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Daulton Isaac
Embry-Riddle Aeronautical University

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Methodologies for the Formation of a Zinc Oxide and Poly(Vinylidene Fluoride) Piezoelectric Device

Daulton Isaac¹, NASA Ames Research Center, Moffet Field, CA, 94035

The advent of nanotechnology has brought about innovative ideas for the solving of the world’s problems. For example, Zinc Oxide nanowires, being piezoelectric, pose a simple solution to the big problem of renewable energy. Piezoelectric materials produce an electric current when they are deformed. In particular, this is an attractive property for systems whose operation produces high frequency vibrations, such as aircraft. Using a simple sandwich of a conductive substrate, Zinc Oxide nanowires coated in PolyVinylideneFluoride (PVDF), and a conductive top layer, an electricity generating device can be built. Forming the device involves obtaining an appropriate thickness for the piezoelectric PVDF film and a layer with minimal cracking. In this work, an introduction of the fundamental concepts related to the device will be given along with a summary of the PVDF activities pursued thus far. It will be shown that such a device is indeed theoretically sound. Also, obtaining a uniform PVDF layer is possible, but an acceptable thickness proves challenging to obtain.

Nomenclature

\[ \alpha = \text{One of the orthorhombic crystal phases of PVDF} \]
\[ \beta = \text{Another orthorhombic crystal phases of PVDF most piezoelectric} \]
\[ \delta = \text{Another orthorhombic crystal phases of PVDF} \]
\[ \gamma = \text{The monoclinic crystal phases of PVDF} \]

I. Introduction

The word piezoelectricity arises from the Greek for pressure and electricity. The relation between these two concepts in certain materials was discovered by the brothers Pierre and Jacques Curie in 1880 [1]. A piezoelectric material, when mechanically deformed, produces an electric current; conversely, inducing an electric current causes a mechanical deformation. A solid material is said to be a crystal or crystalline when its structure is regular and repeating [2]. In order to possess piezoelectricity, a crystal must lack a center of symmetry in the crystal structure. That lack of symmetry is present in 21 of the 32 crystal classes, but only 20 of the classes exhibit the piezoelectric effect. This effect is present in materials, such as crystalline quartz, Rochelle salt, barium titanate, and tourmaline, and these have extensive use in devices, such as band-pass filters, microphones, headphones, and loudspeakers [3].

Consistently high vibrations, and therefore deformations, are a characteristic of commercial aircraft operation. United States commercial aircraft operations both scheduled and unscheduled as well as domestic and international flights consumed 17,594.7 million gallons of fuel costing 50,488.1 million dollars in 2012 [9]. Small improvements in the airline industry yield significant results, so the implication of a piezoelectric device, depending on implementation and operation costs, could save thousands of dollars. Also, considering the general rise in fuel prices, such a device could prove even necessary.

¹ Student Intern, Entry Systems and Vehicle Development Branch (Code TSS), Center for Nanotechnology
II. Device Theory and Formation

The material Zinc Oxide exhibits piezoelectricity. These wires can be grown by Vapor-Liquid-Solid (VLS) synthesis, self catalyzed, and the hydrothermal methods. This research utilized the self catalyzed method to grow wires on an Iron Chromium Aluminum substrate coated with Indium Tin Oxide. The wires obtained thus far are about 10 µm high, but the ideal height is 100 µm. Although the growth of ZnO nanowires involves variables that can be adjusted to maximize height, that aspect will not be addressed in this paper.

The polymer PolyVinylideneDiFlouride(PVDF), produced through the polymerization of vinylidene fluoride also possesses piezoelectricity [4]. The material also exhibits pyroelectricity which is ability to produce an electric charge when its temperature changes [5]. PVDF can exist in α, β, δ, and γ crystal phases, and it is well known that the β phase is the one which produces the material’s piezoelectric effect [5]. However, processing is required to get PVDF into this phase, and much research has been done on this delicate area. The regular process seems to be stretching the film through some mechanical means at high temperature and then poling it in an electric field. This process was reported to create piezoelectric films that could be used in a microfluidic flow sensor [6]. Other experiments have shown that predominantly β phase PVDF films can be obtained by controlling the rate of evaporation of the solvent because that rate influences the crystallization rate. The investigation showed that low evaporation rates produced predominantly β phase films while high rates produced α phase. A special note was also mentioned that these results were true as long as a good solvent of PVDF was used. Such solvents were noted as dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), and hexamethylphosphoramide (HMPA). Acetone was specifically mentioned as a bad solvent of PVDF and one which did not form a homogenously transparent solution as did the other solvents [8]. Related research has shown that films of predominant β phase PVDF/HFP, a copolymer of PVDF, can be obtained without mechanical stretching by introducing a hydrated salt, Mg(NO3)2·6H2O, into the PVDF/HFP solution [5]. For most research X-ray Diffraction and Fourier transform infrared spectroscopy (FTIR) were the instruments used to ascertain and verify the crystal phase of the PVDF.

Figure 1 Showing a simplified Representation of the Piezoelectric Device

An electricity generating device can be formed by a conductive substrate, Zinc Oxide nanowires coated in PVDF, and a conductive top layer. An illustration of such a device is shown in Figure 1. The device, being lightweight and compact, can then be placed within the frame of aircraft wings, engine cowlings, or wherever intense vibrations occur. The electricity produced by such devices could then power passenger electronic devices, signal lights, or sensors on the aircraft. The fundamental idea is that energy wasted in vibrations, the energy ultimately coming from expensive aircraft fuel, will be recovered and used. It should be noted that such a device is applicable in any system involving high vibrations or motion that would deform the nanowires and the PVDF film, such as industrial machines.
III. Experiments Performed

A. Method

The focus of this work was obtaining an acceptably thick PVDF layer with minimal cracking. For all experiments, the solvent used in the PVDF (Alfa Aesar CAS: 24937-79-9) solution was Acetone. Solutions were sonicated in a VWR Model 150 D for varying times depending on the concentration of the solution. A syringe, without a needle, was used to deposit the solution onto a Silicon wafer. The solution was spin coated on the substrate using a Laurel WS-650-23. The deposition was done either before or after starting the spinning process in order to determine which technique better achieves the objectives. The substrates were not heated, heated only before deposition, or heated before and after deposition. The heat was involved in an attempt to avoid cracking. Solutions of different weight percent PVDF were investigated, along with varying RPMs and spinning time intervals. In the experiments where deposition was before spinning, various accelerations were also attempted, but such variations were not necessary when the solution was dropped after spin initiation. Samples were analyzed using a Hitachi S-4800 II Field Emission Scanning Electron Microscope (SEM) in conjunction with a Hitachi TM-1000. The conductive top layer in the device can easily be formed by Gold or Platinum being sputtered on top of the nanowire polymer composite, and is not discussed herein.

B. Results Discussion

One of the first issues that were addressed is whether depositing the solution before or after the spin coater was activated would produce the best film. A few initial attempts showed that deposition after activation was better since the alternative would produce highly cracked films that would not adhere to the Silicon wafer. However, this was found to be true for relatively low accelerations and RPMs. When a high acceleration was used to quickly gain an RPM of about 3000, acceptably uniform yet thin films were obtained for depositions before spinning. Regardless, the results discussed, unless otherwise mentioned, are for depositions done after initiating spinning. The seemingly ideal RPM discovered from various attempts is a range from 1500 to 2000. Likewise a preferable composition for the solution was found to be about 22 percent. The vast majority of experiments with varying composition, time, and RPM yielded highly cracked layers as depicted in Figure 2. Experiments involving heat generally yielded coatings with a rough and thus undesirable topography (see Figure 3). However, in some cases the uniform layer shrunk when heated. Table 1 summarizes the parameters of the notable results. Figure 4 shows a relatively uniform layer compared to Figure 2, but the 3 µm height makes it unacceptable. An SEM image of the layer shown in Figure 4 is also shown in Figure 5 revealing that the height of this layer is around 3 µm. Figure 5 also reveals that the layer is made by a conjugation of tiny PVDF beads. Whether such a rough consistency affects the piezoelectric performance of the coating is unknown, but experiments have shown that heating the layer after it is formed dissolves the beads.
IV. Conclusions

The electricity generating device, from a theoretical standpoint, is fully possible. ZnO nanowires are much studied, understood, and easily produced; however, the formation of an acceptably thick PVDF film proves challenging under the current techniques. The ideal parameters for a uniform layer seem to be a composition of 22% PVDF and a RPM range of 1500-2000 deposited while spinning. These factors yielded a uniform coating of about 3 µm thick. Most parameters outside the ones stated yielded layers with intense cracks, but involving heat in the process produced layers with a rough contour or a uniform but decreased thickness. Further work, such as multiple coatings of the favorable parameters or small variations in spin time and composition will have to be performed in order to obtain a thicker layer. Also, continued work would include efforts to ensure the piezoelectric property of the PVDF film and the construction of a mechanism to measure the electricity produced from the entire device. Future studies would also include an analysis of expected electrical gains based on typical aircraft in-flight behavior.

Acknowledgements

The author would like to express appreciation to mentors Michael Oye and Jovi Gacusan for allowing this opportunity and making available their resources for the pursuance of this project. The work discussed herein was performed at the University of California Santa Cruz Materials Analysis for Collaborative Science (MACS) facility at the NASA Ames Research Center.
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