



# Dielectric barrier discharge plasma enhances room-temperature ammonia sensing in ZnO thin films for rapid environmental monitoring

Tirtha Raj Acharya<sup>a,b,c,\*</sup>, Rajesh Shrestha<sup>d</sup>, Prajwal Lamichhane<sup>d,e</sup>,  
Shambhu Bhandari Sharma<sup>f</sup>, Roshan Chalise<sup>c,d,g</sup>, Keshav Raj Chapagain<sup>h</sup>, Dario Alfè<sup>f,i,j</sup>,  
Dinesh Kumar Chaudhary<sup>d,\*\*</sup>

<sup>a</sup> GSK Carbon Neutral Laboratories for Sustainable Chemistry, University of Nottingham, Jubilee Campus, Triumph Road, Nottingham, NG7 2TU, United Kingdom

<sup>b</sup> School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

<sup>c</sup> Department of Physics, St. Xavier's College, Tribhuvan University, Kathmandu, 44600, Nepal

<sup>d</sup> Department of Physics, Amrit Campus, Tribhuvan University, Kathmandu, 44600, Nepal

<sup>e</sup> Laboratory of Adsorption and Catalysis (LADCA), University of Antwerp, Groenenborgerlaan 171, 2020, Antwerpen, Belgium

<sup>f</sup> Department of Earth Sciences, University College London, Gower Street, London, WC1E 6BT, United Kingdom

<sup>g</sup> Central Department of Physics, Tribhuvan University, Kirtipur, 44613, Kathmandu, Nepal

<sup>h</sup> Central Department of Chemistry, Tribhuvan University, Kirtipur, 44613, Kathmandu, Nepal

<sup>i</sup> London Centre for Nanotechnology, University College London, London, WC1E 6BT, United Kingdom

<sup>j</sup> Dipartimento di Fisica Ettore Pancini, Università di Napoli Federico II, Monte S. Angelo, I-80126, Napoli, Italy

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## ABSTRACT

Zinc oxide (ZnO) thin films are widely explored for gas sensing due to their low cost, stability, and intrinsic sensitivity, yet their room-temperature performance is often limited by slow sensing response, poor selectivity, and insufficient active sites. This study reports a scalable strategy to enhance ammonia sensing via dielectric barrier discharge (DBD) plasma treatment of spin-coated ZnO films. Plasma exposure for 6 min (ZnO@P<sub>6</sub>) significantly tailored structural, morphological, optical, and surface chemical properties compared to pristine ZnO. X-ray diffraction and scanning electron microscopy analyses revealed reduced crystallite size and enhanced lattice strain, while Brunauer-Emmett-Teller and Barrett-Joyner-Halenda measurements showed increased surface area (90 m<sup>2</sup> g<sup>-1</sup>) and enlarged mesopores (~5.94 nm). X-ray photoelectron spectroscopy confirmed oxygen-vacancy formation, nitrogen incorporation, while electron paramagnetic resonance spectra demonstrated a strong signal at  $g = 1.965$ , indicating abundant paramagnetic oxygen vacancies that act as shallow donors to enhance charge transport and surface reactivity. Optical studies revealed bandgaps narrowing to 3.206 eV, and water contact angle measurements confirmed improved hydrophilicity. ZnO@P<sub>6</sub> exhibited ultralow detection limits (1 ppm), rapid response/recovery times (6 s/53 s), and a high sensing response of 2925 at 800 ppm NH<sub>3</sub>, markedly outperforming pristine ZnO (sensing response 609 at 800 ppm). Density functional theory simulations corroborated strong NH<sub>3</sub> chemisorption (−0.94 eV) with significant charge redistribution. These results demonstrate that DBD plasma engineering produces defect-rich, high-surface-area ZnO films, providing a robust platform for high-performance, selective, and stable room-temperature ammonia sensing for environmental monitoring.

## 1. Introduction

Ammonia (NH<sub>3</sub>) is a commonly utilized industrial chemical that plays important roles in agriculture, refrigeration, and chemical process industries [1]. However, due to its toxic and corrosive properties, even

minute quantities of ammonia present serious environmental and health hazards [2]. Its inhalation exposure, for instance, results in irritation of the eye, skin, and respiratory tract; high or prolonged exposures, on the other hand, bring serious risks to health [3]. The threshold limit value (TLV) for ammonia, as defined by occupational safety standards, is 25

\* Correspondence to: T. R. Acharya, School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom.

\*\* Corresponding author.

E-mail addresses: [tirtha.acharya@nottingham.ac.uk](mailto:tirtha.acharya@nottingham.ac.uk) (T.R. Acharya), [dinesh.chaudhary@ac.tu.edu.np](mailto:dinesh.chaudhary@ac.tu.edu.np) (D.K. Chaudhary).

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ppm for an 8-h time-weighted average (TWA) and 35 ppm for a 15-min short-term exposure limit (STEL) [4]. These are much higher than those which must be detected early in agriculture, food storage, and refuse environments where early detection at parts-per-million (ppm) or even below-ppm levels is of vital concern [5]. This specifies the need for stable, extremely sensitive, and specific gas sensors with the ability to detect ammonia in real time under ambient conditions. Semiconducting metal oxides (SMOs) are the most studied gas-sensing materials, and one of the most promising among them is zinc oxide (ZnO) [6–8]. ZnO is an n-type semiconductor material with a large band gap (~3.37 eV), with extremely high exciton binding energy (~60 meV), and with excellent physicochemical stability [9–11]. Its operational mechanism is surface adsorption, in which target gas-surface oxygen species interaction modulates electrical conductivity [12]. As ZnO contains inherent defects such as oxygen vacancies and grain boundaries, it is sensitive to a wide range of analytes such as volatile organic compounds (VOCs), nitrogen oxides (NO<sub>x</sub>), hydrogen (H<sub>2</sub>), and NH<sub>3</sub> [13,14]. Moreover, ZnO thin films can also be produced by scalable low-temperature and low-cost processes such as sol-gel, sputtering, chemical vapor deposition (CVD), and hydrothermal growth, making them more feasible for actual applications [15,16].

ZnO sensors suffer from perennial limitations, including non-selectivity, inadequate room-temperature sensing, and sluggish response/recovery kinetics [12,17]. Besides ZnO and ZnO based materials, metal oxides such as SnO<sub>2</sub>, TiO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, and perovskite-based materials have been widely explored for gas sensing due to their tunable electronic properties and chemical stability [18–23]. However, many require high operating temperatures, complex synthesis, or show limited selectivity and slow response/recovery, restricting practical use. ZnO thin films, with their room-temperature processability and defect-mediated sensitivity, are particularly attractive. Conventional enhancement strategies, including doping, noble-metal decoration, or heterojunction formation, often involve multi-step, high-temperature processes, limiting scalability. Thus, a green, facile but low-temperature modification process that effectively controls surface properties of ZnO without compromising structural integrity is highly in demand. Non-thermal plasma (NTP) surface modification (Table S1), especially dielectric barrier discharge (DBD) plasma, has been reported as an effective method to address these issues [24,25]. DBD plasma generates high concentrations of reactive oxygen and nitrogen species (RONS), ultraviolet photons, and hot electrons, and hence can generate surface etching, oxygen vacancy, and polar functional group introduction without degrading the substrate lattice [26,27]. Plasma contributions enhance surface roughness, defect states, and band structure, enhancing gas adsorption, electron transfer, and catalytic activity [28], all being crucial parameters for high-performance gas sensing [29]. Notably, plasma engineering makes ZnO sensors usable with minimal waste at room temperature, which is of significant concern to low-power, portable devices [30].

In the present work, ZnO thin films were deposited on glass substrates by the spin coating route, which was chosen due to its ability to produce uniform, highly reproducible thin films with precise thickness control. The technique is simple, cost-effective, and compatible with low-temperature processing, making it suitable for scalable fabrication of gas sensors [31,32]. Subsequently, the films were treated with DBD plasma for 2, 4, 6, 8 and 10 min, labeled as ZnO@P<sub>2</sub>, ZnO@P<sub>4</sub>, and ZnO@P<sub>6</sub>, ZnO@P<sub>8</sub>, ZnO@P<sub>10</sub> respectively. Compared with other approaches to enhancement, this method offers a scalable, catalyst-free, energy-efficient post-synthesis adjustment with ambient air used as the plasma feeding gas. Comprehensive characterization (XRD, FTIR, UV-Vis, contact angle, XPS, BET, EPR, SEM, and EDX) and DFT calculations show that plasma treatment creates oxygen vacancies, increases surface roughness, and reduces the band gap. These modifications enhance the interaction of the ZnO surface with NH<sub>3</sub> molecules. ZnO@P<sub>6</sub> was the optimal sensing material among the treated samples and exhibited ultrafast response/recovery times, good selectivity, enhanced

humidity resistance, and stability. To the best of our knowledge, this is the first systematic proof of DBD plasma with comprehensive diagnosis as a surface engineering technique for ZnO thin films as ammonia sensors. These results confirm DBD plasma treatment offers a simple, low-temperature, and scalable surface engineering approach, introducing oxygen vacancies and surface hydroxyl groups in ZnO thin films, which leads to ultrafast, selective, and stable NH<sub>3</sub> sensing at room temperature.

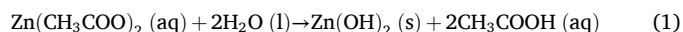
## 2. Experimental setup, instruments, and methodology

### 2.1. Materials

The materials used in this study include commercially available glass substrates (2.5 × 2.5 × 0.1 cm<sup>3</sup>) for thin film deposition. Zinc acetate (Zn(CH<sub>3</sub>COO)<sub>2</sub>, 98%, Sigma-Aldrich, USA) was used as the precursor solution for the ZnO, and diethanolamine (DEA, 99%, Sigma-Aldrich, USA) was used as a stabilizing agent for the ZnO precursor solution. Acetone (≥99.5%, Fisher Scientific, USA) and deionized water were used for cleaning substrates and preparing solutions. Ethanol (≥99.5%, Fisher Scientific, USA) was used for dissolving zinc acetate in the preparation of the ZnO precursor solution. All chemicals were utilized as received without further purification, and solutions were prepared according to the procedures outlined in the methodology section.

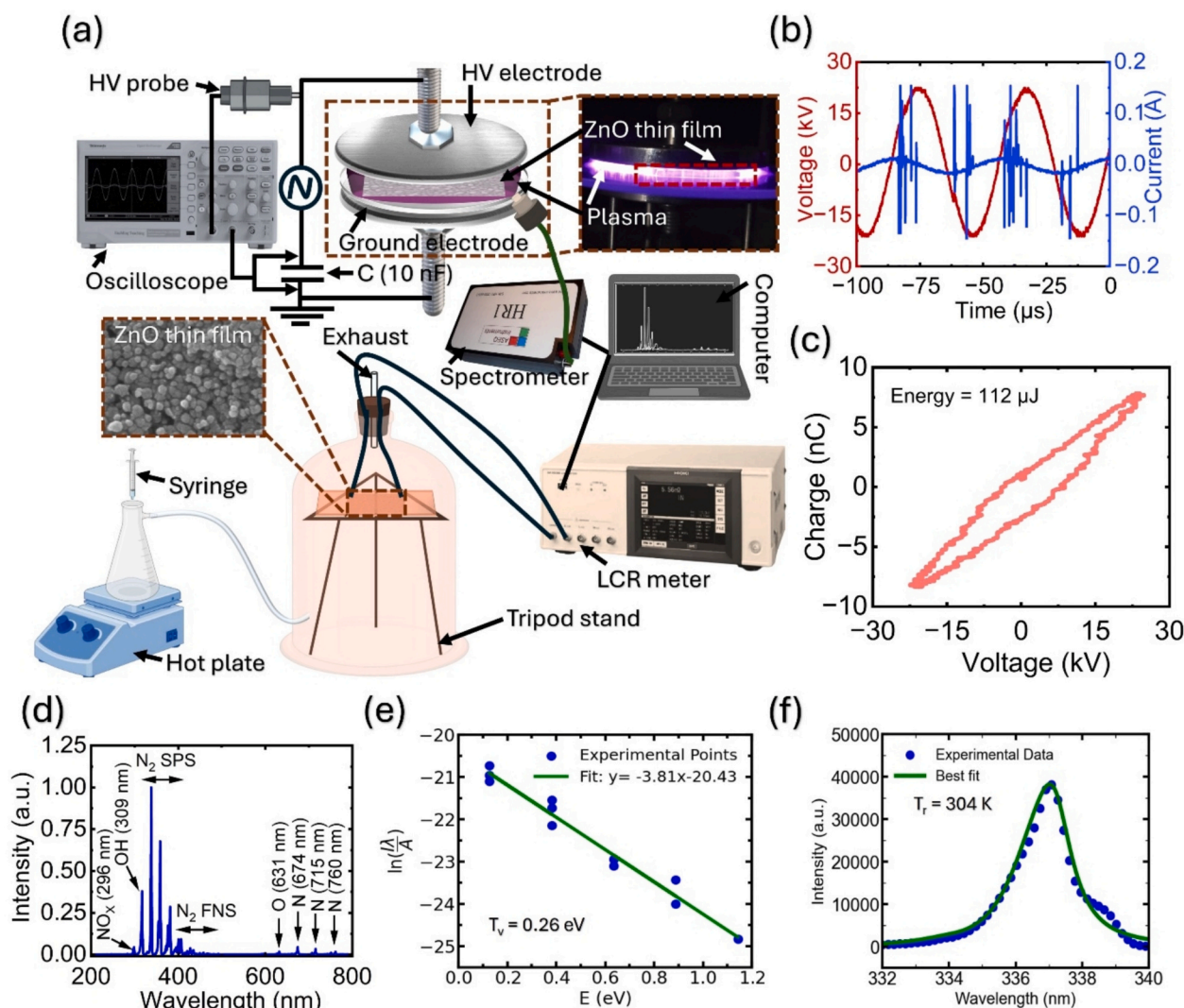
### 2.2. Synthesis chemistry of ZnO thin films

Glass substrates were first cleaned with Labolene detergent and thoroughly rinsed with acetone and deionized water in an ultrasonic bath. The substrates were then dried in a hot oven at 50 °C for 30 min to eliminate residual impurities. For the ZnO thin film preparation, a 0.1 M precursor solution was prepared by dissolving 2.217 g of zinc acetate in 100 mL of ethanol. To this solution, 1.071 g of DEA was added as a stabilizing agent. The mixture was stirred at (60 ± 10) °C for 1 h and aged for 24 h. A 15 μL volume of the precursor solution was deposited onto each cleaned glass substrate using a micropipette and spread uniformly via spin coating at 3000 rpm for 30 s (s). The coated substrates were pre-heated at 120 °C for 5 min and then at 300 °C for 15 min to eliminate residual solvents. This coating and pre-heating cycle was repeated up to five times. Final annealing was performed at (500 ± 5) °C for 2 h in a muffle furnace, leading to the formation of crystalline ZnO thin films (Eqs. 1–2) [33]. The ZnO thin films were then allowed to cool to room temperature before further processing or characterization, as detailed in the previous study [34].



### 2.3. DBD plasma set-up and diagnosis technique

The experimental setup used to treat the surface of ZnO thin film using dielectric barrier discharge plasma is presented in Fig. 1(a). The plasma discharge system is composed of two stainless steel circular electrodes, each with a diameter of 57.15 mm and a thickness of 5.50 mm, and a total gap of 5 mm. A quartz dielectric plate of 1.90 mm thickness and 90.00 mm diameter is inserted between the electrodes as a dielectric barrier. This arrangement establishes a stable plasma zone for treating ZnO thin films to enhance NH<sub>3</sub> sensing. The ZnO films prepared by spin coating, as described above, were subsequently exposed to plasma for 2, 4, 6, 8 and 10 min, respectively. The applied voltage of the plasma was measured using a Tektronix TBS1052B oscilloscope along with a PINTEK HVP-40 high-voltage probe. Current was measured using a 100 Ω, 10 W resistor with a Tektronix TPP0201 probe that also measured voltage across a 10 nF capacitor for discharge analysis. Optical emission spectroscopy (OES) was used for analyzing the plasma characteristics through an HR1 high-resolution spectrometer from ASEQ



**Fig. 1.** Dielectric Barrier Discharge (DBD) plasma setup, diagnostics, and ammonia gas sensor setup for ammonia sensing. (a) Schematic of the DBD plasma setup for ammonia sensing, (b) current-voltage characteristics of the plasma, (c) Lissajous plot for calculating total dissipated energy per cycle, (d) optical Emission Spectroscopy (OES) analysis of the plasma, (e) calculation of vibrational temperature ( $T_v$ ) using the Boltzmann plot of the  $N_2$  second positive system ( $N_2$  SPS), (f) calculation of rotational temperature ( $T_r$ ) by comparing the experimental  $N_2$  SPS peak at 337 nm with the best-fit model.

Instruments. The spectrometer is also equipped with a detection range of 200–830 nm, a grating of  $300 \text{ g mm}^{-1}$ , a resolution of  $0.176 \text{ nm}$ , and a slit width of  $10 \text{ }\mu\text{m}$ . The OES fiber probe was positioned  $5 \text{ mm}$  from the discharge region to capture emission data accurately. Spectral data were taken with an exposure time of  $300 \text{ ms}$  and averaged over 30 scans for stability.

#### 2.4. Characterization of ZnO thin films: Structural, optical, and morphological properties

To analyze the optical and structural properties of the synthesized ZnO and DBD plasma-treated ZnO thin films, a range of advanced characterization techniques was employed. The structural characterization was carried out using an X-ray diffractometer (Ocean Optics Bruker AXS, D2 PHASER A26-X1-A2BOB2A-, Serial No. 207047) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) to determine crystalline phases as well as structural modifications resulting from plasma treatment. Optical properties were studied using a UV-Visible spectrophotometer (Cary 60, Agilent Technologies) to compare the absorbance behavior of the films. The wettability of the films was assessed by measurement of static water contact angles (WCAs) using a Phoenix-MT contact angle analyzer through the sessile drop method. Moreover, Fourier transform infrared

(FT-IR) spectroscopy (PerkinElmer GX) was employed to identify the functional groups in the films and hence offer complementary information on the chemical makeup and molecular architecture of the films. The X-ray Photoelectron Spectroscopy (XPS) measurements were performed using a VG-Scienta MX 650 monochromatic  $\text{Al K}\alpha$  source ( $1486.6 \text{ eV}$ ,  $\Delta E = 0.2 \text{ eV}$ ) with a  $7 \times 2 \text{ mm}^2$  beam spot under a base pressure of  $2 \times 10^{-9} \text{ Torr}$ . Photoelectrons were collected using a VG-Scienta R3000 spectrometer equipped with a four-element electrostatic lens and a hemispherical analyzer ( $0.8 \text{ mm}$  slit,  $100 \text{ eV}$  pass energy), providing an energy resolution of  $200 \text{ meV}$ . The system was calibrated using a clean Au foil by setting the  $\text{Au } 4f_{7/2}$  line to  $(84.00 \pm 0.01) \text{ eV}$ . Spectral fitting was conducted using the KherveFitting program, following the methodology described in the published literature [35]. Brunauer–Emmett–Teller (BET) surface area and porosity measurements were carried out on an ASAP 2020 Plus system (Micromeritics, USA) to determine the specific surface area and pore-size distribution of the materials before and after sulfur loading, using the BET and Barrett–Joyner–Halenda (BJH) analyses, respectively. Due to the extremely low mass of substrate-supported thin films, direct BET measurements are unreliable. Therefore, BET analysis was carried out using powder analogues prepared under identical synthesis and DBD plasma treatment conditions. Approximately  $300 \text{ mg}$  of ZnO powder was

used for each BET measurement. For plasma treatment, the powder was uniformly spread as a thin layer ( $\sim 1\text{--}2$  mm thickness) over an effective surface area of  $\sim 20\text{ cm}^2$  to ensure homogeneous plasma exposure. The BET results are employed for comparative evaluation of plasma-induced textural changes rather than absolute surface area values of the thin films. Electron paramagnetic resonance (EPR) spectroscopy was conducted on a Bruker A300–10/12 instrument to probe unpaired electron states and defect-related paramagnetic centers. Surface morphology and elemental analysis were performed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) using a JEOL system (Japan). ZnO and DBD plasma-treated ZnO grain sizes were determined from image analysis by ImageJ software.

## 2.5. Preparation of sample gases and gas detection setup at room temperature

Fig. 1(a) schematically illustrates the gas sensing apparatus used in this study. The system consists of two connected chambers: a 100 mL chamber for target gas generation and a 1.5 L chamber for gas sensing measurements. Ammonia ( $\text{NH}_3$ ), acetone ( $\text{C}_3\text{H}_6\text{O}$ ), n-butanol ( $\text{C}_4\text{H}_{10}\text{O}$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), formaldehyde ( $\text{CH}_2\text{O}$ ), n-propanol ( $\text{C}_3\text{H}_8\text{O}$ ), and methanol ( $\text{CH}_3\text{OH}$ ) vapors were used as target gases. Ammonia vapor was generated from high-purity aqueous ammonia solution ( $\text{NH}_4\text{OH}$ , 28–35%  $\text{NH}_3$ , Fisher Scientific). A defined volume of the aqueous solution was injected into the preheated 100 mL test chamber using a calibrated gas-tight syringe to achieve the desired  $\text{NH}_3$  concentration. The chamber was maintained at  $(120 \pm 4)^\circ\text{C}$  using a digitally controlled hot plate (TALBOYS  $7 \times 7$  CER HP 230 V ADV, Henry Troemner, LLC), ensuring rapid volatilization of  $\text{NH}_3$ . At this temperature,  $\text{NH}_3$  volatilizes efficiently due to its high vapor pressure, while the contribution of water vapor remains negligible, generating predominantly dry ammonia vapor suitable for room-temperature sensing measurements. Vapors of acetone, n-butanol, ethanol, formaldehyde (from aqueous formalin, 37 wt%  $\text{HCHO}$  with (10–15) vol% methanol stabilizer, Sigma-Aldrich), n-propanol, and methanol (all  $\geq 99.98\%$  purity, Sigma-Aldrich) were generated by controlled heating at  $(120 \pm 4)^\circ\text{C}$  in the same 100 mL chamber. Known microliter quantities of each liquid were injected using a calibrated gas-tight syringe, and the resulting vapors were allowed to equilibrate before exposure to the sensing chamber.

The concentration of the resulting vapor was calculated using the ideal gas law, as described below. The desired target gas concentration,  $C$  (in ppm), was obtained using the following relations (Eqs. 3–6) [9,10]:

$$V_{\text{gas}} = C \times V_s \quad (3)$$

where  $V_{\text{gas}}$  is the volume of the test gas (mL), and  $V_s$  is the volume of the test chamber (mL).

According to the ideal gas law:

$$PV = nRT \quad (4)$$

Hence, the number of moles of the gas introduced is:

$$n_{\text{gas}} = \frac{PV_{\text{gas}}}{RT} = \frac{PCV_s}{RT} \quad (5)$$

Since the injected liquid volume  $V_{\text{inject}}$  is related to its mass by  $V = \frac{Mn}{\rho}$ , obtain:

$$V_{\text{inject}} = \frac{Mn_{\text{gas}}}{\rho} = \frac{MPCV_s}{\rho RT} \quad (6)$$

where  $M$  = molar mass of the target liquid ( $\text{g mol}^{-1}$ ),  $\rho$  = density of the target liquid ( $\text{g mL}^{-1}$ ),  $P$  = pressure inside the test chamber (Pa),  $R$  = universal gas constant ( $8.314\text{ J mol}^{-1}\text{K}^{-1}$ ), and  $T$  = temperature of the test chamber (K). All gases were used without carriers or balancing gases (i.e., the target gases were not mixed with air) to ensure accurate and reproducible sensitivity measurements [9]. The test chamber of volume has two openings for  $\text{NH}_3$  inlet, air, and  $\text{NH}_3$  exhaust. The ZnO thin film,

2.5 cm by 2.5 cm in dimension, is kept facing downwards over the  $\text{NH}_3$  vapor inside the test chamber. Between the ZnO film surface and the base of the sensor, there is 5 cm, and on the ZnO film, two electrodes are created using insulating copper wire and silver paste. The ZnO thin film resistance is tracked using electrodes connected to a DAU that is linked to an LCR meter equipped with a computer. Current-voltage characterization of the ZnO thin-film circuit was also performed before the sensing experiment with satisfactory ohmic behavior. Due to the low density of the  $\text{NH}_3$  vapor, it rapidly moves from the chamber base to the ZnO film surface, thus decreasing the resistance. Humidity was maintained at  $(60 \pm 4)\%$  relative humidity, and ambient temperature at  $(27 \pm 2)^\circ\text{C}$ .

## 2.6. Computational methodology

The first-principles density functional theory (DFT) calculations, as implemented in the Vienna Ab initio Simulation Package (VASP) [36], are performed to study the charge transfer mechanism and electronic properties of the plasma-treated system. The generalized gradient approximation Perdew-Burke-Ernzerhof (GGA) [37] is adopted for describing exchange correlation energy, and the electron-ion interactions are represented by the projector-augmented wave (PAW) method [38]. The Brillouin zone is sampled using a  $3 \times 3 \times 1$  Monkhorst-Pack [39] k-point mesh, with a plane-wave energy cutoff of 530 eV. Structural relaxations are performed until the force on each atom is less than  $0.02\text{ eV/\AA}$ , and the electronic self-consistent field (SCF) iterations are considered converged when the total energy difference between successive steps is below  $10^{-6}\text{ eV}$ . A vacuum region of  $25\text{ \AA}$  is introduced along the z-axis to prevent interactions between periodic images, and a dipole correction is applied in the out-of-plane direction to eliminate spurious electrostatic interactions between the slab surfaces. To accurately describe the van der Waals interactions between the surface and the adsorbate, the empirical DFT-D3 method [40] of Grimme, as implemented in the VASP code, is employed. The projected density of states (PDOS) calculations was performed using the same computational setup, including the GGA-PBE functional, PAW potentials, plane-wave cutoff energy, k-point sampling, and convergence criteria, to ensure consistency between the electronic structure analysis and adsorption calculations. The adsorption energies ( $E_{\text{ads}}$ ) are evaluated as (Eq. 7).

$$E_{\text{ads}} = E_{\text{slab+gas}} - E_{\text{slab}} - E_{\text{gas}} \quad (7)$$

where  $E_{\text{slab+gas}}$ ,  $E_{\text{slab}}$ , and  $E_{\text{gas}}$  are the total energies of the surface with the adsorbed gas, the clean surface, and the isolated gas molecule, respectively. Charge density differences are visualized with the VESTA software [41], and the Bader charge analysis is performed using the code developed by Henkelman [42] group to quantify charge transfer between adsorbate and substrate.

## 2.7. Statistical analysis

All experimental measurements were repeated at least three times to ensure reproducibility and statistical reliability. The reported values are presented as the mean  $\pm$  standard deviation (SD). For gas-sensing measurements, multiple exposure–recovery cycles were performed at each  $\text{NH}_3$  concentration, and the average response was used for analysis.

## 3. Results and discussion

### 3.1. Electrical and optical diagnostics of DBD plasma

Fig. 1 comprehensively illustrates the DBD plasma setup and diagnostics employed for the surface modification of ZnO thin films, which is critical for enhancing ammonia sensing capabilities. The experimental schematic in Fig. 1(a) shows the configuration of the high-voltage AC

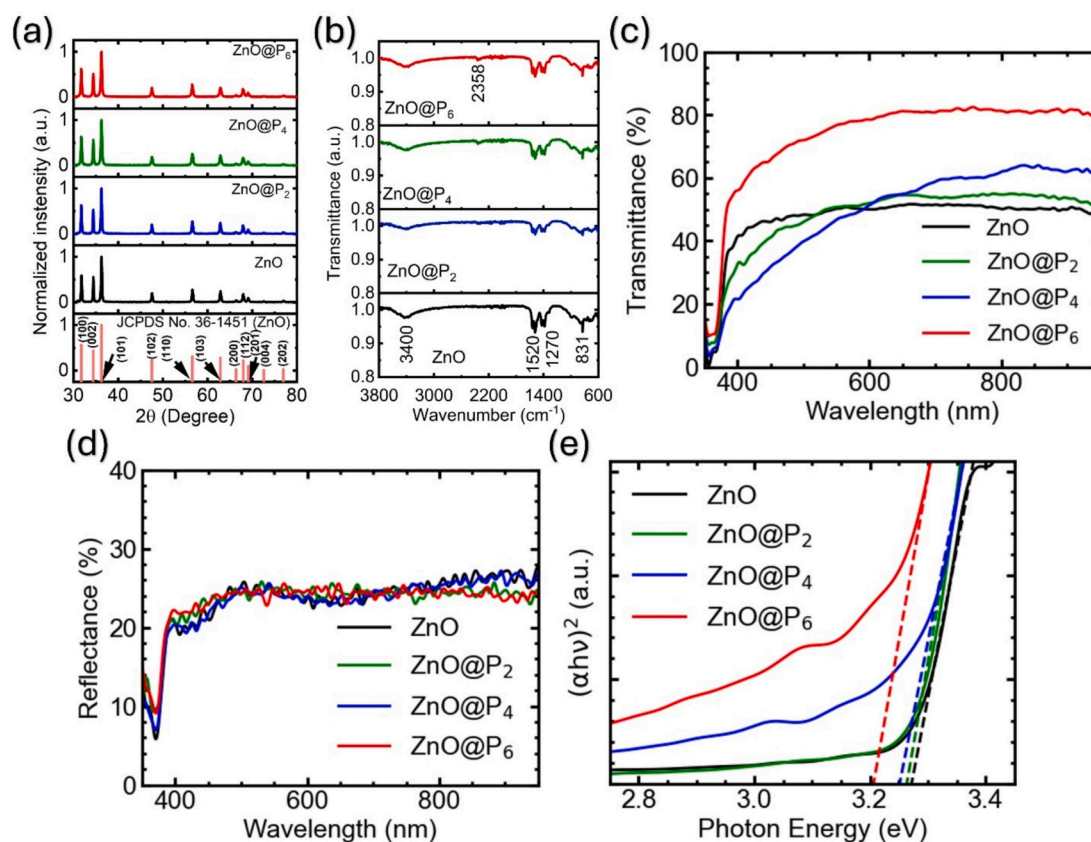
DBD plasma system, where the ZnO-coated substrate is exposed to a plasma discharge generated between a powered high-voltage electrode and a grounded plate, separated by a dielectric barrier. This arrangement ensures non-thermal plasma generation at atmospheric pressure. A suite of diagnostics, including an oscilloscope and spectrometer, facilitates in-situ electrical and optical characterization of the plasma to understand its reactive environment and energy delivery. The voltage-current waveform presented in Fig. 1(b) displays typical DBD behavior characterized by periodic micro discharges. The sinusoidal voltage and transient current spikes confirm non-equilibrium plasma behavior, ensuring surface reactivity without substantial bulk heating. The Lissajous plot in Fig. 1(c), plotting charge versus voltage, represents energy dissipation per AC cycle in the form of a hysteresis loop [43]. The area within the loop quantifies the net power transferred to plasma. The DBD plasma treatment was performed using ambient air as a plasma feeding gas with the flow rate of 15 liters per minute (L/min). The applied voltage had a peak of  $(21.50 \pm 0.54)$  kV and a peak current of  $(0.138 \pm 0.011)$  A. From the Q-V Lissajous figure, the energy per cycle was calculated to be  $(112 \pm 9)$   $\mu$ J, corresponding to a discharge power of  $(2.6 \pm 0.4)$  W at a frequency of  $(23 \pm 0.1)$  kHz. The experiments were conducted under controlled environmental conditions of room temperature  $(27 \pm 2)$  °C, relative humidity  $(60 \pm 4)$  %, vibrational temperature  $T_v = (0.26 \pm 0.02)$  eV, and rotational temperature  $T_r = (304 \pm 5)$  K. These parameters ensure reproducibility of plasma treatment and allow accurate comparison of experimental results.

OES results shown in Fig. 1(d) reveal strong emission lines from OH (A – X) emission at 309 nm, nitrogen second positive system ( $N_2$  SPS) at 311–380 nm,  $NO_x$ -related peaks at 236 nm, and weak emissions from atomic O and N species [44,45]. The spectral signature confirms a chemically rich plasma containing reactive species that can interact with the ZnO surface, leading to bond breakage, functional group formation,

and vacancy generation. The vibrational temperature ( $T_v$ ), calculated from the Boltzmann plot of the  $N_2$  SPS band intensities in Fig. 1(e), is found to be  $(0.26 \pm 0.02)$  eV, indicating a vibrationally excited yet thermally mild discharge [46]. Complementarily, Fig. 1(f) presents the rotational temperature ( $T_r = 304 \pm 5$  K) obtained by fitting the  $N_2$  SPS band head at 337.1 nm to a synthetic spectral model, further confirming the non-thermal nature of the plasma [47]. Collectively, these diagnostic outcomes confirm that the DBD plasma provides a low temperature yet highly energetic environment suitable for inducing precise and tunable modifications in ZnO thin films. The presence of reactive oxygen and nitrogen species, combined with moderate energy input, leads to increased surface oxygen content, improved roughness, and defect-rich ZnO surfaces, conditions that are highly favorable for enhancing gas adsorption, charge transfer, and ultimately, ammonia sensing performance [48].

### 3.2. Structural, optical, and surface characterization of ZnO & plasma-treated ZnO thin films

Fig. 2 presents a comprehensive comparative analysis of ZnO thin films subjected to DBD plasma treatment for varying durations, designated as ZnO, ZnO@P<sub>2</sub>, ZnO@P<sub>4</sub>, and ZnO@P<sub>6</sub>, respectively. The XRD patterns in Fig. 2(a) and Fig. S1 (Rietveld refinement plots) reveal the crystalline phase and structural evolution of the samples. All films exhibit sharp diffraction peaks matching the hexagonal wurtzite structure of ZnO (JCPDS No. 36–1451), with the most intense reflections observed at (100), (002), and (101) planes [49]. Plasma-treated films display slight peak broadening and intensity reduction, particularly for ZnO@P<sub>4</sub> and ZnO@P<sub>6</sub>, indicating a reduction in crystallite size and increased micro strain due to plasma-induced defect formation. These structural distortions are attributed to surface etching, defect



**Fig. 2.** Structural and optical properties of ZnO and DBD plasma-treated ZnO thin films with 0 min (ZnO), 2 min (ZnO@P<sub>2</sub>), 4 min (ZnO@P<sub>4</sub>), 6 min (ZnO@P<sub>6</sub>) of DBD plasma treatments. (a) X-ray diffraction (XRD) analysis to examine the crystalline structure, (b) Fourier Transform Infrared (FTIR) spectroscopy for functional group identification, (c) optical transmittance spectra, (d) reflectance spectra and (e) Tauc plot for band gap calculation.

incorporation (oxygen vacancies), and the introduction of surface disorder by energetic plasma species [48,50]. Table 1 presents the structural analysis of ZnO and DBD plasma-treated ZnO thin films, highlighting major changes in crystallite size, dislocation density, strain, and lattice parameters. Calculations of d-spacing, crystallite size (D), lattice parameters (a, c, and c/a), and Zn–O bond length were performed using the provided Eqs. (8–13) [51,52].

$$2d\sin\theta = n\lambda \quad (8)$$

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (9)$$

$$a = \frac{\lambda}{\sqrt{3}\sin\theta} \quad (10)$$

$$c = \frac{\lambda}{\sin\theta} \quad (11)$$

$$L = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2} \quad (12)$$

with

$$u = \frac{a^2}{3c^2} + 0.25 \quad (13)$$

The dislocation density ( $\delta$ ) consistent with the plane (002) was calculated via Eq. (14).

$$\delta = \frac{1}{D^2} \quad (14)$$

The lattice strain ( $\epsilon$ ) was determined utilizing Eq. (15).

$$\epsilon = \frac{\beta}{4\tan\theta} \quad (15)$$

The crystallite size (D) of ZnO is  $(45 \pm 1)$  nm, which decreases with plasma treatment, reaching  $(37 \pm 1)$  nm for ZnO@P<sub>6</sub>. The decrease in crystallite size with increasing DBD plasma exposure is attributed to plasma-induced lattice distortion and defect generation in the near-surface region of the ZnO thin films. Energetic electrons, ions, and RONS introduce microstrain and increase dislocation density, resulting in XRD peak broadening and an apparent reduction in crystallite size with longer plasma treatment. Such plasma-induced crystallite refinement has been widely reported for ZnO and other metal oxide thin films and is generally associated with surface disorder rather than bulk structural degradation [28,53].

The dislocation density ( $\delta$ ), which is related to structural imperfections, increases from  $7.63 \times 10^{14}$  lines/m<sup>2</sup> (ZnO) to  $1.42 \times 10^{15}$  lines/m<sup>2</sup> (ZnO@P<sub>6</sub>), indicating a higher density of defects in DBD plasma-treated films. Similarly, the strain ( $\epsilon$ ) in the ZnO lattice increases with plasma treatment, reaching a maximum of  $2.65 \times 10^{-3}$  for ZnO@P<sub>6</sub>, which confirms enhanced lattice distortion. The increase in both dislocation density and strain plays a crucial role in modulating the electronic and adsorption properties of ZnO, which are essential for gas sensing applications.

The structural modifications of ZnO thin film after plasma treatment have a direct impact on NH<sub>3</sub> sensing performance. The increased defect density enhances electron transport and surface reactivity, facilitating

stronger interactions between NH<sub>3</sub> molecules and the ZnO surface. Oxygen vacancies function as active sites for NH<sub>3</sub> adsorption, leading to efficient charge transfer and improved sensing response. Plasma-treated ZnO, particularly ZnO@P<sub>6</sub>, exhibits excellent NH<sub>3</sub> sensing due to the optimized balance of defect-induced charge transport and enhanced adsorption capabilities. The higher strain and dislocation density contribute to faster response and recovery times, ensuring stable and long-term ammonia detection at room temperature.

FTIR spectra (Fig. 2b) of ZnO, ZnO@P<sub>2</sub>, ZnO@P<sub>4</sub>, and ZnO@P<sub>6</sub> exhibit common absorption bands at approximately 3400, 1520, 1270, and 831 cm<sup>-1</sup>. The broad band centered at  $\sim 3400$  cm<sup>-1</sup> is attributed to the stretching vibration of surface hydroxyl groups (O–H), originating from adsorbed water molecules and surface –OH species. The band at  $\sim 1520$  cm<sup>-1</sup> corresponds to asymmetric stretching vibrations of carbonate or carboxylate species (CO<sub>3</sub><sup>2-</sup>/–COO<sup>-</sup>), formed due to atmospheric CO<sub>2</sub> adsorption on the ZnO surface. The feature observed at  $\sim 1270$  cm<sup>-1</sup> is associated with C–O stretching and O–H bending modes of surface carbonate or hydroxylated species. The low-wavenumber band at  $\sim 831$  cm<sup>-1</sup> is assigned to Zn–O–H bending and Zn–O lattice vibrations, confirming that the ZnO crystal framework remains intact after plasma treatment [9].

Notably, an additional weak band at  $\sim 2358$  cm<sup>-1</sup> appears in the plasma-treated films and becomes more pronounced for ZnO@P<sub>6</sub> (Fig. S2). This band is attributed to the asymmetric stretching vibration of adsorbed CO<sub>2</sub> species, which preferentially bind to plasma-generated surface defects and oxygen vacancies [54]. The presence of abundant hydroxyl and carboxylate species generated by plasma treatment enhances the surface polarity and density of hydrogen-bonding sites. Consequently, gases capable of donating or accepting hydrogen bonds, such as NH<sub>3</sub>, can interact more strongly with these modified surfaces. This mechanism complements defect-assisted adsorption, as supported by XPS results showing increased defect-related oxygen (O<sub>v</sub>) and surface-adsorbed oxygen/hydroxyl species (O<sub>ads</sub>), as well as EPR measurements revealing a pronounced signal corresponding to singly ionized oxygen vacancies. Together, these results confirm that plasma-induced defect formation and surface activation play a key role in the enhanced NH<sub>3</sub> sensing performance.

The optical transmittance spectra in Fig. 2(c) highlight a marked improvement in transparency across the visible range (350–950 nm) with increased plasma treatment time. The band gap (E<sub>g</sub>) of the ZnO films was determined through the Tauc plot, as described by Eq. (16).

$$(ah\nu)^2 = A(h\nu - E_g) \quad (16)$$

To accurately determine the optical band gap (E<sub>g</sub>) of the films, the absorption coefficient ( $\alpha$ ) was calculated by accounting for both transmittance (T) and reflectance (R) (Fig. 2d) using the relation Eq. (17) [55,56], where  $t$  is the film thickness. This approach accounts for multiple reflections at the air/film/substrate interfaces, which are significant in thin films.

$$\alpha = \frac{1}{t} \ln \left( \frac{(1 - R)^2}{T} \right) \quad (17)$$

Transmittance increases from  $\sim 60\%$  for ZnO to  $\sim 85\%$  for ZnO@P<sub>6</sub>, mainly due to the reduced film thickness after plasma treatment, with minor contributions from the removal of surface contaminants and passivation of nanoscale defects that reduce light scattering, despite slight variations in nanoscale roughness [28,57]. Corresponding Tauc plots in Fig. 2(e) show a reduction in optical band gap energy from 3.272 eV (ZnO) to 3.206 eV (ZnO@P<sub>6</sub>), attributed to enhanced surface defect states and quantum confinement effects. This band gap narrowing supports improved electrical conductivity and charge transfer behavior, favoring ammonia sensing performance.

The contact angle ( $\theta$ ) of a drop of water on a ZnO thin film surface was determined by the surface free energies using Eq. (18) [58].

**Table 1**

Analysis of structural properties for ZnO and DBD plasma-treated ZnO thin films.

| Samples            | D (nm) | Dislocation density ( $\delta$ ) (lines m <sup>-2</sup> ) | Strain ( $\epsilon$ )            |
|--------------------|--------|-----------------------------------------------------------|----------------------------------|
| ZnO                | 45 ± 1 | $(7.63 \pm 0.91) \times 10^{14}$                          | $(2.10 \pm 0.15) \times 10^{-3}$ |
| ZnO@P <sub>2</sub> | 44 ± 2 | $(1.22 \pm 0.03) \times 10^{15}$                          | $(2.45 \pm 0.16) \times 10^{-3}$ |
| ZnO@P <sub>4</sub> | 38 ± 2 | $(1.24 \pm 0.14) \times 10^{15}$                          | $(2.50 \pm 0.14) \times 10^{-3}$ |
| ZnO@P <sub>6</sub> | 37 ± 1 | $(1.42 \pm 0.18) \times 10^{15}$                          | $(2.65 \pm 0.20) \times 10^{-3}$ |

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (18)$$

where  $\gamma_{sv}$ ,  $\gamma_{sl}$ , and  $\gamma_{lv}$  are the solid–vapor, solid–liquid, and liquid–vapor interface energies, respectively.

The contact angle analysis shown in Figs. 3 (a–e) indicates a decrease in water contact angle with increasing plasma treatment time for the ZnO thin films, from 120° for pristine ZnO (Fig. 3a) to 101° (ZnO@P<sub>2</sub>) (Fig. 3b), 88° (ZnO@P<sub>4</sub>) (Fig. 3c), and 74° (ZnO@P<sub>6</sub>) (Fig. 3d), reflecting enhanced surface hydrophilicity. These results are in good agreement with previously reported studies on plasma-treated ZnO-based materials [59,60]. This enhancement (Fig. 3e) is driven by the combined effect of plasma-induced polar surface functional groups (such as hydroxyl, carboxyl, and carbonate species) and nanoscale surface roughness, which together increase surface energy and promotes water spreading [61]. Improved wettability translates into better interaction between the sensing layer and ambient analytes, thereby facilitating faster and more efficient ammonia adsorption and desorption dynamics. Collectively, these structural, optical, and surface modifications confirm that DBD plasma treatment not only introduces beneficial defects and functional groups into ZnO thin films but also optimizes surface chemistry and morphology.

### 3.3. Surface chemistry, defects, and porosity of ZnO & plasma-treated ZnO thin films

XPS analysis (Figs. 4 a–d) reveals that the pristine ZnO thin film contains characteristic Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub> peaks at 1022.31 and 1045.40 eV while C 1 s signal at 285.61 eV arising from surface carbon contamination. Following plasma treatment (ZnO@P<sub>6</sub>) (Figs. 4 e–i), the

Zn 2p peak positions remain essentially unchanged, confirming that the Zn chemical environment and lattice structure are preserved. However, the complete disappearance of the C 1 s peak demonstrates effective removal of adventitious carbon, while the emergence of N 1 s peaks at 403.14, 398.25, and 397.76 eV indicates successful nitrogen incorporation at the surface. The N 1 s spectrum (Fig. 4i) exhibits a doublet at 397.76 eV and 398.25 eV, which can be attributed to nitrogen incorporated into slightly different ZnO lattice environments, corresponding to substitutional or lattice nitrogen (N<sub>lat</sub>). In contrast, the weak component observed at 403.14 eV is characteristic of oxidized or protonated surface nitrogen species (e.g., NO<sub>x</sub>, NH<sub>4</sub><sup>+</sup>) which can be assigned to surface-adsorbed nitrogen-containing groups. The dominance and relative stability of the 398.0–398.3 eV features provide strong evidence for lattice incorporation of nitrogen, while the minor high-binding-energy contribution represents a small population of labile surface species, consistent with previous reports [62,63].

The high-resolution O 1 s XPS spectra of pristine ZnO (Fig. 4c) and ZnO@P<sub>6</sub> (Fig. 4g) thin films were deconvoluted into three characteristic components. For pristine ZnO, peaks located at 530.96 eV, 531.64 eV, and 532.92 eV are attributed to lattice oxygen (O<sub>L</sub>, O–Zn bonds), defect-related oxygen or oxygen vacancies (O<sub>V</sub>), and surface-adsorbed oxygen/hydroxyl species (O<sub>ads</sub>), respectively. Similarly, ZnO@P<sub>6</sub> exhibits corresponding O 1 s components at 530.71 eV (O<sub>L</sub>), 531.23 eV (O<sub>V</sub>), and 532.69 eV (O<sub>ads</sub>). These binding energy positions are in good agreement with reported XPS data for ZnO thin films, where lattice oxygen typically appears at ~529.8–530.2 eV, oxygen vacancies at ~531.0–531.6 eV, and adsorbed species (–OH, H<sub>2</sub>O, CO<sub>x</sub>) at ~532.0–533.5 eV [64]. Owing to the surface-sensitive probing depth of XPS (a few nanometers), surface- and defect-related oxygen species contribute strongly to the O 1 s signal, resulting in a prominent O<sub>V</sub> component, particularly in thin-film systems with high surface-to-volume ratios. After DBD plasma treatment, the increased intensity of the O<sub>V</sub> (~531 eV) and O<sub>ads</sub> (~533 eV) peaks indicate a higher concentration of oxygen vacancies and surface hydroxyl species. These plasma-induced defects act as active adsorption sites and electron donors, facilitating enhanced gas adsorption and charge transfer, which directly correlates with the improved NH<sub>3</sub> sensing response of ZnO@P<sub>6</sub> at room temperature. These modifications are further reflected in the valence band maximum (VBM) (Figs. 4 j–k), which decreases from 3.39 eV (ZnO) to 3.13 eV (ZnO@P<sub>6</sub>), highlighting the defect-driven electronic restructuring induced by plasma treatment.

The specific surface area and pore characteristics of the ZnO and plasma-treated samples were evaluated using N<sub>2</sub> adsorption–desorption isotherms, applying the BET method for surface area determination and the BJH model for mesopore analysis. As shown in Figs. 5(a–b), the ZnO@P<sub>6</sub> sample exhibits the highest specific surface area (90 m<sup>2</sup> g<sup>−1</sup>), exceeding those of ZnO@P<sub>4</sub> (70 m<sup>2</sup> g<sup>−1</sup>), ZnO@P<sub>2</sub> (60 m<sup>2</sup> g<sup>−1</sup>), and pristine ZnO (55 m<sup>2</sup> g<sup>−1</sup>). Complementary pore-size analysis further confirms the greater mesoporosity of ZnO@P<sub>6</sub>, which displays the largest average pore diameter (~5.94 nm) and a broad pore distribution in the 4–30 nm range, compared with ZnO@P<sub>4</sub> (5.45 nm), ZnO@P<sub>2</sub> (5.13 nm), and pure ZnO (4.39 nm). This plasma-induced ordered porosity, with increasing specific surface area and mesoporosity from ZnO to ZnO@P<sub>6</sub>, directly correlates with the observed enhancement in NH<sub>3</sub> sensing response, providing an optimal texture for gas-sensing applications by maximizing active site availability and facilitating rapid analyte diffusion.

Fig. 5(c) presents the EPR spectra of pristine ZnO and ZnO@P<sub>6</sub>, showing a sharp, intense signal at g = 1.965, observed exclusively for ZnO@P<sub>6</sub>. This g-value corresponds to paramagnetic, singly ionized oxygen vacancies (V<sub>O</sub>•), providing direct evidence that the DBD plasma treatment generates a high density of these defects. The deviation from the free-electron g value (2.002) arises from the localization of unpaired electrons at the oxygen vacancy site and their interaction with neighboring Zn<sup>2+</sup> cations through crystal-field effects and spin–orbit coupling. The pronounced EPR signal in ZnO@P<sub>6</sub> indicates a substantial

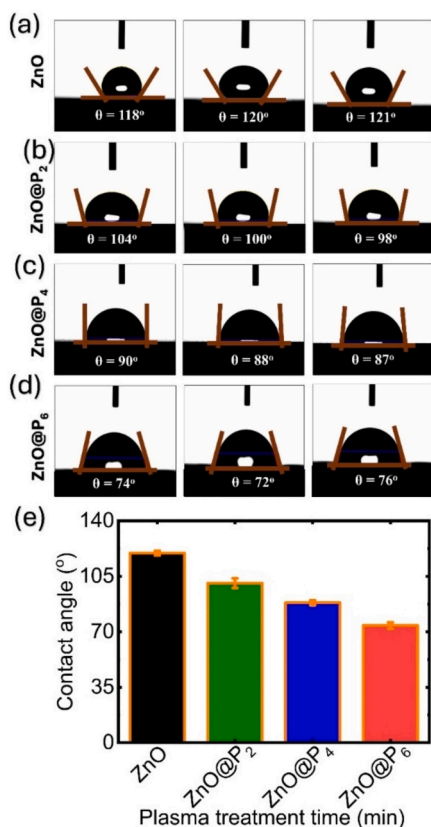
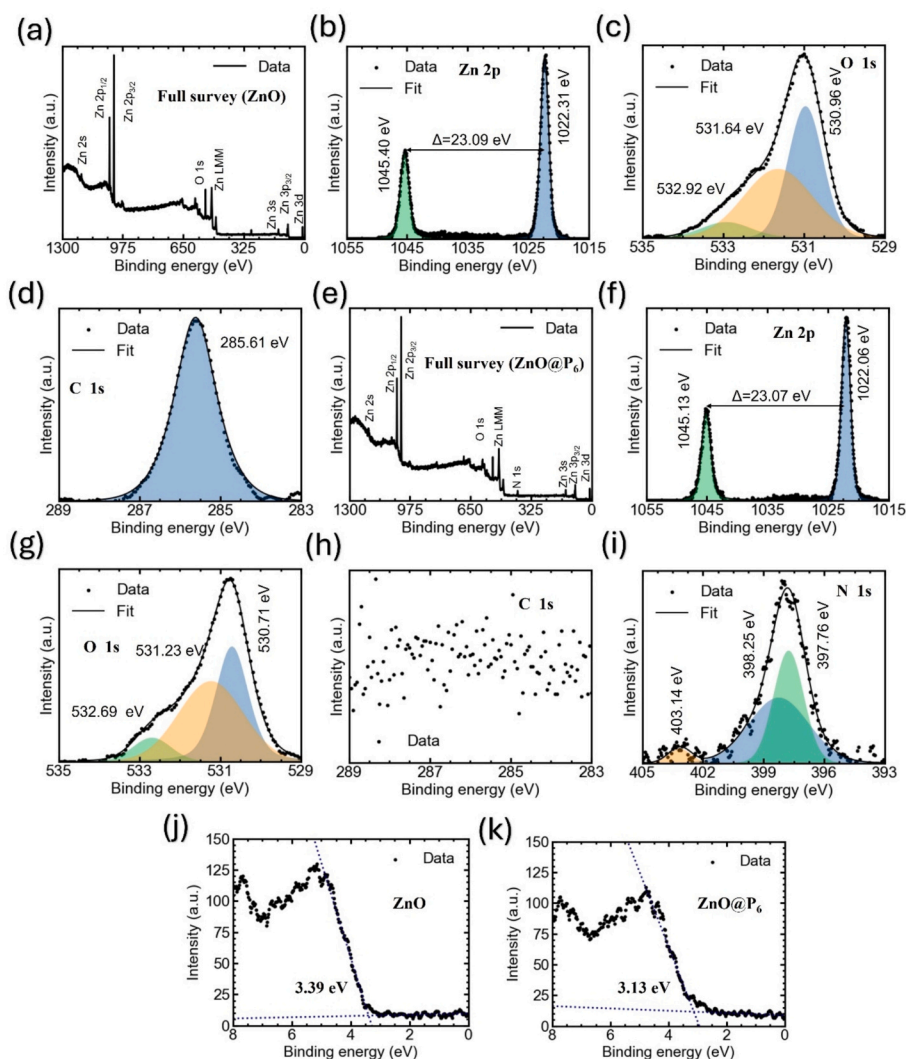


Fig. 3. Surface wettability analysis of pristine ZnO and DBD plasma-treated ZnO thin films. (a–e) Wettability analysis based on water contact angle (WCA) measurements: (a) ZnO, (b) ZnO@P<sub>2</sub>, (c) ZnO@P<sub>4</sub>, and (d) ZnO@P<sub>6</sub>. (f) Bar graph summarizing the water contact angle values for all samples.



**Fig. 4.** X-ray photoelectron spectroscopy (XPS) analysis of pristine ZnO and plasma-treated ZnO (ZnO@P<sub>6</sub>) thin films. (a–d) XPS spectra of pristine ZnO showing the Zn 2p, O 1s, and C 1s core levels. (e–i) XPS spectra of ZnO@P<sub>6</sub> displaying unchanged Zn 2p binding energies, suppression of the C 1s signal, the appearance of N 1s features, and an increased contribution from defect-related oxygen (O<sub>v</sub>) and surface-adsorbed oxygen species (O<sub>ads</sub>) in the O 1s spectrum after plasma treatment. (j–k) Valence band spectra showing a shift of the valence band maximum (VBM) from 3.39 eV (ZnO) to 3.13 eV (ZnO@P<sub>6</sub>).

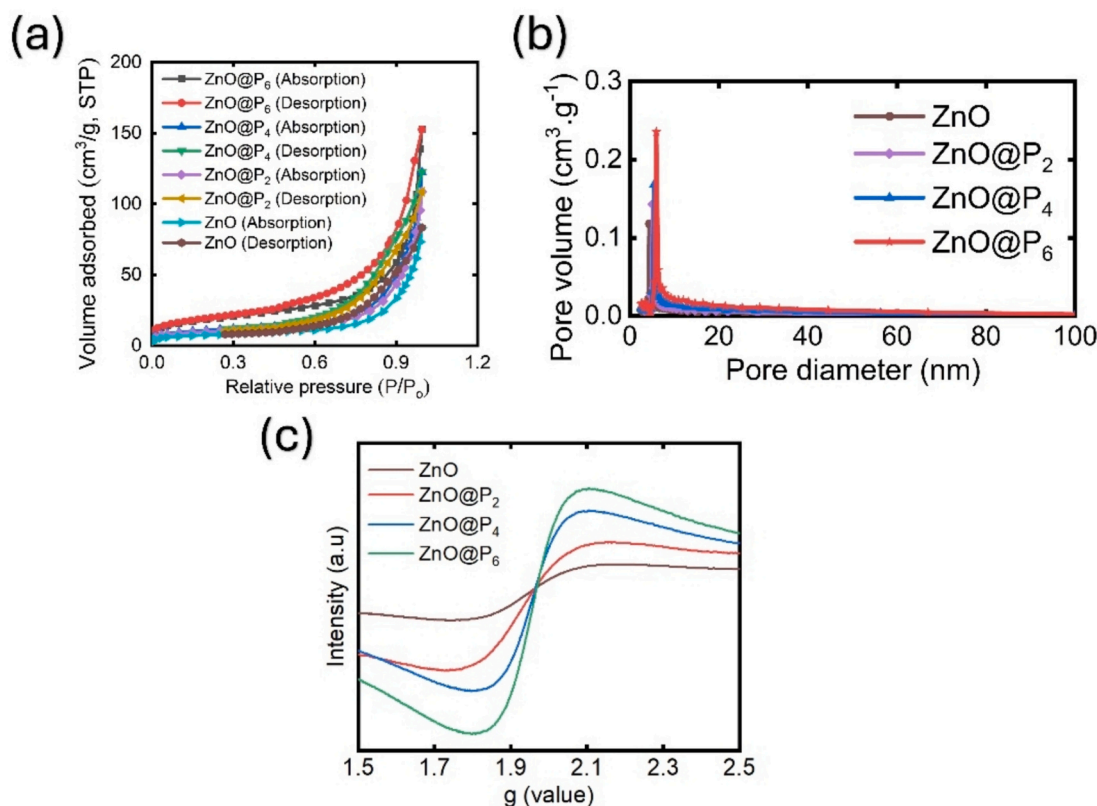
increase in unpaired electrons associated with oxygen vacancies compared to pristine ZnO. These vacancies act as shallow donors, enhancing n-type conductivity and creating active surface sites, which play a critical role in the ultrafast and highly sensitive NH<sub>3</sub> sensing response at room temperature. The formation of these oxygen vacancies through plasma treatment thus underpins the greater sensitivity, rapid sensing response, and high selectivity of ZnO@P<sub>6</sub> toward ammonia detection, consistent with literature reports of similar g-values for oxygen vacancies in ZnO [65,66].

Although EDX analysis indicates an increased oxygen content after DBD plasma treatment, EPR confirms a higher density of oxygen vacancies (V<sub>O</sub>), evidence of an oxygen-deficient lattice. This apparent discrepancy arises because EDX measures total oxygen (lattice and surface-adsorbed species), whereas EPR selectively probes vacancy-related defects. Plasma-generated V<sub>O</sub> sites promote additional surface oxygen adsorption, increasing the EDX signal while preserving the defect density responsible for enhanced NH<sub>3</sub> sensing [28,29,53,67,68].

### 3.4. Morphological characterization of ZnO and DBD plasma-treated ZnO thin films

Fig. 6 presents the structural and morphological analysis of ZnO and

DBD plasma-treated ZnO thin films through Fig. 6(a) top-view SEM images, Fig. 6(b) grain size distribution histograms, and Fig. 6(c) cross-sectional SEM images. The untreated ZnO film exhibits a larger grain size, with well-defined spherical nanoparticles. As plasma treatment duration increases (ZnO@P<sub>2</sub>, ZnO@P<sub>4</sub>, and ZnO@P<sub>6</sub>), the grain size decreases progressively, indicating the influence of plasma-induced etching and surface modification. The progressive reduction in mean grain diameter observed in SEM images is ascribed to plasma-assisted surface etching and grain-boundary modification. Energetic plasma species preferentially interact with high-energy grain boundaries and surface asperities, leading to the fragmentation of larger grains and the formation of a finer surface morphology [28,53]. This plasma-driven grain refinement increases the surface-to-volume ratio and enhances surface reactivity, which is advantageous for improved NH<sub>3</sub> gas-sensing performance. The grain size distribution histograms (Fig. 6b) confirm this trend, showing a decrease in mean grain diameter from (48.34 ± 12.60) nm (ZnO) to (28.53 ± 11.96) nm (ZnO@P<sub>6</sub>). This reduction enhances the surface-to-volume ratio, which is a crucial factor for improving gas sensing performance. The cross-sectional SEM images (Fig. 6c) further demonstrate a decrease in film thickness with plasma treatment, from (185 ± 3) nm (ZnO) to (124 ± 4) nm (ZnO@P<sub>6</sub>). The thinner plasma-treated films provide a shorter diffusion path for charge



**Fig. 5.** BET–BJH and EPR analyses of pristine ZnO and plasma-treated ZnO (ZnO@P<sub>6</sub>). (a–b) N<sub>2</sub> adsorption–desorption isotherms and BJH pore-size distribution showing enhanced specific surface area (90 m<sup>2</sup> g<sup>-1</sup>) and enlarged mesopores (~5.94 nm, 4–30 nm range) for ZnO@P<sub>6</sub> compared to reference ZnO samples. (c) EPR spectra displaying a pronounced signal at  $g = 1.965$  for ZnO@P<sub>6</sub>, indicating increased oxygen-vacancy defects induced by plasma treatment.

carriers and improved surface reactivity, facilitating enhanced NH<sub>3</sub> adsorption and charge transfer [69]. The crystallite size estimated from XRD represents the average size of coherently diffracting domains within the ZnO lattice, which are typically different than the grain sizes observed in SEM images. In contrast, SEM grain size reflects the morphological dimensions of surface grains, which may consist of several smaller crystallites separated by low-angle grain boundaries or internal defects. Therefore, slight differences between the crystallite and grain sizes are expected and consistent with the polycrystalline nature of ZnO thin films.

### 3.5. Elemental characterization of ZnO and DBD plasma-treated ZnO thin films

The elemental composition and surface distribution of Zn and O in ZnO thin films before and after DBD plasma treatment are illustrated in Fig. 7. Fig. 7(a) shows the elemental mapping images, which highlight a progressive increase in oxygen presence and surface uniformity with longer plasma exposure durations (ZnO@P<sub>2</sub> to ZnO@P<sub>6</sub>). ZnO@P<sub>6</sub> exhibits an improved and evenly distributed oxygen signal compared to the untreated ZnO film, indicating successful surface activation. This is further supported by the EDX spectra in Fig. 7(b), where the oxygen peaks intensify with plasma treatment while zinc peaks slightly decrease. These findings suggest that the DBD plasma treatment introduces oxygen-rich functional groups and creates surface defects like oxygen vacancies, which are known to improve gas adsorption and catalytic behavior, crucial for sensing applications [48].

Fig. 7(c) provides quantitative data showing a systematic increase in the atomic percentage of oxygen from 50.00% in untreated ZnO to 58.33% in ZnO@P<sub>6</sub>, while the zinc content decreases accordingly. This shift in stoichiometry confirms that plasma treatment modifies the surface chemistry of ZnO thin films, enhancing their reactivity. The

increased oxygen content and associated surface roughness lead to a higher density of active sites, improving the interaction with ammonia gas molecules. Consequently, these compositional and morphological changes contribute directly to the enhanced ammonia sensing performance observed in plasma-treated ZnO films, particularly ZnO@P<sub>6</sub>, which offers improved sensitivity, faster response time, and better selectivity at room temperature.

### 3.6. Gas sensing characterization of ZnO thin films

Since ZnO is an n-type semiconductor, the gas sensing response ( $R$ ) toward a reducing gas (e.g., NH<sub>3</sub>) was calculated using the sensor's steady-state resistance in air ( $R_a$ ) and in the presence of the target gas ( $R_g$ ). The NH<sub>3</sub> sensing response ( $R$ ) is defined as the ratio of these resistances, as given in Eq. (19):

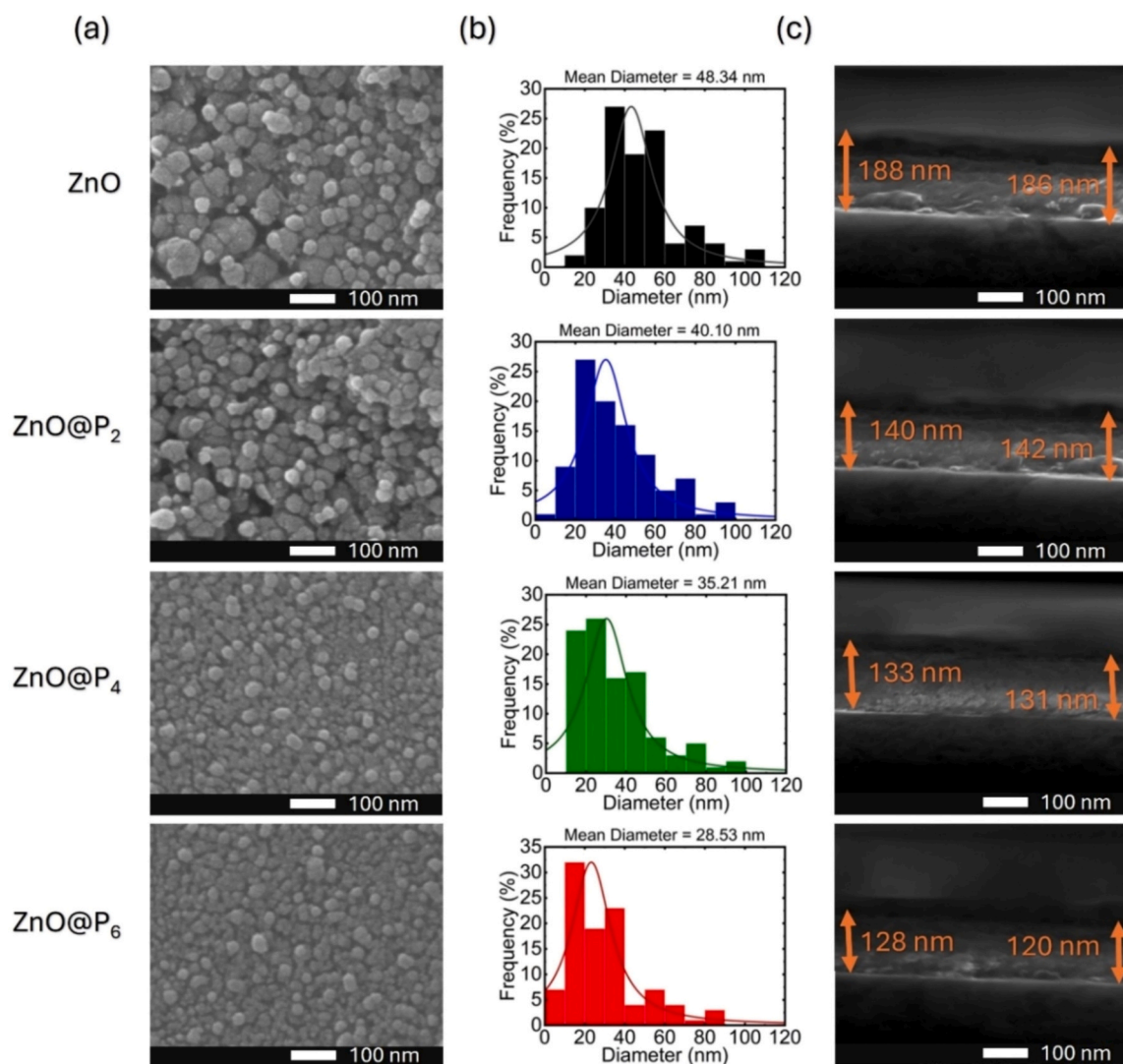
$$R = \frac{R_a}{R_g} \quad (19)$$

Also, similar formula can be used to determine the sensitivity response ( $S$ ) of the ZnO thin film resistive sensor, for n-type semiconductor for reducing gas (Eq. 20) [10,70].

$$S = \frac{R_a - R_g}{R_g} \quad (20)$$

The DBD plasma treatment duration was optimized by testing 0–10 min, and 6 min (ZnO@P<sub>6</sub>) was identified as the optimal condition based on NH<sub>3</sub> sensing at 100 ppm (Fig. S3). This treatment provides the best balance between defect density and structural integrity, enabling efficient and stable NH<sub>3</sub> sensing at room temperature.

Fig. 8 demonstrates the ammonia gas sensing performance of pristine ZnO and DBD plasma-treated ZnO thin films (ZnO@P<sub>2</sub>, ZnO@P<sub>4</sub>, ZnO@P<sub>6</sub>), measured in terms of resistance ( $R_{dc}$ ) and sensing response

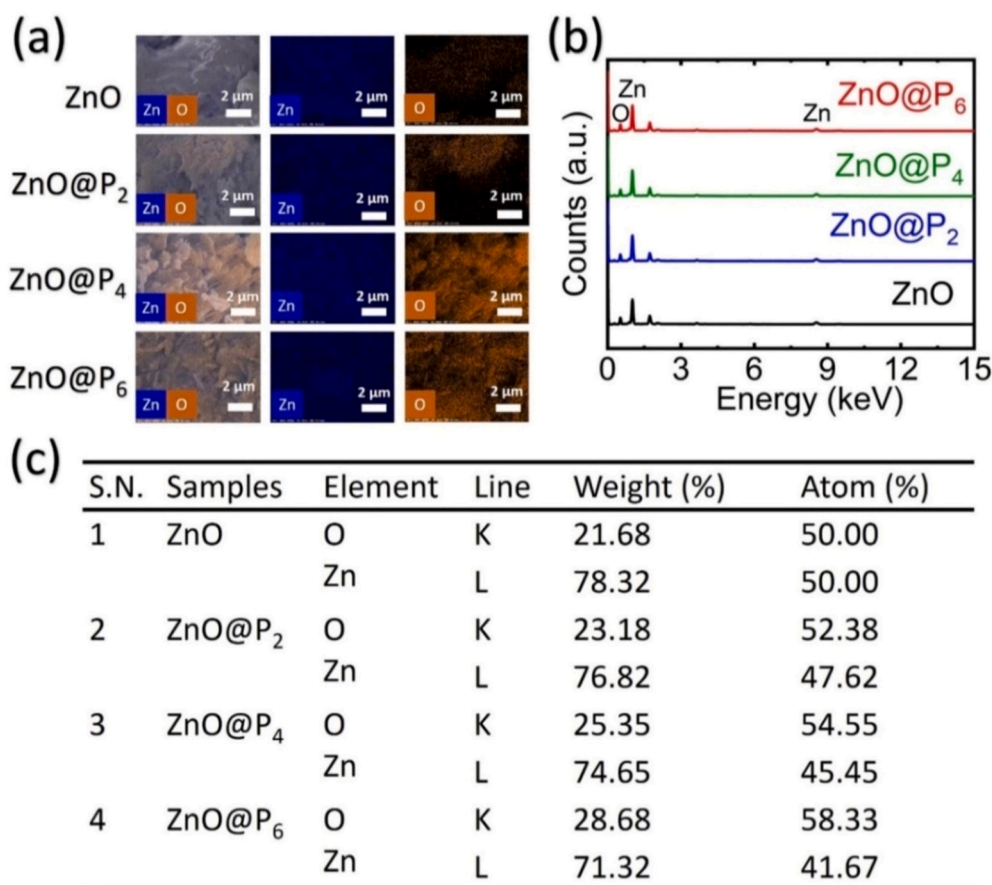


**Fig. 6.** Morphological analysis of ZnO and DBD plasma-treated ZnO thin films, (a) Scanning Electron Microscopy (SEM) images showing the grain size of ZnO nanoparticles, (b) size distribution of ZnO nanoparticles, (c) SEM cross-sectional images depicting the film thickness.

( $R_a/R_g$ ) over a broad concentration range (1–800 ppm) and multiple exposure cycles at room temperature ( $27 \pm 2$  °C). The pristine ZnO sensor Figs. 8(a–b) exhibits a measurable sensing response to ammonia starting from 12 ppm and increases with concentration; however, the sensing response curve saturates at higher concentrations and shows slower response/recovery dynamics, highlighting limitations in surface reactivity and adsorption kinetics. In contrast, the DBD plasma-treated sensors exhibit increased performance, with ZnO@P<sub>2</sub> and ZnO@P<sub>4</sub> (Figs. 8(c–f)) showing progressively stronger and faster sensing responses due to plasma-induced surface activation. Most notably, the ZnO@P<sub>6</sub> sensor (Figs. 8(g–h)) displays a highly sensitive and stable sensing response across all ammonia concentrations, including detectable signals at concentrations as low as 1 ppm. The ZnO@P<sub>6</sub> sensor exhibits a near-linear response to NH<sub>3</sub> in the low-to-moderate concentration range (1–200 ppm), reflecting efficient adsorption and electron transfer at abundant surface-active sites. A sharp increase in response is observed between 5 and 25 ppm, likely due to the small, uniformly distributed spherical grains and the large surface-to-volume ratio of the nano-structured film. At higher concentrations (>200 ppm), the response curve saturates because most surface-active sites are occupied and multilayer adsorption of NH<sub>3</sub> may occur, limiting further interaction with the gas. This saturation behavior is characteristic of chemiresistive sensors and does not compromise the reproducibility or stability of the

sensor, indicating that ZnO@P<sub>6</sub> is particularly suitable for low-to-moderate NH<sub>3</sub> detection while remaining stable at higher concentrations [71,72]. The plasma treatment increases the density of oxygen vacancies and active surface sites, which significantly enhances gas adsorption, electron transfer, and desorption efficiency [25,48]. The dynamic  $R_{dc}$  profiles exhibit well-resolved and repeatable resistance (Fig. S4) drops with each ammonia exposure cycle, confirming robust signal reproducibility and sensor stability.

The concentration-dependent response of ZnO and plasma-treated ZnO sensors arises from surface site availability and adsorption dynamics. At low NH<sub>3</sub> concentrations (1–25 ppm), only a fraction of oxygen vacancies and surface hydroxyl/carboxylate groups are occupied, leading to slower adsorption and electron transfer. At higher concentrations (>50 ppm), abundant NH<sub>3</sub> molecules are available, resulting in fast diffusion. Hence, abundant NH<sub>3</sub> molecules reached to the detecting surface rapidly, accelerating the interaction with adsorbed oxygen ions, charge transfer, and resistance modulation, resulting in faster response kinetics. Plasma-induced surface modifications, including increased oxygen vacancies, surface hydroxylation, and roughness, further enhance redox reaction rates, explaining the faster sensing response at higher concentrations. Among the tested samples, DBD plasma-treated ZnO thin films (ZnO@P<sub>4</sub> and ZnO@P<sub>6</sub>) exhibit excellent sensitivity, with detectable responses at concentrations as low as 1 ppm, well below



**Fig. 7.** Compositional analysis of ZnO and DBD plasma-treated ZnO thin films. (a) Energy Dispersive X-ray (EDX) mapping images showing the distribution of Zn and O elements in ZnO thin films, (b) EDX spectra indicating the elemental composition of Zn and O, and (c) elemental analysis presenting Zn and O content in weight percentage and atomic percentage.

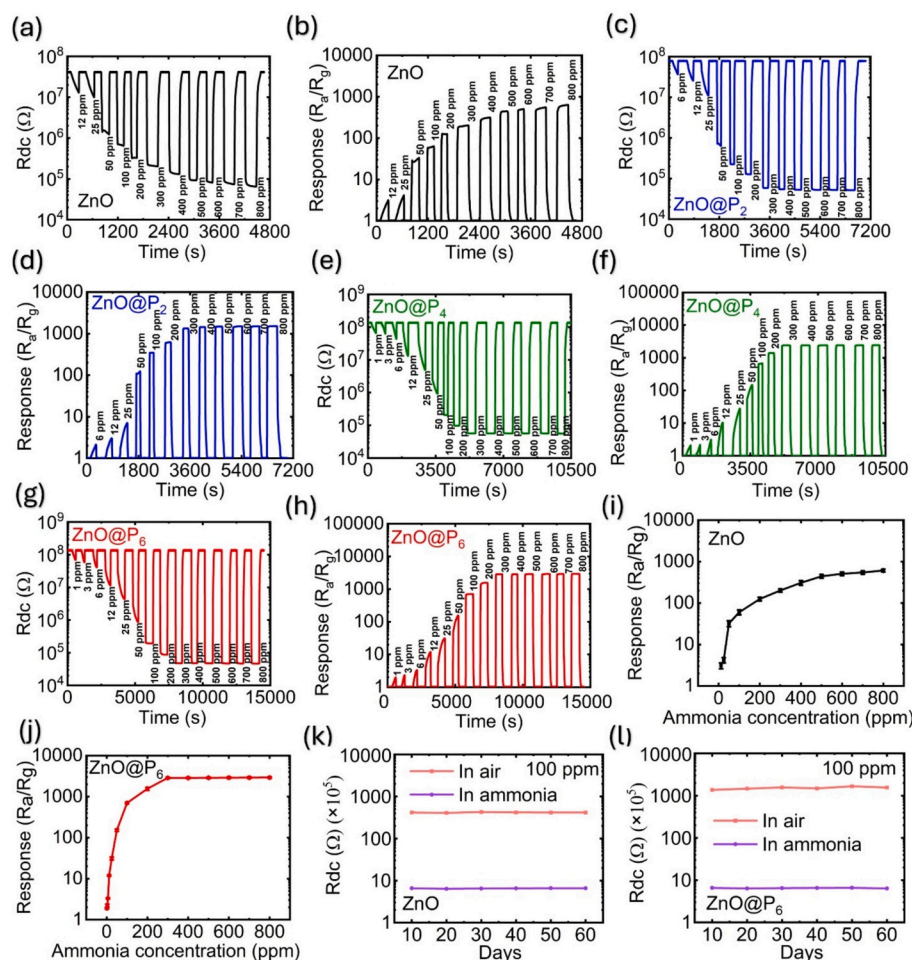
the occupational TLV, highlighting their suitability for early warning and real-time NH<sub>3</sub> monitoring.

Figs. 8(i–j) provide a direct comparison of the sensing response intensity ( $R_a/R_g$ ) as a function of ammonia concentration for ZnO and ZnO@P<sub>6</sub>, respectively. The ZnO@P<sub>6</sub> sensor displays a near-linear increase in sensor response at low concentrations (1–200 ppm) followed by saturation beyond 300 ppm with ammonia gas sensing response of 2860, reflecting efficient interaction and charge modulation at the sensor interface. In contrast, the pristine ZnO shows a lower sensitivity (800 ppm of ammonia with 609 response) and saturation from 500 to 800 ppm of ammonia gas, due to a limited number of adsorption-active sites and slower kinetics. Long-term stability, a critical factor for practical gas sensor deployment, is evaluated in Figs. 8(k–l). Both ZnO and ZnO@P<sub>6</sub> sensors were assessed over 60 days using 100 ppm ammonia. The pristine ZnO exhibits minor signal drift in both air and ammonia, indicating surface passivation or degradation. In contrast, ZnO@P<sub>6</sub> maintains a highly stable baseline and sensing response profile, demonstrating excellent repeatability and resistance to aging. This excellent stability is attributed to the plasma-treated surface's robustness and the sustainable defect-engineered interface, which resists contamination and degradation over time. These results confirm that DBD plasma treatment significantly enhances the ZnO thin film's sensitivity, selectivity, and stability toward ammonia gas. In particular, the ZnO@P<sub>6</sub> sample shows promise for real-time, low-level ammonia detection under ambient conditions, making it suitable for applications in environmental monitoring, industrial safety, and medical diagnostics.

Fig. 9 evaluates the sensing response and recovery behavior, humidity tolerance, and gas selectivity of ZnO and DBD plasma-treated ZnO sensors, providing key performance benchmarks for practical

ammonia sensing applications. In Fig. 9(a), the time-resolved sensing response ( $R_a/R_g$ ) to 100 ppm NH<sub>3</sub> shows a dramatic improvement in the dynamic sensing behavior after plasma treatment. ZnO@P<sub>6</sub> exhibits the highest and fastest sensing response of 700, followed by the response of 676 for ZnO@P<sub>4</sub> and 349 for ZnO@P<sub>2</sub>, while pristine ZnO displays the weakest and slowest response of 63. This hierarchy highlights the role of plasma-induced surface activation in facilitating rapid adsorption and charge transfer [48]. The time-domain resistance measurements for each sample in Figs. 9(b–e) further quantify response and recovery durations. ZnO@P<sub>6</sub> achieves a rapid response in just 6 s and recovers within 53 s, outperforming pristine ZnO, which requires 9 s to respond and 26 s to recover. The response times of ZnO@P<sub>2</sub> and ZnO@P<sub>4</sub> are similarly improved but slightly longer than ZnO@P<sub>6</sub>, reflecting the progressive enhancement with plasma duration. Fig. 9(f) consolidates the response and recovery time metrics, illustrating an inverse trend. While plasma treatment shortens the response time due to faster surface reactions, the recovery time increases slightly with plasma exposure.

The remarkably fast recovery of the ZnO@P<sub>6</sub> sensor at room temperature can be attributed to the synergistic effects of the DBD plasma treatment. Firstly, the plasma-treated surface, rich in oxygen vacancies and disorder, facilitates weaker binding of reaction products, as supported by the optimal NH<sub>3</sub> adsorption energy of  $-0.94$  eV calculated by DFT. This allows for easier desorption of N<sub>2</sub> and H<sub>2</sub>O. Secondly, the plasma-induced hydrophilic surface (Fig. 3e) and the confirmed presence of H<sub>2</sub>O (via FTIR in Fig. S6) promote a hydroxyl-assisted mechanism that cleanses the active sites. Finally, the narrowed bandgap and elevated Fermi level of ZnO@P<sub>6</sub> lower the energy barrier for electron transfer, significantly accelerating the re-adsorption of atmospheric oxygen molecules ( $O_2 + e^- \rightarrow O_2^-$ ) to restore the baseline. In summary,



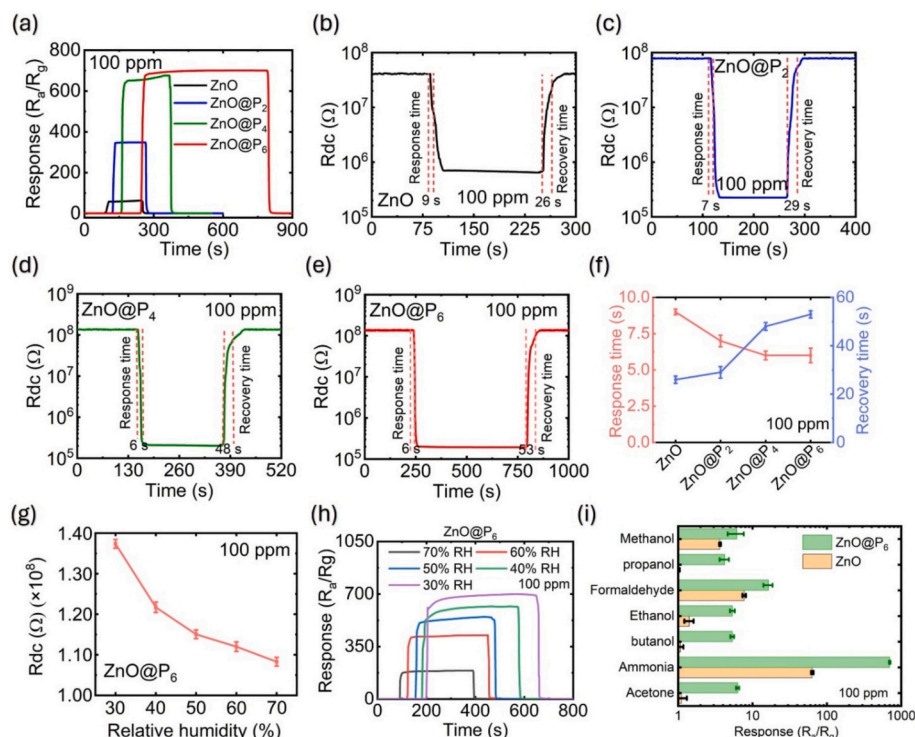
**Fig. 8.** Ammonia gas sensing performance of pristine and plasma-treated ZnO thin films. Time-dependent resistance ( $R_{dc}$ ) and sensing response ( $R_a/R_g$ ) of: (a, b) ZnO, (c, d) ZnO@P<sub>2</sub>, (e, f) ZnO@P<sub>4</sub>, and (g, h) ZnO@P<sub>6</sub> thin films upon exposure to NH<sub>3</sub>. Concentration-dependent sensing response of (i) ZnO and (j) ZnO@P<sub>6</sub> over 1–800 ppm NH<sub>3</sub>. Long-term stability of the sensors: (k) ZnO and (l) ZnO@P<sub>6</sub>, measured over 10–60 days at 100 ppm NH<sub>3</sub>.

the plasma treatment uniquely optimizes the surface for both efficient product desorption and rapid re-adsorption of oxygen, overcoming the typical kinetic limitations at room temperature.

The influence of humidity, a crucial parameter for real-world gas sensing applications [73], is analyzed in Figs. 9(g–h) and (Fig. S5) for ZnO@P<sub>6</sub>. As the relative humidity (RH) increases from 30% to 70%, a slight reduction in the baseline resistance ( $R_{dc}$ ) was observed, attributed to the adsorption of water molecules, which enhances the material's conductivity. Despite this variation, the sensor's response to NH<sub>3</sub> remains distinct and discernible across all humidity levels. The recorded responses to NH<sub>3</sub> at different RH levels of 30%, 40%, 50%, 60%, and 70% are 700, 617, 547, 424, and 189, respectively. These results demonstrate that ZnO@P<sub>6</sub> retains effective sensing capabilities under humid conditions, underscoring its suitability for reliable operation in ambient environments. The influence of humidity on ZnO@P<sub>6</sub> can be further understood mechanistically. At higher relative humidity, water molecules compete with NH<sub>3</sub> for adsorption on surface active sites, slightly reducing the number of NH<sub>3</sub> molecules that can interact with the sensor. Simultaneously, surface hydroxyl groups formed under humid conditions can mediate proton transfer, promoting partial NH<sub>3</sub> adsorption and redox reactions. This dual effect explains the observed reasonable decrease in sensing response at elevated RH, while the sensor retains effective NH<sub>3</sub> detection across 30–70% RH [74].

Selectivity, a vital criterion for gas sensor performance, is evaluated in Fig. 9(i) by exposing the sensors to various interfering gases (acetone, ammonia, butanol, ethanol, formaldehyde, propanol, and methanol) at

100 ppm. ZnO@P<sub>6</sub> demonstrates exceptional selectivity for ammonia, with a sensing response of 700, significantly higher than for other gases, attributed to strong interactions with surface oxygen species or defects, enhancing charge transfer [48,75]. In contrast, pristine ZnO shows minimal differentiation, with only a sensing response of 64 for ammonia, highlighting poor selectivity. The high selectivity of ZnO@P<sub>6</sub> toward NH<sub>3</sub> arises from its small kinetic diameter, electron-rich nature, and strong hydrogen-bonding ability, which enable efficient chemisorption and electron donation at plasma-engineered active sites [72,76]. The smaller kinetic diameter enables it to enter the small porous of the sample and hence interacts with the additional number of adsorbed oxygen ions, resulting in a high response. Other gases, such as butanol, propanol, ethanol, acetone, and formaldehyde, interact weakly due to their larger kinetic diameter, lower electron density, and weaker hydrogen-bonding capability, leading to significantly lower sensing responses [77]. These results confirm that DBD plasma treatment markedly enhances sensitivity, response time, humidity tolerance, and selectivity in ZnO@P<sub>6</sub>, making it a promising candidate for real-time, room-temperature ammonia detection in diverse environments. Table 2 presents a comparison of non-thermal plasma-treated ZnO-based gas sensors from the current study and previous works. It highlights key parameters such as fabrication methods, sensor performance, operating conditions, gas sensitivity, and response times. This comparison provides insights into the advancements in ZnO-based gas sensing technology, emphasizing the improvements achieved through non-thermal plasma treatment. It also displays the effectiveness of the current study's



**Fig. 9.** Ammonia sensing performance, response dynamics, humidity effect, and gas selectivity of pristine and plasma-treated ZnO thin films. (a) Comparison of sensing responses of ZnO, ZnO@P<sub>2</sub>, ZnO@P<sub>4</sub>, and ZnO@P<sub>6</sub> at 100 ppm NH<sub>3</sub>. Time-resolved response and recovery for (b) ZnO, (c) ZnO@P<sub>2</sub>, (d) ZnO@P<sub>4</sub>, and (e) ZnO@P<sub>6</sub>. (f) Comparison of response and recovery times for ZnO and ZnO@P<sub>6</sub> at 100 ppm NH<sub>3</sub>. Effect of relative humidity on ZnO@P<sub>6</sub>: (g) resistance and (h) sensing response at varying RH levels. (i) Gas selectivity of ZnO@P<sub>6</sub> toward acetone, ammonia, butanol, ethanol, formaldehyde, propanol, and methanol at 100 ppm, highlighting the most selective response to NH<sub>3</sub>.

**Table 2**

Comparison of non-thermal plasma-treated ZnO-based gas sensors in current and previous studies.

| Thin film type                  | Fabrication method                             | Plasma treatment type/time (min)             | Target gas                         | Operational temp. (°C) | Gas concentration (ppm)   | Response/sensitivity (%)                | Ref.      |
|---------------------------------|------------------------------------------------|----------------------------------------------|------------------------------------|------------------------|---------------------------|-----------------------------------------|-----------|
| ZnO                             | Sol-gel                                        | Oxygen plasma/8                              | NH <sub>3</sub>                    | RT                     | None specified            | 50% improvement over untreated          | [78]      |
| ZnO                             | DC reactive magnetron sputtering               | None specified                               | NH <sub>3</sub>                    | RT                     | 50*                       | 91                                      | [79]      |
| ZnO/Ag                          | Magnetron sputtering and annealing             | None                                         | NH <sub>3</sub>                    | 300                    | 300*<br>10#               | 61%<br>25%                              | [80]      |
| WO <sub>3</sub>                 | Atmospheric plasma spraying and heat treatment | Low-temperature argon plasma/ None specified | NO <sub>2</sub>                    | 95–240                 | 0–450                     | Enhanced sensitivity                    | [81]      |
| g-C <sub>3</sub> N <sub>4</sub> | Cd-probe deposition                            | Nitrogen plasma/ None specified              | H <sub>2</sub> S                   | Visible light exposure | 40–10,000 (pM level)      | Improved photocurrent response          | [82]      |
| Perovskite graphene             | Immobilization of perovskite on graphene       | Oxygen plasma/5                              | CO <sub>2</sub>                    | RT                     | 6.9                       | Threefold improvement                   | [83]      |
| Carbon nanowalls                | RF-PECVD                                       | Hydrogen plasma/ None specified              | H <sub>2</sub> and CH <sub>4</sub> | RT                     | 200*<br>1000#             | Enhanced gas adsorption and sensitivity | [84]      |
| SWCNT network                   | Spray deposition                               | Oxygen plasma/ None specified                | NH <sub>3</sub>                    | RT                     | 64*<br>4#                 | ≈ 3<br>≈ 2                              | [85]      |
| Fe-ZnO                          | Spin Coating                                   | None                                         | NH <sub>3</sub>                    | RT                     | 100                       | 294                                     | [73]      |
| ZnO                             |                                                | None                                         |                                    |                        | 800*<br>100<br>100<br>12# | 632<br>63<br>3                          |           |
| ZnO@P <sub>2</sub>              |                                                | Air DBD/2                                    | NH <sub>3</sub>                    | RT                     | 800*<br>100<br>6#         | 1517<br>349<br>2                        |           |
| ZnO@P <sub>4</sub>              | Spin coating                                   | Air DBD/4                                    |                                    |                        | 800*<br>100<br>1#         | 2437<br>676<br>2                        | This work |
| ZnO@P <sub>6</sub>              |                                                | Air DBD/6                                    |                                    |                        | 800*<br>100<br>1#         | 2925<br>700<br>2                        |           |

Note: Here, RT denotes room temperature and

\* denotes maximum analytical gas concentration, while

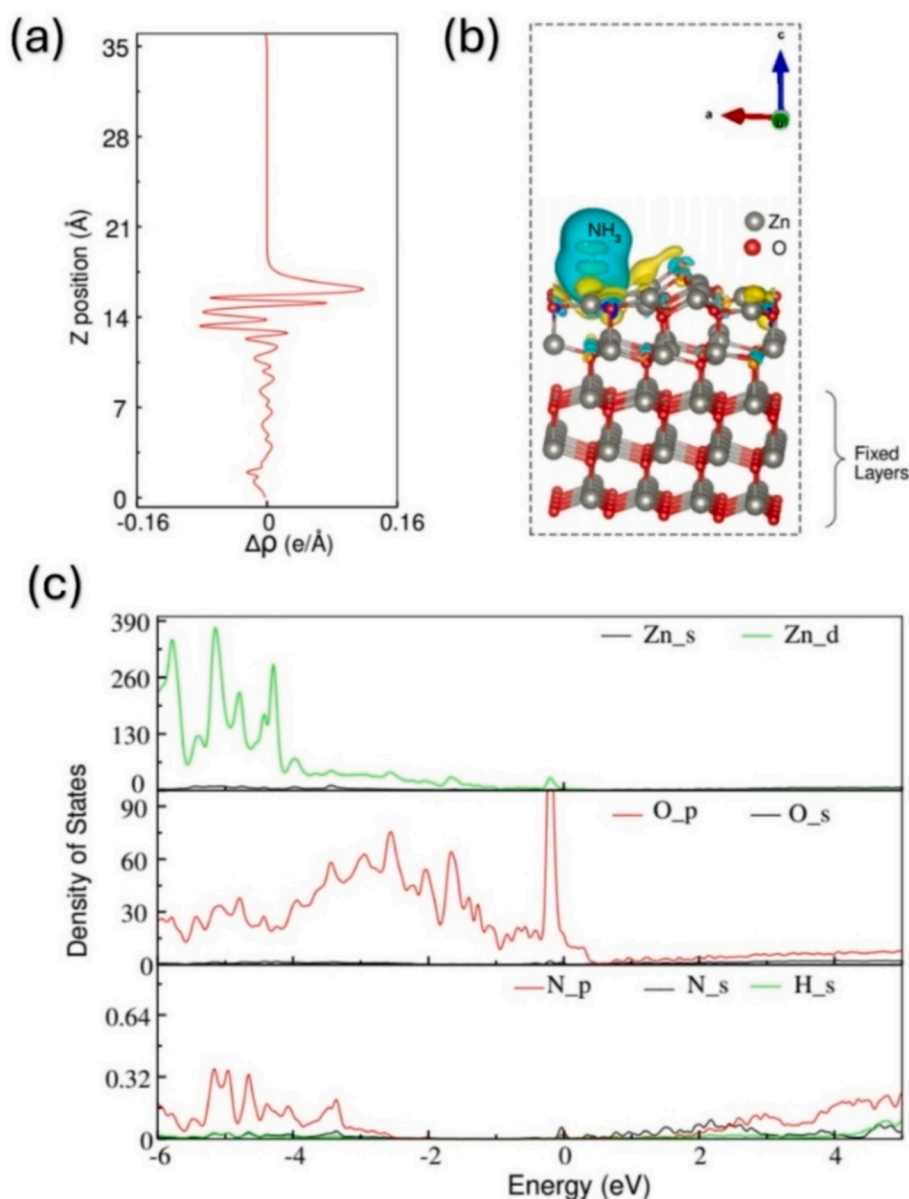
# signifies minimum analytical gas concentration.

sensors relative to earlier research, helping to identify trends and areas for further enhancement.

### 3.7. Orbital hybridization and electronic interactions driving $\text{NH}_3$ chemisorption on plasma-treated ZnO film

In the present study, the Zn-terminated polar surface of wurtzite ZnO (0001) is employed as a plasma-treated surface model to investigate the charge transfer and electronic properties. Among the various crystal facets of ZnO, the wurtzite polar facet exhibits one of the most favorable gas sensing properties due to its improved chemisorption ability and enhanced sensitivity toward target gas molecules [86]. The ZnO(0001) surface slab is constructed by cleaving the optimized bulk structure along the (0001) plane. The resulting surface model is then geometrically optimized while constraining the bottom three atomic layers to their bulk positions to preserve the bulk-like character of the substrate. Surface defects, including oxygen adatoms and oxygen vacancies, based on earlier works [87,88], are incorporated into the ZnO(0001) model to

design the plasma-treated surface. To investigate  $\text{NH}_3$  adsorption, the gas molecule is placed on the plasma-treated surface and allowed to undergo full geometric relaxation until the energetically most favorable adsorption site and configuration are achieved. The computed adsorption energy of  $-0.94$  eV for  $\text{NH}_3$ , calculated using Eq. (7), signifies strong chemisorption with favorable thermodynamics, confirming both the stability of the adsorbed state and the exothermic nature of the adsorption process. The relatively large magnitude of the adsorption energy ( $E_{\text{ads}} = -0.94$  eV), together with the substantial charge transfer revealed by the charge density difference and Bader analyses, provides a microscopic explanation for the enhanced sensing response after plasma treatment. Strong chemisorption of  $\text{NH}_3$  is expected to induce pronounced modulation of the surface depletion layer and charge carrier concentration, thereby leading to the experimentally observed increase in resistance response and improved detection characteristics. This result is comparable to the charge transfer mechanism examined by calculating the charge density difference ( $\Delta\rho$ ) and corresponding planar-averaged profile, which provides insight into the electronic



**Fig. 10.** Charge density distribution and PDOS of  $\text{NH}_3$  on plasma-treated ZnO thin film. The planar averaged differential (a) charge density and the charge density difference (b) ( $\Delta\rho = 0.003 \text{ e}/\text{\AA}^3$ ) calculated for the  $\text{NH}_3$ /plasma-treated Zn-terminated ZnO(0001) surface. (c) The PDOS of atomic species in  $\text{NH}_3$ /plasma-treated Zn-terminated ZnO(0001) surface.

redistribution occurring upon gas molecule adsorption on the surface. Figs. 10(a-b) shows the three-dimensional charge density difference plot, where yellow and cyan isosurfaces correspond to electron accumulation and depletion regions, respectively. Additionally, the planar averaged differential charge density confirms the charge accumulation and depletion, and activity happens on the surface region, highlighting the surface chemical activity. Bader charge analysis provides quantitative insight into the charge redistribution, showing that the nitrogen atom of  $\text{NH}_3$  gains  $0.65 e^-$ , the hydrogen atoms collectively transfer  $0.30 e^-$ , while the surface zinc atom gain approximately  $0.85 e^-$  upon adsorption.

The orbital contributions of constituent atomic species in the  $\text{NH}_3/\text{plasma-treated surface system}$  were investigated through PDOS analysis, which provides insight into the electronic interactions at the molecular level. From the PDOS analysis within the vicinity of the Fermi level, Fig. 10(c), it is evident that Zn  $d$  orbitals contribute significantly to the energy range of  $-6 \text{ eV}$  to  $-4 \text{ eV}$ , while O  $p$  orbitals contribute strongly near the Fermi level at the valence band maximum (VBM). The  $\text{NH}_3$  molecular orbitals are present near both the conduction band minimum (CBM) and VBM, indicating orbital hybridization and electronic coupling between  $\text{NH}_3$  and the ZnO surface states. This electronic interaction supports pronounced chemisorption on the plasma-modified surface and aligns with the experimentally observed enhancements in selectivity and sensor response. It is worth noting that similar results have been reported for oxygen plasma treatment, enhancing the gas-sensing performance of ZnO toward  $N$ -methyl pyrrolidone [48], underscoring the general effectiveness of plasma-engineered ZnO

surfaces for improving sensor sensitivity and selectivity across diverse analytes [89].

### 3.8. Ammonia gas sensing mechanism

The ammonia sensing mechanism of pristine ZnO and DBD plasma-treated ZnO ( $\text{ZnO@P}_6$ ) thin films is illustrated in Fig. 11, revealing the interplay of gas adsorption, surface redox reactions, charge carrier modulation, and depletion layer dynamics. In ambient conditions, oxygen molecules adsorb onto the ZnO surface and are chemisorbed by extracting electrons from the conduction band (CB), leading to the formation of negatively charged oxygen species ( $\text{O}_2^-$ ,  $\text{O}^-$ ,  $\text{O}^{2-}$ ) via the reactions in Eqs. (21–23) [78,80,90,91]:



The type of oxygen ion adsorption is temperature-dependent [73,92]. Below  $200^\circ\text{C}$ ,  $\text{O}_2^-$  species are adsorbed, while  $\text{O}^-$  or  $\text{O}^{2-}$  species dominate at higher temperatures. In this study, gas sensing measurements were conducted at room temperature; therefore,  $\text{O}_2^-$  adsorption is considered. This process induces the formation of a surface depletion layer in the n-type ZnO semiconductor, reducing free carrier concentration and thereby increasing the film's resistance. Upon exposure to reducing gases like ammonia ( $\text{NH}_3$ ), these adsorbed oxygen

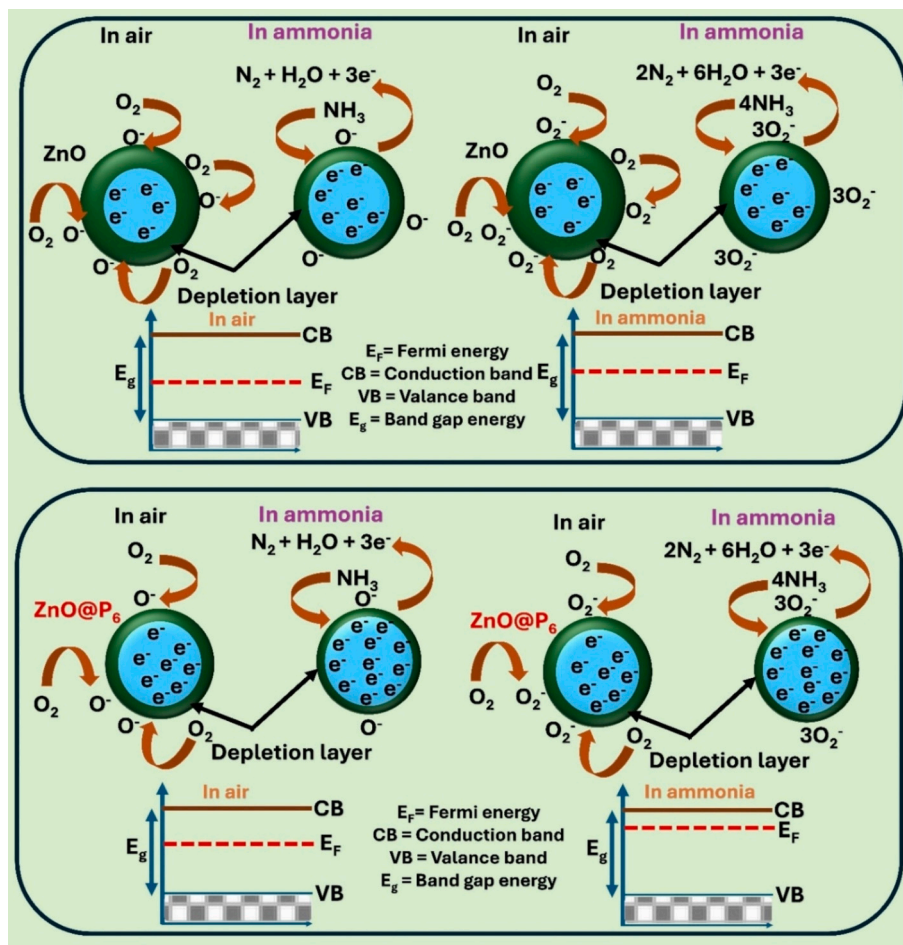
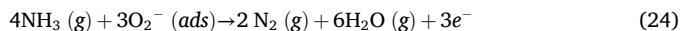


Fig. 11. Proposed gas sensing mechanism of ZnO and DBD plasma-treated ZnO thin films showing the ammonia detection process involving adsorption, charge transfer, conductivity modulation, desorption, and enhanced sensitivity due to DBD plasma treatment.

species engage in redox reactions with  $\text{NH}_3$ , resulting in the release of electrons back into the conduction band and a consequent reduction in resistance. The primary reactions can be represented as Eq. (24) [78,80,91].



Nitrogen doping from DBD plasma also plays a critical role in tuning the electronic properties of ZnO and enhancing its gas-sensing performance. The incorporation of nitrogen introduces defect-related states and acceptor-like levels near the valence band, leading to modified carrier concentration and increased electronic disorder. These N-related defects facilitate efficient charge transfer between the adsorbed  $\text{NH}_3$  molecules and the ZnO surface, thereby amplifying the modulation of the surface depletion layer during gas exposure. Furthermore, the coexistence of nitrogen dopants and plasma-induced oxygen vacancies creates synergistic active sites that promote stronger gas adsorption and faster surface redox reactions. As a result, N-doped ZnO exhibits enhanced sensitivity, faster response kinetics, and improved selectivity toward  $\text{NH}_3$  at room temperature. The results obtained are consistent with previously reported literature [93–95].

Fig. S6 presents the in situ FTIR spectra of the exhaust gas collected from the sensor chamber under an inlet concentration of about 1000 ppm  $\text{NH}_3$ , measured in the presence and absence of the  $\text{ZnO@P}_6$  thin film. To transport efficiently the reacted gas from the sensor chamber to the FTIR gas cell, an Ar carrier flow between 100 sccm was applied; within this range, stable gas displacement is ensured without diluting the  $\text{NH}_3$  signal beyond the FTIR detection capability. Without the  $\text{ZnO@P}_6$  film, only two characteristic  $\text{NH}_3$  absorption bands appeared at  $3333\text{ cm}^{-1}$  and  $1625\text{ cm}^{-1}$ . With the introduction of the  $\text{ZnO@P}_6$  film, these two  $\text{NH}_3$  bands were significantly reduced in intensity, and a new absorption band representing  $\text{H}_2\text{O}$  appeared at  $3708\text{ cm}^{-1}$ . The concurrent attenuation of the  $\text{NH}_3$  features and emergence of the  $\text{H}_2\text{O}$  band constitute direct proof of the oxidation of  $\text{NH}_3$  on the  $\text{ZnO@P}_6$  sensor surface at room temperature, consistent with the reaction pathway suggested in Eq. (24). Additionally, the reversible decrease in sensor resistance observed in Figs. 8 (a, c, e, and g) corresponds to electron injection into the ZnO conduction band, which is expected during the  $\text{NH}_3$  surface redox process. These, in-situ FTIR results and the electrical response behavior thus jointly confirm strongly and self-consistently the ammonia oxidation mechanism operating on the ZnO-based sensor.

In the case of DBD plasma-treated ZnO ( $\text{ZnO@P}_6$ ), the enhanced performance can be attributed to the synergistic effect of increased oxygen vacancy ( $V_{\text{O}}$ ) concentration, surface disorder, and improved surface roughness resulting from plasma-induced surface engineering [48,95]. Plasma treatment increases the number of adsorption sites, enabling a higher density of reactive oxygen species to be chemisorbed. As shown in the energy band diagrams in Fig. 11 [96,97], the plasma-treated ZnO demonstrates a slightly elevated Fermi level ( $E_{\text{F}}$ ) and a narrower bandgap ( $E_{\text{g}}$ ), which lowers the energy barrier for electron transport and enhances charge transfer efficiency. The presence of additional  $V_{\text{O}}$  sites and surface hydroxylation further accelerates the redox reaction kinetics between  $\text{NH}_3$  and surface oxygen species [98]. The cumulative result is a more pronounced and rapid modulation of resistance upon ammonia exposure, with significantly faster response and recovery times. This optimized surface state in  $\text{ZnO@P}_6$  yields higher sensitivity and selectivity toward  $\text{NH}_3$ , even at low concentrations, establishing the efficacy of DBD plasma surface modification for next-generation room-temperature gas sensors.

#### 4. Conclusion

DBD plasma treatment is demonstrated as an effective strategy for defect engineering of ZnO thin films, enabling enhanced physicochemical properties and improved room-temperature  $\text{NH}_3$  sensing performance. Plasma diagnostics confirm the presence of a non-thermal reactive environment that facilitates controlled surface modification

without compromising the ZnO lattice structure. The optimized  $\text{ZnO@P}_6$  film exhibits refined microstructural features and a higher density of surface defects, which promote adsorption and charge-transfer processes essential for gas sensing. As a result, the sensor shows high sensitivity, rapid response and recovery, strong selectivity toward ammonia, and stable operation under varying humidity conditions. Density functional theory calculations further support the experimental findings by revealing strong  $\text{NH}_3$  chemisorption and effective charge redistribution at the plasma-modified ZnO surface, confirming the role of defect-induced active sites in enhancing sensing behavior. These combined experimental and theoretical insights establish a clear structure–defect–performance relationship governing the sensing mechanism. Despite these promising outcomes, several challenges remain, including improving selectivity in complex gas environments, ensuring long-term stability of plasma-induced defects, and achieving scalable and reproducible plasma processing for practical deployment. Future research should therefore focus on selectivity engineering, optimization of plasma parameters, and integration of plasma-treated ZnO films into miniaturized and portable sensing platforms, followed by validation under real environmental and industrial conditions. Overall, this work highlights DBD plasma surface engineering as a scalable, low-temperature approach for tailoring ZnO thin films and advancing next-generation room-temperature sensors for environmental monitoring, industrial safety, and healthcare applications.

#### CRediT authorship contribution statement

**Tirtha Raj Acharya:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization, Supervision. **Rajesh Shrestha:** Visualization, Methodology, Investigation, Data curation. **Prajwal Lamichhane:** Visualization, Methodology, Investigation, Data curation. **Shambhu Bhandari Sharma:** Writing – review & editing, Methodology, Investigation, Data curation. **Roshan Chalise:** Visualization, Methodology, Funding acquisition, Data curation. **Keshav Raj Chapagain:** Visualization, Methodology, Data curation. **Dario Alfè:** Writing – review & editing, Visualization. **Dinesh Kumar Chaudhary:** Writing – review & editing, Validation, Methodology, Data curation, Conceptualization.

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#### Declaration of competing interest

The authors affirm that there are no known competing commercial interests or personal relationships that could have influenced the findings presented in this paper.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.175514>.

#### Data availability

Data will be made available on request.

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