REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)*	**2. REPORT TYPE**	**3. DATES COVERED** *(From - To)*
08/06/2012	Final Technical	05/05/2010 -05/04/2012

4. TITLE AND SUBTITLE
Piezoelectric and Semiconducting Ribbon for Flexible Energy Harvesting

5a. CONTRACT NUMBER

5b. GRANT NUMBER
N66001-10-1-2012

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Michael McAlpine

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
The Trustees of Princeton University
4 New South Building
P O Box 36
Princeton, NJ 08544

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Space and Naval Warfare Systems Command

10. SPONSOR/MONITOR'S ACRONYM(S)
SPAWAR

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Available to the Public

13. SUPPLEMENTARY NOTES

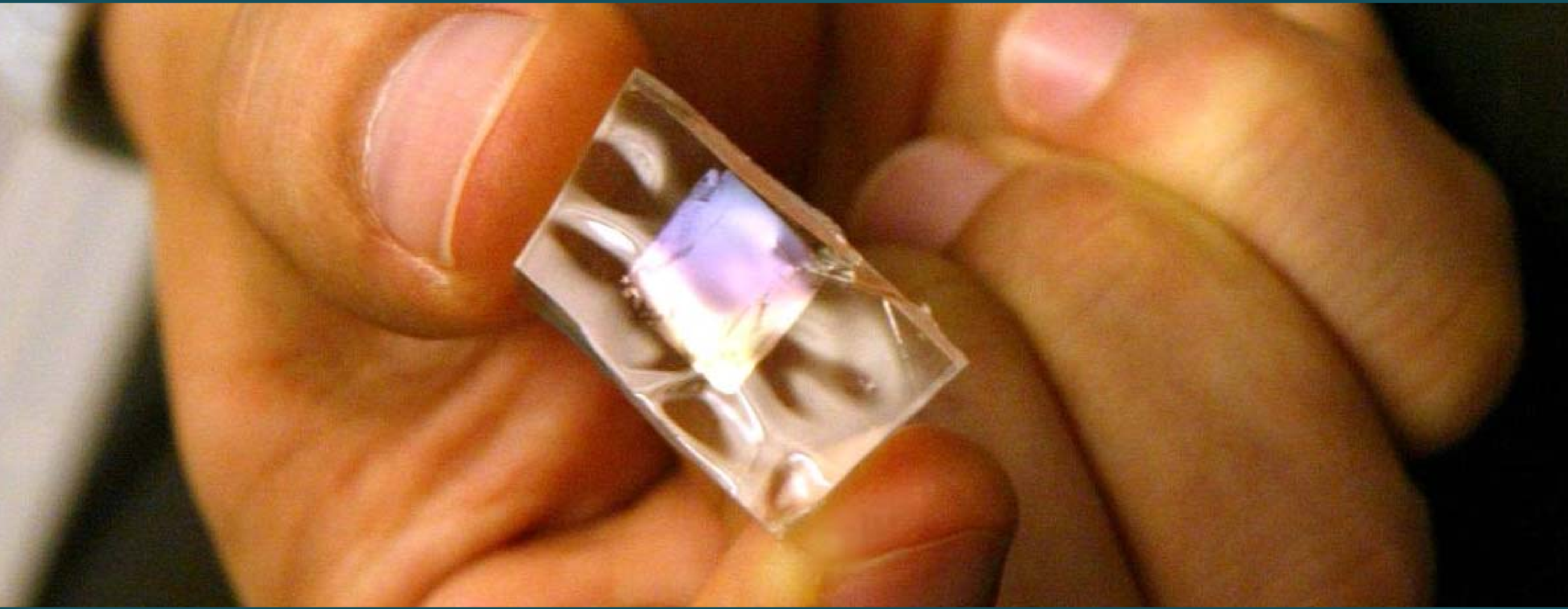
14. ABSTRACT
The objective of this proposal is the hierarchical assembly of piezoelectric and semiconducting ribbons onto a common polymeric platform for thin, flexible energy harvesting. In particular, we aim to reach a target output of 5 mW at 100 Hz. The development of a method for integrating highly efficient energy conversion materials onto stretchable, biocompatible rubbers could yield breakthroughs in implantable or wearable energy harvesting systems. Being electromechanically coupled, piezoelectric crystals represent a particularly interesting subset of smart materials which function as sensors/actuators, bioMEMS devices, and energy converters. Yet, the crystallization of these materials generally requires high temperatures for maximally efficient performance, rendering them incompatible with with temperature-sensitive plastics and rubbers. Here, we propose overcoming these limitations by presenting a scalable and parallel process for transferring crystalline piezoelectric ribbons of lead zirconate titanate (PZT) from host substrates onto flexible plastics over macroscopic areas. The ribbons are fabricated from single crystal, stoichiometric films of PZT, allowing for exceptional control over the composition and, consequently, the performance characteristics of these materials.

15. SUBJECT TERMS
Nanotechnology, Electromechanical energy harvesting, Biocompatible piezoelectrics, Nanomaterials

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Michael McAlpine
U	U	U	UU	45	**19b. TELEPHONE NUMBER** *(Include area code)* 609-542-0275

Reset

Biointerfaced Nanopiezoelectrics



Michael McAlpine
Princeton University

Milestones (5/5/10–5/5/12)

Tasks	*Accomplishments*
1 – PZT Ribbon Fabrication (a) Optimize film growth (b) Fabrication of ribbons	***1 – PZT Ribbon Fabrication*** ✓ Single-crystal, stoichiometric films have been grown and nanoribbons defined over 2” diameter areas
2 – PZT Ribbon Transfer to Plastic (a) Optimize transfer to flexible substrates (b) Scale transfer process to 2” areas	***2 – PZT Ribbon Transfer to Plastic*** ✓ We have been able to achieve transfer onto a variety of substrates, including elastomers, plastics, and silk, over 2” diameter areas
3 – Charge Constant Metrics (a) Maximize d_{33} on MgO by PFM (b) Maximize d_{33} on plastic by PFM	***3 – Charge Constant Metrics*** ✓ We have achieved the highest piezoelectric charge constant (d_{33} = 150 pm/V) ever on a flexible platform
4 – PZT Energy Harvesting Device (a) Interdigitated electrode fabrication (b) Power output test	***4 – PZT Energy Harvesting Device*** ✓ Achieved voltage outputs of 1.5 V (peak-to-peak) and power outputs of 10 mW/cm^3 in both stretching and flexing operation modes
5 – Heterogeneous Interfacing With Body (a) Integration of piezoelectric nanomaterials directly with the body for energy harvesting	***5 – Heterogeneous Interfacing with Body*** ✓ Demonstrated interfacing with cells, and direct biointerfacing with cow lungs for implantable on-body energy harvesting

Return on Investment – 1

- Total # of people employed: 1 Faculty (Prof. Michael C. McAlpine), 1 graduate student (Thanh Nguyen, graduating 6/2013), 2 postdocs (Dr. Yi Qi, now at GLOBALFOUNDRIES; Dr. Jihoon Kim, now at AZ Electronic Materials)
- # of new hires as a result of this funding: 1 (Dr. Jihoon Kim)
- # of newly trained scientists in this area: 3 (Nguyen, Kim, Qi)
- # of PhD theses initiated based on this work: 0 (I have only been as assistant professor for 4 years, not long enough to graduate someone yet)
- Discoveries utilized on other efforts / Follow-on funding: The results that we have achieved have led directly to a number of new projects and funding:
  - Army Research Office, “Buckled Piezoelectric Nanoribbons: Morphology, Nanomechanics, and Flexoelectricity,” $120k/yr for 3 yrs ($360k total)
  - Lockheed Martin, “Investigation of Wireless Energy Harvesting,” $50k total
  - Essig-Enright and Insley Blair Pyne Funds, “Studying Neuron Biomechanics via Interfacing with Piezoelectric Nanowires,” $52.5k/yr for 2 yrs ($105k total)
- Patents Filed: 2
  - M. C. McAlpine, Y. Qi. Buckled and Wavy Piezoelectric Ribbons for Stretchable Energy Harvesting Devices. U.S. Patent Pending 61/422,808.
  - M. C. McAlpine, Y. Qi. Flexible Piezoelectric Structures and Method of Making Same. U.S. Patent Pending 12/727,798.

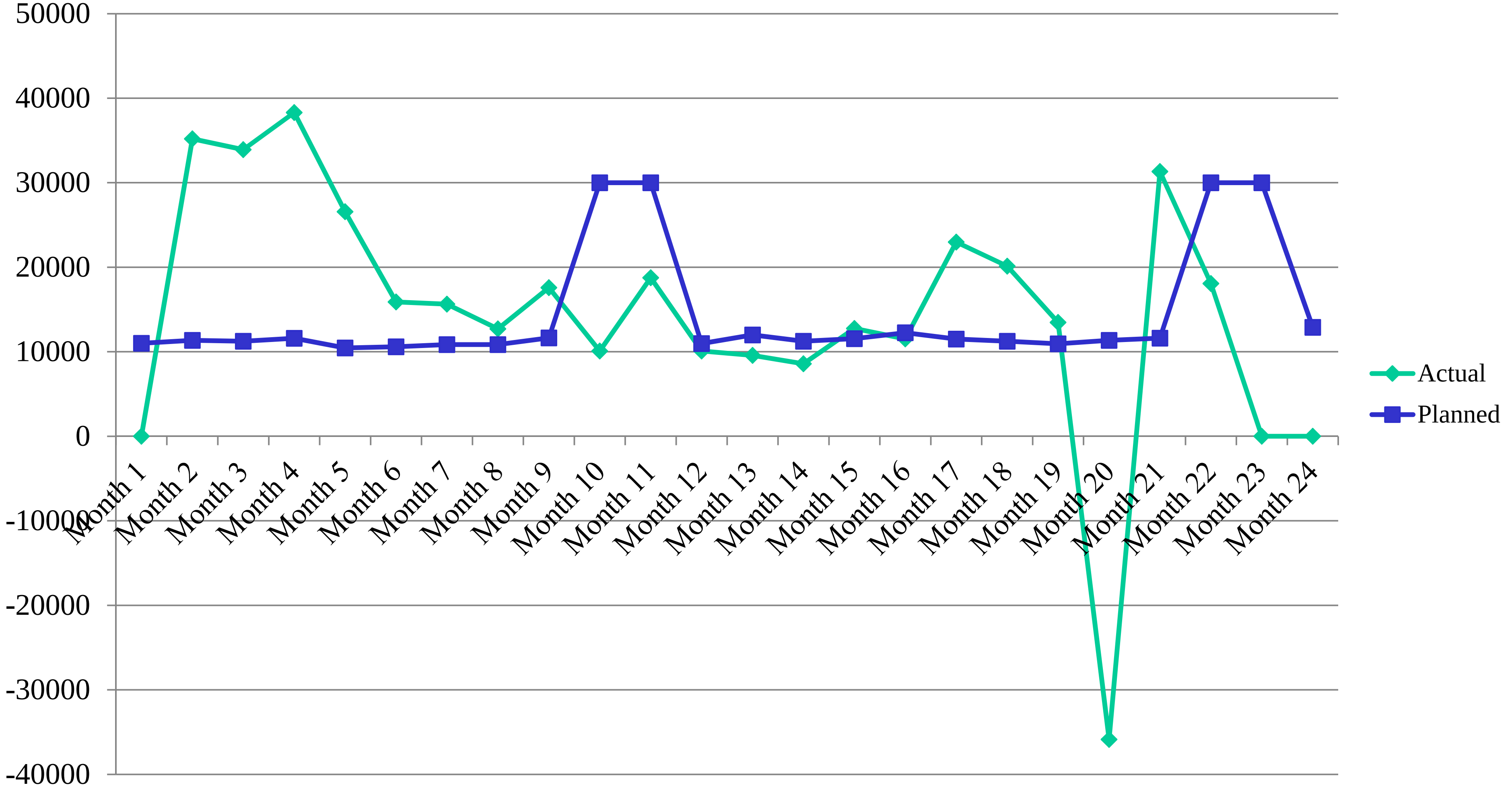
Return on Investment – 2

- Papers and Books Published: 6 total:
  - T. D. Nguyen, N. Deshmukh, J. M. Nagarah, T. Kramer, P. K. Purohit, M. J. Berry, M. C. McAlpine. "Piezoelectric Nanoribbons for Interfaced Cellular Nanomechanics." *Nature Nanotechnology* (2012).
  - Y. Qi, T. D. Nguyen, J. Kim, M. C. McAlpine. "Stretchable Piezoelectric Nanoribbons for Biocompatible Energy Harvesting." Invited Book Chapter, in Stretchable Electronics, ed. Takao Someya (2013).
  - Y. Qi, J. Kim, T. D. Nguyen, B. Lisko, P. K. Purohit, M. C. McAlpine. "Enhanced Piezoelectricity and Stretchability in Energy Harvesting Devices Fabricated from Buckled PZT Ribbons." *Nano Lett.* **11**, 1331-1336 (2011). [Featured in *Nature*: M. H. Lee, A. Javey. "Power Surfing on Waves." *Nature* **472**, 304-305 (2011).]
  - T. D. Nguyen, J. M. Nagarah, Y. Qi, S. S. Nonnenmann, A. V. Morozov, S. Li, C. B. Arnold, M. C. McAlpine. "Wafer-Scale Nanopatterning and Translation into High Performance Piezoelectric Nanowires." *Nano Lett.* **10**, 4595-4599 (2010).
  - Y. Qi, M. C. McAlpine. "Nanotechnology-Enabled Flexible and Biocompatible Energy Harvesting." *Energy Environ. Sci.* **3**, 1275-1285 (2010).
  - Y. Qi, N. T. Jafferis, K. Lyons, Jr., C. M. Lee, H. Ahmad, M. C. McAlpine. "Piezoelectric Ribbons Printed onto Rubber for Flexible Energy Conversion." *Nano Lett.* **10**, 524-528 (2010).

Return on Investment – 3

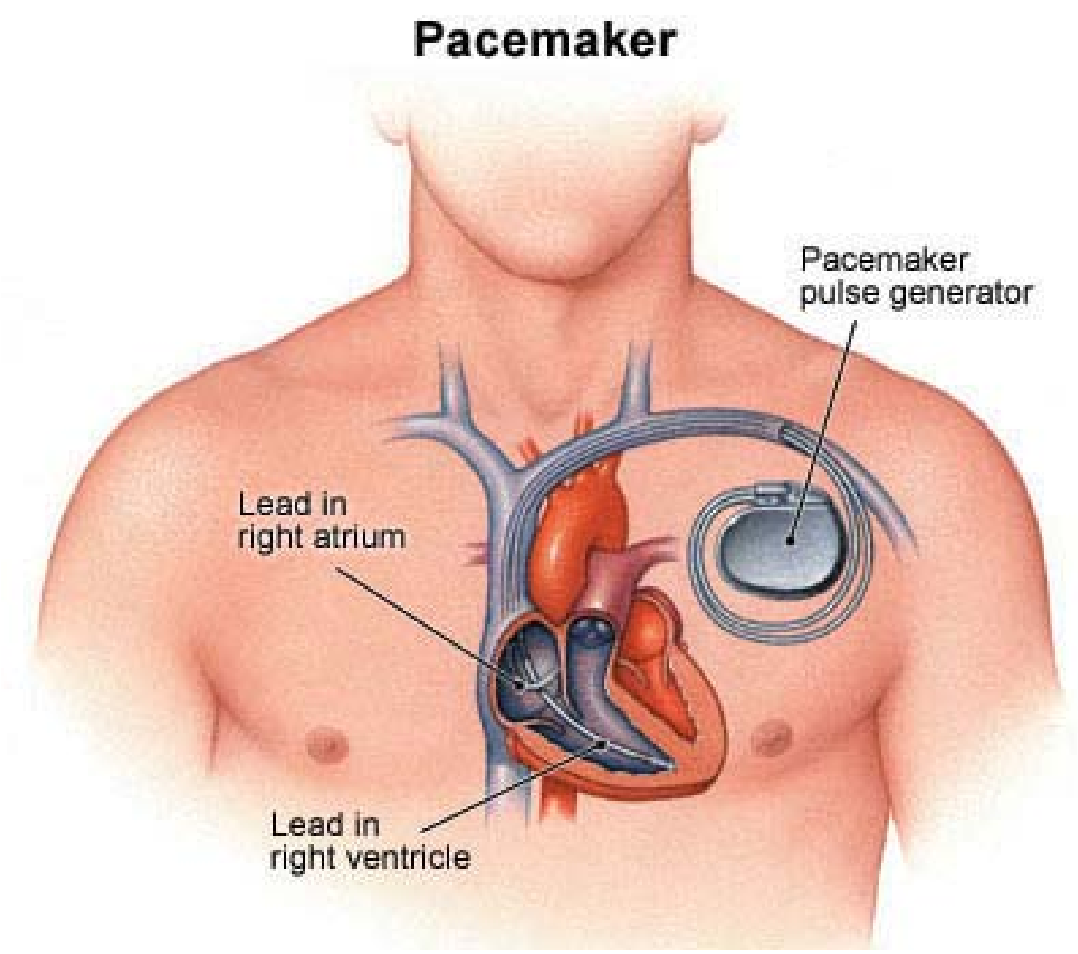
- Invited Presentations Related to This Work:
- 19. “Biointerfaced Nanodevices,” New York University, 10/31/12 (New York, NY).
- 18. “Biointerfaced Nanodevices,” University of California - Berkeley, 10/2/12 (Berkeley, CA).
- 17. “Biointerfaced Nanodevices,” Microsoft Research, 6/11/12 (Redmond, WA).
- 16. “Nanotechnology-Enabled Advances in Piezoelectric Energy Harvesting,” ONR International Workshop on Acoustic Transduction Materials and Devices, 5/10/12 (State College, PA).
- 15. “Nanotechnology-Enabled Advances in Biomedical and Energy Research,” University of Pennsylvania, 4/24/12 (Philadelphia, PA).
- 14. “Nanotechnology-Enabled Advances in Biomedical and Energy Research,” University of Texas at Austin, 3/28/12 (Austin, TX).
- 13. “Nanotechnology-Enabled Advances in Biomedical and Energy Research,” Georgia Institute of Technology, 3/19/12 (Atlanta, GA).
- 12. “Nanotechnology-Enabled Advances in Biomedical and Energy Research,” University of Illinois at Urbana-Champaign, 2/16/12 (Urbana-Champaign, IL).
- 11. “Nanotechnology-Enabled Device Interfacing with the Human Body,” Drexel University, 11/10/11 (Cherry Hill, NJ).
- 10. “Nanotechnology-Enabled Device Interfacing with the Human Body,” Lockheed Martin Advanced Technology Laboratories, 10/28/11 (Cherry Hill, NJ).
- 9. “Nanotechnology-Enabled Device Interfacing with the Human Body,” DuPont Central Research and Development, 6/25/11 (Wilmington, DE).
- 8. “Nanotechnology-Enabled Device Interfacing with the Human Body,” Keynote Speech at Freescale Technology Forum, 6/22/11 (San Antonio, TX).
- 7. “Nanotechnology-Enabled Interfacing of Devices with the Human Body,” Google Tech Talk, 6/6/11 (Mountain View, CA).
- 6. “Nanotechnology-Enabled Flexible Energy Harvesting,” SPIE Defense, Security, and Sensing Conference, 4/28/11 (Orlando, FL).
- 5. “Nanotechnology-Enabled Flexible Energy Harvesting,” Materials Research Society (MRS) Fall Conference, 12/1/10 (Boston, MA).
- 4. “Nanotechnology-Enabled Flexible Energy Harvesting,” IDTechEx Energy Harvesting & Storage USA, 11/17/10 (Boston, MA).
- 3. “Nanotechnology-Enabled Flexible Energy Harvesting,” Technology Review EmTech@MIT 2010 Conference, 9/23/10 (Cambridge, MA).
- 2. “Nanotechnology-Enabled Flexible Energy Harvesting,” Workshop on Nanomaterials for Alternative Energy Applications, University of British Columbia, 6/21/10 (Vancouver, BC, Canada).
- 1. “Nanotechnology-Enabled Flexible Energy Harvesting,” Princeton Technology Center, Schlumberger, 6/3/10 (Princeton, NJ).

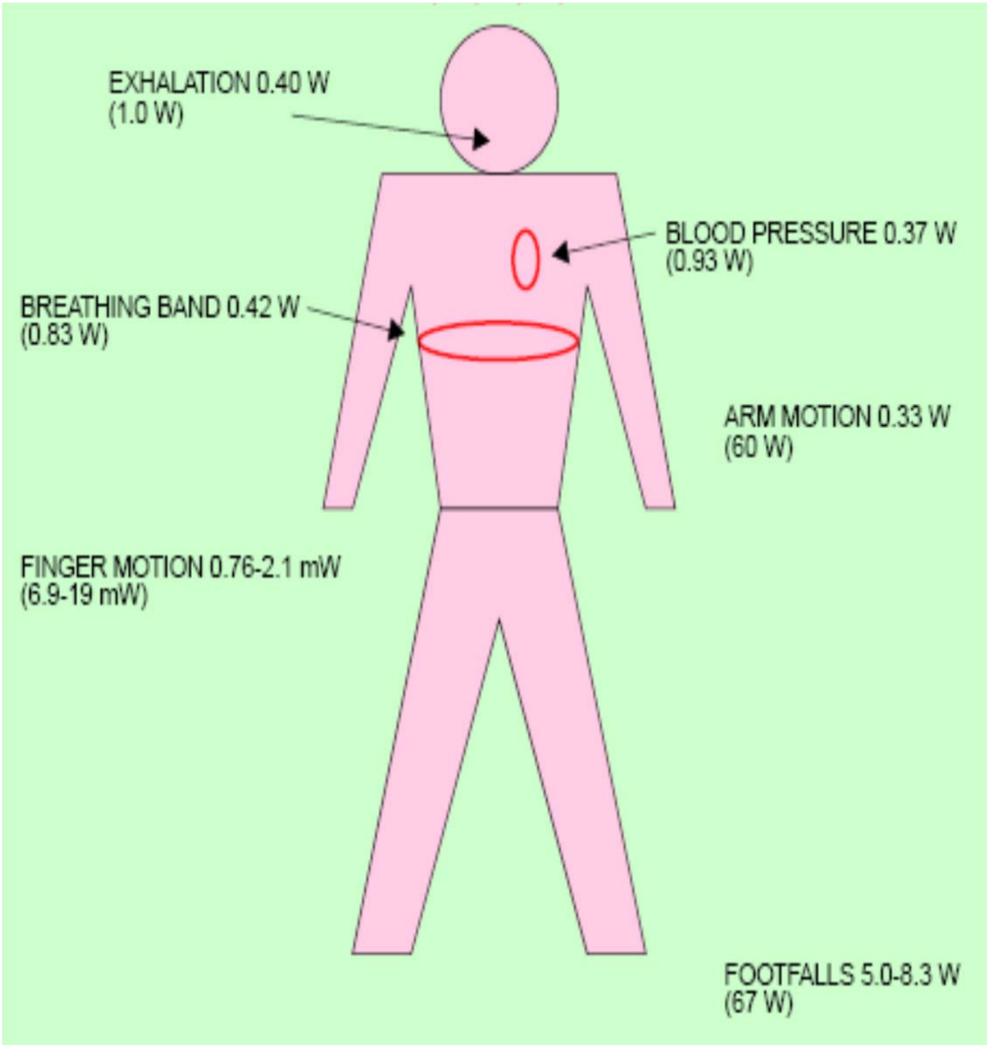
Spend Chart



Financials: 1) Percent of funds expended: 100%, 2) Total of funds expended: $347,193, 3) Total of funds remaining: $0

Human Power



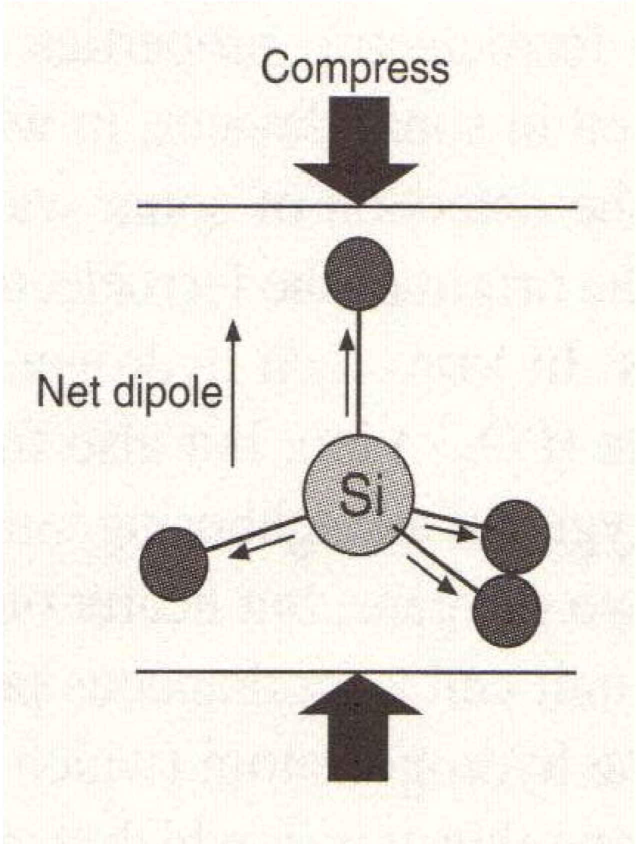


T. Starner, *IBM Syst J* 35, 618–629 (1996)

Piezoelectricity

Mechanical Energy

Sensor



Actuator

Electrical Energy

Energy

$$E \propto d_{33}^2 \sigma^2 V$$

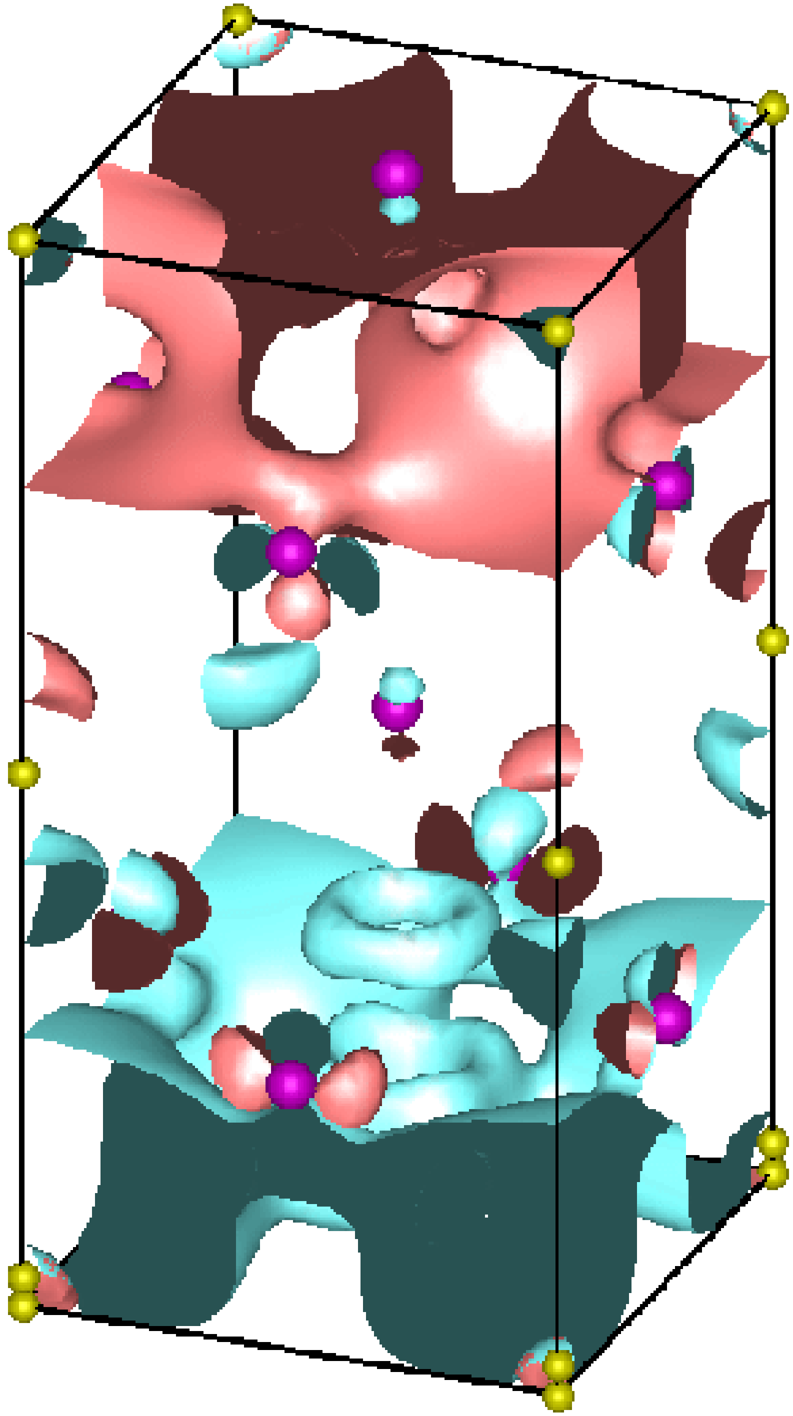
d_{33} (pm/V)	PZT	PVDF	Quartz	Bone
	250	25	2.5	.25

$$k_{33} \propto d_{33}$$

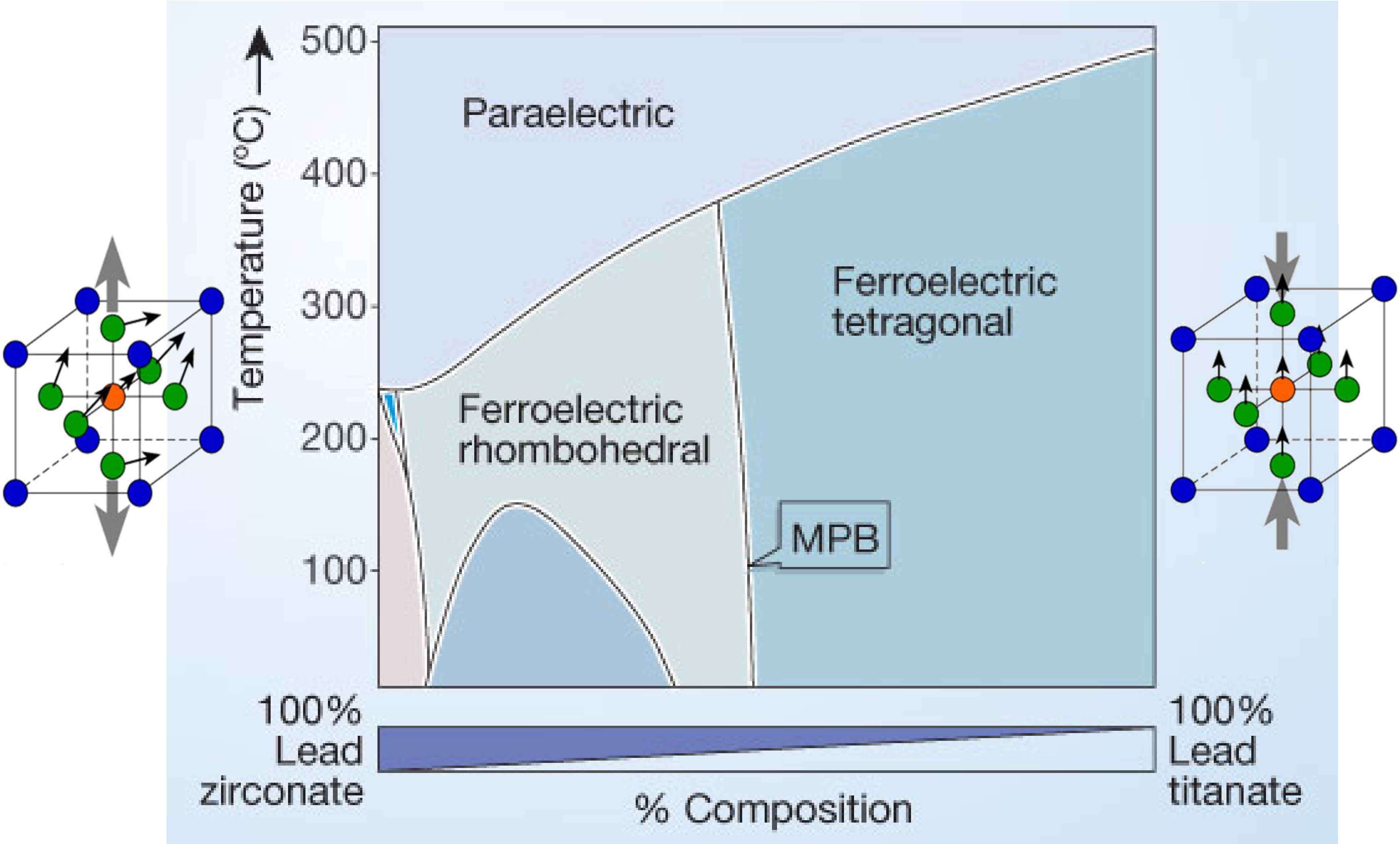
PZT > 80% Conversion Efficiency

S. R. Platt, *et al*, *IEEE Trans Mech* 10, 240-252 (2005)

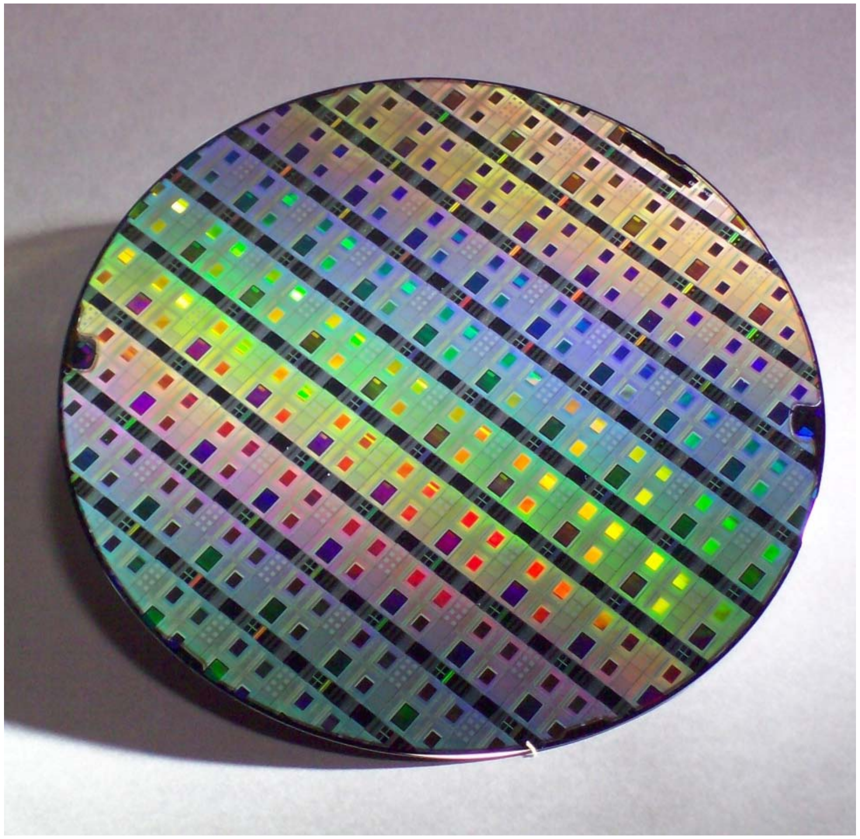
PZT



Phase Diagram

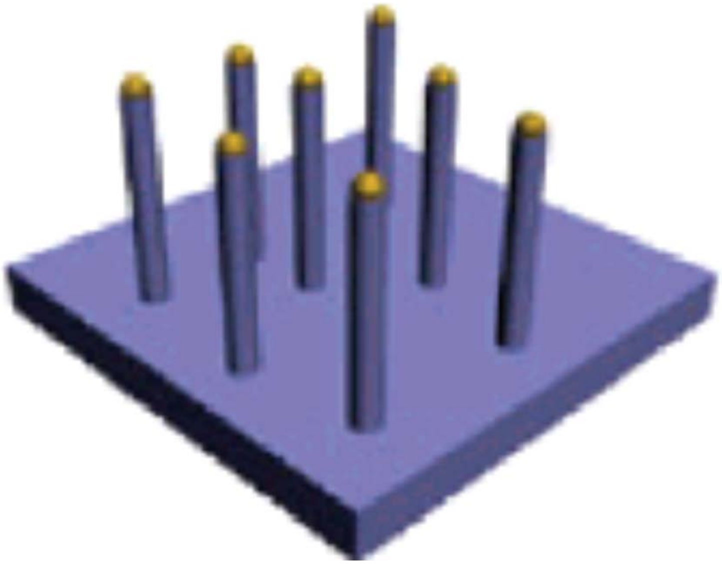


Dichotomy



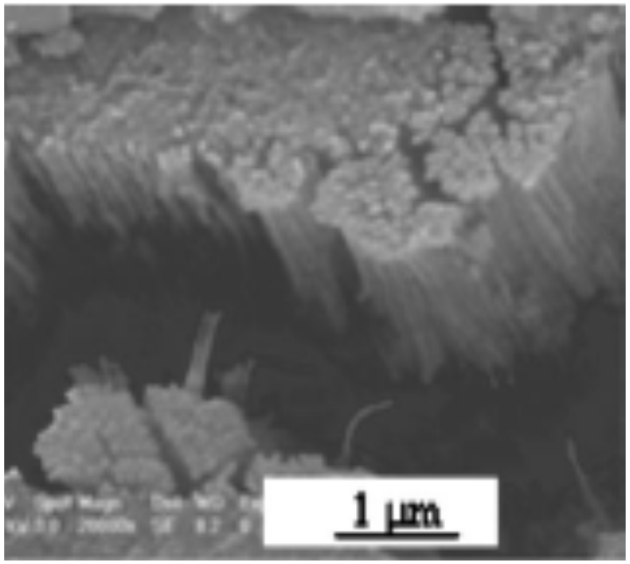
PZT Nanowires

VLS Growth – Lack of Catalysts



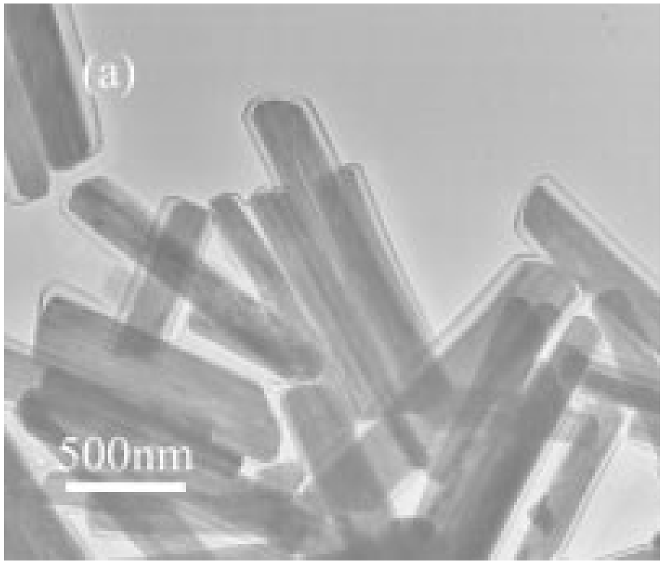
C. Zhou, *et al*, *Nano Lett* 4, 1241-1246 (2004)

Confined Templates – Polycrystallinity



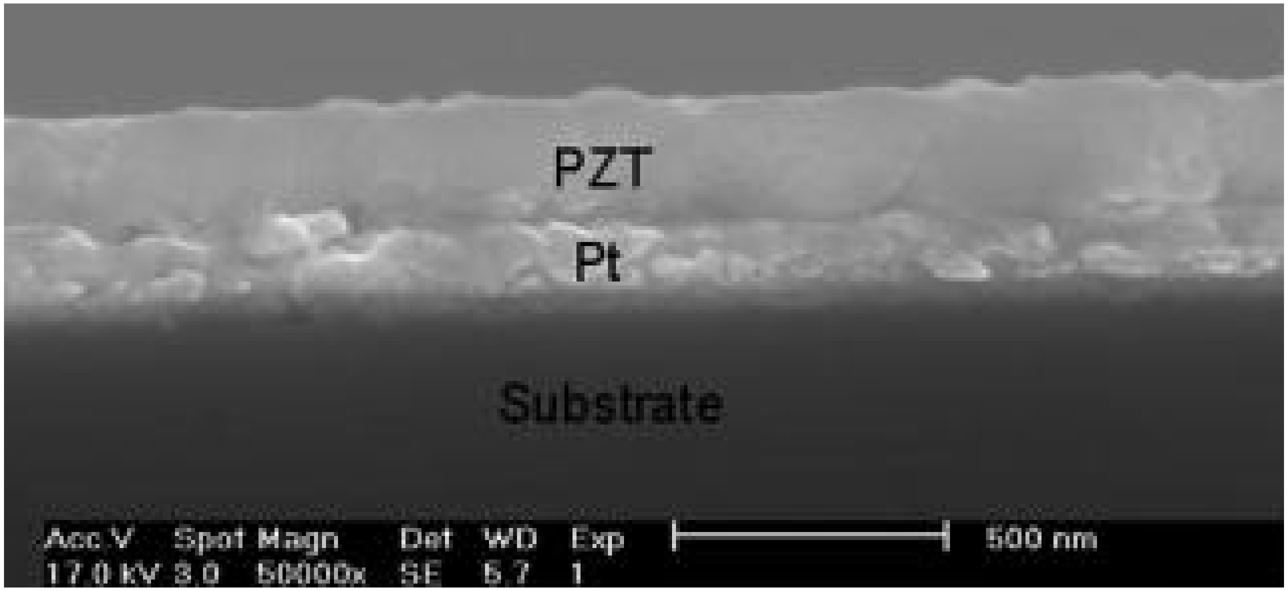
M. Alexe, *et al*, *Appl Phys Lett* 83, 440 (2003)

Hydrothermal – Stoichiometry

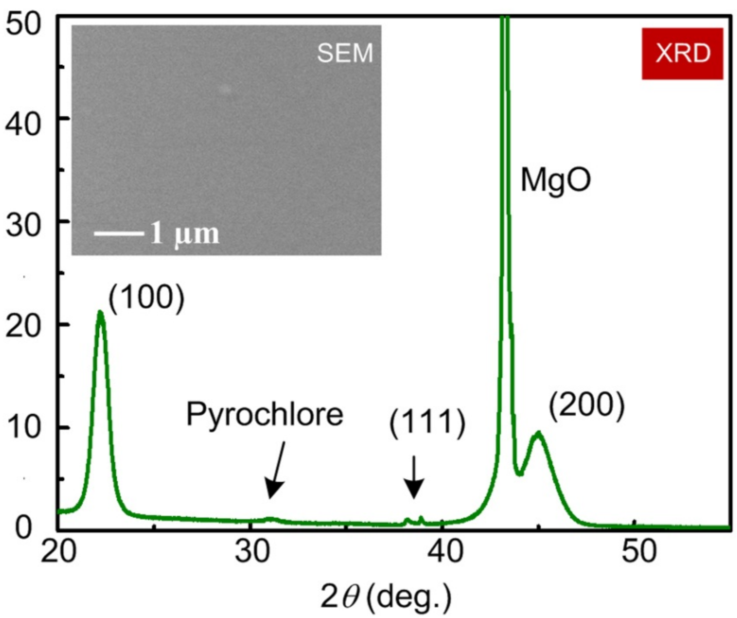


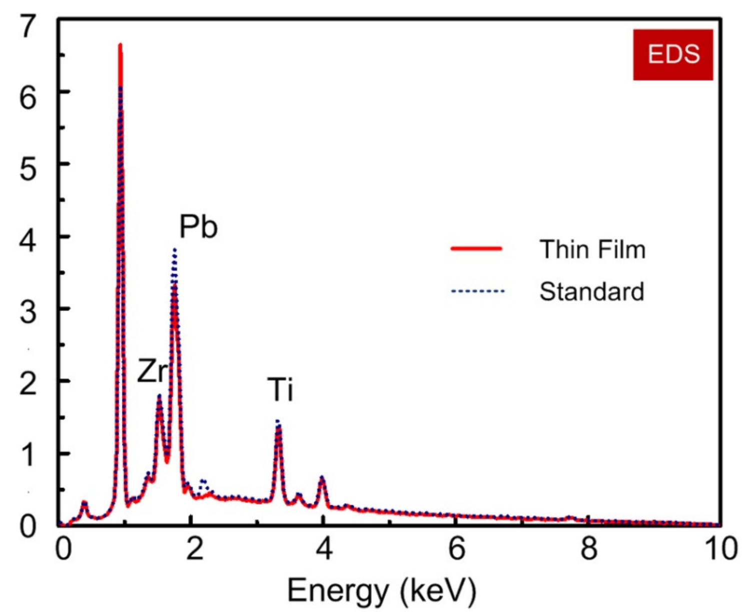
G. Han, *et al*, *Adv Mater* 17, 907-910 (2005)

Thin Film



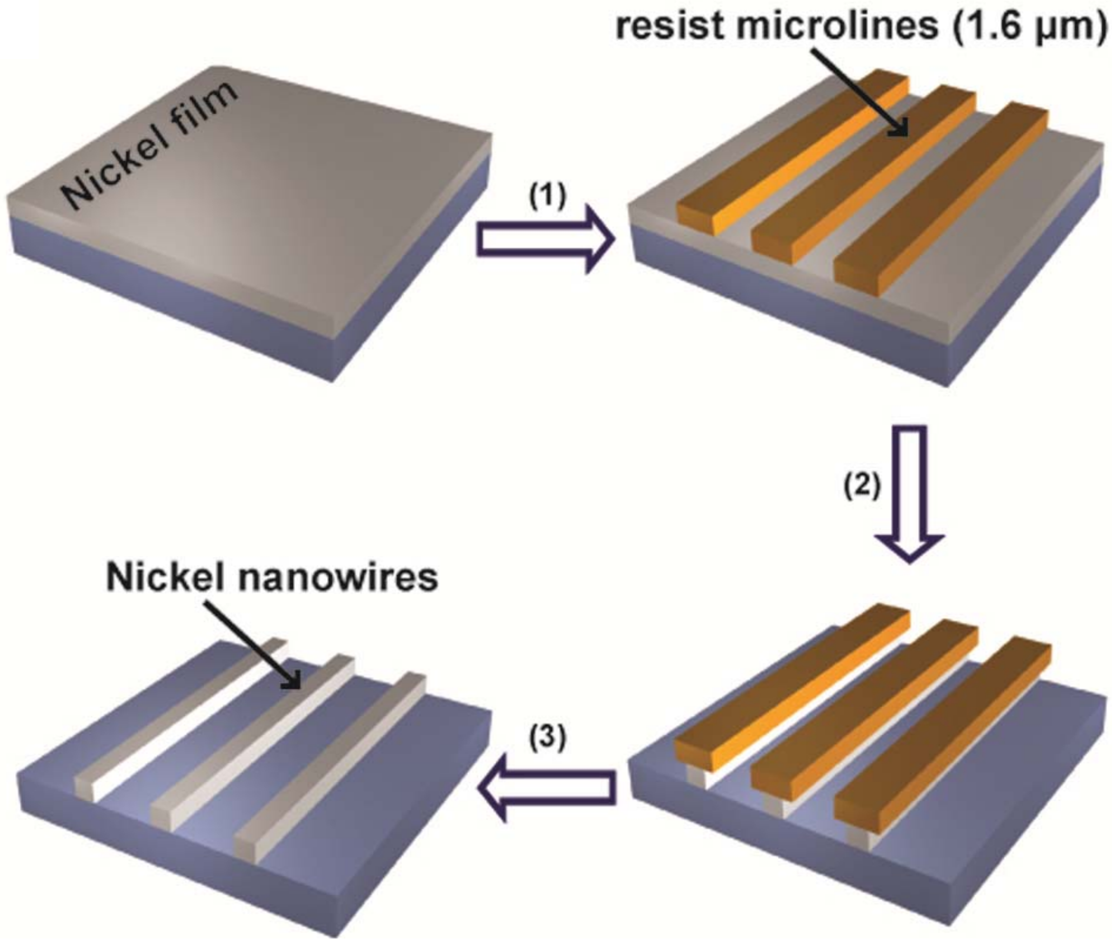
MgO	4.21
PZT	4.05
$SrTiO_3$	3.91

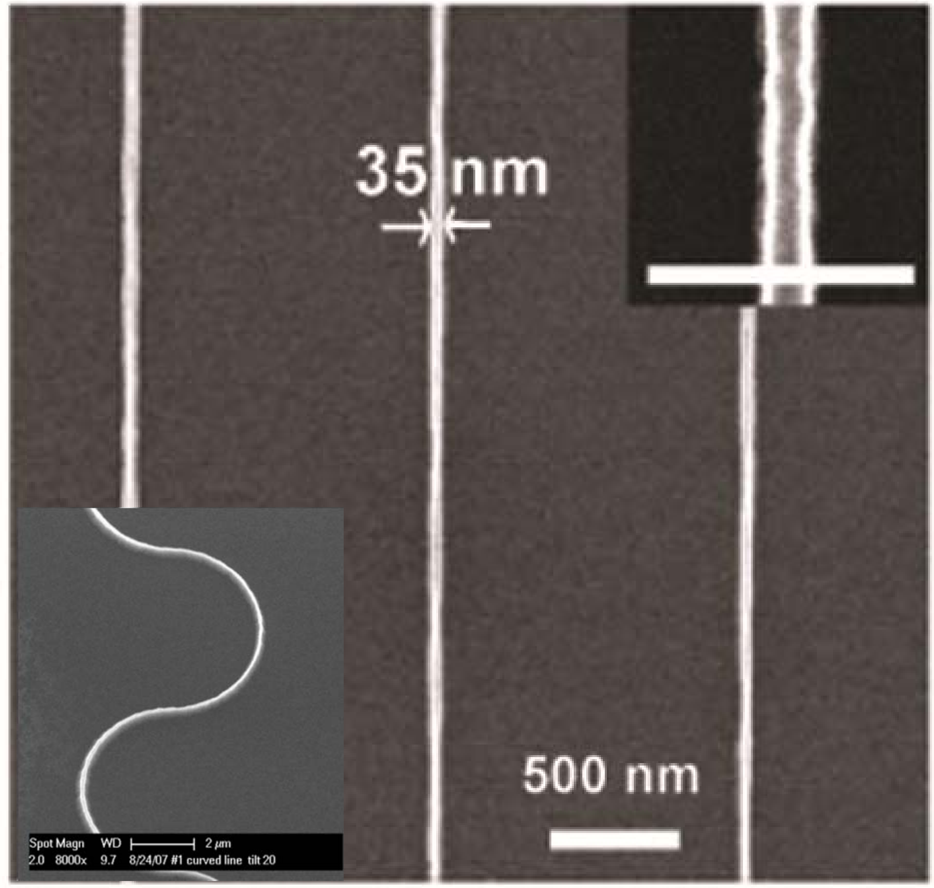




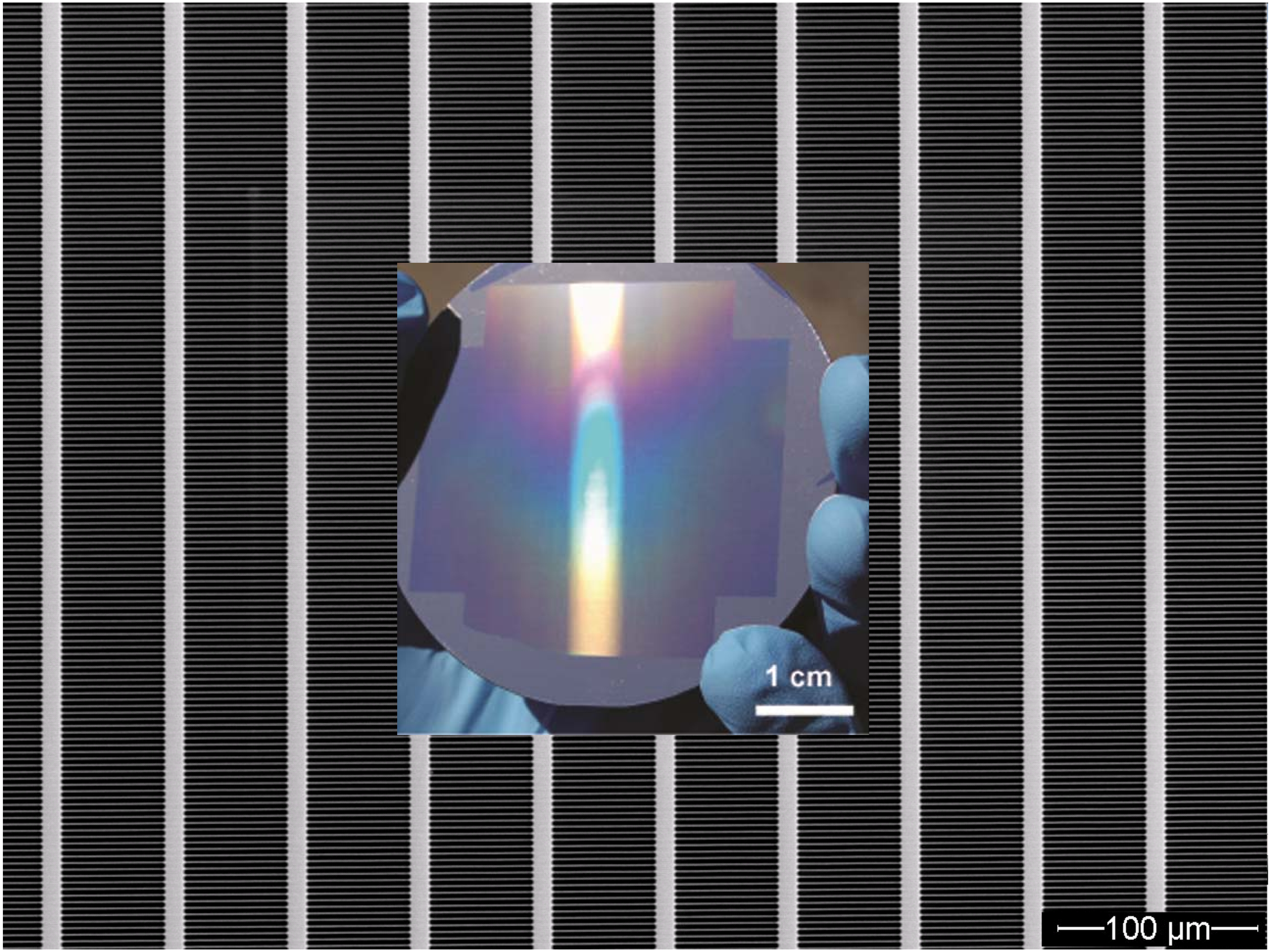
Post-anneal at 700 °C

PENCiL

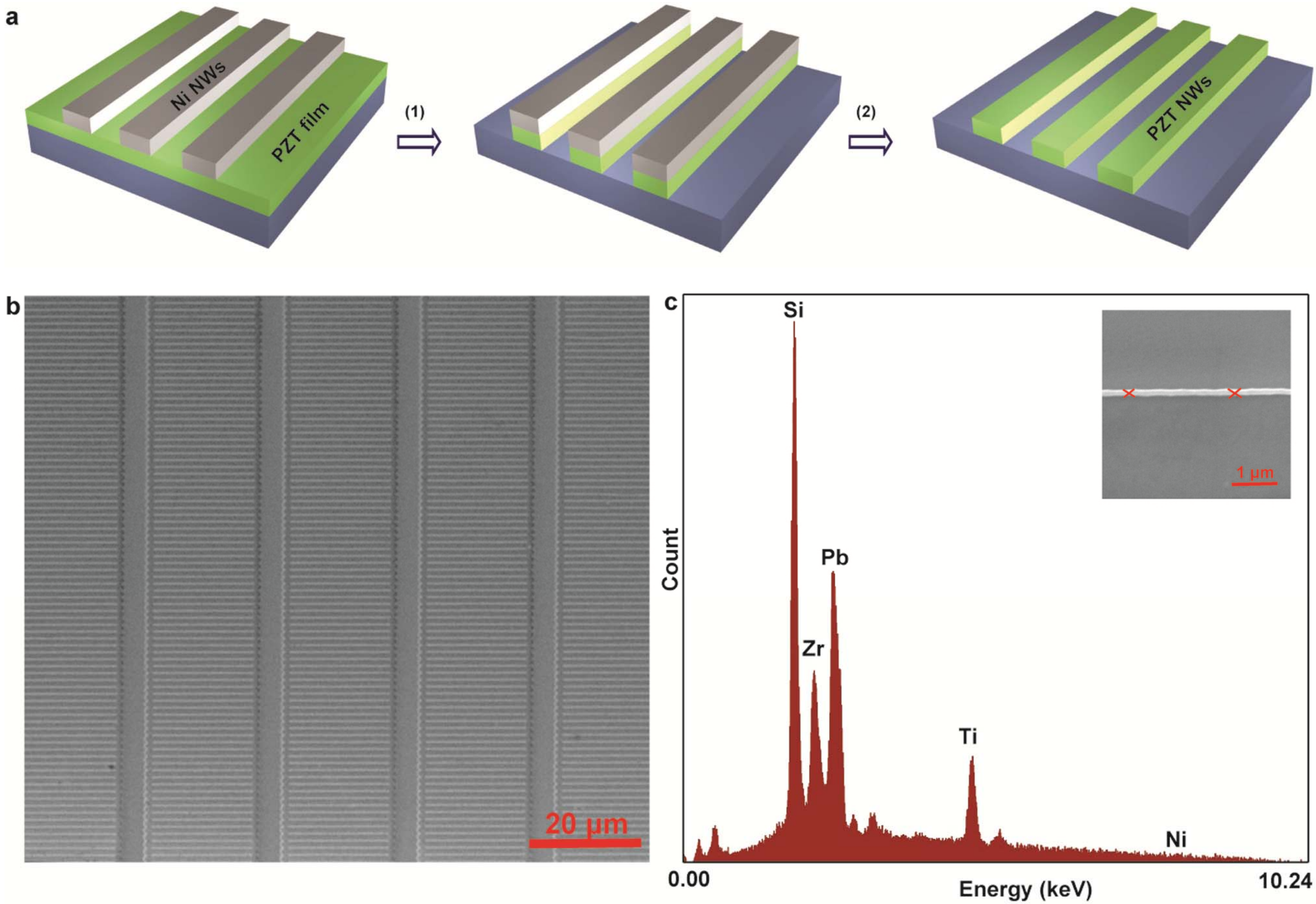

resist microlines (1.6 µm)
Nickel film
(1)
(2)
Nickel nanowires
(3)


35 nm
500 nm
Spot Magn WD 2 µm
2.0 8000x 9.7 8/24/07 #1 curved line tilt 20

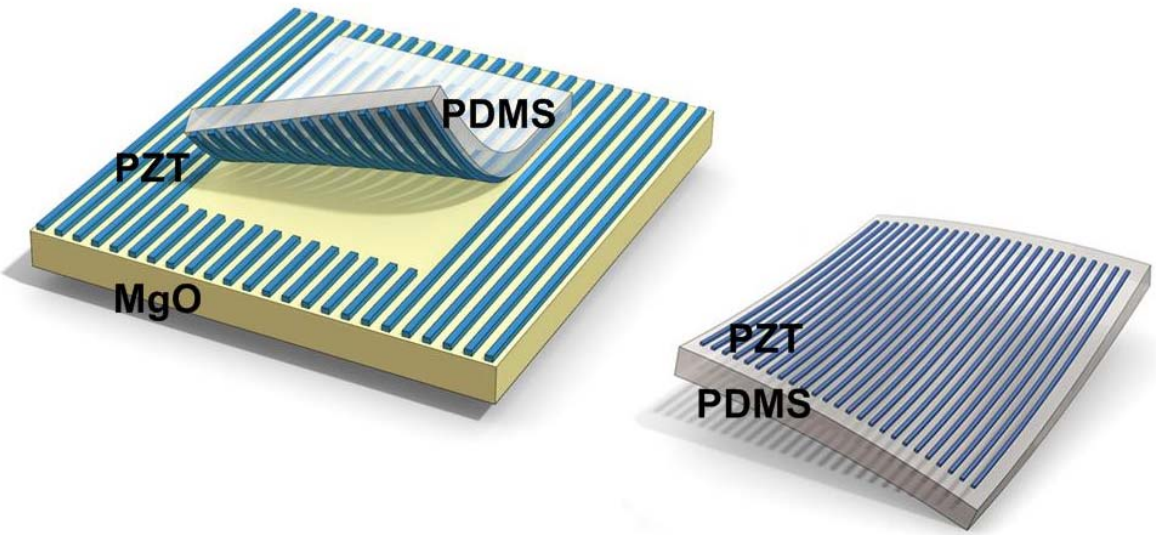
Wafer

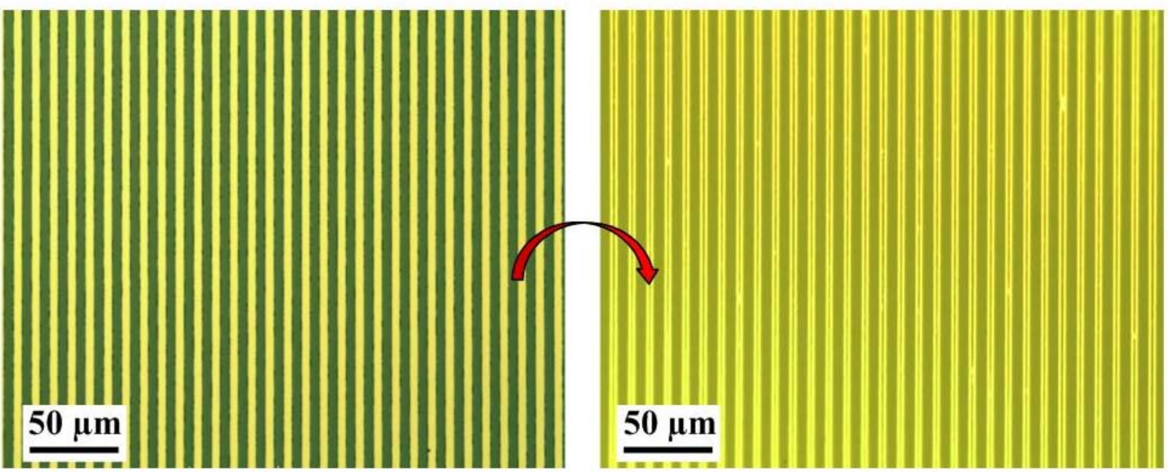


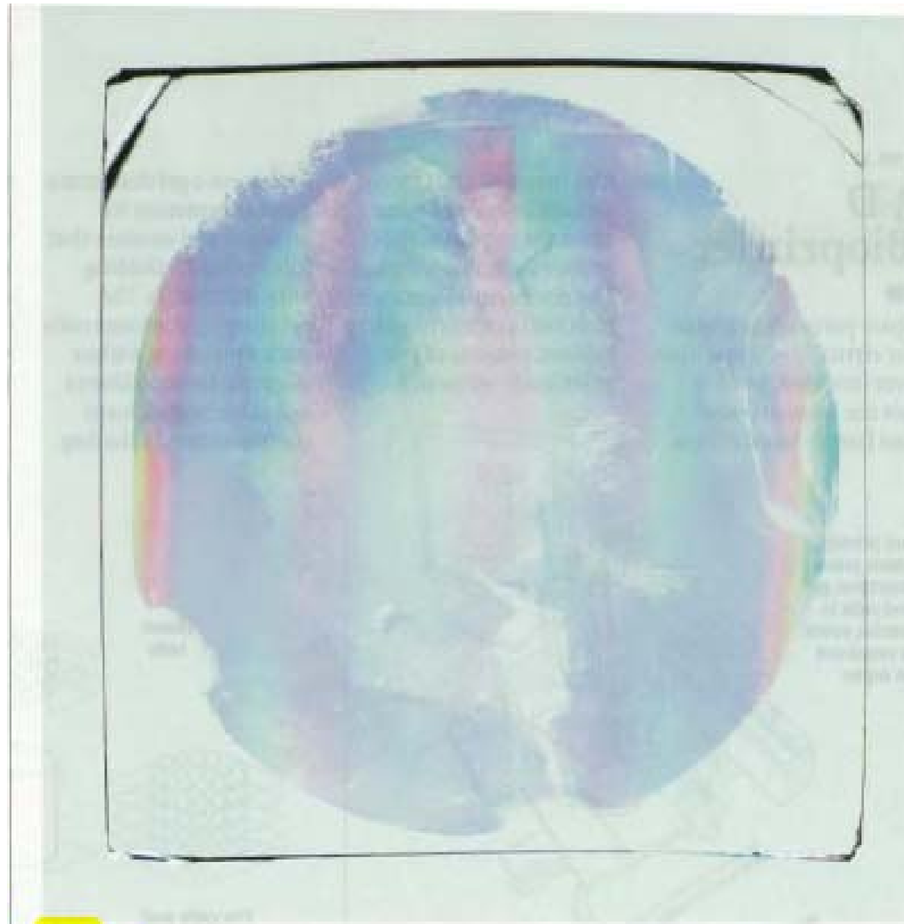
PZT NWs


a
Ni NWs
PZT film
(1)
(2)
PZT NWs
b
20 µm
c
Si
Pb
Zr
Ti
Ni
Count
0.00
Energy (keV)
10.24
1 µm

Printing





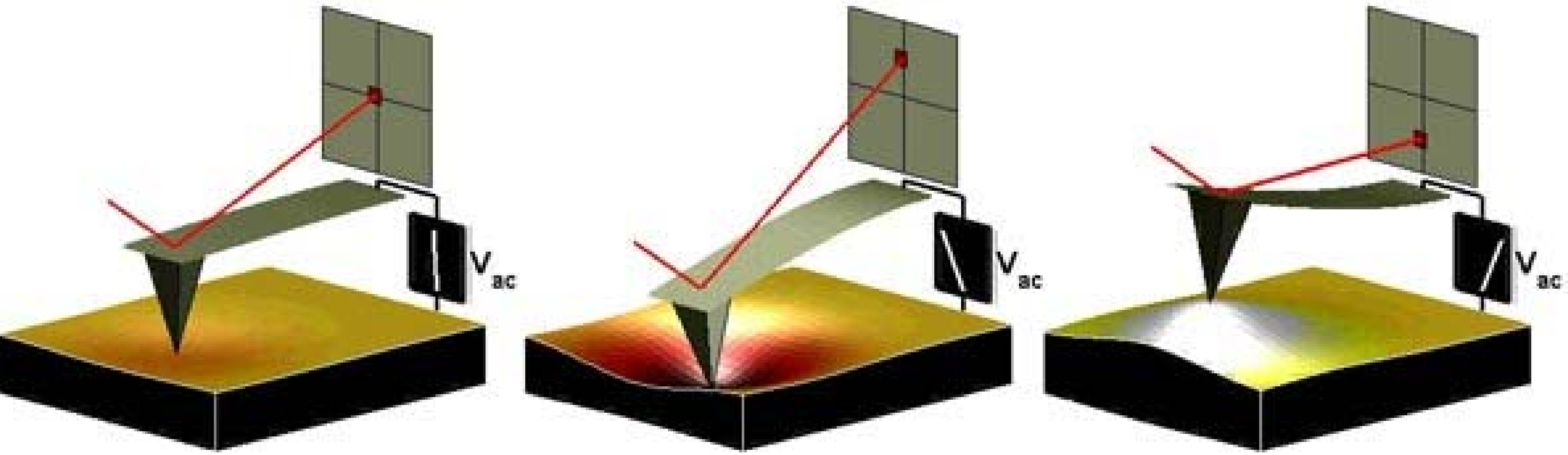


NOS. 40-42

Body-Powered Devices

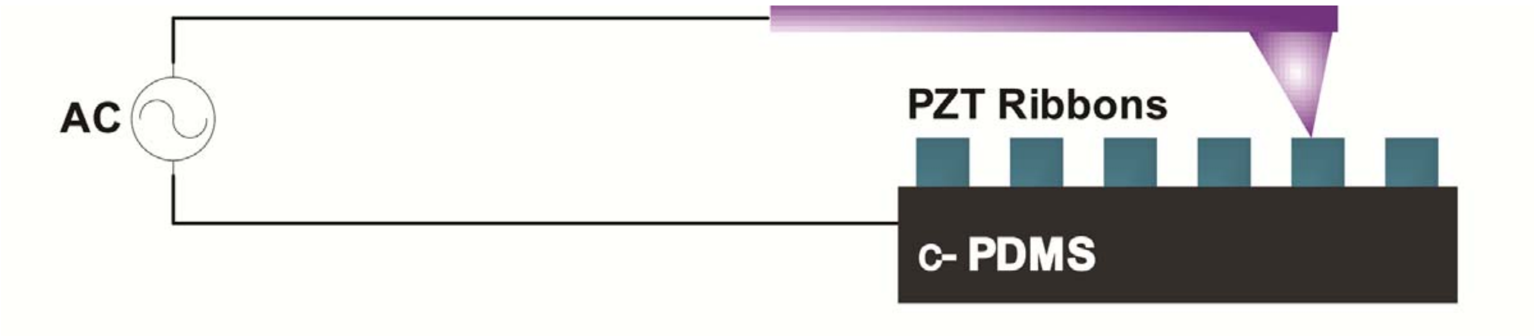
Everything we do generates power—about 1 watt per breath, 70 watts per step. This year, Michael McAlpine of Princeton University and colleagues figured out how to turn locomotion into power by embedding **piezoelectric crystals** into a flexible, biocompatible rubberlike material that, when bent, allows the crystals to produce energy.

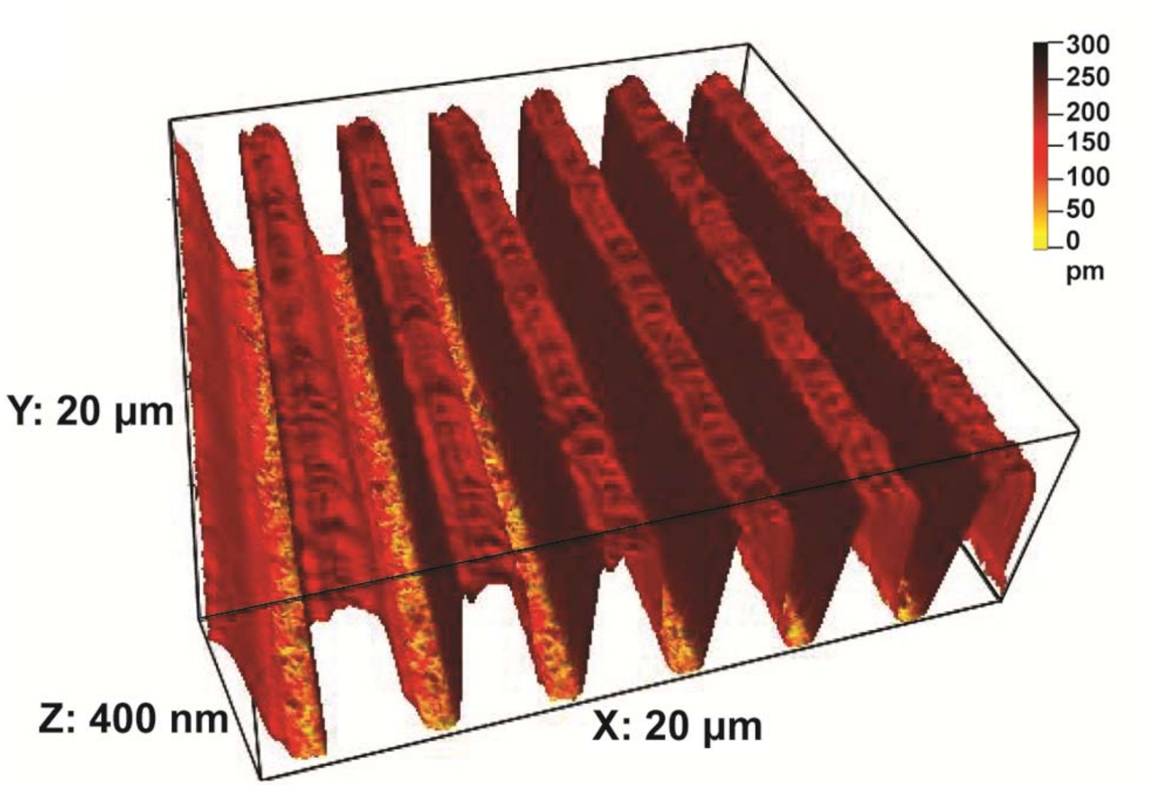
Piezoforce Microscopy

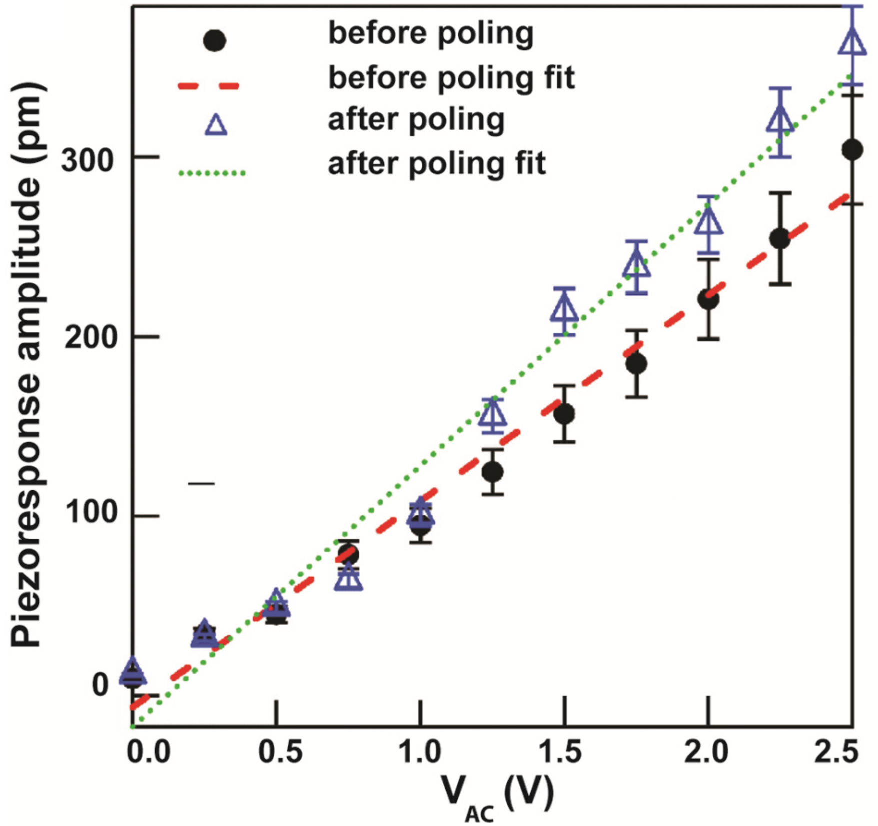


$$d_{eff} = A_{VIB}/V_{AC}$$

PFM

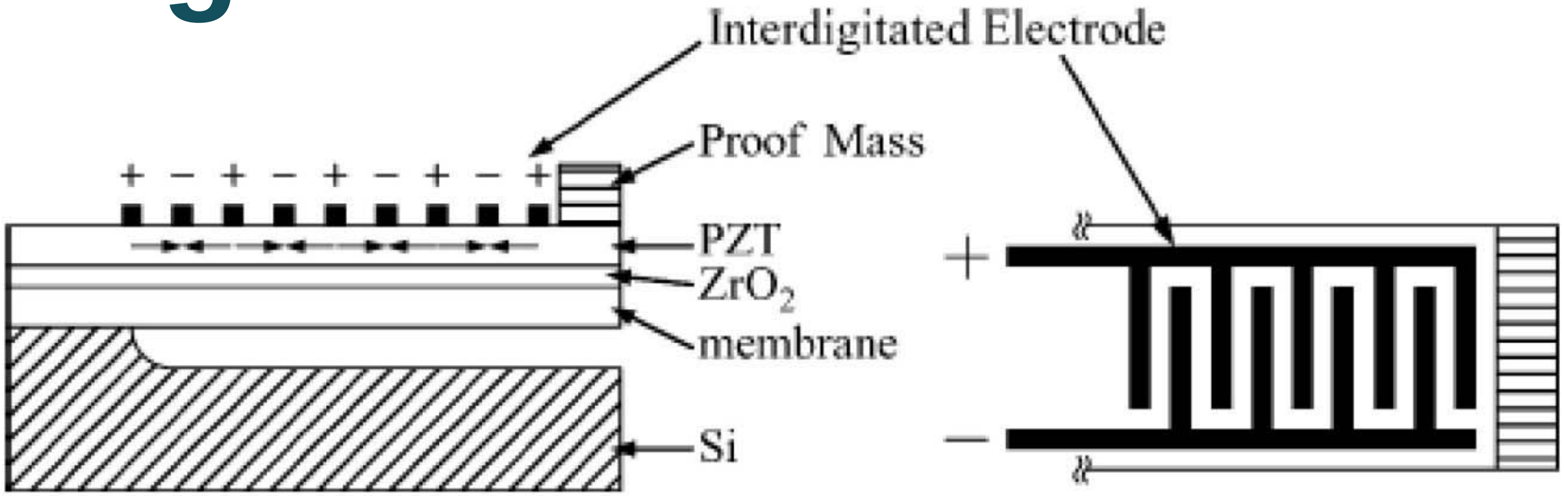


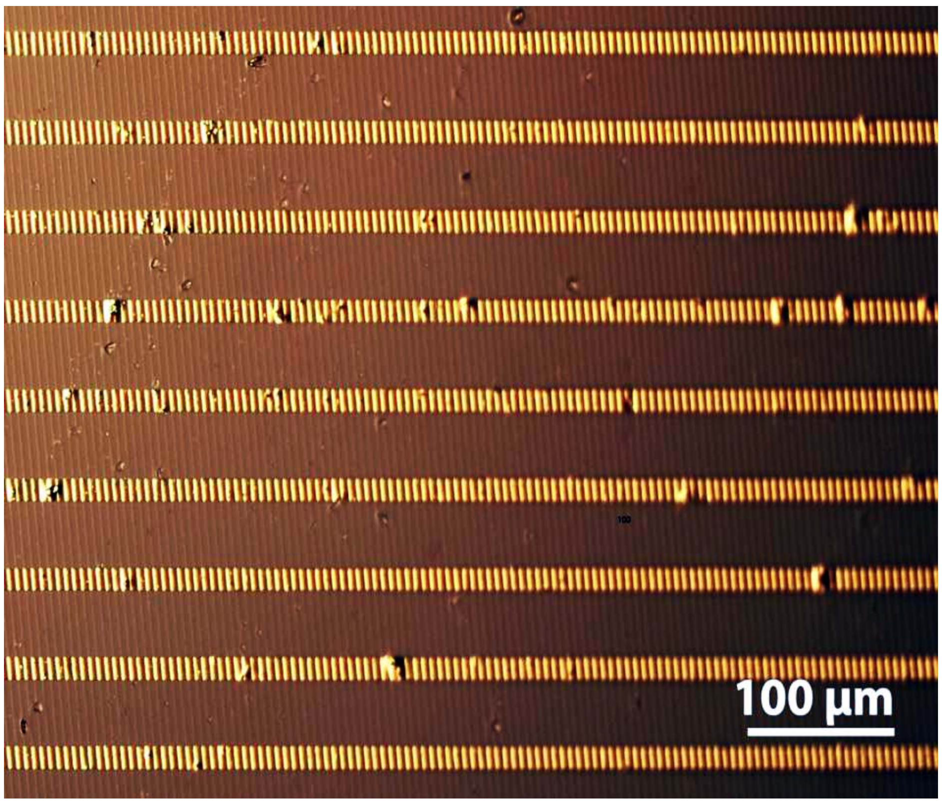


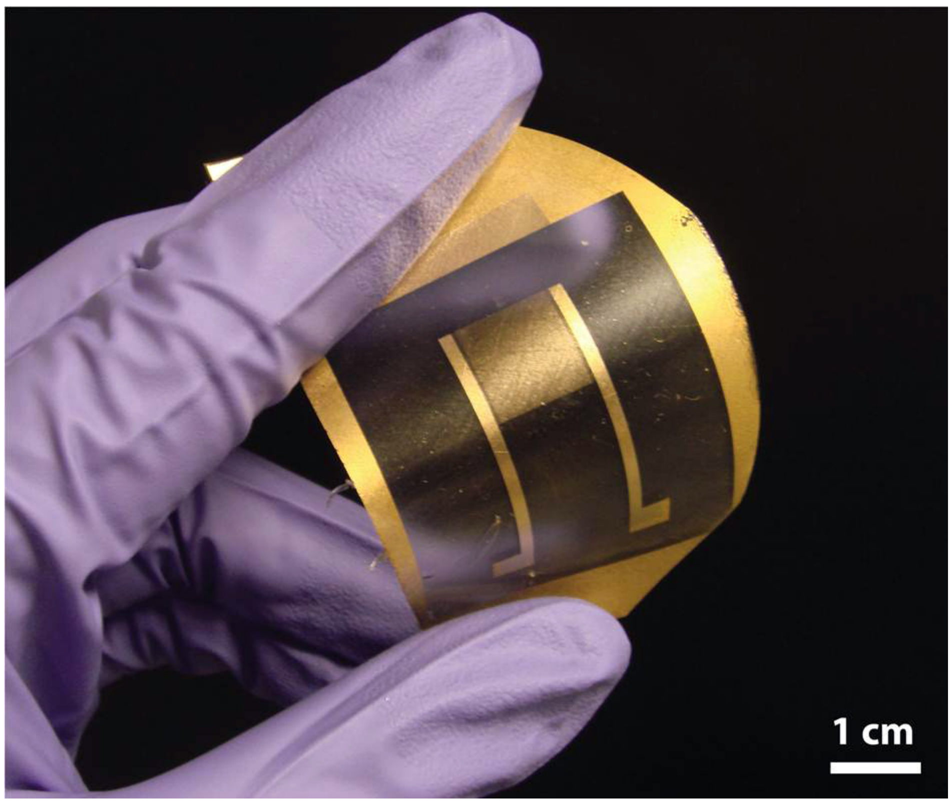


d_{33} = 100 pm/V

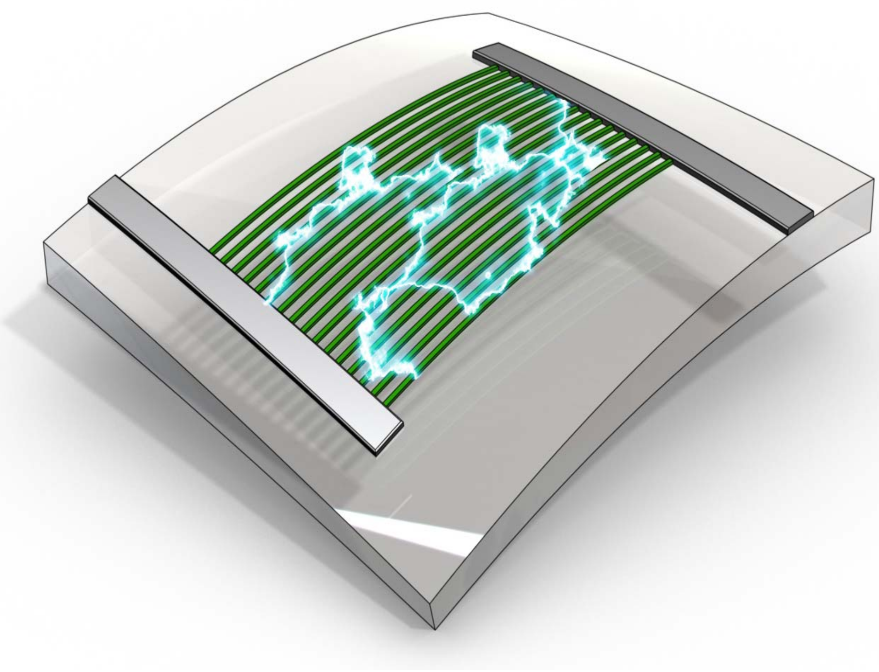
Interdigitated

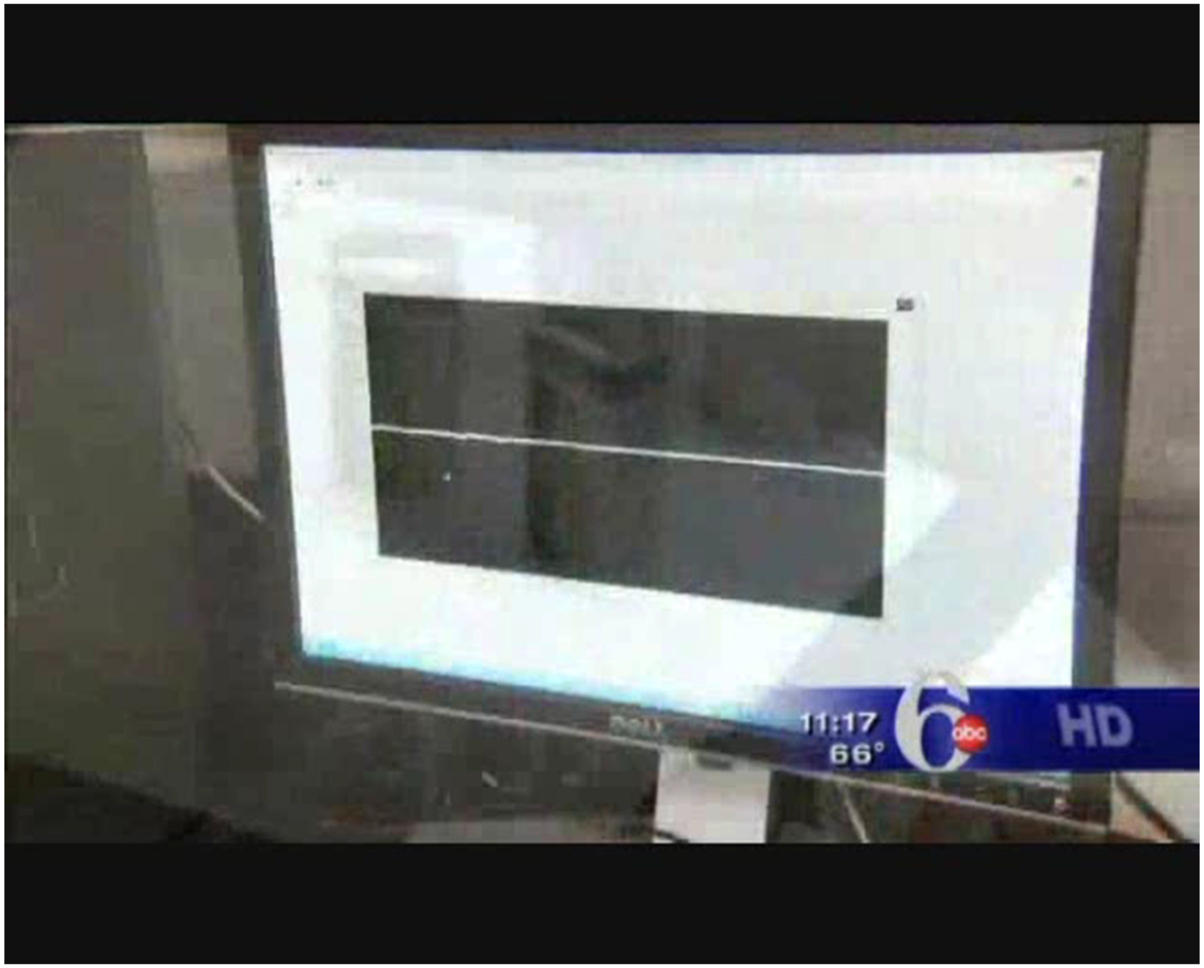




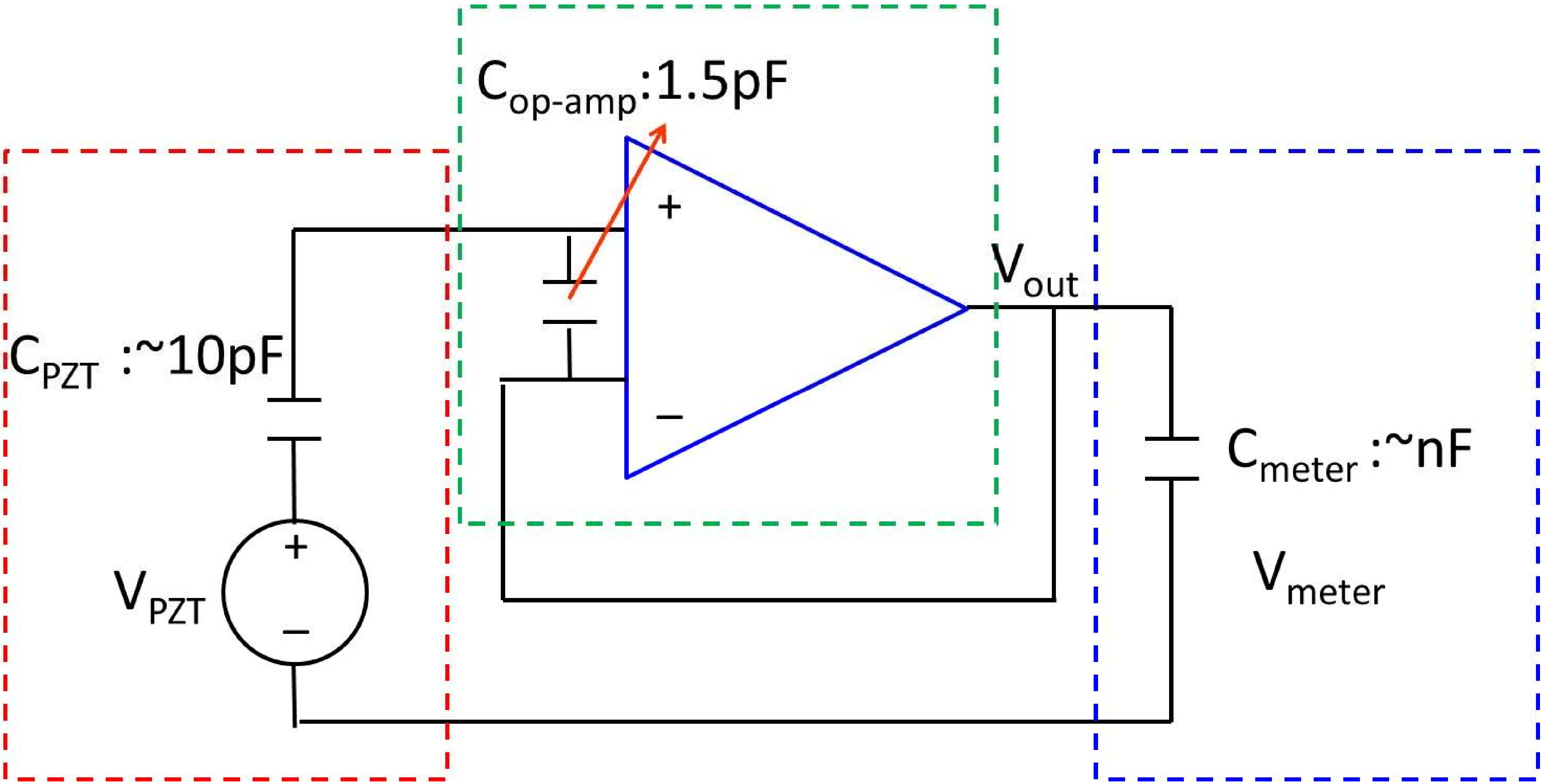


Prototype

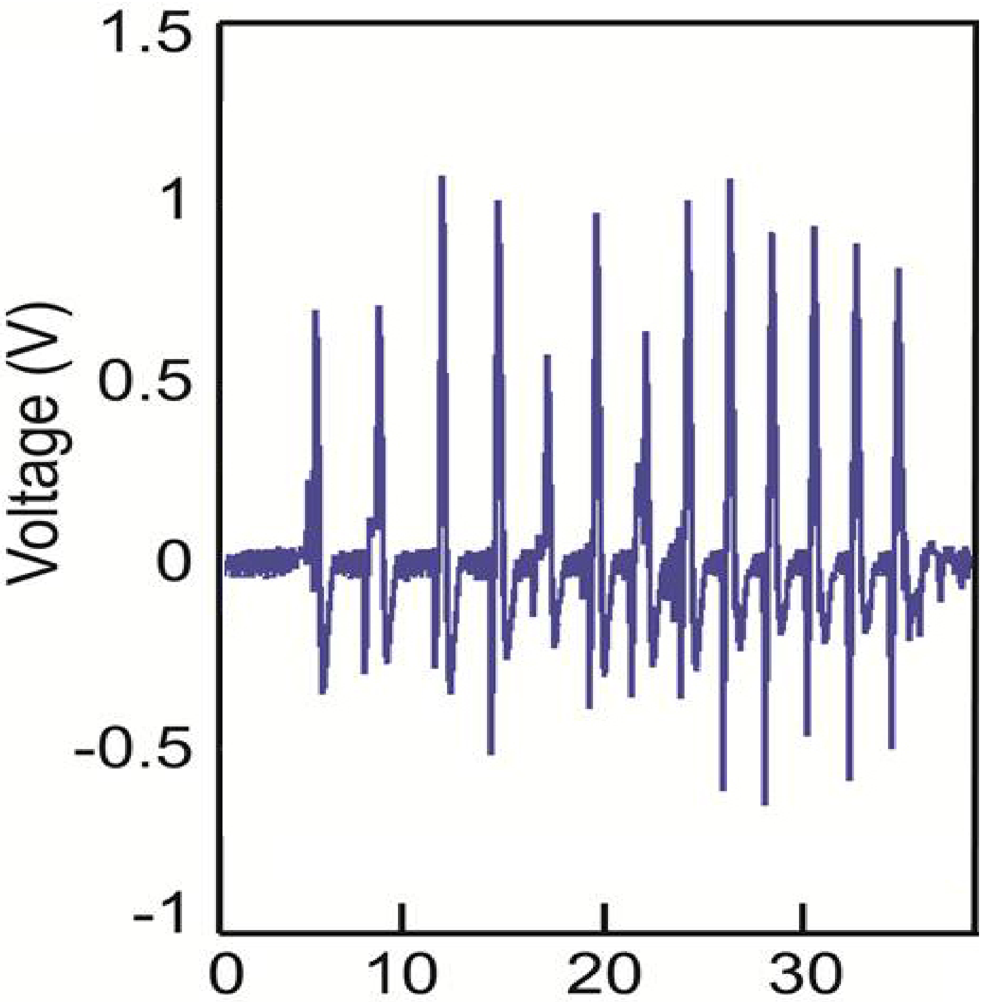


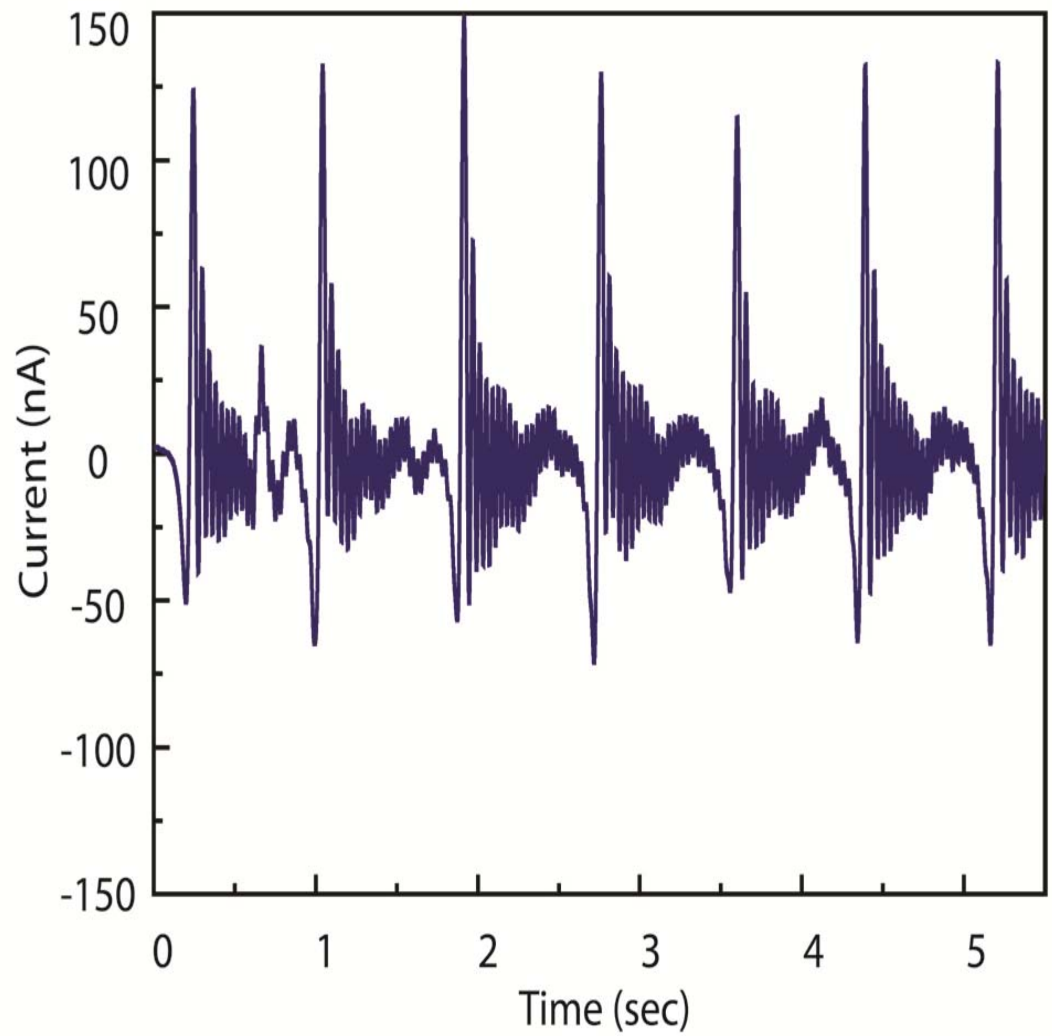


Impedance Matching



Power



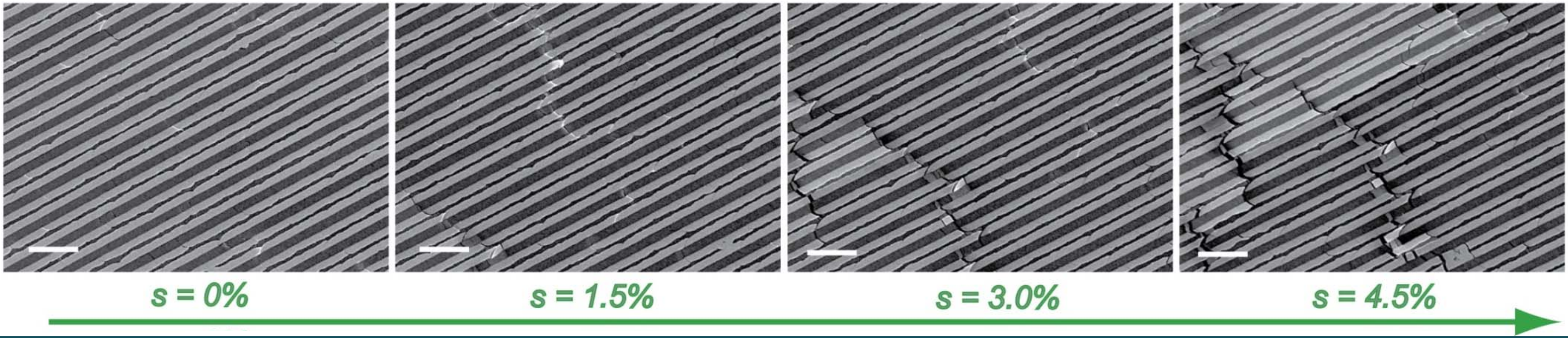


Power = 10 mW/cm³

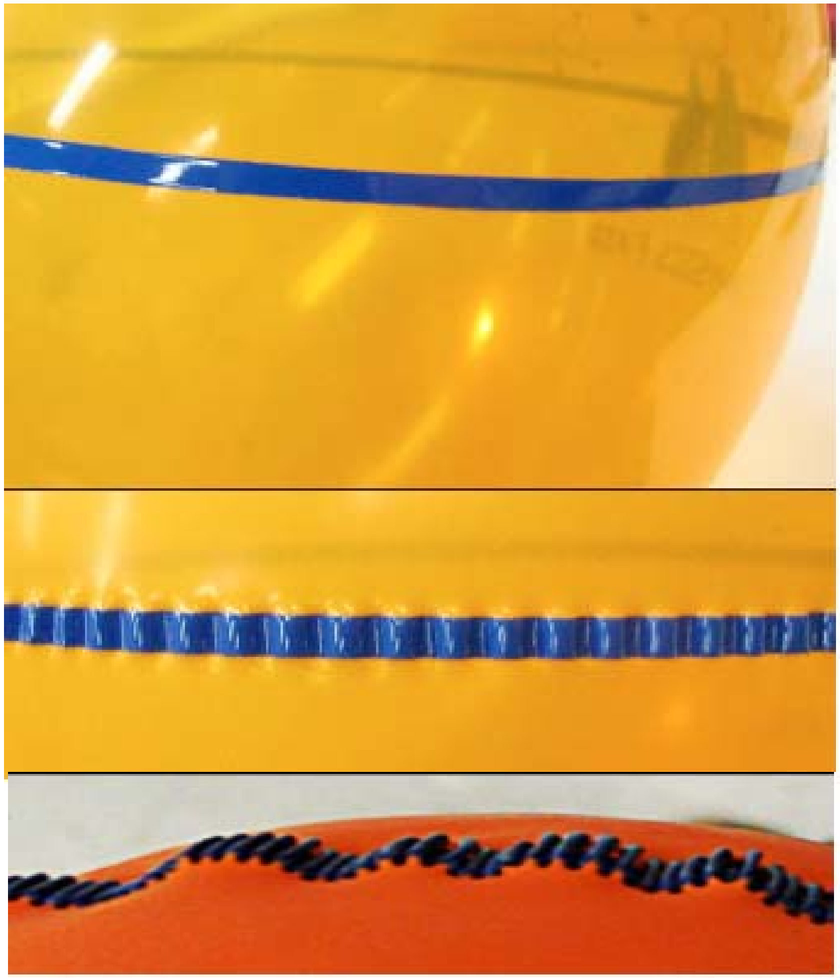
Comparison

This work Printed PZT Nanoribbons	Voltage: 1.5 V Current: 200 nA Power: 0.3 μW Power Density: 10 mW/cm^3
Chen, Xu, Yao, Shi PZT Nanofibers Nano Letters 10.1021/nl100812k	Voltage: 1.63 V Current: 20 nA Power: 30 nW Power Density: Unknown
Xu, Hansen, Wang PZT Nanowire Arrays Nature Communications 10.1038/ncomms109	Voltage: 0.7 V Current: 100 nA Power: 100 nW Power Density: 2.8 mW/cm^3

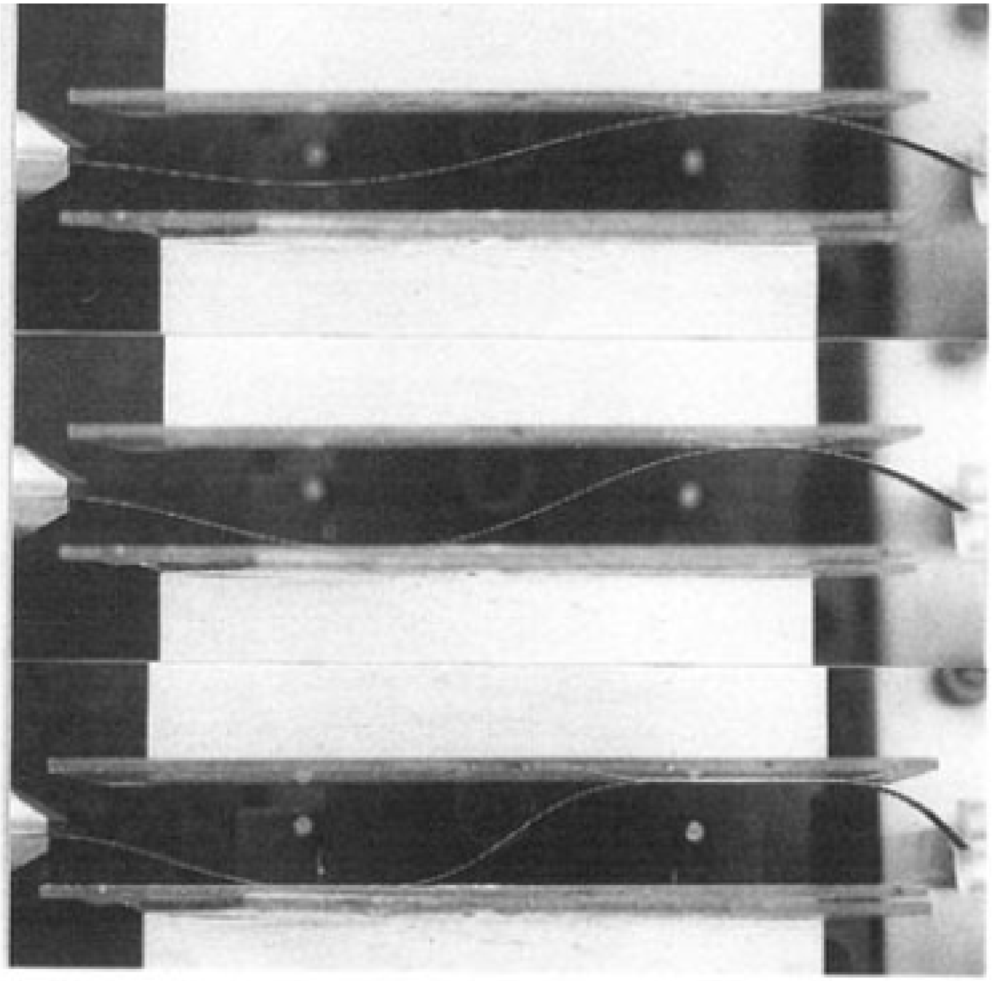
Failure



Buckling

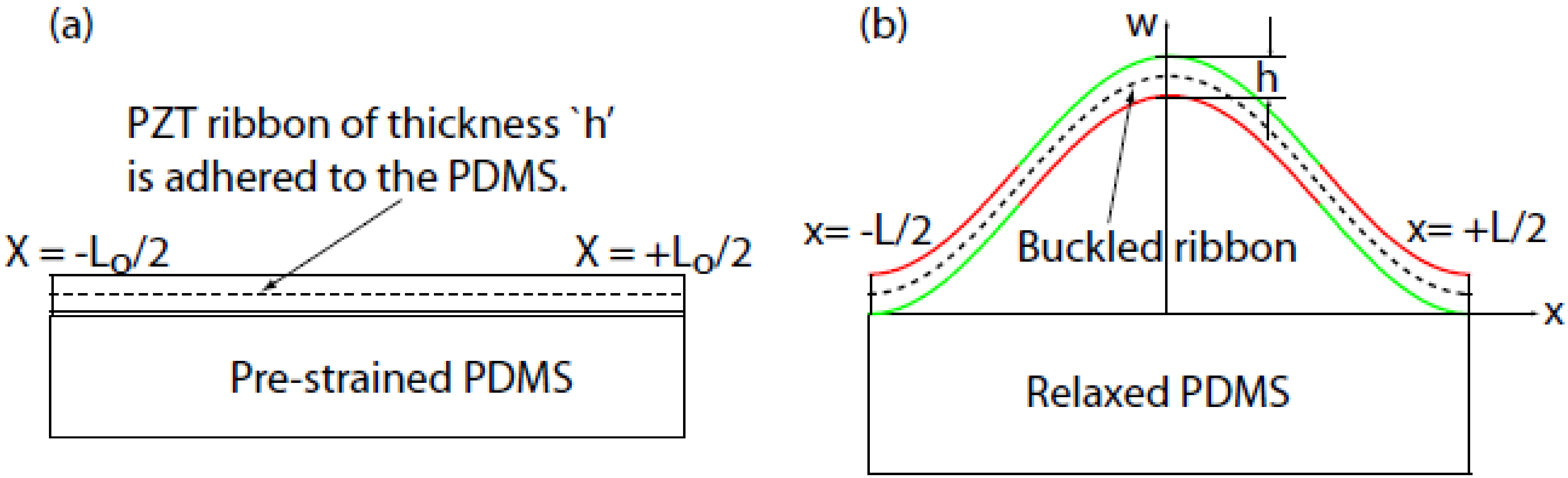


A. Concha, J. W. Melver III, P. Mellado, D. Clarke, O. Tchernyshyov, R. L. Leheny, *Phys Rev E* 75, 016609 (2007)



G. Domokos, P. Holmes, B. Royce, *J Nonlinear Sci* 7, 281-314 (1997)

Parameters



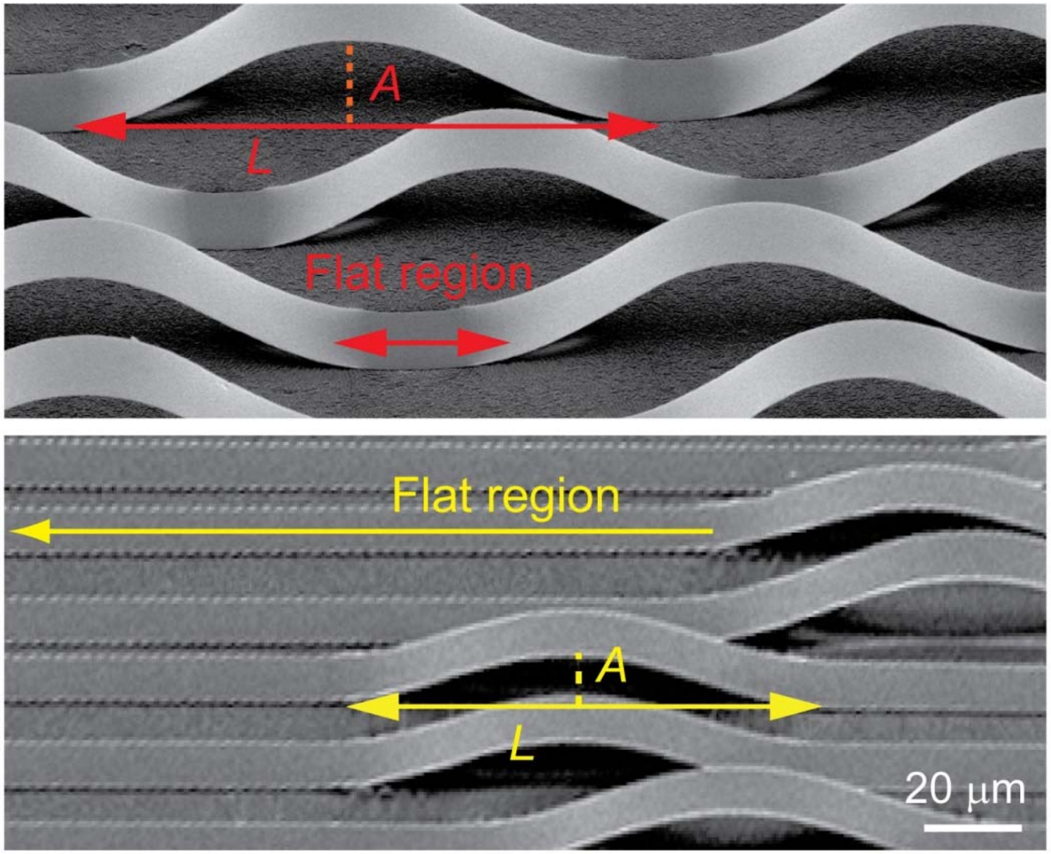
$$U^{bend} = \int_{-\frac{L_0}{2}}^{+\frac{L_0}{2}} \frac{1}{2}\frac{Eh^3}{12}\left(\frac{d^2w}{dX^2}\right)^2 dX = \frac{Eh^3}{12}\frac{\pi^4 A^2}{L_0^3},$$

$$U^{mid} = \int_{-\frac{L_0}{2}}^{+\frac{L_0}{2}} \frac{1}{2}Eh\epsilon_{mid}^2\, dX = \frac{1}{2}EhL_0\left(\frac{\pi^2 A^2}{4L_0^2} - \frac{\epsilon_{pre}}{1+\epsilon_{pre}}\right)^2$$

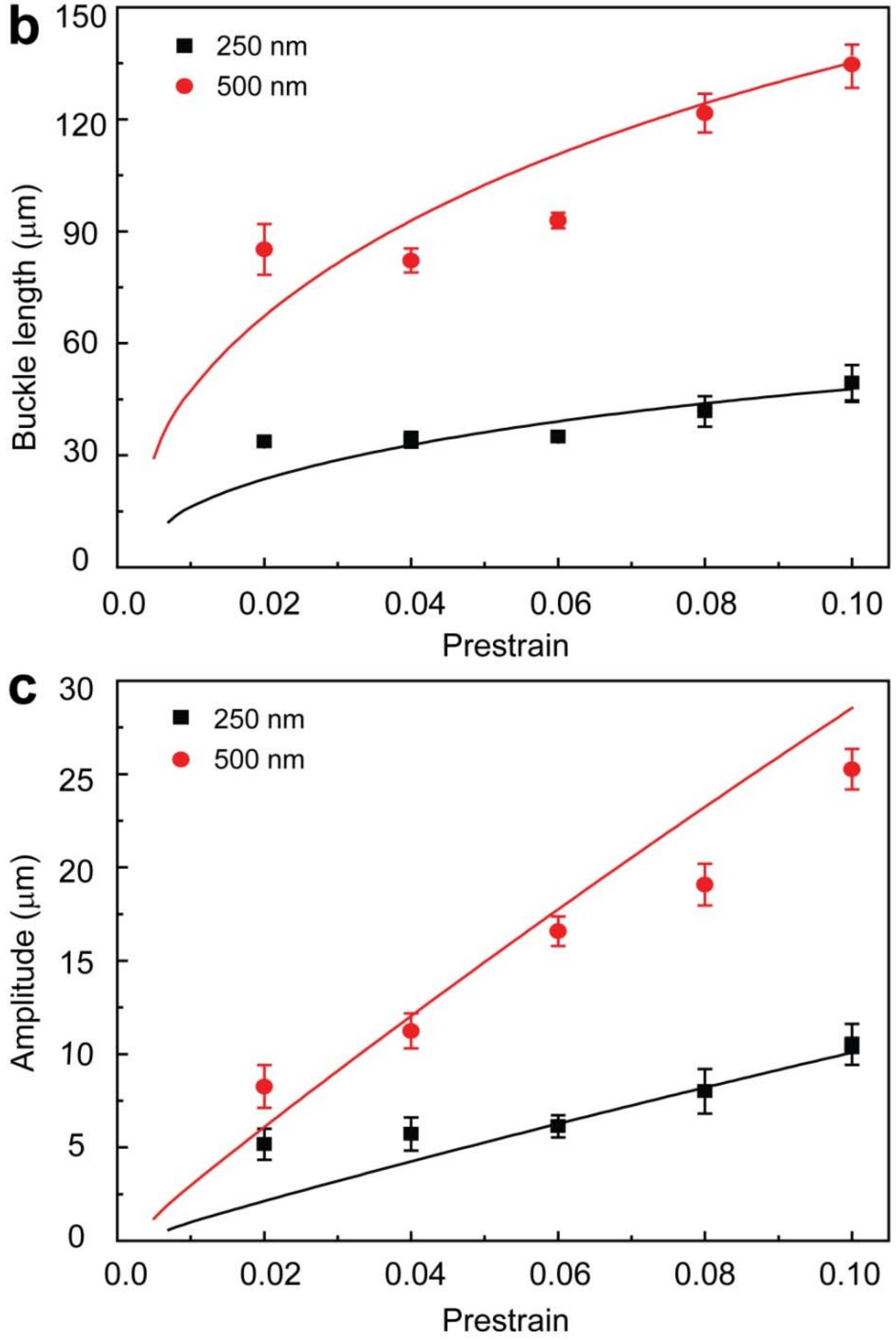
$$U^{adh} = W_{ad}L_0.$$

Waveforms

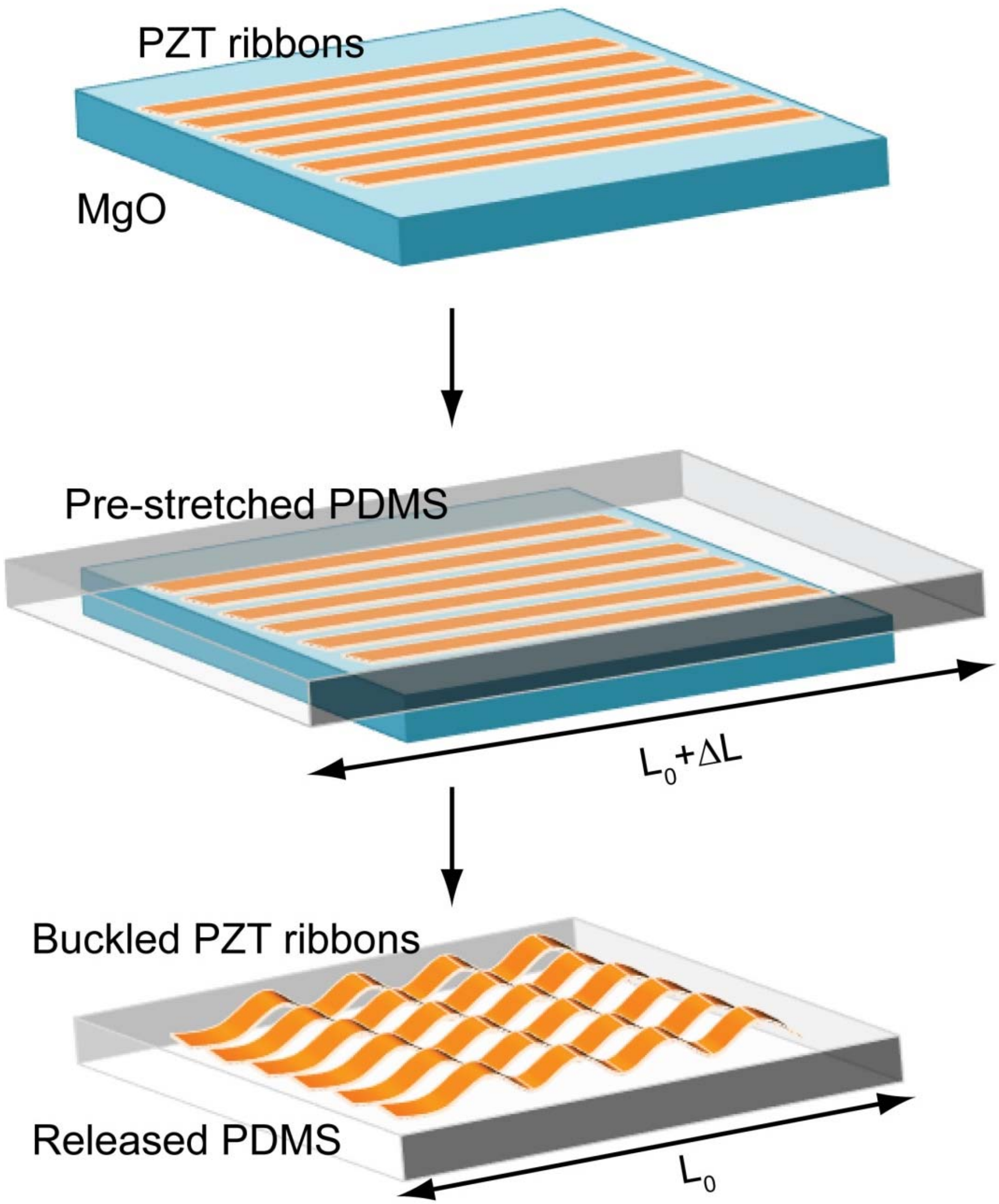
8% Prestrain



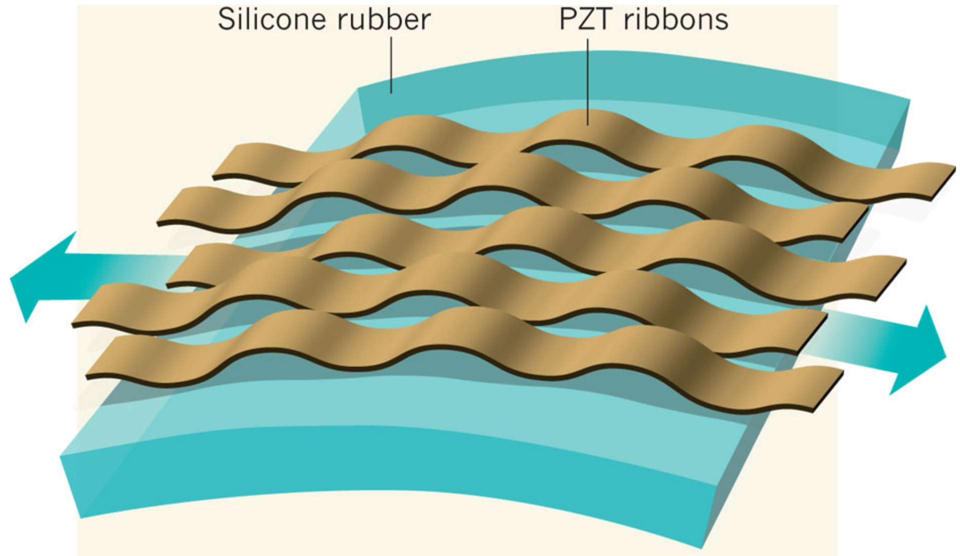
2% Prestrain



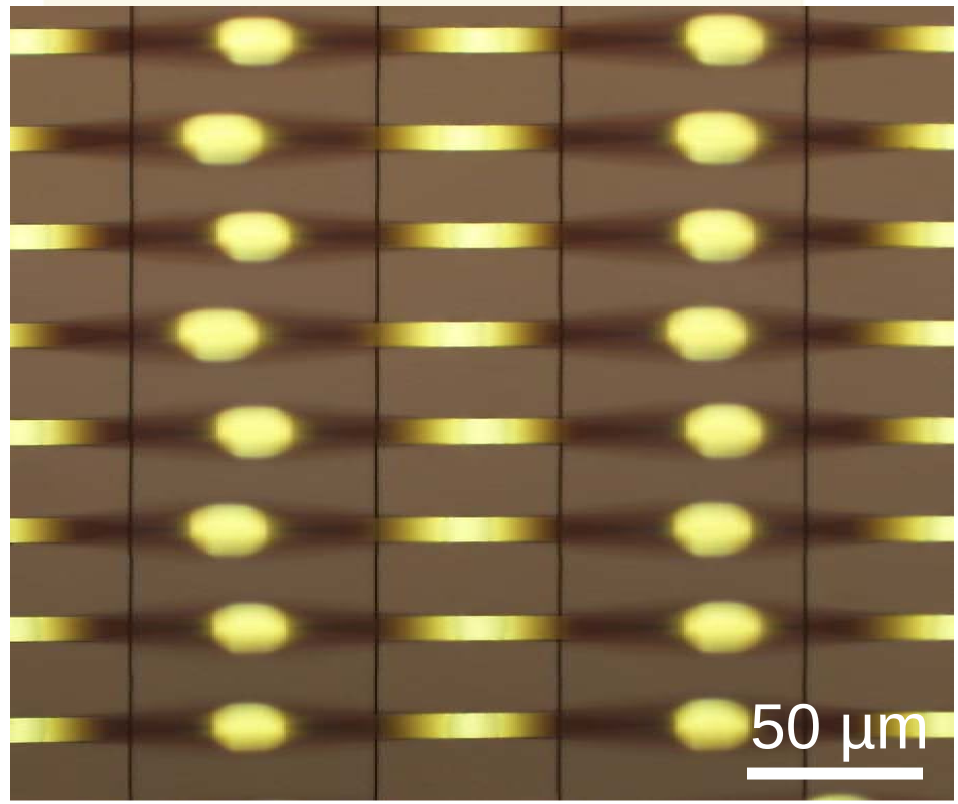
Buckled PZT



PZT ribbons
MgO
Pre-stretched PDMS
$L_0+\Delta L$
Buckled PZT ribbons
Released PDMS
L_0

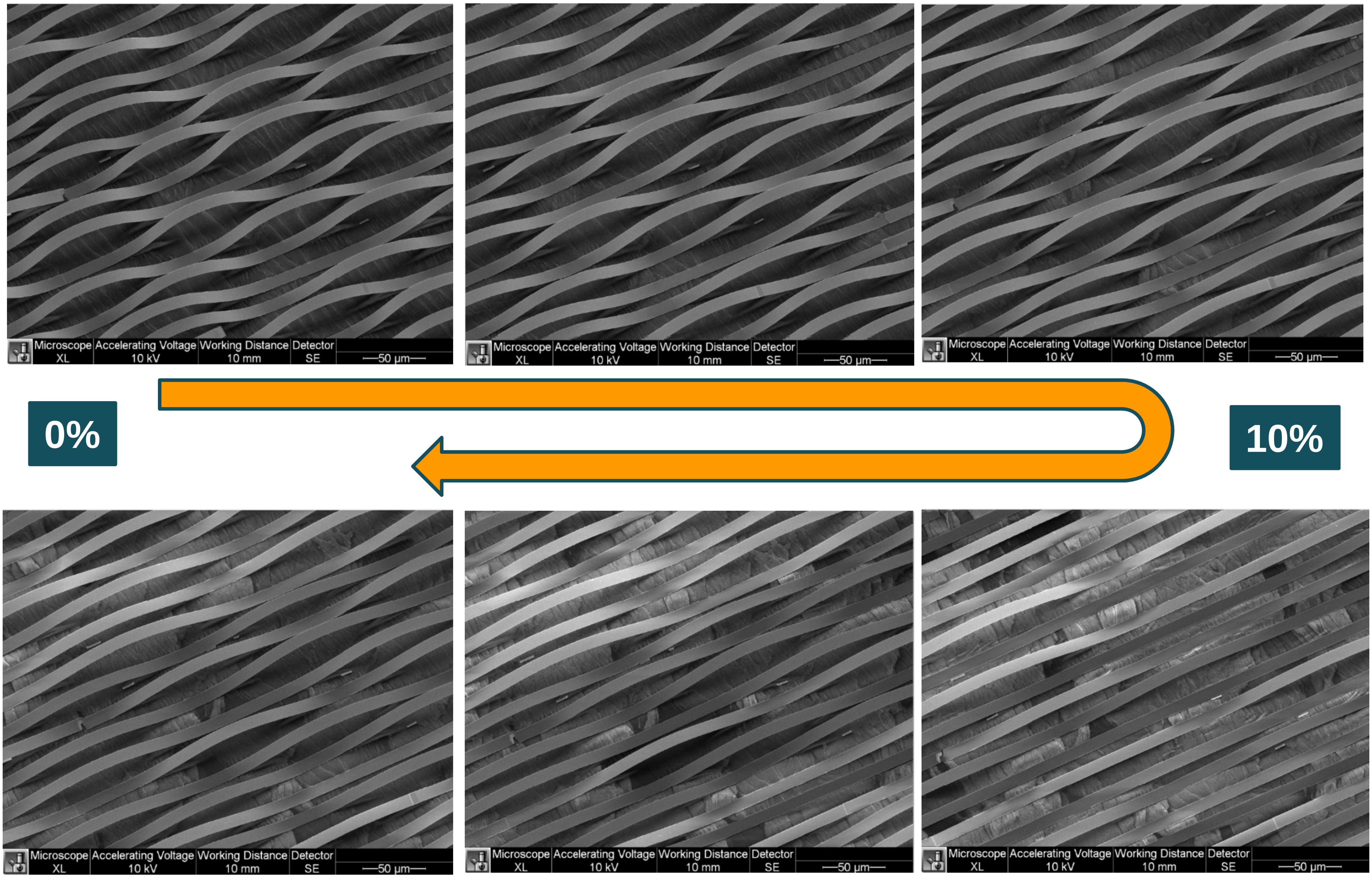


Silicone rubber
PZT ribbons

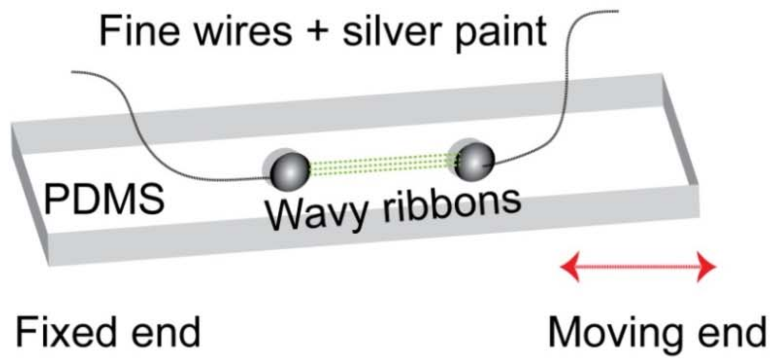


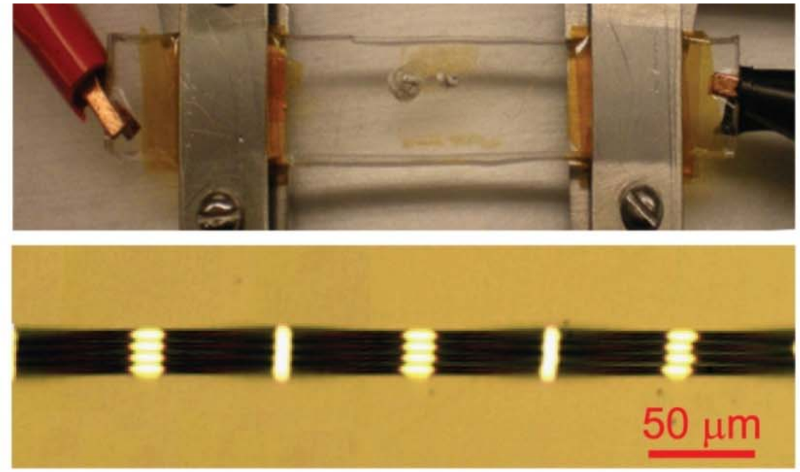
50 µm

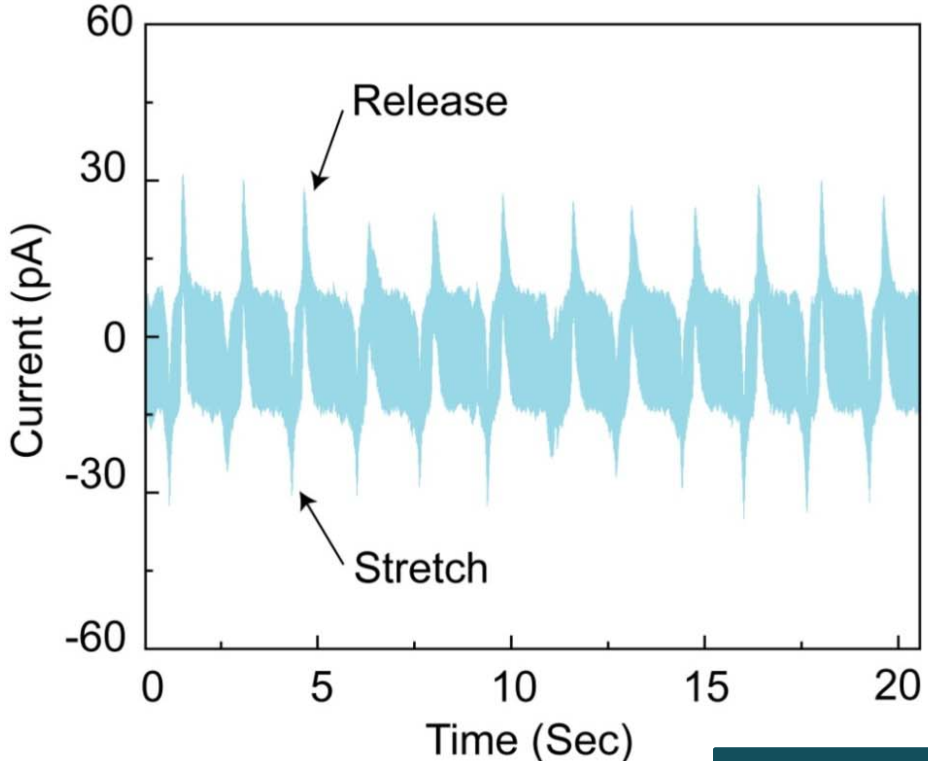
Stretchability

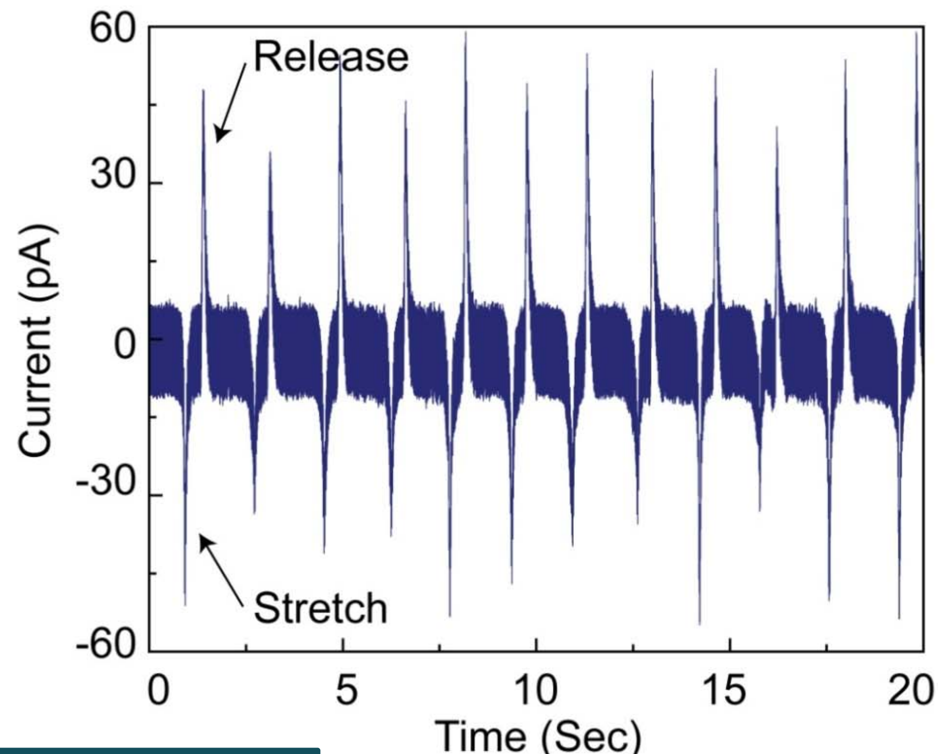


Generator









0.25 mA/cm^2

Science and Nature

Nanogenerators Tap Waste Energy To Power Ultrasmall Electronics

Tiny devices that convert movements into electricity won't power cities. But they may soon be efficient enough to power arrays of invisible sensors and hand-held electronics

—ROBERT F. SERVICE

www.sciencemag.org SCIENCE VOL 328 16 APRIL 2010

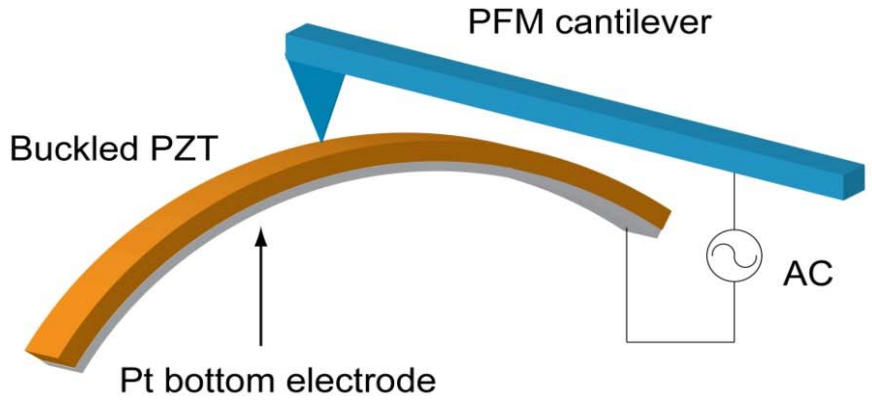
Power surfing on waves

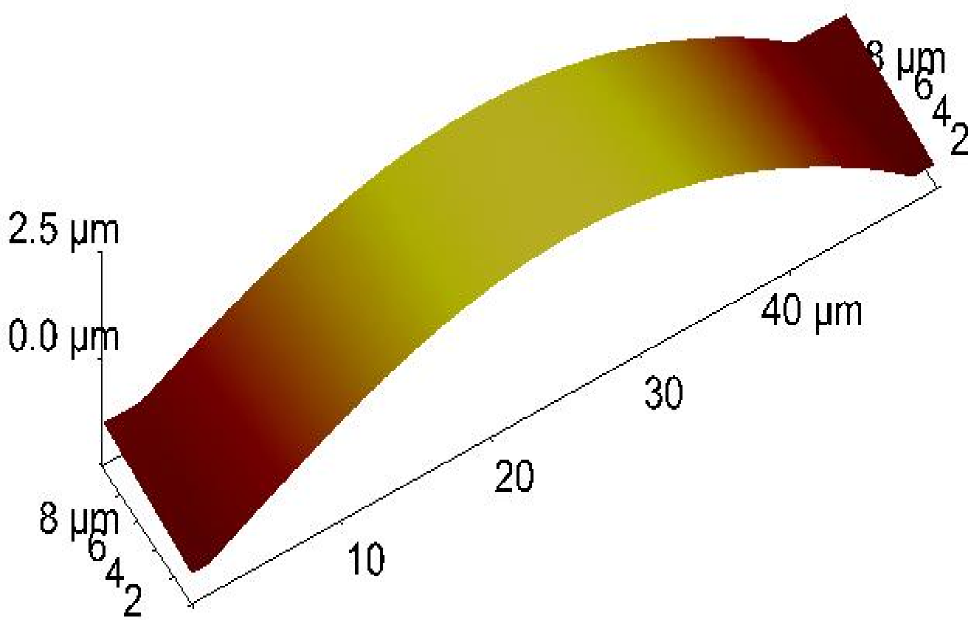
Wavy strips of piezoelectric materials on stretchable substrates can both withstand larger applied mechanical strain without cracking and harvest energy more efficiently than their flat counterparts.

MIN HYUNG LEE & ALI JAVEY

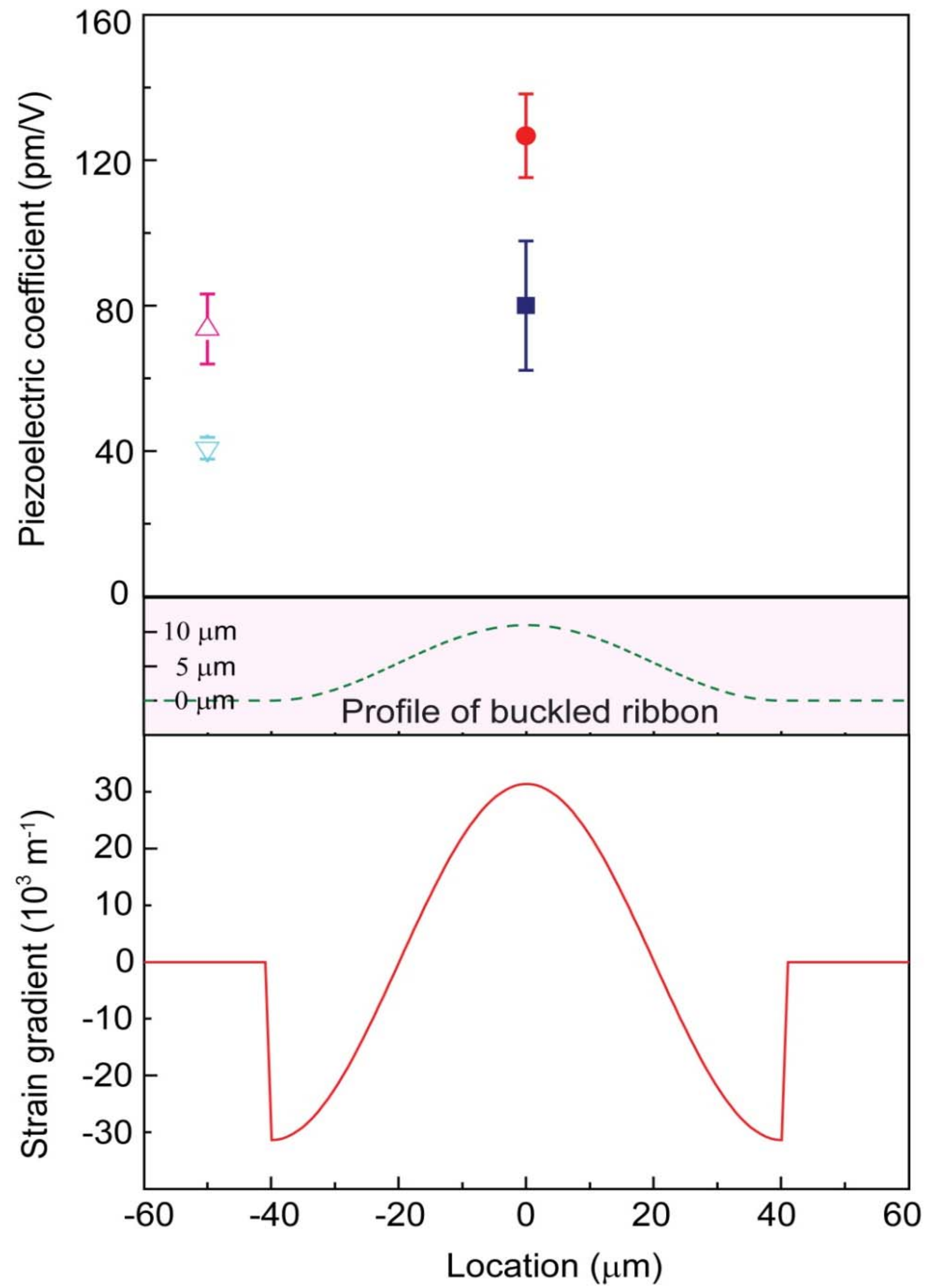
304 | NATURE | VOL 472 | 21 APRIL 2011

Local Probing

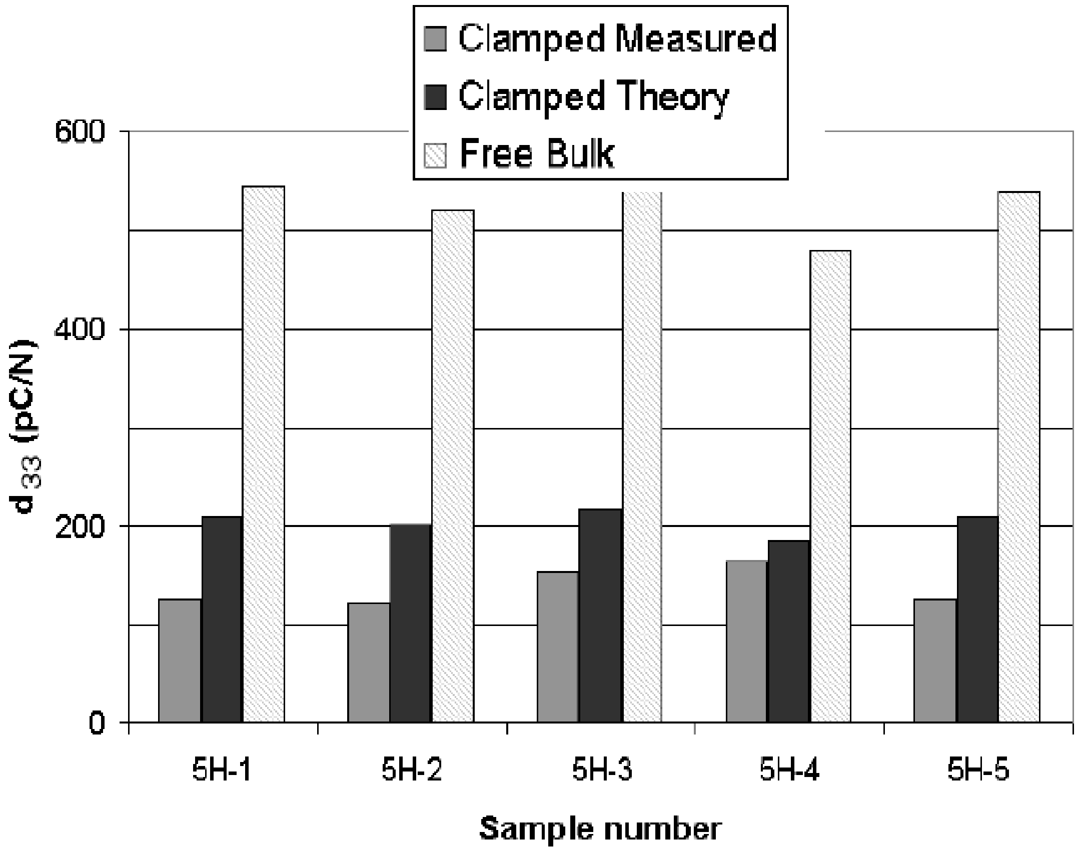


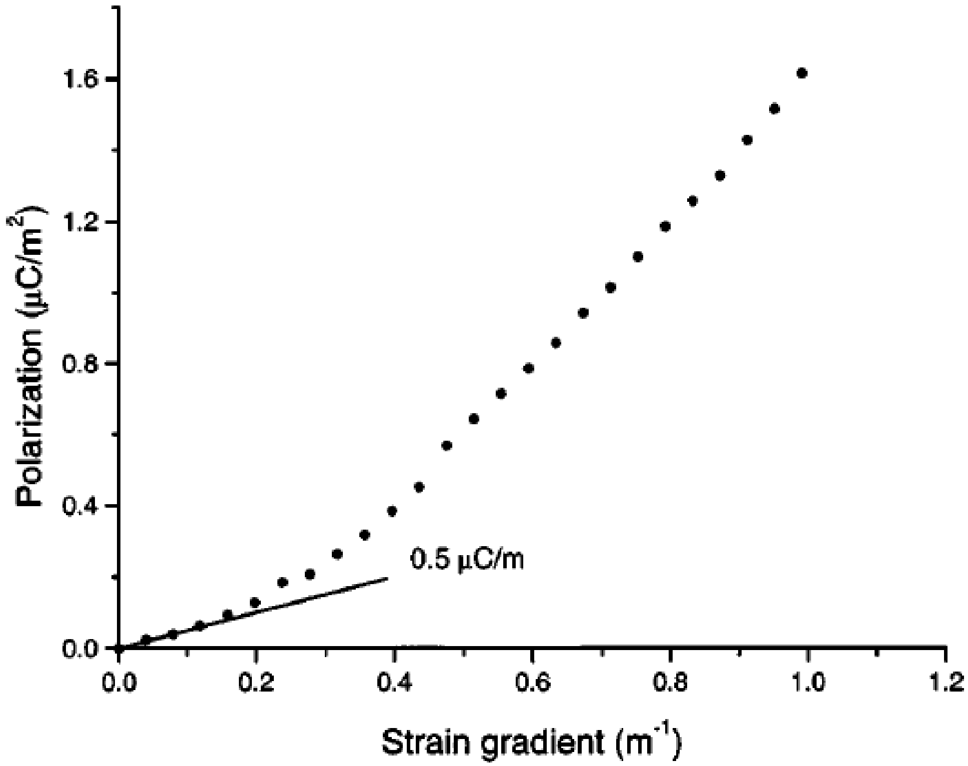


Voltage (V)



Enhancement



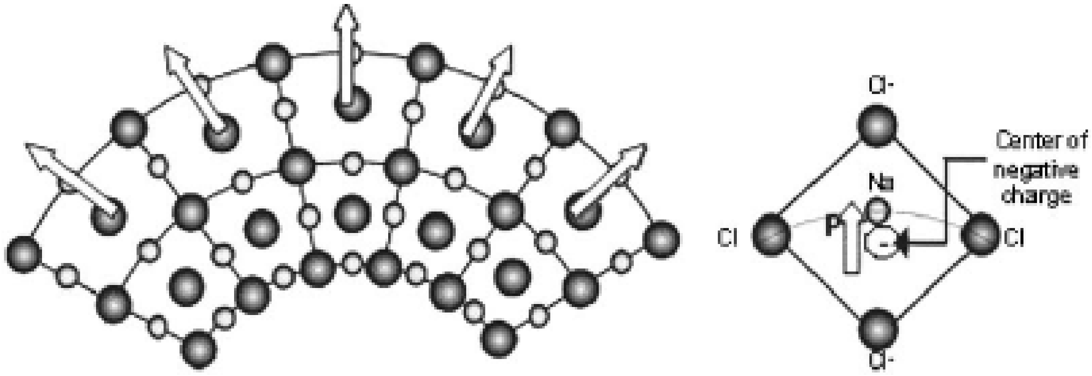


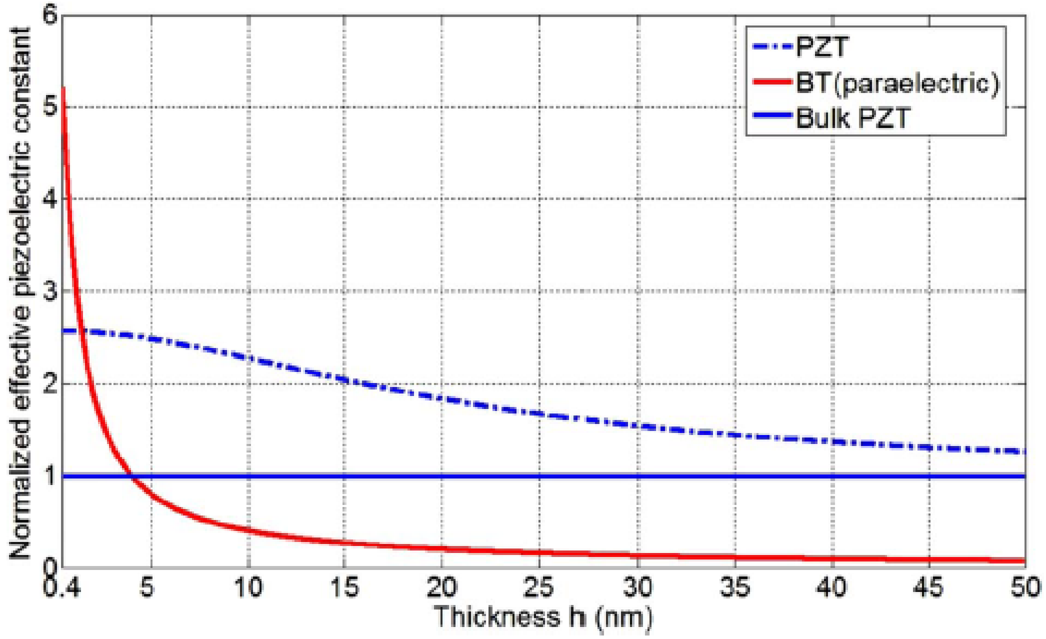
Torah, Beeby, White, *J Phys D* 37, 1 (2004)

W. H. Ma, L. E. Cross, *Appl Phys Lett* 82, 3293 (2003)

Flexoelectricity

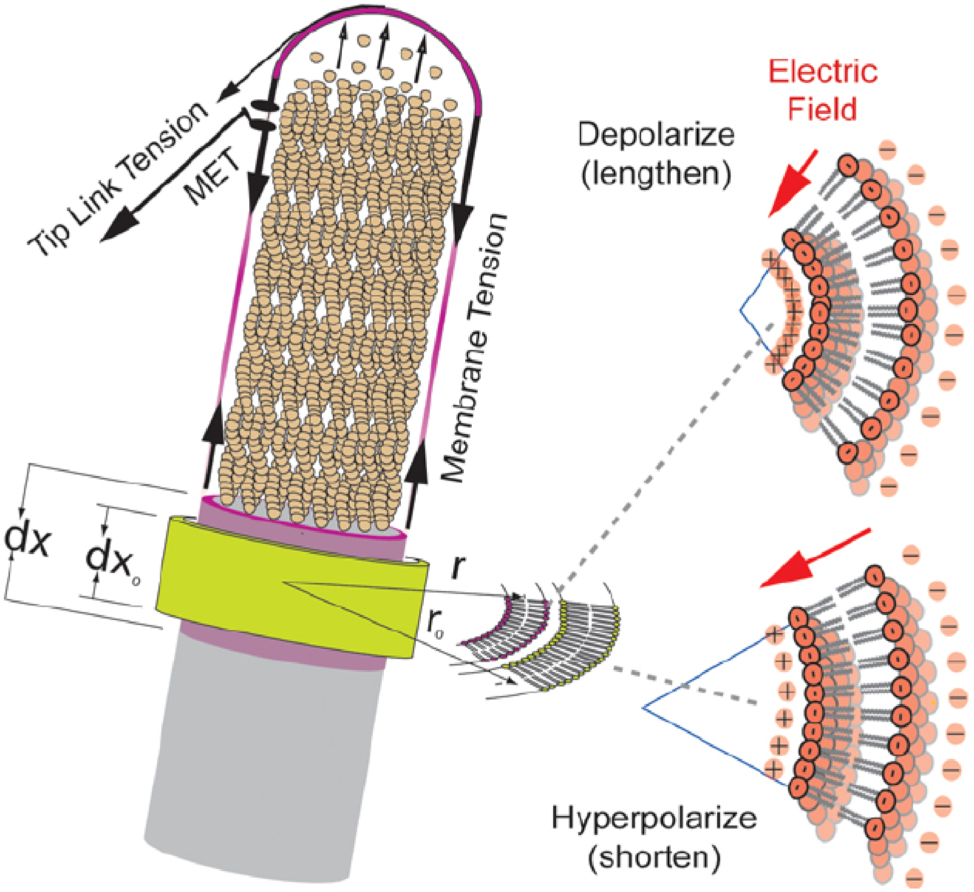
$$(\mathbf{P})_i = (\mathbf{d})_{ijk}(\varepsilon)_{jk} + (\mathbf{f})_{ijkl}\nabla_l(\varepsilon)_{jk}$$

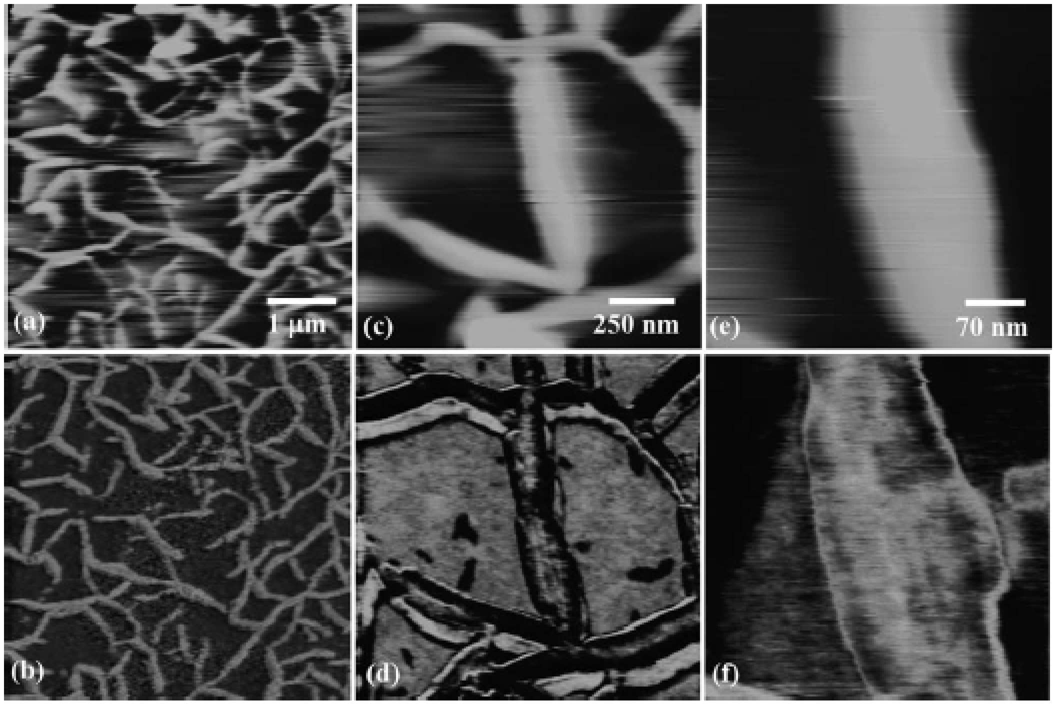


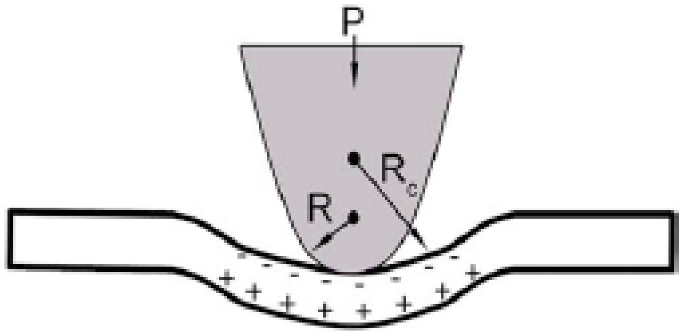


Maranganti, Sharma, Sharma, *Phys Rev B* 74, 014110 (2006)

Soft Matter



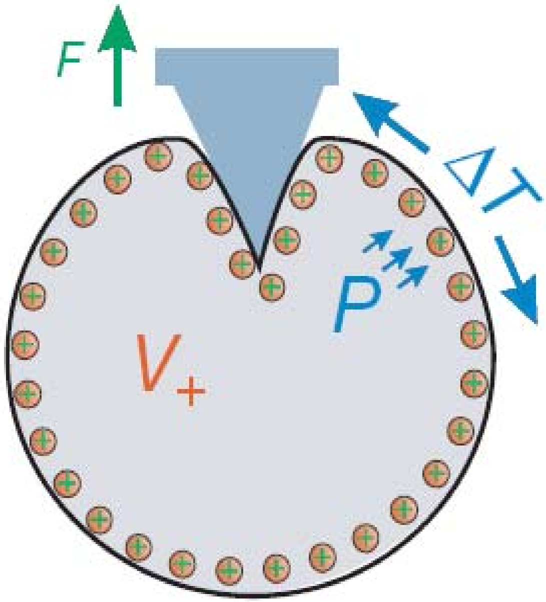


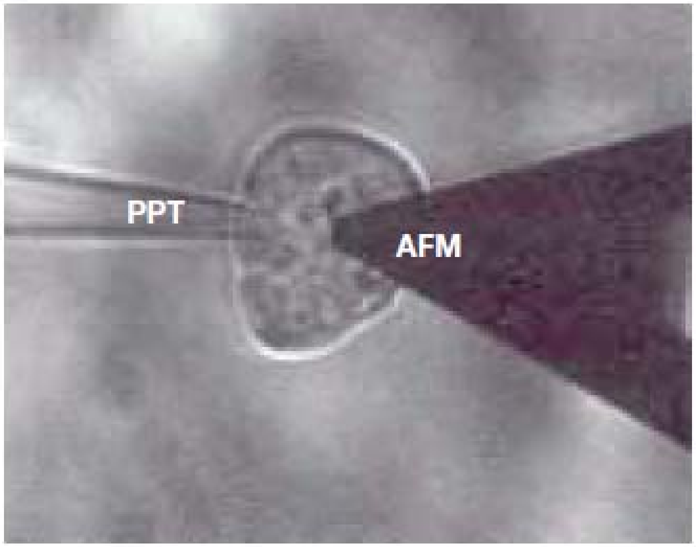


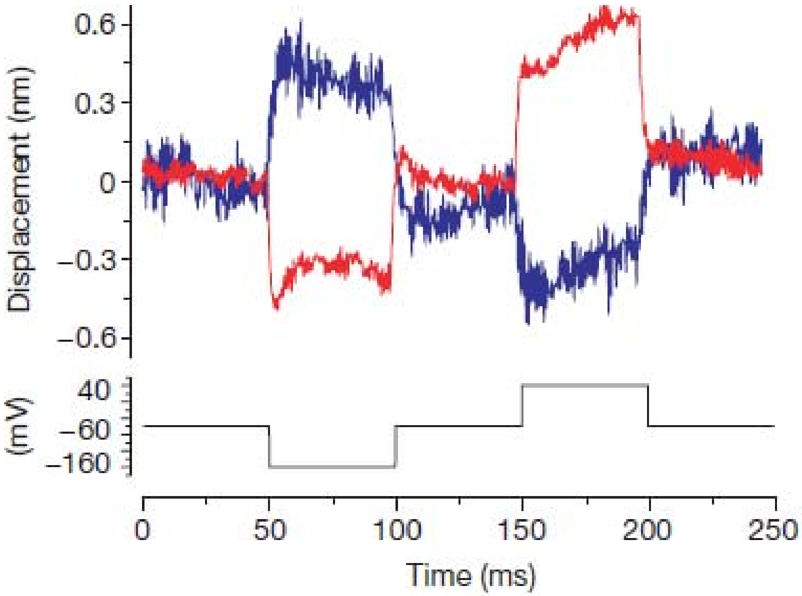
K. D. Breneman, W. E. Brownell, R. D. Rabbitt, *PLoS One* 4, e5201 (2009)

Kalinin, Jesse, Liu, Balandin, *Appl Phys Lett* 88, 153902 (2006)

Cell Nanomechanics

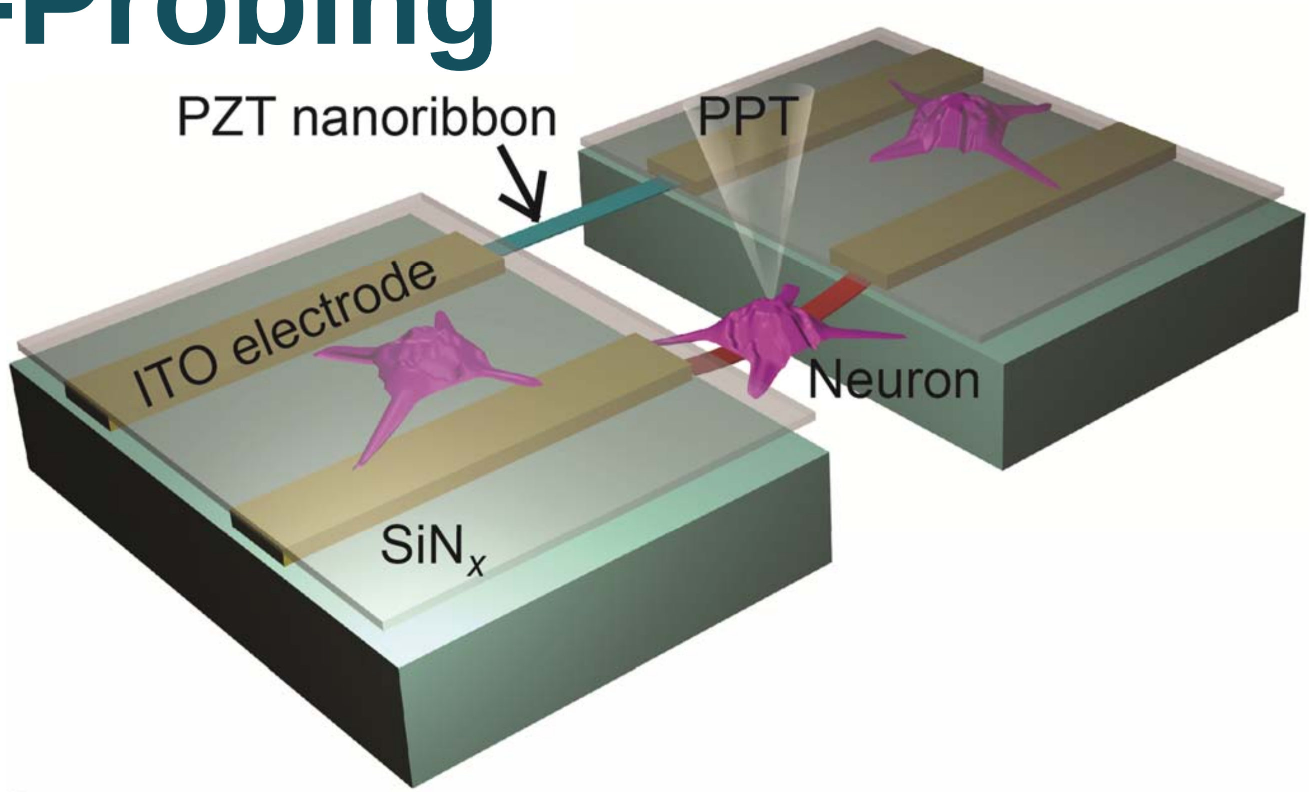


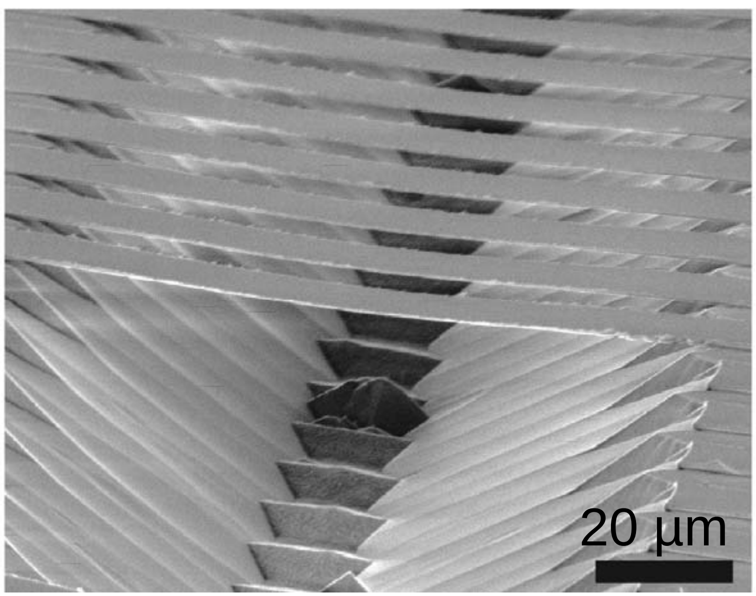


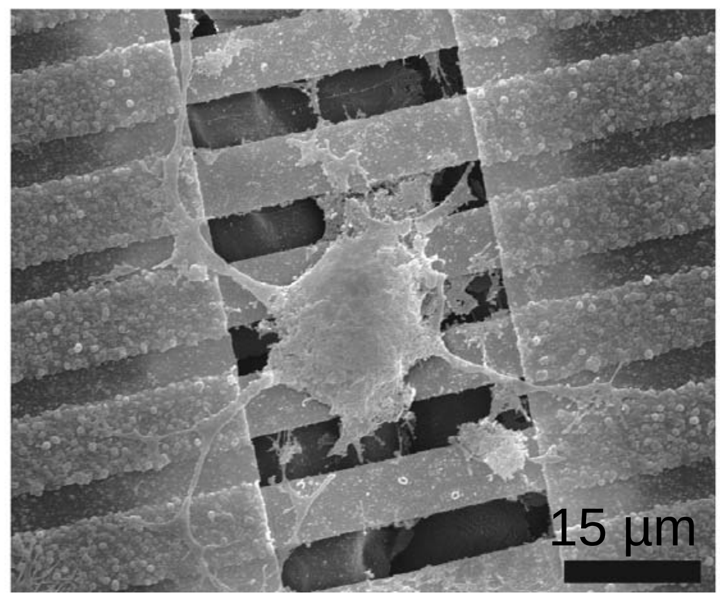


P. Zhang, A. Keleshian & F. Sachs, *Nature* 413, 428 (2001)

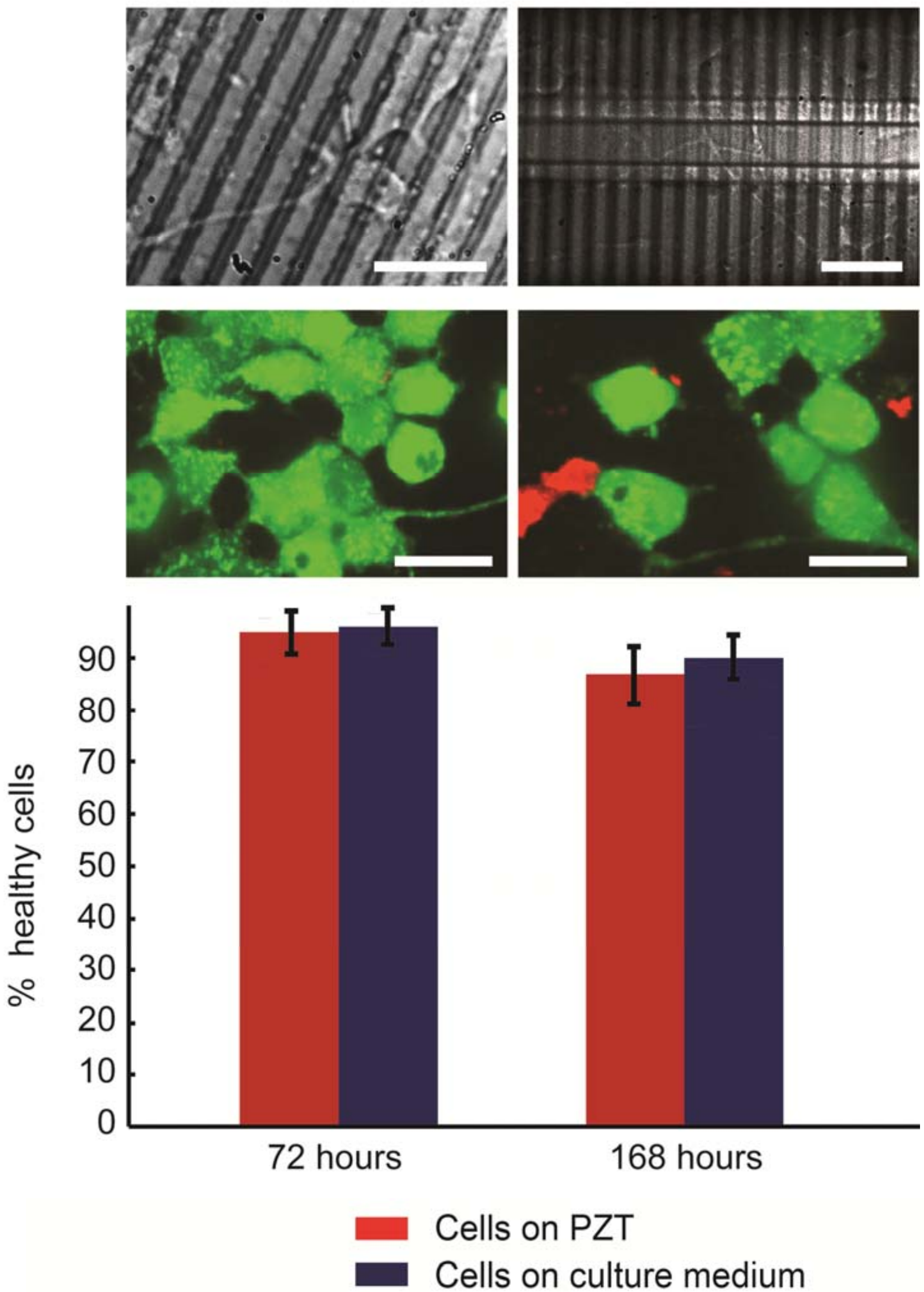
Piezo-Probing



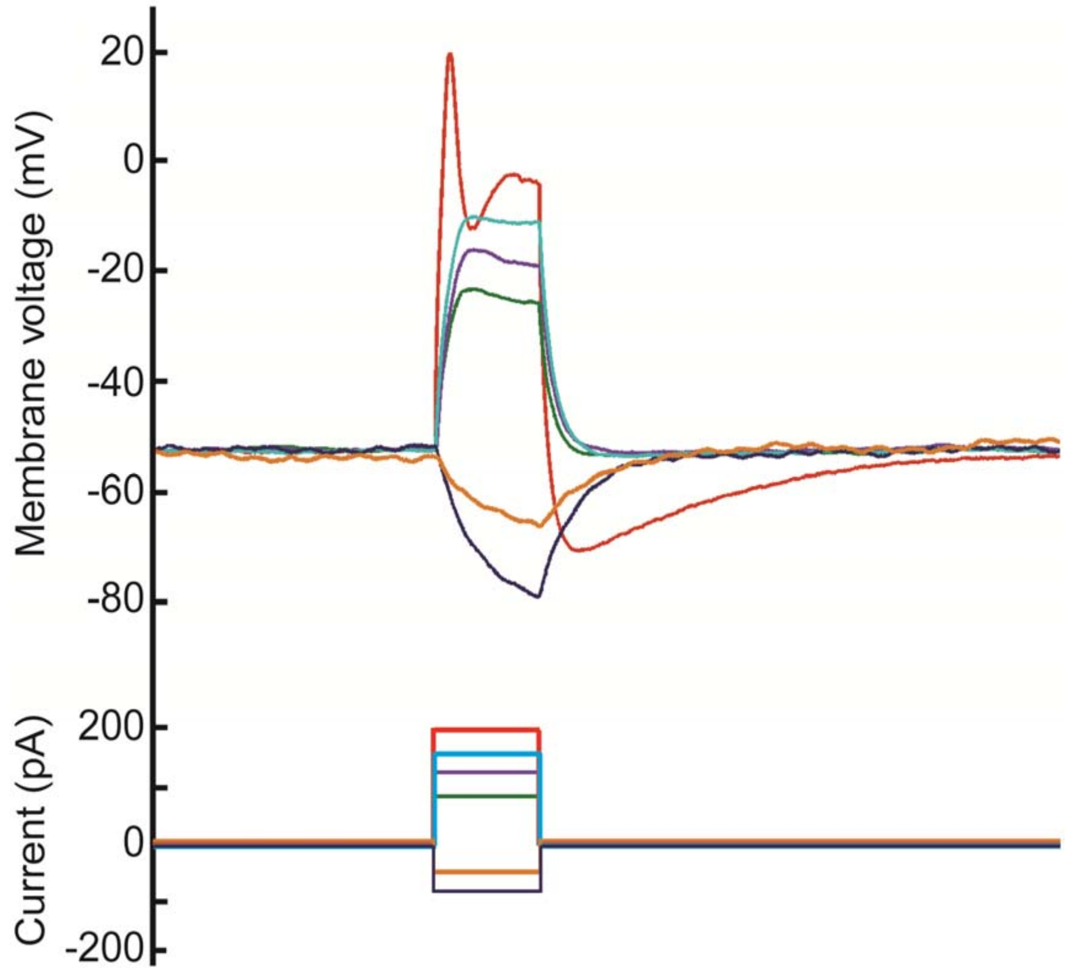




Viability

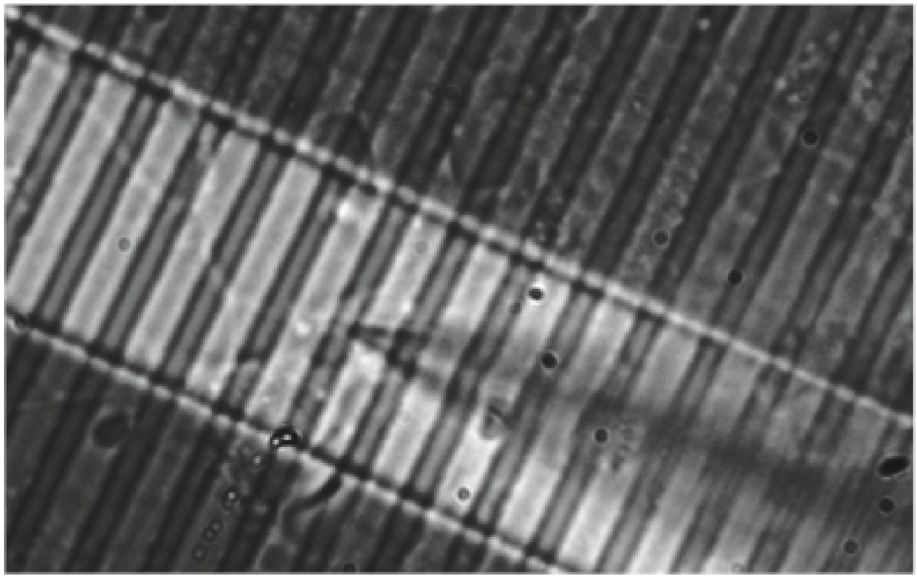


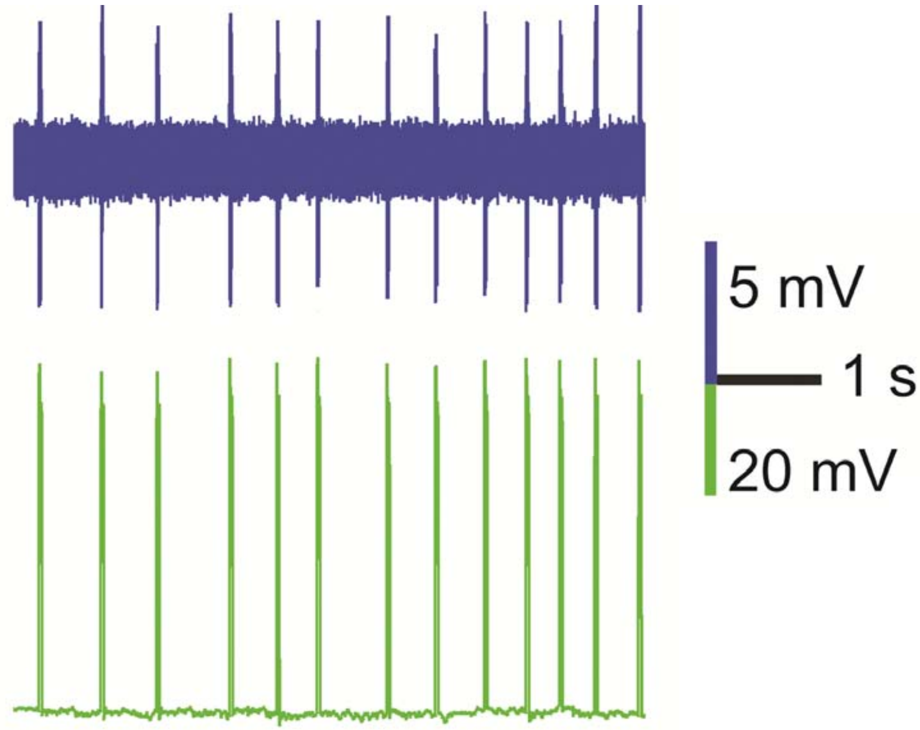
% healthy cells
0
10
20
30
40
50
60
70
80
90
72 hours
168 hours
Cells on PZT
Cells on culture medium

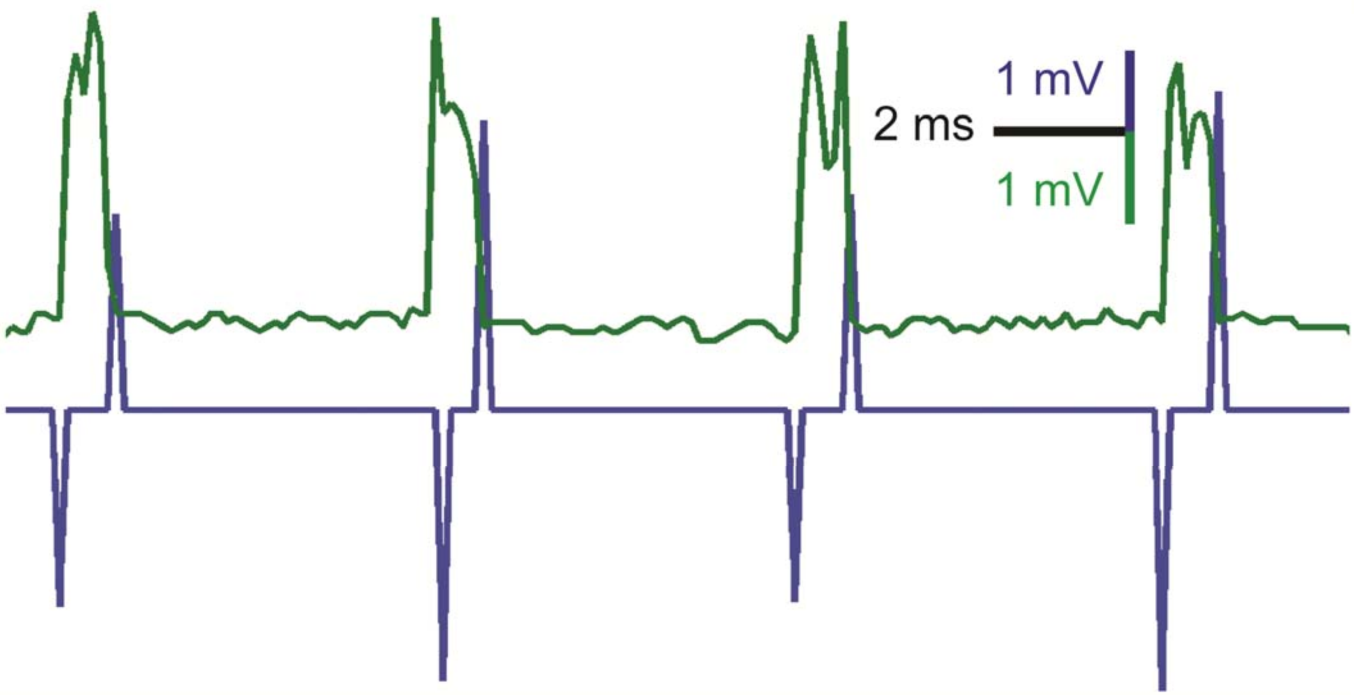


Membrane voltage (mV)
20
0
-20
-40
-60
-80
Current (pA)
200
0
-200

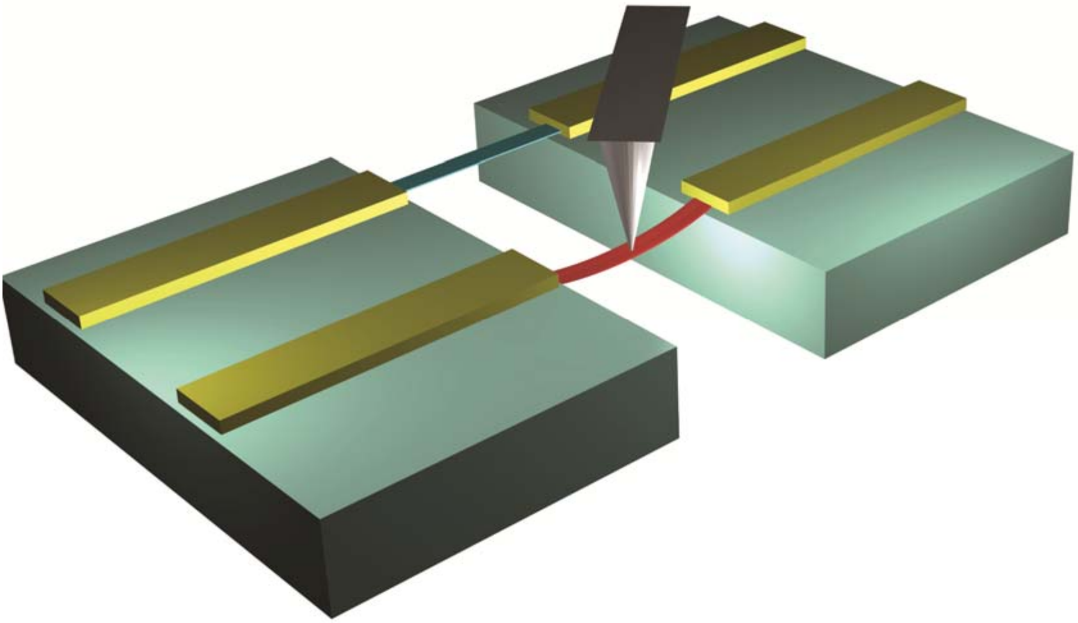
Neurointerfacing

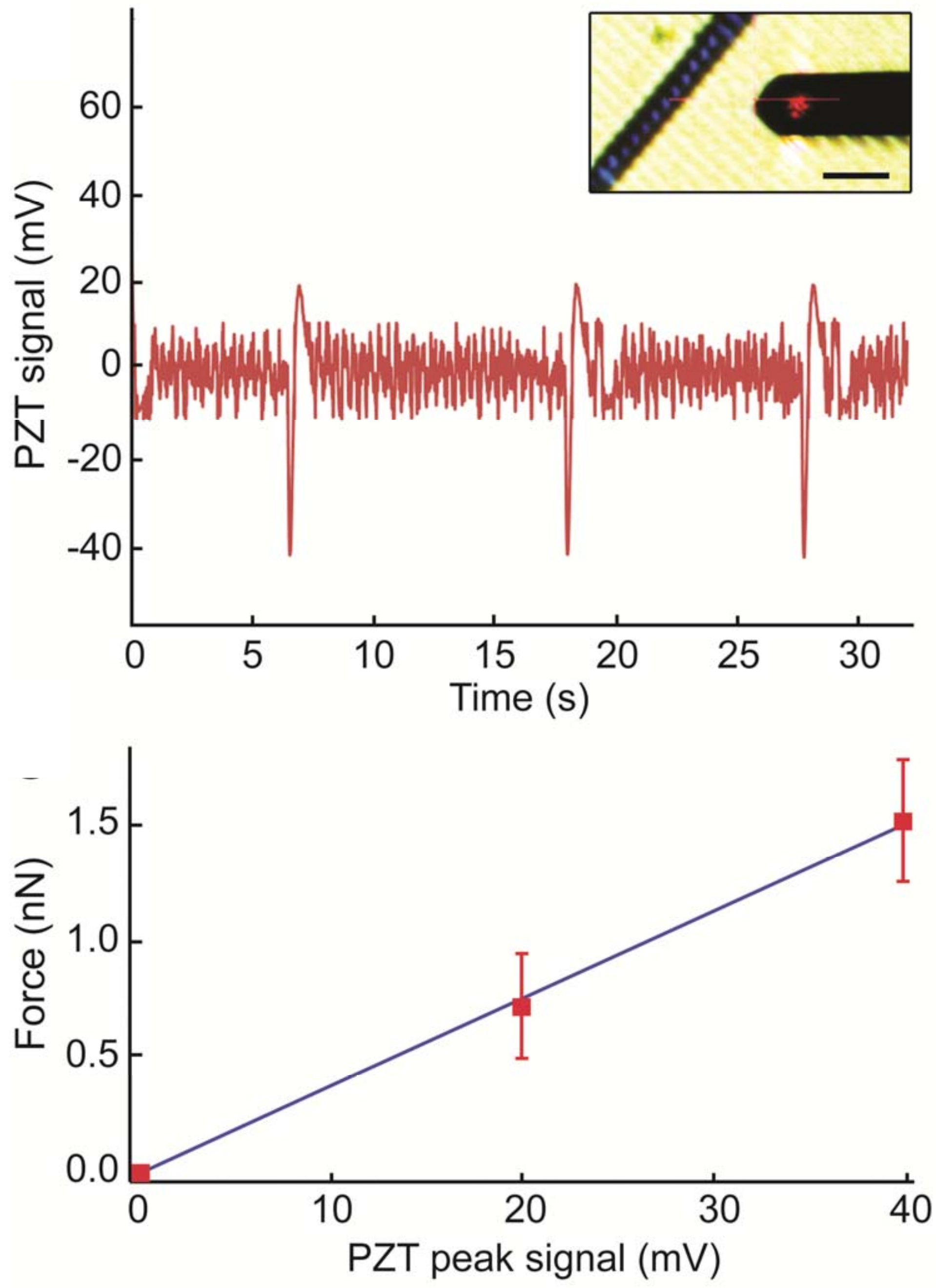




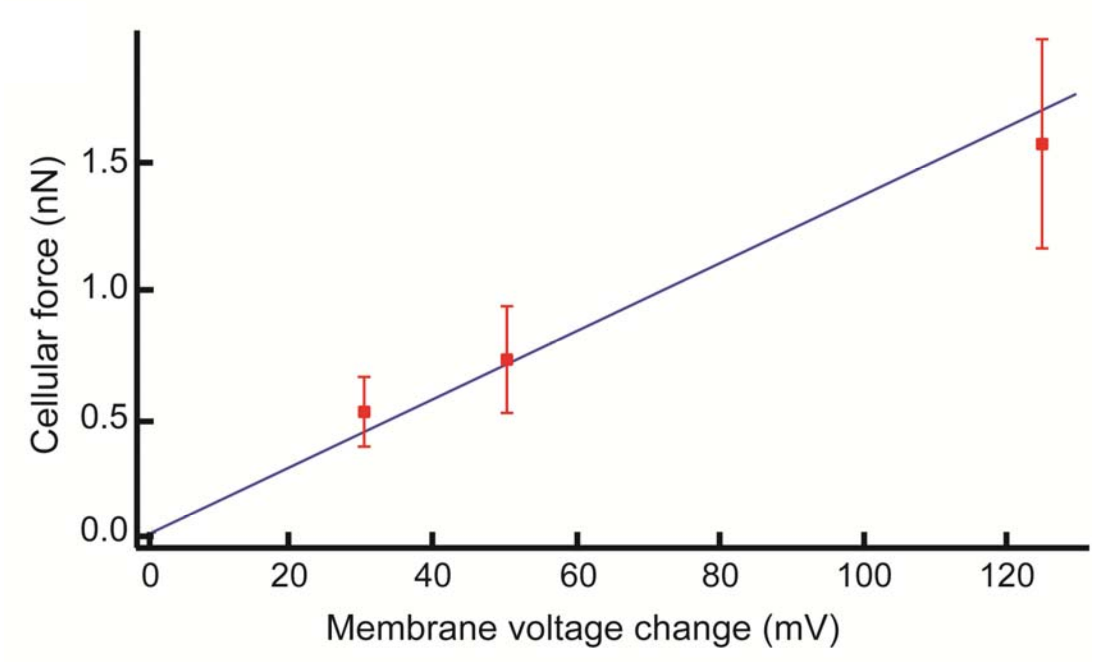


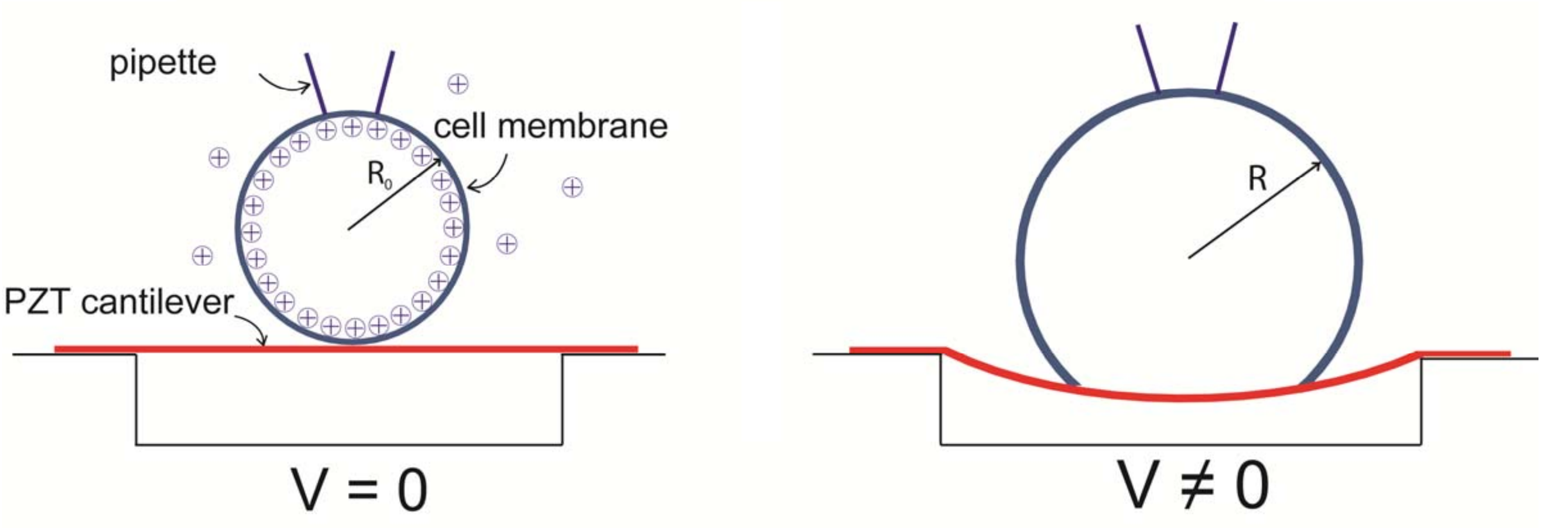
Calibration





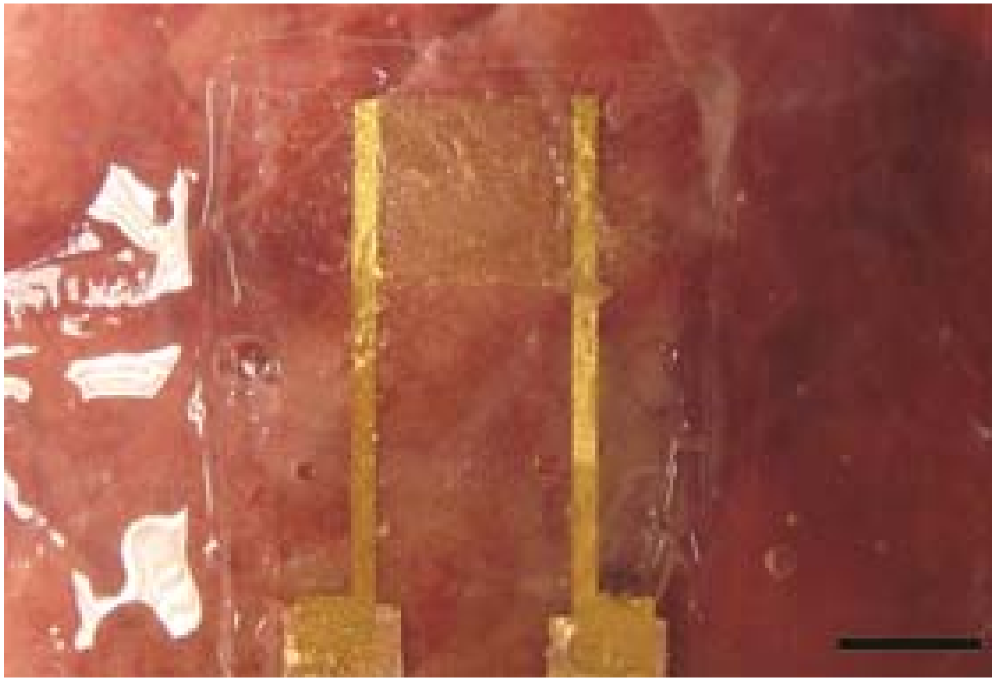
Quantification

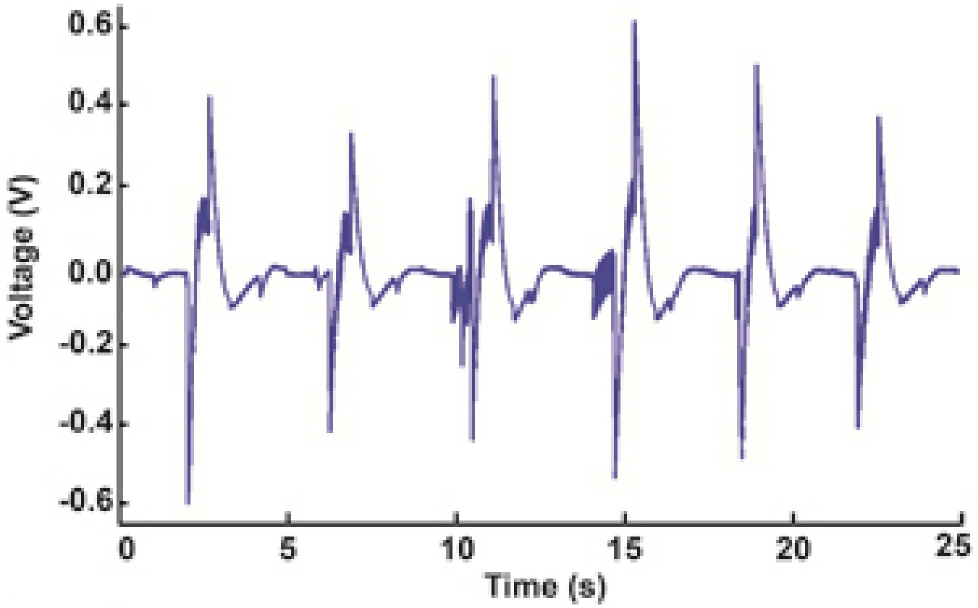


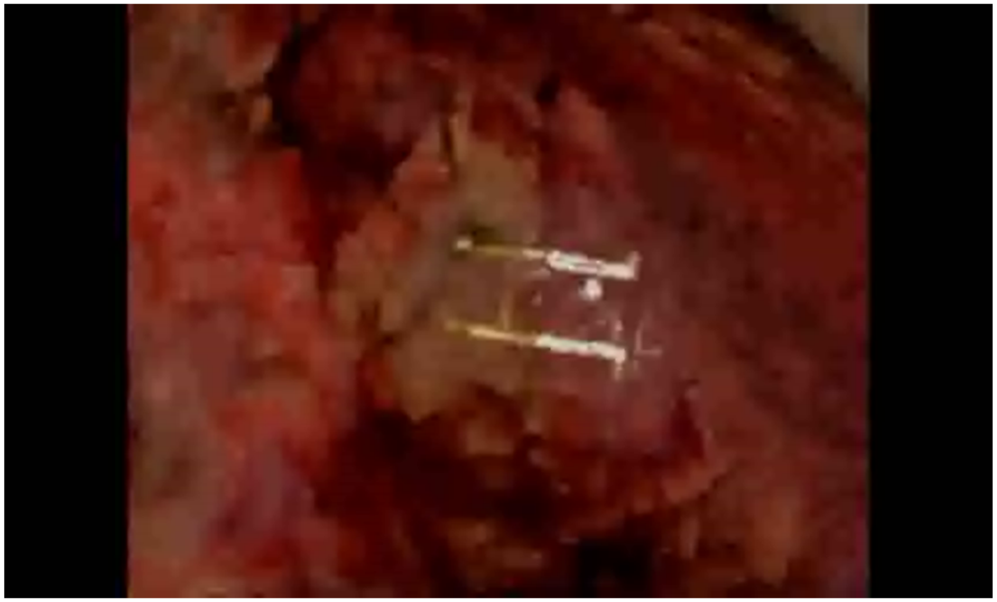


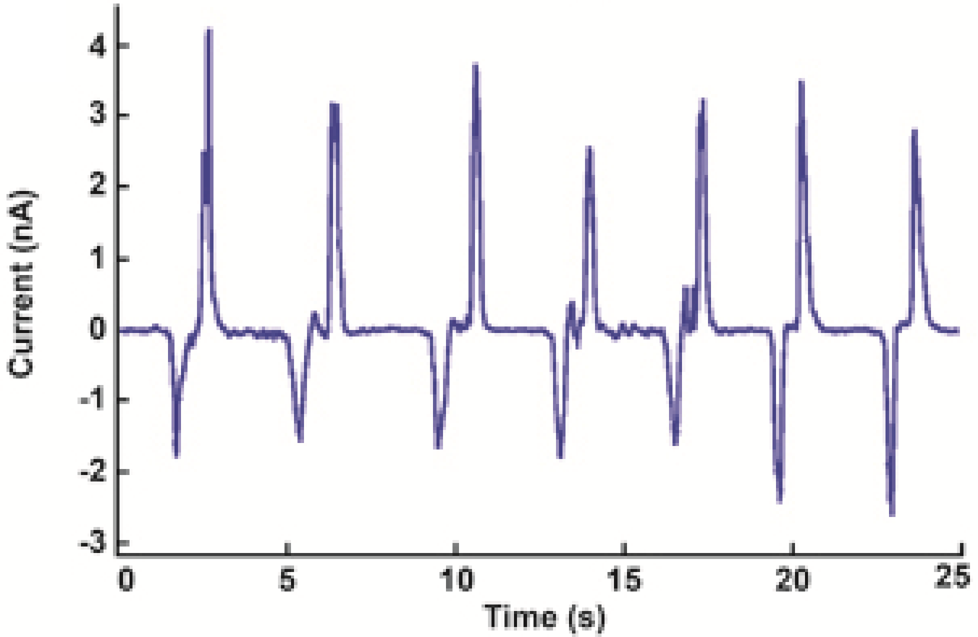
Force ~ 1.5 nN | Deflection ~ 1 nm

Biointerfacing

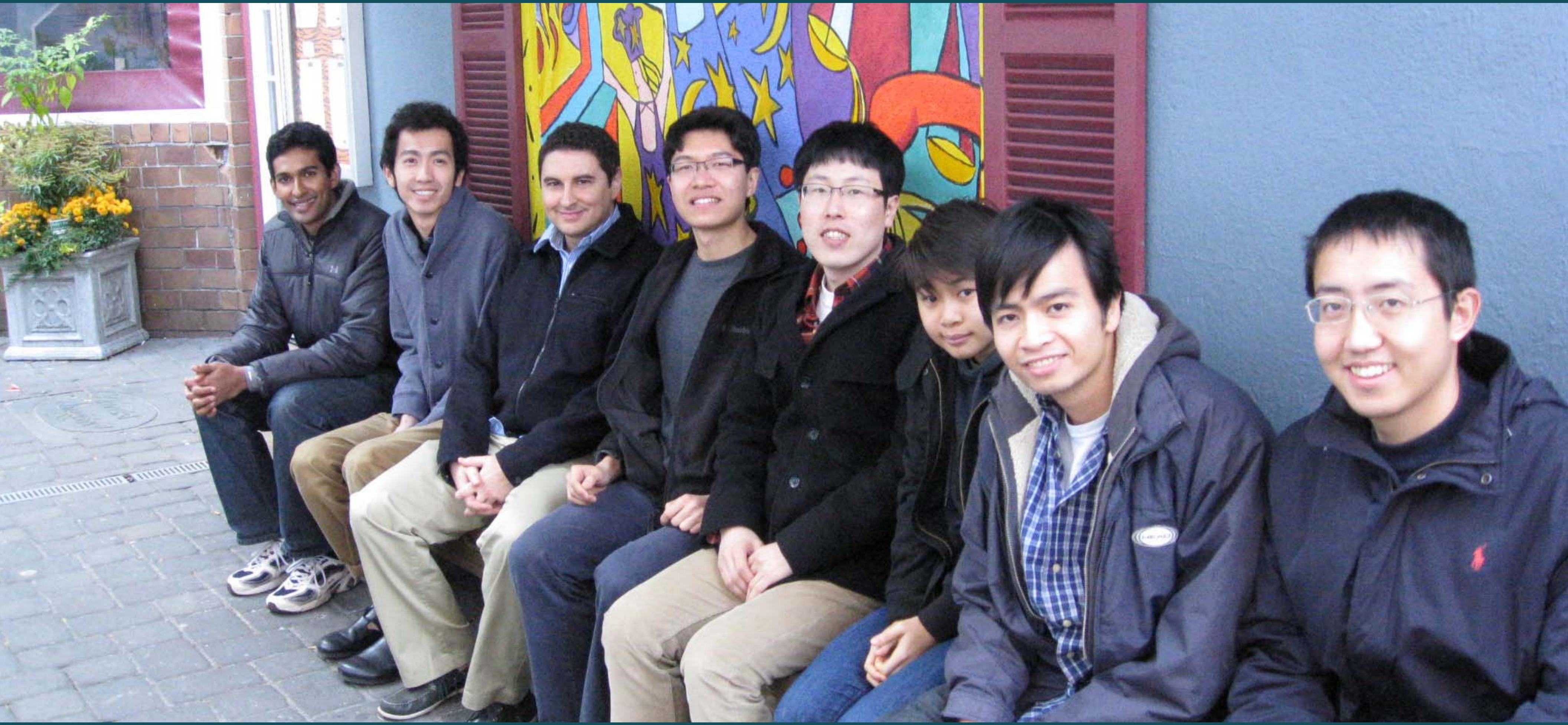








Thanks



DARPA | ARO | LM | AFOSR | AAF | NSF | IC | DUPONT

Prashant Purohit (Upenn) | Michael Berry (Princeton)