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14. ABSTRACT
The goal of this project is to develop cost-effective, sensitive, flexible and adaptive Surface Acoustic Wave (SAW) devices that will provide for improved detection of corrosion on aircraft. To accomplish this goal, polymeric sensory materials (pristine and nanocomposites) were synthesized and optimized to provide for enhanced piezoelectric properties, improving sensor performance. SAW devices were designed and fabricated, integrating these novel materials on the sensor surface. TSU faculty as well as undergraduate and graduate students were involved in conducting research on this project to achieve the project goals.

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Office of Naval Research (ONR)

Research Performance Progress Report (RPPR)

"Design of Microsensors for the Detection of Corrosion on Aircraft"

Final Report
Accomplishments
2020-2021

Dr. Frances Will ams (Principal Investigator)
Dr. Richard Mu (Co-Investigator)
Tennessee State University

2020-2021 Accomplishments

Major Goals

The goal of this project is to develop cost-effective, sensitive, flexible and adaptive Surface Acoustic Wave (SAW) devices that will provide for improved detection of corrosion on aircraft. To accomplish this goal, polymeric sensory materials (pristine and nanocomposites) will be synthesized and optimized to provide for enhanced piezoelectric properties, improving sensor performance. SAW devices will be designed and fabricated, integrating these novel materials on the sensor surface. Finally, these devices will be tested for the proposed naval application. TSU faculty as well as undergraduate and graduate students will be involved in conducting research on this project to achieve the project goals.

Accomplishments under Goals

During this past year, two graduate students and two undergraduate students (Majors: Electrical, Mechanical, and Computer and Information Systems Engineering) participated in research on this project under the supervision of the PI (Dr. Frances Williams) and Co-PI (Dr. Richard Mu). Supplies and equipment were procured to enable the researchers to perform their research tasks on this project.

1) <u>Investigation of Substrate Surface Assisted Pristine PVDF Thin Film Fabrication:</u>
   - Built upon our previous approach of using ZnO thin film as the seed layer to drop case and spin coating methods, we have built and tested a new electrospraying system to fabricate PVDF thin film. This technique has two clear advantages over the previous two techniques used: *a)* Much better controlled film thickness and uniformity; *b)* Circumvented the problem of wettability; and *c)* the vertical electrical fie d can potentially leads to piezoelectric properties with no need of electrical poling process.
   - Verified the previously obtained results suggesting that we can indeed achieved the macroscopic dipole moment alignment.
   - A manuscript was prepared for publication.
2) <u>Synthesis of PVDF + GO Nanocomposite Materials</u>
   - Graphene oxide PVDF polymer films have been obtained with drop-castirg, spin-costing and electro spraying techniques.
   - Comparative study through materials characterization and testing were completed to understand how the fabrication and processing parameters affect Beta-phase (functional piezoelectric phase) formation.
   - A manuscript was prepared for publication.

3) <u>SAW Device Design, Fabrication, and Evaluation</u>
   - Investigation of electrode materials and conductivities for multifunctional device fabrication
   - Used QCM device to evaluate sensing principles and SAW device testing protocols
   - Design, fabricate and test SAW devices

Significant Results

I. The use of ZnO seed layer to enhance polar phase formation

Major Activities: We have used *a*) ZnO seed layer as the substrate to deposit PVDF films with three different techniques. They are: drop casting of PVDF on a ZnO seed layer, electrospray PVDF on ZnO seed layer and spin-coating and the used of confocal Raman to study the crystal structure of the films. With **specific objectives** to enhance polar phase formation due to the polar face of the ZnO. The **significant results** and **key outcomes or other achievements** from the study show *a*) more polar phase formation is observed when PVDF is dissolved in pure DMF than in DMF-acetone (60:40), *b*) Electrospraying PVDF on ZnO seed layer also showed an enhancement of polar phase content and the enhancement is much stronger, *c*) In the case of spin-coating, use of a ZnO seed layer did not show enhancement of polar phase content. For spin-coating, wettability and viscosity are more important than the interaction between PVDF and the ZnO seed layer. In all, this suggests that a ZnO seed layer does have the ability to improve fabrication of PVDF.

II. The fabrication of a free standing piezoelectric PVDF composite substrate for SAW device applications

Major Activities: The material synthesis begins using PVDF powder suspended in the solvent DMF and sonicated until the PVDF completely dissolved. The PVDF suspension is made at 1% by weight in solvent. A separate suspension is synthesized using dopant materials specifically chosen with material properties to enhance the PVDF functionalities. Graphene oxide in the reduced (rGO) and non-reduced (GO) were chosen as dopants. The film was produced with the electrospray technique which has been previously demonstrated to be more effective and Confocal Raman has been used for crystal structure characterization with **specific objectives** to enhance polar phase formation due to 2-dimensional nature of GO and rGO. The **significant results** and **key outcomes or other achievements** are *a*) the PVDF thickness profile was mapped out using time dependent depositions where thickness increased over time, *b*) the roughness was also shown to increase for longer depositions, *c*) The deposited PVDF was shown to have the highest structural properties at a 1% concentration based on Raman and also confirmed with XRD, and *d*) rGO electrospray samples has higher functional phase content then GO.

III. Investigation of electrode materials and conductivities for multifunctional device

Major Activities: Four conductive materials are deposited on to PVDF film and evaluated for potential SAW device application. They are: ITO, Nickle, Molybdenum, and Aluminum deposited on both sides of a PVDF thin film with two **specific objectives** in mind: *a*) obtaining the film thickness at which the percolation threshold is achieved and *b*) exploring the potential to use the electrode materials that are optically transparent so that multifunctional devices can be developed. The **significant results** and **key outcomes or other achievements** are: *a*) the 5 nm ITO were not obtained and it is believed to be due to the brittleness of such a thin layer of the material. Data was also unable to be collected for the 5 nm aluminum. This may be due to the lack of continuity of the film, *b*) The high values of resistivity for 10 nm ITO and 10 nm molybdenum are thought to be the result of the probes cracking or possible puncturing the thin film, *c*) the 20 nm thin films provided the best results which is more than likely due to film continuity and rigidity and the 20 nm aluminum film and the 10 nm nickel film gave the best value for resistivity, and *d*) ITO electrode may be used for optical devices when the deposited film thickness is more than 10 nm. And optical transparency can still be in 60 – 80% range.

IV. Use QCM device to evaluate sensing principles and SAW device testing protocols
Major Activities: In order to effectively evaluate acoustic devices, we have designed both a temperature and environmental controlled chamber. The chamber is capable of 1) achieving mTorr vacuum and/or purged with various gases and 2) elevating temperature from 25 °C to 300 °C with two identical sensor platforms to house both reference and sample devices. Both adsorption and desorption experiments which result in mass changes of sensing materials. One **major and specific objective** in this effort is to validate the laboratory-built chamber to test various acoustic devices including SAW device to be fabricated. The **significant results** and **key outcomes or other achievements** are: *a*) two sets of dual QCM sensors, one set has silver coated clean surfaces and the other is with PVDF + carbon nanotube (CNT) coated sensing surface, have been tested for adsorption and desorption. The results showed high sensitivity and are consistent with the expectation. *b*) Organic molecules, acetone and ethanol vapor, were used for adsorption experiment and monolayer surface adsorption coverage can be observed. Likewise, the same level of desorption sensitivity can also be obtained. *c*) Effective purging and temperature control results in high level repeatability and reliability of sensor testing and *d*) *in-situ* device testing can be routinely conducted.

V. Design, Fabricate and Test SAW Devices
Major Activities: Two graduate students have been trained to use the clean room at Vanderbilt Interdisciplinary Nanoscale Science and Engineering (VINSE) facility ranging from software design tools, optical and focus-ion beam lithography, materials deposition and lifting techniques, and device evaluation methods. Two SAW device design have been conducted with the expected SAW frequency of 100 MHz and 10 MHz. 100 MHz SAW device is more challenging because the electrode width is a few microns. Both interconnectivity and longevity have presented problems for device testing. 10 MHz device design have been accomplished but there were some delays due to VINSE facility

COVID-related closures and staffing issues. However, there should be no major challenges from the technical aspects. There are two **major and specific objectives** in this effort. They are: 1) successfully use free standing PVDF films to fabricate SAW devices and 2) evaluate these devices of adsorption and desorption kinetics with the laboratory-built chamber. The **significant results** and **key outcomes or other achievements** are: 1) We have successfully fabricated a set of devices and are able to evaluate and improve device fabrication techniques; 2) A number of new techniques have developed through our device making processes, including overcoming wrinkle problems with 28 micrometer film, addressing electrostatic charging, bonding materials to mount film onto supporting substrates, *etc.* Addressing such issues allowed us to fabricate quality SAW devices that were integrated with the new materials synthesized in our lab and achieve the main goal of the proposal.

Results Dissemination

1. Three manuscripts have been prepared for publication. 2. Three major research and educational proposals are funded as a result of new capabilities and collaborations related to this research (DOD Instrumentation, NSF-RISE, NSF-PREM Seed grants)

Honors and Awards

Frances Williams was recognized on the list of "1,000 Inspiring Black Scientists in America" by Cell Mentor (web resource that provides support and resources for emerging scientists) (2020)

Training Opportunities

Two graduate students have been trained to use the clean room at Vanderbilt Interdisciplinary Nanoscale Science and Engineering (VINSE) facility ranging from software design tools, optical and focus-ion beam lithography, materials deposition and lifting techniques, and device evaluation methods. Graduate and undergraduate students have also been trained and educated on the synthesis and characterization of advanced materials as well as in the development and fabrication of micro- and nano-scale devices at TSU. They implemented SAW device design and learned and mastered materials characterization techniques such as confocal Raman, SEM, TEM, XRD, and FTIR. Working with mentors, the team designed and established two stand-alone electrospray systems (which are opened to other research teams on campus) and collaborated with faculty members at Fisk and Vanderbilt Universities. The faculty researchers served as mentors to the students on their projects and helped guide them on their research tasks.

Participants

Frances Williams (PD/PI), Richard Mu (Co-PD/PI), Omari Paul (graduate student), Anthony Thai (graduate student), Shaniqua Jones (undergraduate student), Marvel Ridley (undergraduate student)