Monoclinic Zirconium Oxide Nanostructures having Tunable Band Gap Synthesized Under Extremely Non-Equilibrium Plasma Conditions

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Outline

- Introduction
- Fabrication of ZrO_2 nanostructures using modified dense plasma focus device
- Results and Discussion
- Conclusions

Introduction

ZrO_2 has

- ❑ Wide band gap of ~ 5.0 eV
- ❑ High melting point
- ❑ High mechanical and thermal resistance
- ❑ High dielectric constant
- ❑ Low electrical conductivity
- ❑ Excellent hardness and biocompatibility

These properties of ZrO_2 render it as a potential candidate for applications in …………

- ✓ making fuel cells
- ✓ protective coatings for mirrors
- ✓ optoelectronic devices

The band gap of ZrO_2 decreases on increasing the processing temperature making it more conductive and hence used in applications-oriented research.

ZrO_2 possess high dielectric constant making it an ideal candidate for replacement of conventional gate oxide in field effect transistors (FETs).

ZrO_2 nanostructures have emission peaks in UV region having applications

- in making read heads of compact discs (CDs)
- increasing storage density of CDs.

Band gap of ZrO_2 can be tuned at nanoscale which increases the efficiency of fabricated devices.

- Fabrication of ZrO_2 nanostructures have been reported in the literature mainly using chemical methods which introduce impurities due to precursors etc.
- Thereby reducing the efficiency of fabricated devices.
- Plasma-assisted methods can overcome this disadvantage.
- Fabrication of ZrO_2 nanostructures using plasma-assisted method is not yet reported in the literature.

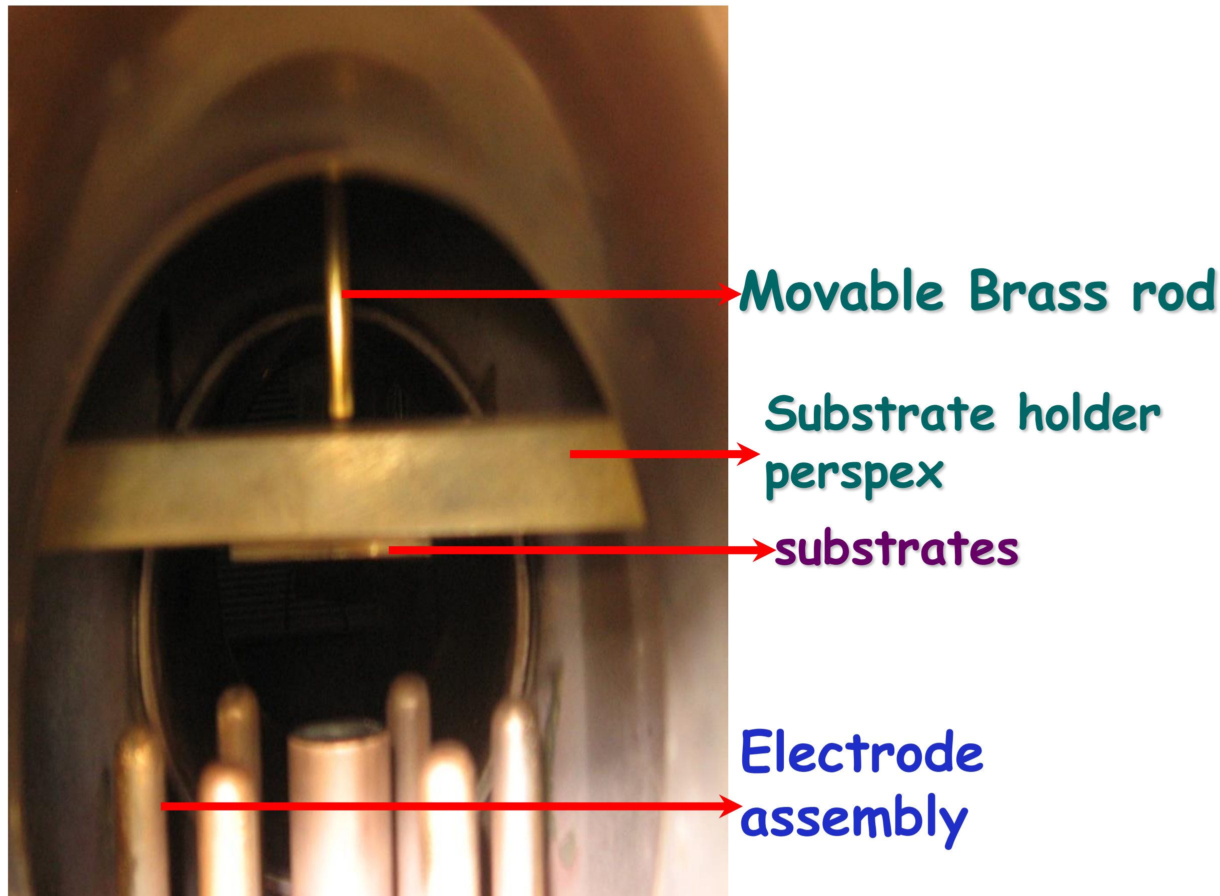
- Arc discharge, DC, RF and magnetron sputtering, pulsed laser deposition and modified dense plasma focus (DPF) device are few plasma based methods used commonly for nanofabrication.
- Most of them have disadvantages of substrate heating or biasing or post annealing of deposited material.
- Modified DPF device overcome these disadvantages and also reduces the number of processing steps for nanofabrication.

The modified DPF device is used for phase change of as-deposited thin film, thin film deposition and recently for nanofabrication- First time by Plasma research group at DU

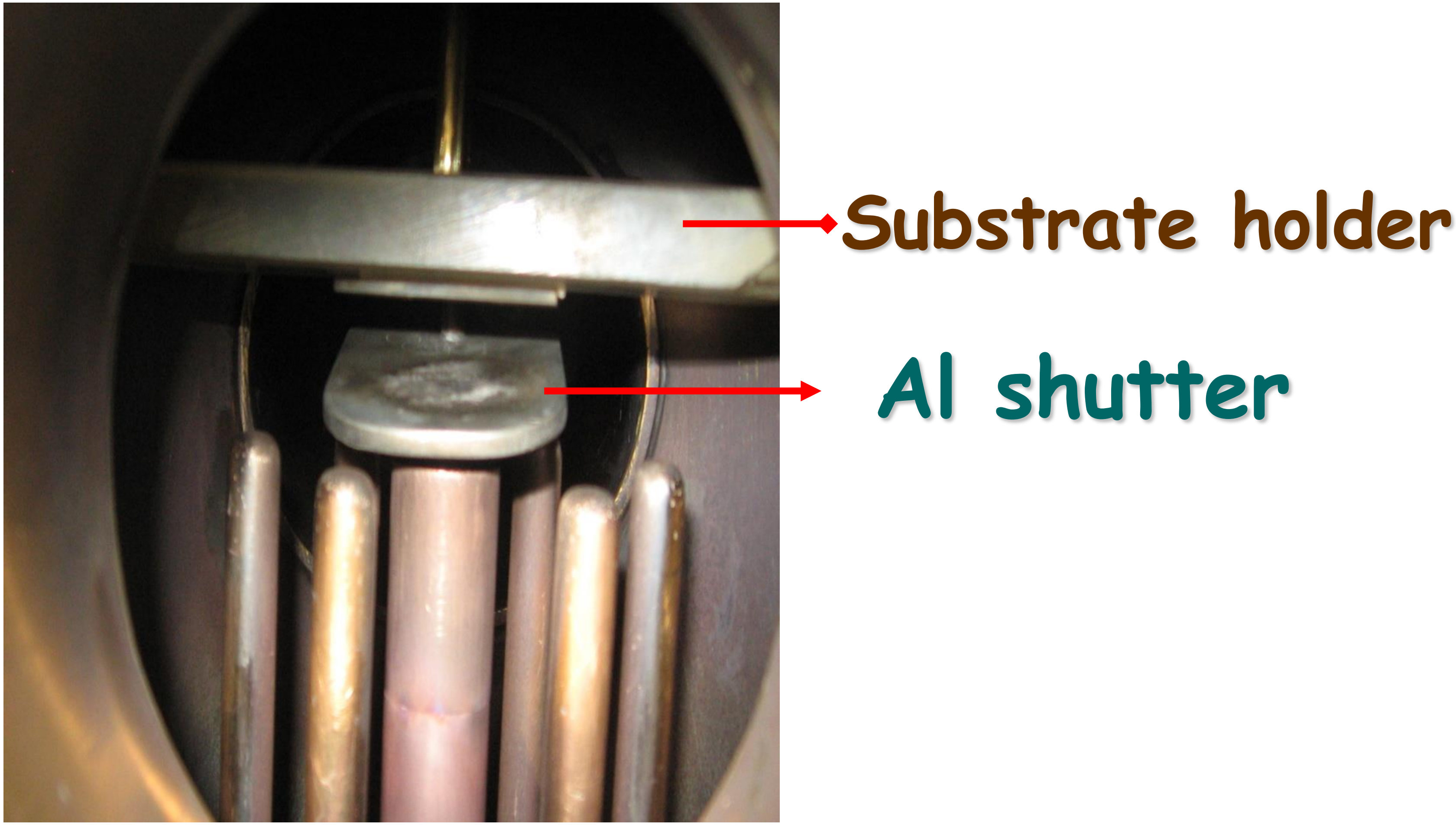
Modifications to DPF device

Anode was modified to host a disc/ pellet on top

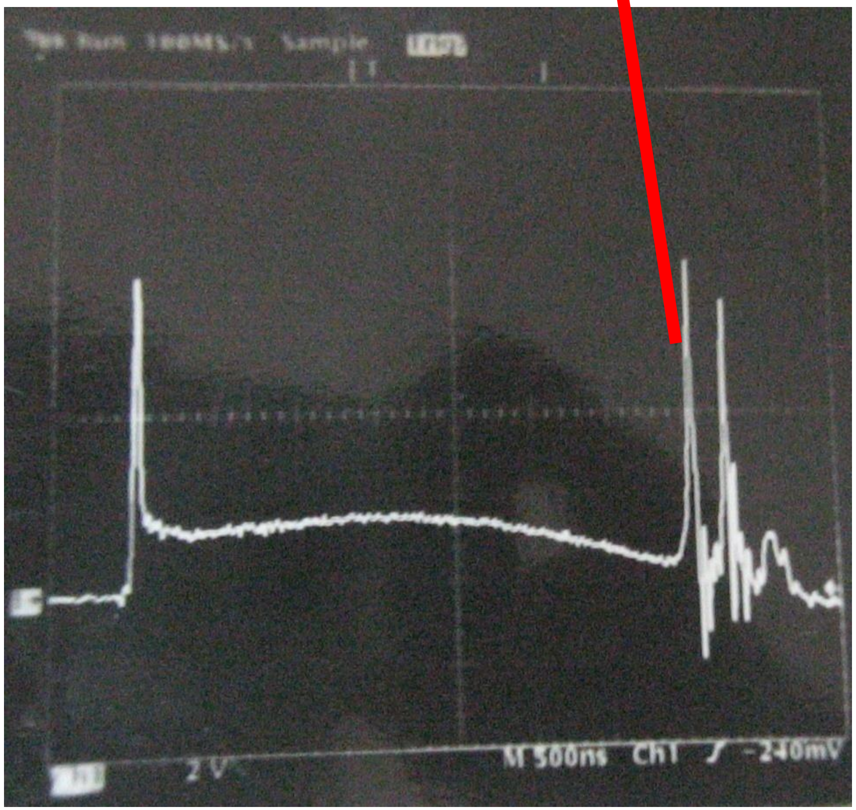
In top flange of plasma chamber arrangements were made to insert substrate and its holder attached to cylindrical moveable brass rod at one end and the other end outside the chamber through which the height of the substrate from anode is adjusted.



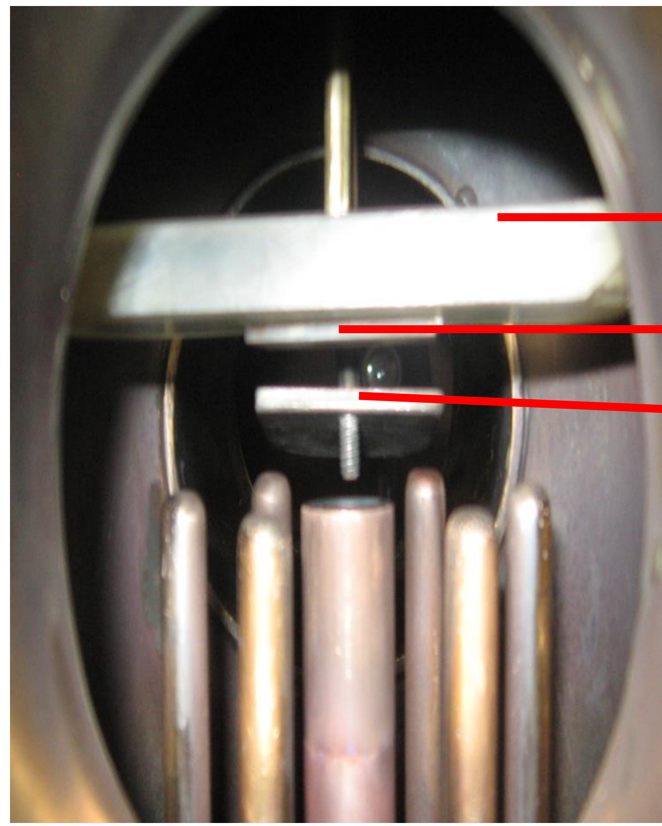
- Another moveable brass rod is inserted from top flange of plasma chamber to insert aluminum shutter between top of the anode and substrates in order to avoid the unfocused ions hitting the substrates.



Evidence of good focusing in Voltage Probe Signal obtained on Digital Storage Oscilloscope shown as



Once the focused plasma is formed the shutter is removed



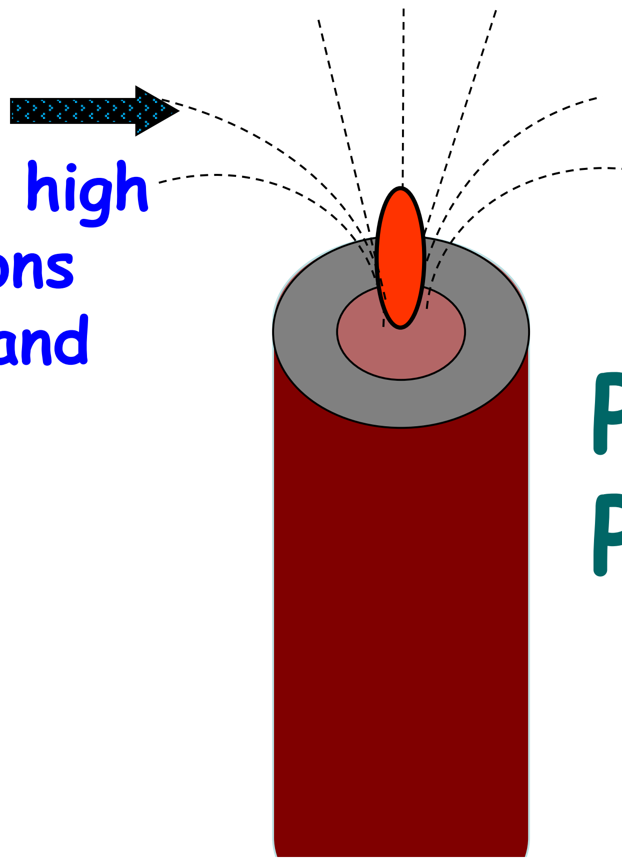
Fabrication of ZrO_2 nanostructures

- Pellets of ZrO_2 powder (99.99% pure) were made by compressing it at a pressure of 10 MPa and subsequently sintering them at 800°C for 6h.
- The ZrO_2 pellet is fixed on the top of the modified anode.
- Quartz substrates were placed at a distance of 5.0 cm from anode top.

- ZrO_2 pellet fixed at top of the anode is brought into ionized state by hot and dense argon plasma producing material ions.

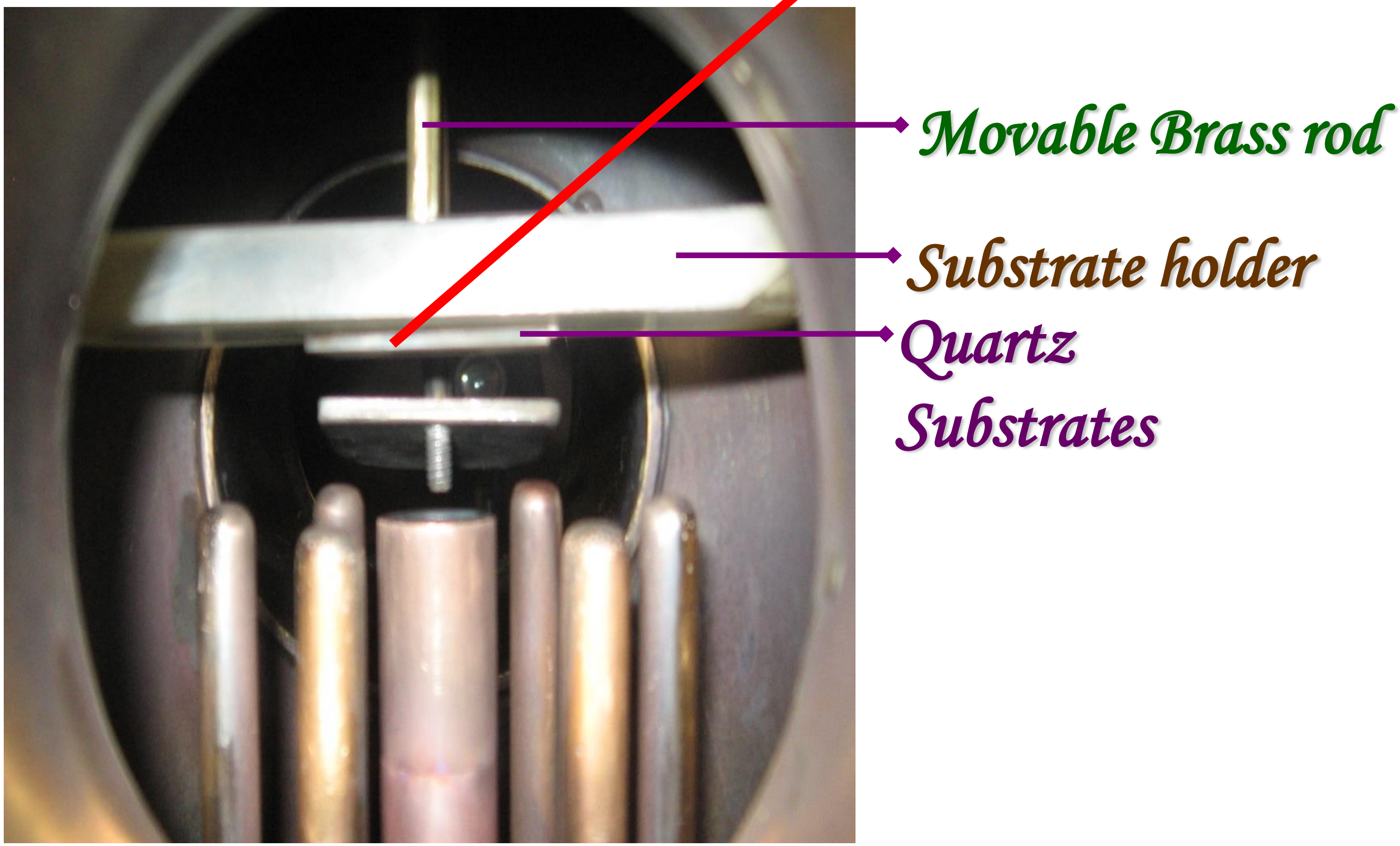
- These ions along with argon ions move vertically upward in a fountain shape in post focus phase.

Highly energetic high fluence ions of ZrO_2 and argon



Post Collapse Phase

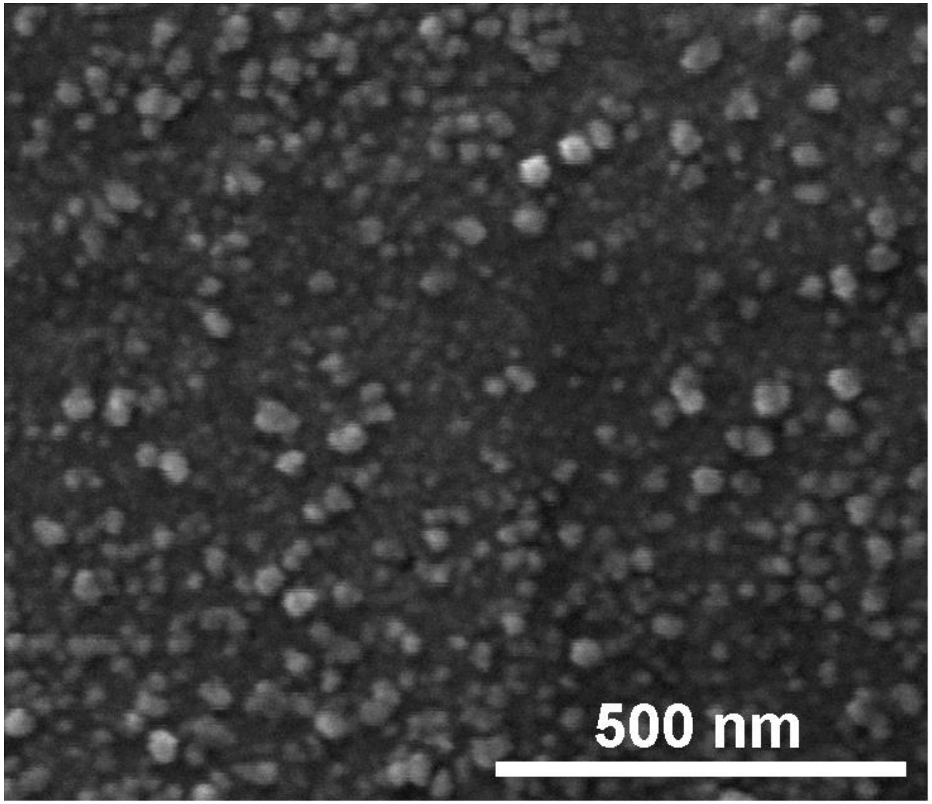
ZrO_2 material ions hit the substrate, lose energy, cool down and deposited on quartz substrate

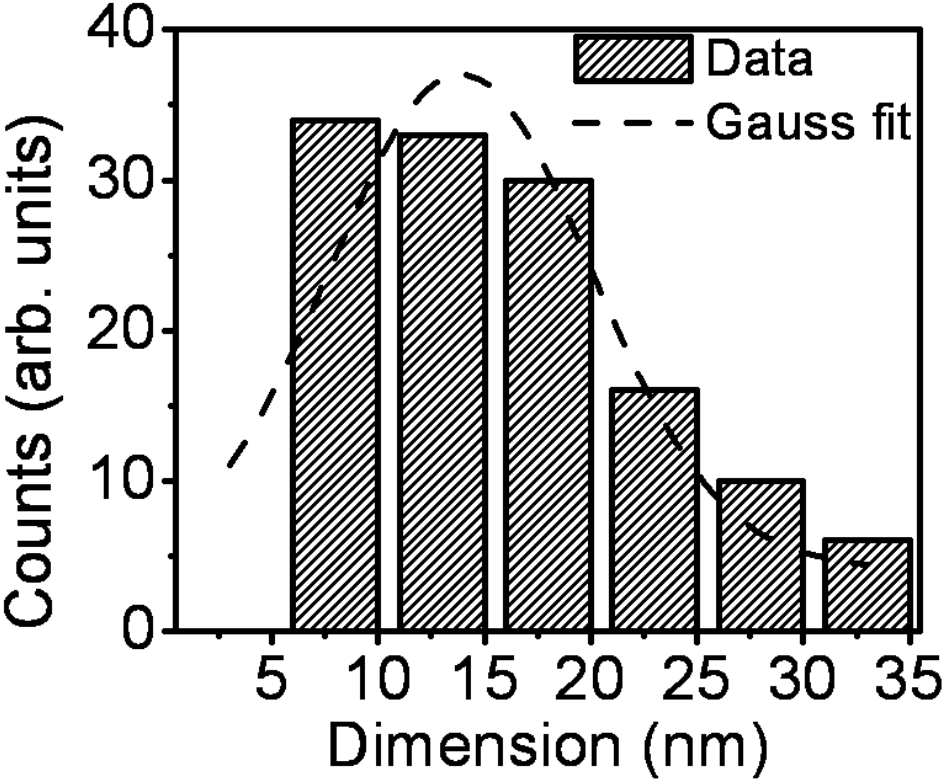


- ZrO_2 nanostructures are fabricated with 2 bursts of focused plasma

Surface morphology of ZrO_2 Nanostructures-SEM

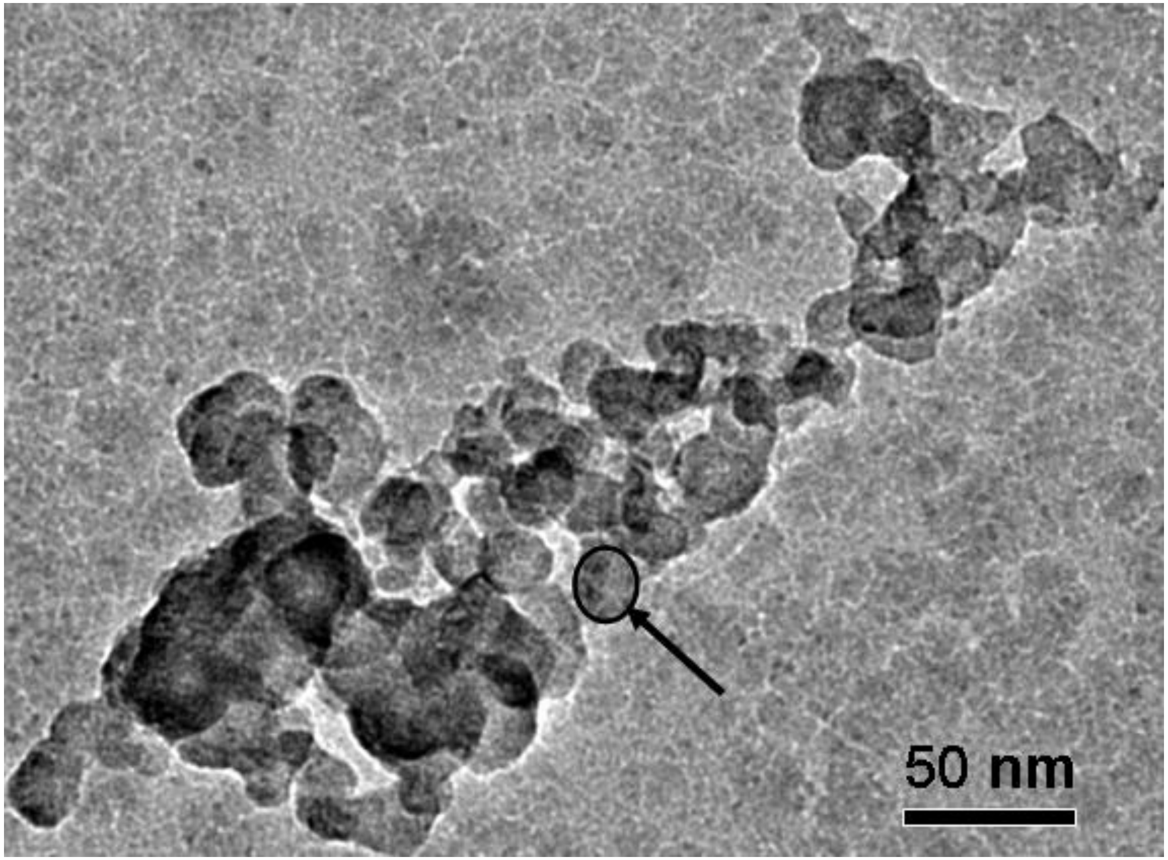
- Uniformly distributed nanostructures with average size ~ 14 nm.
- Surface density is ~ 4100 nanostructures/μm^2.



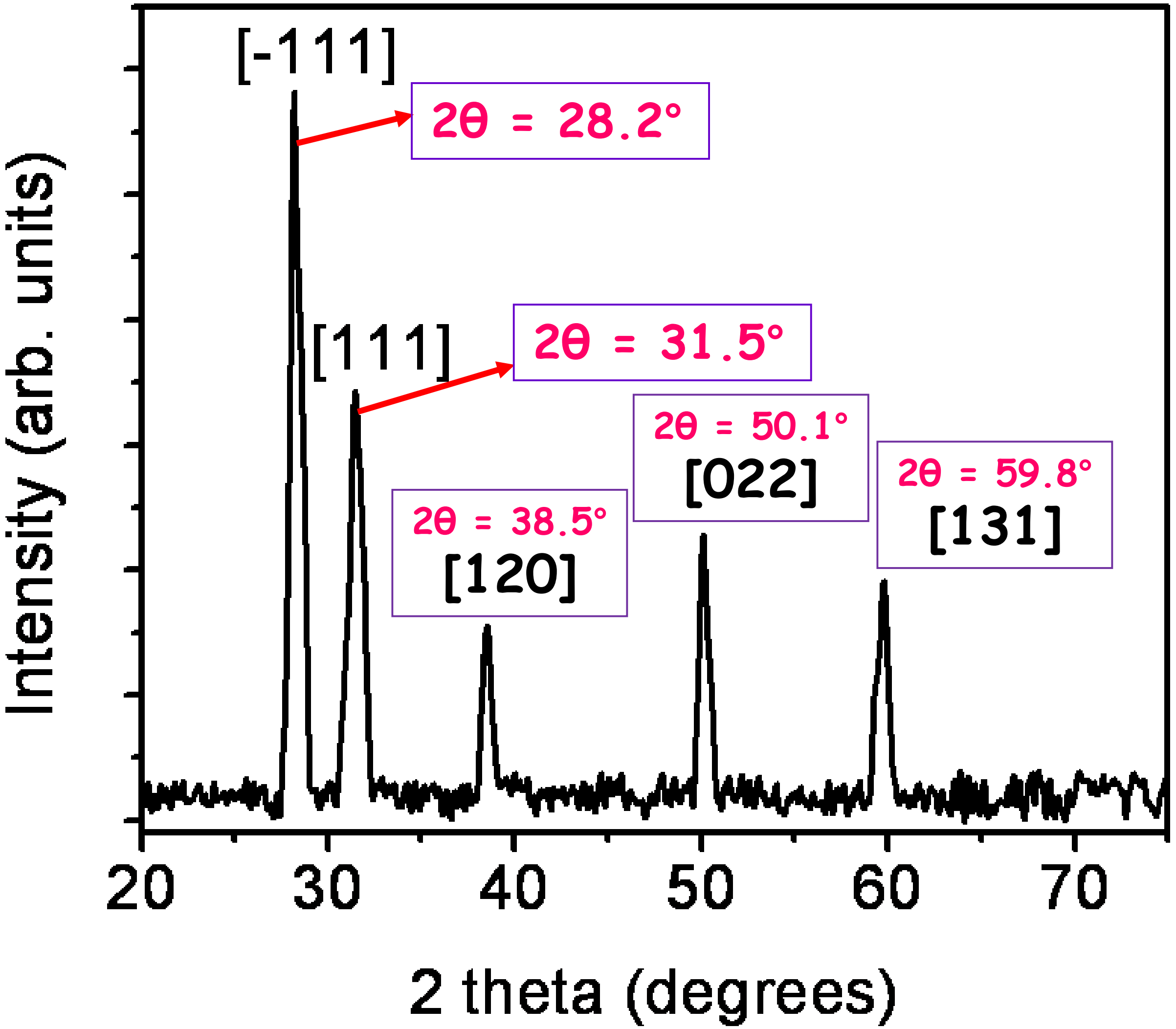


Surface morphology of ZrO_2 Nanostructures-TEM

- Nanostructure shown by arrow has size ~ 15 nm.
- Morphology and dimension obtained from TEM is in good agreement with SEM.



Structural properties of ZrO_2 nanostructures- XRD



- XRD pattern show nanocrystalline behavior with diffraction peaks corresponding to monoclinic phase of ZrO_2.
- Average grain size found from Scherrer's formula is 14 nm and the average strain produced in nanostructures is ~ 2.5×10^{-3}.

Structural parameters of ZrO_2 nanostructures obtained from XRD pattern

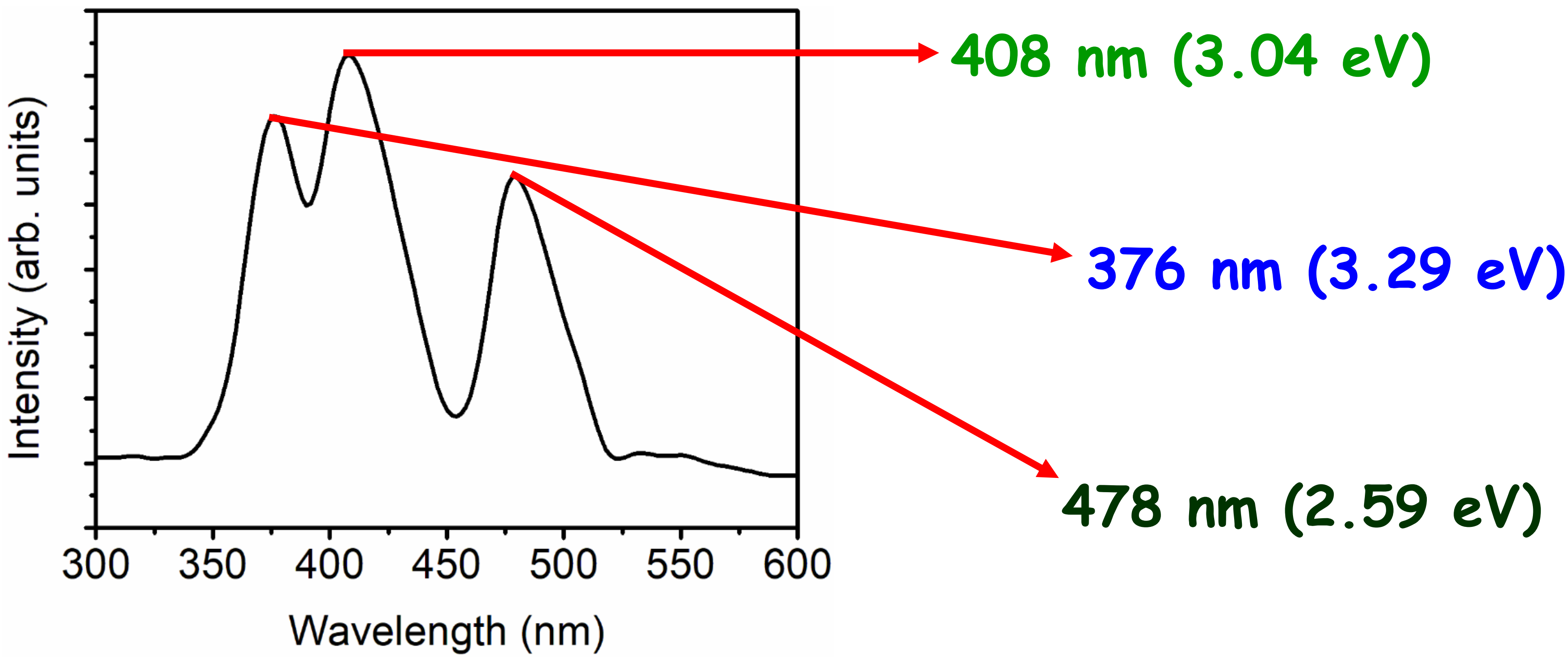
2θ (°)	θ (°)	β (radians)	D (nm)	δ (x 10^{-3} nm^{-2})	ε (x 10^{-3})
28.2	14.1	0.01166	12	6.94	2.83
31.5	15.75	0.01307	11	8.26	3.14
38.5	19.25	0.00865	17	3.46	2.04
50.1	25.05	0.00936	16	3.91	2.12
59.8	29.9	0.01089	15	4.44	2.36

- θ is angle of diffraction corresponding to peak
- β is full width at half maxima (FWHM) in radians
- D is grain dimension in nm
- δ is length of dislocation per unit volume i.e. dislocation density
- ε is strain produced in nanostructures due to dislocations

Emission spectra of ZrO_2 nanostructures

PL spectra

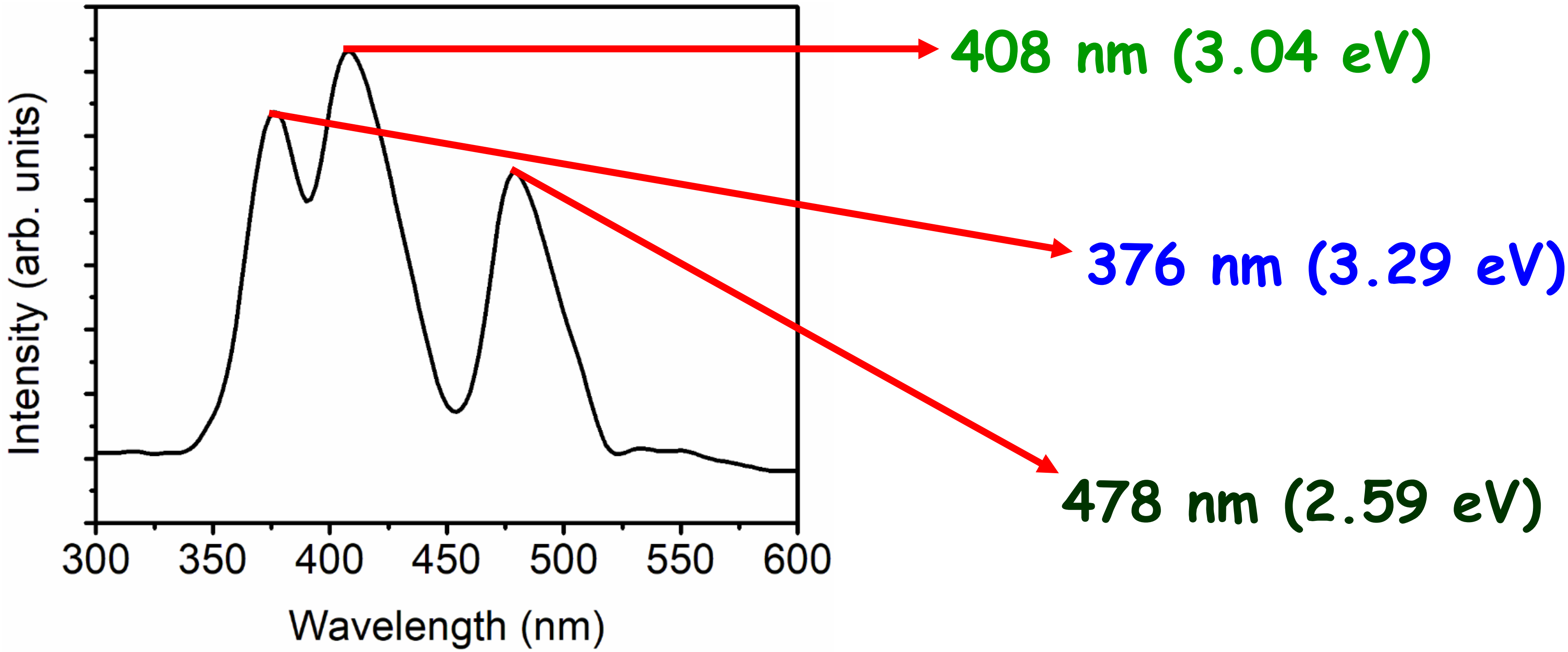
- Peak at 376 nm (3.29 eV) lies in UV region which arises due to oxygen vacancies in nanostructures
- These oxygen vacancies make extrinsic states between valence and conduction band yielding radiative transition at energy lower than band gap of ZrO_2
- The decrease in energy of this radiative transition is also associated with size and crystal quality of nanostructures which ultimately shift the emission spectra



Emission spectra of ZrO_2 nanostructures

PL spectra

- Peak at 408 nm (3.04 eV) lies in near-UV region which arises due to transition from mid-gap trap state to valence band
- The mid-gap trap states are formed mainly due to surface defects such as dislocations which are prominent in nanostructures
- Peak at 478 nm (2.59 eV) is characteristic peak of monoclinic ZrO_2
- The observed monoclinic phase is in good agreement with XRD results.

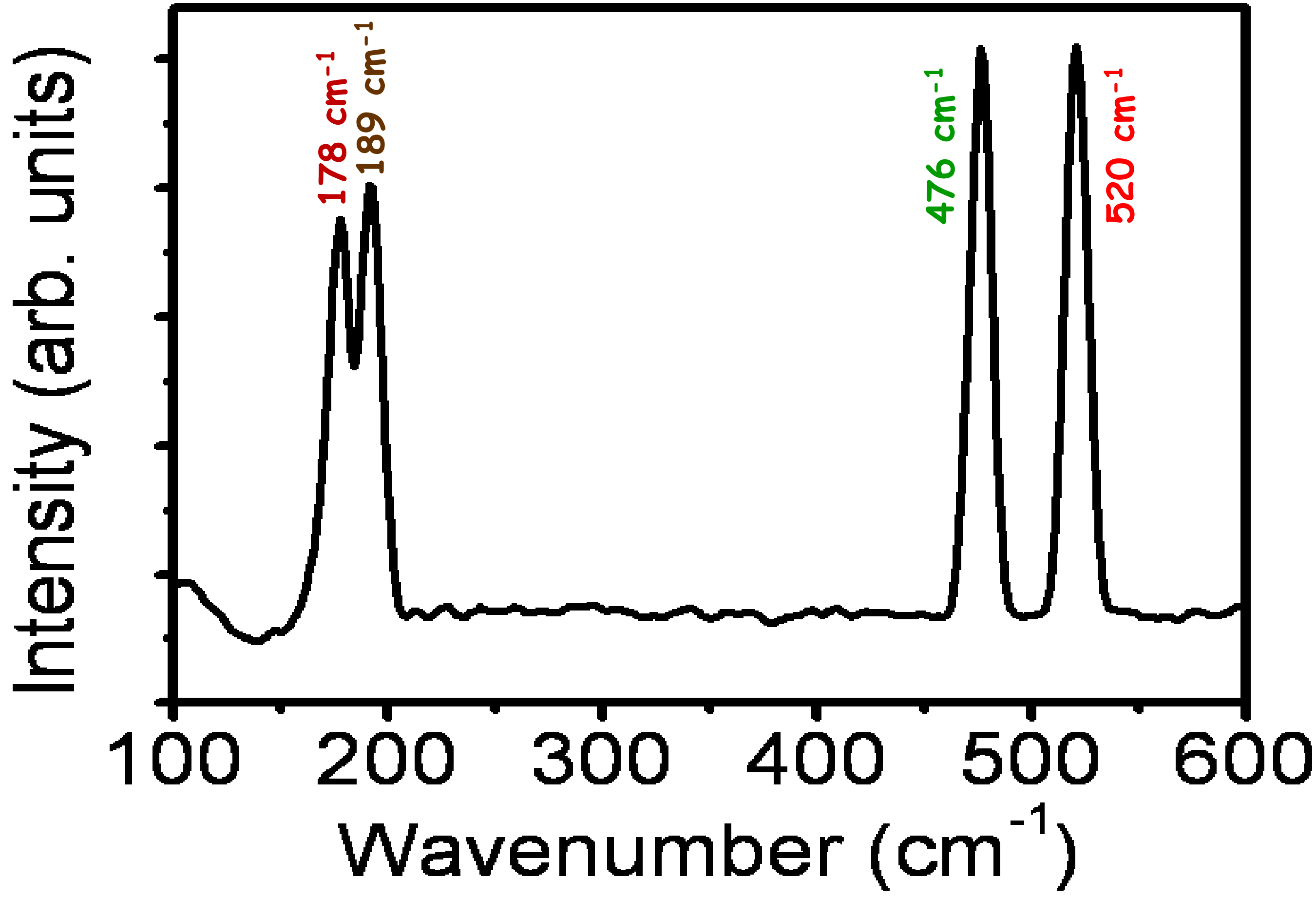


PL spectra of ZrO_2 nanostructures deposited by chemical methods have single broad band which limits the optical range of fabricated devices.

Whereas PL spectra of ZrO_2 nanostructures deposited using modified DPF device have multiple peaks in UV, near-UV and visible regions thereby increasing the optical range of fabricated optoelectronic devices.

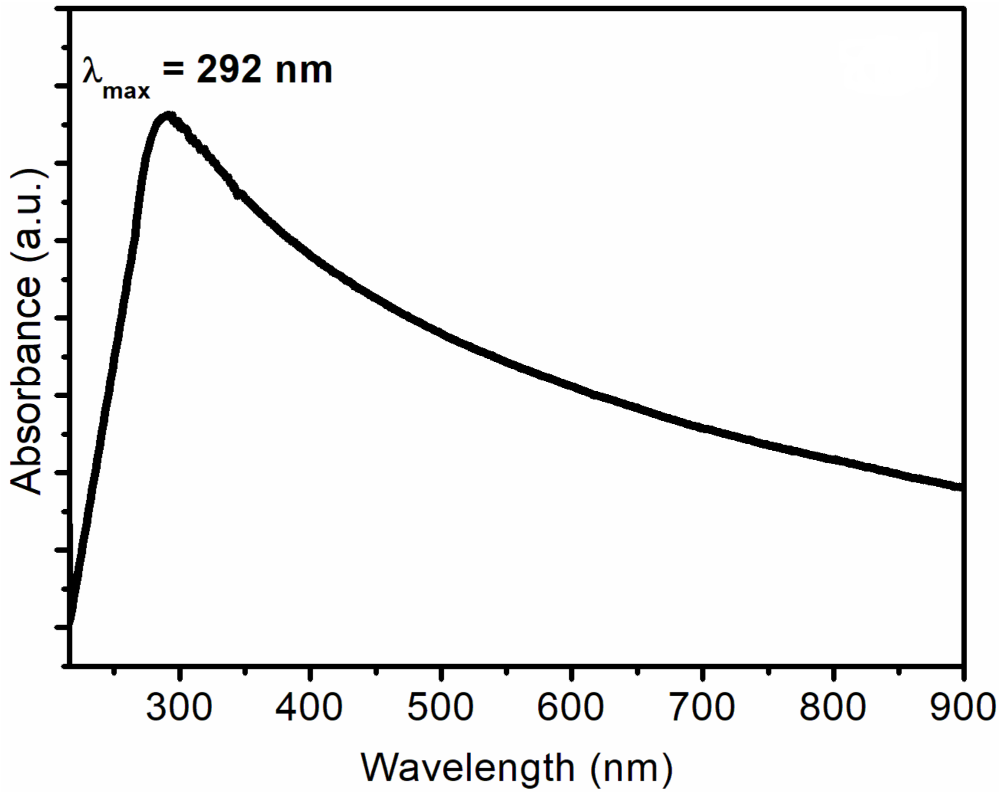
Raman spectra of ZrO_2 nanostructures

- Raman spectra have peaks at 178 cm^{-1}, 189 cm^{-1}, 476cm^{-1} and 520 cm^{-1}
- All these Raman peaks are attributed to monoclinic phase of ZrO_2
- The monoclinic phase observed in Raman is in confirmation with the same observed in PL and XRD results.



Absorption spectra of ZrO_2 nanostructures

- Absorption spectra show peak at 292 nm due to transition from valence band to conduction band in ZrO_2 nanostructures.
- The transition involved in this peak is due to Zr^{3+} ions in the interstitial.
- This transition is the main characteristics of the monoclinic phase of ZrO_2 nanostructures.

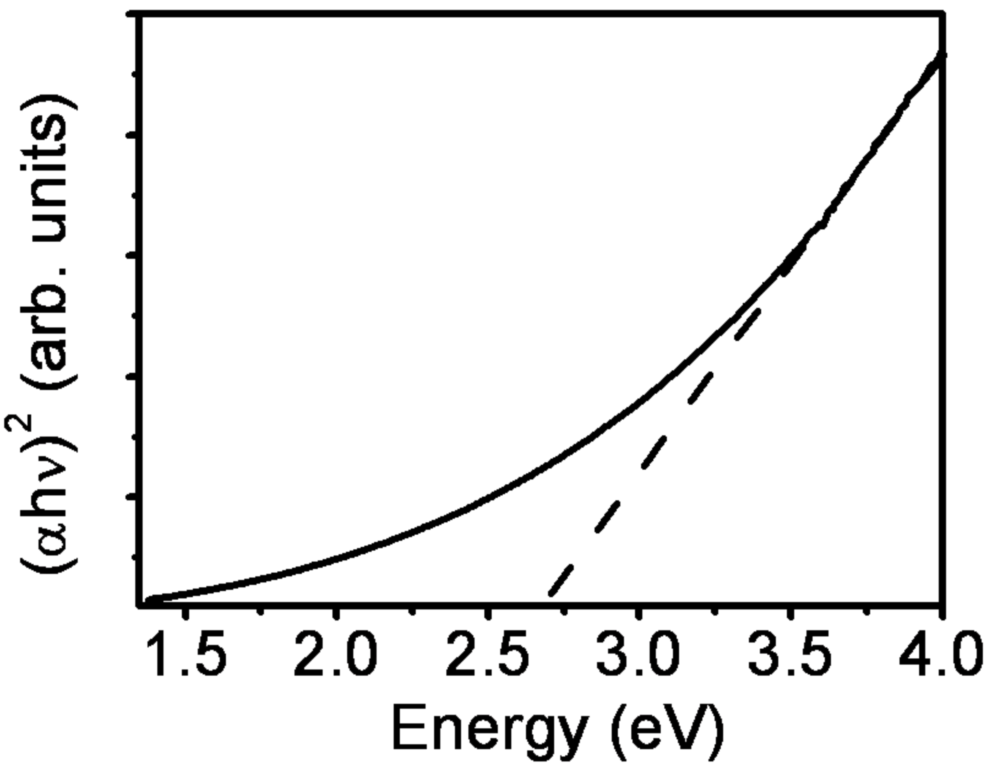


Band gap studies of ZrO_2 nanostructures

Tauc plot

- Tauc plot show band gap of nanostructures ~ 2.67 eV.
- The band gap value is in fair agreement with PL peak (2.59 eV), thereby confirming the tuning of band gap of ZrO_2 nanostructures.

The tunability of band gap suggests possible applications in enhancement of solar cell efficiency



Conclusions

- Monoclinic ZrO_2 nanostructures having mean size of ~ 14 nm, are fabricated on quartz substrates in a modified DPF device.
- PL spectra show intense emission peaks in UV and near-UV regions due to oxygen vacancies and dislocations, respectively.
- PL spectra also show peak in visible region from monoclinic phase of nanostructures.
- Raman spectra show peaks corresponding to monoclinic ZrO_2 nanostructures.
- Absorption spectra show peak from monoclinic phase.
- Tauc plot show band gap in visible region.
- Band gap values are found to be tuned in nanostructures.
- Tuning of band gap suggest possible applications of nanostructures in optoelectronic devices and efficiency enhancement of solar cells.

THANK YOU