Fabrication and Analysis of High Sensitivity Biochemical Sensors Using PMN-PT Single Crystal Thin Membranes

Michael Frank, Saravana Pitchaikani, Kee S. Moon+, Samuel K. Kassegne++

+ Mechatronics Lab, ++MEMS Research Lab,

Department of Mechanical Engineering, College of Engineering, San Diego State University,

5500 Campanile Drive, San Diego, CA 92182-1323. Tel: (619)-594-4046

SAN DIEGO STATE UNIVERSITY

ABSTRACT

In this poster, we report the results of the Hydrochloric Acid (HCl) wet etching process to fabricate a PMN-PT single crystal piezoelectric thin membrane. A piezoelectric thin membrane can offer the ability to passively sense vibrations without power requirements. Furthermore the new generation oxide material exhibits extraordinary piezoelectric properties. The material, the single-crystal solid-solutions (1-x)Pb(Mg1/3Nb2/3)O3-xPbTiO3 (PMN-PT), has been shown to possess piezoelectric coefficients and electromechanical coupling responses significantly larger than conventional ceramics. A four-fold enhancement in piezoelectric coefficients and much higher efficiencies in electrical to mechanical energy conversions have been found. Use of a PMN-PT sensor to detect, with high sensitivity, minute amounts of waterborne pathogenic bacteria such as E. coli O157:H7 is one promising direct application. Design of a compact and portable PMN-PT sensor device used in produce packaging facilities and grocery stores is a primary focus. In this paper, we present the research results produced from the experimental work for the PMN-PT wet etching in HCl solution.

INTRODUCTION

PMN-PT is a piezoelectric transducer which can be used with a biochemical sensing element (gold) to measure the effect of surface mass change on the resonant frequency of the sensor. Resonant frequency changes are directly proportional to mass changes on the sensor, such that an increase in the mass of the sensor results in a decrease in the resonant frequency. The physics for this relationship is based upon Sauerbrey's formula (listed in the box below).

Possible uses for PMN-PT are widespread because of its high sensitivity, high quality value, high dielectric constant, low dielectric loss, high electromechanical coupling coefficient, and high piezoelectric coefficient. Piezoelectric single crystals of PMN-PT have shown superior properties to piezoelectric ceramics and piezoelectric films in device applications. The wet etch rate of PMN-PT with concentrated HCl at 80ºC to form a thin PMN-PT membrane (5µm) is determined.

Equation from Sauerbrey's Formula

$$\Delta f = -\frac{2 f_0^2 \Delta m}{A\sqrt{\rho_q \mu_q}} = -2.26\times 10^6 f_0^2 \frac{\Delta m}{A}$$

f_0 – Resonant frequency (Hz)

Δf – Frequency change (Hz)

P – Density (quartz = 2.648 g/cm³)

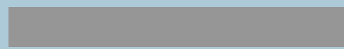
μ - Shear modulus (quartz = 2.947 x 10^11 g/cm.s²)

A – Piezoelectrically active area between electrodes (m²)

Δm – Mass change (g)

FABRICATION OF THE CHIP

Silicon Wafer



Single crystal PMN-PT (20µm)

Electrode pattern (circular interdigitated electrode) Gold And Chromium (100 µm each)

Wet etching of silicon

Thinning PMN-PT film to 5 µm using Conc. HCl

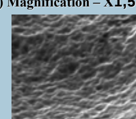
Table 1: Etching Rate of PMN-PT in Conc. HCl at 80ºC

Time Etched (in minutes)	Total Thickness Etched (in µm)	Total Etch Rate (in µm/min)	Per Side Etch Rate (in µm/min)
20	12	0.6	0.3
40	20	0.5	0.25
180	100	0.556	0.278

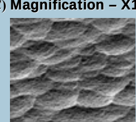
Figure 1: PMN-PT Surface After 3 Hours of Etching in Conc. HCl at 80ºC

A) Magnification – X150

B) Magnification – X1,500



C) Magnification – X10,000



PMN-PT PATHOGEN DETECTION DEVICE

Figure 2: Exploded view of various layers of PMN-PT microbalance system with PMN-PT chip and PDMS

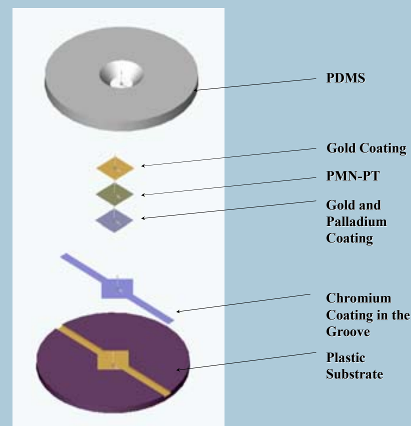
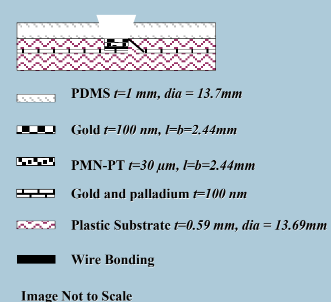


Figure 3: Cross-section of Various Layers of PMN-PT Microbalance System with PMN-PT Chip and PDMS



ACKNOWLEDGEMENT

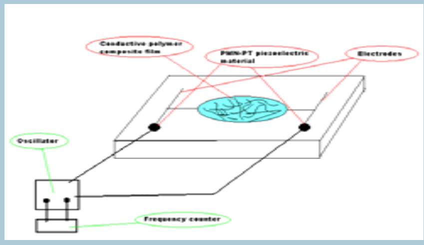
We would like to thank our research advisors Sam Kassegne, PhD and Kee Moon, PhD for their continuous follow-up on this project, valuable comments, and useful suggestions. Also, we received assistance from INRF-UCI, Matthew Haynes, and Tricia Nguyen. Our sincere thanks goes to SDSU CSRC for printing this poster.

CONCLUSION

Our research represents the first study of its kind to specify the etch rate of PMN-PT in concentrated HCl (38% acid) at 80ºC. The use of HCl to etch PMN-PT represents an economic alternative to Deep Reactive Ion Etching (DRIE). After repeating the etch rate experiment with HCl multiple times, we found that pre-treating the PMN-PT sample in HCl for 5-10 minutes makes for a suitable substrate to ensure good adherence to SU-8 when it is applied. SU-8 is a common photoresist used in negative photolithography.

Additionally, the use of PMN-PT for pathogen detection is a viable option which will be further explored. Anthrax spores have been detected *in situ* using a thin membrane PMN-PT layer within an aqueous environment at a very high sensitivity and high quality value [1]. Our group will continue to focus on creation of a PMN-PT sensor device that can detect food and waterborne pathogenic bacteria such as *E. coli* O157:H7 and *Salmonella*.

Another pursuable application for PMN-PT is to couple it with a thin layer conducting polymer sensitive to gas in order to measure specific oscillation frequencies for volatile gases like acetone, methanol, and benzene. Composite conducting polymers swell to varying degrees when exposed to volatile gases. Polypyrrole/Poly(methylmethacrylate) (PPy/PMMA) composite film exposed to acetone demonstrated a higher amount of swelling in PMMA than in PPy, thus decreasing the conductivity of the composite film [2]. Polyaniline/Polystyrene (PAni/PS) composite film exposed to polar alcohols (e.g. methanol) increased the conductivity of PAni due to higher solubility and greater swelling compared to PS [3]. A change in conductivity sensed by electrodes connected to PMN-PT would register a specific resonant oscillation measurable by a frequency counter.



REFERENCES

[1] McGovern, J.P.; Shih, W.Y.; Shih, W.H. *In situ* detection of *Bacillus anthracis* spores using fully submersible, self-exciting, self-sensing PMN-PT/Sn piezoelectric microcantilevers. *Analyst* 2007, 132, 777-783.

[2] Ruangchuay, L.; Sirivat, A.; Schwank, J. Polypyrrole/poly(methylmethacrylate) blend as selective sensor for acetone in lacquer. *Talanta* 2003, *60*, 25-30.

[3] Segal, E.; Tchoudakov, R.; Narkis, M.; Siegmann, A.; Wei, Y. Polystyrene/polyaniline nanoblends for sensing of aliphatic alcohols. *Sens. Actuators B* 2005, *104*, 140-150.