



E-MRS 2016 **Spring Meeting**



Selective growth of ZnO nanosheets and their application in piezoelectric and triboelectric energy harvesting devices



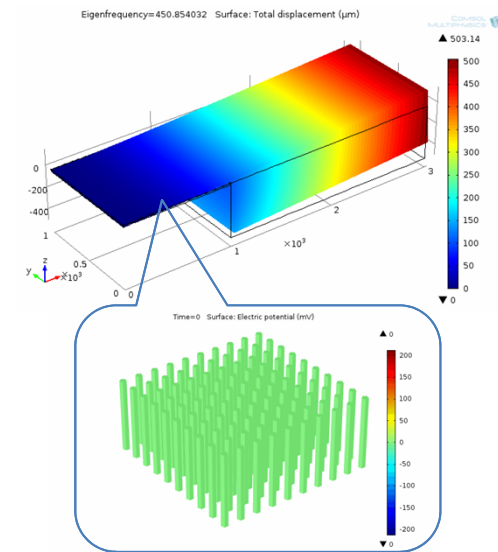
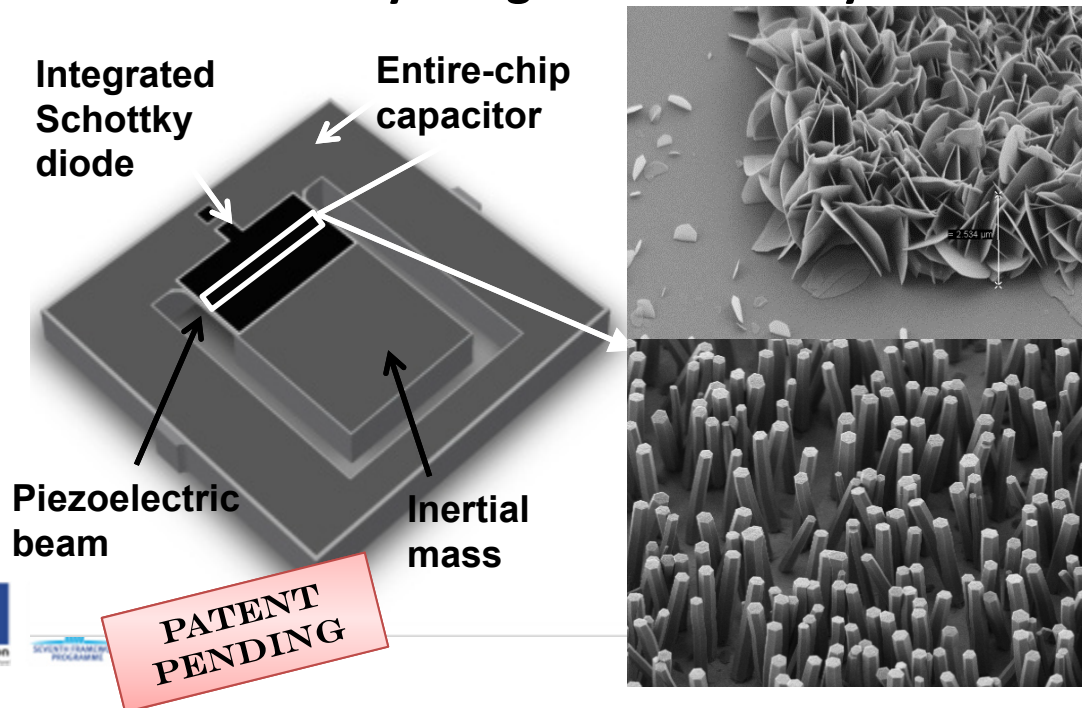
Symposium W
Lille, May 5, 2016

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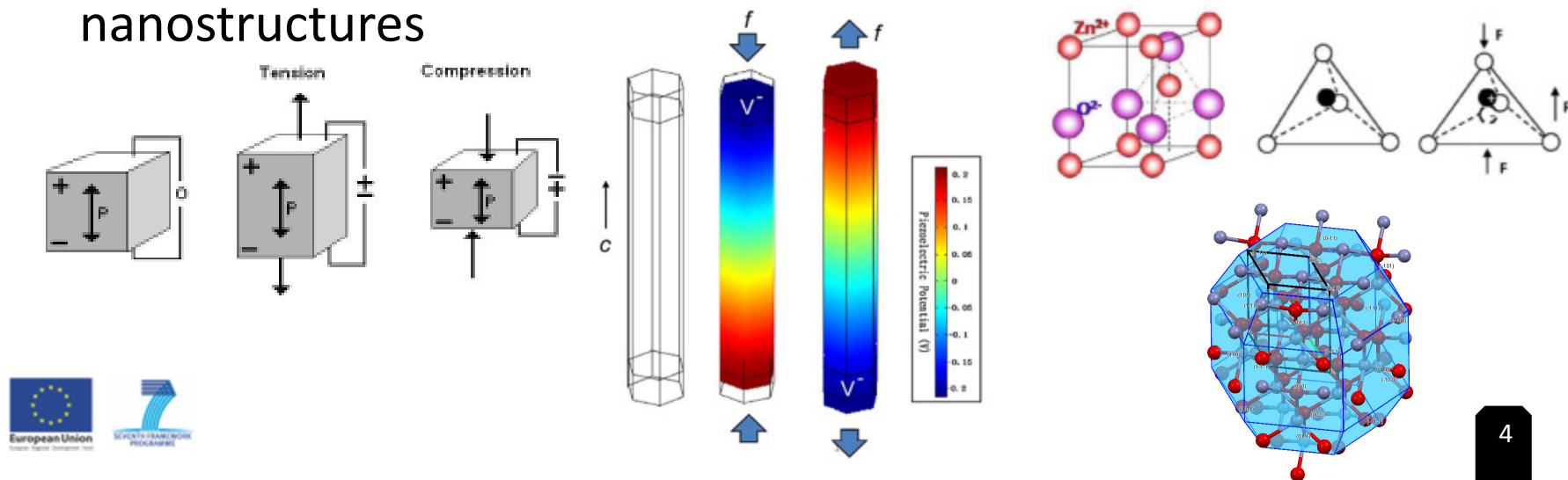
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Introduction

- **Piezoelectric Energy Harvesters: our final target**
 - Silicon mass and cantilever beam based on DRIE of an SOI wafer
 - **ZnO nanostructures** (nanowire and nanosheet) as piezoelectric material
 - Polymer encapsulation of NW/NS network
 - **Monolithically integrated Schottky diode and capacitor**

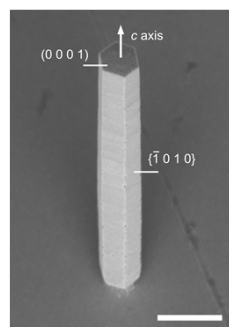


- Why ZnO nanostructures?
- ZnO is a semiconductor that presents a piezoelectric behavior and direct band-gap
- ZnO nanostructures are easy to grow and integrate with silicon
- More flexible and robust than thin-films
- Compatible with VLS silicon technologies
- ZnO is also a hot-topic and low-cost solution to grow nanostructures

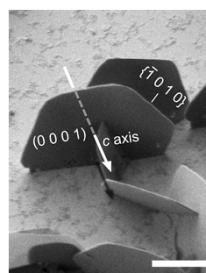
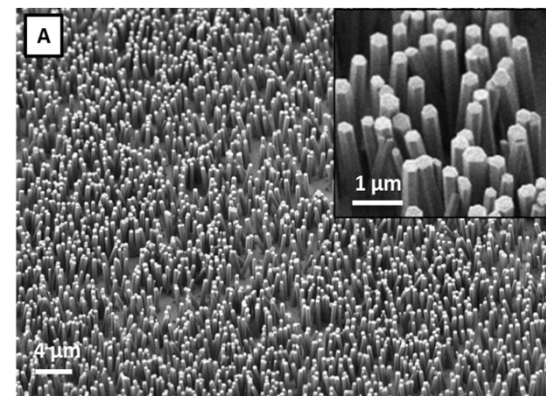
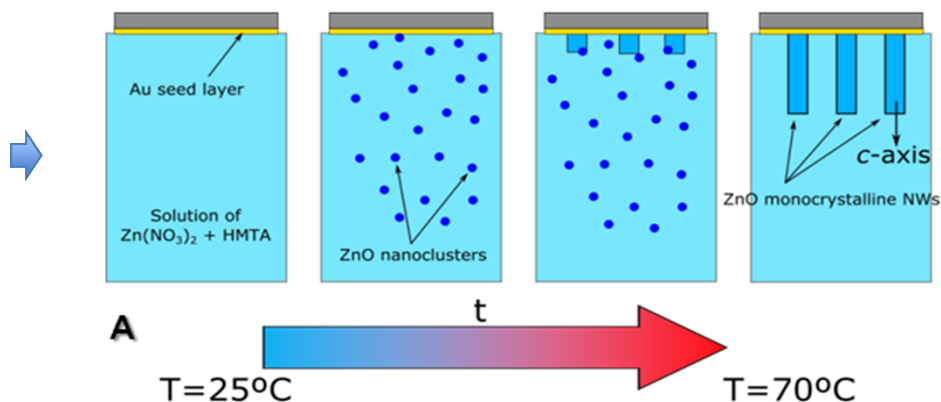


Growth of ZnO nanosheets (NSs) and nanowires (NWs)

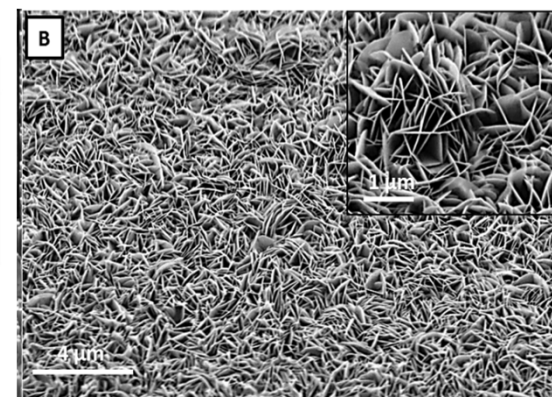
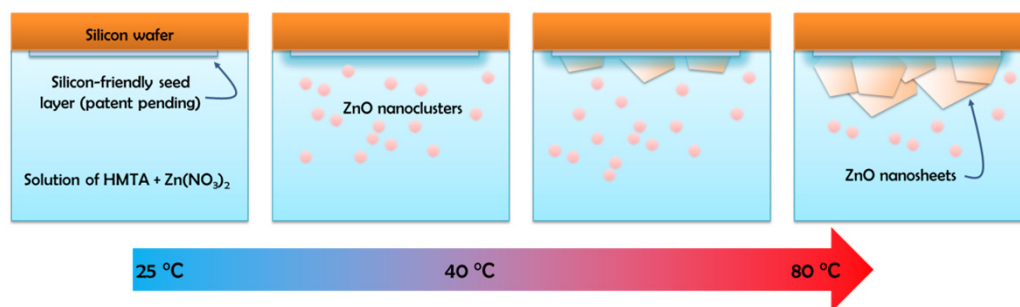
Hydrothermal process (cheap, low T, wafer level and selective)



NW



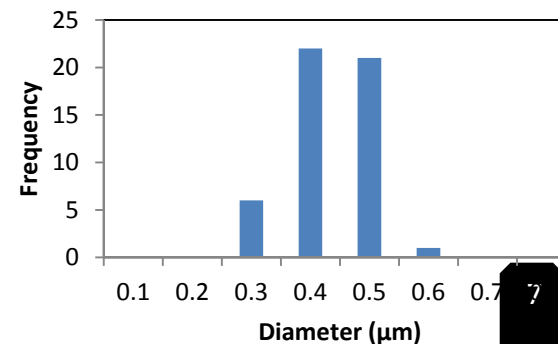
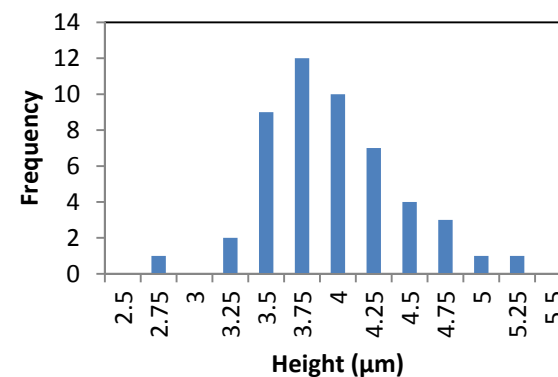
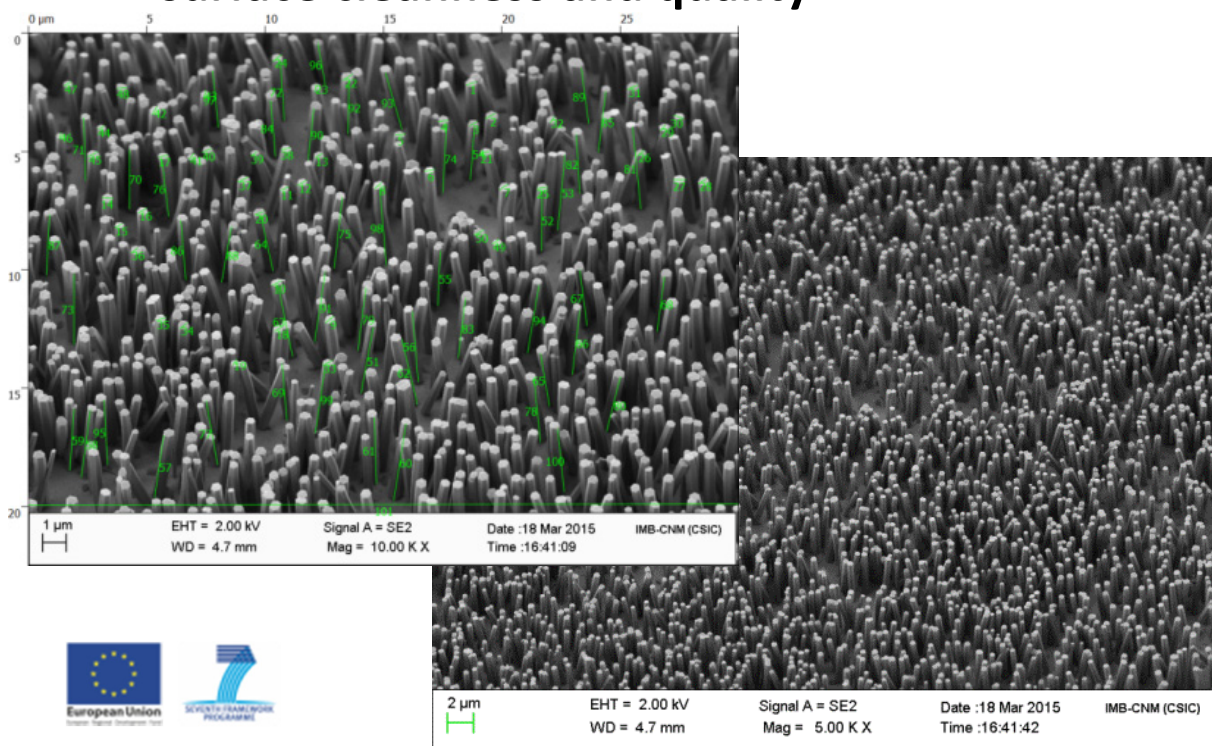
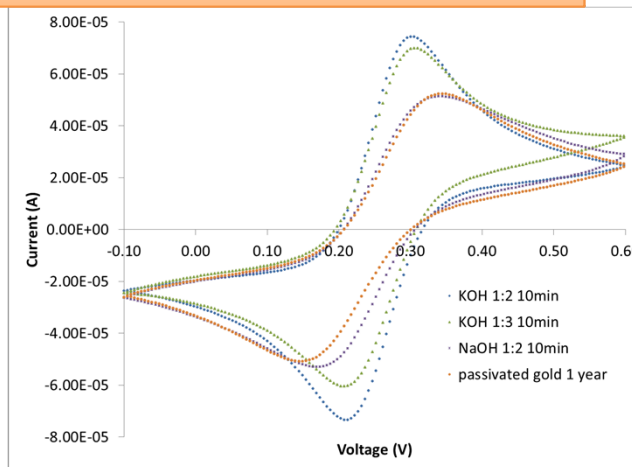
NS



Growth Characterization of NW over gold seed layer

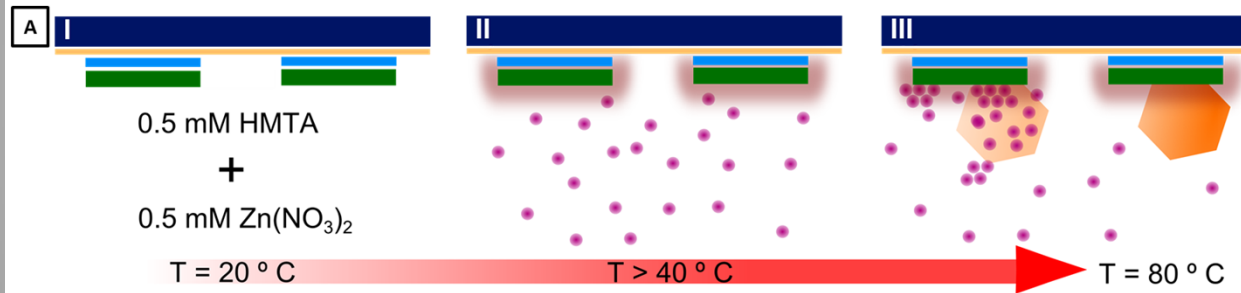
Density = 124 NW/100 μm^2

- Activation process developed with H_2O_2 :KOH (1:3 and 1:2), H_2O_2 :NaOH (1:3 and 1:2) or HNO_3 .
- Relationship between cyclic voltammetry and surface cleanness and quality

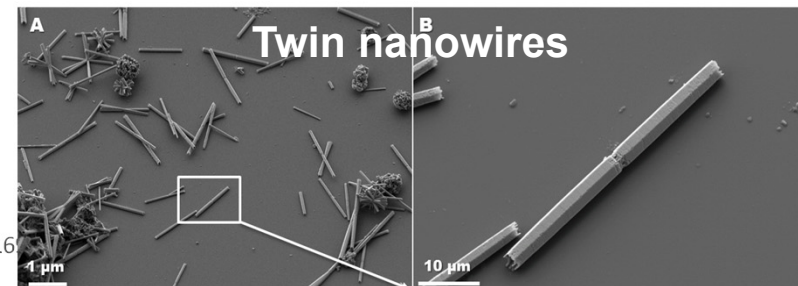
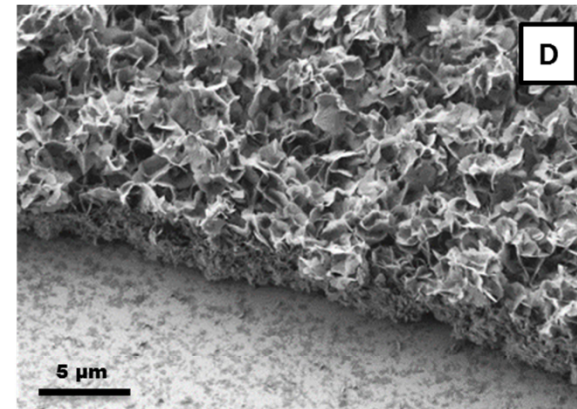
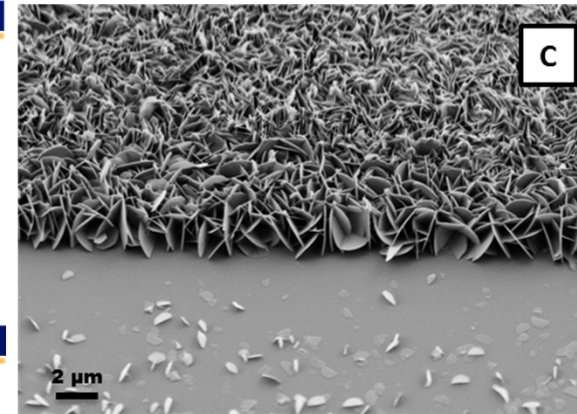
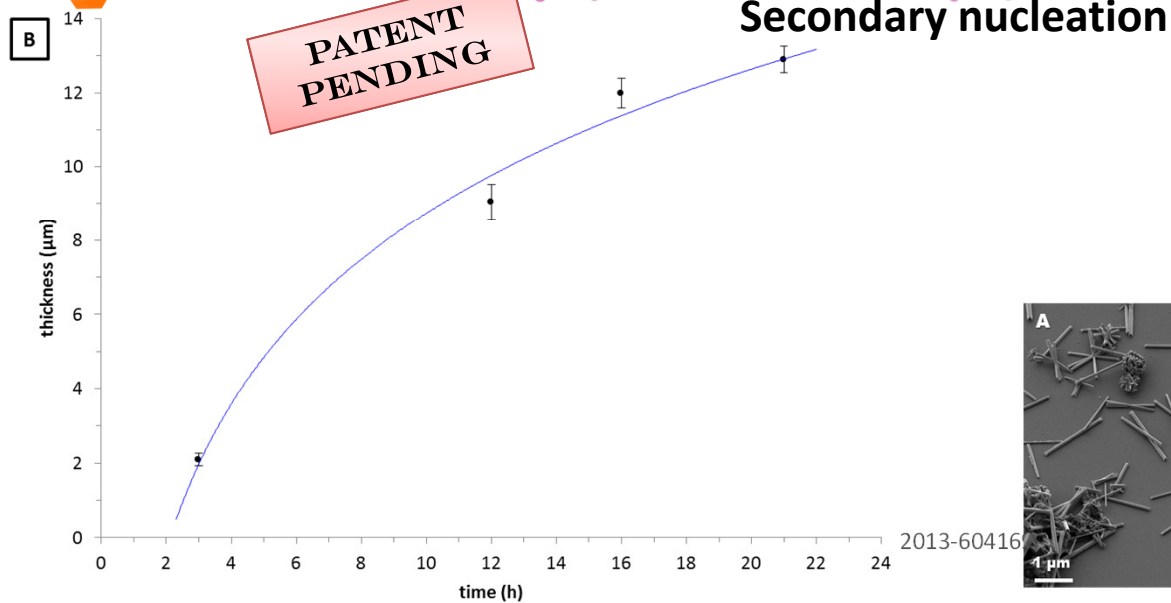




ZnO NS synthesis: working principle



- (1 0 0) Si wafer
- CVD SiO₂
- Ti/Pt layer
- Seed layer
- Local pH gradient
- ZnO nanocluster
- ZnO nanosheet



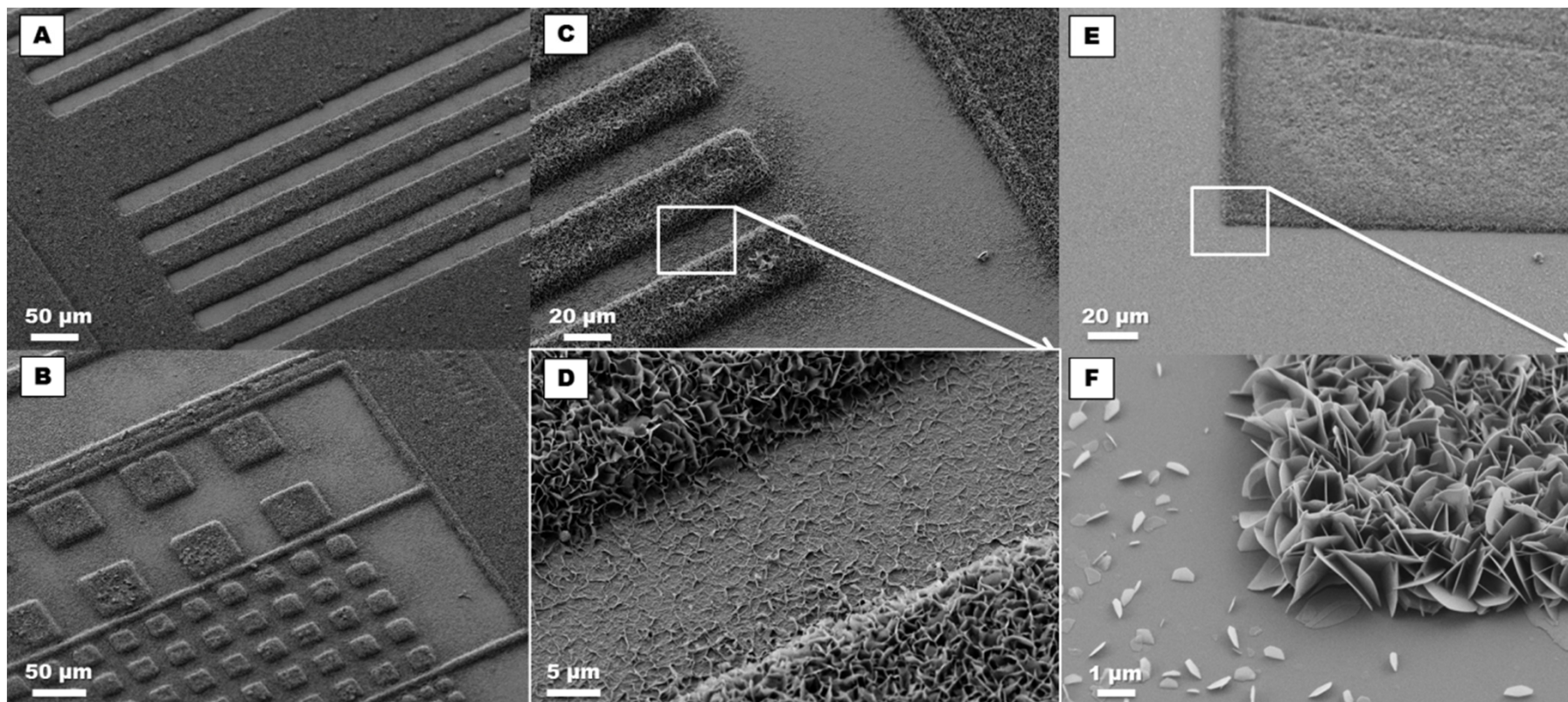
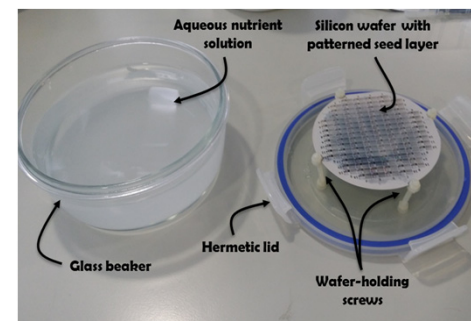
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Selective area ZnO NS synthesis at wafer level

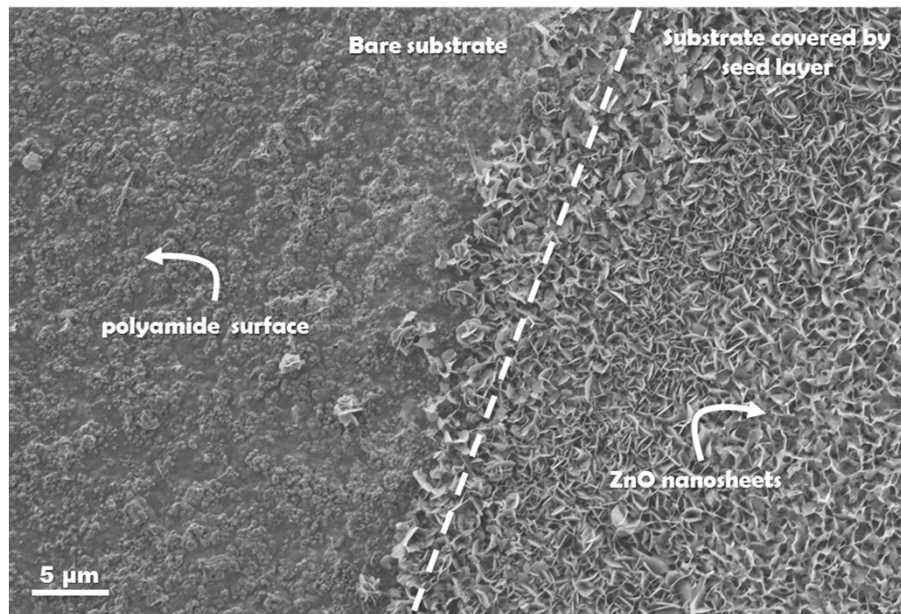
Selective area growth on silicon wafers

- Micrometric features can be obtained with high selectivity at wafer level.

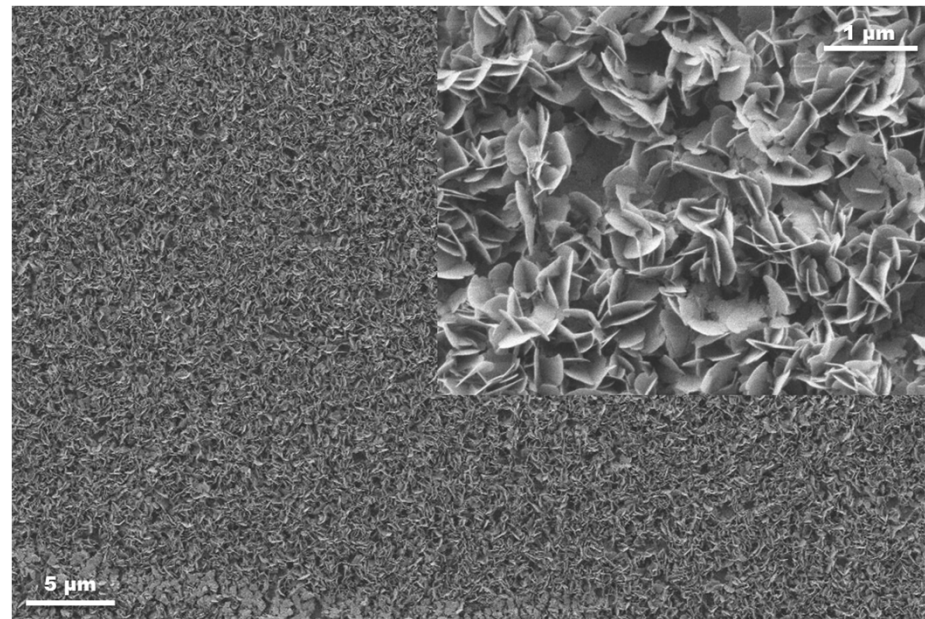


ZnO NS synthesis on other substrates

- Performed in flexible substrates such as polyimide
- It can be grown on top of glass (transparent device)
- Wafer-level synthesis



polyimide

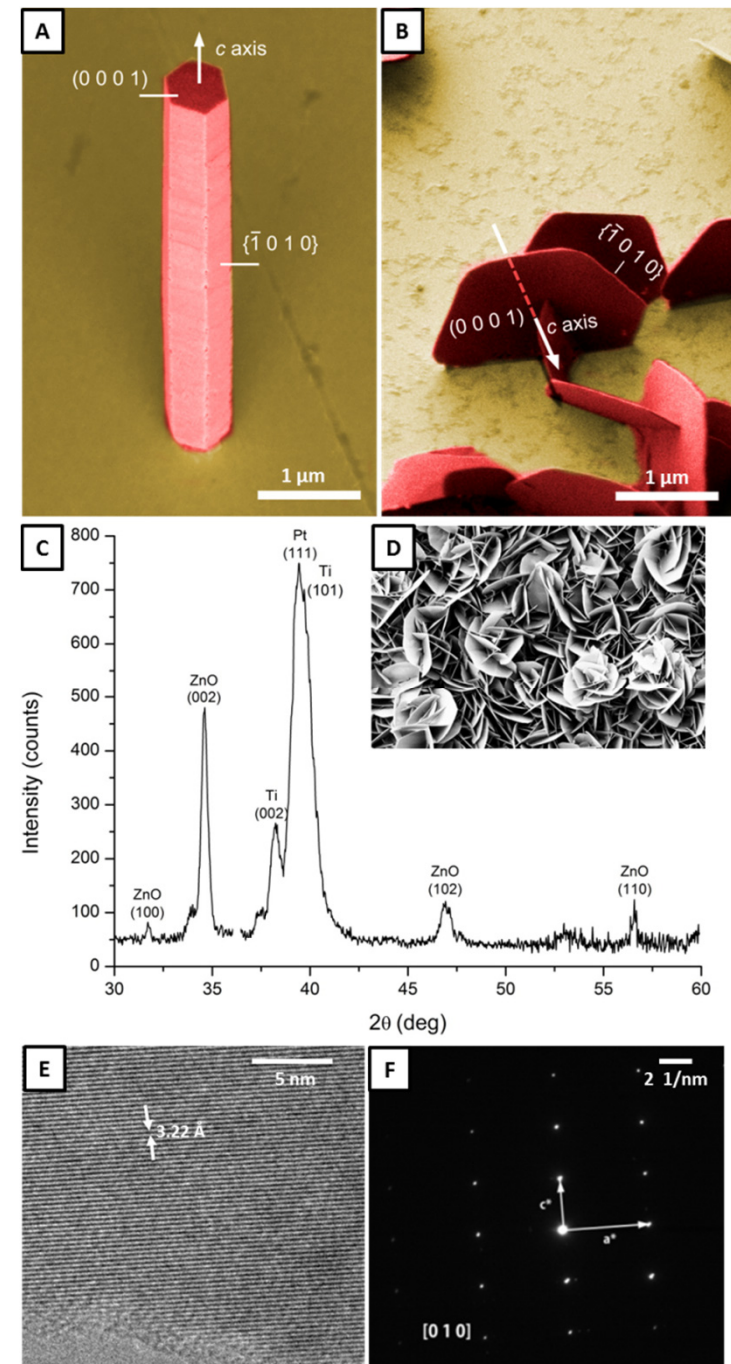


glass

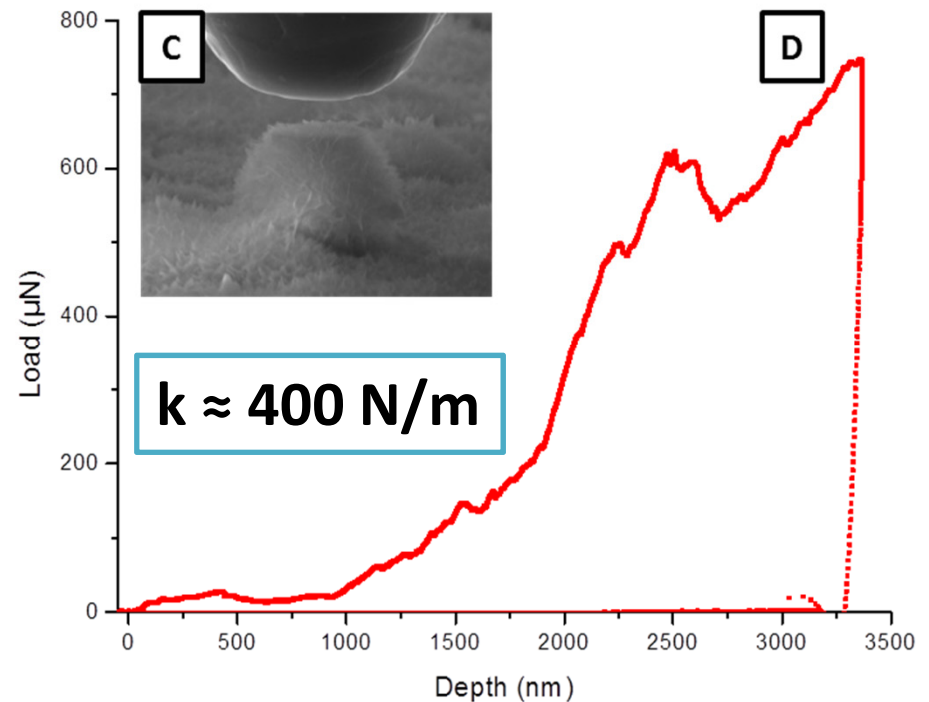
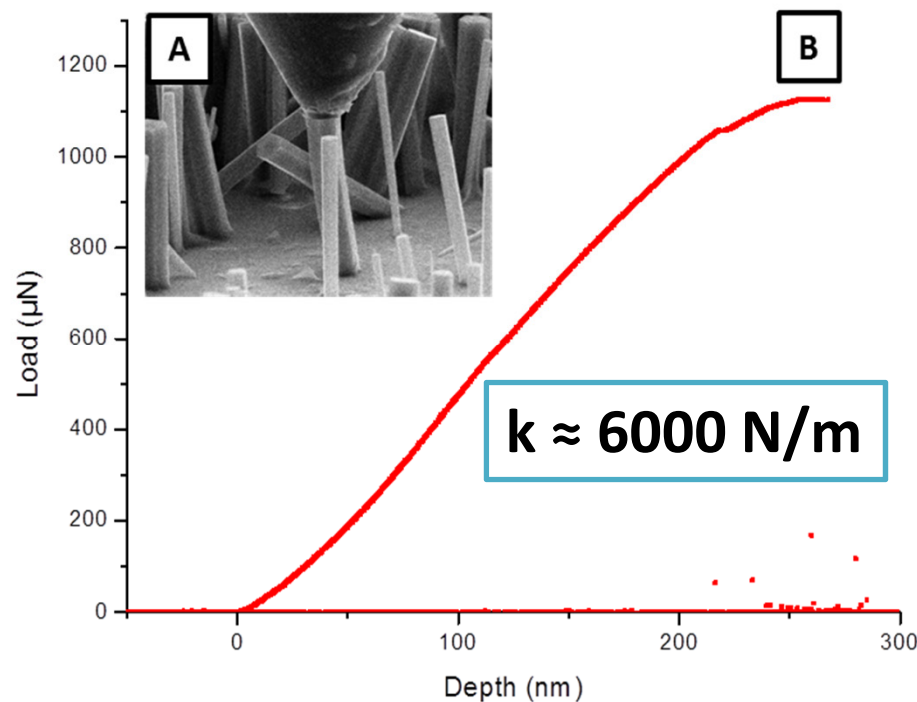
Material characterization

Characterization by HRTEM, SEM and XRD:

- ZnO NWs & NWs show a **good crystalline** structure.
- NS: Thickness < 20 nm, several μm long; **high aspect ratio**
- NS: Extremely high-density, **reproducible and fast**
- Growth along (0001) face is inhibited by the local pH gradient around seed layer
- **Seed layer is an insulator** which **avoid screening effect** of external carriers going into the ZnO

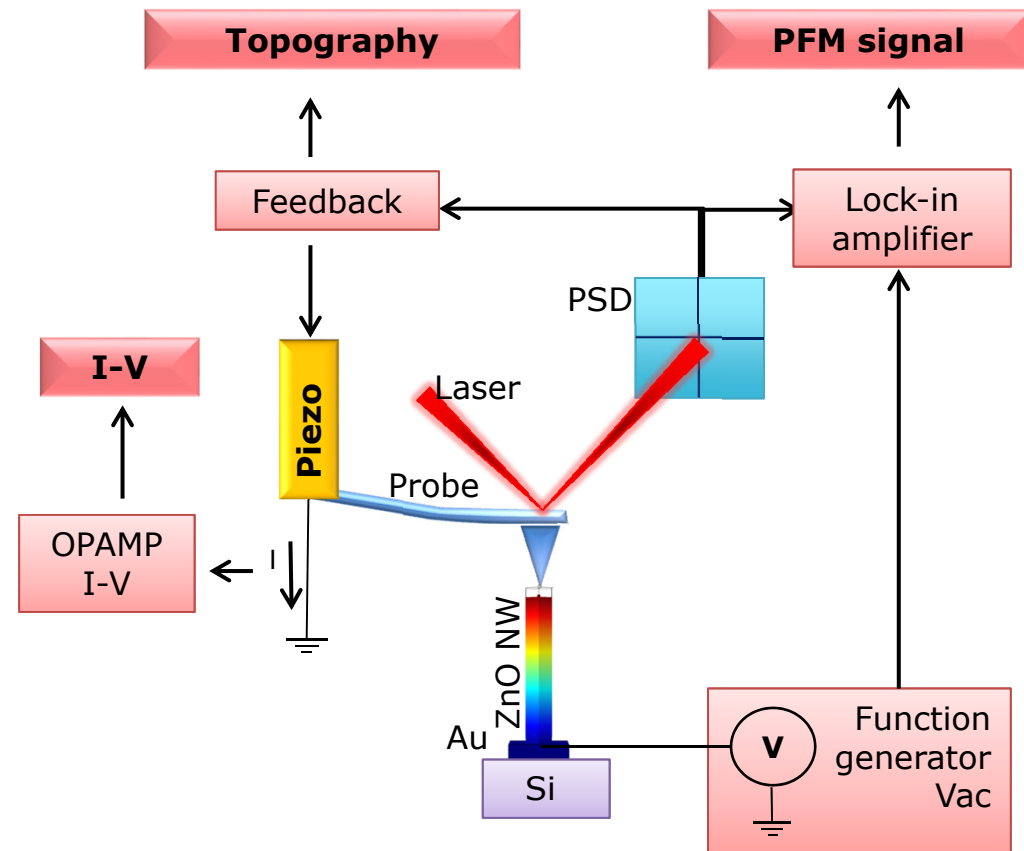


- ZnO nanostructures allow higher compression without fracture.
- It has been demonstrated that a single ZnO NW can stand for a compressing force of more than 1mN!



Piezoresponse Force Microscopy (PFM):

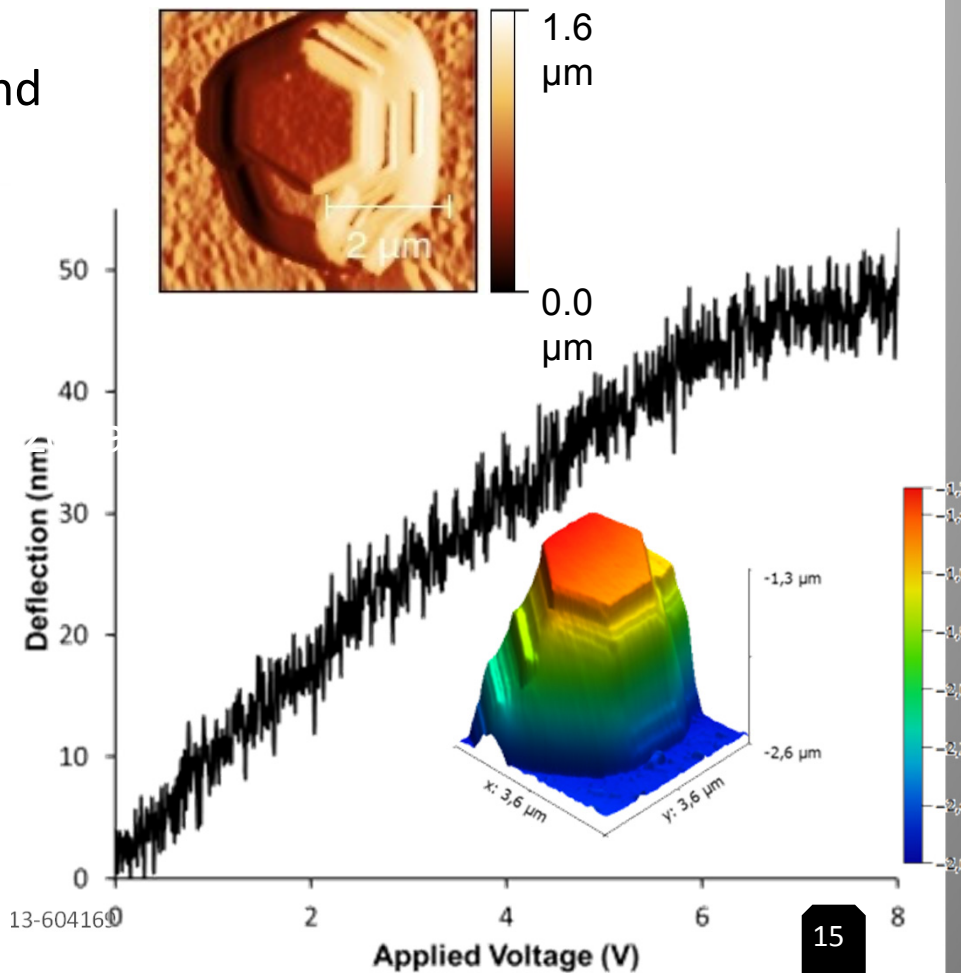
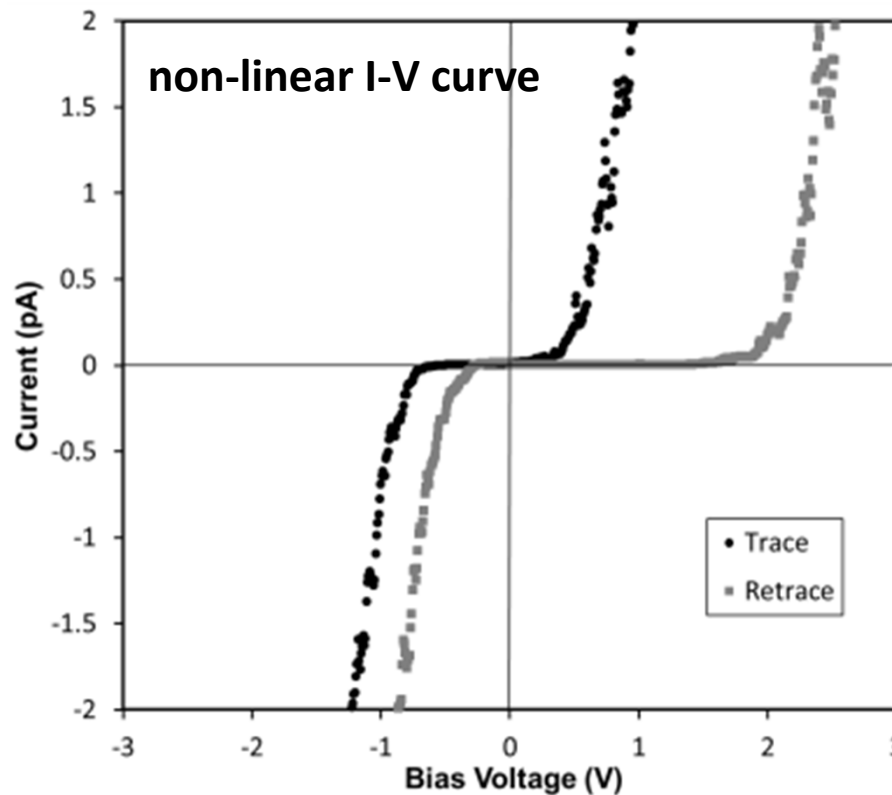
- AFM technique based on the converse piezoelectric effect
- Conductive tip used to measure the mechanical response when an electrical voltage (usually ac-voltage) is applied to the surface



- I-V and piezoresponse characterization

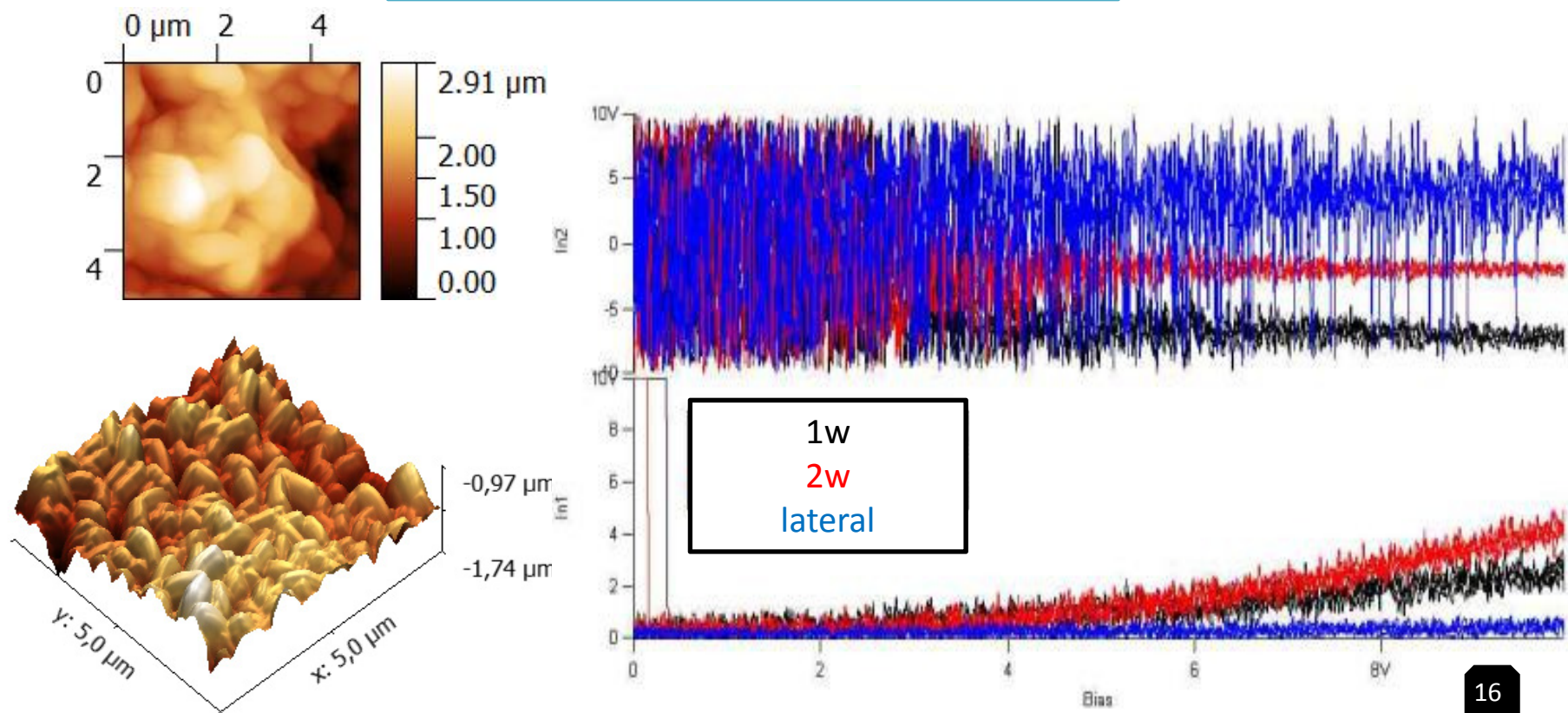
ZnO nanowire: $d_{33} \approx 8.6 \text{ pm/V}$

Piezoresponse AFM (PFM) measurement of ZnO nanowires and nanosheets at 37kHz.



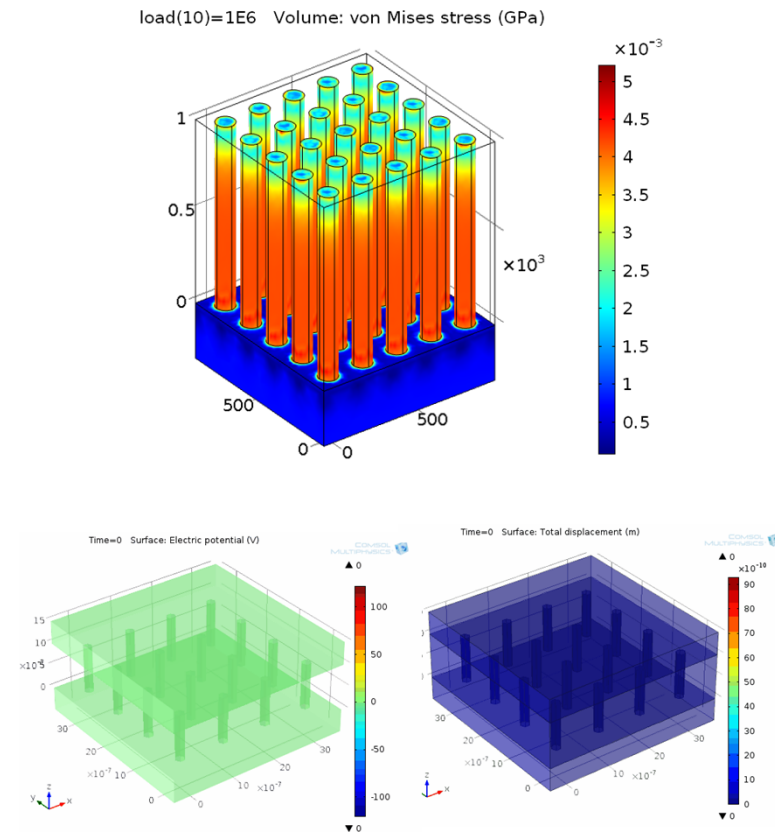
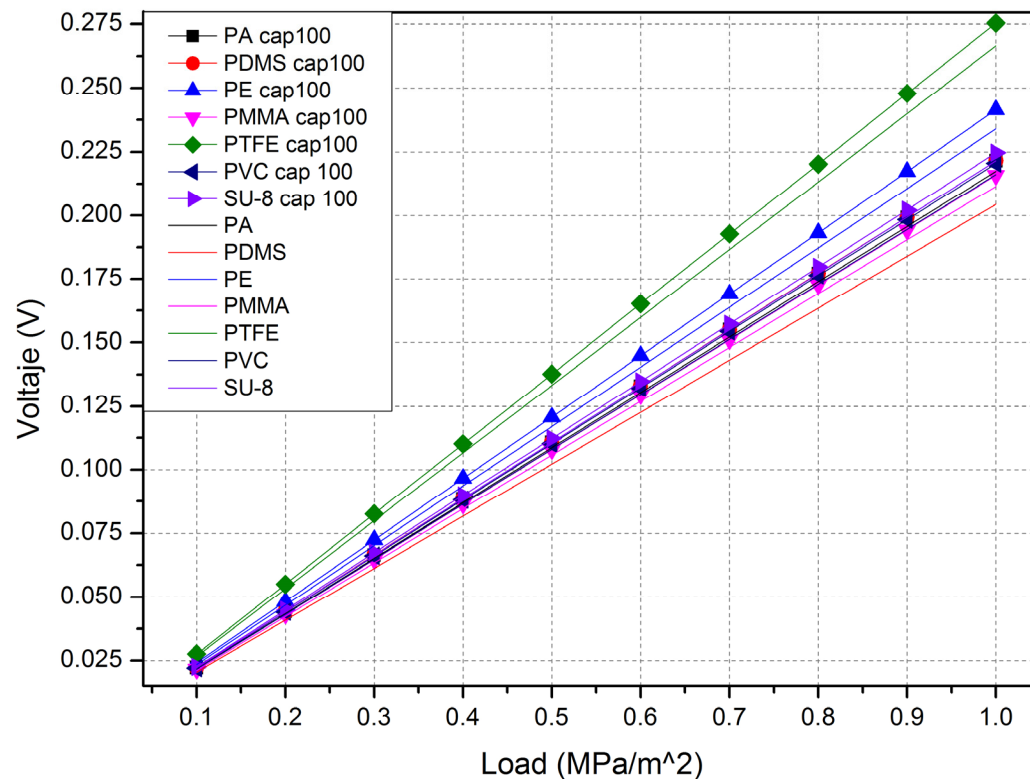
- PFM characterization
 - Piezoresponse of ZnO nanowires and nanosheets at 37kHz.

ZnO nanosheet: $d_{31} \approx 6 \text{ pm/V}$

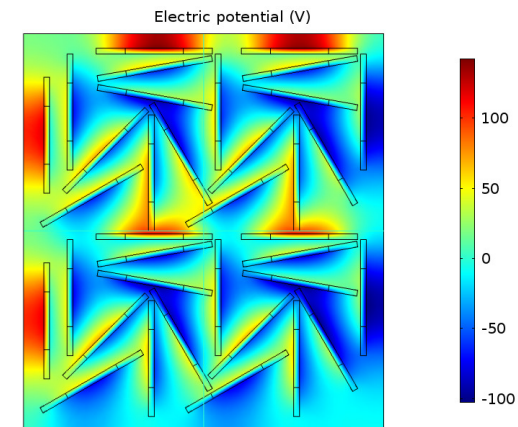
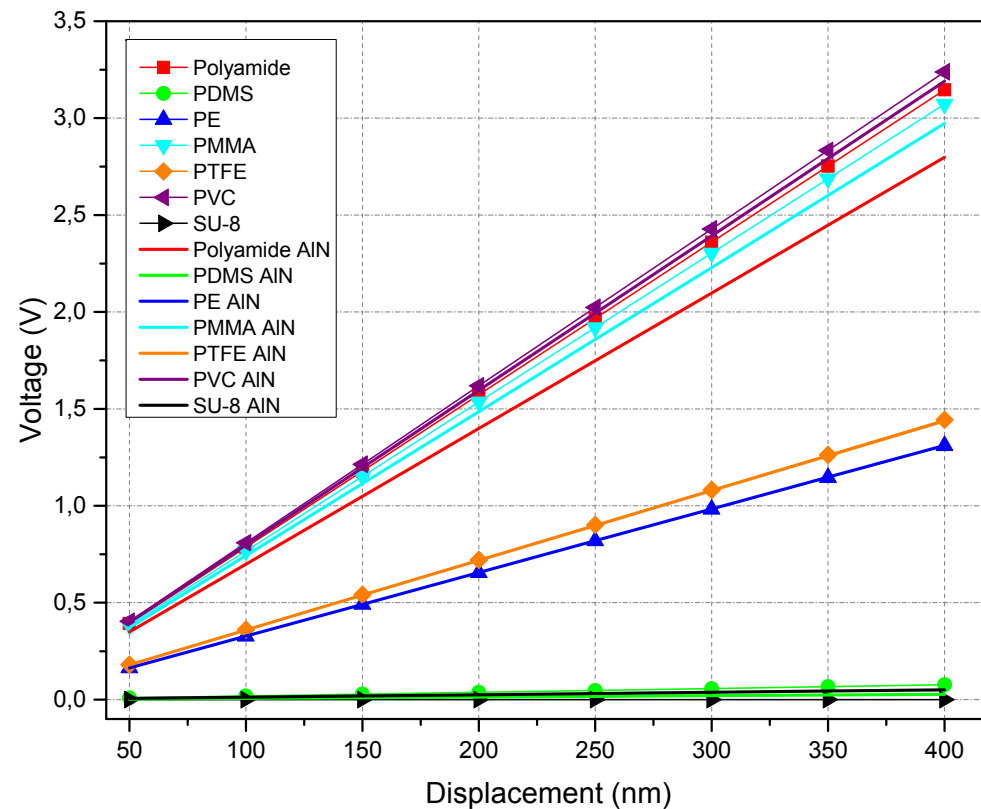


Piezoelectric and triboelectric applications: preliminary results

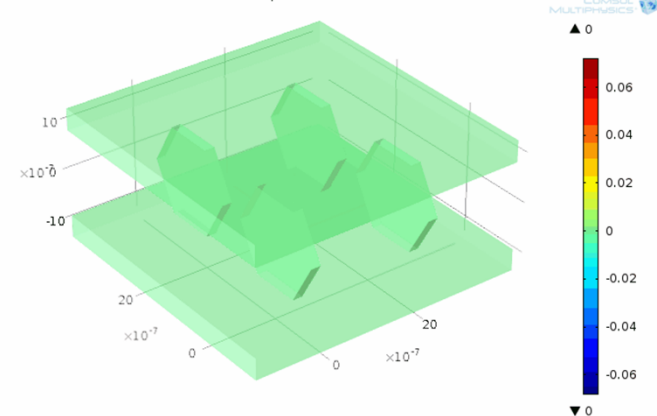
- ZnO nanowires
 - Study of more suitable polymer to encapsulate ZnO NWs in terms of open circuit voltage:



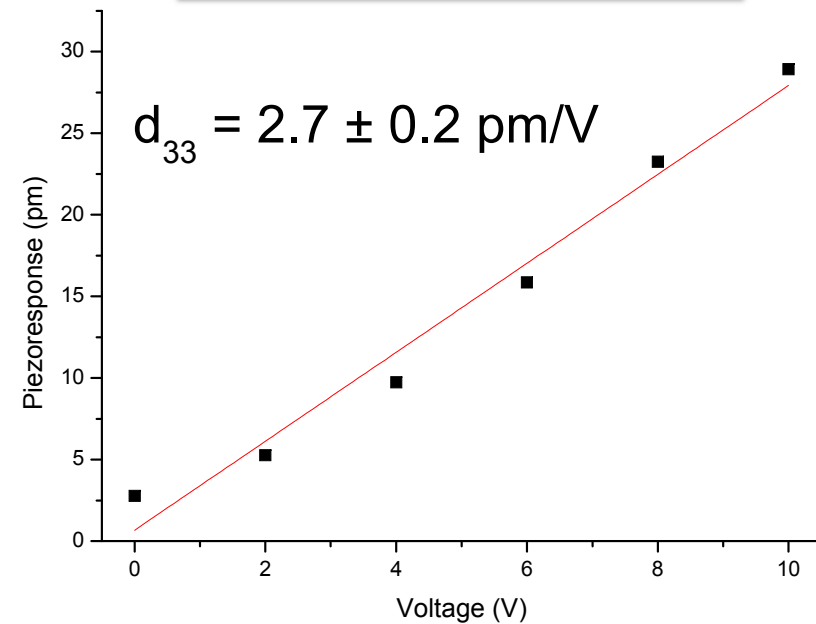
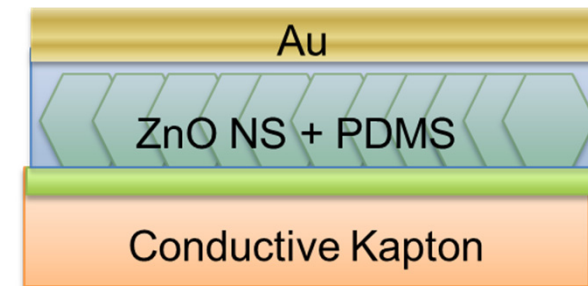
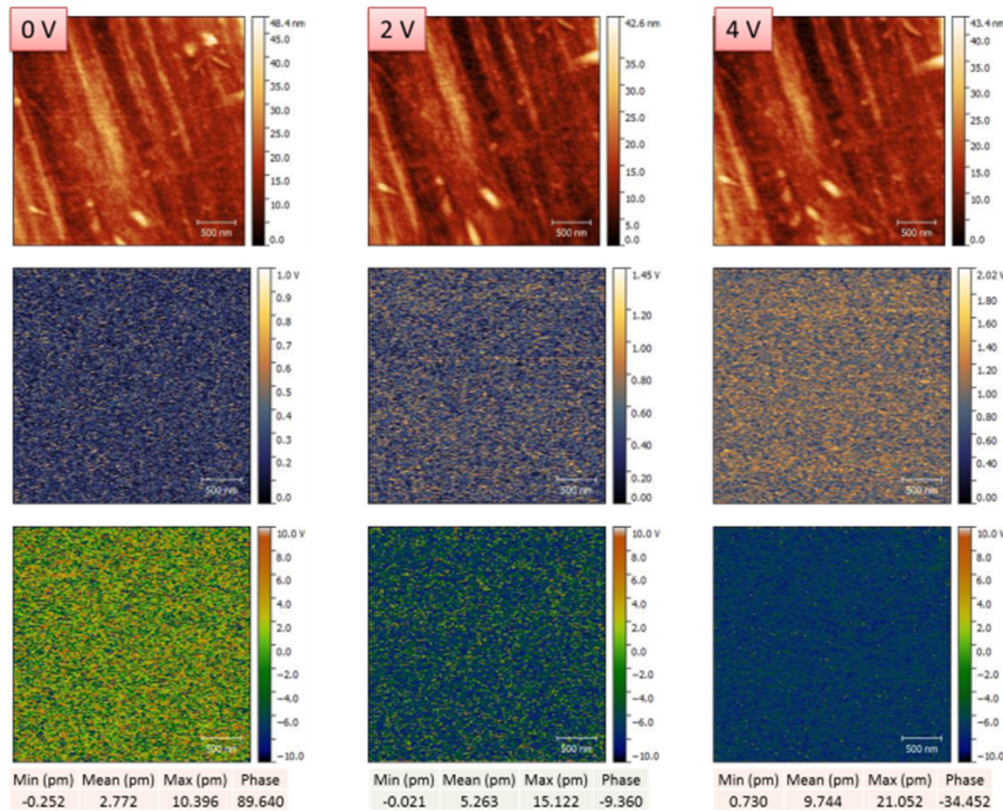
- ZnO nanosheets:
 - Study of more suitable polymer to encapsulate ZnO NSs in terms of open circuit voltage:



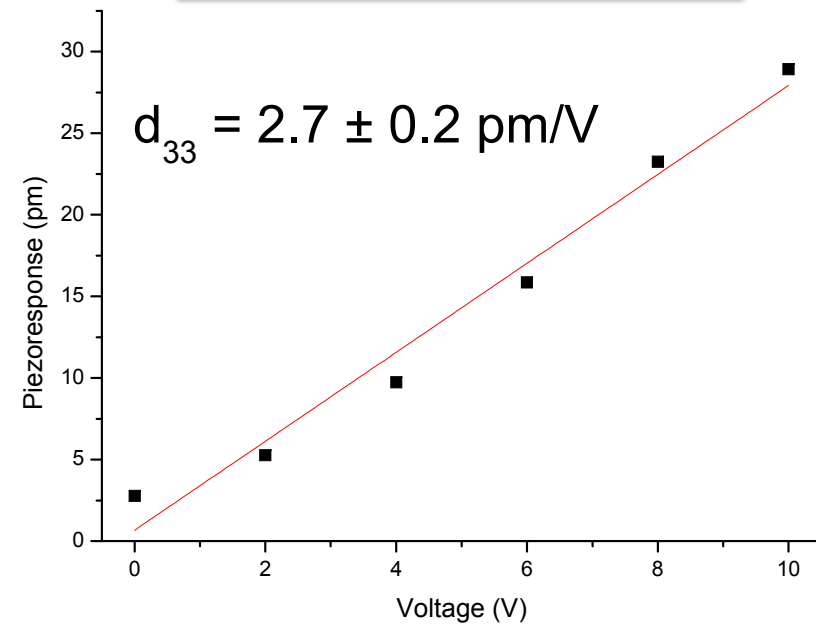
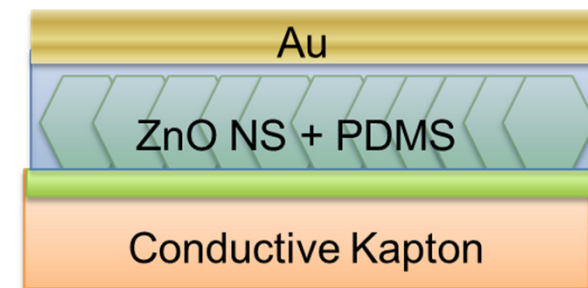
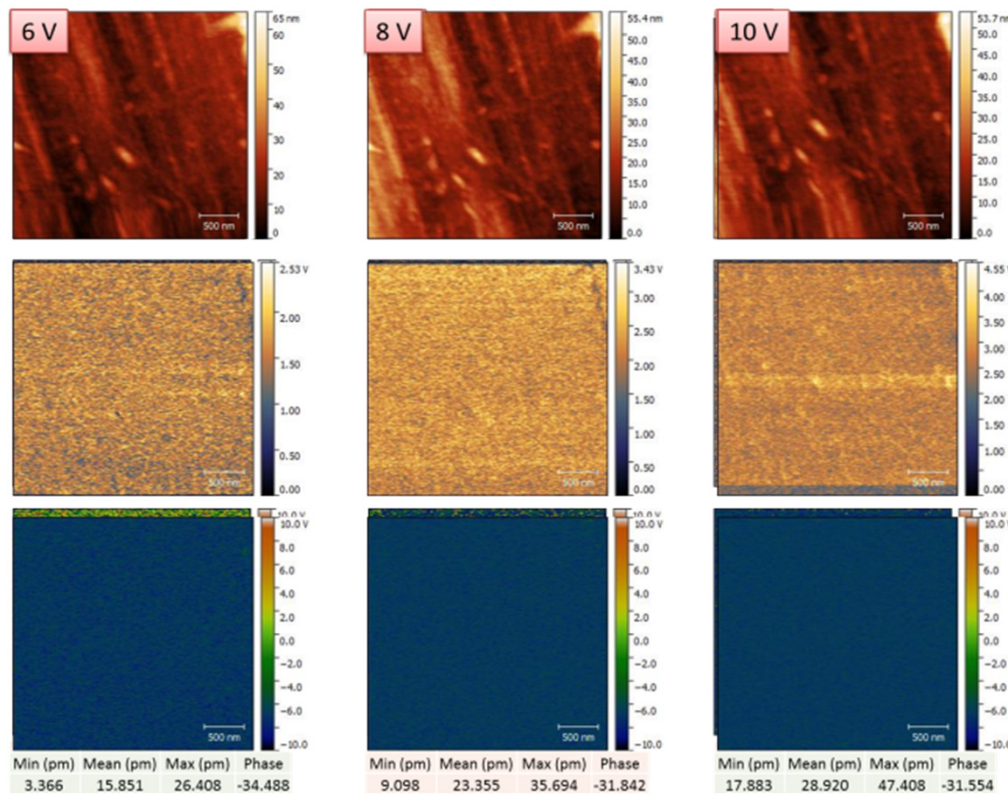
Time=0 Surface: Electric potential (V)



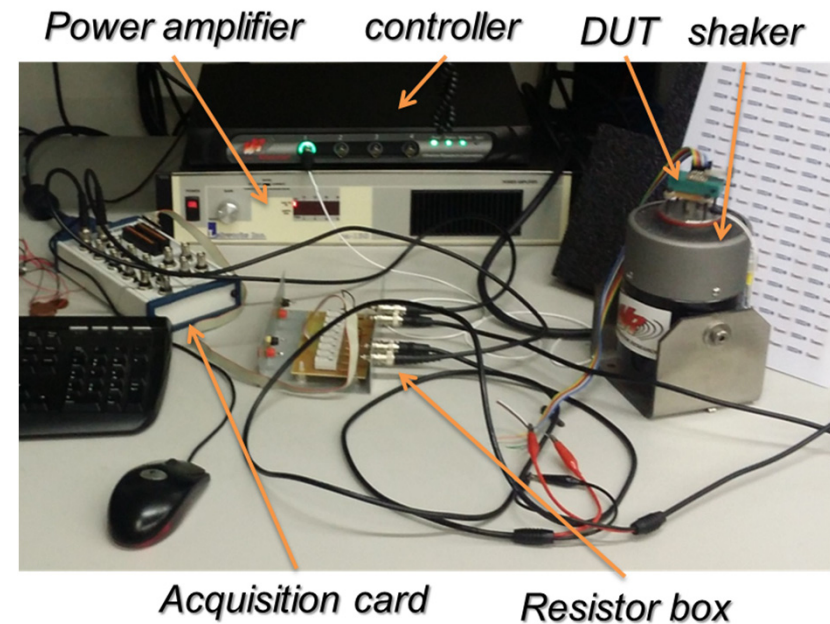
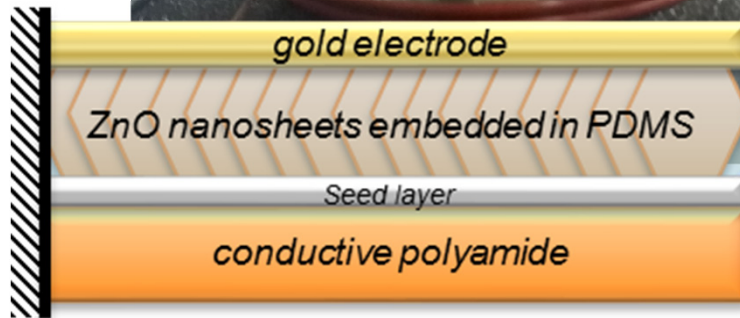
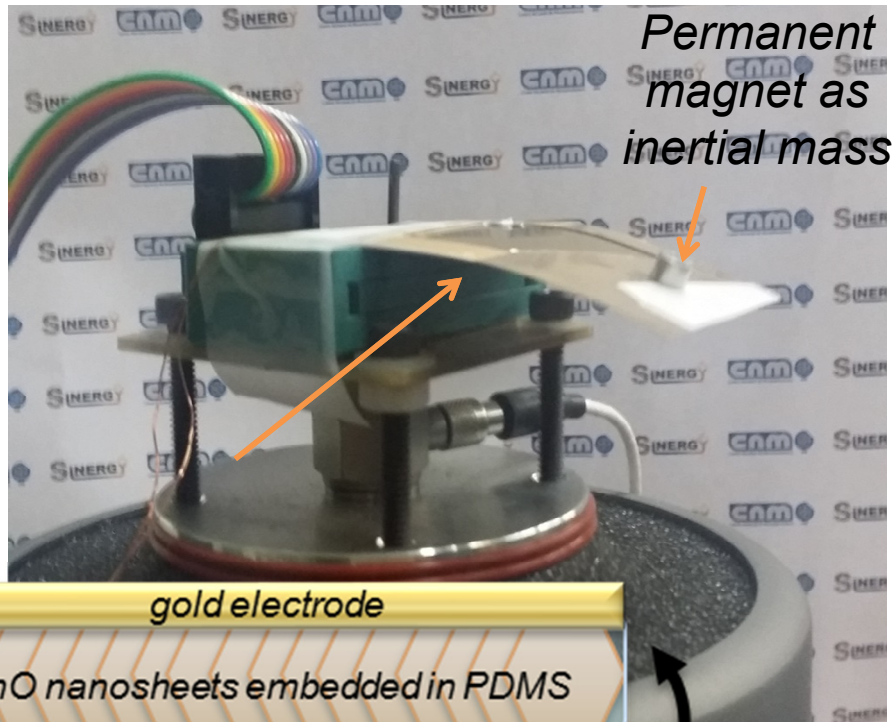
PFM of Flexible generator based on ZnO NS + PDMS



PFM of Flexible generator based on ZnO NS + PDMS



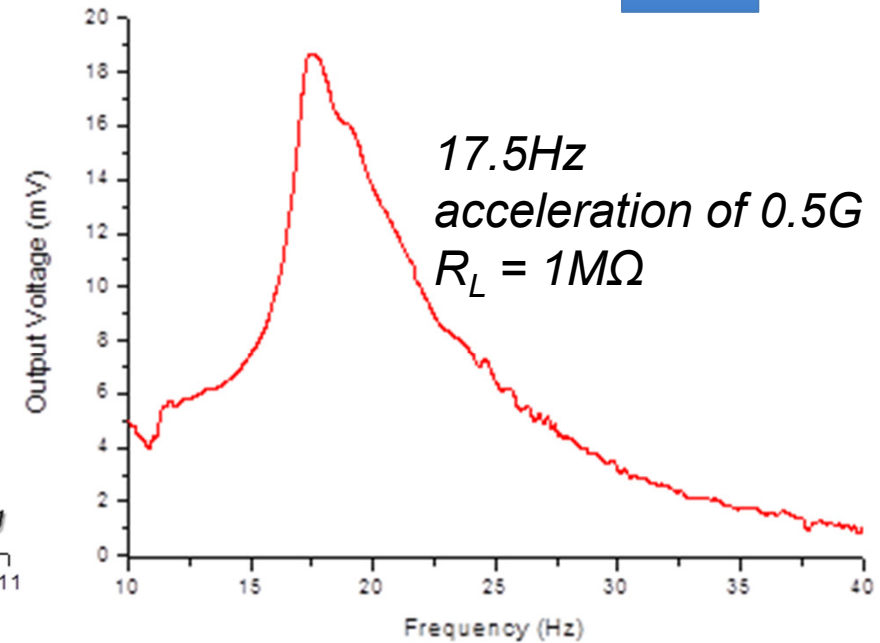
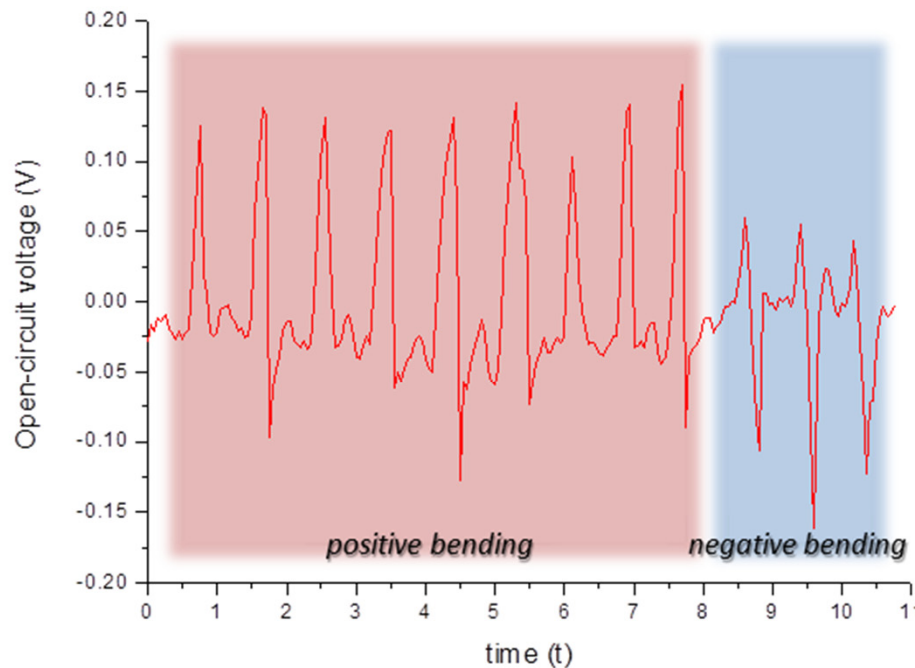
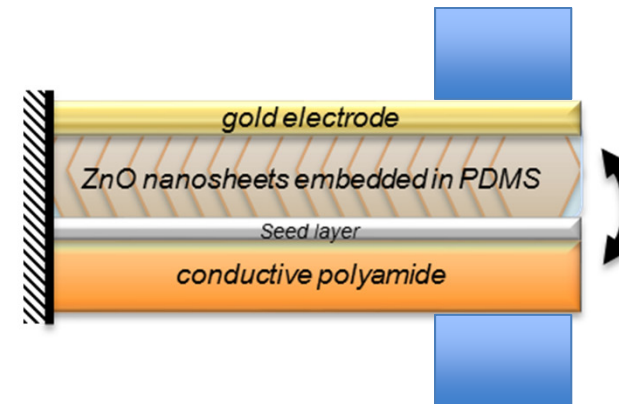
- Flexible energy harvester
 - Vibrational device characterisation
 - Tip mass made with two magnets



NMP3-SL-2013-604169

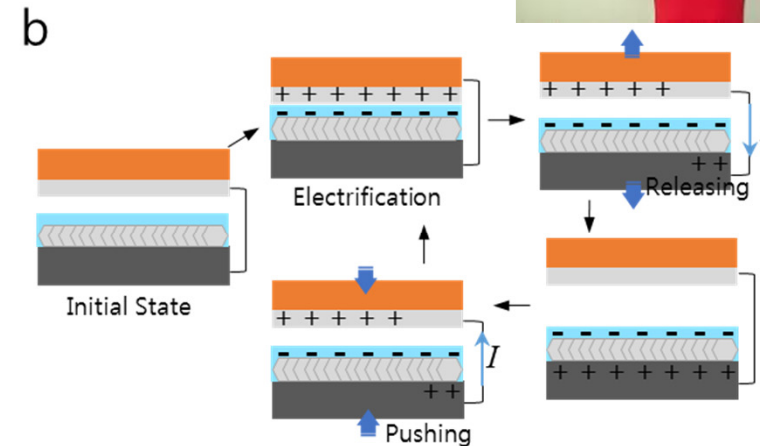
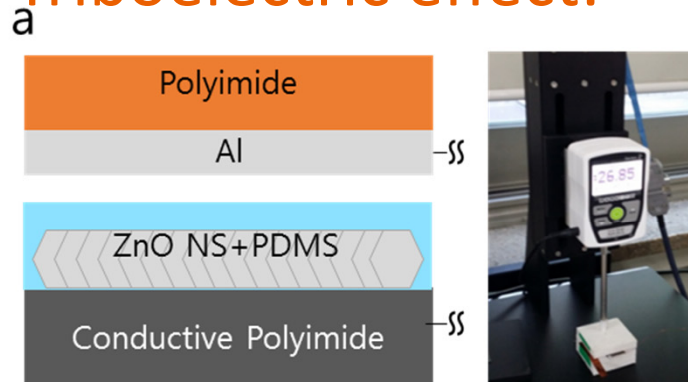
- Piezoelectric effect

Flexible device mounted on top of an electromagnetical shaker to be tested at a controlled vibration at a certain frequency and acceleration

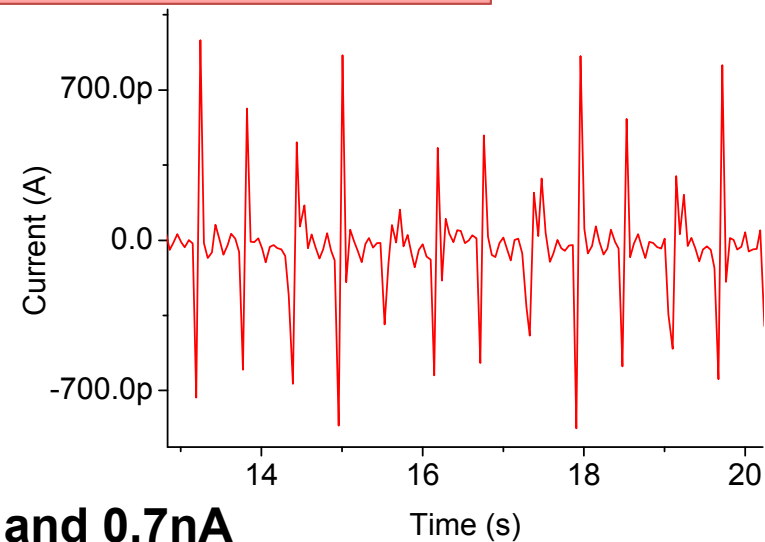
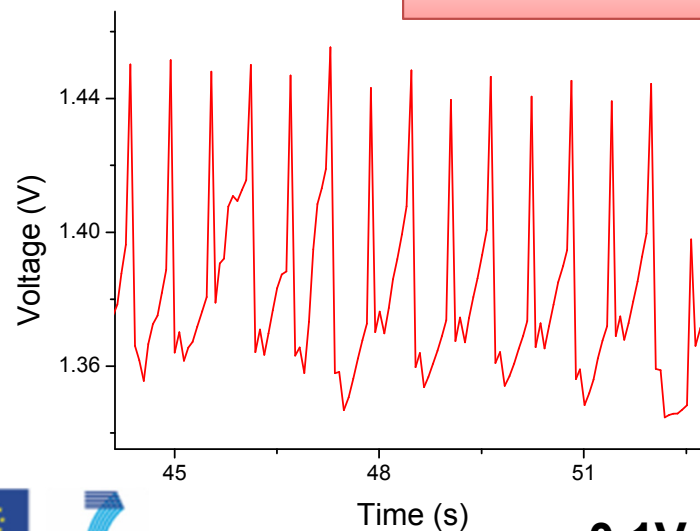




- Triboelectric effect:



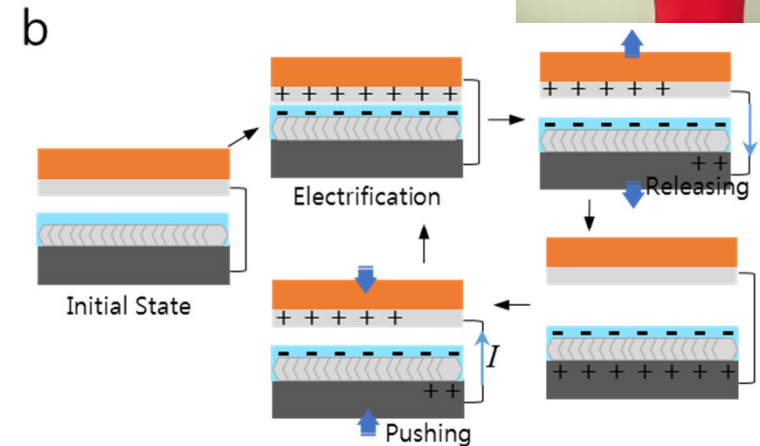
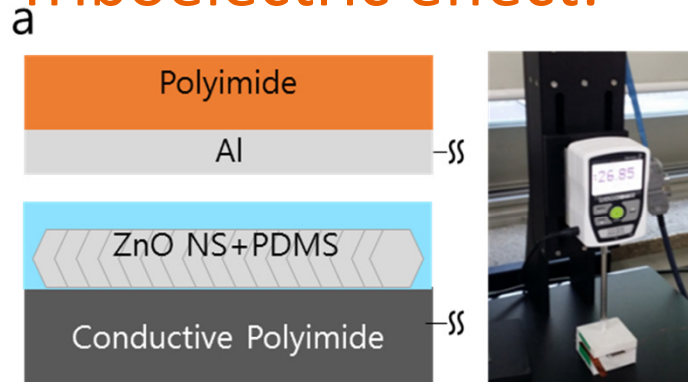
Close contact: piezoelectric contribution



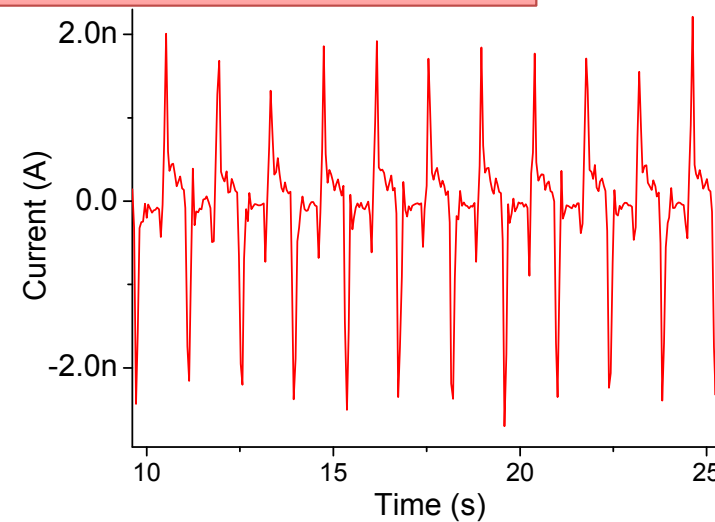
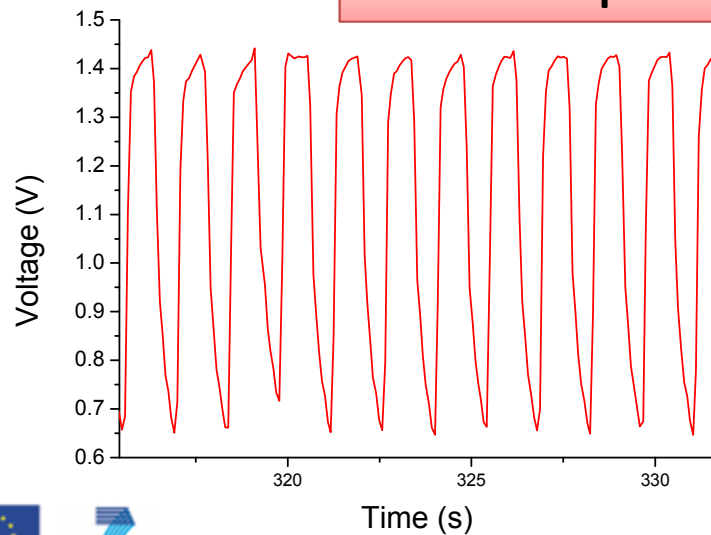
0.1Vpp and 0.7nA



- Triboelectric effect:



5 mm of separation: triboelectric contribution



0.78Vpp and 2nA

Conclusions

- Our novel seed layer allows **selective area growth of ZnO NSs**
- This growth is **inexpensive, fast, reproducible, at wafer level** and over transparent, flexible and silicon substrates
- Piezoelectric coefficients of ZnO NWs and NSs have been measured
- A **flexible NS-based prototype** has been fabricated and electrically characterized
- Some preliminary results show a promising application of ZnO NSs in **triboelectric and piezoelectric devices**

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(a) Centro Nacional de Microelectrónica (IMB-CNM, CSIC), Bellaterra 08193, Spain;
(b) Department of Physics, Inha University, Incheon 22212, South Korea;
(c) CEA/DEN/DTEC/SGCS, F-30207 Bagnols-sur-Cèze, France

Thank you! Any question?

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