Fabrication of n-ZnO/p-Si++ Hetero-junction Devices for Hydrogen Detection: Effect of Annealing Temperature

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Abstract
In the present study, we report the fabrication of n-ZnO/p-Si++ hetero-junction devices for the detection of hydrogen leakage in ambient air environment. For the fabrication of n-ZnO/p-Si++ hetero-junction devices, high quality ZnO thin films are grown by controlled thermal evaporation technique on the highly doped p-type silicon substrates at 400 °C. The two sets of films deposited at 400 °C are further annealed at 500 and 600 °C to examine the effect of annealing temperature on the structural, morphological, electrical and gas sensing properties of the deposited films. It is revealed from the x-ray diffraction studies that the crystallite size, and the density of the films increase from 22.55 to 24.95 nm, and from 5.65 to 5.68 g/cm³, respectively, on increasing the fabrication temperature from 400 to 600 °C. In contrast to this, the grain boundary specific surface area decreases from 8.79 × 10⁷ to 7.88 × 10⁷ m⁻¹ on changing the fabrication temperature from 400 to 600 °C. The hydrogen gas sensing responses of the fabricated devices have also been recorded at different operating temperatures and different hydrogen concentrations (200 to 1000 ppm) in air ambient. It is found that the gas sensing responses of the fabricated devices increase with increase in operating temperature up to 100 °C and decease beyond this temperature. The gas sensing responses of the devices fabricated at 400, 500 and 600 °C are found to be 97.22, 64.23 and 40.77 % respectively at 1000 ppm of hydrogen. A decrease in gas sensing response with fabrication temperature is attributed to the increase in crystallite size (quantum size effect), density of film (i.e. lower penetration) and decrease in grain boundary specific surface area (i.e. active sites) with annealing temperature. The mechanism of the gas sensing in these devices has also been systematically analyzed under different models.

Keywords ZnO thin films · Hydrogen sensing · Freundlich’s isotherm · Hetero-junctions

1 Introduction
Hetero-junction devices always remain the center of attention for their eclectic range of applicability in rectifying diodes, lasing devices, photodetectors, light emitting diodes and transistors, etc. [1–5]. However, for a longer time, these optoelectronic devices remained dependent on a costly and sophisticated silicon based technology. In contrast to this, in recent years, metal oxide based hetero-junction devices received significant attention because of their low cost, easy and eco-friendly fabrication technologies [3–7]. Apart from the optoelectronic applications of the metal oxide based hetero-junctions, the gas sensing devices have also shown augmented device performances towards many hazardous gases [6, 7]. This includes the detection of H₂S, chloroform, ammonia, CO₂, NO₂, NH₃ and the most vulnerable hydrogen gas [7, 8]. However, hydrogen finds diverse range of utility in health sectors, nuclear power plants, and as a highly clean and sustainable renewable source of energy for automobile industries and space exploration, etc. [9, 10]. In spite of these sundry applications, hydrogen is the most vulnerable gas for human being because of its colorlessness, odorlessness, highly inflammable and explosive nature [11]. Thus, to avoid any serious accident, the continuous monitoring of hydrogen at low ppm levels is essential. Researchers are continuously exploring for highly sensitive, stable and robust sensing elements to trace out the leakage of hydrogen in working environment. A variety of metal oxide based semiconductors are widely studied for the detection of wide range of gases. Out of these metal
oxide semiconductors, zinc oxide (ZnO) is an intrinsically n-type semiconductor, which was first time used by Seiyama et al. [12] for the detection of flammable gases in thin film form. Henceforth, ZnO thin films were utilized for the detection of variety of gases by numerous researchers in different modular forms such as MOS capacitors, Schottky diodes, MOSFETs, simple resistors, etc. [13, 14]. Ominously, the pristine ZnO thin films have poor hydrogen detection ability. These films generally have higher operating temperature and low sensitivity and selectivity for hydrogen. Therefore, different device fabrication strategies and methods have been employed to enhance the sensing ability of ZnO for hydrogen gas. This includes the decoration of ZnO by noble metals like platinum (Pt), palladium (Pd), etc., doping and formation of nanocomposites of ZnO with different metal oxide and post deposition treatments, [11, 14], etc. The hetero-junction device based on metal oxide (particularly ZnO) is one of such choices that can be employed for enhancing the device performance. It is reported that fabrication of metal oxide based hetero-junction device decreases the possibility of electron-hole recombination by altering the charge transfer process and electronic structure of the device, and thus, improved the gas sensing performance [15-17]. Therefore, in the present study, the hetero-junctions of n-ZnO/p-Si are fabricated by thermal evaporation technique at 400 °C. The post-deposition heat treatment has also been done at 500 and 600 °C to investigate the effect of annealing temperatures on the sensing ability of the fabricated devices towards hydrogen gas. The effect of annealing temperature on the structural and morphological properties has also been investigated.

2 Experimental Details

2.1 Growth of n-ZnO Thin Films

The n-type ZnO (n-ZnO) thin films were grown by simple thermal evaporation technique on the heavily doped p-type silicon substrates at a substrate temperature of 400 °C. For the deposition of high quality n-ZnO thin films, the high purity (99.99 %) ZnO dust was thermally evaporated under constant vacuum condition (3.2 × 10^{-3} mbar) maintained through a continuous flow of well-prepared mixture of argon (80 %) and oxygen (20 %). Before the deposition of n-ZnO thin films, a base vacuum of ~2.1 × 10^{-5} mbar was achieved in the deposition chamber with the help of diffusion and rotary pumps. The precursor material (ZnO powder) was placed in a molybdenum boat, which was maintained at a distance of 12 cm from the substrate holder. The substrates were heated to a temperature of 400 °C using a substrate heater attached with the substrate holder. The ZnO powder was slowly evaporated by passing a low current and the thickness of the films was constantly supervised using the thickness monitor fixed with sample holder. After achieving the thickness of ~250 nm, evaporation process was stopped and the films were left to cool naturally inside the deposition system and taken out next day. The deposition of n-ZnO thin films on p-Si++ substrates result into the fabrication of n-ZnO/p-Si++ hetero-junction devices. Out of several deposited samples, two sets of thin films were further annealed at 500 and 600 °C to examine the effect of heat treatment on the properties of the deposited thin films. These three sets of n-ZnO/p-Si++ thin films were designated as n-ZnO/p-Si++ at 400 °C, n-ZnO/p-Si++ at 500 °C, and n-ZnO/p-Si++ at 600 °C, respectively.

2.2 Characterization of Deposited Thin Films

The structural and phase analysis of the deposited thin films was carried out using x-ray diffractometer (D8 discover), ASX-Bruker made. The surface examination was done using high resolution field emission scanning electron microscopy, Gemini-500, Zeiss, Germany. The conduction behavior of the charge carrier in air and hydrogen (H₂) ambients was examined using Keithley’s 2410 source measure unit. The current-voltage (I-V) characteristics of all three sets of films were recorded in gridded sandwich structure Pt/n-ZnO/p-Si++/Pt. The Pt electrodes of ~50 nm were deposited on both sides of the hetero-junction devices using the thermal evaporation technique. The room temperature I-V measurements were performed in ambient air and hydrogen environments. The schematic diagram of the gridded structure of the Pt-electrodes and different layers of fabricated p-n heterojunction are shown in Fig. 1. The transient hydrogen gas sensing measurements on all three sets of hetero-junction devices were performed at 100 °C at different concentrations (200, 400, 600, 800 and 1000 ppm) of hydrogen gas using Keithley’s 2410 source measure unit.

Fig. 1 Schematic representation of the fabricated heterojunction gas sensing device.
3 Results and Discussion

3.1 Structural and Morphological Studies

Figure 2(a) shows the XRD patterns of the ZnO thin films consist of various sharp reflections located at 31.73, 34.44, 36.24, 47.51, 56.56, 62.79, and 67.99°, which are related with the polycrystalline (hkl) planes (100), (002), (101), (102), (110), (103) and (112), respectively [2, 18, 19]. These peak positions related with different (hkl) planes are well corroborated with JCPDS Card No. 36-1451 corresponding to the hexagonal wurtzite structure of ZnO [15–17]. All these peaks are purely associated with the high quality ZnO and thus, negate the possibility of any impurity present in the deposited films. The n-ZnO thin film deposited at 400 °C has been further annealed at 500 and 600 °C to investigate the effect of heat treatment on the structural and other properties of the deposited film. The structural change in the deposited film can be examined in terms of various structural parameters like crystallite size (λ), lattice parameters ‘a’ and ‘c’, stress and strain, volume of the unit cell and density of the deposited films. Therefore, these structural parameters have been evaluated for all three sets of films. The well-known Debye-Scherrer’s formula [18–21] given below is used to determine the crystallite size,

\[ \Delta = \frac{0.91 \lambda}{\beta \cos \theta} \]  

(1)

Where, λ is the wavelength (~1.5406 Å) of CuKα source used for the irradiation of the films and, θ is the angular position of a particular plane used for the determination of crystallite size and β is the full width at half maximum of the corresponding peak of the plane measured in radians. The average crystallite sizes for n-ZnO thin films grown at 400, 500 and 600 °C are found to be ~ 22.55, 23.88 and 24.95 nm, respectively. It is observed that the crystallite size of the deposited film at 400 °C increases slightly with increase in annealing temperature to 500 and 600 °C. This is because of that the annealing temperature provides the necessary energy for crystallization and adjustment of atoms/molecules of the film for the formation long order crystal structure. The calculated average crystallite sizes for the deposited films are further used to examine the average defect densities in the films using the relation [18, 19]

\[ \delta = \frac{1}{\Delta^2} \]  

(2)

It is found that the average defect density for ZnO film deposited at 400 °C decreases from 1.97 × 10^{15} to 1.75 × 10^{15} and to 1.61 × 10^{15} m^{-2} with increase in annealed temperature to 500 and to 600 °C, respectively. The decrease in defect density with increase in annealing temperature suggests the increase in the quality of the deposited film with heat treatment. The observed values of the defect density for the present thin films are in the range of reported values for ZnO thin films [19, 20].

The inter-planer spacing (d) for the deposited films has been estimated by utilizing the well-known Bragg’s law

\[ 2d \sin \theta = n \lambda \]  

(3)

Where, symbols have their usual meanings. The obtained values of the d-spacing for the (hkl) plane (002) are found to be 2.605, 2.602, and 2.601 Å for the films heat treated at 400, 500 and 600 °C, respectively. A slight decrease in inter-planer spacing with increase in annealing temperature can be attributed to the re-arrangement/adjustment of atoms at higher temperature due to presence of sufficient energy for crystallization.

The obtained values of the d-spacing are further used to estimate lattice parameters ‘c’ and ‘a’ [22] using the relation

\[ \frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + h k + k^2}{a^2} \right) + \left( \frac{l^2}{c^2} \right) \]  

(4)

For the crystalline plane (002), the above Eq. (4) reduces into the relation

\[ c = \frac{\lambda}{\sin \theta} \]  

(5)

and the obtained values of ‘c’ parameter are found to be 5.210, 5.205 and 5.202 Å and the values of the parameter ‘a’ are found to be 3.256, 3.253 and 3.251 Å for the devices fabricated at 400, 500 and 600 °C, respectively. A small decrease in lattice parameter values is observed with annealing temperatures.

The obtained values of the lattice parameters ‘a’ and ‘c’ are further used to estimate the volume of the unit cell [22] using the relation

\[ V = \frac{\sqrt{3}}{2} a^2 c \]  

(6)

And the observed values of the unit cell volumes for different sets of films are presented in Table-1. The effect of annealing temperature on the lattice stress (S) and strain (ε) has also been examined for the deposited films [19–21] using the relations

\[ S = \frac{\lambda}{\Delta \sin \theta} - \frac{\beta \tan \theta}{\tan \theta} \]  

(7)

and

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  

(8)

The obtained values of lattice stress and micro-strain for the n-ZnO thin films obtained at different annealing temperature
are tabulated in Table 1. It is found that the values of both stress and strain decrease with increase in annealing temperature. The obtained values of these parameters are well matched with the reported values of the parameters for the deposited ZnO thin films [18–21].

The grain boundary specific surface area ($S_a$) and theoretical density ($D_T$) of deposited films are crucial parameters for the surface structure dependent applications like gas sensing, photodetectors, etc. Therefore, the effect of annealing temperature on these parameters has also been investigated. The grain boundary specific surface area ($S_a$) is estimated [20, 23] using the formula

$$S_a = \frac{1.65}{\Delta}$$

And the theoretical density is estimated [24] using the relation

$$D_T = \frac{2M}{NV} \text{ (g/cm}^3\text{)}$$

Where, $M$ is the molecular weight, $N$ is Avogadro’s number, and $V$ is the volume of the unit cell. The values of these parameters are presented in Table 1. It is found that the value of grain boundary specific surface area decreases, whereas, the density of the films increases with increase in annealing temperature.

Figure 2(b-d) shows SEM images of the deposited films at different temperatures. It can be seen from the SEM micrographs that the ZnO nanoparticles of size about 200 nm are

![Figure 2](image-url)
uniformly distributed throughout the film surface. However, it is found that the annealed films at 500 and 600 °C have relatively larger agglomeration of the nanoparticles with respect to the film deposited at 400 °C. The observed surface structures of thin films at higher temperature are obvious behavior. Such behavior is commonly observed due to fusion of nanoparticles at higher temperatures.

### 3.2 Conduction Behavior and Hydrogen Gas Sensing Properties

Figure 3(a-b) shows the current-voltage (I-V) characteristics of the n-ZnO/p-Si++ hetero-junction devices fabricated at different temperatures, recorded in air and hydrogen ambients. It is found that the current flowing through all three heterojunction devices is non-linear with applied bias voltage. The forward current flowing through the devices increases slowly at lower voltages, say up to ~0.7 V and then increases very rapidly beyond 0.7 V. However, the current flowing through all the devices in reverse bias condition is almost constant. Such behavior of the hetero-junction devices with applied bias can be attributed to the well-known diodic behavior [25]. It has also been observed that the current flowing through the n-ZnO/p-Si++ hetero-junction device fabricated at 400 °C is greater than the devices fabricated at 500 and 600 °C. Similar kinds of the behaviors of the fabricated hetero-junction devices with applied bias and annealing temperatures have also been observed in hydrogen ambient. However, a slight increase in current values of the devices is observed in hydrogen environment with respect to air ambient. For example, the current values increase from 0.503 mA to 0.879 mA and from 0.131 mA to 0.176 mA at a bias voltage of 1.5 V in the heterojunction devices fabricated at 400 and 500 °C, respectively, on changing the environment air to hydrogen. However, a relative change in current values (I_H2/I_a = 1.352) of the heterojunction device fabricated at 500 °C is lower than the device fabricated at 400 °C (I_H2/I_a = 1.748) at room temperature. These values of currents correspond to the percentage sensitivities of 74.93 and 34.18 % towards hydrogen gas at room temperature for the devices fabricated at 400 and 500 °C, respectively i.e. the fabricated devices exhibit significant sensitivity towards hydrogen gas even at room temperature. Thus, to investigate the gas sensing behavior of the fabricated devices, the current flowing through the devices at different temperatures in air and hydrogen ambients has been recorded. The obtained values of current in hydrogen and air are used to calculate the temperature dependent sensitivity/response of the fabricated devices using the relation

\[
\text{Response(\%)} = \frac{I_{\text{H}_2} - I_a}{I_a} \times 100
\]  

Where, \( I_{\text{H}_2} \) and \( I_a \) are the current values of the device in hydrogen and air environments.

Figure 4a shows the temperature dependent sensing response (%) for the hetero-junction device fabricated at 500 °C. It is observed that the sensitivity of the fabricated device increases with increase in operating temperature up to 100 °C and decrease beyond this temperature, which is an obvious behavior of the metal oxides. Such temperature dependent behavior of metal oxides can be understood through three physical/chemical processes generally takes place at different temperature. At lower temperatures near room temperature, the physisorption of oxygen molecules takes place on the film surface [11, 26] that can be understood by the processes

\[
\begin{align*}
\text{O}_2(\text{molecule}) & \rightarrow \text{O}_2(\text{ads. at film Surf.}) \quad (i) \\
\text{O}_2(\text{ads at film Surf.}) + e^- (\text{pull}) & \rightarrow \text{O}^2_2(\text{ads at lower temp.}) \quad (ii)
\end{align*}
\]

This process of adsorption of oxygen (O_2) molecules on the film surface and dragging out of electron from film surface to form oxygen ions (O^2_2), results into the generation of a lower conductive region on the film surface called the depletion layer. Larger be the adsorption of oxygen molecules, more will be the length of depletion layer and lower be the electrical conductivity of the deposited film in air ambient. The surface adsorbed oxygen ions interact with hydrogen gas molecules in hydrogen ambient. The electrons are returned back to the
conduction band that results into the decrease in depletion layer thickness and increase in electric current in hydrogen environment. This caused in an increase in sensing response of the fabricated devices. This process can be understood [9, 11, 26] by the relation

\[
\text{H}_2 + \text{O}_2^- (\text{ads at ZnO Surf.}) 
\rightarrow \text{H}_2\text{O} (\text{ejected as vapor}) 
\rightarrow + 2e^- (\text{returned back to C.B.})
\]

The length of depletion layer \(L_D\) depends upon the temperature, which can be given by the relation [27, 28]

\[
L_D = \sqrt{\frac{\varepsilon_0 kT}{ne^2}}
\]

Where, \(n\) is the number of the charge carriers, \(\varepsilon_0\) is the static dielectric constant and other parameters have their usual meanings. At further higher temperature, the physisorbed oxygen ions (\(\text{O}_2^-\)) chemically react to each other to form chemisorbed oxygen ions (say \(\text{O}_2^2^-\) or \(2\text{O}^-\)) at film surface. Such processes can be given by [6, 11, 29, 30]

\[
\text{O}_2 (\text{ads at ZnO Surf.}) + 2e^- (\text{pull}) 
\rightarrow 2\text{O}^- (\text{ads in mid-temp. range})
\]

\[
\text{O}_2 (\text{ads at ZnO Surf.}) + 4e^- (\text{pull}) 
\rightarrow 2\text{O}^2^- (\text{ads at higher temp.})
\]  

In this temperature range, the depletion width has the maximum value. i.e. in this temperature range, there are maximum number of active sites or oxygen ions for compensation by the analyte gas (\(\text{H}_2\)) molecules. And the process of compensation [10, 26, 31] can be rewritten as

\[
\text{H}_2 + 2\text{O}^- (\text{ads.in mid.temp.range}) 
\rightarrow \text{H}_2\text{O} (\text{vapor}) + 2e^- (\text{returned back to C.B.})
\]

The fabricated devices having maximum sensitivity in this temperature range (around 100 °C in present case). Beyond a specifically higher operating temperature (>100 °C), the fabricated devices or ZnO films show well-known semiconducting behavior in which thickness of the depletion layer decreases due to increase in charge carrier concentration. And thus, the sensitivity of the fabricated devices decreases beyond a particular temperature.

To investigate the effect of hydrogen concentrations on the sensing response of the fabricated devices, the change in electric current has been recorded at different concentrations of hydrogen, ranging from 200 to 1000 ppm at an operating temperature of 100 °C. Figure 4(b-d) shows the transient sensing response of the fabricated hetero-junction devices at 200, 400, 600, 800 and 1000 ppm of hydrogen. It is found that the
sensing responses of the fabricated devices increase with increase of hydrogen concentrations. However, the sensing response of the fabricated devices decreases with increase in annealing temperature. i.e. the observed sensing response of ~97.22 % for the device fabricated at 400 °C decreases to 64.23 % for the device fabricated at 500 °C and finally to ~40.77 % for the device fabricated at 600 °C at 1000 ppm of hydrogen gas. The observed sensing responses of the fabricated devices are of the order or better than the reported values of sensing response [32–38]. The comparative values for the sensing responses are presented in Table 2. The cyclic response of all three devices at five different concentration of hydrogen suggests the cyclic stability and repeatability of the fabricated devices.

The transient gas sensing responses of the fabricated devices can be understood by adsorption kinetic of the gas molecules on the surface of the sensing device. One of such adsorption kinematics was introduced by the Langmuir based upon the homogeneity of the surface. Some basic assumptions of this theory are that (i) the adsorbing surface should be homogeneous, (ii) the adsorbing surface contains some specific number of actives sites, which are available for adsorption, and each site can accommodate only one gas molecule. As soon as a site is occupied by the analyte gas (i.e. if one monolayer complete), no further adsorption takes place [39, 40] on that site. This assumption corresponds to the saturation of gas sensing response with time, and (iii) all the sites are equivalent and independent i.e. the presence of other molecules do not affect the occupancy (energy of adsorption) of newly arriving molecule. However, this theory of the homogeneous surface was later modified by Freundlich for the heterogeneous surfaces and semiconducting materials [39–41]. Since, the surface morphology/structure of the deposited films strongly dependent on the deposition techniques and process conditions i.e. temperature and pressure, etc. Thus, the discontinuity and heterogeneity of the film surface is obvious, which results into the non-uniform adsorption of the analyte gas molecules.

Therefore, the transient gas sensing response of the present devices can be determined by the modified Freundlich adsorption isotherm for the non-uniform adsorption of hydrogen molecules and/or desorption of oxygen molecules in hydrogen environment. Thus, the rise in sensing responses of the fabricated devices in hydrogen environment with time can be fitted with modified Freundlich relation for the desorption of oxygen molecules or adsorption of hydrogen molecules [39, 40] given by

\[
R = R_{a1} \left(1 - e^{-1/\tau_{a1}} \right) + R_{a2} \left(1 - e^{-1/\tau_{a2}} \right)
\]

Where, \(R_{a1}\) and \(R_{a2}\) are the pre-exponential factors of the rising of sensing response, and \(\tau_{a1}\) and \(\tau_{a2}\) are the time constants for sensing response.

Whereas, on the removal of hydrogen gas molecules from the sensing cavity, the adsorption of the oxygen molecules starts and the sensing device approaches to its original state. The current flowing through the device falls during the desorption of hydrogen gas molecules or adsorption of oxygen molecules and corresponding decrease in sensing response is recorded. Thus, the transient decay of sensing response is fitted with the modified Freundlich’s equation for the desorption of hydrogen molecules or adsorption of oxygen molecules given by [39, 40]

\[
R = R_{d1} \left(e^{-t/\tau_{d1}} \right) + R_{d2} \left(e^{-t/\tau_{d2}} \right)
\]

### Table 2
Comparative sensing responses of the fabricated devices

| S. No. | Device structure | \(H_2\) Conc. (ppm) | Response (%) | Operating temperature (°C) | Ref. |
|-------|------------------|----------------------|--------------|-----------------------------|-----|
| 1     | rGO/ZnO Hetero-junction | 500 | 96% | ----- | [6] |
| 2     | MXene/SnO₂ Hetero-junction | 50 | 40% | ----- | [7] |
| 3     | n-ZnO/p-NiO Hetero-junction | 100 | 53% | 237 | [32] |
| 4     | Au/ZnO Schottky | 1000 (~1 %) | 48% | 210 | [33] |
| 5     | ZnO@SnO₂ Resistive | 500 | 70% | 400 | [34] |
| 6     | ZnO-SnO₂ Resistive | 1000 | 45% | 200 | [35] |
| 7     | ZnO Resistive | 1000 | 43% | 150 | [36] |
| 8     | Ni-ZnO-rGO | 100 | 63.8% | 150 | [37] |
| 9     | ZnO resistive | 150 | 6 | 400 | [38] |
| 10 | n-ZnO/p-Si Hetero-junction | 1000 | 97% | 100 | [This work] |

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Where, $R_{d1}$ and $R_{d2}$ are the pre-exponential factors for decaying sensing response. $\tau_{d1}$ and $\tau_{d2}$ are the time constants for decaying sensing response.

The transient rising and decaying sensing responses of the fabricated devices are fitted with Eqs. (13) and (14), respectively. And the fitting parameters for the rise and decay in sensing responses are presented in Tables 3 and 4, respectively. It is found that the Eqs. (13) and (14) very well fit the response and recovery parts of the transient sensing behaviors of all the fabricated devices.

The transient sensing response curves have also been used to calculate the response ($\tau_{res}$) and recovery ($\tau_{rec}$) times for different cycles recorded at different hydrogen concentrations as shown in Fig. 4(b-d). It is found that the response and recovery times increase with increase in hydrogen concentration as well as fabrication temperature. The values of response time increase from 84 to 159 s, 126 to 228 s and 144 to 225 s on changing the hydrogen concentration from 200 to 1000 ppm for the devices fabricated at 400, 500 and 600 °C, respectively. Similarly, the values of recovery time increase from 51 to 93 s, 85 to 111 s and 88 to 135 s on changing the hydrogen concentration from 200 to 1000 ppm for the devices fabricated at 400, 500 and 600 °C, respectively. The lower value of recovery times as compared to response times for all the fabricated devices discards the possibility of strong chemical reaction (or absorption) of hydrogen gas molecules.

### Table 3
Freundlich’s fitting parameters for the adsorption of hydrogen molecules for the fabricated hetero-junction devices

| Sample Name          | H$_2$ (ppm) | 200   | 400   | 600   | 800   | 1000  |
|----------------------|-------------|-------|-------|-------|-------|-------|
| n-ZnO/p-Si at 400°C  | $R_{a1}$    | -15415.39 | -72680.49 | -16848.88 | -257432.82 | -459208.62 |
|                      | $\tau_{a1}$ | 32.23  | 105.69 | 159.68 | 251.29 | 330.76 |
|                      | $R_{a2}$    | 15458.22 | 72757.69 | 168593.62 | 257371.23 | 393541.26 |
|                      | $\tau_{a2}$ | 32.39  | 106.25 | 160.82 | 248.73 | 343.64 |
|                      | Exactness   | 0.99441 | 0.99299 | 0.99591 | 0.99215 | 0.97887 |
| n-ZnO/p-Si at 500°C  | $R_{a1}$    | -15366.33 | -39411.16 | -35432.76 | -1655033.79 | -277244.40 |
|                      | $\tau_{a1}$ | 41.61  | 122.65 | 136.05 | 110.70 | 212.84 |
|                      | $R_{a2}$    | 15390.92 | 39461.04 | 35496.10 | 1655098.05 | 277519.44 |
|                      | $\tau_{a2}$ | 41.65  | 123.29 | 140.31 | 113.07 | 218.69 |
|                      | Exactness   | 0.9919 | 0.98827 | 0.98833 | 0.99057 | 0.9918 |
| n-ZnO/p-Si at 600°C  | $R_{a1}$    | -32946.50 | -23004.16 | -1227706.57 | -1228786.19 | -1018930.76 |
|                      | $\tau_{a1}$ | 69.22  | 287.51 | 222.51 | 303.95 | 86.15 |
|                      | $R_{a2}$    | 32969.81 | 233100.17 | 1227762.32 | 1228857.59 | 1018976.04 |
|                      | $\tau_{a2}$ | 69.26  | 287.69 | 222.55 | 304.06 | 134.64 |
|                      | Exactness   | 0.99541 | 0.98476 | 0.98817 | 0.99435 | 0.98618 |

### Table 4
Freundlich’s fitting parameters for the desorption of hydrogen molecules for the fabricated hetero-junction devices

| Sample Name          | H$_2$ (ppm) | 200   | 400   | 600   | 800   | 1000  |
|----------------------|-------------|-------|-------|-------|-------|-------|
| n-ZnO/p-Si at 400°C  | $R_{d1}$    | 52975.1 | 13.48 x10$^7$ | 62.02 x10$^10$ | 2.17 x10$^{17}$ | 3.34x10$^{23}$ |
|                      | $\tau_{d1}$ | 21.59  | 30.65 | 34.52 | 31.93 | 31.75 |
|                      | $R_{d2}$    | 55920.2 | 13.49 x10$^7$ | 63.01 x10$^{10}$ | 2.17 x10$^{17}$ | 2.99 x10$^{21}$ |
|                      | $\tau_{d2}$ | 21.58  | 30.66 | 34.51 | 31.93 | 35.93 |
|                      | Exactness   | 0.97782 | 0.97555 | 0.97137 | 0.98439 | 0.99336 |
| n-ZnO/p-Si at 500°C  | $R_{d1}$    | -15.78 x10$^6$ | 29.33 x10$^5$ | 52.75 x10$^9$ | 33. x10$^{10}$ | 2.74 x10$^{15}$ |
|                      | $\tau_{d1}$ | 18.48  | 41.39 | 36.59 | 51.02 | 51.14 |
|                      | $R_{d2}$    | 14.45 x10$^6$ | 29.22 x10$^5$ | 12.46 x10$^{10}$ | 42.90 x10$^{10}$ | 2.73 x10$^{15}$ |
|                      | $\tau_{d2}$ | 18.69  | 41.40 | 36.61 | 51.02 | 51.15 |
|                      | Exactness   | 0.99716 | 0.95882 | 0.97399 | 0.97401 | 0.95029 |
| n-ZnO/p-Si at 600°C  | $R_{d1}$    | -45.83 x10$^5$ | -72.96 x10$^7$ | 30.09 x10$^7$ | 33.12 x10$^9$ | 1.25 x10$^{12}$ |
|                      | $\tau_{d1}$ | 18.44  | 37.94 | 45.72 | 55.81 | 66.13 |
|                      | $R_{d2}$    | 43.02 x10$^5$ | 72.42 x10$^2$ | 30.11 x10$^9$ | 33.12 x10$^9$ | 1.25 x10$^{12}$ |
|                      | $\tau_{d2}$ | 18.61  | 37.97 | 45.71 | 55.82 | 66.12 |
|                      | Exactness   | 0.99494 | 0.99758 | 0.98613 | 0.98285 | 0.94829 |
on the film surface. Thus, simple adsorption-desorption processes can be attributed as the mechanism of gas sensing in these devices.

Figure 5 shows the sensing response of the fabricated hetero-junction devices as a function of hydrogen concentration. It is found that the gas sensing responses of all three devices increase almost linearly with hydrogen concentration. The gas sensing response of the fabricated devices as a function of analyte gas concentration can also be understood in terms of Freundlich's relation given by [39, 41, 42].

\[
\text{Response} = \alpha C^\beta
\]

where, \(\alpha\) and \(\beta\) are the Freundlich's undeterminants related with the surface structures and \(\beta\) can have value between 0 and unity, \(C\) is the concentration of analyte gas (say \(H_2\) in present case). The beauty of Eq. (15) is that this equation accounts for the heterogeneity of the deposited films.

However, there is an incongruity with this model is that Freundlich's isotherm tends to infinity as \(C\) tends to infinity, i.e. there is no restriction on the adsorption of gas molecules on the film surface or in a monolayer. This results into the infinitely rising in sensing response of the fabricated device with analyte gas concentration, which is unphysical. Thus, a modified Freundlich's eq. could be good choice to explain the concentration dependent gas sensing response of the device. The modified Freundlich's eq. for concentration dependent gas sensing response can be given by [39, 41, 42]

\[
\text{Response} \propto \frac{\alpha C^\beta}{1 + \alpha C^\beta}
\]

For the lower concentrations of the analyte gas, the above Eq. (16) reduces into the Eq. (15), whereas, for very high concentrations, R.H.S. of Eq. (16) approaches to 1 and gas sensing response approaches to a constant/saturated value. Thus, concentration dependent gas sensing responses of the deposited films are fitted with Eq. (16) and the obtained values of \(\alpha\) and \(\beta\) for the fabricated devices are shown in Fig. 5 along with the goodness of fitting. It is found that all the curves are very well fitted with Freundlich's relation with goodness of fitting better than 97.5 \%. Furthermore, the value of \(\beta\)-parameters increases from 0.57±0.05 to 0.68±0.05 and to 0.74±0.08 on increasing the fabrication temperature from 400 to 500 °C and to 600 °C, respectively. The increase in \(\beta\)-parameter with fabrication temperature can be attributed to the faster saturation of gas sensing response i.e. accommodation of lower number of analyte gas molecules in the first monolayer or lower active sites in case of device fabricated at higher temperature.

### 3.3 Mechanism of Gas Sensing in Hydrogen Environmental

The mechanism of hydrogen sensing (i.e. change in electric current) in n-ZnO/p-Si++ hetero-junction devices fabricated at different temperatures can be further understood by three more elegant models such as space charge region current control model (ii) grain boundary specific surface area and potential barrier height current control model and (iii) valence state current control model [11]. The current controlled by these three processes under hydrogen environment can be analyzed one by one, as follows

(i) Space charge region current control model: according to this model, in air ambient, oxygen (O\(_2\)) molecules are adsorbed on the active sites of film surface (Fig. 6a) and dissociated into two atomic oxygen atoms at moderate temperature (say 100 °C in present case) to occupy two active sites [11, 43] The electrons are transferred to these atomic oxygen (Fig. 6b) via reaction mechanism (iv) and thus, the electrons are depleted from the grains and grain boundary regions (or from the conduction band) near the upper surface of the films. This electron depleted region is called space charged or depletion region as shown in Fig. 6c. The reduced electrons concentration in depletion region results into the decrease in electrical current (conductivity) flowing through the heterojunction devices in air ambient. The length of this lower conductive region (L\(_D\)-Debye length) can be given by Eq. (12), which is an inverse function of carrier concentration. The decrease in carrier concentration means large thickness of this region and hence, lower conductivities of the fabricated devices in air ambient (Fig. 3a).

On the other hand, in hydrogen ambient, the reaction mechanism of type Eq. (vi) will take place. The electrons are
become free and returned back to the conduction band, which means an increase in carrier concentration and hence, a decrease in the thickness of depletion layer. This ultimately results into the increase in electric current flowing through the hetero-junction devices in hydrogen environment and responsible for hydrogen gas sensing. This process can be understood schematically through Fig. 6(d-e). In hydrogen environment, \( \text{H}_2 \) molecules adsorbed on the active sites of the film surface (Fig. 6d) and these adsorbed \( \text{H}_2 \) molecules interact with oxygen ions of the depletion layer (Fig. 6e) to form \( \text{H}_2\text{O} \) molecules. These water molecules evaporate from film surface at the operating temperature (Fig. 6f) and electrons are given back to the film. This results into the decrease in the thickness of depletion layer, as can be depicted from Fig. 6f.

Larger the number of grains and grain boundaries means larger the active sites for interaction. Thus, a decrease in gas sensing response of the hetero-junction devices with increase in fabrication temperature from 400 to 600 °C can be attributed to the decrease in number of grains and grain boundaries as observed from the increase in crystallites’ size and decrease in grain boundaries specific surface area measured from XRD patterns. Furthermore, the observed density of the fabricated films from XRD studies also found to increase with fabrication temperature, which means lower penetration of hydrogen molecules into the bulk of films. This again cause a decrease in the number of active sites for interaction and hence, the lower sensitivity of the devices fabricated at higher temperatures.

(ii) Grain boundary current control model: The growth of the lower conductive space charge region upon the capriciously scattered ZnO grains results into the development of potential barriers between two grains [44, 45] (i.e. at the grain boundaries) as shown in Fig. 6g. For the transport of the charge carriers (i.e. electrons), carriers have to jump over this potential barrier or crossover the grain boundaries (inset of Fig. 6g). Thus, the electrical properties or the currents flowing through the fabricated devices are determined by the height of the potential barrier or the contact resistance between of the grains [46], given by relation:

\[
I = I_o \exp \left( \frac{-e\Phi_B}{kT} \right) \tag{17}
\]

Where, \( I_o \) is the pre-exponential factor referred as the current flowing through the device at zero Kelvin and \( \Phi_B \) is the potential barrier height, which is related with the width of depletion layer \( W_D \) at the grains boundaries by the relation:

\[
W_D = \sqrt[2]{\frac{2e\Phi_B}{N_d \epsilon_0}} \tag{18}
\]

Where, \( N_d \) is the donor density and \( \epsilon_0 \) is the permittivity of free space.

The value of the potential barrier height for the fabricated devices can be estimated using the Richardson’s relation, wherein the reverse saturation current and the potential barrier height are inter-related by the expression

\[
I_0 = \frac{AA^*T^2\exp\left(-\frac{e\Phi_B}{kT}\right)}{\exp\left(\frac{e\Phi_B}{kT}\right)} \tag{19}
\]

where, \( A^* \) is the Richardson’s constant having the value of \( 32 \text{ Acm}^{-2} \text{ K}^{-2} \) and \( A \) is the area of Pt electrodes \( (=0.785 \text{ cm}^2) \). And the obtained values of the potential barrier height estimated in air ambient for the devices fabricated at 400, 500 and 600 °C are 0.402, 0.425 and 0.434 eV, respectively. The increase in potential barrier height with annealing temperature is attributed to the corresponding decrease in electric current flowing through the devices.

On the other hand, the values of the potential barrier height decrease in hydrogen environment to 0.384, 0.409 and 0.421 eV for the devices fabricated at 400, 500 and 600 °C, respectively. The \( \text{H}_2 \) molecules interacts with oxygen ions to form \( \text{H}_2\text{O} \) molecules near the grain boundaries (Fig. 6h) and the water molecules are evaporated from the film surface resulting in decrease in depletion width at the grain boundaries (Fig. 6i) and a corresponding decrease in potential barrier height is observed. The decrease in potential barrier height is the responsible factor for the observed increase in electric current in hydrogen environment. Thus, the proportionate change in potential barrier height \( (\Delta\Phi_B=0.018, 0.016 \text{ and } 0.013 \text{ eV}) \) in hydrogen ambient is responsible for the relative change in electric current and given by

\[
I_R = I_o \exp\left\{-\frac{-e\Delta\Phi_B}{kT}\right\} \tag{20}
\]

Lower the change in potential barrier height means lower the sensing response as observed for the devices fabricated at higher temperature.

(iii) Valence state controlled current conduction: A third mechanism that can contribute in the gas sensing responses of the fabricated devices is the valence state current control mechanism. According to this mechanism, because of high reducing ability of hydrogen gas, on exposure of ZnO surface with hydrogen gas molecules, the ZnO molecules reduce into the \( \text{Zn}^+ \) ions. In this process, \( \text{Zn}^+ \) ions are incorporated into the ZnO surface that produced metallization effect and change the valence state of Zn [11, 47, 48].
This effect drastically increases the electrical conductivity of the fabricated device. However, metallization effect generally occurs at relatively higher temperatures and thus can have only a small contribution in the electrical gas sensing measured at 100 °C in the present case. Thus, the major contribution in hydrogen gas sensing comes from the earlier mechanisms.

4 Conclusions

In summary, the hetero-junction devices based on n-ZnO/p-Si++ were fabricated at three different temperatures of 400, 500 and 600 °C. For the fabrication of these devices, ZnO thin films were grown by thermal evaporation technique, wherein, high quality Zn dust was evaporated slowly on the highly doped p-type silicon substrates maintained at 400 °C. Other two sets of films were obtained after annealing the deposited films at 500 and 600 °C. The structural analysis carried out under x-ray diffraction revealed that the crystallite size, grain boundary specific surface area and the density of the films increases with increase in fabrication temperature. I-V characteristics of the fabricated hetero-junction devices showed non-linear diodic behaviors in air and hydrogen gas environments. I-V characteristic of the fabricated devices also revealed the increase in electric current, when the devices are exposed to hydrogen environment. The fabricated hetero-junction devices are further analyzed for the detection of hydrogen gas at different concentrations (200 to 1000 ppm). It is found that the gas sensing responses of the fabricated devices increase with increase in operating temperature (up to 100 °C) as well as the hydrogen concentration. However, the sensing responses of the fabricated devices decrease from 97.22 to 64.23 and to 40.77 % with increase in annealing temperature from 400 to 500 and to 600 °C at 1000 ppm of hydrogen in ambient air. The sensing response of the device fabricated at 400 °C is found to increase from ~40.07 to 97.22 % and for the device fabricated at 500 °C from 23.73 to 64.23 on increasing the hydrogen concentration from 200 to 1000 ppm in air ambient. The mechanism of gas sensing has been systematically analyzed under space charge region control, grain boundaries control and valence state control current conduction. The values of response time increase from 84 to 159 s, 126 to 228 s and 144 to 225 s on changing the hydrogen concentration from 200 to 1000 ppm for the devices fabricated.
at 400, 500 and 600 °C, respectively. Similarly, the values of recovery time increase from 51 to 93 s, 85 to 111 s and 88 to 135 s on changing the hydrogen concentration from 200 to 1000 ppm for the devices fabricated at 400, 500 and 600 °C, respectively.

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Ishpal Rawal: Supervision, Conceptualization, Validation, Software, Reviewing and Editing.

Vipin Kumar: Data collection, Methodology, Visualization.

Data Availability Data will be provided on request.

Declarations

Ethics Approval The work presented here authors original work. Contributions of all the workers are declared here. No animal or human being harmed during this work.

Conflict of Interest The authors declare that there are no any kinds of conflicts of interest to declare.

Research Involving Human Participants and/or Animals No human or animal participant was involved by any of authors for this work.

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