Ion irradiation on ZnO and other metal oxides: prospects, challenges and future directions

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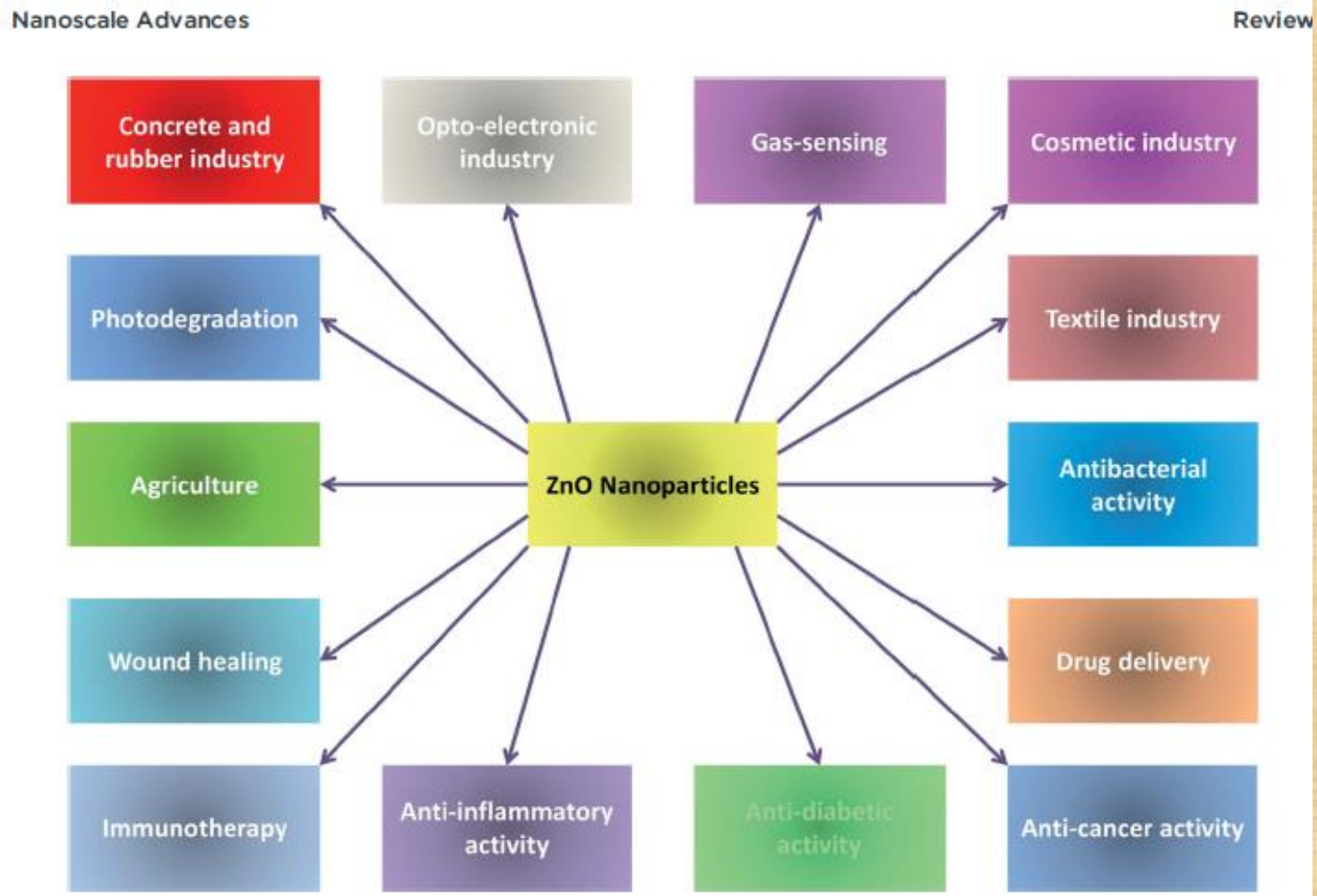
ZnO as material

- ZnO is a well-known wide band gap (3.37 eV at room temperature), extremely radiation hard semiconductor.
- The exciton binding energy of ZnO is ~ 60 meV. Intense luminescence in the ultra-violet region due to exciton recombination is seen from ZnO at room temperature.
- ZnO is intrinsically n type and making it p type is challenging.
- Undoped ZnO is diamagnetic but becomes ferromagnetic due to intrinsic or extrinsic defects.
- In brief, ZnO is a promising candidate for opto-electronic devices, particularly useful in high radiation environments as in spacecrafts.
- Defect accumulation in this radiation hard semiconductor bears immense importance. Well planned energetic particle irradiation can serve in a big way on this regard.
- Understanding vacancy clusters in ZnO, their formation, growth and recovery is necessary to achieve a defective state for technological need.
- ZnO is a benchmark material for theoretical calculations.

Defect Probing in ZnO

Positron annihilation, Raman, photoluminescence, Rutherford backscattering spectroscopy, several microscopic techniques and synchrotron based spectroscopic probes have been employed in literature.

Methodology and outcome on ZnO can be used to investigate other metal oxide semiconducting materials such as TiO_2, CeO_2, Ga_2O_3 and others, specially ion beam irradiation effects

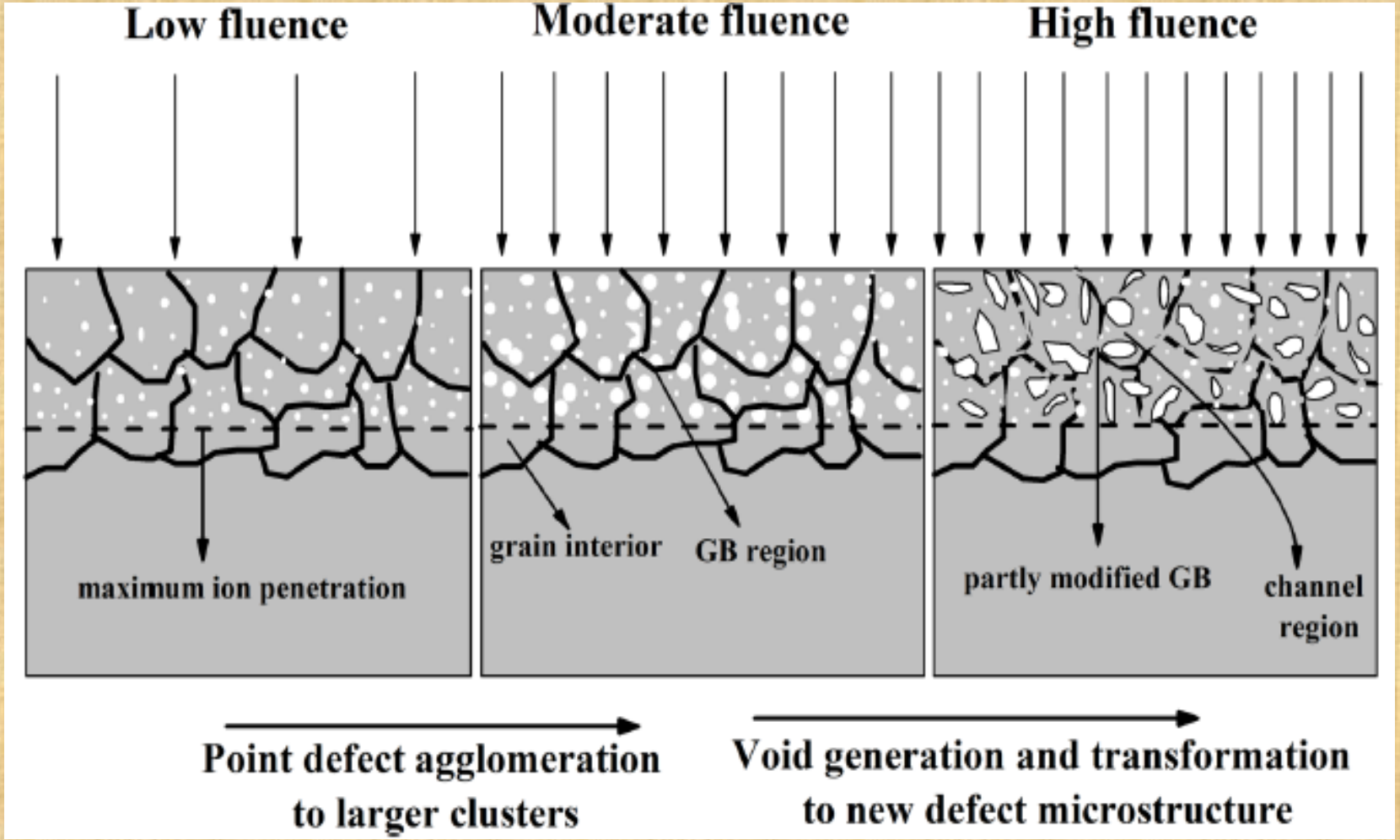


Nanoscale Adv. 4 (2022) 1868

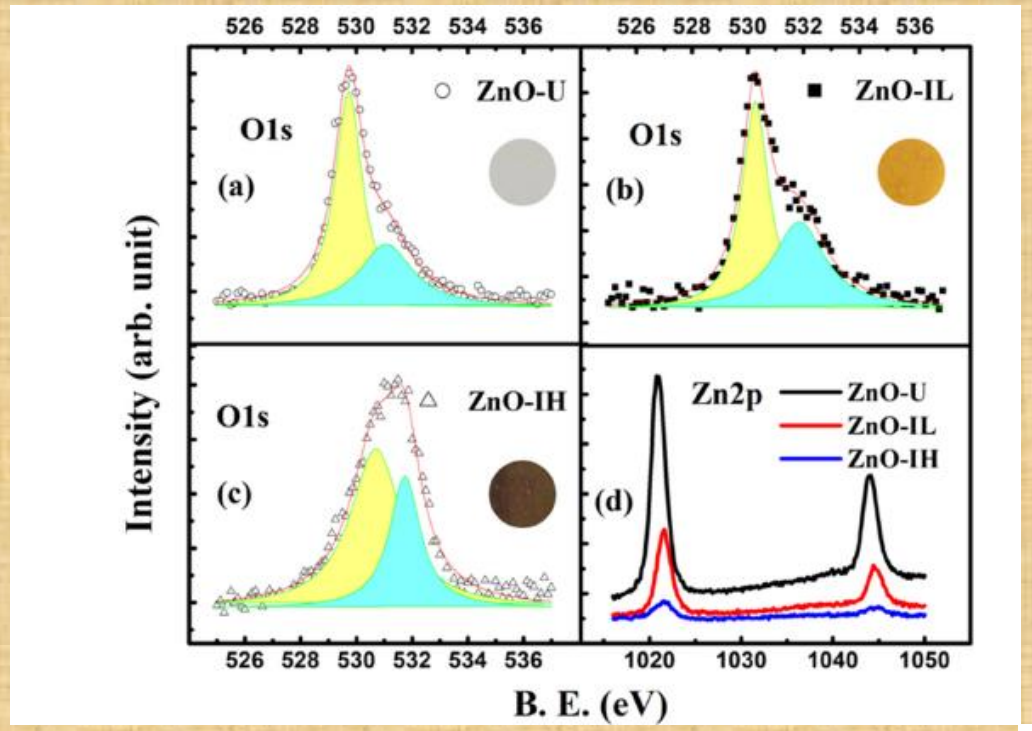
Plan of the presentation

- **A general overview of damage accumulation in ion irradiated ZnO and its possible consequences.**
- **Few case studies on Ar, O, H irradiated ZnO.**
- **Defect probing by positron annihilation spectroscopy, Raman spectroscopy and photoluminescence spectroscopy.**
- **Understanding defective state of ZnO with an aim towards technological and bio-medical requirements.**
- **Extension of the knowledge to other metal oxide semiconductors**
- **Possible use of stable isotope ion beams**
- **Possible use of radioactive ion beams**

A general overview on damage build up in polycrystalline ZnO



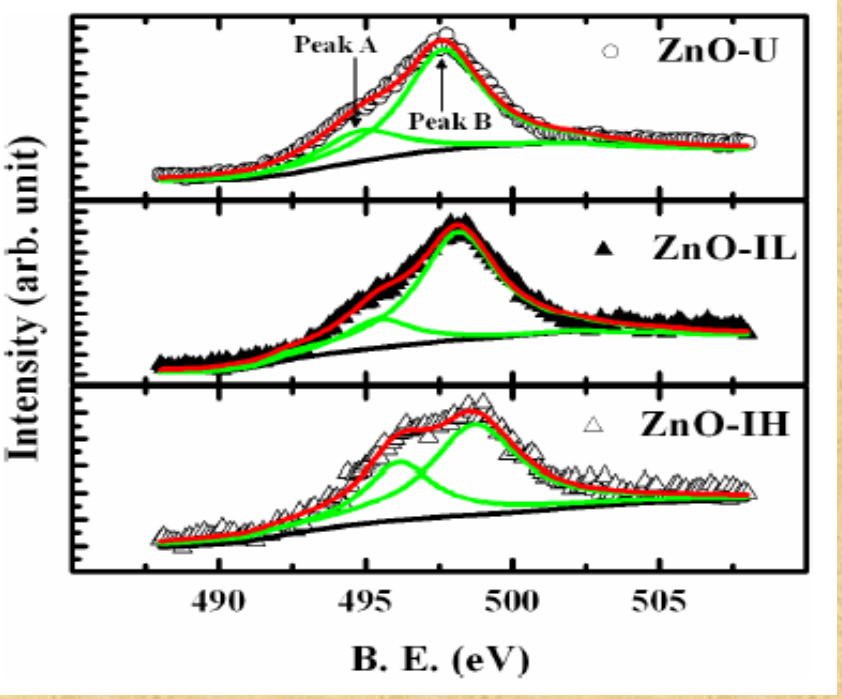
J. Phys. D: Appl. Phys. 51 (2018) 105107



1.2 MeV Ar ion fluence, XPS study

ZnO-IL 1×10^{14} ions/cm^2
ZnO-IH 1×10^{16} ions/cm^2

To reveal the possible metallic Zn segregation, Zn(LMM) Auger transition spectra for all three samples have been shown. Each Zn (LMM) signal is resolved into two peaks by fitting Lorentzian distribution. The ZnO-IH spectra clearly show that the weight of the lower binding energy peak (peak A) has been notably increased compared to the ZnO-U and ZnO-IL spectra. The peak at lower energy side corresponds to the metallic Zn whereas the other (peak B) is the signature of Zn-O bond of ZnO.



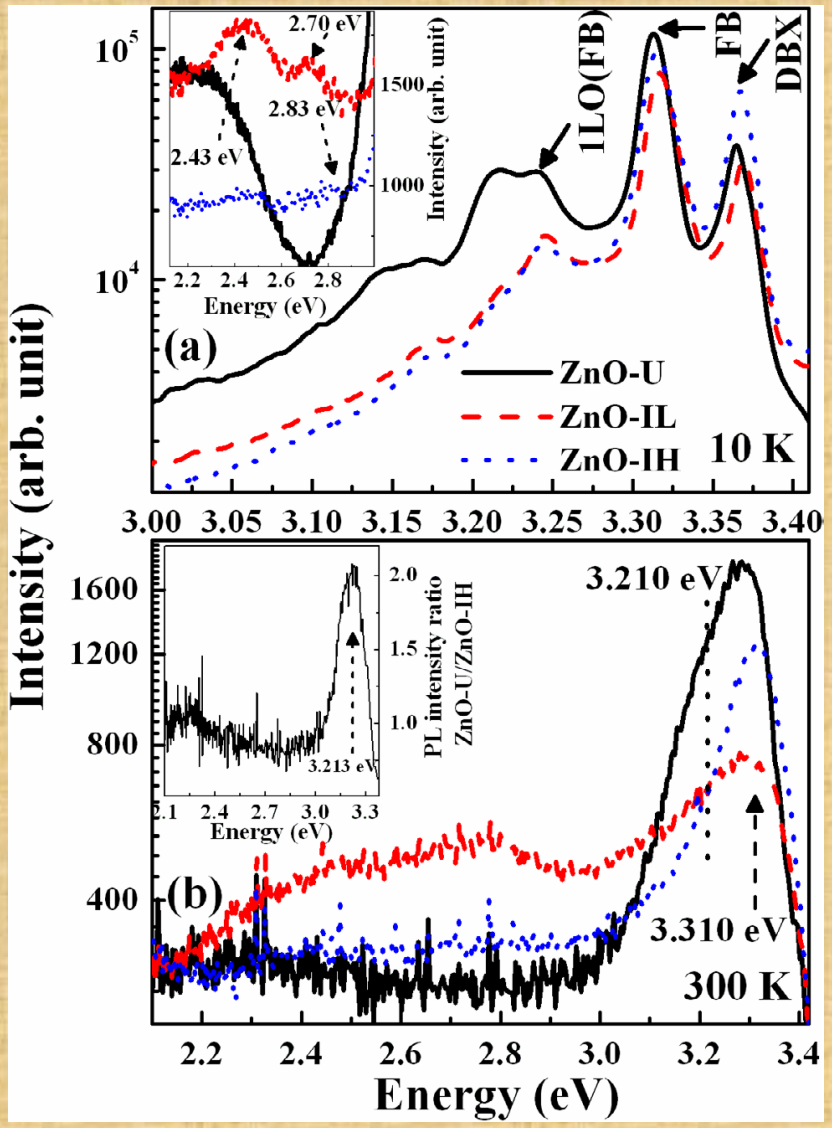
Amorphization is hardly achievable if a material can efficiently generate voids in application of energetic ion irradiation. Generation of voids depends on the diffusion coefficient of the concerned open volume defects (material property) and also on the sample temperature. On the other hand, presence of foreign atom (chemical impurity, like As in GaSb alloy) can hinder void formation during ion irradiation and amorphization can be reached [J. Phys. D: Appl. Phys. 50 (2017) 125101]. Till date, limited report exists in ZnO such as Si implantation induced secondary phase formation and amorphization.

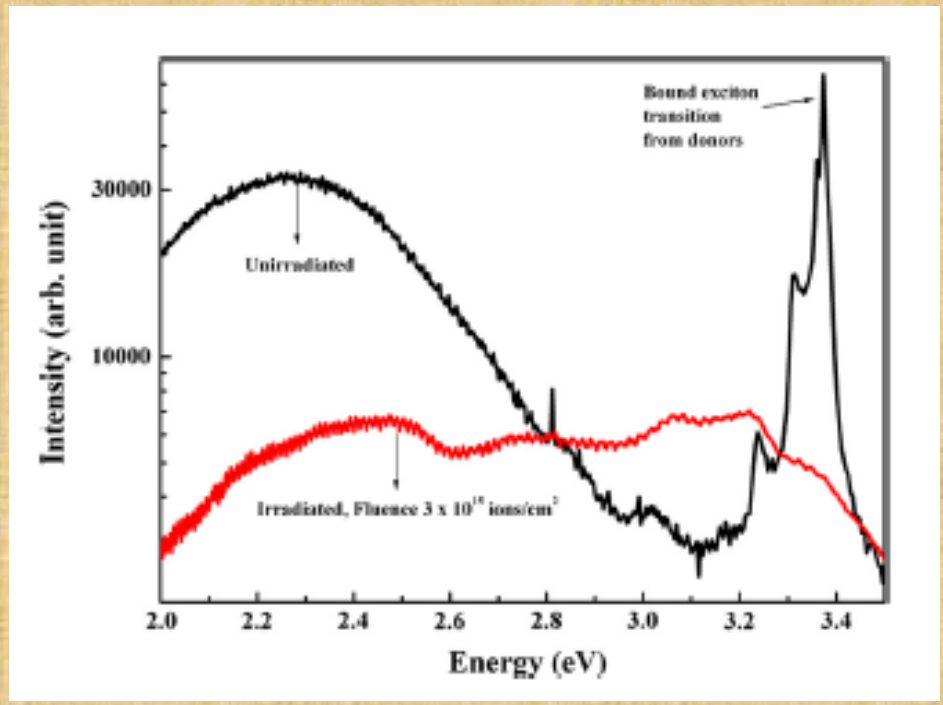
After reaching this new defective state, the overall defect as probed by RBS or positron annihilation spectroscopy will show a saturation of defects with increasing irradiation fluence further. This is because voids now act as both sink and source of vacancies and the two distinctly different regions are in defect equilibrium. In fact, a recent work envisages that buried extended defects can make ZnO more resistant for incorporating more disorder [Appl. Phys. Lett. 110 (2017) 172103].

Due to dominant I_{Zn} species (donor defects) in the nano channels, it is impossible to achieve p-type conductivity in high fluence ($\geq 10^{16}$ ions/cm^2) irradiated ZnO. High concentration of implanted dopants like N (or Li) may form N_2 in voids (or form metal clusters) without being substituted at V_{Zn} sites and generating N_{Zn} (Li_{Zn}) acceptors.

The scenario in single crystalline ZnO will be different as such system has less in-built disorder (particularly GB regions) compared to that of granular materials. For example, Ar fluence of 3×10^{14} ions/cm^2 on ZnO single crystal (hydrothermally grown, MTI Corp., USA) sample can reduce drastically its NBE PL emission [NIM B 311 (2013) 20] even at 10 K.

To note, no track formation in ZnO is till reported even for very high electronic energy deposition regime.





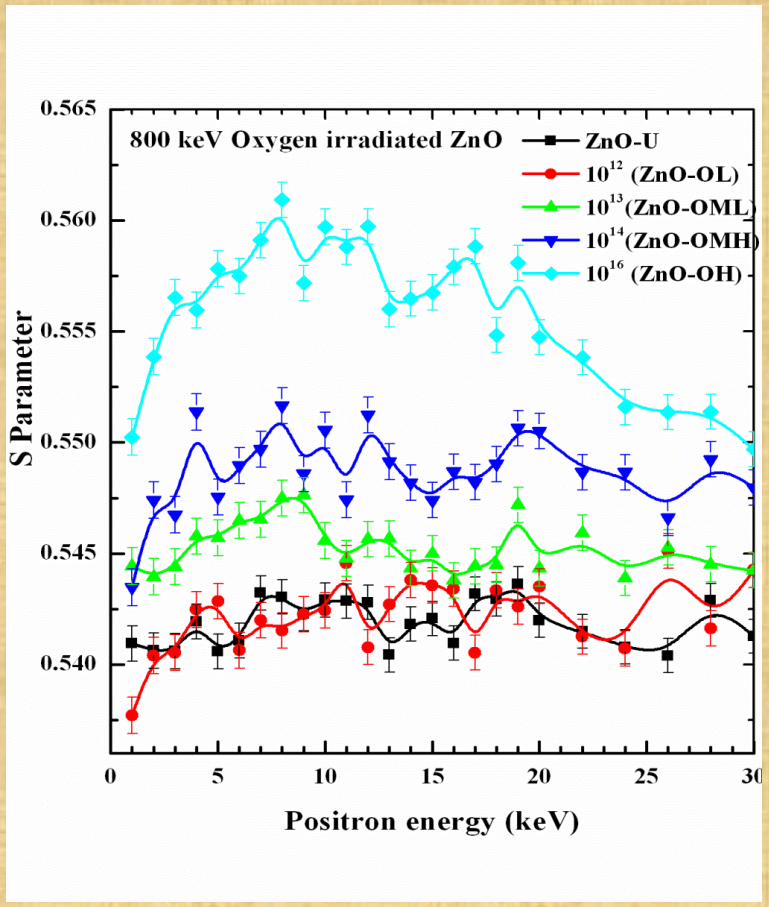
Nucl. Instrum. Meth. B 311 (2013) 20

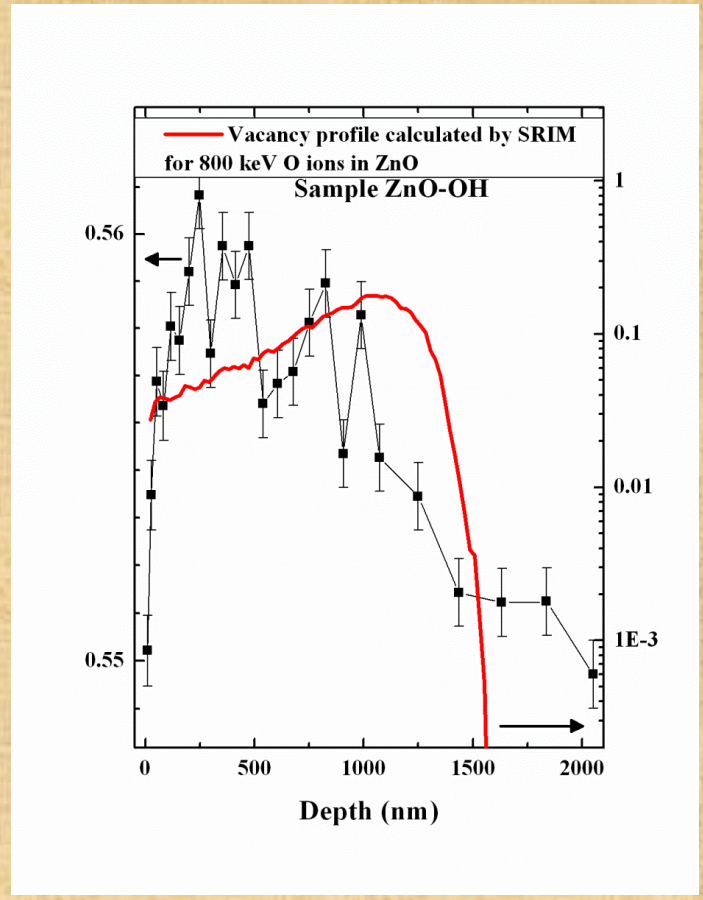
J. Phys. D: Appl. Phys. 51 (2018) 105107

For a much lower fluence, single crystalline ZnO has drastically lost it near band edge PL emission ~ 3.368 eV even at 10 K

Comparison and further insight…..

- ZnO pellets have been irradiated by 1.2 MeV Ar and 800 keV O ions. In both cases SRIM (Stopping and Range of Ions in matter) simulation predicts ratio of Zn and O vacancies (V_{Zn}/V_O) to be ~ 1.7.
- Electron-positron annihilated γ ray (511 keV) line shape have been measured using variable energy positron beamline at TU Munich.
- S and W parameters are well known in 511 keV line shape measurements. They are defect sensitive parameters.

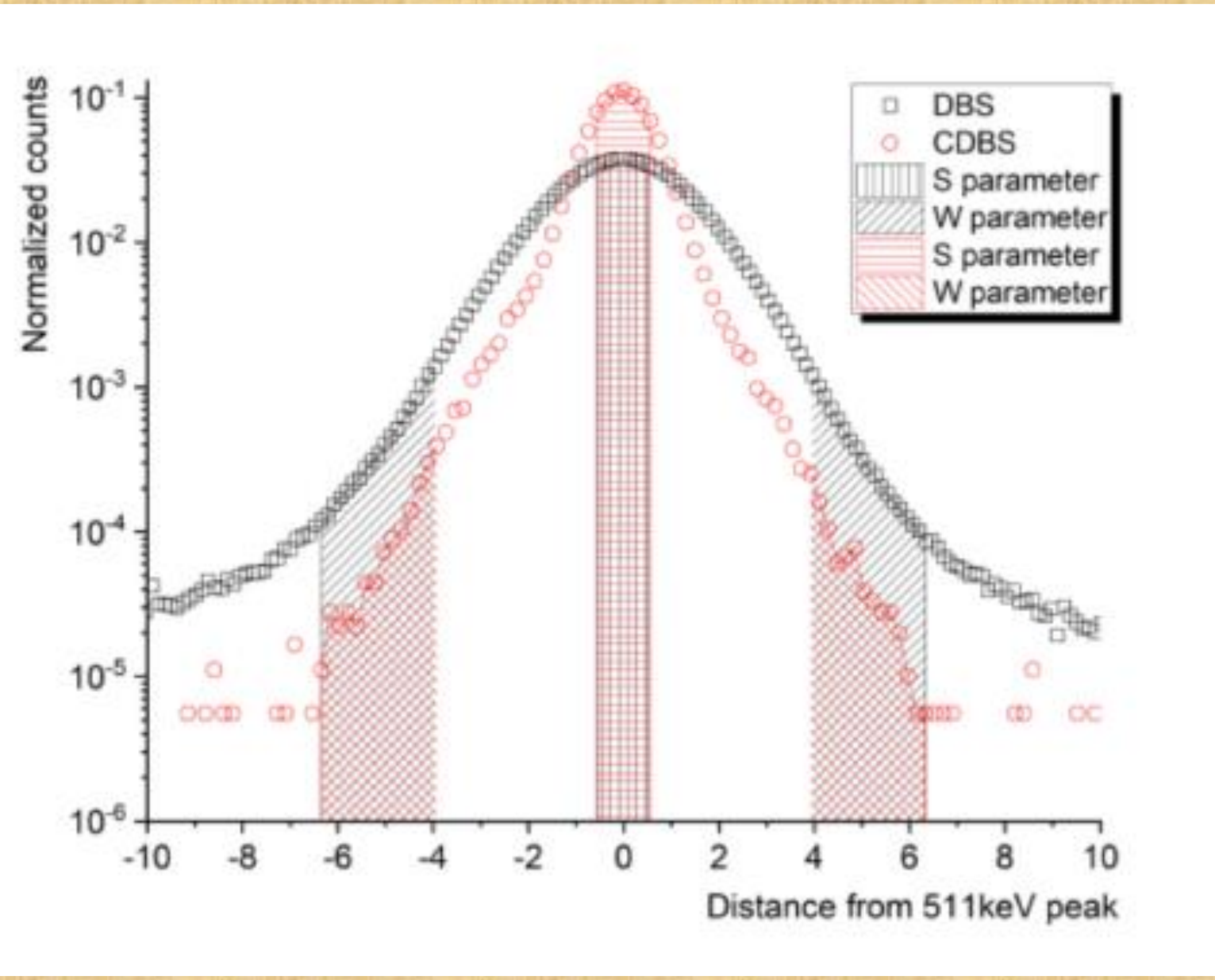




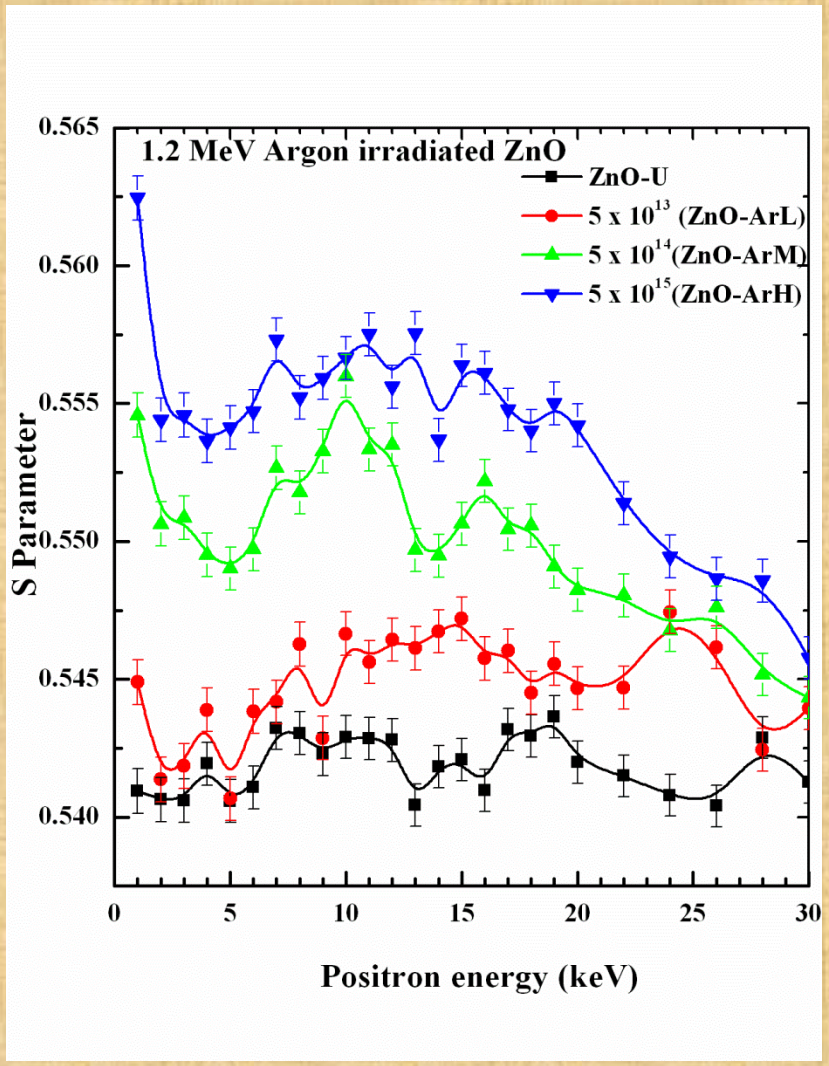
Please note the regions

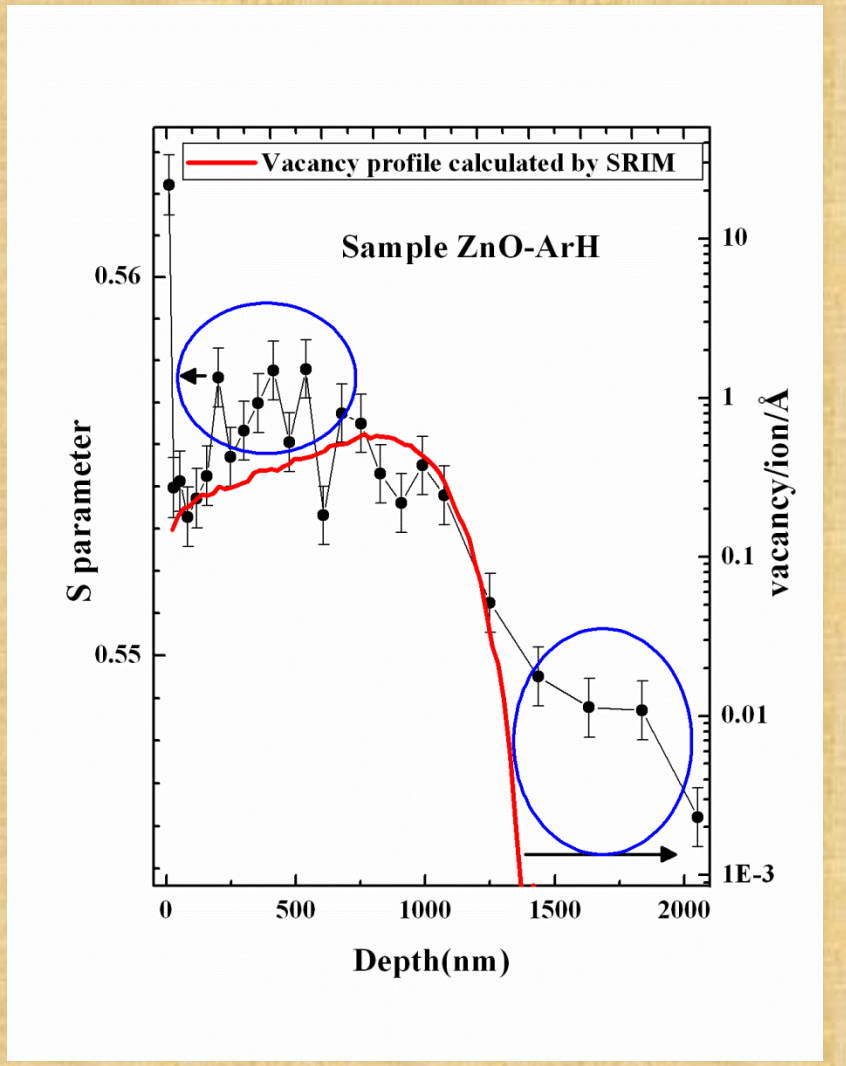
~ 250 nm below the surface

Beyond the penetration depth of the O ions

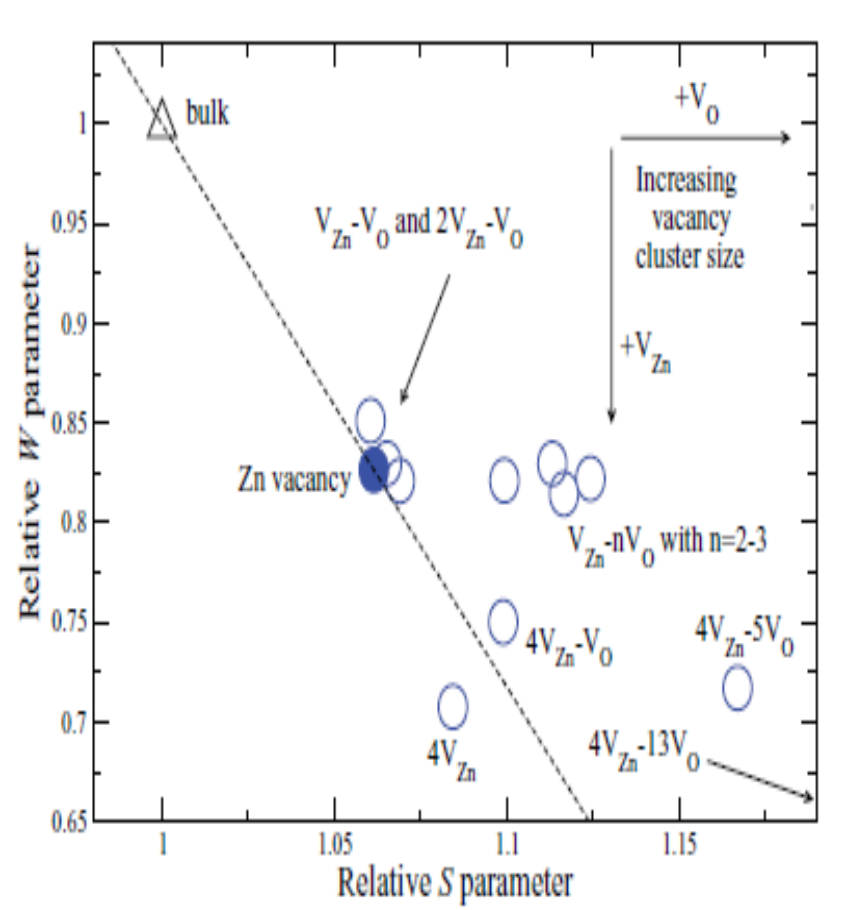

Normalized counts
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
-10
-8
-6
-4
-2
0
2
4
6
8
10
Distance from 511keV peak
DBS
CDBS
S parameter
W parameter
S parameter
W parameter

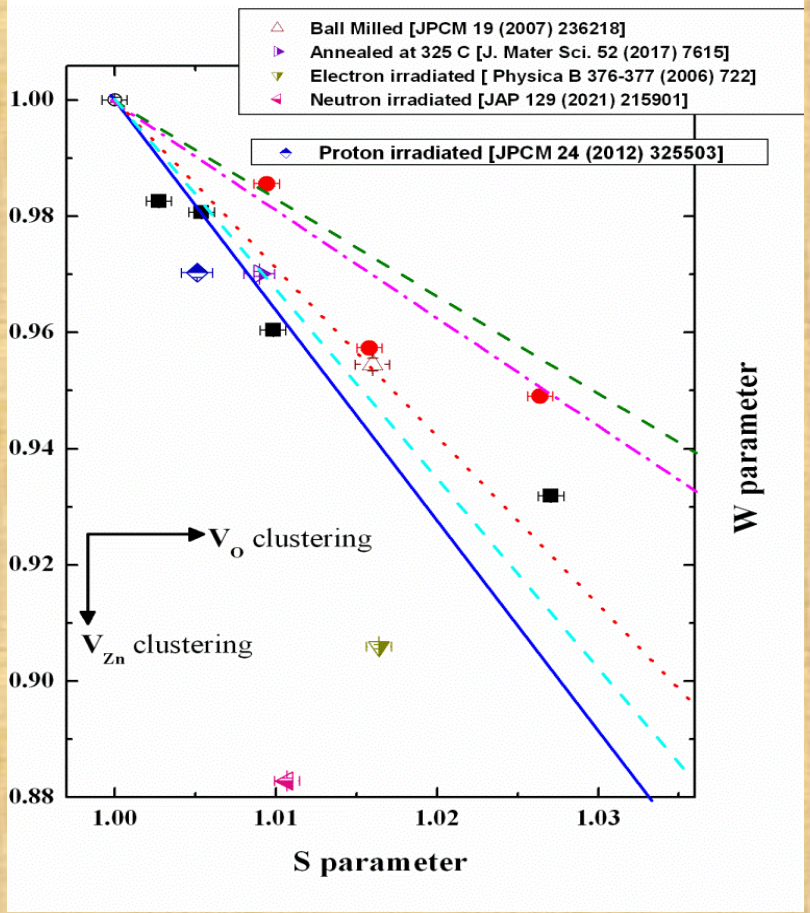
Similar feature for Ar ion irradiation





J. Phys.: Condens. Matter 32 (2020) 085703

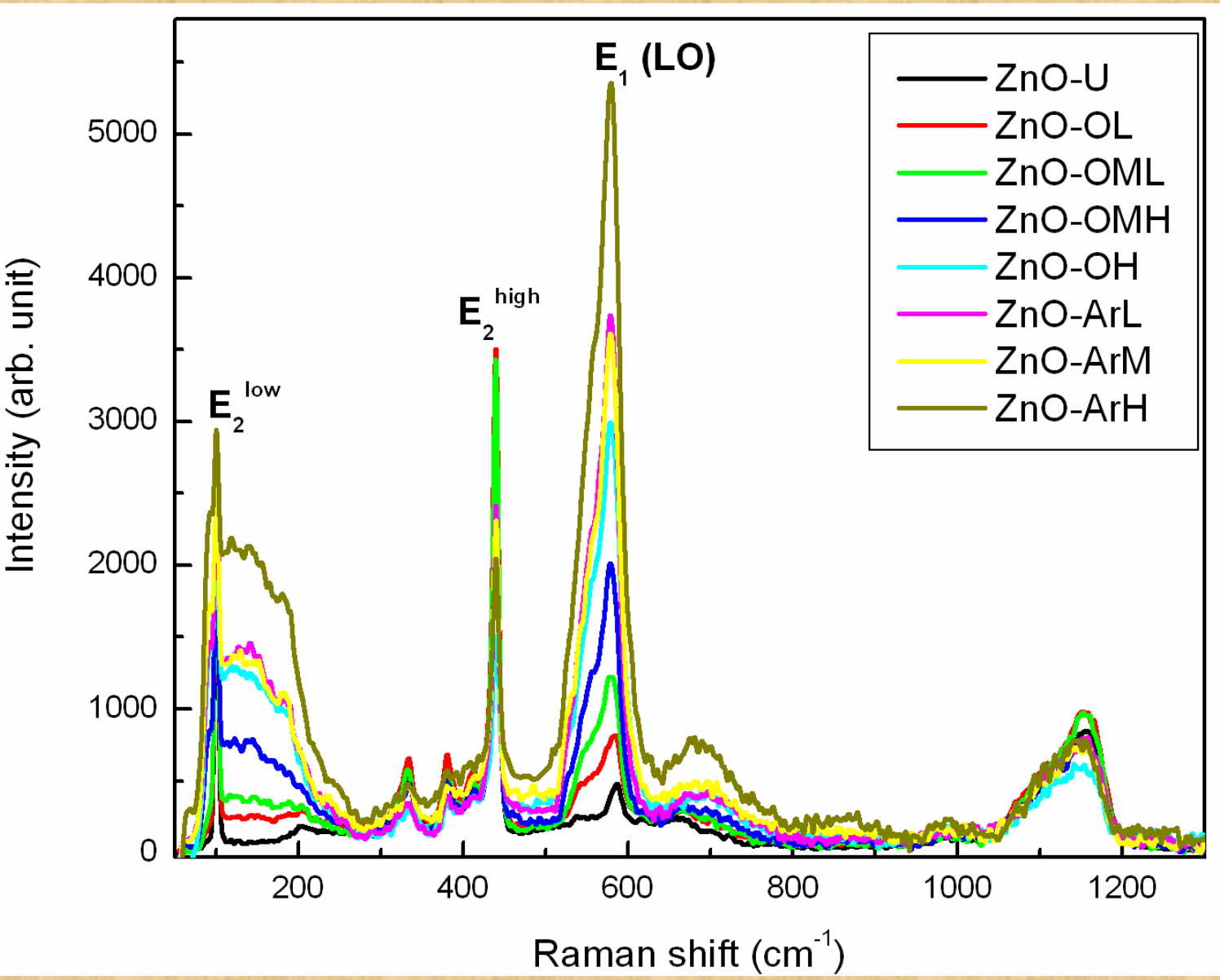




J. Phys.: Condens. Matter 28 (2016) 224002

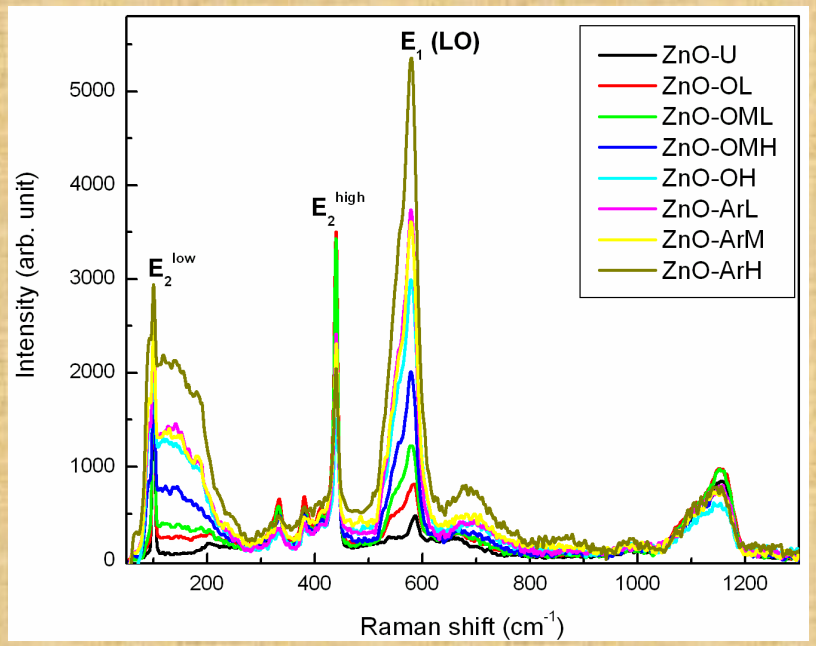
Red sphere: Ar irradiation (present data)
Black square: O irradiation (present data)
Blue line : V_{Zn} [J. Phys.: Condens. Matter 28 (2016) 224002] (Th.)
Dassed cyan: O irrd. [Appl. Phys. Lett. 110 (2017) 172402]
Dot red: N irrd. [J. Mater. Res. 28 (2013) 1977]
Dash dot magenta: Ga doped ZnO [Sci. Rep. 9 (2019) 3534]
Dassed green: $4V_{Zn}$-$5V_O$ (Th.)

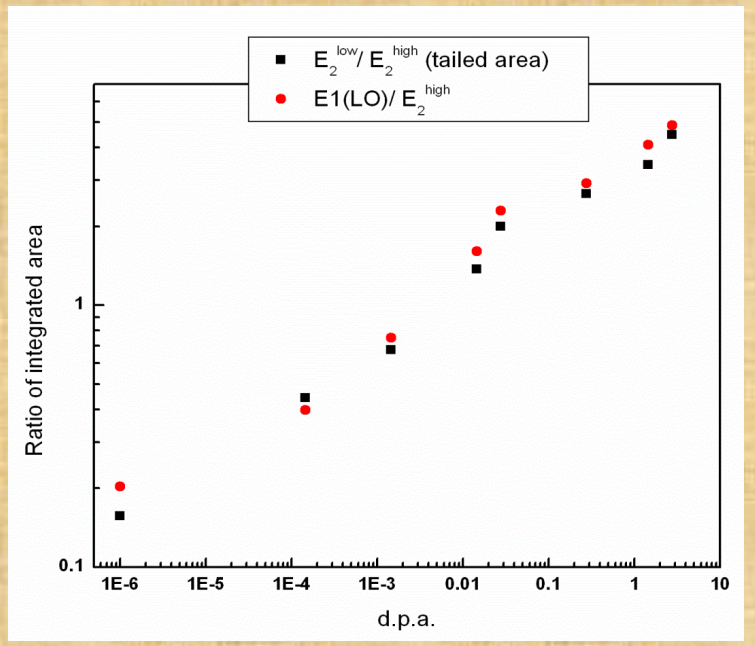
Measuring S & W parameters one can have an idea regarding the nature and size of the vacancy clusters

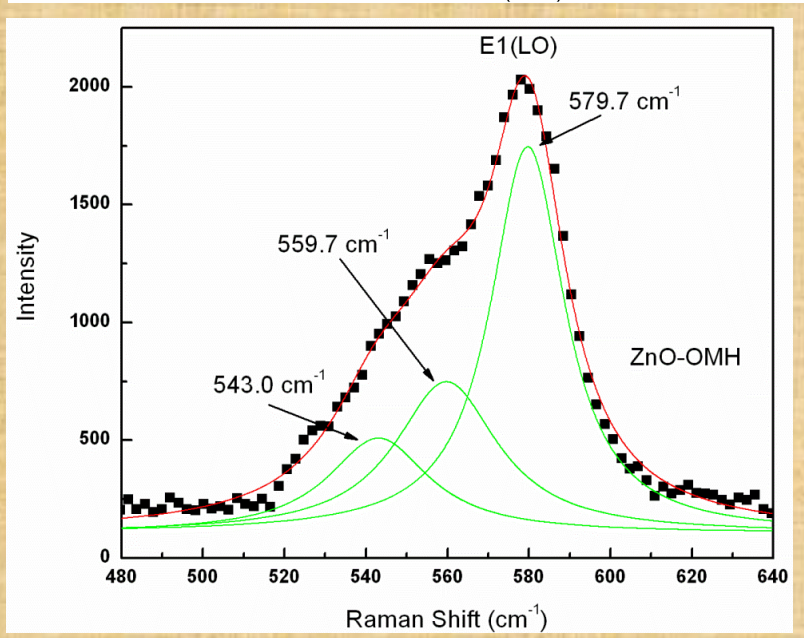


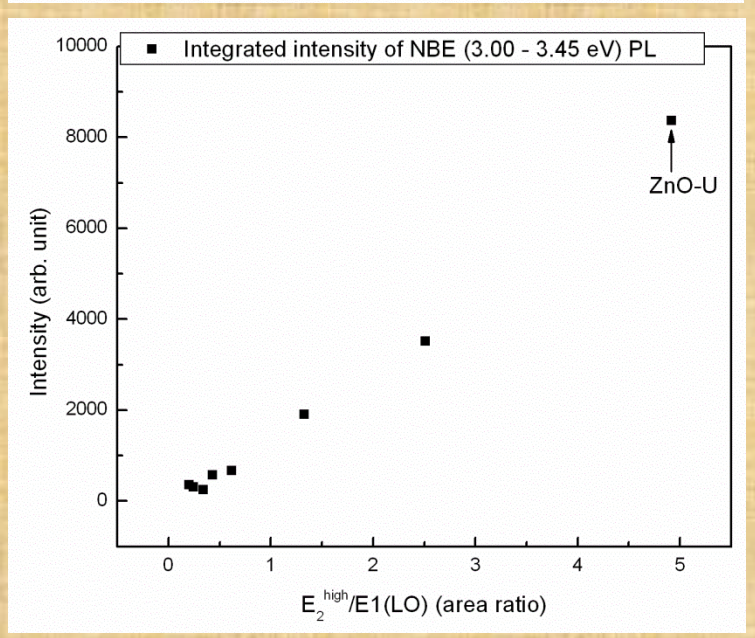
Room temp. Raman spectra (488 nm excitation) of unirradiated and irradiated ZnO samples.

Symmetry modes, E_2^{low} and E_2^{high} as well as disorder related E_1 (LO) of ZnO lattice and their evolution is clearly seen. The tailing of E_2^{low} is related with generation of vacancy clusters. The intensity ratio of E_1 (LO) and E_2^{high} can also be a disorder sensitive parameter [J. Raman Spec. 50 (2019) 1926].

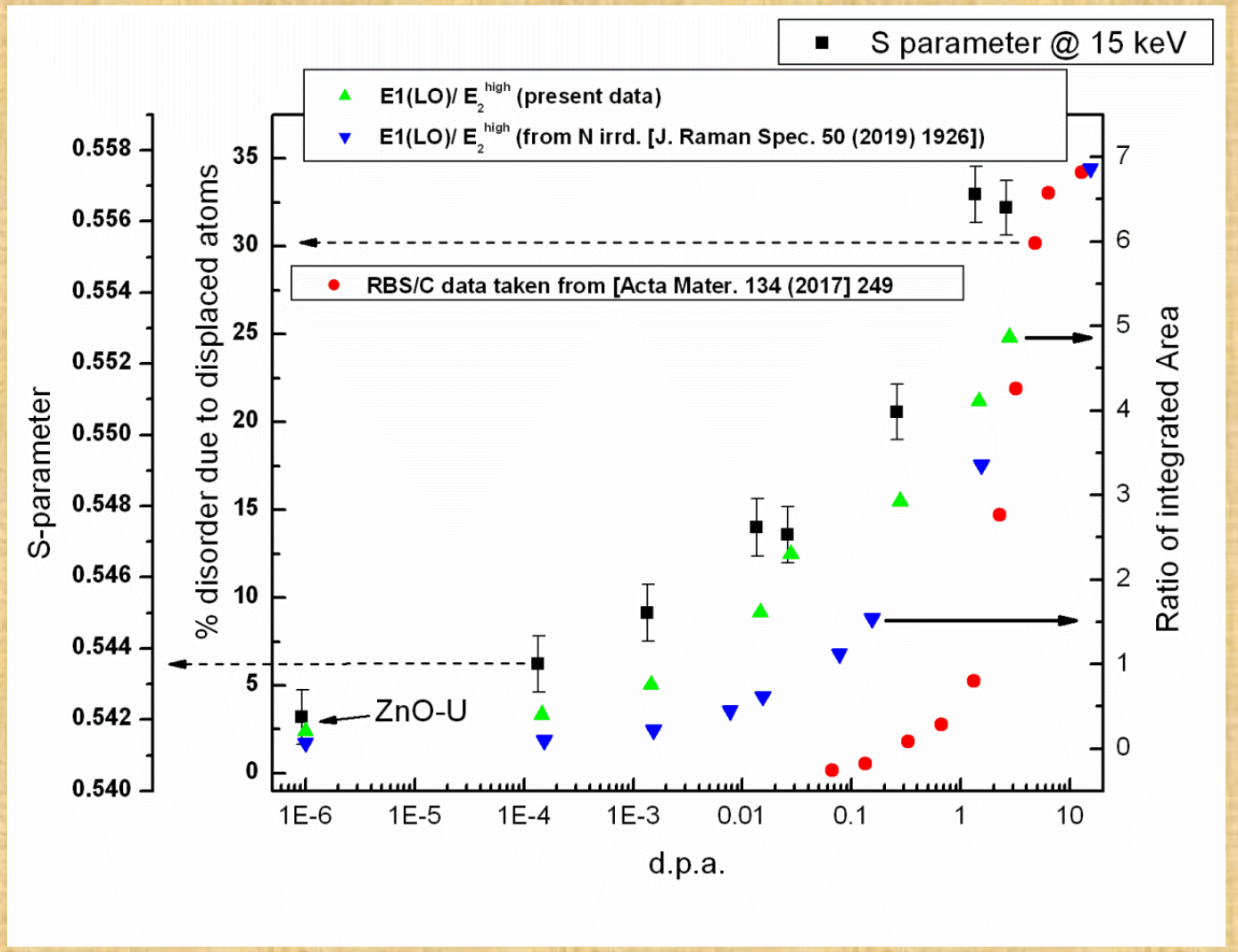






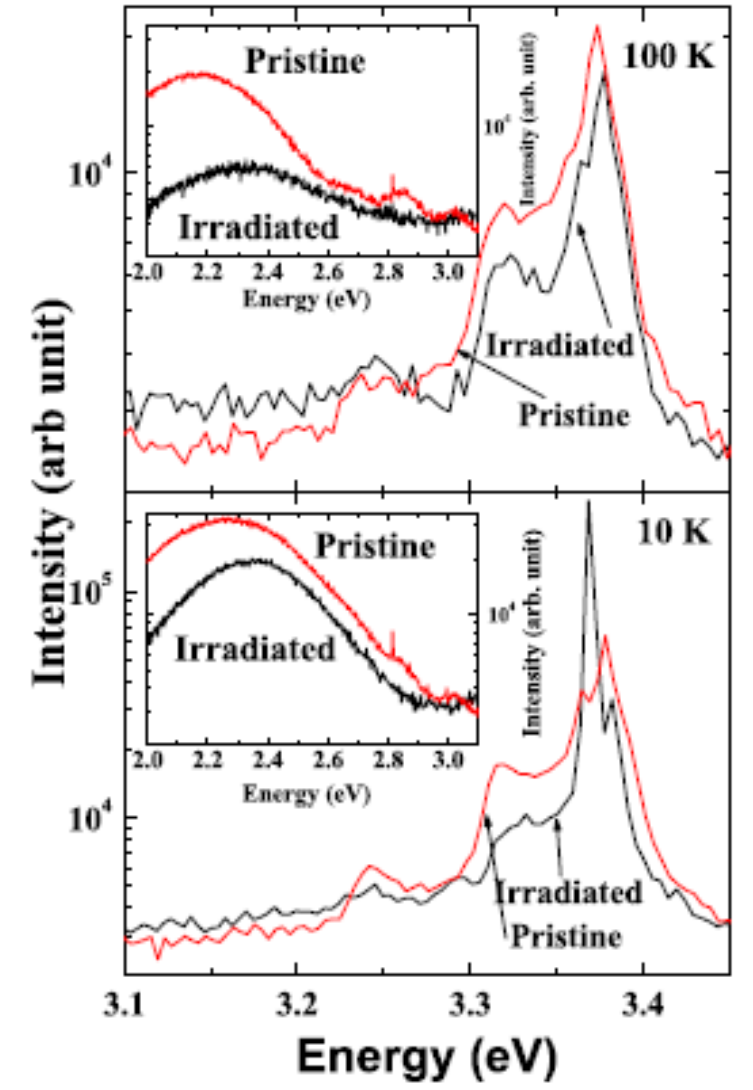


It is nice indeed that both the area ratios vary in a similar way. Also the variation is almost linear in a log-log scale with incorporated disorder (d.p.a.) in the present ZnO samples. This has been earlier noted in N implanted ZnO for a wide fluence regime. The inverse parameter E_2^{high} / E_1 (LO) scales with the integrated NBE PL of ZnO.



In the lower disorder regime (low d.p.a.) positron data as well as Raman data is very much effective to assess the defective nature of ZnO.

6 MeV proton irradiation



Whereas H implantation induces doping in ZnO, high energy H ions can induce rearrangement of doped/interstitial H in ZnO.

The increase of positron lifetime is onle (164 ps to 175 ps) 11 ps for a fluence of 5×10^{14} ions/cm^2 H fluence.

Our proposition is in built V_{Zn}-2H defects are transformed to V_{Zn}-1H causing small increase of positron lifetime.

At the same time, H interstitial defects occupy substitutional O (irrd. generated) position, causing intense H_O related transition at 10 K.

Both electronic and nuclear energy deposition play role in such rearrangement of defective state.

J. Phys.: Condens. Matter 24 (2012) 325503
J. Phys.: Condens. Matter 23 (2011) 155801
J. Phys.: Condens. Matter 25 (2013) 385501

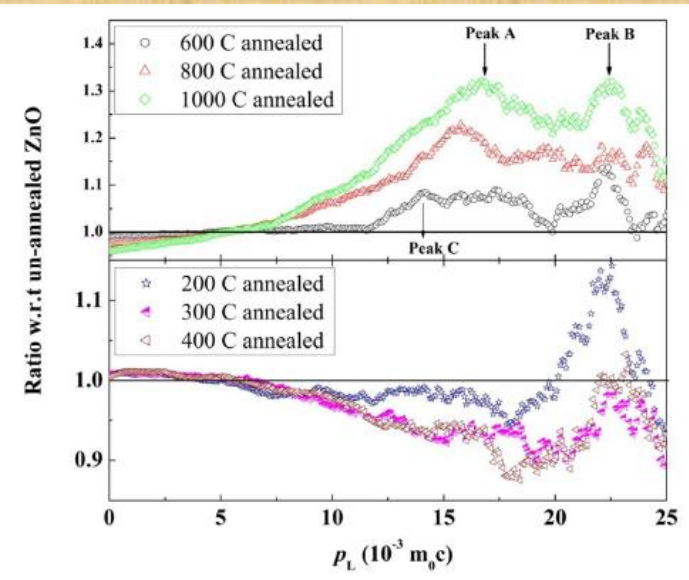
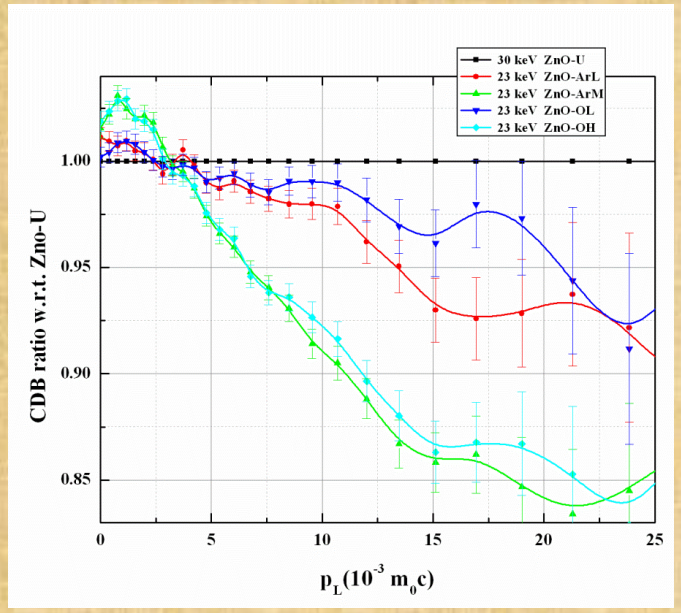
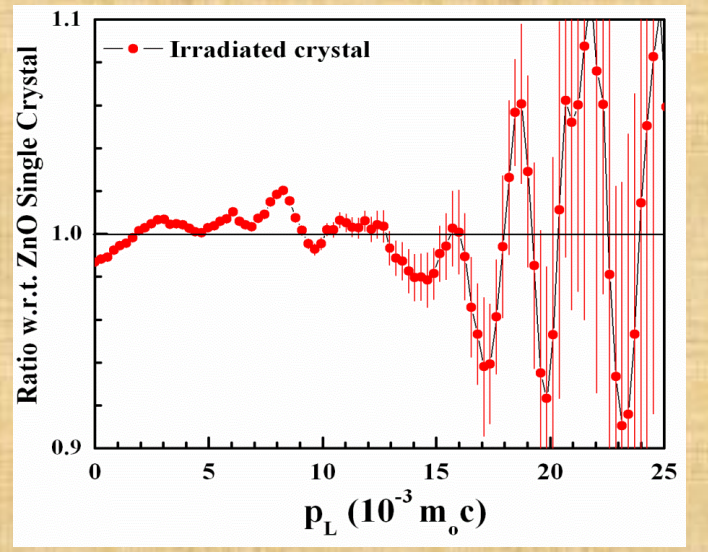


Figure taken from [J. Appl. Phys. 98 (2005) 053513]



J. Phys.: Condens. Matter 32 (2020) 085703



J. Phys.: Condens. Matter 24 (2012) 325503

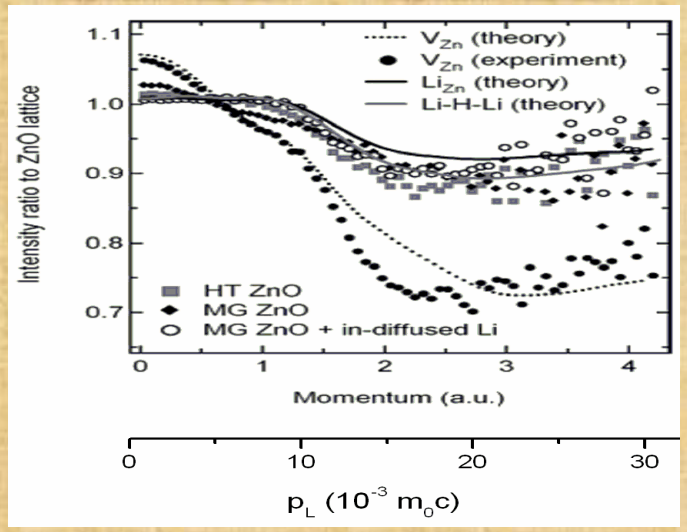
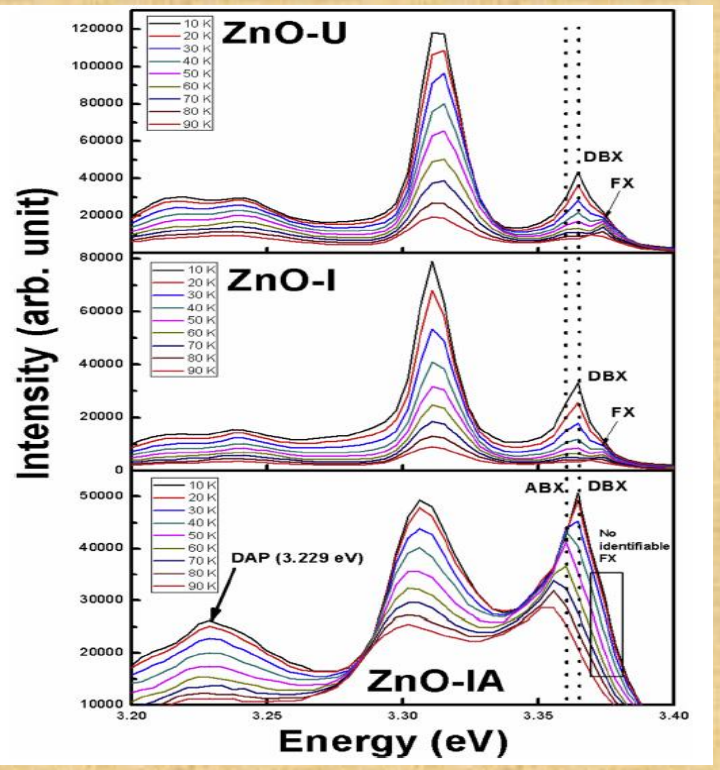
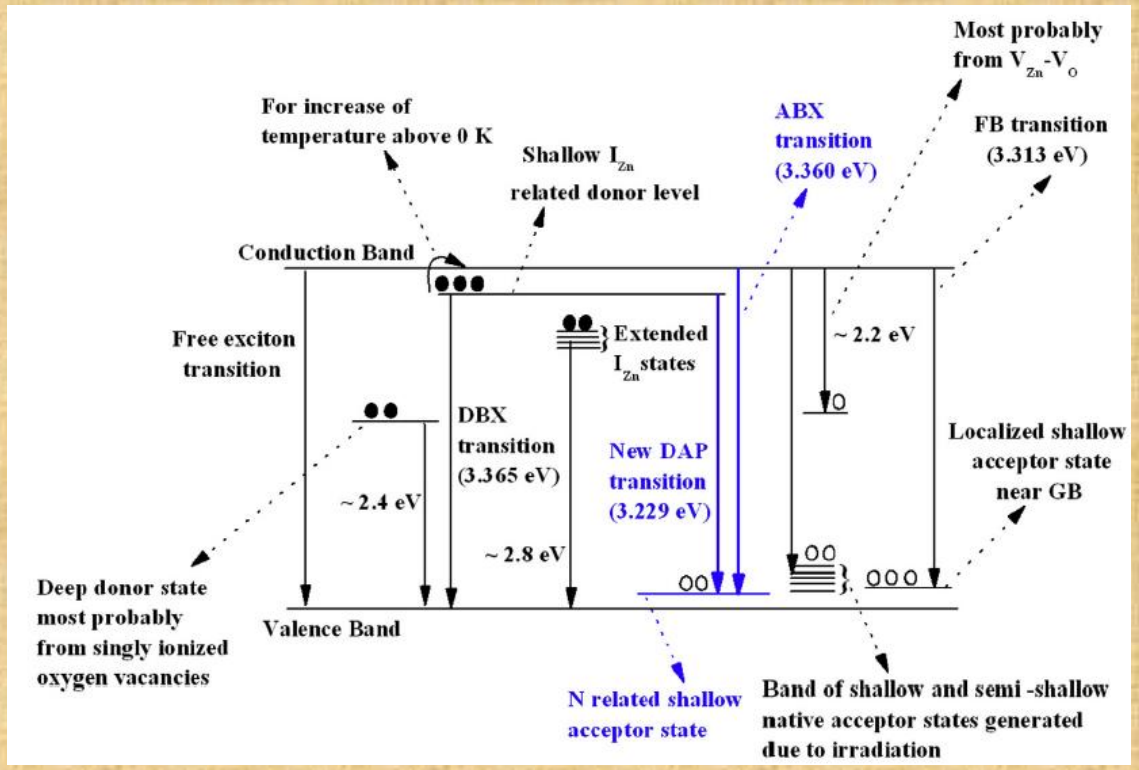


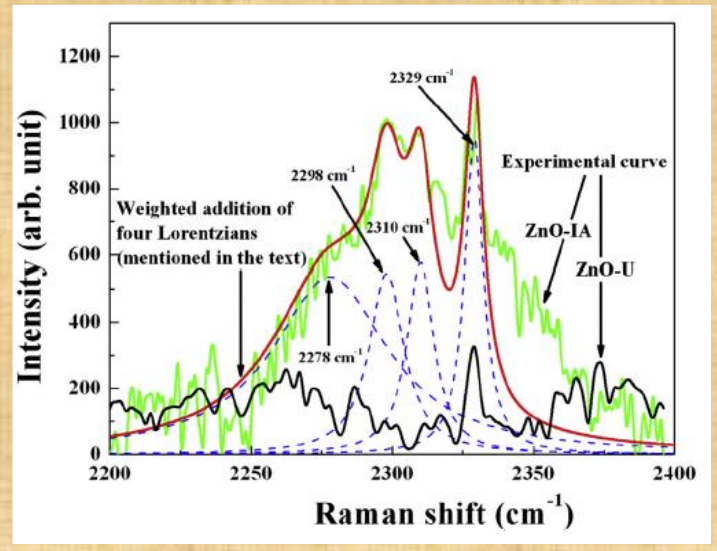
Figure taken from [Phys. Rev. B 83 (2011) 245208]

Peak A, B & C corresponds to positron annihilation with Zn 3p, Zn 3s and O 2s core electrons respectively [Phys. Rev. B 56 (1997) 14303]. So corresponding dip or peak like structure reflects lower or higher (respectively) positron annihilation with these electrons [Mater. Res. Express 4 (2017) 035909].



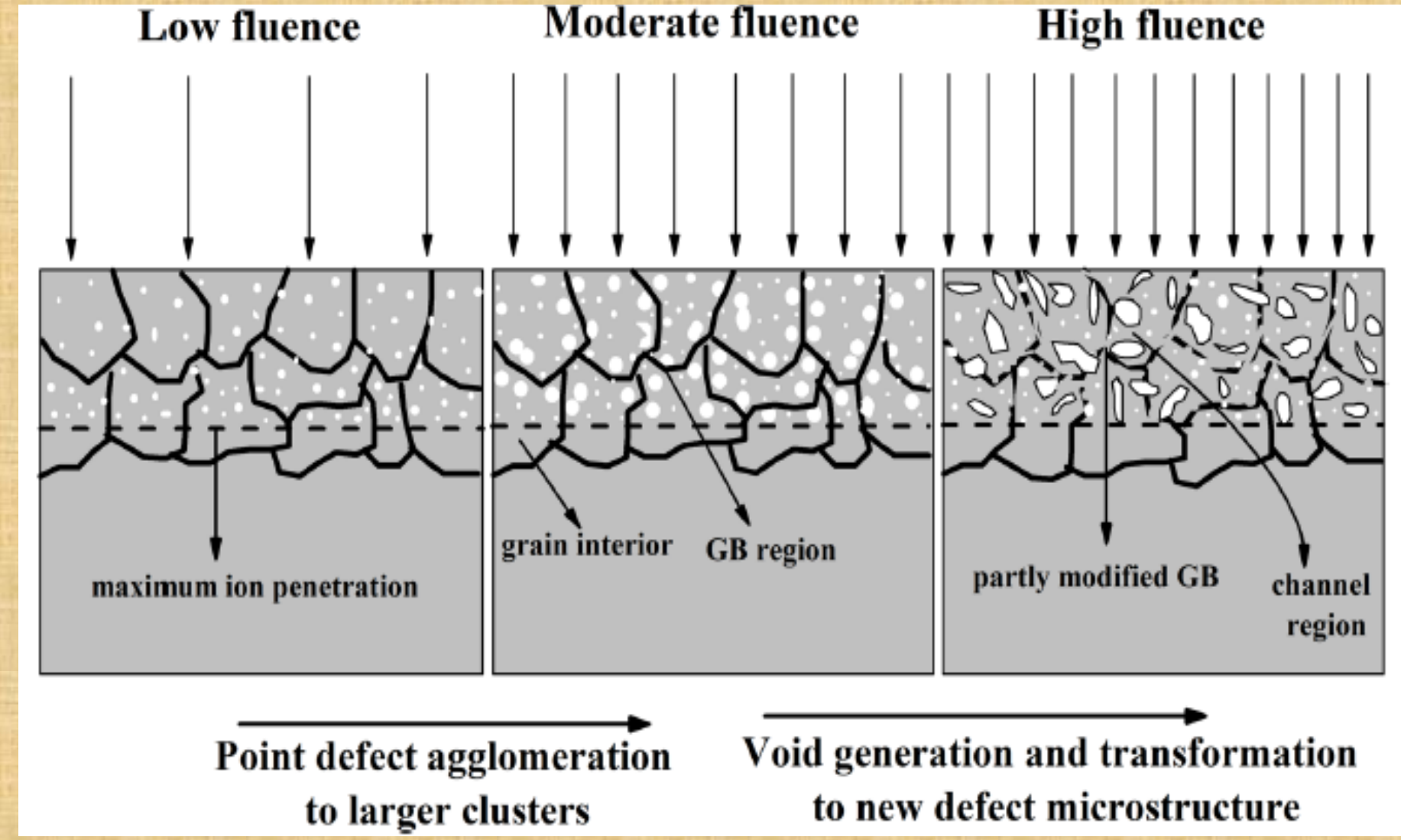


ZnO-I : 96 MeV O ion irradiated, ZnO-IA: post annealed at 300 ^oC



J. Alloys. Comp. 703 (2017) 26

Effect of N_2 incorporation via irradiated surface and thereby generation of shallow acceptor state when doped at V_{Zn}/V_{Zn}-V_O open volume defects


Low fluence
Moderate fluence
High fluence
maximum ion penetration
grain interior
GB region
partly modified GB
channel region
Point defect agglomeration to larger clusters
Void generation and transformation to new defect microstructure

nature COMMUNICATIONS

ARTICLE

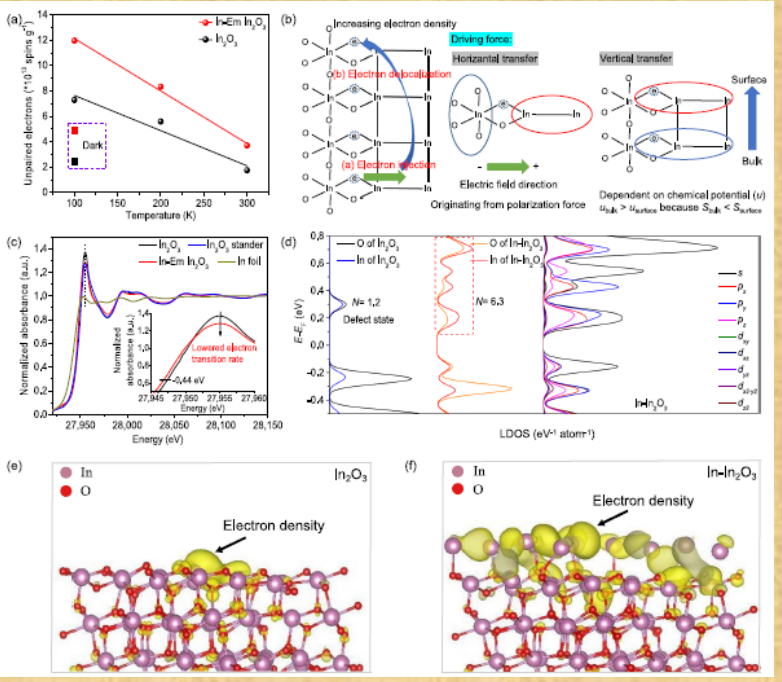
https://doi.org/10.1038/s41467-022-30958-5 OPEN

Subsurface oxygen defects electronically interacting with active sites on In_2O_3 for enhanced photothermocatalytic CO_2 reduction

Weiqin Wei[1], Zhen Wei[2], Ruizhe Li[1], Zhenhua Li[3], Run Shi[3], Shuxin Ouyang[1✉], Yuhang Qi[4], David Lee Philips[2] & Hong Yuan[1]

Oxygen defects play an important role in many catalytic reactions. Increasing surface oxygen defects can be done through reduction treatment. However, excessive reduction blocks electron channels and deactivates the catalyst surface due to electron-trapped effects by subsurface oxygen defects. How to effectively extract electrons from subsurface oxygen defects which cannot directly interact with reactants is challenging and remains elusive. Here, we report a metallic In-embedded In_2O_3 nanoflake catalyst over which the turnover frequency of CO_2 reduction into CO increases by a factor of 866 (7615 h^{-1}) and 376 (2990 h^{-1}) at the same light intensity and reaction temperature, respectively, compared to In_2O_3. Under electron-delocalization effect of O-In-(O)V_O-In-In structural units at the interface, the electrons in the subsurface oxygen defects are extracted and gather at surface active sites. This improves the electronic coupling with CO_2 and stabilizes intermediate. The study opens up new insights for exquisite electronic manipulation of oxygen defects.

Nature Commun. 13 (2022) 3199



IOP Publishing Journal of Physics D: Applied Physics

J. Phys. D: Appl. Phys. 47 (2014) 025001 (5pp) doi:10.1088/0022-3727/47/2/025001

Room temperature ferromagnetic ordering in 4 MeV Ar^{5+} irradiated TiO_2

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Abstract

Room temperature ferromagnetic ordering has been observed in a rutile TiO_2 polycrystalline sample after 4 MeV Ar^{5+} ion irradiation. The sheet resistance of the irradiated sample decreases from 10^7 to $3 \times 10^3\ \Omega\,cm^{-2}$. *Ab initio* calculation in the density-functional theory indicates that both oxygen vacancy (V_O) and titanium vacancy (V_{Ti}) can lead to ferromagnetism. However, the drastic lowering of resistance and change of colour (from white to black) indicate the formation of V_O. Experimental results along with the theoretical calculation suggest that presence of V_O in the irradiated sample plays the main role in inducing ferromagnetism.

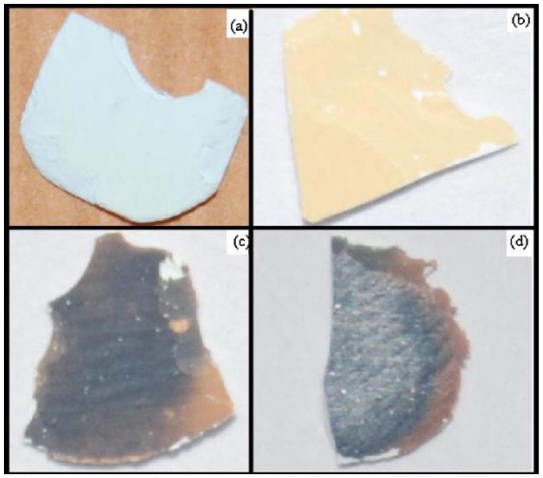

FIG. 3. (Color online) Color of ZnO samples, (a) unirradiated and irradiated with fluence, (b) 1×10^{15}, (c) 5×10^{15}, and (d) 5×10^{16} ions/cm^2.

Simultaneous appearance of ferromagnetism, low resistance and black colouration in TiO_2 and ZnO

J. Appl. Phys. 107 (2010) 113516

A General Method for Large-Scale Fabrication of Semiconducting Oxides with High SERS Sensitivity

Xudong Zheng,[†] Feng Ren,[*,†,‡] Shunping Zhang,[‡] Xiaolei Zhang,[†] Hengyi Wu,[†] Xingang Zhang,[†] Zhuo Xing,[†] Wenjing Qin,[†] Yong Liu,[‡] and Changzhong Jiang[*,†,‡]

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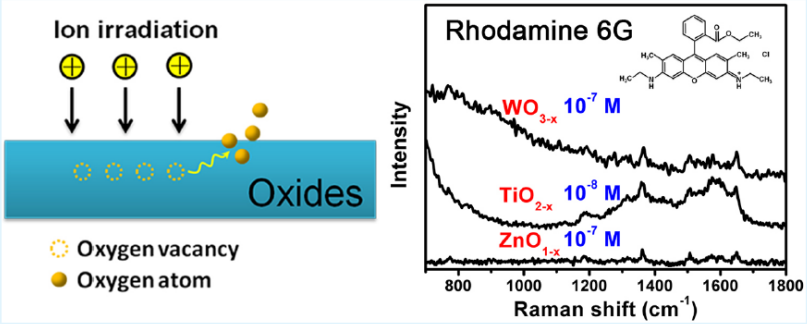
Supporting Information



ABSTRACT: Surface-enhanced Raman spectroscopy (SERS) is a versatile and powerful spectroscopic technique for substance analysis and detection. So far, the highest detection sensitivities have been realized on noble nanostructure substrates, which, however, are costly, unstable, and non-biocompatible. While semiconductor substrates could in principle be used, existing realizations have either resulted in substrates with low sensitivities or used methods that have poor technical control. Here we report a general and versatile method, based on ion irradiation and vacuum annealing, for fabricating large-scale reduced semiconducting oxide SERS substrates with high sensitivities. The SERS enhancement mainly stems from oxygen vacancy-associated electronic states created by the ion irradiation of sample; these states enhance the charge-transfer (CT) mechanism between the oxide substrate and the adsorbed molecules and thus significantly magnify SERS signals. The improved carrier mobility by vacuum annealing and the introduction of impurity energy levels and nanostructures enhances further the CT efficiency. A detection limit as low as 5×10^{-8} M was achieved; this is the highest sensitivity among the reported semiconductors, and it even compares to noble metals without the aid of "hot spots". The method is general—we demonstrate it on WO_3, ZnO, and TiO_2 substrates using Ar^+ and N^+ ion beam irradiation—and broadly applicable to produce noble-metal-free SERS substrates with high sensitivities.

KEYWORDS: *ion irradiation, semiconducting oxide, oxygen vacancy, charge transfer, surface-enhanced Raman scattering*

ACS Appl. Mater. Inter. 9 (2017) 14534

Finally, in 2D materials…….

Supported Two-Dimensional Materials under Ion Irradiation: The Substrate Governs Defect Production

Silvan Kretschmer,*[,†] Mikhail Maslov,[†,‡] Sadegh Ghaderzadeh,[†] Mahdi Ghorbani-Asl,[†] Gregor Hlawacek,[†] and Arkady V. Krasheninnikov*[,†,§]

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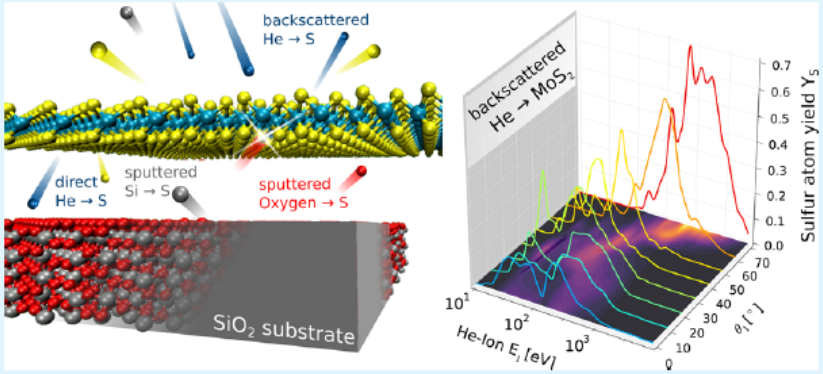
Supporting Information

ABSTRACT: Focused ion beams perfectly suit for patterning two-dimensional (2D) materials, but the optimization of irradiation parameters requires full microscopic understanding of defect production mechanisms. In contrast to freestanding 2D systems, the details of damage creation in supported 2D materials are not fully understood, whereas the majority of experiments have been carried out for 2D targets deposited on substrates. Here, we suggest a universal and computationally efficient scheme to model the irradiation of supported 2D materials, which combines analytical potential molecular dynamics with Monte Carlo simulations and makes it possible to independently assess the contributions to the damage from backscattered ions and atoms sputtered from the substrate. Using the scheme, we study the defect production in graphene and MoS_2 sheets, which are the two most important and wide-spread 2D materials, deposited on a SiO_2 substrate. For helium and neon ions with a wide range of initial ion energies including those used in a commercial helium ion microscope (HIM), we demonstrate that depending on the ion energy and mass, the defect production in 2D systems can be dominated by backscattered ions and sputtered substrate atoms rather than by the direct ion impacts and that the amount of damage in 2D materials heavily depends on whether a substrate is present or not. We also study the factors which limit the spatial resolution of the patterning process. Our results, which agree well with the available experimental data, provide not only insights into defect production but also quantitative information, which can be used for the minimization of damage during imaging in HIM or optimization of the patterning process.



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Cu-doping of ZnO by nuclear transmutation

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Zinc oxide single crystals were doped with copper acceptors by means of the nuclear transmutation doping method, which gives highly uniform dopant distributions and has a much higher probability of controlling the dopant locations in the lattice. The Cu doping was confirmed by the infrared absorption signature of Cu^{2+} at 5780 cm^{-1}. Hall-effect measurements were performed to study the effect of Cu_{Zn} on the electrical properties of ZnO. These measurements indicated that the Cu acceptor level lies 0.160 eV below the conduction-band minimum. © *2011 American Institute of Physics*. [doi:10.1063/1.3662014]

TABLE I. Zn stable isotope percentage in ZnO nanorod samples measured by APM; plus standard values for natural Zn isotope abundance. Uncertainties represent the expected standard deviation for each measurement.

Sample	^{64}Zn	^{66}Zn	^{67}Zn	^{68}Zn	^{70}Zn
^{nat}ZnO	49.28±0.02%	27.83±0.02%	4.20±0.01%	18.12±0.01%	0.562±0.003%
^{64}ZnO enriched	71.47±0.06%	15.60±0.03%	2.30±0.01%	10.30±0.02%	0.334±0.005%
^{66}ZnO enriched	6.44±0.02%	90.26±0.06%	0.88±0.01%	2.33±0.01%	0.078±0.002%
Natural abundance[24]	49.17±0.75%	27.73±0.98%	4.04±0.16%	18.45±0.63%	0.61±0.10%

Nuclear transmutation of ^{64}Zn to ^{65}Zn using neutron irradiation, ^{65}Zn decays to stable ^{65}Cu. Similarly, ^{68}Zn transmutes to ^{69}Zn which decays to ^{69}Ga. Cu and Ga at Zn sites are acceptor and donor (respectively) in ZnO.

Suitable isotope enrichment and simultaneous neutron irradiation can be effective for p-n junction fabrication using ZnO thin films.

Also important for bio-imaging!

Hot probe measurements on neutron irradiated, isotope enriched ZnO nanorods

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ABSTRACT

We report on neutron transmutation doping (NTD) of isotopically (^{64}Zn) enriched ZnO nanorods to produce material with holes as the majority mobile carrier. Nanorods of ZnO enriched with ^{64}Zn were synthesised and the abundance of ^{64}Zn in these samples is ~ 71%, compared to the natural abundance of ~ 49 %. The enriched material was irradiated with thermal neutrons which converts some ^{64}Zn to ^{65}Zn. The ^{65}Zn decays to ^{65}Cu with a half-life of 244 days and the Cu can act as an acceptor dopant. After 690 days, a hot probe technique was used to determine the majority charge carriers in non-irradiated and neutron irradiated nanorod samples. Non-irradiated samples were measured to be to have electrons as the majority mobile carrier and the irradiated samples were measured to have holes as the majority mobile carrier.

Use of stable heavier isotope ion beams

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Heavy Hydrogen Doping into ZnO and the H/D Isotope Effect

Ryo Nakayama,* Mitsuhiko Maesato,* GyeongCheol Lim, Makoto Arita, and Hiroshi Kitagawa*

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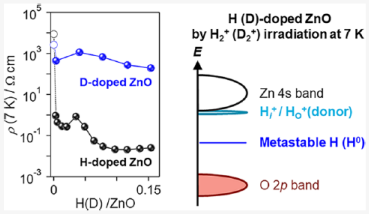
ABSTRACT: Hydrogen (H) can drastically change the physical properties of solids by the doping of host materials with minimum perturbation to the lattice because of its small size, quantum nature, and a variety of charged states from −1 (hydride, H^-) to +1 (proton, H^+). While the H-doping amount is limited under equilibrium conditions, H_2^+ ion irradiation at low temperature is a promising method for introducing a large amount of hydrogen into any material. Although the application of this method offers the potential for exploring unforeseen fascinating properties, the effects of nonequilibrium H doping at very low temperature below 10 K are largely underexplored and are not well understood. In this article, we report heavy H (D) doping into ZnO films by H_2^+ (D_2^+) irradiation at 7 K, which resulted in metallic conductivity and an isotope effect on the conductivity at 7 K. The H/D isotope effect is attributable to metastable H (D) trapping sites generated by the effect of irradiation. The isotope effect is decreased at low acceleration voltage. Furthermore, the subsequent thermal excursion induces a large irreversible decrease in resistivity, indicating the migration of H (D) from metastable trapping sites upon heating. This work provides a new strategy to control the physical properties of materials and to investigate the H (D) migration occurring with increasing temperature after excess H doping at very low temperature.



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Isotopic study of the nitrogen-related modes in N⁺-implanted ZnO

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Micro-Raman measurements were performed to study the nitrogen-related modes in ZnO samples implanted with N^+. The two stable N isotopes, ^{14}N and ^{15}N, were implanted. Distinct peaks at 277 and 512 cm^{-1} are observed irrespective of the implanted isotope, both before and after rapid thermal annealing. The insensitivity of the mode frequencies to the implanted isotope rules out the explanation of these modes as local vibrational modes involving N motion. These modes were not detected in ZnO samples implanted with Zn^+, O^+, or P^+, which suggests that they may be associated with distortions/defects favored by the presence of N. © *2007 American Institute of Physics.*

Use of radioactive ion beams

A large number of RIBs are being provided by ISOLDE, CERN.

For metal oxides, important beams are ^{57}Mn which decays to ^{57}Fe, and ^{72}Ga which decays to ^{72}Ge.

Location of Fe inside ZnO and/or TiO_2 lattice is important because both can excellent photoicatalytic compounds.

Ge is a shallow donor both in ZnO and Ga_2O_3. Doping Ga in ZnO (stays as impurity) or in Ga_2O_3. Conversion of Ga to Ge will generate high conductivity at room temperature.

Summary and future directions

- **Damage build up in the bulk and subsurface regions has been investigated in ion irradiated ZnO.**
- **Positron and Raman spectroscopy both are very efficient to detect evolution of low disorder in ZnO.**
- **With correctly selected parameters, Positron and Raman spectroscopy can detect the defective state of ZnO within a short time scale.**
- **The methodology can be extended to other metal oxide semiconductors**
- **Sub-surface defects are very much important for technological purposes.**
- **Neutron transmutation doping can start a new avenue of technological use of ZnO, specially for opto-electronic devices and bio-medical imaging.**
- **Stable isotope ion beams enhance our knowledge on irradiation induced defects and their control**
- **Use of two radioactive isotope ion beams have also been discussed**
- **Radioactive as well as stable isotope ion beams, along with electron, proton and neutron beams can open huge possibilities from material science point of view.**
- **Thin film deposition unit, Depth resolved positron beam, Depth resolved cathodoluminescence, Raman spectrometer, high quality metal-semiconductor contact fabrication, I-V measurement set up, sample temperature variation (77-500 K), are needed to exploit fully the above mentioned irradiation facilities.**

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