Center for Environmental Research and Technology

Improved piezoelectric performance of mechanically stable ZnO nanopyramidal array

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Abstract

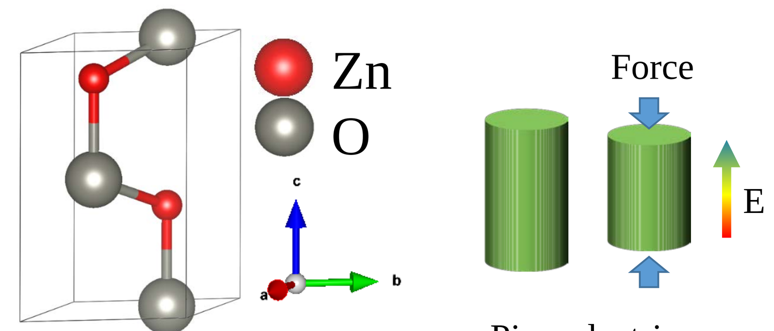
Zinc oxide (ZnO) is a well-known versatile material which is a wide-bandgap semiconductor having photocatalytic, piezoelectric and pyroelectric properties. Due to its wide bandgap nature, the ZnO shows high visible light transparency which allows it to be applied for diverse applications including functional surface coatings. Piezoelectric power generation is a clean and renewable energy generation from the mechanical forces such as vibrational energy. ZnO shows the piezoelectricity due to the absence of centro-symmetry in its crystal structure. The ZnO is polarized along the c-axis direction so the piezoelectric performance along the c-axis shows highest piezoelectric coefficient (d_{33}). However, in practice, most of the piezoelectric ZnO nanostructures cannot utilize the main axial piezoelectric operation due to structural limitations (e.g. ZnO nanowires are vulnerable to mechanical stress). Therefore, the morphological modification of the ZnO is desired to apply for high performance piezoelectric devices.

In this poster, a crystal growth method to synthesize the mechanically stable ZnO array for the piezoelectric applications is introduced. Through our modified chemical vapor deposition synthesis technique, the conditions are well-controlled to achieve the targeted morphology which is hexagonal step-wise nanopyramid. The as-synthesized ZnO has crystal defects which inhibits the piezoelectric performance of ZnO so that the thermal annealing under the oxygen environment was applied. The crystal growth, morphology and crystal defect control, piezoelectric and optical properties are discussed in this poster.

Background

- **Zinc Oxide (ZnO)**
  - ✓ Wide bandgap (3.37 eV) semiconductor
  - ✓ Intrinsic n-type semiconductor
  - ✓ Visible-transparent
  - ✓ Hexagonal wurtzite crystal structure
  - ✓ Photocatalytic properties
  - ✓ Piezoelectric and pyroelectric properties

- **Piezoelectricity**
  - ✓ Absence of centro-symmetry
  - ✓ Dipole moment induced by mechanical force



ZnO Unit cell

Piezoelectric operation

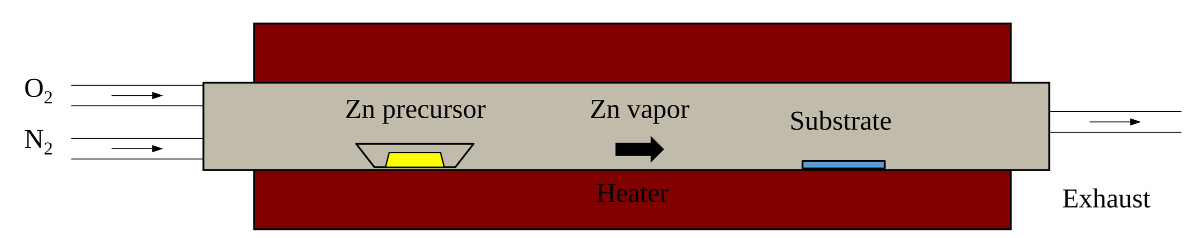
- **Research Objectives**
  - ✓ Achieve higher performance piezoelectric ZnO
  - ✓ Achieve mechanically stable ZnO array
  - ✓ Achieve a low-temperature ZnO synthesis process
  - ✓ Control morphology of synthesized ZnO
  - ✓ Analyze crystal structure and defects

Experimental Work

- **Piezoelectric Performance of Mechanically Stable ZnO**

To utilize the highest performance piezoelectric operation mode, d_{33}, vertically aligned crystal growth along c-axis is desired. The mechanical stability of the synthesized ZnO can be achieved by using pyramidal morphology of ZnO. The piezoelectric performance of the ZnO is characterized by piezoelectric force microscopy (PFM), which is a type of scanning probe microscopy measuring amplitude change in response to the applied electric field.

- **CVD Synthesis Process**

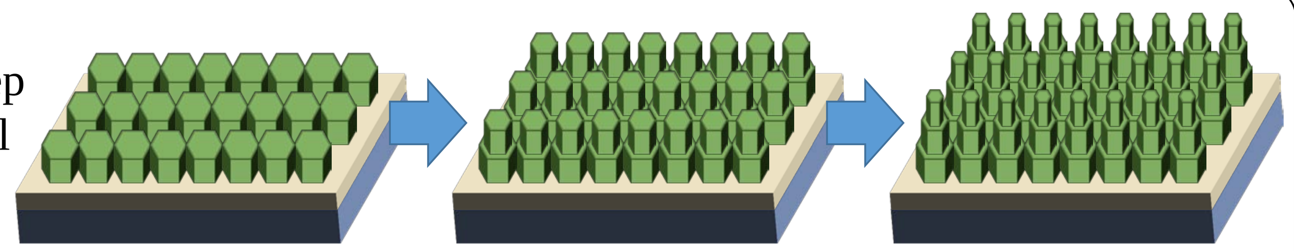


Schematic of CVD synthesis process

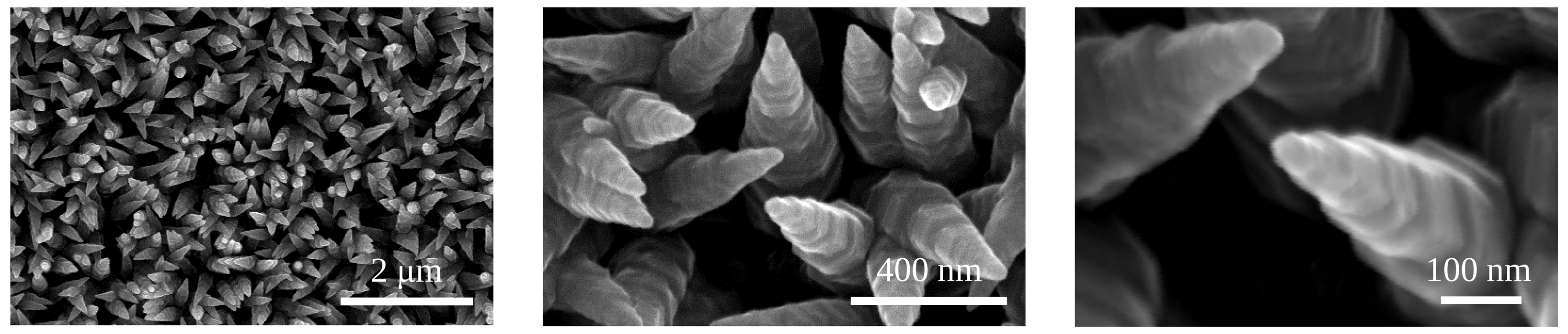
A horizontal tube furnace is used as the CVD reactor. When the bowl-shaped precursor boat is used, a ZnO layer on top of the Zn precursor is formed by the premature oxidation of liquid Zn, inhibiting the supply of Zn reactant. To control the morphology of ZnO, a small quartz test tube-shaped boat is used as the precursor boat. Positive pressure generated by the evaporation of Zn inhibits the premature oxidation of Zn precursor, resulting in the tapered structure of ZnO nanopyramids.

- **Crystal Growth of ZnO Nanopyramidal Array**

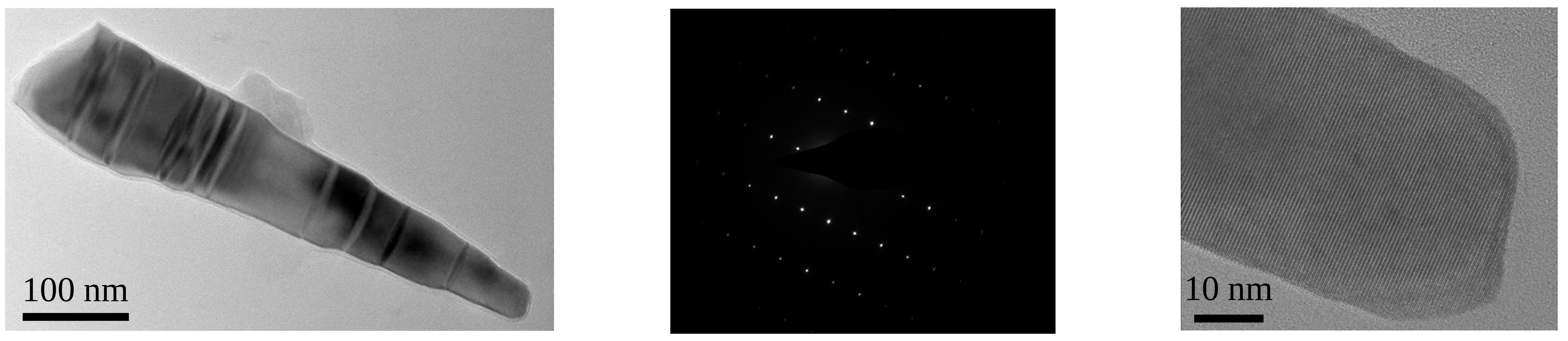
Crystal growth of step-wise ZnO hexagonal nanopyramidal array



- **Morphology and Crystal Structure Analysis**



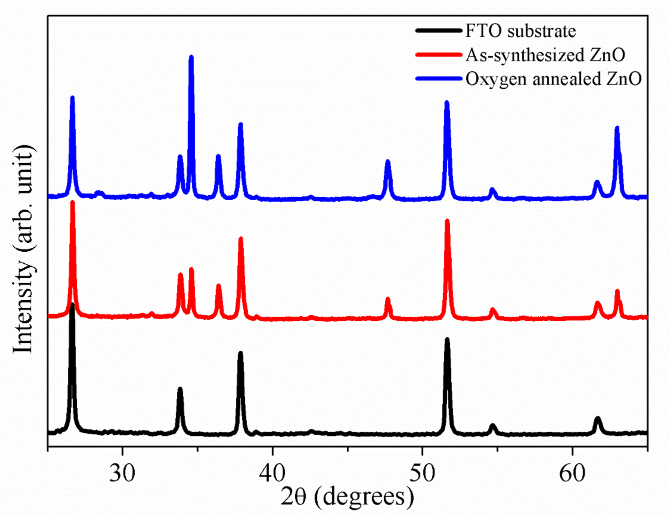
SEM images of synthesized ZnO nanopyramidal array



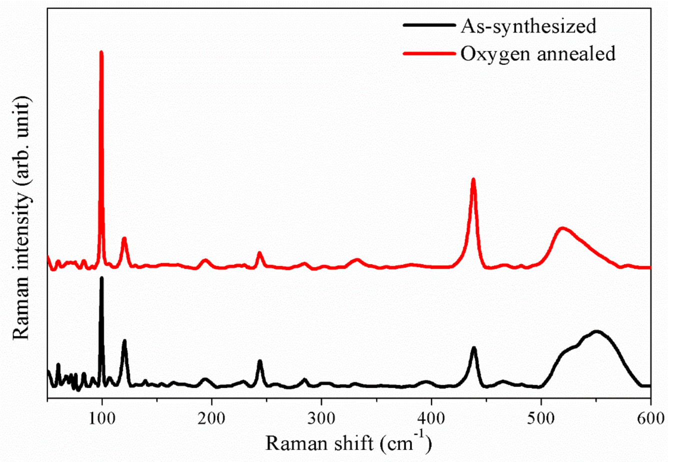
TEM SAED HRTEM

Results and Discussion

- **Crystal Structure**

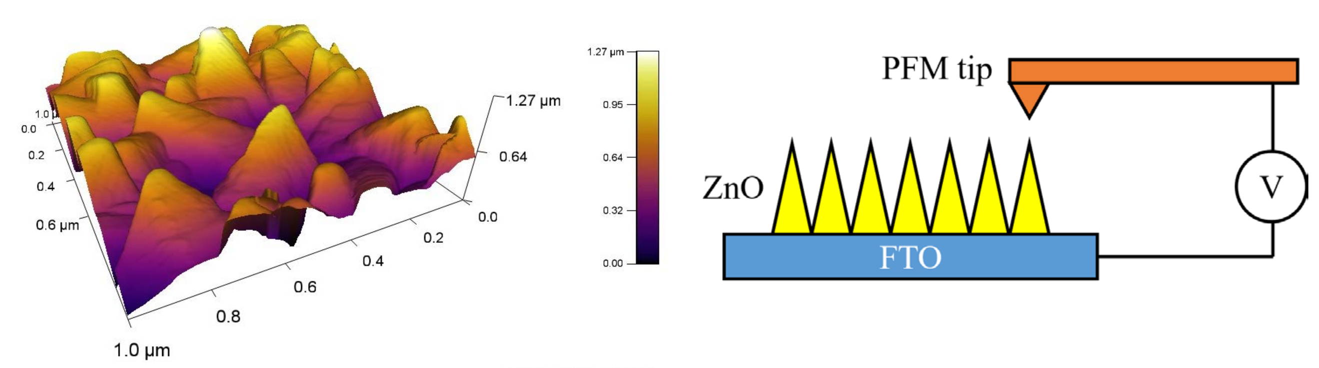


As-synthesized ZnO shows wurtzite XRD pattern on the FTO substrate, and the peak from (002) plane at 2θ=34° is significantly increased after the oxygen annealing.

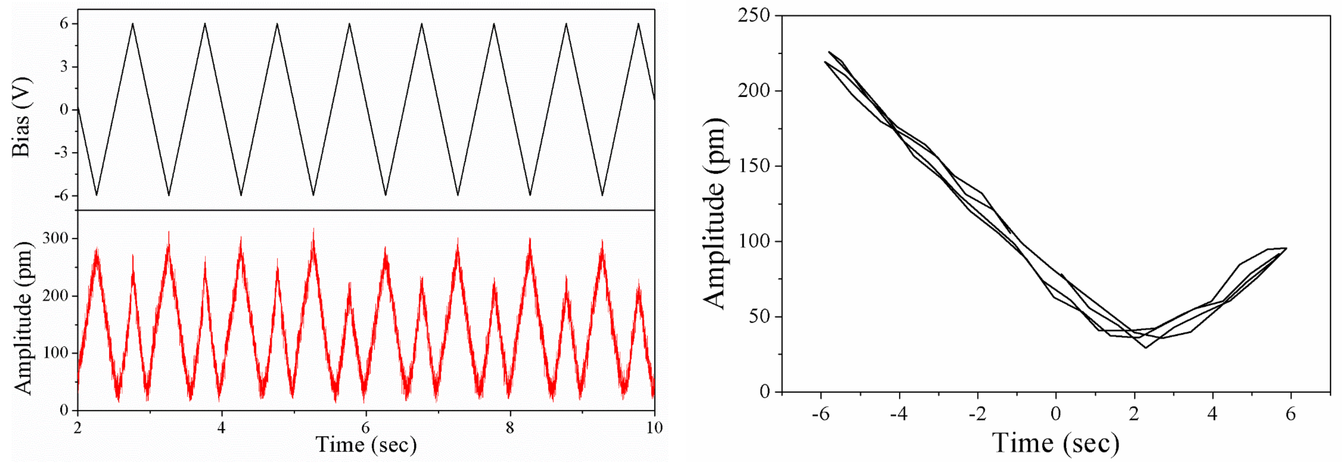


The point and planar crystal defect in the as-synthesized ZnO was decreased by the oxygen annealing proven by Raman spectroscopy.

- **Piezoelectricity**

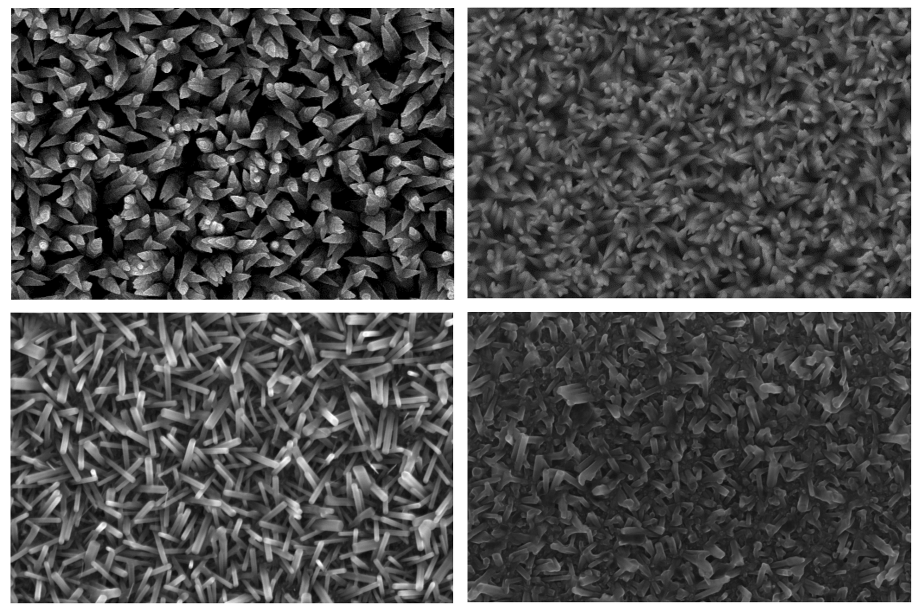


The surface topography was characterized prior to the piezoelectric performance measurement. The piezoelectric force microscopy (PFM) was performed at the apex of a pyramidal structure.



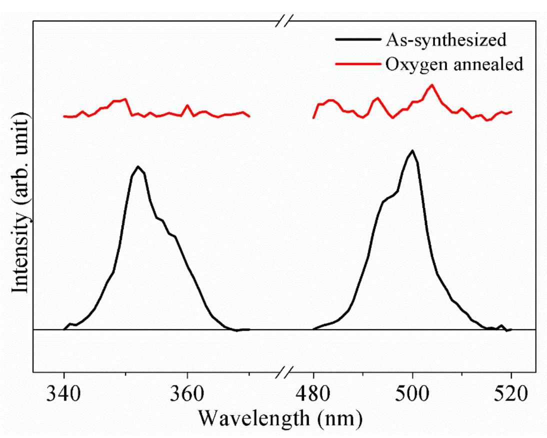
The as-synthesized ZnO shows piezoelectric coefficients d_{33} of 10.58 pm/V and it was improved to 23.08 pm/V after the oxygen annealing. The improvement of the piezoelectric performance by the oxygen annealing is due to the reduced crystal defects as observed with XRD and Raman spectroscopy.

- **Mechanical Stability**



The synthesized ZnO nanopyramids have superior mechanical stability proven by the ultrasonication test. The pyramidal ZnO is durable while the ZnO nanorods were broken

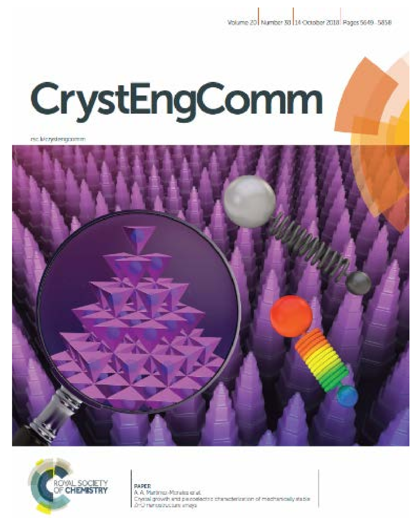
- **Photoluminescence Spectroscopy**



The oxygen vacancy defects were decreased during the oxygen annealing process proven by the PL spectroscopy. The green fluorescence emission at 500 nm is from the oxygen vacancy and it is reduced after the oxygen annealing.

Conclusion

In conclusion, the improved piezoelectricity of ZnO was achieved by modifying its morphology to the step-wise pyramidal structure. The pyramidal ZnO array was successfully synthesized by controlling the Zn precursor supply in the CVD synthesis process. The synthesized ZnO nanopyramids show superior mechanical stability to utilize its highest piezoelectric operation mode d_{33}. The as-synthesized ZnO nanopyramids have planar and point crystal defects proven by XRD, HRTEM, Raman, and PL spectroscopy. The piezoelectric performance of ZnO was further improved by reducing the crystal defects to increase its crystallinity. The partial results of this research has been published in CrystEngComm (2018, **20**, 5688–5694) and highlighted as the cover article.



Future Plan

The future plan of this research is to utilize the mechanically stable piezoelectric ZnO nanopyramidal array for diverse applications such as a piezo-enhanced photocatalyst and piezoelectric nanogenerator. Since the ZnO nanopyramid structure is durable against external physical stress, it is suitable for the piezoelectric power generation. In addition, the photocatalytic operation can be assisted by piezoelectric polarization under the presence of mechanical forces (e.g. ultrasonic power).

Acknowledgement

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Electron microscopy was performed on the Nova NanoSEM 450 and Titan 300 in CFAMM at UC Riverside.

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