7
Effect of Gamma Irradiation on Vertically Aligned ZnO Nanorods based Hydrogen Sensor

In this chapter, the impact of gamma irradiation on performance of ZnO nanorods based hydrogen sensor will be perused. Effect of Gamma irradiation on structural, surface morphology and optical characterization will be studied. Then, effect of gamma irradiation with incremental doses rates on Schottky contacted ZnO NRs based nanosensor's response and response/recovery time will be taken into account for 1% and 5% hydrogen concentration at 150 °C operating temperature. As discussed earlier, Schottky contacted ZnO NRs based nano-sensor's response was relatively correlated with modified structural, optical and electrical properties and as an output, gave enhanced sensor response at low gamma doses. In addition, overall effect of irradiation on sensing mechanism will be discussed.

7.1 INTRODUCTION

Gamma radiations are highly penetrable as compared to alfa (α)and beta (β) radiations due to the fact that they are the most vigorous electromagnetic radiation sources with energy ranging from 100 keV to few MeV [L'Annunziata, 2012]. Key applications of gamma irradiations are in the area of medicines, industries, military, nuclear power plants and research [chamielewski and Haji-Saeid, 2004]. Penetration and absorption of gamma rays in a material produces changes in the internal configuration of mater. Subsequently, it brings change in the structural, electrical and optical properties of metal oxide [Al-Sofany *et al.*, 2014; Indluru *et al.*, 2013]. When these energetic photons travel through semiconductor materials, energy is released in the form of ionizing (core-level ionization, electron hole pair generation) and non-ionizing process (displacement damage effect) [Srour *et al.*, 2003]. Primary lattice defects such as vacancies and interstitials are created at low dose of gamma rays. At high gamma dose, disordered regions are created which exhibit displacement damage effects. Radiation induced primary and secondary defects and heat from the radiation modifies the structural, optical, electrical properties and surface morphology which then resulted in enormous change in nanosenor based sensor's response. Al-Hamdani *et al.* in [Al-Hamani *et al.*, 2014], described the effect of gamma irradiation on ZnO thin film, where increase in gamma irradiation dose caused decrease in grain size and optical band gap. Gas sensing properties of metal oxides based gas sensors gets strongly influenced by gamma irradiation [Azmy *et al.*, 2014; Wang *et al.*, 2014; Duy *et al.*, 2015]. Yin *et al.* in [Yin *et al.*, 2014], irradiated Ag/Ag_2SnO_3 nano-particles with different gamma rays ranging from 0 kGy-500 kGy and, result revealed enhanced 6.3-fold response of ethanol sensor in comparison with un-irradiated Ag_2SnO_3.

From this chapter, we will learn about the effects of gamma irradiation on structural, optical and gas sensing properties of Au/ZnO NRs based hydrogen nanosensors with gamma doses ranging from 1 kGy to 10 kGy. Furthermore, hydrogen sensor's relative response with various gamma doses at 150 °C for 1% and 5% hydrogen concentration will be considered. Finally, effect of low and high gamma doses on ZnO NRs conjoined with gas sensing mechanism will also be learned.

7.2 EXPERIMENTAL SETUP

RF Magnetron Sputtering System was used to grow ZnO NRs on n-type silicon substrate. The growth parameters were set at optimized levels corresponding to base pressure of $1x10^{-6}$ mbar, sputtering gas (Argon) with constant flow of 60 sccm, target to substrate distance of ~14cm and substrate temperature at 600 °C. RF power, pressure and deposition time were kept at 150 W, $2x10^{-2}$ mbar, 2 hours 15 minutes, respectively. Circular Schottky contacts of gold were grown on ZnO NRs using thermal evaporation having diameter of 500µm, thickness of 200nm and a physical mask was used to keep spacing between two circular contacts of ~500µm. After fabrication, Au/ZnO NR/n-Si/Au nano-sensors were irradiated in air at room temperature using a ^{60}Co gamma irradiation source. Gamma irradiation chamber was irradiated at dose rate of 3 kGy/hr and sample irradiation with various gamma dose of 1 kGy, 2 kGy, 5 kGy and 10 kGy.

Effect of gamma irradiation doses on ZnO NRs were studied using structural characterization (XRD) and optical characterization with the help of photoluminescence spectra (PL). Morphology was investigated by means of Field-Emission Scanning Electron Microscope (FESEM). After irradiating Au/ZnO NR/n-Si/Au nano-sensors at different irradiation doses, hydrogen gas sensing was performed. Effect of gamma irradiation on Au/ZnO NRs based nanosensors response were studied in presence of 1% and 5% hydrogen in pure argon concentration. Change in resistance with respect to time was measured at operating temperature of 150 °C using two-probe semiconductor characterization system. Table 7.1 shows deposition, gamma irradiation and gas sensing parameters for Schottky contacted ZnO NRs based nanosenor.

Table 7.1: Deposition, gamma irradiation and gas sensing parameters for Schottky contacted ZnO NRs based nanosensor

Substrate	2 inch n-Si (100)
Sputtering target	ZnO (99.999% purity)
Base pressure	1×10^{-6} mbar
Deposition pressure	2×10^{-2} mbar
Deposition time	2.15 hour
RF power	150 W
Sputtering gas	Argon (60 sccm)
Substrate temperature	600 °C
Target to substrate distance	14 cm
Metallization technique	Thermal evaporation
Metal contact	Au (500 µm dia, 200nm thickness) Spacing between two metal contact~500 µm
Gamma irradiation source	^{60}Co source
Irradiation chamber temperature	RT
Gamma irradiation doses rate	3 kGy/hr
Sensor's gamma irradiation doses	1 kGy/hr, 2 kGy/hr, 5 kGy/hr, 10 kGy/hr
Gas sensor operating temperature	150 °C
Hydrogen concentration	1% and 5% (in pure argon)

7.3 EFFECTS OF GAMMA IRRADIATION ON SURFACE MORPHOLOGY

FESEM was used to examine surface morphology of un-irradiated ZnO NRs. Figure 7.1 (a) and (b) shows cross-sectional and top views FESEM images of un-irradiated ZnO NRs, respectively. FESEM images clearly demonstrates growth of well-aligned ZnO NRs on Si (100) substrate with an average height and diameter of 850 nm and 80 nm, respectively as earlier discussed in chapters 4 & 6.

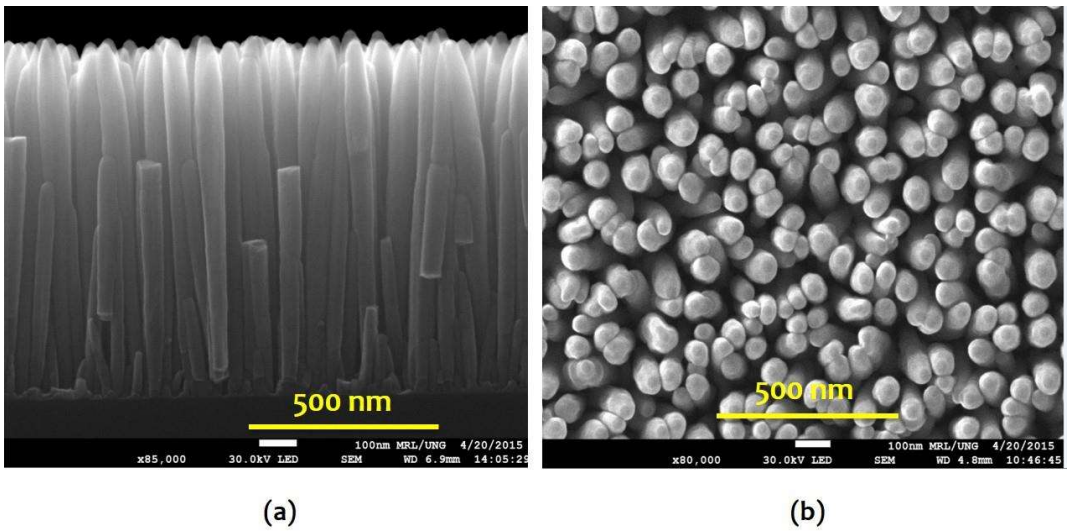
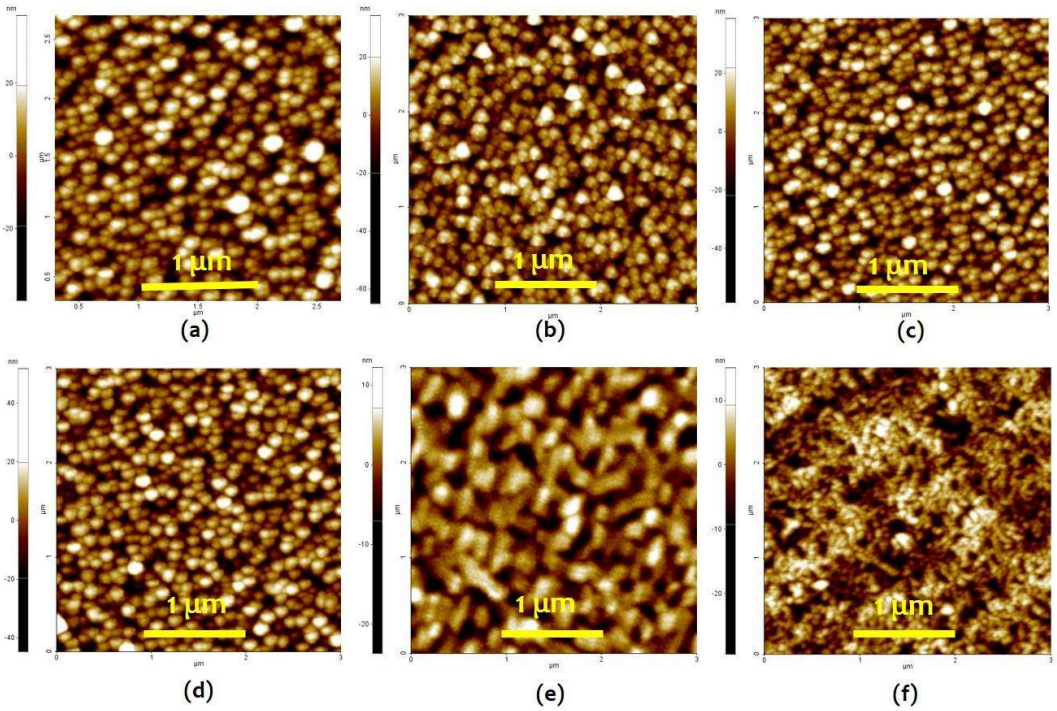


Figure 7.1: (a) Cross sectional view, (b) Top view of FESEM images of un-irradiated ZnO NRs



Figures 7.2: 2D AFM Images of (a) Un-irradiated and gamma-irradiated ZnO NRs with irradiation doses of (b) 1 kGy, (c) 2 kGy, (d) 5 kGy, (e) 8 kGy and (f) 10 kGy, respectively

The effect of gamma irradiation on surface morphology was also studied with the help of atomic force microscopy (AFM) images. Figures 7.2 (a), (b), (c), (d), (e) and (f) shows 2D AFM images of un-irradiated and gamma-irradiated ZnO NRs at irradiation doses of 1 kGy, 2 kGy, 5 kGy, 8 kGy and 10 kGy, respectively. The pristine ZnO NR 2D images show uniform distribution of ZnO NRs throughout the substrate as earlier confirmed in FESEM images. At low gamma doses up to 5 kGy, there is negligible change in surface morphology. As gamma doses increases

up to 8 kGy and 10 kGy, ZnO NRs gets distorted and coalesce due to generation of local heating during gamma irradiation. At 10 kGy gamma doses, ZnO NRs gets entirely merged into each other.

7.4 EFFECTS OF GAMMA IRRADIATION ON STRUCTURAL PROPERTIES

Effect of gamma irradiation on structural properties of ZnO NRs were studied. Crystal structure before and after exposure to gamma irradiation doses ranging from 1 kGy to 10 kGy were characterized by x-ray diffraction. Figures 7.3 (a), (b), (c), (d) and (e) shows X-ray diffraction (XRD) patterns of un-irradiated and gamma-irradiated ZnO NRs with irradiation doses of 1 kGy, 2 kGy, 5 kGy, and 10 kGy, respectively. XRD spectra depicts single peak of (0002) at 34.64°, which confirms the growth of a hexagonal wurtzite structure of ZnO NRs along c-axis [Campo *et al.*, 2016]. Comparative studies of XRD spectra after exposure to low doses of gamma irradiation varying from 1 kGy to 5 kGy show no significant change in crystal structure. After exposure to high gamma irradiation doses of 10 kGy, XRD spectra showed decreased (0002) peak intensity along with the presence of a few extra peaks of ZnO such as $(10\bar{1}0)$, $(10\bar{1}1)$ and $(10\bar{1}2)$, which validated polycrystalline nature of ZnO NRs [Guerguerian *et al.*, 2012]. Due to high dose rate of gamma irradiation, displacement damages along with many defect states and centres were produced, which may degrade ZnO NR's crystallinity.

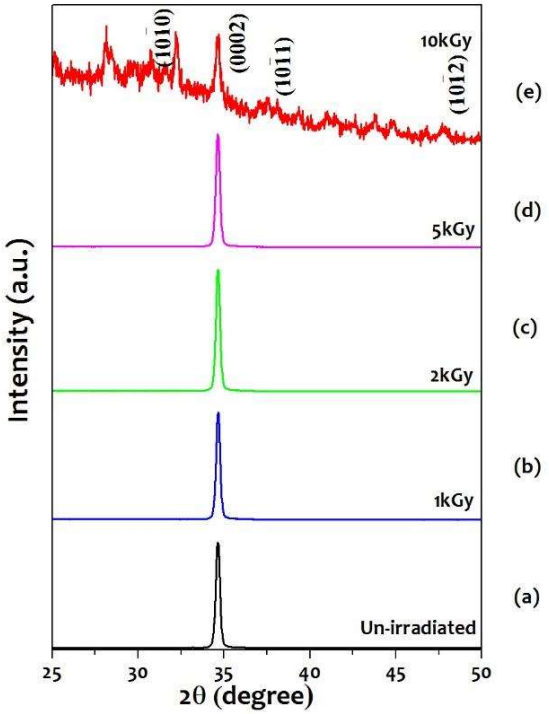


Figure 7.3: (a), (b), (c), (d) and (e) X-Ray diffraction (XRD) patterns of un-irradiated and gamma-irradiated ZnO NRs with irradiation doses of 1 kGy, 2 kGy, 5 kGy, and 10 kGy, respectively

7.5 EFFECTS OF GAMMA IRRADIATION ON OPTICAL PROPERTIES

Gamma irradiation also induced structural and intrinsic defects into crystal structural. Optical characterization was carried out using PL spectroscopy. Room temperature PL spectra of ZnO NRs is shown in Figure 7.4 for un-irradiated and irradiated ZnO NRs with a 10 kGy gamma irradiation dose. Un-irradiated ZnO NRs PL spectra showed a sharp peak around 376 nm, identified as a near-band emission (NBE) transition. PL spectra with missing broadband emission regions confirmed that there were no structural defects in the growth of ZnO NRs [Chen *et al.*, 2013]. After irradiation with a 10 kGy gamma irradiation dose, the NBE peak got suppressed and a strong peak was observed at 425 nm. The presence of structural defects such as zinc interstitials

(Zni), caused deep-level emission and lead to recombination of photo-generated electrons and holes. A green emission region was observed in the range from 400 nm to 600 nm, assigned to double-ionized zinc vacancies (Vzn) with a deep level of defects (528 nm–543 nm) such as antisite oxygen (Ozn) or oxygen interstitial (Oi) [Biriju *et al.*, 2014].

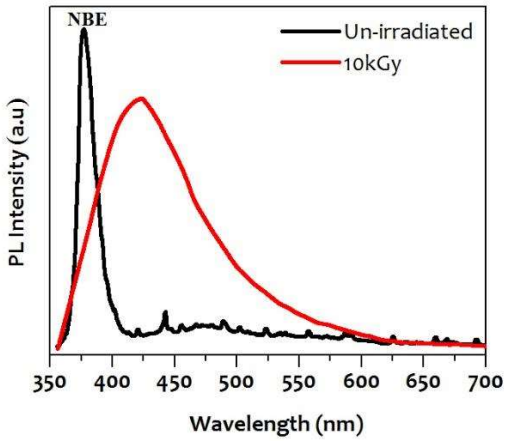


Figure 7.4: Room temperature PL spectra of un-irradiated and gamma irradiated ZnO NRs with 10 kGy dose

7.6 EFFECTS OF GAMMA IRRADIATION ON HYDROGEN GAS SENSING PROPERTIES

The effect of gamma irradiation on Au/ZnO NRs/Si/ ZnO NRs/Au heterojunction-based nano-sensors with respect to un-irradiated devices at 150 °C for 1% hydrogen and 5% hydrogen in pure argon concentration was studied. Figures 7.5 (a) and (b) shows a resistive response curve of the gas sensor with time for un-irradiated and irradiated ZnO NRs based sensor at gamma irradiation doses ranging from 1 kGy to 10 kGy at a moderate operating temperature of 150 °C for 1% and 5% hydrogen concentration in argon, respectively.

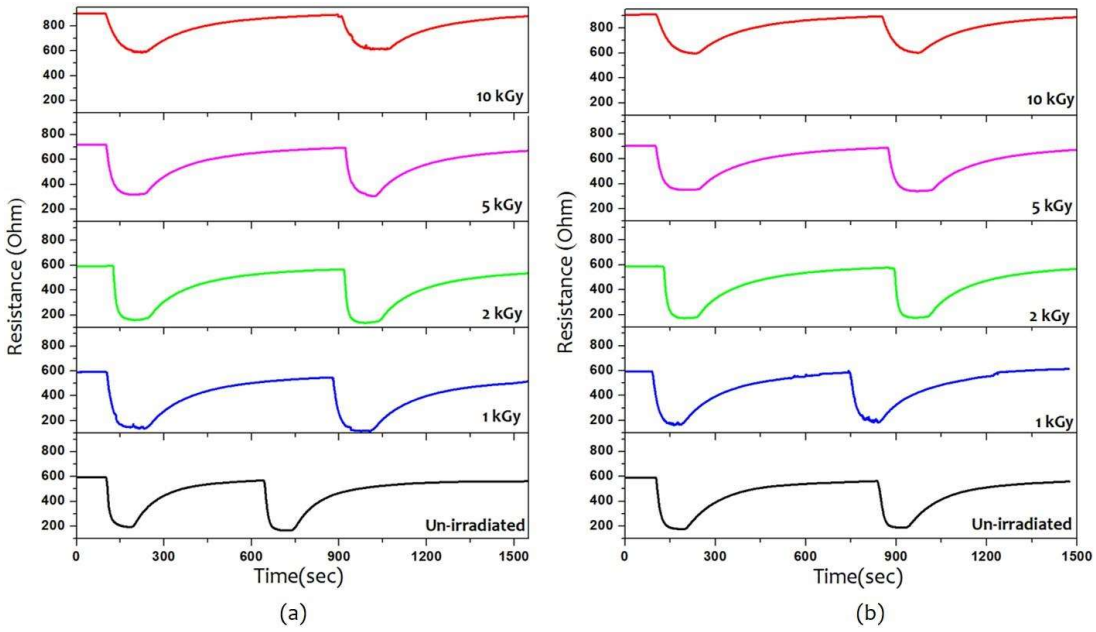


Figure 7.5: Resistive response curve of un-irradiated and gamma irradiated ZnO NRs based sensors with irradiation doses of 1 kGy, 2 kGy, 5 kGy and 10 kGy at 150 °C operating temperature: (a) 1% and (b) 5% hydrogen concentration in pure argon

It was observed that at 150 °C, the ZnO NR-based hydrogen sensor endures significant change in resistance during loading/deloading of hydrogen in sensing chamber. At moderate operating temperatures, ZnO NRs with Schottky contact gave a high rate of adsorption/desorption of reactive gases. Gamma irradiation with various dose rates also significantly affects the resistive response. When a nanosensor was irradiated with gamma irradiation with low doses ranging from 1 kGy to 2 kGy, the resistive response curve showed huge change in resistance while loading/deloading of 1% and 5% hydrogen concentration. Gamma irradiation created some charge centres and defects on the surface and in the bulk of the NRs through ionization process, which caused more adsorption of environmental oxygen on the ZnO NR's surface and created adsorbed oxygen ions (O^-, O_2^-, O^{2-}). So, the loading of hydrogen decreased the depletion region largely with respect to the un-irradiated ZnO NR based sensor. At low doses, surface defects played an important role and increased the sensitivity. At higher doses of gamma irradiation (5 kGy, 10 kGy), bulk defect density was observed due to which, the base resistance was increased. Thus, at higher doses, the resistive response curve decreased and a huge increase in response/recovery time in comparison to the unirradiated ZnO NR-based hydrogen sensor for both hydrogen concentrations (1% and 5%) was measured. Data in figures 7.5 (a, b) also shows that the base resistance increases with high gamma irradiation doses changing from 5 kGy to 10 kGy. This can be explained by the formation of a larger number of permanent displacement damage defects in the ZnO NRs and saturation of adsorbed oxygen ions on ZnO NRs, which increases the depletion region and shows less change in resistance during loading/deloading of hydrogen. When incident gamma particles interact with target material, they displace atoms in the crystal structure that acts as a scattering centre and decreases carrier mobility [Srour *et al.*, 2003].

Response and recovery time for the sensor's relative response defines sensors performance. Exponential fitting of the response and recovery cycle for the resistive response curve gives the response and recovery time for the sensor. Figure 7.6 (a) and (b) shows response and recovery time with various gamma irradiation doses ranging from 0 kGy to 10 kGy at 150 °C for 1% and 5% hydrogen concentrations, respectively. At a low dose range varying from 1 kGy to 2 kGy, response time falls within ~10–18 s, similar to un-irradiated NRs and recovery time varies in the range of 116–168 s, which is higher in comparison to the un-irradiated ZnO NR-based nanosensor, for both 1% and 5% hydrogen concentration. At high gamma irradiation doses up to 10 kGy, the response time increases up to ~56 s and ~39 s for 1% and 5% hydrogen concentrations, respectively. Huge increase in response and recovery time at high doses of gamma irradiation in comparison to the un-irradiated nanosensor are due to the degraded crystal structure and the presence of more permanent displacement damage defects in the crystal. These structural defects slow down response and recovery time of the sensor.

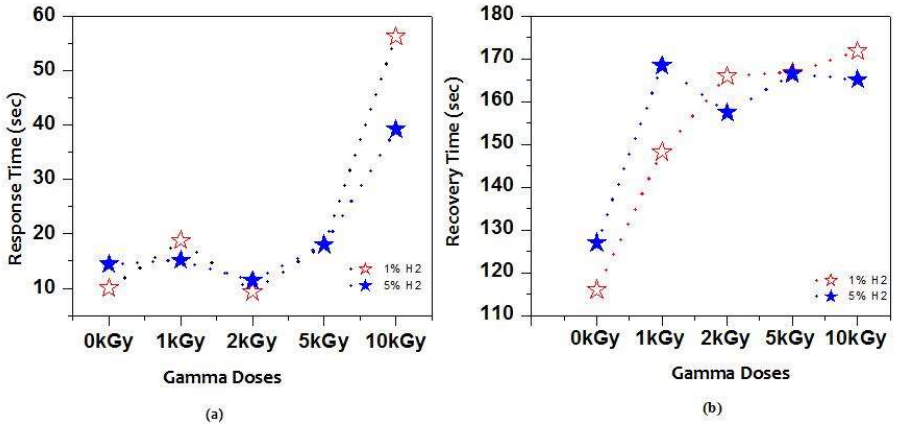


Figure 7.6: (a) Response time and (b) Recovery time for un-irradiated and gamma irradiated ZnO NRs based sensors with irradiation doses of 1 kGy, 2 kGy, 5 kGy and 10 kGy at 150 °C operating temperature at H_2 concentrations of 1% and 5%.

The relative response of the gas sensor is defined as relative change in resistance with respect to base resistance (resistance in the presence of air). Figures 7.7 (a) and (b) shows relative response curve with respect to gamma irradiation doses at 150 °C for 1% and 5% hydrogen concentrations, respectively. It is observed that when we increase gamma irradiation doses up to 1 kGy, the relative response increases approximately ~14.9% and 11.4% with respect to pristine ZnO for 1% and 5% hydrogen concentration, respectively. At higher gamma irradiation doses of 5 kGy and 10 kGy, the sensor's relative response is degraded from 77% and 74% to 33.5% and 34% for 1% and 5% hydrogen concentrations, respectively.

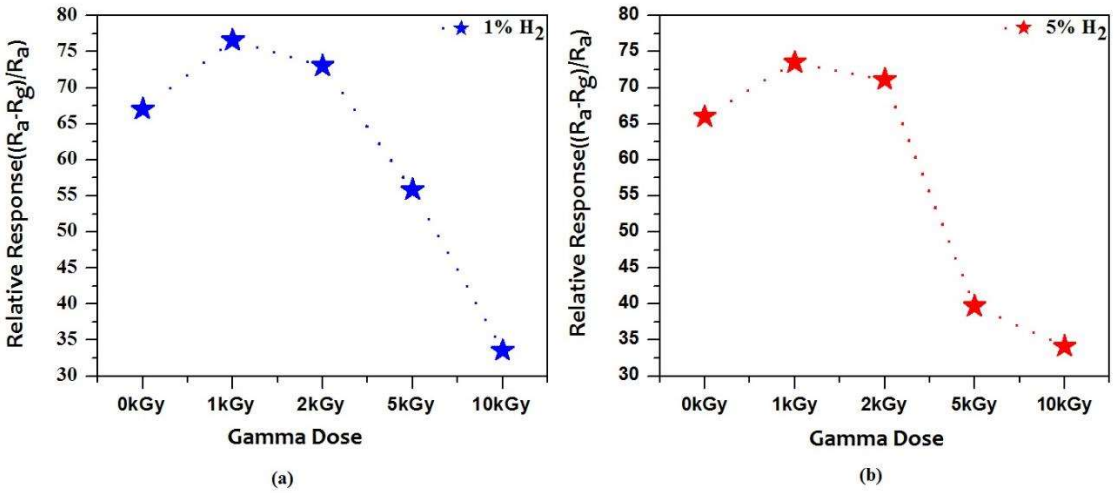


Figure 7.7: Relative response of ZnO NRs based hydrogen sensor as a function of un-irradiated and gamma irradiated for various irradiation doses for: (a) 1% and (b) 5% H_2 concentration

7.7 PROPOSED GAS SENSING MECHANISM

Gas sensing mechanism have been proposed to study effect of gamma irradiation on hydrogen gas sensing of Schottky contacted ZnO NRs based nanosensors. Figure 7.8 (a) and (b) show basic gas-sensing mechanism where, when ZnO NRs come into contact with atmospheric oxygen at moderate operating temperatures, absorbed oxygen extracts electrons from conduction band and creates oxygen ions (O^-, O_2^-, O^{2-}) on the NR surface. Absorbed oxygen ions create a depletion region which increases nanorod's resistance. During hydrogen loading, these oxygen ions react with hydrogen and increases electron concentration in the conduction band. This chemisorbed reaction leads to the reduction in the depletion region in ZnO NRs and, henceforth, NR resistance decreases. At a constant operating temperature, the sensor's sensing parameters such as relative response and response/recovery time can be tailored by using gamma irradiation. Figure 7.8 (c) and (d) show schematics of relative change in the gas-sensing mechanism in presence of low and high gamma irradiation doses. When ZnO NRs are irradiated with a 1 kGy gamma irradiation dose, ionization process creates some charge centres and defects on the ZnO NR surfaces. These generated electrons then attracts more oxygen, thus, increasing absorbed oxygen ions on the ZnO NR surfaces. When oxygen ions react with hydrogen, the depletion region is decreased to a larger extent, while the relative response of the gas sensor increases with respect to un-irradiated ZnO NRs. At the highest gamma irradiation dose of 10 kGy, displacement damage defects in ZnO NRs like isolated vacancies interstitials and atom displacement in crystal structure are generated, which expands the depletion region. Although, at this point, the ionization process saturates the absorbed oxygen ion to its maximum value, this saturation process does not decrease the depletion region to the extent to which low-dose irradiated ZnO NRs do. At high irradiation doses, the crystal structure also degrades which, in

turn, decreases the sensor response. Thus, the results suggests that ZnO NR-based sensor's response can be enhanced in the presence of low gamma dose rates and can be used as an excellent hydrogen sensor application that detects hydrogen of concentrations as low as 1% and 5%.

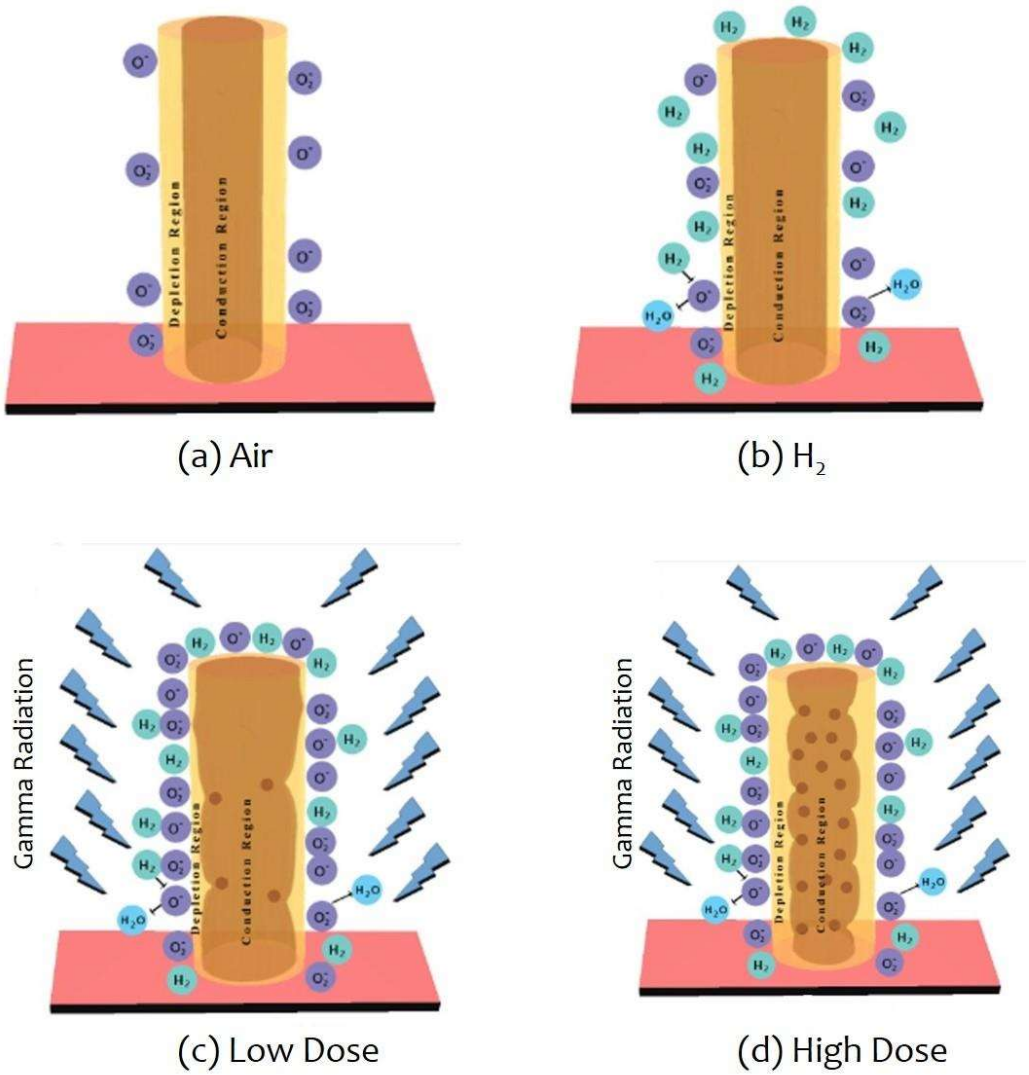


Figure 7.8: Schematic diagram of hydrogen gas sensing mechanism of un-irradiated ZnO NRs: (a) In air, (b) In hydrogen, (c) Effect of low gamma dose and (d) Effect of high gamma dose

7.8 CONCLUSION

Throughout in this chapter, the effect of gamma irradiation on the hydrogen gas-sensing characterization of a ZnO NR-based sensor was explained. Un-irradiated ZnO NRs showed single crystalline and defect-free c-oriented growth of NRs, which was confirmed using structural (XRD) and optical properties (PL) characterization. As gamma irradiation doses were increased up to 10 kGy, ZnO NRs became polycrystalline from a single crystalline structure and confirmation was made by x-ray diffraction spectra. High gamma doses suppressed NBE peak and created structural defects and atomic displacement damages in the crystal structure, which was confirmed by the presence of a wide-band emission region (defects) in the PL spectra. The relative response of the gas sensor was highly affected by gamma irradiation doses. At a low gamma dose of 1 kGy, the relative response of the ZnO NR-based sensor increased from 67% to 77% and 66% to 73.5% for 1% and 5% hydrogen concentrations, respectively. With low gamma doses at 150 °C operating temperature, sensors showed fast response time of ~15–18.75 seconds.

As the gamma dose was increased up to 10 kGy, the sensor's relative response decreased to ~34%. An increase in baseline resistance was observed for both hydrogen concentrations due to degraded crystallinity and occurrence of structure defects in ZnO NRs. This proves that the gamma irradiation with low dose rates can significantly improve ZnO NRs based hydrogen sensor's sensitivity without changing operating temperature and hydrogen concentration.

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