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Comparison of Thermal Annealing vs Hydrothermal Treatment Effects on the Detection Performances of ZnO Nanowires

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ABSTRACT

A comparative investigation of the post-electroplating treatment influence on the gas detecting performances of single ZnO nanorod/nanowire (NR/NW), as grown by electrochemical deposition (ECD) and integrated into nanosensor devices, is presented. In this work, hydrothermal treatment (HT) in H_2O steam and conventional thermal annealing (CTA) in a furnace at 150 °C in ambient were used as post-growth treatments to improve the material properties. Herein, the morphological, optical, chemical, structural, vibrational, and gas sensing performances of the as-electrodeposited and treated specimens are investigated and presented in detail. By varying the growth temperature and type of post-growth treatment, the morphology is maintained, whereas the optical and structural properties show increased sample crystallization. It is shown that HT in H_2O vapors affects the optical and vibrational properties of the material. After investigation of nanodevices based on single ZnO NR/NWs, it was observed that higher temperature during the synthesis results in a higher gas response to H_2 gas within the investigated operating temperature range from 25 °C to 150 °C. CTA and HT or autoclave treatment showed the capability of a further increase in gas response of the prepared sensors by a factor of ~8. Density functional theory (DFT) calculations reveal structural and electronic band changes in ZnO surfaces as a result of strong interaction with H_2 gas molecules. Our results demonstrate that high-performance devices can be obtained with high-crystallinity NWs/NRs after HT. The obtained devices could be key element for flexible nanoelectronics, wearable electronics and have attracted a great interest due to its unique specifications.

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1. INTRODUCTION

Quasi-one-dimensional (Q-1D) micro- and nano-structures, like wires, rods, fibers and tubes of metal oxides are key elements for nanoelectronics, especially for flexible or wearable electronics, including nanosensors, and have attracted a great interest in research of high-performance devices with unique specifications.[1] ZnO Q-1D nanostructures are investigated due to their immense application potential,[1] e.g. optoelectronic microdevices or even flexible nanoelectronics,[2,3] gas nanosensors,[2] light emitting diodes,[4] transistors, etc. [5]

Different techniques have been engaged to fabricate ZnO NWs/NRs, including chemical and physical methods,[6] as well as various other methods that have been employed to enhance the gas sensing properties. For example, Drobek *et al.* reported on a general methodology for improving the selectivity of semiconductor metal oxides nanowires sensors, based on the coverage of ZnO nanowires with a thin molecular sieve membrane, Weber *et al*. reported a synergy effect of Pd nanoparticles with other nanomaterials.[7-10] Among the wide range of techniques, electrochemical deposition (ECD) has become an advantageous technique for the synthesis of ZnO Q-1D structures, being cost-efficient and having a possibility of large-area deposition of structures with excellent optical properties. Furthermore, NWs/NRs can be deposited at lower temperatures compared to various techniques.[6] ECD method also allows the efficient doping of ZnO NWs/NRs with a diversity of ion metals, namely Cd, Eu, Ag, Cu, Cl, Al, etc.[2,11,12] Recently, the one-step surface doping and functionalization with Pd and Au nanoparticles was achieved by ECD method.[13,14] Based on individual nano- and microstructures grown by ECD method, such as Ag-doped ZnO NW, Au-modified NW, Pd-modified ZnO NW, high performance nanosensors for the detection of H_2 gas in the 25 – 150 °C operating temperature range were developed.[2,13,14] For example, by Al-doping of ZnO NWs it is possible to detect volatile organic compounds at room

temperature with excellent longterm stability.[15] Another advantage of ECD method is the possible synthesis of ZnO NWs on flexible substrates,[16] which is important for application in flexible and wearable electronics, including gas sensors and UV photodetectors.[17,18]

While the doping and surface functionalization effects on ultraviolet light and gas detecting performances of single ZnO NRs/NWs obtained by ECD method have been studied extensively, less attention has been given on the influence of post-deposition thermal treatments. Previous works revealed that thermal treatment of ZnO NWs has an essential influence on structural and optical properties of the samples.[19,20] However, conventional thermal annealing (CTA) could not be realized on flexible or other substrates for wearable electronics or else, which cannot survive at high temperatures (>200°C) due to melting, contamination or deterioration processes.

Thus, a thorough comparison of the influence of post-synthesis temperature treatments, like hydrothermal treatment (HT), autoclave treatment (AUT) or CTA in different ambient (air or in water vapor steam ambient) is essential. Specifically, their effects on the structural, electronic and gas sensing properties of electrodeposited ZnO NWs/NRs grown from a chloride medium need to be investigated.[16,19] The post-growth thermal annealing in air and hydrothermal treatment in water vapor ambient are important methods for improving the quality of the ECD ZnO NWs/NRs and changing their surface properties.[19] As the sensing properties of individual nanostructures with high surface-to-volume ratio are highly dependent on the surface properties,[2] the stabilizing effect for future devices on flexible substrates is expected.

The ZnO NR/NW arrays studied in the present work, were grown by ECD followed by post-growth HT in H_2O vapor and CTA in normal ambient at the same temperatures and durations for the sake of a comparative study.[20] The structural, chemical, vibrational, optical, and sensor performances of the as-electroplated and treated samples were investigated in

detail. The individual ZnO NRs/NWs were incorporated into micro-devices employing focused ion beam/scanning electron microscopy (FIB/SEM) equipment. The gas and UV detection measurements demonstrated that the performances of the fabricated devices could be significantly improved by increasing the electrodeposition temperature, as well as by the post-growth treatment, especially by HT with a water steam at 150 °C for 12 h. The results obtained in this research represent a meaningful step forward for the elaboration of higher-performance gas sensor devices based on a single ZnO NR/NW for flexible nanoelectronics.

2. EXPERIMENTAL DETAILS

2.1. Electroplating

ZnO NR/NW arrays were grown by the electrodeposition approach from a 0.20 mM $ZnCl_2$ (Merck, 99.0%, CAS- 7646-85-7) solution in H_2O hold at 70°C, then increased with a step of 10 °C/specimen up to 90°C, as reported elsewhere.[16,19-21] 0.1 M of KCl (Sigma-Aldrich, 99.5%, CAS- 7447-40-7) was accessed as an additive, to confirm a reliable electrical conductivity in the H_2O – based electrolyte.[19] Based on reports on the synthesis of ZnO by electrodeposition, the chloride content is always higher (> ~22 times) than the zinc content in the ECD solution. [16,19-21] The ZnO NRs/NWs were electrodeposited on a glass substrate having a conductive fluorine-tin-oxide (FTO) layer on top (sheet resistance of 10 Ω/□).[2,13,21,22] The FTO/glass was employed as the working electrode (WE) in a classical 3 electrode setup for electrodeposition of ZnO NRs/NWs. [16,19-21] Before ECD, the FTO substrates were cleaned in an ultrasonic bath first with acetone (100%, CAS-67-64-1), then C_2H_5OH (100%, CAS-64-17-5) for 5 min each and rinsed afterwards with deionized H_2O (18.22 MΩ·cm) for 10 s. [16,19-21] The substrates with FTO layer were dipped in HNO_3 (45%, diluted from 68%, CAS-7697-37-2) for 60 s and also rinsed with deionized H_2O in the ultrasonic bath for 5 min.[19] The

cleaned substrate with FTO layer was attached to a rotating working electrode.[19] The reference electrode was mounted in a separated cell arm-tube at room temperature as reported in previous works.[15,19,23] The counter electrode (CE) used during the electrodeposition was a platinum (Pt) spiral-wire.[19] The ECD process was done at –1.0 V controlled with an Autolab PGSTAT30a galvanostat/potentiostat,[19] controlled by the AutoLabsoftware. The WE was rotated constantly with a speed ω=300 rev/min.[19] The pH-value of the ECD bath in the beginning was around 5.50. [15,19,23] The ECD cell was introduced in a larger second bath with thermoregulation and kept constant at 70°C, 80°C or 90°C,[24] with an uncertainty of ± 0.2 °C for three different experiments, respectively.[21] The electrolyte was saturated with extra pure O_2 for 50 min prior and during the ECD. [25] The ECD for the syntheses of ZnO NR/NW arrays on FTO was stopped when the passed electrical charge during synthesis was about 15.4 C·cm^{-2} at 70 °C, 14.3 C·cm^{-2} at 80 °C and 11.2 C·cm^{-2} .[25]

The main physicochemical reactions during the cathodic zinc oxide NR/NW array growth in an aqueous $ZnCl_2$ solution can be described as followed: [19]

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad E^o = 0.4V / NHE \qquad (1)$$

The oxygen reduction reaction in electrochemical process proceeds:[26,27]

$$Zn^{2+} + 2(OH)^- + 4e^- \rightarrow Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O \qquad E^o = 0.4V / NHE \qquad (2)$$

ZnO NRs/NWs are grown as following:[19,28]

$$Zn^{2+} + \frac{1}{2}O_2 + 2e^- \rightarrow ZnO \qquad E^o = 0.93V / NHE \qquad (3)$$

The ZnO NWs/NRs were ECD on FTO at –1.0 V, and the changes with time of electrical current density (*j*) was saved in AutoLab software.[19] **Figure S1** represents the time dependent changes of electrical current density for electrodeposition of ZnO NWs/NRs at several different temperatures. The illustrated curves indicate clearly that the ECD ZnO NR/NW are electrical conductors, due to the electrical current densities collected at the electrode that are maintained at necessary values. [19] Steady state current densities of pure zinc oxide NRs/NWs are about 1.9 (at 70 °C), 1.8 (at 80 °C) and 1.2 $mA \cdot cm^{-2}$ (at 90 °C) after 3000 seconds of ECD. **Figure S2** shows the cyclic voltammograms on FTO substrates for specimens grown at 70 °C and 80 °C measured with a scanning rate of 11 $mV \cdot s^{-1}$.[11] The cathodic wave started at about − 850 mV vs a saturated calomel electrode (SCE). The maximum current density was about 1.13 mA/cm^2 at − 1.29 V vs SCE for specimens grown at 70 °C and 1.26 mA/cm^2 at − 1.29 V vs SCE at 80 °C. This peak can be designated to the electrochemical reduction of molecular oxygen.[11,25] The small hysteresis, observed in both cases can be described by large coverage on the FTO surface/substrate with zinc oxide NRs/NWs upon the forward scan.[11,25]

After the ECD process, the prepared ZnO NRs/NWs were first dipped with DI-H_2O to clean the sample from chloride salts and other unwanted species and then cut into three equal parts.[21] Whereas one part was used as the reference specimen, the other two parts were heat treated using CTA and HT at 150°C in air for 12 h and post-growth hydrothermal treatment at 150 °C, 12 h, in water steam ambient, respectively.[19,20] The hydrothermal treatment HT was performed at 150°C in a stainless steel autoclave with an inner liner of 100 mL made from Teflon.[16] To exclude the direct contact of ZnO NWs/NRs with water, the sample was fixed at about 3.5 cm above the DI H_2O surface.[16] Thus, to evaluate the influence of CTA and HT on the ZnO NWs/NRs three sample sets of each were prepared in the same conditions.

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2.2. Characterization of electrochemically prepared ZnO NWs/NRs and fabrication of gas nanosensors

Details of the experimental procedures, as well as samples characterization methods can be found in previous reports.[11,19,21,29,30] To investigate the effect of HT and CTA on the gas sensing performances of samples, the prepared nano- and microstructures were integrated into nanodevices. The procedure of nanodevice fabrication using FIB/SEM equipment can be found elsewhere (see references).[2,13] According to this technique up to eight individual nano- and microstructures of different oxides and other materials with diameter down to 20-30 nm can be integrated in one device consisting of a specially designed chip based on a SiO_x/Si 800 nm substrate with pre-patterned Au/Cr contacts.[14] The individual structures were contacted with Au pre-pads using the electron beam maskless Pt complex nanodeposition in a dual beams FIB/SEM instrument to avoid Ga implantation or Ga milling when using Ga for Pt complex deposition exposing only edges of NWs for shorter time. Using dual beam FEI (5.0 kV, 0.175 nA),[2] the Au/Pt/ZnO/Pt/Au structures with two contacts were formed. This makes the ZnO NW-based nanodevices presented below feasible. The electrical and gas detection measurements were realized as reported elsewhere. [2,13]

2.3. Computational Details

Computational studies are performed using the DFT and its generalized gradient approximation (GGA). The Perdue–Burke–Ernzerhof (PBE)[31] exchange–correlation functional and the projected augmented wave (PAW)[32,33] approach was used through its implementation in the Vienna *ab initio* Simulation Package (VASP).[34] Using the conjugate gradient method,[35] the bulk structure of ZnO was fully optimized till the maximum residual force acting on each atom becomes < 0.00010 eV/Å. The energy convergence criterion used is

$1 \cdot 10^{-7}$ eV/cell having a plane wave cutoff energy of 520 eV. For modelling the bulk ZnO structure, 5 × 5 × 4 Monkhorst-Pack *k* points were used,[36] while surfaces are computed using the 4 × 4 × 1 Monkhorst-Pack *k* points. For the determination of the Methfessel–Paxton smearing scheme partial occupancies with smearing width of 0.10 eV were used. A vacuum space of 20.0 Å was involved to avoid any interaction with a ZnO (0001)/ZnO ($10\bar{1}0$) surface and its periodically repeated images along the *c* axis. Surface energies were calculated using a combination of calculations for the relaxed and unrelaxed surfaces. Here, the Coulomb effect (U) for the localized 3d electrons of metal atoms were investigated and a negligible effect on the results was obtained, hence this is not incorporated in the calculations.

The DFT- D2 approach as expressed by Grimme[37] was involved to incorporate the long-range dispersion corrections while investigating gas molecule interactions. The adsorption energy of a gas molecule was computed following the:

$$E_{ads} = E_{surf+mol} - (E_{surf} + E_{mol}) \quad (4)$$

where $E_{complex}$ - total energy of the surface with molecule, $E_{surface}$ - energy of the surface slab without molecule, and $E_{molecule}$ - energy of the isolated molecule. $E_{molecule}$, was calculated by modelling the isolated molecule in the center of a broken symmetry cell with lattice constants of 20 Å, inspecting only the Gamma-point of the Brillouin zone with the same truthfulness specification as construe for the surfaces.

3. RESULTS AND DISCUSSION

3.1. Characterization of structure and morphology characteristics of ZnO NRs/ NWs

Figure 1a illustrates the XRD diffractograms of as-electrodeposited ZnO samples at 70, 80 and 90 °C, while **Figure 1b** exhibits the XRD diffractograms of ZnO samples

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electrodeposited at 70 °C and treated by AUT and CTA at 150 °C. The peaks which originate from the SnO_2 substrate (according to the PDF 01-077-0488 card [19]) were marked with red dots. The detected reflection with highest intensity is at 2θ values of 34.43°, which correspond to the lattice (002) plane. Other reflections with significantly lower intensity were detected at 31.8°, 36.2°, 47.5°, 56.7°, and 62.8° corresponding to the (100), (101), (102), (110) and (103) lattice planes, respectively. The obtained results show that ZnO NWs/NRs grow with a (002)-preferred direction, i.e. nanowire arrays have the excellent overall *c*-axis alignment arrays over the large FTO substrate area.

From **Figure 1b** it can be observed that after AUT and CTA treatment at 150 °C the intensity of the peak corresponding to the (002)-plane remains with higher intensity in comparison to the other peaks, demonstrating that post-growth thermal treatment does not induce changes in orientation of ZnO NWs/NRs in the *c*-axis. The full width at half-maximum (FWHM) values of the (002) peak of oxide NWs/NRs arrays on FTO substrate are 0.1248°, 0.0936° and 0.0930° (see **Figure 1b**) for the samples as-deposited, after CTA and AUT at 150°C, respectively. These low values of FWHM widths indicate a high crystallinity of the electrodeposited material, even at lower temperature of 70 °C, which can be further improved by HT or CTA treatment.[19] **Figure S3** shows crystallinity of ECD ZnO NWs before and after post growth-treatments.

SEM investigations were involved to characterize the morphology of the as-electrodeposited NWs/NRs and the influence of HT and CTA treatment (see **Figure 2**). The aspect ratio of ZnO NWs/NRs were not changed essentially after annealing, following recent results on ZnO samples synthesized by ECD method.[19] According to the top view and the cross-section (see **Figure 2**) a diameter of 70-100 nm was estimated. For samples electrodeposited at 70 °C the average diameter (*D*) of ~ 100 nm is the same over the entire

surface having uniformity and a fully covered surface. The length of NRs is ~ 1 μm with clearly observable hexagonal end planes. No significant changes in morphology after CTA or HT treatments at 150 °C were observed. However, after the HT treatment smoother surfaces of the NRs were observed, the NRs grown at 80 °C are thinner in diameter than those grown at 70 °C, with a diameter of D ~ 70 - 90 nm, and a length of ~ 2 μm. Also, for these samples, the average NR-diameter was almost similar across the entire surface. It can be observed that the nanowires are quasi-aligned (see **Figure 2**). For specimens grown at 90 °C, the ZnO NWs/NRs with a wider range of diameters is found. The individual diameters of these structures are non-uniform, varying between 70 - 200 nm, while the average length is about ~ 3 μm. In **Figure 2** an influence of the growth rate is observed showing an increasing rate for samples electrodeposited at 70 °C to 80 °C and 90 °C; even though the electrical current density is the highest for samples deposited at 70 °C. Furthermore, the HT-treatment does not cause any significant changes, which is in accordance with the above reported XRD results. However, after the post-growth HT at 150 °C for 12 h in water vapors or steam, the lateral facets become smoother (see **Figure 2f**).

Transmission electron microscopy (TEM) was operated to find the properties of structure for the as-electrodeposited zinc oxide NRs/NWs, in conjunction with study of the HT and CTA treatments influence. **Figure 3** reports typical TEM and high-resolution TEM (HRTEM) images presenting the general morphology of the electrodeposited ZnO NRs-nanorods grown at 70, 80 and 90 °C. Nanorods grown at 70 °C (see **Figure 3a**) have a diameter of about 100 nm and are 1.3 μm in length. It is also important to note that the diameter varies along the nanorod length (see **Figure 3a**). This phenomenon is less manifested for the nanorods grown at 80 °C. According to our observations, the TEM images (see **Figure 3b**) show that the diameter is uniform from one nanorod to another for the same

sample electrodeposited at 80 °C. The tip of the NR is round-shaped with about 10 nm radius, as presented in **Figures 3a, 3b**. In the case of samples electrodeposited at 90 °C (see **Figure 3c**) a larger diameter of 100 – 200 nm was observed. The atomic arrangements of the ZnO nanorods are seen in **Figure 3d-f**, showing that ZnO NWs/NRs grown along the [0001] direction, which is in concordance with XRD data.[38] The calculated distance between ZnO (0001) fringes perpendicular is 0.26 nm.[38] Also, it confirms that the NRs have a single crystalline structure in the investigated area. The obtained results confirm that the zinc oxide NRs/NWs are well-crystalline and possess a hexagonal crystal lattice.

Typical selected area electron diffraction (SAED) patterns of ZnO NRs/NWs electrodeposited at 70°C, 80°C and 90°C are presented in **Figure 3g-i**. Independent of the electrodeposition temperature the ZnO NRs/NWs are single-crystalline with distinct diffraction spots, and, to a smaller extent, nanocrystalline with diffuse diffraction rings.[39]

3.2. Chemical characterizations (EDX and XPS)

For a characterization of the chemical composition of ZnO NRs/NWs, energy dispersive x-ray spectroscopy (EDX) analysis at the TEM was performed. **Figure S4** represents the EDX spectrum of individual ZnO NW scratched from the electrodeposited material on the FTO substrate. Here, peaks of the two essential constituent's Zn and O in the zinc oxide nanorod/nanowire can be distinguished, as well as peaks of C and Cu originating from the holey carbon film and the copper TEM grid. No evidence of other impurities was found in the EDX spectrum.

X-ray photoelectron spectroscopy (XPS) were done to observe the chemical characteristics of electrodeposited ZnO nanomaterial in chloride medium in more detail, as well as the effect of AUT and CTA post-growth treatment. The adventitious carbon peak (C-1s) at 285.0 eV was used as a reference in order to calibrate the binding energy.[19] Because all

samples were maintained in air before measurements, the presence of residual quantities of adventitious carbon/carbonyl conglomerate are inevitable.[19,40]

XPS survey spectra are demonstrated in **Figure S5**, from which the following elements were detected: O, Zn, C (adventitious), and Sn. The Sn signal originates from the FTO substrate. The low intensity peaks detected at ~ 230 eV and ~ 400 eV for as-grown sample at 70 °C can be attributed to Mo-3p and Mo-3d core levels, respectively, which can originate from the partially exposed sample holder.[20] No other elements from the electrodeposition bath were detected. **Figure S5b-d** presents high-resolution XPS spectra of (b) Cl-2p; (c) Sn-3d and (b) C-1s core level regions. **Figure 4** presents XPS spectra of the core level regions for (a) Zn-2p and (b) O-1s of the synthesized samples. The ZnO NRs/NWs display a doublet at 1021.71 eV and 1044.81 eV which can be associated with the core levels Zn-$2p_{3/2}$ and Zn-$2p_{1/2}$ of ZnO (see **Figure 4a**).[19] These binding energy (BE) values are in agreement with previously prepared pure ZnO samples from our group. [29,41-43] The presence of residual Cl compounds from our preparation method was discarded based on XPS measurements from the Cl-2p BE region (**Figure S5b**), in agreement with previous works.[19,44] I.e., no detectable amounts of Cl were observed in our XPS measurements, which are in accordance with EDX studies performed from a single ZnO NW in TEM. The asymmetric peak detected in the region of O-1s, **Figure 4b**, was deconvoluted by sub-spectral components including (i) stoichiometric ZnO (530.2 eV), (ii) defective ZnO_x (531.6 eV), (iii) adventitious CO (531.1 eV),[45] and (iv) adventitious CO_2 (532.5 eV).[46-48] The relative content of each compound is shown in **Table 1**. The $ZnO_x(OH)_y$ stoichiometry was considered using the intensity ratios of O-1s/Zn-2p peaks.[19,49]

The peak detected in the O-1s region is asymmetric (see **Figure 4b)** and thus deconvoluted by 4 components: (i) stoichiometric ZnO (530.20 eV), (ii) defective ZnO_x (531.60 eV), (iii) adventitious CO (531.10 eV),[45] and (iv) adventitious CO_2 (532.50 eV).[46,47]

Table 1 illustrate the relative content of each compound extracted from the fittings. Zordan *et al*.[49] and Jiazhong *et al*.[50] detected similar components in their O-1s spectra and assigned the high BE peak (531.6 eV) to Zn-OH species. Because of their O-1s/Zn-2p ratios, the stoichiometry of $ZnO_x(OH)_y$ have been proposed.[49] The 531.6 eV component found in investigated specimens may be assigned to $ZnO_x(OH)_y$. Furthermore, it is reported that ZnO_x defective is reduced after HT.[49] The XPS spectra of CTA samples was presented in the previous work and showed the similar effect and spectral features.[19]

3.3. Micro Raman scattering

Figure 5 illustrates the micro-Raman spectra of the ZnO NRs/NWs electroplated on FTO recorded at room temperature. For all samples, the presence of high intensity vibrations at 440 and 100.1 cm^{-1} is characteristic, corresponding to E_{2high} and E_{2low} modes, accordingly. The broad peaks marked with red dots can be attributed to FTO substrate.[19] The presence of weak peak at 410.1 cm^{-1} corresponds to an E_{1TO} mode.[51] Because the Raman selection rules predict that TO modes are forbidden in the case of incident light parallel to the *c* axis of ZnO NWs/NRs, the presence of E_{1TO} mode can suggest that not all structures are oriented perpendicular to the substrate.[51] Therefore, it could be suggested that ZnO NWs/NRs are quasi-*c*-axis oriented, which is in conformity with previous SEM and XRD results.[52] An increase in intensity of the E_{2high} and E_{2low} modes, a characteristic for the wurtzite lattice, is caused by the increase in synthesis temperature from 70 to 90 °C and can be observed in **Figure 5a**. **Figures 5b-d** show that the HT and CTA treatments results in further increase in intensity and sharpening of the E_{2high} and E_{2low} modes. Moreover, the HT treatment results in better samples crystallization and therefore i.e. is more effective in improving the optical properties.[16,20,53] From **Figure 5** it can also be observed that the intensity of E_{2high} and E_{2low}

modes is increasing after HT or CTA treatment in all investigated cases, independent on the growth temperature, which also can indicate an increased crystal quality of the treated samples.[16,20,53]

3.4. Optical characterization

Transmission spectra of ZnO NWs electrodeposited on a substrate covered with FTO at 60 °C, 70 °C, 80 °C and 90 °C are presented in **Figure 6**. For all samples, the excellent transparency in the visible range and in the UV region (over 90%) was observed. It was found that the optical transmittance could be enhanced by a rise in temperature of the ECD bath, which can be associated with the decrease in surface roughness, as observed during SEM and TEM studies (see above). No essential shift in absorption edge was observed. **Figure S6** shows transmission spectra of ZnO NRs/NWs ECD on FTO substrates at 60 °C (a), and 80 °C (b).

Figure 7 illustrates the photoluminescence (PL) spectra of ZnO NRs/NWs, recorded at room temperature. The PL spectra demonstrate a high UV and a low visible emission peak in the as-deposited ZnO nanostructures. The UV line for the as-electrodeposited ZnO at about 381 nm is assigned to a free exciton and a neutral donor bound exciton.[19] No shift of UV exciton-related emission peak was observed for heat treated samples, i.e. by HT or CTA.[19]

The FWHM values of the UV peaks from all samples are ranging from 1400 to 2000 cm^{-1}. This could be explained by the fact that, after annealing, the variation of defects can take place as follows:[54,55]

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$$V_O + \frac{1}{2}O_2 = O_O \quad (5)$$

$$Zn_i + \frac{1}{2}O_2 = Zn_{Zn} + O_O \quad (6)$$

where $[Zn_i], [Zn_{Zn}]$ and $[O_O]$ are the concentrations of the interstitial Zn, Zn in the lattice place and oxygen in the lattice place, respectively. These equations show that by an increase in treatment temperature during ECD of ZnO NWs/NRs a decrease in defect concentration can be obtained.[19] Therefore, it was observed that the intensity of the UV peak increases and the intensity of the visible PL emission peak decreases.[19] For thermal treated ZnO NWs/NRs the visible PL emission peak is difficult to see from the inset of **Figure 7**. The ratio between intensity of the near-band-edge (NBE) UV vs the visible PL emissions is about 42 for the as-grown sample and 50 and even 100 for the CTA and HT annealed samples, respectively.

From **Figure 7a** it could be observed that samples electrodeposited at 80 °C have a higher emission at the band-gap emission compared to samples electrodeposited at 70 °C. ZnO NWs electrodeposited at 90 °C has the highest near-bandgap emission. The visible emission was not observed as the intensity is two orders of magnitude lower than the UV emission. According to the data reported in **Figure 7b-d** it can be concluded that synthesized samples that were subjected to CTA at 150 °C for 12 h in air, independent of the growth temperature, show an increase in UV emission. However, samples after HT treatment in ambient H_2O vapors have a higher UV emission compared to CTA samples or as grown samples. These experimental data are in concordance with transmission, XRD, Raman and XPS data. Thus, the increased UV emission intensity after CTA or HT can be a result of the enhanced crystallinity of the electrodeposited ZnO NWs/NRs as well as a reduced defect concentration in the crystalline material.

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3.5. Gas sensing performances of ECD ZnO NRs/NWs

To investigate the room temperature sensing properties of ZnO NRs/NWs electrodeposited at different temperatures to reducing gases, the individual nanostructures were integrated into devices. SEM images of individual as-electrodeposited ZnO NWs/NRs synthesized at different temperatures and integrated on a specially designed chip are presented in **Figure 8a-c**.[14] Because the gas response is highly reliant on the width changes of the surface electron depletion region of ZnO NW/NR due to adsorption/desorption processes of gaseous/vapor species,[56] the use of nanostructures with smaller diameter is crucial for fabrication of high performance gas nanosensors.[56] In our case, the ZnO NWs/NRs with a diameter in the same range were integrated. This is of major importance, since the structure diameter value is one of the most important factors that determine the gas detection properties of devices, especially in the case of individual structures, while the length of NW has a minor role according to previous study.[14,57] Also, the dependence of the gas sensitivity on various temperatures of the electrolyte growth solution needs to be considered. As can be observed from **Figure 8a-c** the radius of NWs/NRs changes is in the order of about 85 to 110 nm along the structure.

The typical current-voltage characteristics of the device based on individual ZnO NW grown at 90 °C is presented in **Figure S7a**. Such quasi-linear behavior was observed for all tested samples. This demonstrates a low barrier formed at the Pt/ZnO interface and indicates that the gas response originates mainly from modulation of electron depletion region, which will be discussed later in the next section. [2,58,59]

The gas sensing performances were investigated at working temperature varying between 25 °C – 150 °C. Higher operating temperatures were not applied to prevent damage of the Pt/ZnO contacts. **Figure 8d** presents the gas response versus working temperature of

devices to 100 ppm of hydrogen gas. According to the obtained data, the gas response is increasing when rising the operating temperature from 25 °C to 150 °C. Also, a rise in temperature of the electrolyte solution for growth of ZnO NWs/NRs from 70 °C to 90 °C show a higher gas response. The highest gas response of ~ 60 was detected for ZnO NW grown at 90 °C and measured at a work temperature of 150 °C.

In **Figure 9**, the dynamic gas response at 150 °C of individual ZnO NW synthesized at 70 °C to multiple exposures of H_2 gas with 100 ppm is presented. Here, the good repeatability of the fabricated sensors is demonstrated. The residual standard deviation of the gas response for all samples is limited to 10 %. In **Figures 9a** and **9b** the dynamic response to H_2 gas with different concentrations at an operating temperature of 150 °C for individual ZnO NW synthesized at 80 °C and 90 °C is presented. A complete recovery of the signal to the starting electrical baseline after evacuating the H_2 gas from the testing chamber is observed. This is very important for real-time application in monitoring of hydrogen gas concentrations. The response time and recovery times for detecting 100 ppm H_2 gas is 26 s and 35 s for NWs grown at 70 °C, 21 s and 20 s for NW grown at 80°C, 17 s and 16 s for NWs grown at 90°C. Therefore, **Figures 9a-c** indicate that NWs grown at higher temperatures have a faster saturation of the gas response and a faster recovery of the signal in comparison to samples ECD at lower temperature.

Figure 9d shows the gas response value versus hydrogen gas concentration at 150 °C for individual ZnO NW/NR synthesized at different temperatures, demonstrating a power law dependence of gas response on hydrogen concentration.[60] The $I_{gas}/I_{air} > 1.2$ criterion was used to determine the lower detection limit (LDL) of the nanosensor.[57] For NWs grown at 90°C, 80°C and 70°C the estimated LDL value is ~ 1.1 ppm, ~ 1.8 ppm and ~ 5.0 ppm, respectively. Overall, these results demonstrate that ZnO NWs/NRs synthesized at the higher temperatures,

especially at 90°C, are preferable to fabricate gas nanosensors with higher performances, including gas response, response/recovery time and lowest detection limit.

Next, the influence of post-growth conventional thermal annealing (CTA) in air and hydrothermal (HT) annealing in water vapors at 150°C for 12 h on the gas detection was investigated. Here, ZnO NWs/NRs grown at 80°C were used. **Figure 10a** presents the gas response of individual ZnO NWs to 100 ppm of hydrogen gas as a function of working temperature and different treatments. Both post-growth treatments led to a further enhancement of the gas response value for the electrochemically deposited ZnO NRs/NWs. The highest increase in response was obtained for HT by hydrothermal annealing in water steam. At 150 °C, the response value to 100 ppm of H_2 is 45, 93 and 380 for as-grown, CTA and HT treated ZnO NRs/NWs, respectively. The post-growth annealing does not affect the optimal operating temperature of the specimens showing still the highest response at 150°C.

The time-dependent response at 150 °C to 100 ppm of hydrogen gas of single ZnO NW synthesized at 80 °C by ECD and treated CTA or HT is presented in **Figures 10b** and **10c**, respectively, showing excellent repeatability and total recovery of the signal. The responses and recovery times are ~ 5 s and ~ 10 s for CTA treatment and ~ 11 s and ~ 10 s for HT treatments, respectively. To check the selectivity of the ZnO NRs/NWs, the gas detection measurements were performed at 150 °C working temperature to 100 ppm of ammonia, 2-propanol, butanol, acetone, ethanol and hydrogen (see **Figure 10d**). In all cases, no detectable sensitivity/response to other vapors was found, demonstrating the high selectivity of ZnO NRs/NWs to H_2 gas.

The fabricated nanosensors were also tested under UV light, as reported previously.[54] **Figure S7b** shows the UV response of individual nanowires grown at 70, 80 and 90°C. The UV response value was determined using the relation I_{UV}/I_{Dark}, where I_{UV} and I_{Dark} are the electrical currents under UV illumination and in the dark. The UV response of nanowires

grown at 70, 80 and 90 °C is ~ 1.80, ~ 2.7 and ~ 3.75, respectively. Therefore, the highest UV response was obtained for the nanowire grown at 90 °C. Analyzing **Figure S7b**, it can be noticed that the response times are much shorter than the recovery times. The similar conclusions were reported by Liu *et al.*, i.e. higher UV sensing performances of ZnO NW with higher crystallinity.[61] However, in our study this is demonstrated namely for individual structures, where no influence of NW-NW junction effect is present.

3.6. Gas sensing mechanism

For single nanostructures of semiconducting oxides the gas sensing mechanism is associated to the surface phenomena.[2,62] As an outcome of the enormous surface-to-volume ratio, the adsorption/desorption of gas molecules can lead to dramatic modifications in electrical properties.[56,57] At exposure of individual ZnO NWs/NRs to ambient air in the temperature range of 25 °C to 150 °C, mainly oxygen species are adsorbed on the surface by extracting free electrons from ZnO as follows:[2,63]

$$O_2(g) + e^- \rightarrow O_2^-(ads) \qquad (7)$$

this extraction will produce the formation of an electron depletion region (EDR) at the ZnO NWs/NRs surface and to the narrowing of the conduction channel through NWs/NRs, i.e. a rise of device resistance.[58] The observed tendency of an increase in gas response when rising the working temperature can be discussed based on the increased thermal energy of H_2 molecules and their reaction with adsorbed oxygen as follows:[2,64]

$$H_2(g) + \frac{1}{2}O_2^-(ads) \rightarrow H_2O(g) + e^- \quad (8)$$

This results in a narrowing of the EDR, leading to the decrease of device resistance. The excellent selectivity of individual ZnO NRs/NWs to H_2 gas can be explained based on the presence of Pt as contacts.[58] Pd or Pt due to the high catalytic properties for binding and dissociating the H_2 molecule, Pd or Pt are known to contribute significantly to enhanced selectivity of hydrogen gas response.[65]

The integrated ZnO NRs/NWs synthesized at different temperatures show different gas responses, although they show practically the same diameter of the structure. From investigations of the structural and optical properties, it was found that the higher temperature of ECD bath can result in a nanomaterial with better crystallinity. Therefore, the main cause of improved gas sensing performances can be the higher crystallinity of materials that results in the formation of contacts with higher quality. Also, it was observed that the CTA and HT treatment can result in further improvements of gas sensing properties. This can be also explained by a significantly improved crystallinity,[16] as well as in an efficient lowering of the concentration of Cl ions, as was demonstrated by our results and in previous works.[16,19,20] Also, as demonstrated by other studies, the doping of ZnO NWs with Cl may lead to metallic conduction that could negatively affect the gas detection properties of the devices.[12] **Table S1** shows a comparison of different sensors on individual nanomaterials.

3.7. DFT Calculations: H_2 gas molecule interaction with ZnO (0001) *and ZnO* $(10\bar{1}0)$ *surfaces*

In order to understand better the H_2 gas molecule interaction with ZnO NWs/NRs, DFT calculations on two active surfaces of ZnO were performed. Both Zn-terminated polar

(0001) and nonpolar ($10\bar{1}0$) surfaces have been found very active surfaces and studied extensively for gas sensing and catalytic experiments.[66] Here, calculations on both these two surfaces to understand the H_2 gas sensing on ZnO NWs/NRs were done. Firstly, the modelled bulk wurtzite structure and calculated lattice parameters [a = b = 3.19571 Å, c = 5.14371 Å, α = β = 90°, γ = 120°] (see **Figure S8**) were found to match well with the experiments (a = b = 3.2490 Å, c = 5.2052 Å, α = β = 90°, and γ = 120°).[67] Calculated parameters of the lattice in this study are also in agreement with the earlier DFT computed results of Cook *et al.* (a = b = 3.1959 Å, c = 5.1585 Å, α = β = 90°, and γ = 120°).[68]

The macroscopic dipole of polar (0001) surface was quenched by removing one Zn atom from top and one oxygen atom from the bottom of the surface. The top layer of this ZnO (0001) surface consists of 3 Zn and 4 O atoms with the lattice parameters of a = 6.51 Å; b=6.51 Å. Hereby, total 6 atomic layers in the slab model and fixed bottom four layers to their bulk positions were considered, while the top 2 layers were allowed to relax. The surface energy with a value of 2.28 $J.m^{-2}$, was calculated as described in the SI.

It was observed that after relaxation of the ZnO (0001) surface, the Zn-O bond in the top layers shrinks (Zn-O bond length changes to 1.85 and 1.92 Å from 1.88 and 1.94 Å respectively) forming a stronger bonding arrangement (see **Figure S9**). Next, a hydrogen molecule was placed closed to all the possible surface sites. It shows that the hydrogen molecule dissociates from the surface having an adsorption energy of -4.42 eV (see this value comparing **Figures 11(a, b))**. This spontaneous dissociation of the H_2 molecule was also found earlier for doped ZnO (0001) surfaces.[69] Next Bader charge analysis was performed to quantify the charge transfer. It was noticed that -0.06 Bader charge is transferred to the molecule from the surface, as a result of surface-molecule interaction as shown in the charge density difference plot in **Figures 11(c, d)**. To further quantify the electronic structure changes, the electronic density of states (DOS) was calculated. The results show that there are

considerable shifts in valence and conduction band states as a result of H_2 molecule interaction as shown in **Figures 11(e, f)**. Here, the Fermi energy changes from -2.735 eV for the ZnO (0001) surface to -1.352 eV after H_2 molecule adsorption over this surface.

In order to study the H_2 molecule interaction with the ZnO $(10\bar{1}0)$ surface, our recently modelled structure of the $(10\bar{1}0)$ surface was used where similar to earlier works,[68,70] a termination (**Figure S10**) with a surface energy of 1.119 $J.m^{-2}$ was observed showing more stability compared to others.[68,70] The relaxed structure of the $(10\bar{1}0)$ surface is presented in **Figure S10**.

Here again, a H_2 molecule was placed closed to all possible sites of the surface. The results show that the molecule is physisorbed with a weak energy for adsorption of -0.258 eV, as can be seen in **Figure 12(a, b).** Bader charge analysis and charge density-difference plots show a very weak charge transfer to the molecule from the surface, as can be seen in **Figures 12(c, d)**. Moreover, electronic-DOS also suggests a weak interaction of the H_2 molecule as shown in **Figures 12(e, f),** with slight change in Fermi energy, as it values changes from -2.3761 for the ZnO $(10\bar{1}0)$ surface to -2.3655 when H_2 molecule is adsorbed over this surface. Overall, the results show that ZnO$(10\bar{1}0)$ interacts weakly with H_2 molecule, while the ZnO (0001) surface interacts strongly with an H_2 molecule.

4. CONCLUSION

ZnO NRs/NWs were electrodeposited on fluorine-doped tin oxide substrates at different temperatures of electrolyte solution, namely 70 °C, 80 °C and 90 °C, to study its influence on structural, chemical, optical and sensing performances of devices based on single nanostructures, integrated into nanosensor devices. The effects of post-growth relatively low temperature annealing/treatment and HT at 150 °C for 12 h on the morphology, structural

properties, optical transmission, absorption, chemical composition, electronic structure and photoluminescence of ZnO NWs/NRs were investigated in detail. It was demonstrated that the use of higher temperatures during synthesis, as well as the exposure to post-growth annealing in water vapors HT can lead to improvements in the crystallinity of the electrodeposited ZnO-based nanomaterial. The individual ZnO NRs/NWs were integrated into micro- and nanodevices by the FIB/SEM technique for detailed detection tests. The experimentally obtained results demonstrate that hydrothermal annealing HT in water vapors-steam of ZnO NRs/NWs is an efficient method to achieve high performances in the gas sensing of H_2 gas. At a temperature of 150 °C the gas response of ~ 380 to 100 ppm of H_2 gas detected. DFT calculations indicate that H_2 gas binds strongly with the ZnO (0001) surface and results in electronic bands shifts that are indicative of a better sensing capability of ZnO NRs/NWs. The developed nanodevices could be key element for e.g flexible nanoelectronics and/or wearable electronics.

■ ASSOCIATED CONTENT

Supporting Information: Additional information on DFT calculations of relaxed surface energy. Dynamic dependence of current density and cyclic voltammograms on FTO substrate, the EDX spectrum and the overview XPS spectra corresponding to ZnO NWs/NRs. Transmission after different annealing of ZnO NW array grown at 80 °C. Typical current-voltage characteristic of device based on individual ZnO NW grown at 80 °C. UV response of individual ZnO nanowires. Crystallinity of ECD ZnO NWs before and after post growth-treatments. Figures of ZnO Bulk Structure, 2*2 supercell of the ZnO (0001) and $(10\bar{1}0)$ surfaces. The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org

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■ AUTHOR CONTRIBUTIONS

O.L. and Th.P. synthesized the nanomaterial and developed the synthesis-treatment methodology. L.K.O. and B.R.C. carried out XPS measurements and XPS data analysis. B.V. and O.L. carried out photoluminescence investigations and PL data analysis. O.L. and Th.P. carried out all Raman experiments and data discussion. O.L. and L.C. fitted a technology pathway for material integrations in the devices. N.M., V.P., O.L. performed the measurements of the detection characteristics of the nanomaterials and investigated the data. H.H. and L.C. investigated the TEM-HRTEM. O.L., N.M., S.H., R.A., H.K. and V.P. analyzed the experimental data/results, then the revised work. R.K.M. and A.K.M. accomplished the computational and DFT draft. A.K.M. performed and analyzed the computational results. O.L., N.M., S.H., V.P., L.K.O., B.R.C. and R.A. prepared the manuscript draft. O.L., Th.P., S.H., L.C. and R.A. accomplished the concept of this study and design. All gave the approval of the final version for manuscript to be submitted. This work was written based on all authors contributions. All of our co-authors reviewed the draft and have given approval to the final version of the manuscript.

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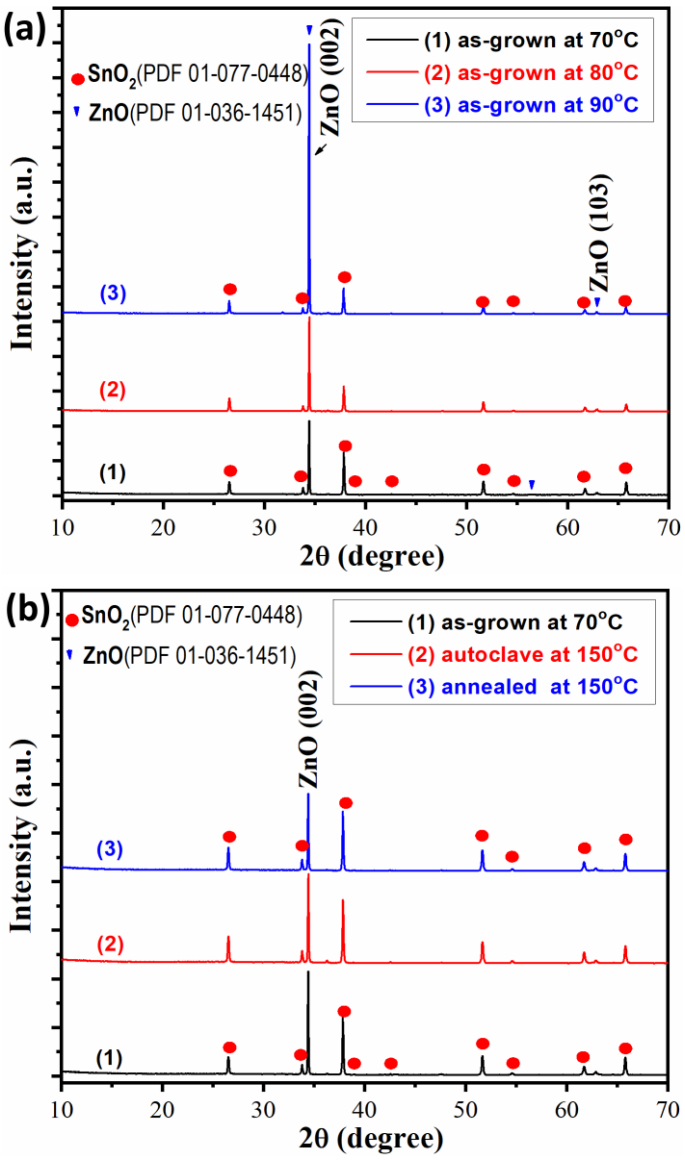

Figure 1. XRD diffractograms of ZnO NRs/NWs electrodeposited at: (a) 70 °C, 80 °C, and 90 °C. (b) at 70 °C and CTA at 150 °C in air and hydrothermal treated-HT at 150 °C in autoclave with H_2O vapors in the ambient.

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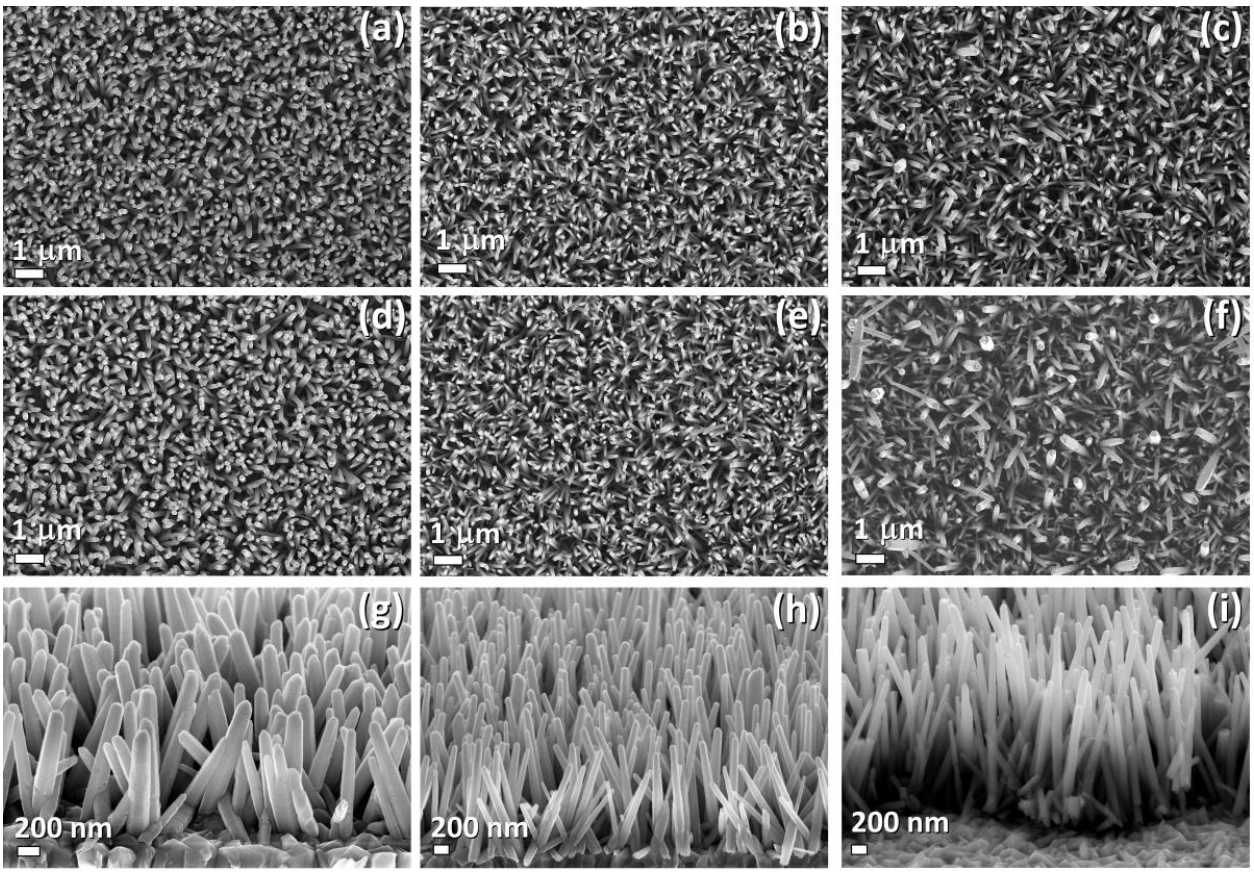

Figure 2. SEM images of electrodeposited ZnO NRs/NWs (top view) initially and after post-synthesis treatment/annealing: (a) as-grown at 70°C (2.5 h); (b) as-grown at 80 °C (2.5 h); (c) as-grown at 90 °C (2.5 h); (d) grown at 70 °C (2.5 h) and hydrothermal treated HT at 150 °C in H_2O vapor ambient, 12 h; (e) grown at 80 °C (2.5 h) and HT at 150°C, 12 h in an autoclave; (f) grown at 90 °C (2.5 h) and treated- HT at 150 °C, 12 h; (g) 65°-tilted-view of image (d); (h) 65°-tilted-view of image (e); (i) 65°-tilted-view of image (f).

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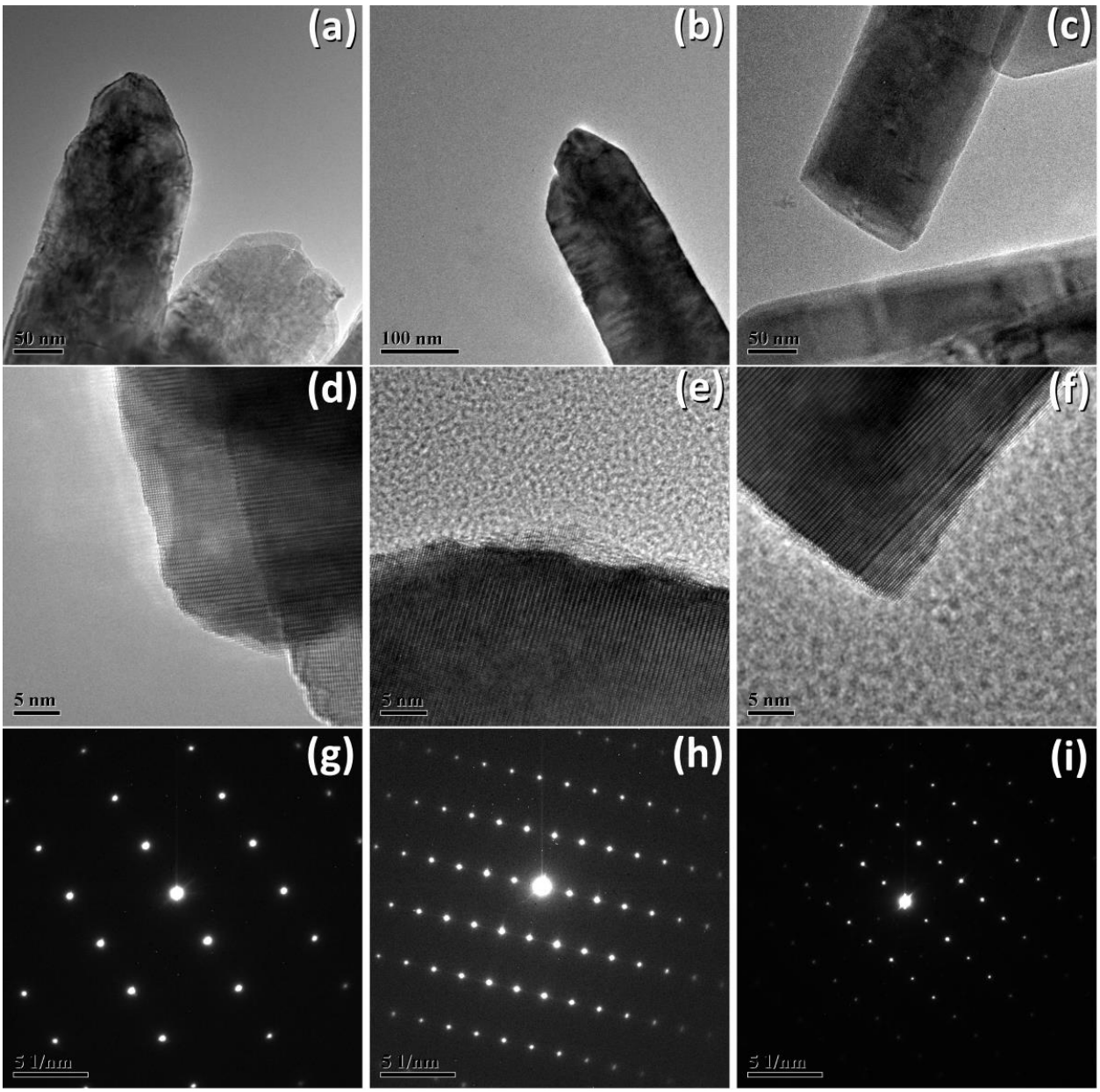

Figure 3. TEM of ZnO NRs/NWs grown by electrodeposition: (a) as-grown at 70 °C (2.5 h); (b) grown at 80 °C (2.5 h); (c) grown at 90 °C (2.5 h) and treated HT at 150 °C, 12 h in an autoclave. HRTEM of ECD ZnO NRs/NWs: (d) as-grown at 70 °C(2.5 h); (e) grown at 80 °C (2.5 h); (f) grown at 90 °C (2.5 h) and treated- HT at 150 °C, 12 h. Typical SAED patterns of ZnO NRs/NWs grown by electrodeposition at: (g) 70 °C, (h) 80 °C and (i) 90 °C.

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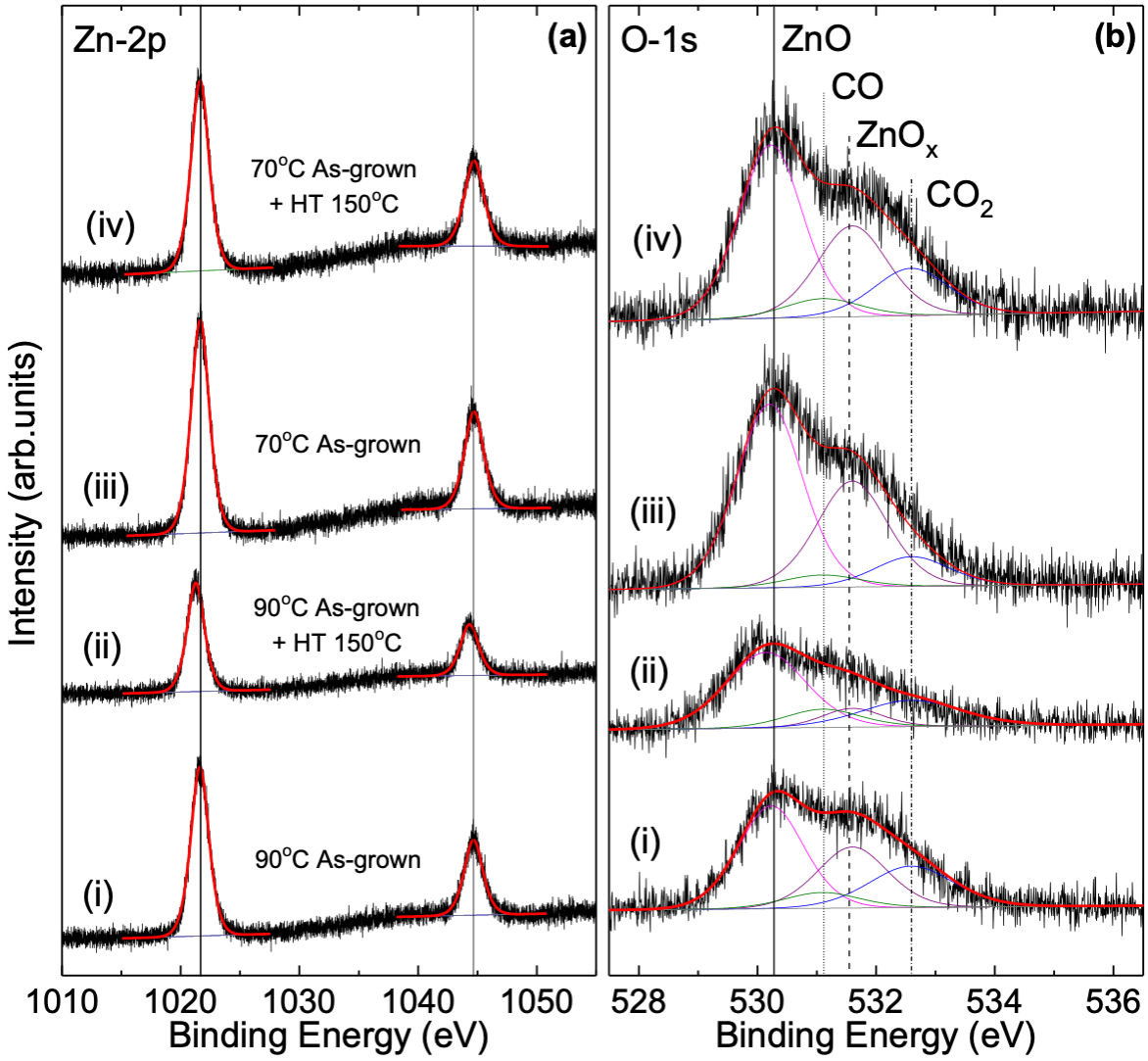

Figure 4. XPS spectra (Al-K$_\alpha$ = 1486.6 eV) investigated to the (a) Zn-2p and (b) O-1s core level regions of ZnO NWs synthesized on FTO/glass substrates. The vertical lines in (b) indicate the binding energies of O-1s in stoichiometric and defective ZnO, as well as in adventitious CO and CO_2. Samples were grown at (i) 90 °C and (ii) subsequently treated HT at 150 °C, 12 h in autoclave. The second set of samples consist of (iii) 70 °C and (iv) subsequently treated HT at 150 °C, 12 h in autoclave.

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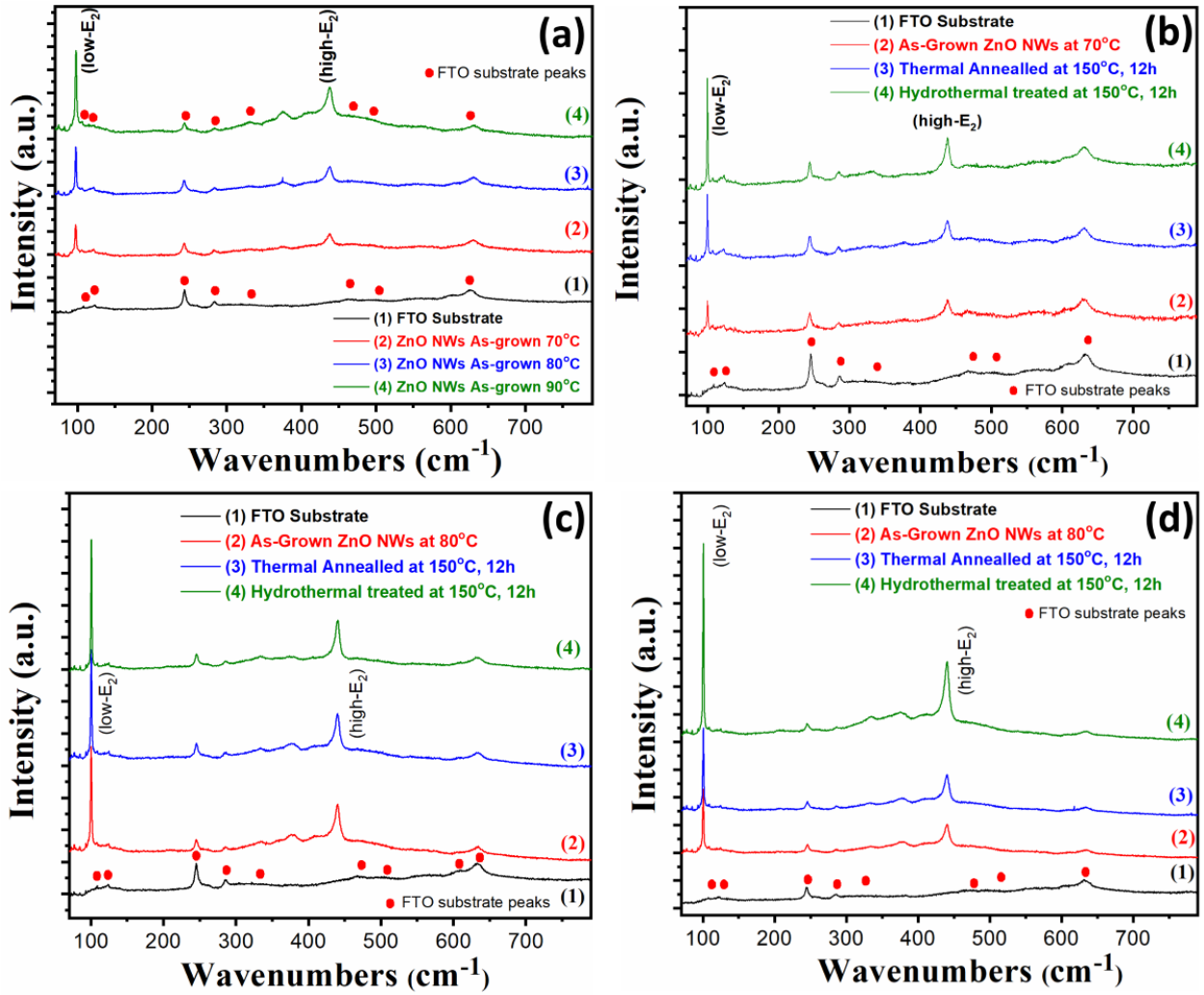

Figure 5. Raman spectra for initially and annealed/treated-HT ZnO nanorod/nanowire arrays on FTO substrate measured at room temperature: (a) comparison of samples grown at different temperatures 70 °C, 80 °C, and 90 °C; (b) comparison of samples grown at 70 °C and subjected to different post-growth treatments; (c) comparison of samples grown at 80 °C; and (d) comparison of samples grown at 90 °C and subjected to different post-growth treatments.

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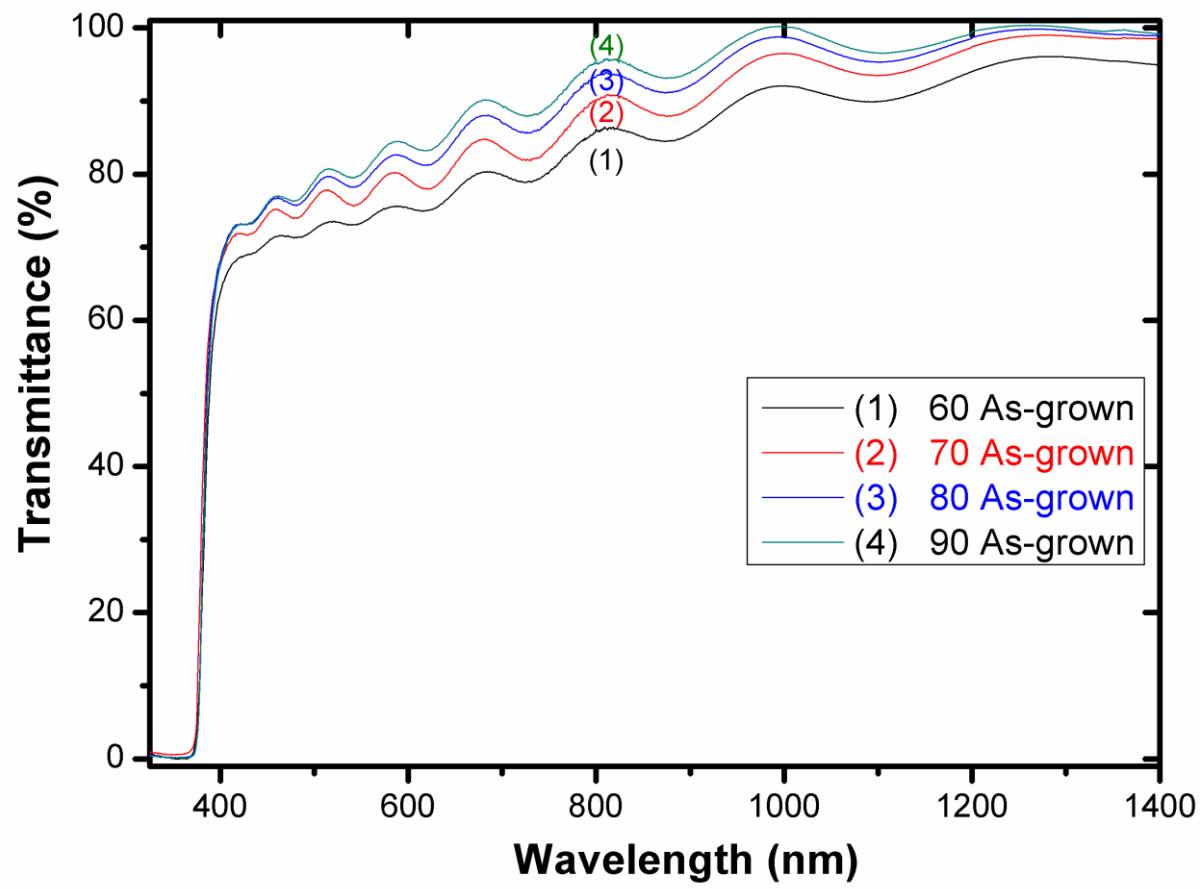

Figure 6. Transmission spectra of as-synthesized ZnO NRs/NWs electrochemically grown on FTO substrates at 60 °C, 70 °C, 80 °C, and 90 °C.

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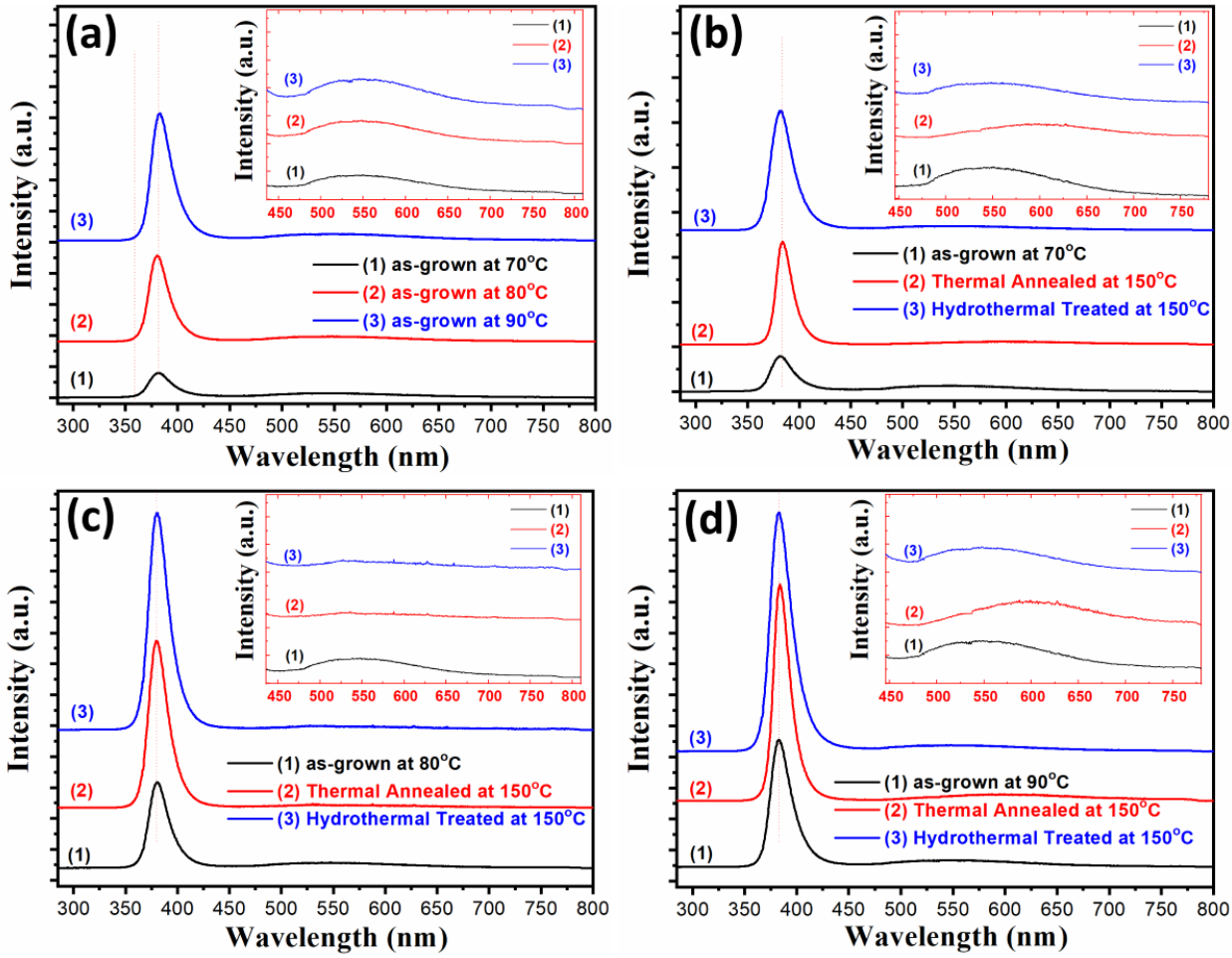

Figure 7. PL room-temperature spectra for as-synthesized and annealed/treated-HT ZnO NRs/NWs arrays on FTO: (a) comparison of samples grown at various temperatures as indicated on graph; (b) comparison of samples obtained at 70 °C and subjected to different post-growth treatments; (c) comparison of samples grown at 80 °C; and (d) comparison of samples grown at 90 °C and subjected to different post-growth annealing/treatments-HT. Insert represents zoom-in visible regions of the same photoluminescence spectra.

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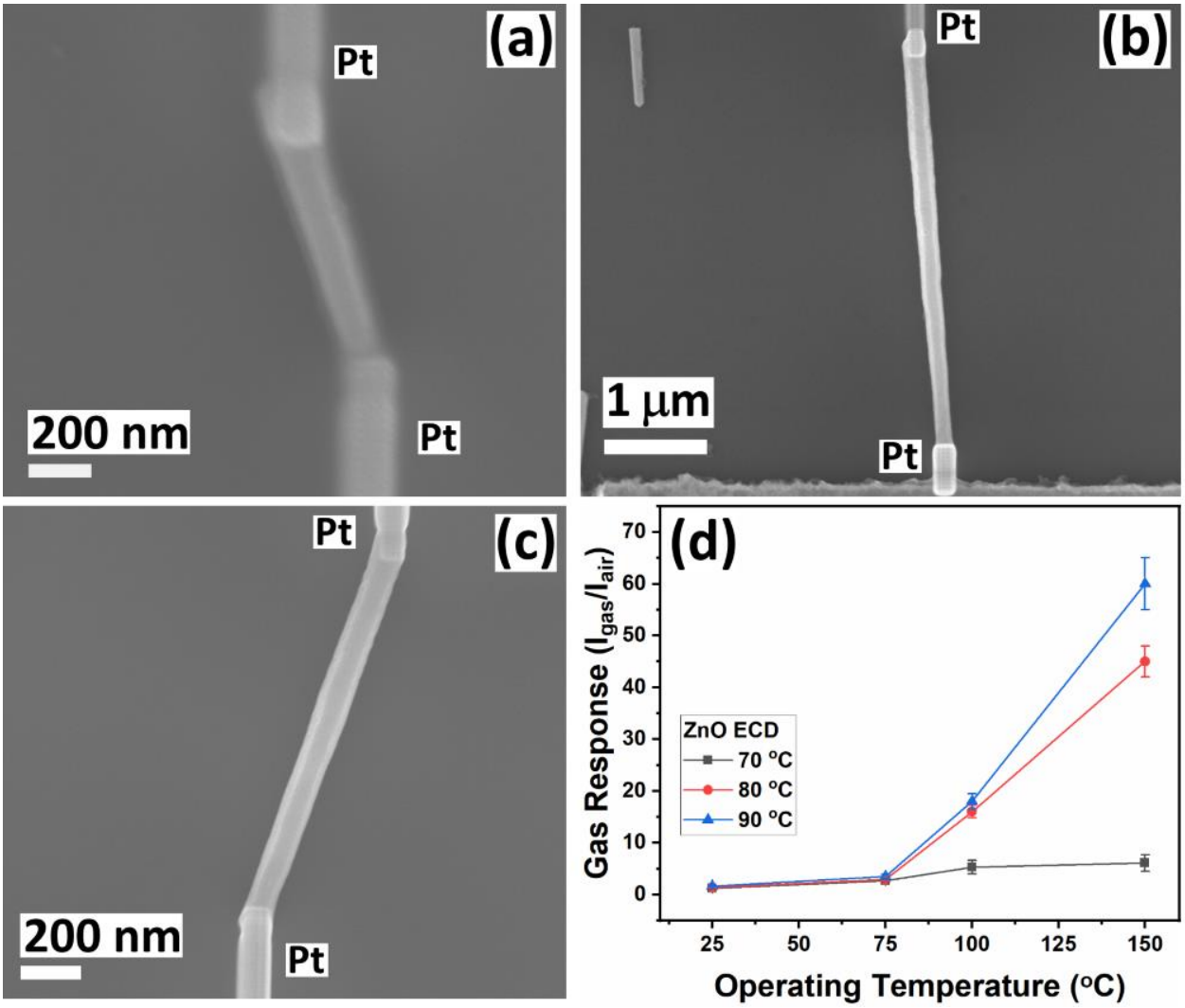

Figure 8. SEM images of microdevices/sensors constructed on individual ZnO NRs/NWs synthesized at: (a) 70 °C, (b) 80 °C and (c) 90 °C. (d) Response vs working temperature of devices to 100 ppm of hydrogen.

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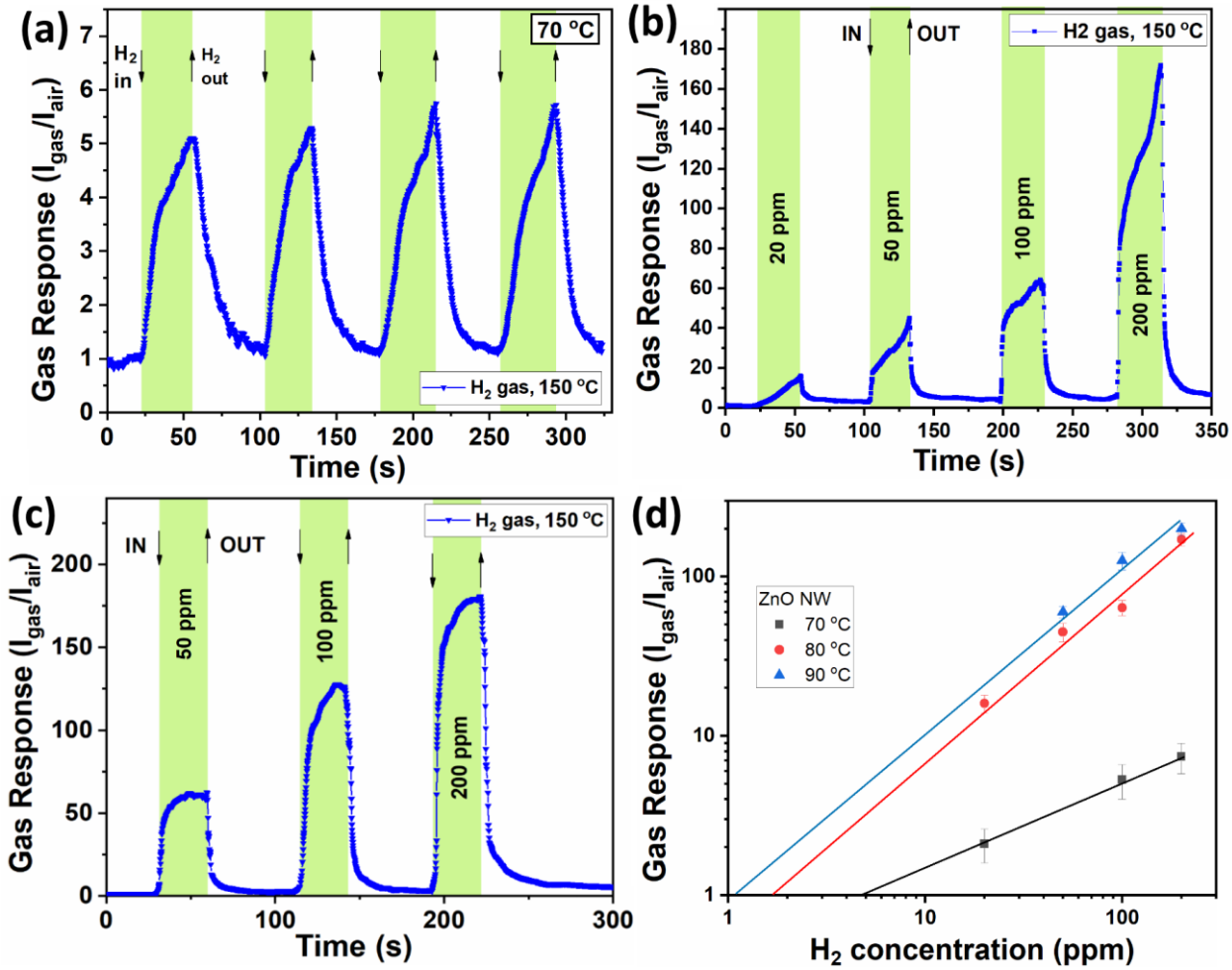

Figure 9. (a) Dynamic gas response at 150 °C of individual ZnO NRs/NWs synthesized at 70 °C to multiple exposures of H_2 gas with 100 ppm as well as to different concentrations of hydrogen gas for a single ZnO NRs/NWs synthesized at: (b) 80 °C and (c) 90 °C. (d) Dependence of gas response on gas H_2 concentration at 150 °C for individual ZnO NRs/NWs synthesized at 70 °C, 80 °C and 90 °C.

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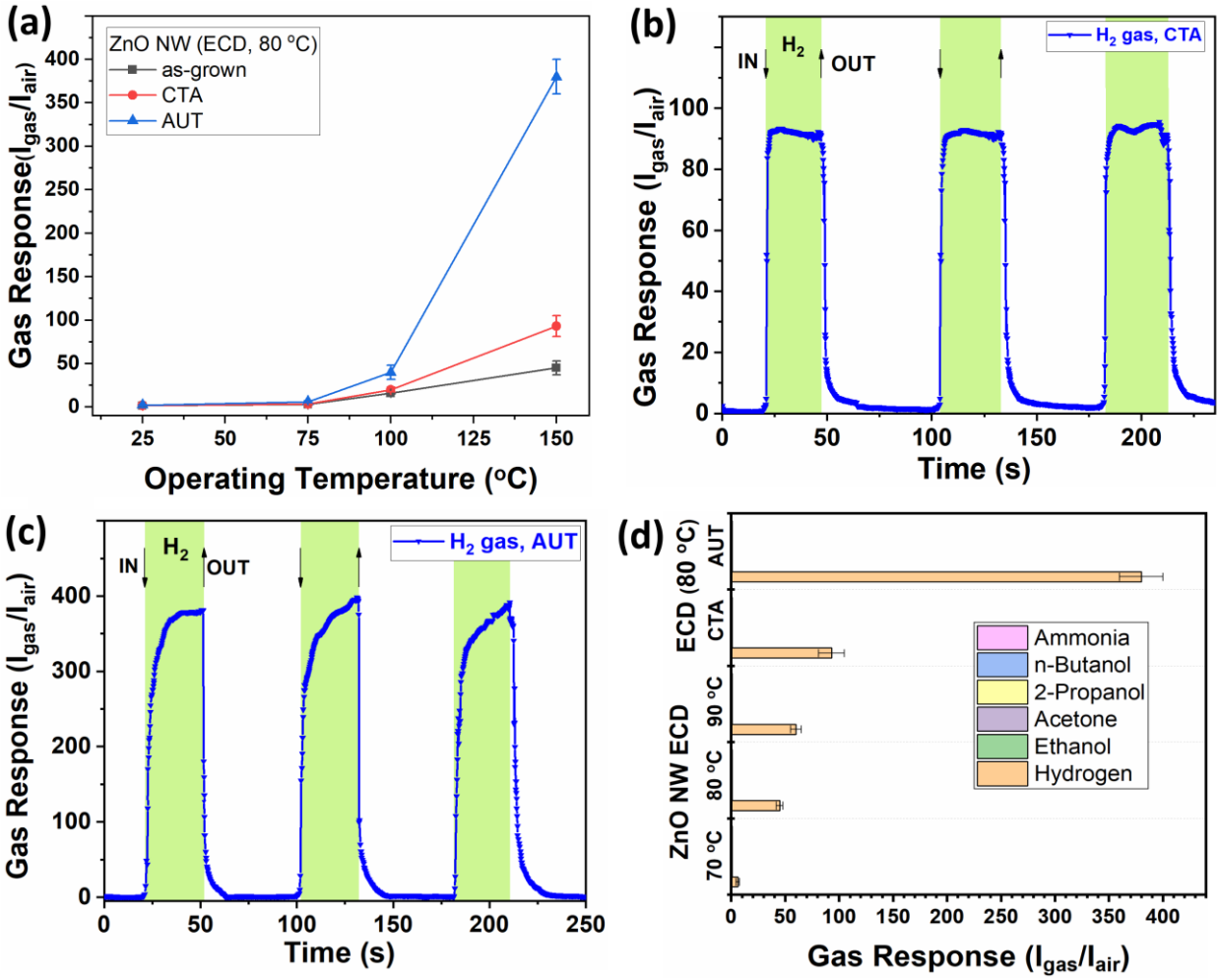

Figure 10. (a) Response vs working temperature of individual ZnO NRs/NWs synthesized at 80 °C and treated CTA or treated HT at 150 °C, 12 h in an autoclave to 100 ppm of hydrogen gas. Response in dynamic mode at 150 °C to 100 ppm of H_2 gas of a single ZnO NRs/NWs synthesized at 80 °C and treated by: (b) CTA or (c) HT at 150 °C, 12 h in an autoclave. (d) Gas response of the fabricated devices at 150 °C to 100 ppm of various gases and vapors (ammonia, *n*-butanol, 2-propanol, acetone, ethanol and hydrogen).

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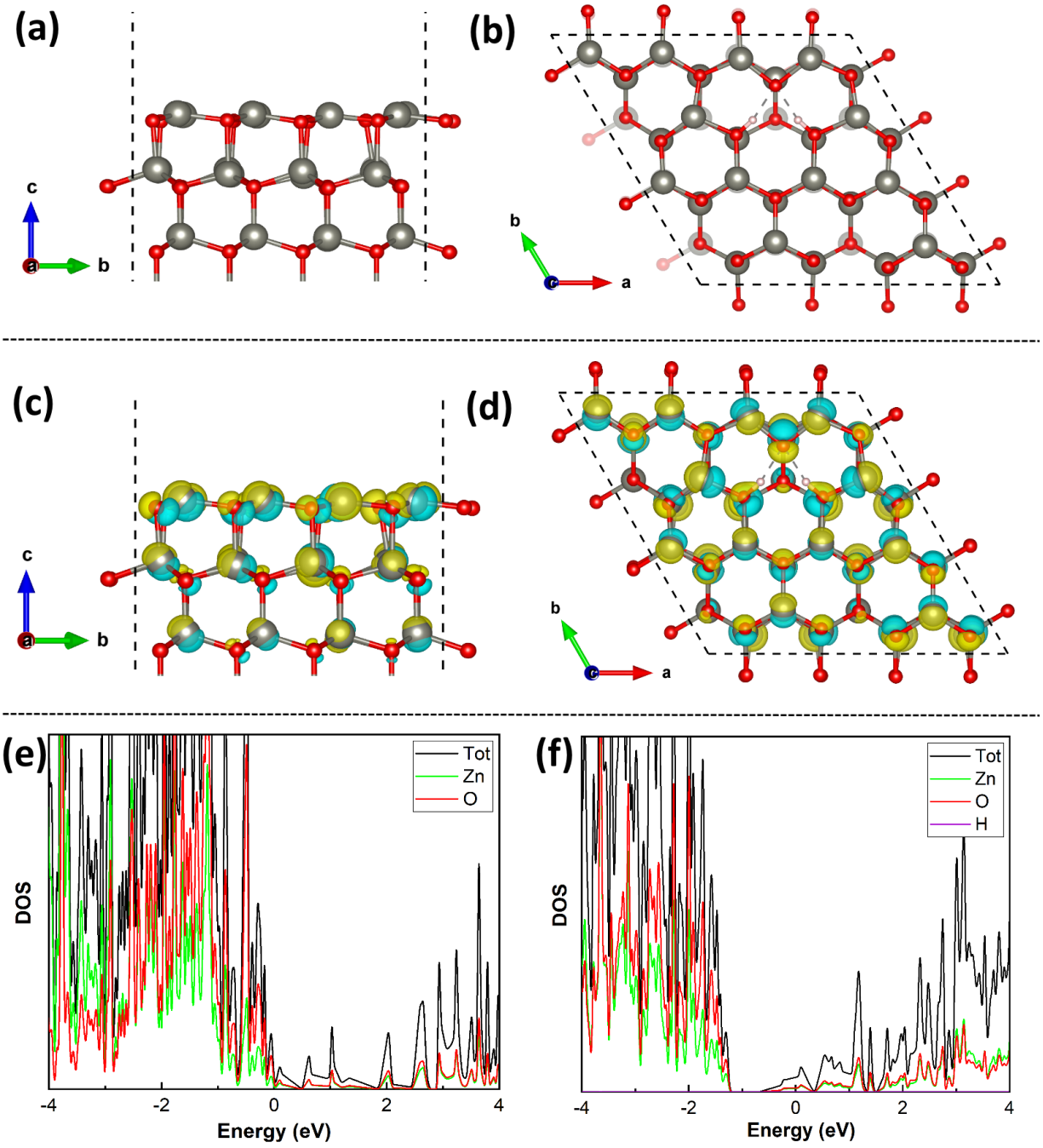

Figure 11. Interaction of hydrogen gas molecule on ZnO (0001) surface with: side (a) and top (b) views. Charge density difference plot of H_2 molecule interaction on ZnO (0001) surface with: side (c) and top (d) views, where yellow and blue colors indicate positive and negative

charge densities in (e/Bohr^3). Density of states for: (e) ZnO (0001) surface and (f) of H_2 molecule over ZnO(0001) surface.

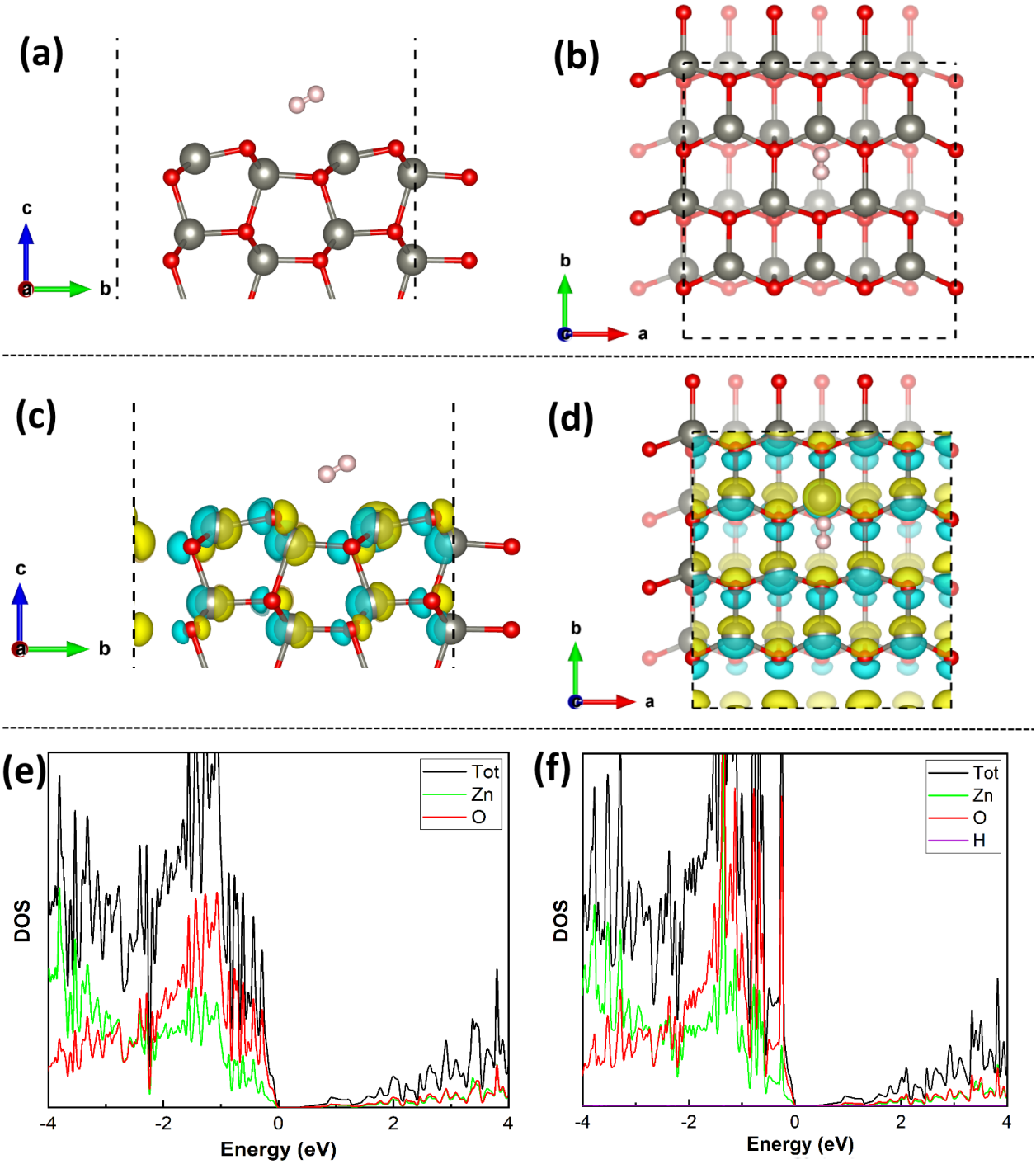

Figure 12. Interaction of H_2 molecule with ZnO $(10\bar{1}0)$ surface with: side (a) and top (b) views. Charge density difference plot of hydrogen molecule interaction on ZnO $(10\bar{1}0)$ surface with: side (c) and top (d) views, where positive and negative charge densities in

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(e/Bohr^3) are indicated by yellow and blue colors. Density of states of ZnO($10\bar{1}0$) surface (e) and of hydrogen molecule closed ZnO ($10\bar{1}0$) surface (f).

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Table 1. Relative concentration of ZnO, CO_2 and CO species calculated from the spectral area of the O-1s XPS binding energy region. The data correspond to samples annealed at different temperatures.

	ZnO (at %) (530.21 eV)	ZnO_x / $ZnO_x(OH)_y$ (at %) (531.61 eV)	CO (at %) (531.11 eV)	CO_2 (at %) (532.51 eV))
(i) As-grown at 90°C	42.8	27.3	22.3	7.6
(ii) As-grown at 90°C followed by HT 150ºC, 12 h	53.8	10.2	23.6	12.4
(iii) As-grown at 70°C	53.1	32.9	9.9	4.1
(iv) As-grown at 70°C followed by HT 150ºC, 12 h	49.2	28.6	15.9	6.3

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TOC Figure