV), interconnected arrays that concurrently collect data profiles, or tracking salinity profiles of marine organisms of all sizes.
Traditional Microfabrication Techniques

Sensors and microsystems, such as those used by CTD instruments are created by microfabrication techniques. Traditional microfabrication starts with photolithography, which is the technique used to transfer copies of a master pattern onto the surface of a substrate material. A photomask of the desired pattern is generated using either film acetate and emulsion or optically flat glass with a metal (e.g., chromium) absorber pattern. The absorber pattern on the photomask blocks ultraviolet light, whereas the film acetate or glass is transparent to UV. The photomask is placed directly on the photoresist coated substrate, and is exposed to ultraviolet radiation using a UV light box, thus creating a 1:1 image of the pattern. Since these masks make physical contact with the substrate, they have the tendency to degrade over time due to wear. This degradation limits the lifespan of the mask (Madou, 1997). [A light field or dark field image can be generated on the photomask that is dependent upon the type of photoresist is used for pattern transfer.] The photoresist is a polymer that changes structure when exposed to radiation. It is applied to the surface of the substrate either by spinning or lamination. There are two types of photoresists, positive and negative. Positive photoresists have polymer chains that become weakened when exposed to UV radiation, thus causing the resist to become more soluble in developing solutions. Negative photoresists are strengthened by cross-linkage caused by UV exposure, thus becoming less soluble. Several factors dictate which type of resist to use, such as pattern feature size, photospeed, adhesion to substrate, thermal stability, and wet chemical resistance (Madou, 1997). Once the pattern has been transferred onto the surface of the substrate via photomask and UV radiation, a developer is used to create a relief image in the
photoresist. This relief image serves as a mask during other additive and subtractive processes such as etching and metallization.

Traditional microfabrication of sensors and devices uses silicon wafers as a substrate (Sheats and Smith, 1998). The silicon wafer has the ability to conduct electricity in a very controlled manner, making it an ideal substrate for the construction of most advanced semiconductor devices.
Motivation and Scope of Thesis

The motivation of this work was to develop a miniature, low cost CTD system using novel PCB MEMS fabrication techniques combined with liquid crystal polymer (LCP) material that measures salinity in natural waters. By using a novel photolithography technology developed at COT, combined with LCP material, it is possible to rapidly produce expendable conductivity and temperature microsensor prototypes that can be easily reconfigured for extensive experimentation, thus allowing quick development and mass quantity fabrication of ocean sensors (Fries et al., 2002).

The main scope of this work addresses two important milestones in conductivity and temperature sensors. The first milestone was construction of LCP-based conductivity and temperature sensors using novel PCB MEMS fabrication techniques without an expensive cleanroom environment. The second was miniaturization of the sensors. Small sensor size increases the range of applications from open-ocean profiling to monitoring microscale processes. The combination of these factors ultimately lead to the production of low-cost sensors, thereby allowing greater accessibility to the scientific, academic, public and private communities. These milestones led to the design of a planar thin-film four-electrode conductivity cell and a thin-film copper resistive temperature device.

Once the two microsensors were fabricated and tested in the laboratory, they were then combined with a commercially available piezoresistive pressure sensor to produce the entire CTD system. Along with the development and fabrication of the sensors, the integration and packaging of the CTD system in a watertight housing for the marine environment was investigated and developed in this work. Once the CTD system was
packaged, the sensors were calibrated, and field-tests were performed. Field deployment of the completed CTD system was performed in Bayboro Harbor, St. Petersburg, Florida.

Oceanographic researchers are exploring various new tools, such as instrumented animals, in order to study the physical, chemical and biological structure of the oceans, (Boehlert et al., 2001). Salinity measurements acquired from these autonomous environmental samplers (pinnipeds, cetaceans, fishes) is of interest to oceanographers investigating density structure and mixed layer depth (Freeland et al., 1997). However, limitations in the size and cost of CTD instruments have prohibited the extensive collection of salinity data by this method (Hooker and Boyd, 2003). The development of small, expendable, inexpensive CTD systems would be beneficial in the collection of salinity data sampled using autonomous biological vehicles, thus providing scientists with an additional data source.
CHAPTER II
DEVELOPMENT OF NOVEL MICROFABRICATION
TECHNIQUES

Maskless Photolithographic Patterning Tool

As stated previously, traditional microfabrication techniques involve photomasks generated from film acetate or glass with an absorber pattern. These photomasks have limited usage duration due to damage that results from physical contact with the substrate and operator. The pattern on the mask has a tendency to become scratched and therefore no longer viable for the application. The Center for Ocean Technology Systems Group developed a tool that replaces the physical photomask with a projected UV photomask (Figure 3). This tool (SF-100), has been licensed by Intelligent Micro Patterning LLC, St. Petersburg, Florida.

The maskless photolithographic patterning tool technology utilizes reflective micro optics in combination with mixing and imaging lenses to allow direct circuit image projection onto a substrate surface. In this technique, reflective microoptoelectromechanical (MOEM) elements are used to spatially modulate light such that light can be controlled on the several micron-sized regime, simultaneously over a 13 mm x 10 mm sized field of view. The desired pattern is designed and stored using conventional computer-aided drawing tools and is used to control the positioning of the
individual elements in the spatial light modulator to reflect the corresponding desired pattern.

In addition, an automated stage with 6-inch by 6-inch travel has been incorporated with the system to allow for stitching of larger patterns on a substrate, while maintaining small feature size. The stage is capable of movement in the X, Y, Z and theta directions with a stepping resolution of 1 µm. The stage is controlled with software that accepts bitmap images and breaks them into 1024 x 768 pixel size images for exposure. The software exposes the first frame and then moves the stage into the correct location for the
next exposure of the pattern. The tool’s shutter is also controlled by the stage software and once programmed the stage will automatically expose the entire pattern, thus allowing the user to do other tasks.

This patterning tool, by eliminating the use of traditional contact photomasks, provides distinct photolithographic advantages over conventional methods. Once the pattern has been designed using the desired software, it can be changed and manipulated in much less time than required to generate a traditional photomask. Pattern changes can be performed from seconds to minutes. This allows for rapid generation of numerous prototypes. Traditional photomasks must be filed and stored in a clean, temperature and humidity controlled environment. The patterns generated for the maskless tool are electronically stored in a memory file on a computer, thus eliminating mask contamination and the need for proper storage space. The maskless photolithographic tool eliminates the need for photomask generating tools such as cameras, printers and harsh chemicals, along with the separate UV exposure unit. Low cost microsensors and microsystems can be fabricated rapidly by using the novel maskless photolithographic tool.
Liquid Crystal Polymer Material

Liquid crystal polymer (LCP) is a thermoplastic dielectric material developed specifically for single layer and multilayer substrate constructions with unique structural and physical properties. The polymer contains rigid and flexible monomers that link together. Once in the liquid state, the rigid monomers align next to each other in the direction of shear flow. When this orientation is formed, the structural alignment of monomers persists, even after the LCP has cooled below melting temperature (Jayaraj and Farrell, 1998). As a result of this unique structure, LCP exhibits a combination of electrical, thermal, mechanical and chemical properties that other polymers do not. LCP material is characterized by low and stable dielectric constant and dielectric loss (0.004). LCP has good dimensional stability and low modulus, allowing it to bend easily for flex and contour applications. LCP has extremely low moisture absorption (0.04%) and low moisture permeability, which allows the material to maintain stable electrical, mechanical and dimensional properties in humid environments. LCP has very high chemical resistance and is unaffected by most acids, bases and solvents (Culbertson, 1995). The combination of these physical properties make LCP material well suited for underwater sensor applications (Table 2).

LCP material is commercially supplied in a predefined thickness ranging from 25 µm to 3 mm. The material may have an 18 µm thick copper cladding layer laminated to one or both sides. In this work, 200 µm thick (8 mil), double-copper clad LCP material was supplied by Rogers Corporation, AZ.
**Lamination**

The fabrication of PCB MEMS devices and sensors can be achieved with LCP material. A lamination process has been developed that allows the LCP to be thermally bonded to MEMS materials. With the correct applied temperature and pressure, the material will flow and bond to another layer of LCP as well as to other materials such as glass, copper, gold or silicon (Wang et al., 2003). This lamination process allows thicker (0.008 inch) LCP material to be produced, which can be used to fabricate more rigid layers or microsensors. It also allows the fabrication of complex multi-layer, three-dimensional structures.

**Etching**

Even though LCP is highly chemical resistant, it is possible to chemically attack and dissolve the material. By using a strongly alkaline, caustic solution (KOH @ 90 °C), LCP can be surfaced etched or completely dissolved. When this process is combined with PCB MEMS techniques, it is possible to fabricate microfluidic channel devices and metallized microsensors. LCP material has been surfaced etched using a reactive ion etching (RIE) process. This process utilizes an oxygen plasma RIE machine that increases the surface roughness of the LCP material (Wang et al., 2003).

**Metallization**

LCP material can be metallized using several different processes such as lamination, resistive evaporation and electrodeposition. Generally, the LCP material is clad with 18 µm thick copper. This copper layer is laminated to one or both sides of the
LCP material using a vacuum press at a temperature around the melting point of the polymer material (Jayaraj and Farrell, 1998). Wang et al. (2003) has evaporated aluminum onto LCP to serve as an etch mask. In this work, an electrodeposition process that produces additive metal structures (nickel) above the LCP surface is discussed. This process, commonly used for printed circuit board material such as FR4 (fiberglass), allows the deposition of a large number of metals, such as Au, Ag, Cu, Ni, Pt, Pd… etc, to be electroplated to the surface of the material once a Pd seed layer has been catalytically deposited (Kovacs, 1998).
Table 2. LCP physical properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
<th>Test Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanical Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimensional Stability MD</td>
<td>0.01</td>
<td>0.06</td>
<td>%</td>
</tr>
<tr>
<td>CMD</td>
<td>-0.05</td>
<td>-0.03</td>
<td></td>
</tr>
<tr>
<td>Peel Strength</td>
<td>0.95 (5.2)</td>
<td>0.95 (5.2)</td>
<td>N/mm (lbs/in)</td>
</tr>
<tr>
<td>Initiation Tear Strength, min</td>
<td>1.4 (3.1)</td>
<td>1.4 (3.1)</td>
<td>Kg (lbs)</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>120 (17.5)</td>
<td>200 (29)</td>
<td>MPa (Kpsi)</td>
</tr>
<tr>
<td>Tensile Modulus</td>
<td>2400 (350)</td>
<td>2255 (327)</td>
<td>MPa (Kpsi)</td>
</tr>
<tr>
<td>Density</td>
<td>1.4</td>
<td>1.4</td>
<td>gm/cm³, Typical</td>
</tr>
<tr>
<td><strong>Thermal Properties</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTE (30°C to 150°C)</td>
<td>17</td>
<td>17</td>
<td>ppm/°C</td>
</tr>
<tr>
<td>X</td>
<td>17</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>150</td>
<td>150</td>
<td></td>
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<tr>
<td>Solder Float, Method B (288°C)</td>
<td>Pass</td>
<td>Pass</td>
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<tr>
<td>Melting Temperature</td>
<td>290</td>
<td>315</td>
<td>°C (Typical)</td>
</tr>
<tr>
<td>Relative Thermal Index - RTI</td>
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<td></td>
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<tr>
<td>mechanical</td>
<td>190</td>
<td>190</td>
<td>°C</td>
</tr>
<tr>
<td>electrical</td>
<td>240</td>
<td>240</td>
<td>°C</td>
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<tr>
<td>Thermal Conductivity</td>
<td>0.5</td>
<td>0.5</td>
<td>W/m/°K (Typical)</td>
</tr>
<tr>
<td>Thermal Coefficient of ε, -50°C to 150°C</td>
<td>(+) 24</td>
<td>(+)24</td>
<td>ppm/°C (Typical)</td>
</tr>
<tr>
<td><strong>Electrical Properties</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Dielectric Constant, 10 GHz, 23°C</td>
<td>2.9</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>Dissipation Factor, 10 GHz, 23°C</td>
<td>0.002</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Surface Resistivity</td>
<td>1 x10⁶</td>
<td>1 x10⁶</td>
<td>Mohm</td>
</tr>
<tr>
<td>Volume Resistivity</td>
<td>1 x10³²</td>
<td>1 x10³²</td>
<td>Mohm-cm</td>
</tr>
<tr>
<td>Dielectric Breakdown Strength</td>
<td>1378 (3500)</td>
<td>1378 (3500)</td>
<td>KV/cm (V/μl)</td>
</tr>
<tr>
<td><strong>Environmental Properties</strong></td>
<td></td>
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<tr>
<td>Chemical Resistance</td>
<td>98.7</td>
<td>98.7</td>
<td>%</td>
</tr>
<tr>
<td>Water Absorption (23°C, 24 hrs)</td>
<td>0.04</td>
<td>0.04</td>
<td>%</td>
</tr>
<tr>
<td>Coefficient of Hygroscopic Expansion, CHE (60°C)</td>
<td>4</td>
<td>4</td>
<td>ppm%/RH</td>
</tr>
<tr>
<td>Flammability</td>
<td>VTM-0</td>
<td>VTM-0</td>
<td>UL-94</td>
</tr>
</tbody>
</table>

Table courtesy of Rogers Corporation, www.rogerscorporation.com
Novel PCB MEMS Fabrication Techniques

In recent years, there has been considerable interest in the development of microelectromechanical systems (MEMS) fabricated with printed circuit board processing techniques (Ramadoss et al., 2003). The advantages of the PCB MEMS based approach include low cost, suitability for batch fabrication, ease of integration with electronics, and high volume manufacturing (Palasagaram et al., 2005). The use of liquid crystal polymer has emerged recently as a suitable substrate for MEMS, replacing silicon. LCP’s low cost, flexible fabrication and packaging techniques, and physical and chemical properties, not available in silicon materials, allow large arrays of conductivity and temperature sensors to be fabricated using roll-to-roll flexible printed circuit processing systems for large area applications (Wang et al., 2003).

In the past, planar conductivity sensors have been fabricated using alumina or quartz glass substrates. Farrugia and Fraser (1984) have used a multi-layer screening technique for fabrication of a conductivity cell using alumina. Norlin et al. (1998) used micromachining and MEMS techniques for fabrication of planar Pt conductivity electrodes and Pt thermistors using quartz glass wafer. In this work, novel LCP material is combined with the maskless photolithographic tool to fabricate PCB MEMS-based conductivity and temperature sensors.

Figure 4 illustrates the novel PCB MEMS process used to fabricate the two oceanographic sensors. The process steps include photoresist application, maskless pattern exposure, pattern development, and etching of copper and/or LCP material. This process allows the construction of the desired architectures used to fabricate sensors such
as through holes and blind vias. This novel microfabrication technique (figure 4) allows for the rapid construction of a cost effective miniature CTD system.

Figure 4. PCB MEMS process using LCP
CHAPTER III
SENSOR DEVELOPMENT AND SYSTEM INTEGRATION

Conductivity Cell

Design

The conductivity sensor design was a planar, thin film, four-electrode cell (Figure 5). It consists of four metallic rings plated to a LCP substrate. The rings consist of three metal layers: electroless nickel, electroless gold and platinum black, respectively. The electroless nickel exhibits uniform thickness and low porosity, thus making it an effective corrosion-protection agent against seawater (Schlesinger and Paunovic, 2000). The thin electroless gold layer improves the adhesion of the platinum black. The porous platinum black layer finalizes the construction, which increases the surface area and reduces the metal to seawater interfacial polarization impedances (Jacobs et al., 1990). Traces (on the backside) then run to contact points under each of the four rings, where plated thru-holes were made to connect the traces to the rings. The holes are within the geometry of each ring and do not interfere with the cell. Electrical contact fingers were attached to the traces to connect the circuit to the sensor circuit board (figure 5B). The circuit and contact fingers were also plated with electroless nickel and gold simultaneously with the conductivity electrodes. The gold layer makes an excellent electrical conductor for the circuit.
Figure 5. Schematics of the conductivity cell (A. Front, B. Back)
The overall diameter of the conductivity sensor was approximately 10 mm. The three outermost rings are approximately 310 µm with a distance of 665 µm between them. The center ring has an approximate diameter of 4 mm. Figure 6 shows a magnified (4x) section of the conductivity cell rings with their measured widths.

Figure 6. Conductivity cell rings with measurements

Rings 1 and 4 are the drive rings while rings 2 and 3 are the sense rings (Figure 5A). Current flows through the two drive rings (ring 1 and ring 4), while the voltage drop is sensed by the two inside rings (ring 2 and 3). The cell excitation is an alternate
current (AC) signal that is produced by a Wein bridge oscillator. The oscillator runs at 10 kHz, but its feedback circuitry allows the amplitude to be controlled by a direct current (DC) signal from the microcontroller’s digital to analog (D/A) converter. The AC signal remains at a constant amplitude and is applied as an AC voltage across the drive rings. To eliminate the need for split supplies for the electronics, the signal is shifted up by adding 2.5V DC. No DC potential can be present in the cell since corrosion and calcium deposits will destroy it promptly. Thus, the signal is low pass filtered and the DC potential is applied to the inside ring, while the shifted AC is applied to the outside ring. There are extra connections to the current carrying rings that allow the user to observe any losses in the connection to the sensor itself, and the amplifier circuitry uses that as part of the feedback such that the exact signals are applied to the rings. The current required for the cell is applied through a current sensing resistor before the feedback, so the resistor does not form part of the sensor, but rather part of the driving circuit. The voltage drop across the resistor is then fed to a precision peak detector and then buffered. The current is derived using the formula:

\[ I_{cell} = \frac{V_{peak}}{R_{ref}} \]  

\[ V_{peak} = \text{Voltage peak measured} \]  

\[ R_{ref} = \text{Resistance (Reference)} \]
Since the amplitude of the voltage used for the cell excitation and the current required to drive the potential are known, the conductance (Siemens) of the cell can easily be calculated using the formula:

\[ S = \frac{I}{V} \]  

\[ S = \text{Siemens (amps/volts)} \]
\[ I = \text{Current (amps)} \]
\[ V = \text{Voltage (volts)} \]
Possible problems with the sensor are biofouling, biofilming, corrosion and/or mineral deposition of the sensor that can change the geometry of the field, increase contact resistance, and reduce the contact area. Biofouling and biofilming of the conductivity cell can be caused by sea surface oils, bacterial colonies and marine organisms that adhere to the electrodes (Varney, 2000). The current carrying electrodes are the most vulnerable to this sort of damage, while the voltage sensing electrodes will most likely have to withstand only salt effects. Therefore, they are hooked up to a differential amplifier with very low input bias current, which is also fed to a buffered peak detector, such that we now have a 3rd feedback point for measurements. As the sensor becomes corroded, a difference would become observable between the voltage sensing rings and the programmed AC signal, such that we could predict the state of the sensor over time.

Due to the constant potential biasing scheme, the sensor can measure salinities down to DI water levels, as well as the full range up to 70mS/cm. The resolution across the entire range remains unchanged, while maintaining a linear response. By using the programmed AC potential and the current measurements, a volume measurement is made, which encompasses the water up to 1mm from the surface of the electrodes. When fouling begins to affect the current carrying electrodes, this method could potentially begin to exhibit higher order responses. In this case, the voltage measurement electrodes can be used to replace the programmed AC potential in the conductance equation since they will not be subject to deterioration affecting their geometry. This will yield a surface measurement that affects only the primary ion path. However, this method is more accurate at higher conductivities since more current paths are created away from the
surface of the cell by the increasing ion concentration. To achieve maximum resolution, the two calibration models can be used, where the micro controller can select the right one based on the current range.
Novel Fabrication Process

The conductivity cell was fabricated using PCB MEMS techniques combined with the maskless photolithographic tool and 8-mil thick double copper-clad liquid crystal polymer material. An overview of the process sequence is shown in figure 8. The first step of the process was to clean the surface of the copper clad LCP material with a sodium persulfate solution for 1 minute. This solution performs a micro-etch of the surface by removing a thin layer of copper, thus exposing a clean, dull layer. Next, the copper surface of the LCP was laminated with a negative dry-film photoresist (Dupont 950) and exposed for 9 seconds with the conductivity cell contact pad pattern (backside) using the maskless photolithographic tool. After development of the photoresist (NaCO₃, 1%, 1 minute), the pattern was used as a template to drill the five thru-holes. The thru-holes bridge the conductivity cell rings (front side of sensor) to the electrical contact pads and fingers (backside of sensor). Once the thru-holes were drilled, the copper was entirely etched away using sodium persulfate (approximately 6 minutes) and then the LCP was uniformly micro-etched for 5 to 10 minutes in a KOH solution (32%, 20% ethanolamine, 90°C) to roughen the surface for metallization (Technic and Crane ECIT). After the micro-etch, the surface of the etched LCP material was examined and measured against the surface of a non-etched piece of LCP using a Veeco Wyco NT 3300 Optical Profiler (Figure 9 and Figure 10). The Ra measurements resulted in a difference in surface area from 913.80 nm (before micro-etch) to 955.88 nm (after micro-etch). The images produced show a change in surface topography where the etched piece has a rougher surface compared to the non-micro-etched piece. Also the LCP thickness was
measured before (0.00845 inch) and after (0.00790 inch) the micro-etch resulting in a 0.00055 inch loss of surface material.

Figure 8. Conductivity cell process sequence
Figure 9. LCP 3D surface topography measurement before micro-etch

Figure 10. LCP 3D surface topography measurement after micro-etch
After the micro-etch, the LCP substrate was catalyzed for metallization. The catalysation deposition process (Shipley, Marlborough, MA) involves several steps:

1) Cleaner (3320)    5 minutes
2) Deionized Water Rinse   1 minute
3) Deionized Water Rinse   1 minute
4) Pre-dip (Cataposit 404)   1.5 minutes
5) Catalyst (Cataposit 44)   5 minutes
6) Deionized Water Rinse   1 minute
7) Deionized Water Rinse   1 minute
8) Deionized Water Rinse   1 minute
9) Accelerator (Accelerator 19)  6 minutes
10) Deionized Water Rinse   1 minute

Once the LCP was catalyzed with the palladium solution (Cataposit 44), it was plated with a thin-film (0.4 microns) of electroless nickel (Enthone 425, West Haven, CT) at 90 °C for 2 minutes. After the deposition of electroless nickel, Dupont 950 photoresist was laminated to the front and back of the nickel-plated LCP substrate. Then the electronically generated conductivity cell patterns (figure 11) were exposed onto the surface using the maskless photolithographic tool. The exposure time used was 9 seconds. The circuit with contact fingers was exposed first to insure proper registration for the plated thru-holes. This pattern was a two-step exposure. Then the substrate was turned over and the cell rings were exposed.
Figure 11. Dark field artwork for conductivity cell (A Front, B Back)
After pattern exposure, the images were developed for 1 minute using NaCO$_3$ (1%) (Fisher Scientific, Pittsburg, PA). After development, the excess nickel was etched away using an aqua regia solution (66% HCl, 33% HNO$_3$, Fisher) for 60 seconds, leaving the desired pattern in the thin plated nickel. The conductivity cell pattern was cleaned in an acid dip solution (HCl 20%) for 2 minutes and re-deposited with 25- micron thick layer of electroless nickel (Enthone 425, 2 hours). Once the nickel metal was built up, a thin layer of electroless gold (Bright Electroless Gold, Transene, Danvers, MA) was chemically deposited for 10 minutes. Then a porous layer of platinum black metal (Yellow Springs Instruments, Yellow Springs, OH) was deposited using a current density of 0.1 A/cm$^2$ for 5 minutes (Gileadi et al., 1975) (Figure 12).
Figure 12. (A) conductivity cell electrode rings, (B) conductivity cell electrodes
Resistive Temperature Device

Design

The temperature sensor designed was a linear resistive temperature device (RTD), which is a thin film metallic circuit that exhibits a linear change in resistance with change in temperature. The electrical resistance of the conductor at any temperature can be calculated by using the formula:

\[ R_T = R_f (1 + \alpha (T-T_f)) \]  

Where:

- \( R_T \) = resistance of conductor at temperature (T)
- \( R_f \) = resistance of conductor at reference temperature (T_f) and
- \( \alpha \) = temperature coefficient of resistance at reference temperature

It was fabricated by etching copper clad LCP into a single filament that was wound orthogonally to the center of the sensor. The entire sensor was then tin plated to prevent corrosion and oxidization, which can cause errors and deterioration of its performance. The traces run parallel to improve noise immunity and then terminate in a four-wire hookup for best accuracy (Figure 13). The width of the traces was approximately 41.5 \( \mu \)m and the length 106 cm (Figure 14). The entire size of the sensor (with electrical contact fingers) was 26 mm x 10 mm. The use of LCP material enables the sensor to be flexible or rigid, depending on the thickness. Copper was chosen as the base metal because it exhibited linear results over the desired water temperature range (-5 to 65 °C), and was cost effective because it was pre-clad on the LCP material.
Figure 13. Light field artwork for resistive temperature device

Figure 14. RTD traces magnified 4x with measurements
The temperature circuit allows a microcontroller equipped with a D/A converter to control the constant current bias for the sensor. The main supply voltage was filtered and then fed to a NPN transistor that supplies the sensor, which was then connected to ground by a current sensing resistor. An opamp looks directly at the D/A DC signal and matches the voltage drop across the sensing resistor. The current to the temperature sensor was fed through 2 of its 4 wires. The current develops a voltage drop across the sensor and it is, in turn, measured by a precision instrumentation amplifier. The output of the amp was fed to the A/D converter in a differential fashion using the 2.5V precision reference as the offset.

Figure 15. Block diagram of the temperature circuit
Novel Fabrication Process

As with the conductivity cell, the temperature sensor was fabricated using novel PCB MEMS techniques, the maskless photolithographic tool, and 8-mil thick Cu-clad LCP material. First the copper had to be cleaned with the sodium persulfate solution (D & L Products). Then the copper-LCP substrate was coated with a positive, liquid spin-on photoresist (Shipley 1827), which was exposed with the temperature sensor pattern for 3.8 seconds. The pattern was developed for 60 seconds in 453 Developer (Shipley). After development, the pattern was etched in the copper metal using sodium persulfate for 6 minutes. The photoresist was then removed (Acetone, Fisher) and the temperature sensor was plated with electroless tin (Transene) to protect it from oxidation. Once completed, the resistivity of the sensor was measured at room temperature and recorded (approximately 85 ohms).
Figure 16. Photo of resistive temperature device (26 mm x 10 mm)
Depth Sensor

The depth sensor used for the miniature CTD system was a commercially available SMD-hybrid device (MS5535 14 bar Pressure Sensor Module) manufactured by Intersema Sensoric SA (Bevaix, Switzerland), which includes a piezoresistive pressure sensor and an ADC-Interface IC. The MS5535A is a low-power, low-voltage device with automatic power down (ON/OFF) switching that provides pressure and temperature measurements. The pressure range measured was 0-14 bar (200 psi) or 140 meters depth. The size of the sensor was 7.3 mm diameter. The reported accuracy was 0.020 bar with a resolution of 0.0012 bar. The internal temperature sensor had an accuracy of 0.8 °C and a resolution of 0.015 °C.

Figure 17. Piezoresistive pressure sensor (7.3 mm diameter), Intersema
CTD System Integration

Once the conductivity and temperature sensors were fabricated, they had to be integrated with the rest of the CTD system, which included the pressure sensor, sensor circuit board, microcontroller circuit board and the power circuit board. All circuit boards for the CTD system were designed and populated with the components by Stan Ivanov of the Center for Ocean Technology (St. Petersburg, FL). A small circuit board (19 mm x 10 mm) was fabricated using the novel PCB MEMS process for the pressure sensor (figure 18). All other circuit boards were fabricated by Advanced Circuits (Aurora, CO). All circuit boards were initially designed as single-sided boards for experimentation and troubleshooting purposes.

Figure 18. Depth sensor circuit board (19 mm x 10 mm)
Flexible printed circuitry connectors and cables (Digi-Key, Thief River Falls, MN) were attached to the fingers of the conductivity and temperature sensors and placed through a slit in a plug for electrical interfacing. The pressure sensor was mounted to the circuit board and placed in a plug with connecting wires. The plugs were machined out of Delrin material and the sensors were mounted using a permanent urethane resin (Scotchcast 2130, 3M). The temperature sensor was completely coated with the urethane resin and mounted in the plug to protect it from seawater corrosion. The backside (circuit) of the conductivity sensor was coated with the urethane resin to protect it from corrosion and then mounted into the plug. After the conductivity sensor was mounted in the plug, the electrodeposition of the platinum black was performed.
Underwater Packaging

The underwater packaging of the CTD system for the marine environment was engineered by Chad Lembke, Mark Holly and Gino Gonzales at the Center for Ocean Technology, College of Marine Science, University of South Florida, St. Petersburg, Florida. All three sensors were integrated and packaged in separate plugs to allow for quick exchange once the sensor life was exhausted. The circuit boards were mounted and housed in a clear acrylic vessel. The three sensor plugs were fitted into the top end cap (Figure 19) of the cylindrical vessel with the data and power port connector connected through the bottom end cap. The end caps were fitted with o-rings and screwed into place using stainless steel screws. The dimensions of the instrument were 4-inch outer diameter x 4 inches long (Figure 20). Two underwater communication cables (Impulse Enterprise, San Diego, CA) were mounted to the bottom end cap, one for RS-232 communication and power and the other for programming the microcontroller.
Figure 19. Sensor plugs mounted to end cap
Figure 20. Miniature CTD system prototype
CTD System Description

Electronics

The CTD system electronics is comprised of three individual single-sided circuit boards that control the sensors, microprocessor and power. The sensors are controlled by a low-power MSP430 microcontroller device. It has a 32-bit RISC processor with 64 bit floating point calculations. It is a highly integrated microcontroller with internal accessible flash, D/A, A/D, references, and timing capabilities. A MAX3221 low power RS232 level converter handles communications and an ADC1241 performs a 24bit A/D conversion with a 60Hz digital filter and self-calibration. The sensor biases are handled by the microcontroller’s internally self-calibrated 12-bit D/A converter.

Output

The communications standard for the CTD system is configured to RS-232 with an automatic baud rate of 115200 to 1200 and communicates directly with a computer equipped with a serial port. The communication software used is Telnet or Hyperterminal with the settings 115200 bits per second, 8 data bits, none parity, 1 stop bits, and none flow control.

Logging

The CTD system has the capability of logging data internally to 12 megabytes memory. Currently it can log 900 lines of data, where each line contains the date, time, temperature, conductivity, pressure, and temperature within pressure sensor. The
date/time stamped data is logged based upon a programmable sampling rate from 1 sample every 2 seconds to once every 24 hours.

**Power**

Power for the CTD system can be supplied with an internal or external battery source. The unit requires 3 mA for the RS-232, 800 µA average quiescent, 10 mA sampling deionized water, 22 mA sampling water at 70 mS/cm at 6 to 12 volts DC power.

**Software**

The CTD software is a comprehensive program, which allows the user to communicate with the system through the serial port. The software is a menu driven program that allows the user to set the system clock, sampling start/stop times, sensor bias and calibration curves, memory format, sampling rate and sample mode (raw, parametric or calibrated) (Figure 21). It also controls the downloading of logged files and has real-time data display capabilities. The data has the option of being displayed as raw (voltages), parametric (ohms, Siemens) or calibrated (°C, mS/cm) except for the pressure sensor, which is always displayed as mbars along with its temperature (°C). Salinity measurements are then independently calculated using the temperature and conductivity data with the Practical Salinity Scale 1978 formula.
Figure 21. Menu format of the CTD system
CHAPTER IV
RESULTS AND DISCUSSION

Conductivity Cell

Calibration and Statistical Evaluation

The conductivity cell was calibrated using International Association for the Physical Sciences of the Oceans (IAPSO) standard seawater samples (Ocean Scientific International Limited, Hamshire, England). The conductivity calibration procedure entailed taking consecutive measurements of the standard’s conductivity while varying the temperature of the solution. It is known that a solution’s conductivity is a function of temperature, and there is a mathematical expression that relates these two variables. The conductivity cell was submersed with a platinum resistive temperature device in a beaker of 34.995 salinity sample and heated to 32 °C using a water bath. Once the sample stabilized at the chosen bath temperature a conductance reading (in Siemens) was taken. Temperature readings from the sample were taken to verify actual solution temperature. The temperature of the water bath was reduced by 2 °C increments and measurements were acquired from 32 to 4 °C. The measurements were taken from hot temperature to cold temperature to reduce the formation of bubbles in the standard seawater solution (Brown et al., 1991). Five conductance measurements were recorded and averaged to obtain a stable reading at every given temperature. The conductivity (mS/cm) of the

48
standard seawater sample (34.995) per temperature was calculated using the Electrical Conductivity Method formula as stated in the Standard Methods for the Examination of Water and Wastewater, 20th Edition and TK Solver 5.0 Software. The formula states:

\[ S = a_0 + a_1 R_t^{1/2} + a_2 R_t + a_3 R_t^{3/2} + a_4 R_t^2 + a_5 R_t^{5/2} + \Delta S \]  \[ 4 \]

Where \( \Delta S \) is given by

\[ \Delta S = [t - 15/ 1 + 0.0162 (t-15)] (b_0 + b_1 R_t^{1/2} + b_2 R_t + b_3 R_t^{3/2} + b_4 R_t^2 + b_5 R_t^{5/2}) \]

And:

\[ a_0 = 0.0080 \quad b_0 = 0.0005 \]
\[ a_1 = -0.1692 \quad b_1 = -0.0056 \]
\[ a_2 = 25.3851 \quad b_2 = -0.0066 \]
\[ a_3 = 14.0941 \quad b_3 = -0.0375 \]
\[ a_4 = -7.0261 \quad b_4 = 0.0636 \]
\[ a_5 = 2.7081 \quad b_5 = -0.0144 \]

Valid from \( S = 2 \) to \( 42 \), where:

\[ R = C \text{ (Sample at t)}/C \text{ (KCl solution at t)} \]

The conductance (Siemens) of the conductivity cell was plotted against the calculated conductivity (mS/cm) (Figure 22). As the conductance is a linear function of the conductivity, linear curve parameters were regressed using the method of least squares. The regressed line, \( (y=1165.0615x - 4.8709) \) along with the coefficient of determination \( (R^2=0.9997) \) are also placed in the graph. This equation was then entered into the CTD
software program to calculate the calibrated conductivity (mS/cm) data from the measured conductance (Siemens). The calculated R² value (0.9997) of the conductivity cell indicated very good linear correlation (value close to 1.000). The 95% confidence limits, (defined by α) for the estimated values of ŷ was calculated using the formula:

\[
ŷ ± t_{α/2} s \sqrt{\frac{1}{n} + \left( \frac{x_p - \overline{x}}{SS_{xx}} \right)^2}
\]  

[5]

Where \( t_{α/2} \), a parameter obtained from the t distribution is based on (n-2) degrees of freedom. The variable n is the number of data points, \( \overline{x} \) is the sample mean, s represents the standard deviation, and SS_{xx} is the sum of squares. These limits, which range from +/- 0.28 to 0.59 mS/cm, are illustrated in figure 22 as dotted lines.
A regression model was used to relate the dependent variable $y$ (conductivity) to the independent variables $x_1, x_2, \ldots, x_k$ (conductance) and calculate the predicted $y$ intervals. The experimental evaluation was conducted exactly as stated above for the calibration except only five data points were measured. The conductivity cell was placed in the 34.995 salinity sample and measurements were taken at approximately $32^\circ$C, $24^\circ$C, $18^\circ$C, $10^\circ$C, and $4^\circ$C (+/- 0.80 $^\circ$C) respectively. The conductivity values were calculated using the known standard seawater salinity and the known temperatures. This test was repeated on four separate occasions. The residuals for all data points were calculated and plotted using statistical equations in Excel (Figure 23).
The residual data shows that the experimental error is not random, but depends on the conductivity measured. As the conductivity increases, so does the experimental error. Due to this fact, the standard deviations of the residuals of each repeated conductivity measurement were calculated separately. The conductance (x) and conductivity (y) values for all runs were averaged and the standard deviation of the residuals calculated. Table 3 shows the statistics data for the repeated conductivity cell measurements along with the 2s values for the respective y-values.
Table 3. Average values of Conductivity and Conductance with Standard Deviation

<table>
<thead>
<tr>
<th>Average Conductivity (y)</th>
<th>Average Conductance (x)</th>
<th>Standard Deviation (s)</th>
<th>2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>32.0967</td>
<td>0.03184</td>
<td>0.2603</td>
<td>0.5206</td>
</tr>
<tr>
<td>38.1437</td>
<td>0.03715</td>
<td>0.2900</td>
<td>0.5780</td>
</tr>
<tr>
<td>46.1776</td>
<td>0.0444</td>
<td>0.5652</td>
<td>1.1304</td>
</tr>
<tr>
<td>52.0576</td>
<td>0.0496</td>
<td>0.6248</td>
<td>1.2500</td>
</tr>
<tr>
<td>59.8116</td>
<td>0.05612</td>
<td>0.9071</td>
<td>1.8141</td>
</tr>
</tbody>
</table>

In figure 24 all data points from the five runs (calibration and repeated runs) including the five averaged values are plotted along with the y-error bars associated with those respective points. The y-error bars range from +/- 0.5206 to 1.8141 mS/cm.
Figure 24. Plotted data points of conductivity cell replicates of measured conductance vs. calculated conductivity.
Comparison Test

Once the conductivity cell was calibrated and the sample regression equation was entered into the CTD software program, the cell was tested against a standard laboratory conductivity probe (Mettler Toledo Inlab 730). The Mettler Toledo conductivity probe was calibrated using a standard of 12.88 mS/cm. Conductivity standards (KCl) from Exaxol Chemical Corp. (Clearwater, Florida) were used to perform the test. The standards used were 2000, 5000, 7000, 10000, 12880, 15000, 20000, 30000, 40000, 50000, 60000 and 70000 µMHOs @ 25 °C. The Mettler Toledo conductivity probe is equipped with a temperature sensor, which automatically calculates the temperature compensation for the conductivity measurement. Temperature measurements for each standard were recorded. The conductivity measurement taken from the fabricated cell was corrected using the temperature compensation formula:

\[
\frac{R}{1 + 0.019(T - 25)} \quad [6]
\]

Where:

- \( R \) = measured mS/cm reading
- \( T \) = measured temperature

The temperature compensated conductivity values were then plotted against the Mettler Toledo measurements and the sample regression equation and \( R^2 \) were calculated (Figure 25). The slope of the best-fit regression line indicates a 3% deviation of the straight line. Figure 26 shows an adequate correlation of the two sensors up to 50 mS/cm. The differences calculated between the conductivity cell and the commercial probe were
approximately 3% for each conductivity value and are illustrated in figure 27. The differences show that even though the fabricated sensor performance is a function of the measured range, it performs relatively well until the upper limit (70 mS/cm) was reached.

\[
y = 1.0348x - 0.2340 \\
R^2 = 0.9987
\]

Figure 25. Mettler Toledo conductivity probe vs. fabricated conductivity cell
Figure 26. Measured conductivity for conductivity cell vs. Mettler Toledo probe

Figure 27. Difference calculated between commercial probe and conductivity cell
Resistive Temperature Device

Calibration and Statistical Evaluation

The resistive temperature devices were calibrated using DI water in a temperature controlled water bath. The sensor was submersed in a 200 ml beaker along with a calibrated platinum resistive temperature device. Once the DI water stabilized at the desired water bath temperature, the resistance (ohms) measurement along with the temperature measurement from a calibrated platinum RTD was recorded. Five resistance measurements were averaged to obtain a stable reading at each temperature. The resistance (ohms) of the temperature sensor was plotted against the temperature ($^0\text{C}$) (Figure 28). A linear regression line was plotted through the known x and y-values and the sample regression equation ($y = 3.3904x – 251.6038$) along with the coefficient of determination ($R^2= 0.9998$) that was also calculated. This equation was then entered into the CTD software program to calculate the calibrated temperature ($^0\text{C}$) data from the measured resistance (ohms). Again, the calculated R$^2$ –value (0.9998) indicates good linear correlation between the measured (resistance) and predicted variable (temperature) (values close to 1.000). The 95% confidence limits were calculated using formula [5] and had a range of +/- 0.141 to 0.586 $^0\text{C}$. Figure 28 illustrates these limits with dotted lines.
Once the RTD was calibrated, additional runs were performed to calculate the $y$ prediction interval. The tests were conducted exactly as stated above for the calibration curve, except five data points were measured. Resistance (ohms) data were collected for five different temperatures including 50 $^\circ$C, 35 $^\circ$C, 25 $^\circ$C, 10 $^\circ$C, 5 $^\circ$C. This test was conducted on four separate occasions and plotted along with the calibration curve in an Excel worksheet (Figure 29). The residuals from the straight-line calibration data were calculated and plotted (Figure 30).
Figure 29. Temperature calibration curve and 4 additional runs

Figure 30. Residual plot of temperature data set
The residual data show that the experimental error is randomly distributed along the sensors tested range. This implies that a constant error exists for the sensors response in the entire data range tested. Therefore the $y$ prediction interval can be calculated using the formula:

$$
\hat{y} \pm t_{\alpha/2} s \sqrt{1 + \frac{1}{n} + \left( \frac{x_p - \bar{x}}{SS_{xx}} \right)^2}
$$

[7]

Where $t_{\alpha/2}$ is based on (n-2) degrees of freedom. The variable definitions correspond to those specified in equation 5. The prediction limits for some value of $y$ was illustrated in figure 31 (shown as dotted lines). These limits range from +/- 0.778 to 0.964 $^\circ$C.

\[
y = 3.3904x - 251.6
\]

\[
R^2 = 0.9998
\]

Figure 31. 95% Prediction Intervals
Comparison Test

Once the RTD was calibrated and the sample regression equation was entered, the sensor was tested against a standard laboratory temperature probe (Fluke 80T-1500). Both probes were submersed in a beaker of deionized water and heated to a specific temperature using a recirculating water bath. The temperature devices were measured from 50 °C to 100 °C in increments of 5 °C. The data were plotted and the sample regression and R² values were calculated using Excel (Figure 32). The R²-value (0.9997) shows good linear correlation between the novel RTD and the commercial temperature probe. The regression coefficient or slope (0.9917) of the compared sensors was close to 1.00. Figure 33 is the temperature comparison data of both sensors plotted against the known temperature of the water bath. The differences between the RTD and the commercial probe range from –0.64 to 0.15 °C and are illustrated in figure 34.
y = 0.9917x + 0.7388
\( R^2 = 0.9997 \)

Figure 32. Commercial digital thermometer vs. RTD

Figure 33. RTD and commercial digital thermometer data plotted against calibrated thermometer.
Figure 34. Difference in °C for measured temperature between RTD and commercial digital thermometer.
Depth Sensor

Comparison Test

The Intersema MS5535A pressure module (140 dbar) was tested and compared to another discrete pressure sensor (Keller PA-10, Applied Microsystems, Sidney, BC), in order to insure the appropriate results were obtained from the integration of the pressure module to the sensor circuit board. The Keller PA-10 was a semiconductor bridge strain gauge with a maximum range of 500 dbar. Both sensors were mounted into a pressure vessel and then the vessel was pressurized and depressurized several times. Pressure measurements were recorded for both sensors simultaneously and graphed (Figure 35). The data were plotted and the sample regression and $R^2$ values were calculated using Excel (Figure 36). The $R^2$ - value (0.9999) shows good linear correlation between the Intersema pressure module and the Keller pressure sensor.
Figure 35. Comparison graph of Intersema vs. Keller pressure sensors

Figure 36. Keller pressure sensor vs. Intersema pressure sensor
Once the calibration of the conductivity and temperature sensors was conducted, the complete system was evaluated both in laboratory conditions and in the field. The CTD was placed in a bucket in the laboratory containing a known KCL standard sample of 40000 \( \mu \text{MHOS} @ 25^\circ \text{C} \). The CTD was programmed to take three conductivity and temperature measurements every minute for a 24-hour period. The data were logged internally as well as displayed real-time using RS-232 communication via hyperterminal. The data were plotted in Excel (Figure 37).

The evaluation data revealed a small percentage of points (0.532%) that exhibit extremely high spikes in the conductivity measurements of the known sample. These spikes were caused by the charging of the capacitor by the super diode circuit (Ivanov, private communication, 2005). To conserve energy in the system a reset circuit was incorporated, which drains the holding capacitor. The super diode circuit tries to compensate with more voltage to the capacitor. If the sample is taken when the signal is at the top of the sign wave, the reset circuit releases and causes the super diode to over charge the capacitor. This condition can be fixed by the addition of a capacitor to the reset circuit. Since these spikes can be explained due to an underdamped electrical response, the data were plotted without these data points (Figure 38). The graphed data shows temperature and conductivity changes due to the ambient temperature of the laboratory within the 24-hour period. The conductivity data in figure 38 were not temperature compensated, although when the temperature compensation equation was applied, the average measurement was 38.40466 mS/cm @ 25 \(^\circ\)C, which is consistent with the known KCL standard sample of 40000 \( \mu \text{MHOS} @ 25^\circ \text{C} \). Although the system
did exhibit some drift within the temperature compensated conductivity measurement with a range of 39.34095 to 37.17808 mS/cm. This 2.16287 mS/cm drift is equivalent to a 1.523 drift in salinity @ 25 °C (Figure 39).
Figure 37. CTD system evaluation plot
Figure 38. Twenty-four hour evaluation CTD test with measured conductivity, temperature and depth.
Figure 39. Salinity values for given mS/cm and temperatures.
Field Test

Once the CTD system was packaged in the waterproof housing and the sensors were calibrated, it was placed in a flow-through tank. The tank was situated on a dock within Bayboro Harbor (St. Petersburg, FL) where continuous natural seawater was pumped into and out of the tank. The CTD system was programmed to acquire conductivity, temperature and depth data for a seven-day period. A series of three measurements were taken every thirty minutes and logged internally. The power source for the CTD system was an internal 9-volt battery. After the seven-day period the CTD system was removed from the tank and the data were downloaded and plotted (Figure 40). Also plotted on the chart were the temperature measurements for the Intersema thermometer incorporated within the pressure module and the water level (tide) data. This data was collected by NOS and stored in the CO-OPS database and was retrieved from the website:

http://140.90.121.76/data_retrieve.shtml?input_code=011011111pwl&station=8726520+St.+Petersburg,+FL

Rainfall data were also acquired for the deployment location (Albert Whitted Airport, St. Petersburg, FL) and period (August 17th to 24th, 2005) from NOAA. A substantial rainfall event occurred on August 23, 2005 between 1900 and 2000 hours. This event was captured by the CTD system, which measured a noticeable change in the conductivity and temperature of the seawater.

The graphed data demonstrate the fluctuations of conductivity, temperature and depth vs. time for the period of one week. The resistive temperature device was observed to be consistent with the commercially manufactured sensor (Intersema). The
temperature data showed elevated temperatures during the day and lower temperature during the night hours. The conductivity measurements fluctuated with temperature, but once the parameters were incorporated into the salinity equation and the temperature was compensated, the data was normalized. Bayboro Harbor has a mixed tidal pattern, where successive high tides or low tides are of significantly different heights through the cycle, which causes fluctuations in the salinity (Garrison, 1998). These fluctuations were measured with the CTD system and were calculated using the Practical Salinity Scale 1978 [4] and plotted against time in figure 40.
Figure 40. Field test data of the CTD measurements with water level
CHAPTER V
CONCLUSIONS

Summary

The goal of this work was to develop a miniature, low cost CTD system using novel PCB MEMS fabrication techniques combined with liquid crystal polymer (LCP) material that measures salinity in natural waters. Two milestones had to be achieved to reach this goal. First, the construction of LCP-based conductivity and temperature sensors using novel PCB MEMS fabrication techniques without an expensive cleanroom environment, and second, miniaturization of the sensors. In this work several tasks were accomplished:

- Design and construction of LCP-based conductivity and temperature sensors using PCB MEMS fabrication techniques
- Calibration and statistical evaluation of the conductivity cell and RTD
- Integration of conductivity, temperature and depth sensors to make a CTD system
- Packaging of the CTD system for the underwater marine environment
- Seven-day field evaluation of the CTD system
Conventional PCB MEMS fabrication processes, such as etching and metallization, have been coupled with a novel photolithographic process and applied on LCP. LCP has a unique combination of physical, electrical, chemical and mechanical properties, which makes it a good substrate for sensor applications (Wang et al., 2003).

The experiments performed have demonstrated a prototype of a novel PCB MEMS-based CTD system capable of monitoring conductivity, temperature and depth in natural waters. The research presented includes the design and integration of the sensors as well as the interfacing and packaging of the system for the underwater environment. It also includes the calibration and statistical evaluation of the conductivity and temperature sensors. The calculated $R^2$ values (0.9997 and 0.9998) of the conductivity cell and RTD (respectively) indicated very good linear correlation (values close to 1.000). While the 95% prediction intervals ranged from +- 0.5206 to 1.8141 mS/cm and +- 0.778 to 0.964 $^\circ$C.

The field evaluation test verified that all measurement principles essentially worked as intended, and salinity data was acquired for a seven-day period. This work demonstrates that microsensors for a CTD system can be fabricated using novel low cost PCB MEMS processing techniques combined with liquid crystal polymer material.
Future Research

The next steps in the development of the PCB MEMS-based CTD system should be the further miniaturization of the entire instrument. This can be accomplished by redesigning the three circuit boards that control the sensors, microcontroller and power. The initial boards were designed as separate single-sided boards to quickly troubleshoot electrical problems. These boards can be redesigned as one thin-film multi-layer board, thus miniaturizing the electronics of the system. Also the boards could be fabricated using novel photolithography techniques, which have the capability to fabricate circuit boards with smaller traces than commercial printed circuit board manufacturers. A redesign on the system packaging could also contribute to further minimize the size of sensing device. Most conventional packaging approaches are space inefficient and dwarf the physical size of the system (Lyke, 1995). Several packaging alternatives need to be investigated to protect the system for the underwater environment, such as injection molding and waterproof coatings (Xu, 2002).

Another important issue that would require more development is expendable or disposable sensors for the system. This type of sensors would enable the system to be very flexible in its applications. Sensors that are pre-calibrated and then easily exchanged with old or fouled ones allows for expanded field time for the system. This is especially an issue with the conductivity sensor where biofouling and recalibration are important factors that limit its ability to perform correctly. Large arrays of low-cost disposable systems can be distributed to acquire more data, especially if these sensors are small enough to be attached to living marine organisms.
REFERENCES CITED


