

Al₂O₃/ZnO Heterostructure-Based Sensors for Volatile Organic Compounds in Safety Applications

Oleg Lupan,* David Santos-Carballal,* Nicolae Magariu, Abhishek Kumar Mishra, Nicolai Ababii, Helge Krüger, Niklas Wolff, Alexander Vahl,* Mani Teja Bodduluri, Niklas Kohlmann, Lorenz Kienle,* Rainer Adelung,* Nora H. de Leeuw, and Sandra Hansen*



Cite This: *ACS Appl. Mater. Interfaces* 2022, 14, 29331–29344



Read Online

ACCESS |



Metrics & More

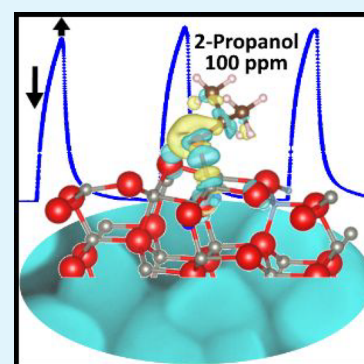


Article Recommendations



Supporting Information

ABSTRACT: Monitoring volatile organic compounds (VOCs) in harsh environments, especially for safety applications, is a growing field that requires specialized sensor structures. In this work, we demonstrate the sensing properties toward the most common VOCs of columnar Al₂O₃/ZnO heterolayer-based sensors. We have also developed an approach to tune the sensor selectivity by changing the thickness of the exposed amorphous Al₂O₃ layer from 5 to 18 nm. Columnar ZnO films are prepared by a chemical solution method, where the exposed surface is decorated with an Al₂O₃ nanolayer via thermal atomic layer deposition at 75 °C. We have investigated the structure and morphology as well as the vibrational, chemical, electronic, and sensor properties of the Al₂O₃/ZnO heterostructures. Transmission electron microscopy (TEM) studies show that the upper layers consist of amorphous Al₂O₃ films. The heterostructures showed selectivity to 2-propanol vapors only within the range of 12–15 nm thicknesses of Al₂O₃, with the highest response value of ~2000% reported for a thickness of 15 nm at the optimal working temperature of 350 °C. Density functional theory (DFT) calculations of the Al₂O₃/ZnO(1010) interface and its interaction with 2-propanol (2-C₃H₇OH), *n*-butanol (*n*-C₄H₉OH), ethanol (C₂H₅OH), acetone (CH₃COCH₃), hydrogen (H₂), and ammonia (NH₃) show that the molecular affinity for the Al₂O₃/ZnO(1010) interface decreases from 2-propanol (2-C₃H₇OH) ≈ *n*-butanol (*n*-C₄H₉OH) > ethanol (C₂H₅OH) > acetone (CH₃COCH₃) > hydrogen (H₂), which is consistent with our gas response experiments for the VOCs. Charge transfers between the surface and the adsorbates, and local densities of states of the interacting atoms, support the calculated strength of the molecular preferences. Our findings are highly important for the development of 2-propanol sensors and to our understanding of the effect of the heterojunction and the thickness of the top nanolayer on the gas response, which thus far have not been reported in the literature.



KEYWORDS: ZnO, Al₂O₃, heterojunctions, VOCs, semiconducting metal oxides, gas sensors, DFT, gas response

1. INTRODUCTION

Volatile organic compounds (VOCs), which originate from multiple sources such as household items, cooking appliances, paint, oil refineries, and vehicle exhaust emissions, are highly hazardous vapors that significantly affect human health and air quality in various industrial environments.^{1–4} Despite having been investigated extensively over the past few years, the sensing properties toward VOCs need to be improved continuously to meet the most up-to-date requirements for specific applications and to withstand the harsh industrial environments, especially when using heterostructures or heterojunctions of two or more metal oxides.^{3–5} The selective detection of low concentrations of VOCs is highly important to underpin the continuous monitoring of human health and for environmental safety.⁵ Among the various types of materials available, the semiconducting–metal oxide-based chemo-resistive sensors are considered to be promising candidates for the detection of VOCs,^{2,6} especially those comprising heterostructures/heterojunctions containing two or

more different oxides, as these materials show excellent potential for their application in portable solid-state devices because of their low cost, high efficiency, simple preparation method, and good stability.^{1–9} In the context of real-world applications, the response parameter is influenced by several factors, including the morphology,¹⁰ microstructure, defects, and heterojunctions of the VOC sensors as well as the relative humidity.⁶ The response and selectivity performance of solid-state gas sensors can be improved further through control of their properties and, especially, by developing new multi-layered or heterostructured oxides with a coating of Al₂O₃

Received: February 28, 2022

Accepted: May 31, 2022

Published: June 15, 2022



nanofilms. These films provide an effective protective layer against harsh environments since they can withstand high temperatures and/or inaccessible environments.^{11–13}

A recently developed approach to improve the sensitivity of chemoresistive sensors toward common VOCs involves the preparation of mixed or heterostructured/multilayered nanomaterials, including copper oxide, zinc oxide, indium oxide, aluminum oxide, titanium oxide, and several other semiconducting metal oxides. The literature includes reports on the fabrication of new heterostructures of TiO₂/CuO,¹⁴ Al₂O₃/CuO,⁵ ZnO/In₂O₃,¹⁵ Mn₃O₄/Fe₂O₃, Mn₃O₄/ZnO,¹⁶ and ZnO–SnO₂¹⁷ and their functionalization with metallic nanoparticles such as Pd, Ag, Pt, and Au.^{14,18,19} These multilayered heteromaterials have been used as sensor devices for the detection of hydrogen gas or volatile organic compounds or in the production of solar cells,²⁰ photodetectors,²¹ photocatalysts,^{15,22} and light-emitting diodes.²³

In this study, we investigate the response of the Al₂O₃/ZnO heterostructure to 2-propanol (2-C₃H₇OH), *n*-butanol (*n*-C₄H₉OH), ethanol (C₂H₅OH), acetone (CH₃COCH₃), molecular hydrogen (H₂), and ammonia (NH₃) vapors in low concentrations. In addition, DFT calculations were used to model the Al₂O₃/ZnO(10 $\bar{1}$ 0) interface and its interaction with the VOCs and molecular hydrogen (H₂). The adsorption energies and structures of the molecules at the interface are evaluated, whereas the charge transfers and electronic densities of states for the most favorable molecular binding modes are calculated to examine the selectivity and sensitivity of the developed heterostructured sensor.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Al₂O₃/ZnO Heterostructures. Columnar zinc oxide thin films were synthesized from chemical solutions (SCS) of zinc sulfate at 95 °C over quartz silica or glass substrates, where the nanocrystalline layers were produced following thermal annealing treatment. Details of the preparation procedure can be found in our previous works,^{24–27} whereas the cross section of the columnar structure of these films has also been reported previously.⁸ Standard thermal treatment in an electrical furnace at 450, 550, and 650 °C for 120 min was used as a postgrowth thermal treatment process, which improved significantly the crystallinity of the SCS deposited columnar ZnO layers.^{24,26,28,29}

Next, a coating of an Al₂O₃ nanofilm was deposited on top of the columnar zinc oxide films and ZnO nanowire model systems³⁰ by using a thermal atomic layer deposition (ALD) method (Picosun's R200) at 75 °C, with different numbers of runs to control the thickness of the top nanolayer.^{5,31} Pico-flow technology was applied to achieve uniform nanolayer coating depositions on high-aspect-ratio structures, such as nanowire networks or materials with difficult morphologies, like interpenetrated column-based films. Trimethylaluminum (TMA) was used as the aluminum source, which was oxidized by using H₂O after chemisorption. Alternating pulses with a duration of 0.2 s per pulse were applied to insert the precursors into the reactor chamber where the Al₂O₃ monolayers were grown. N₂ gas was utilized to carry the precursors' vapors into the reaction prechamber and to remove the byproducts from the reactor.

To study the thickness of the Al₂O₃ thin film coating deposited on the columnar ZnO films, we used a flame synthesis approach³⁰ to prepare a suitable model system consisting of ZnO nanowires, which were homogeneously coated by using the ALD method with identical process parameters. Such nanowires are regarded as highly congruent systems that bypass the advanced sample preparation methods required for electron microscopy imaging.

In addition, the Al₂O₃/ZnO thin film and nanowire heterostructures were thermally treated at 620 °C for 40 min in a furnace to

improve the crystallinity and stability during the sensing measurements.

2.2. Structural, Morphological, Vibrational, Chemical, and Spectroscopic Characterization of the Al₂O₃/ZnO Heterostructures. The morphology of the Al₂O₃/ZnO heterostructures was measured by using a Zeiss Ultraplus scanning electron microscope (SEM) at 7 kV. To study the reproducibility of the deposition technique, the uniformity of the Al₂O₃ layers, and possible crystallization effects during the subsequent thermal annealing, we performed transmission electron microscopy (TEM) experiments of Al₂O₃-coated ZnO nanowires, as a model of columnar Al₂O₃/ZnO heterostructures, using a JEOL JEM2100 instrument equipped with a thermionic LaB₆ cathode operating at 200 kV. Energy-dispersive X-ray spectroscopy (EDXS) was conducted by using an Oxford AztecEnergy/TEM EDXS system with an 80 mm² silicon drift (SD) detector. The line-scan data were low-pass filtered during counts to reduce the signal-to-noise ratio and enhance the X-ray patterns. The crystallographic structures were investigated by using X-ray powder diffraction (XRD) with a Seifert 3000 unit operating with Cu K α ₁ radiation (1.540598 Å) at 40 kV and 40 mA. Micro-Raman experiments were measured by using the 532 nm line from a laser as the excitation light source.

To find additional information about stoichiometry and chemical composition, we performed X-ray photoelectron spectroscopy (XPS, Omicron Nano-Technology GmbH, Al anode, 240 W) on both columnar ZnO and Al₂O₃/ZnO thin film samples grown on quartz glass substrates. The software CasaXPS (ver. 2.3.16) was used to correct potential charging by adjusting the main C-1s line of all experiments to 284.5 eV, which is the reference value of adventitious carbon.^{32,33}

2.3. Density Functional Theory (DFT) Calculations. Calculations based on the DFT were performed by using the generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE)³⁴ exchange-correlation functional and the projected augmented wave (PAW)^{35,36} method, as implemented in the Vienna *ab initio* Simulation Package (VASP).^{37–40} The atomic positions and lattice constants of the ZnO bulk structure were optimized by using the conjugate gradient method until the maximum residual force acting on each atom was less than 0.01 eV/Å, as in our earlier works,^{8,41–43} where the criterion for energy convergence was 10^{–5} eV/cell. Here, a cutoff of 520 eV was used for the kinetic energy of the plane waves, and Γ -centered 5 × 5 × 4 and 5 × 3 × 1 Monkhorst–Pack *k* points meshes⁴⁴ were used to simulate the bulk and (10 $\bar{1}$ 0) surface structures, respectively. The electronic partial occupancies were determined by using the Gaussian smearing technique, which has been used previously to model the ZnO bulk, its (10 $\bar{1}$ 0) surface, and the Al₂O₃/ZnO(10 $\bar{1}$ 0) interface.^{8,41,42} Similar to earlier works,^{45,46} the termination of the (10 $\bar{1}$ 0) surface (Figure S1) with a surface energy of 1.12 J m^{–2} was found to be the most stable. The (10 $\bar{1}$ 0) surface has two different types of cations, with the most exposed surface Zn atoms forming bonds to three oxygen atoms in the top layer, whereas the subsurface Zn atoms are comparatively less exposed, as they form bonds with three oxygen atoms in the top layer and one oxygen atom in the second layer, as shown in Figure S1. The semiempirical method of Grimme (D2) was included in our calculations to account for the long-range dispersion corrections.⁴⁷ Atomic charges were obtained by using the Bader analysis.^{48,49}

To model the Al₂O₃/ZnO (10 $\bar{1}$ 0) interface, three Zn ions from the surface and subsurface layers were replaced with two Al atoms in a 2 × 2 supercell of the ZnO (10 $\bar{1}$ 0) surface. Here, the energies of different configurations were calculated, and the most stable system was identified by replacing two subsurface Zn atoms with Al atoms and removing one most exposed surface Zn atom nearby. After relaxation, it was noted that both substituted Al atoms coordinate four oxygen atoms with bond lengths varying from 1.751 to 1.861 Å, as demonstrated by our results shown in Figure 1.

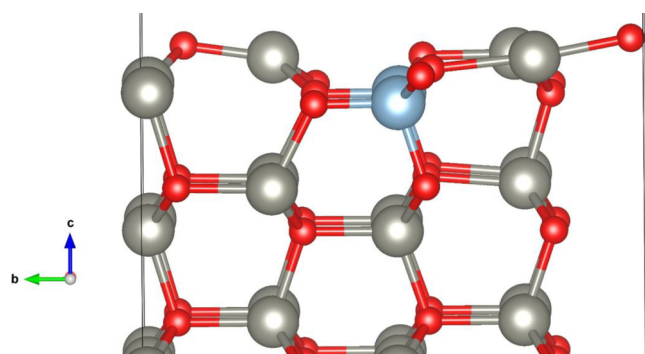


Figure 1. Relaxed structure of the $\text{Al}_2\text{O}_3/\text{ZnO}$ ($10\bar{1}0$) interface. Zn and O atoms are represented in gray and red colors, while the blue color indicates substituted Al atoms.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization of the $\text{Al}_2\text{O}_3/\text{ZnO}$ Heterostructures. As-deposited and annealed $\text{Al}_2\text{O}_3/\text{ZnO}$ nanowire model structures were examined by TEM to determine the layer thickness for amorphous Al_2O_3 coatings targeting 3 to 18 nm (3, 5, 7, 10, 12, 15, and 18 nm; 30, 50, 70, 100, 120, 150, and 180 deposition cycles, respectively) and their resistance to crystallization upon annealing at 620 °C (Figure 2). The ZnO nanowires exhibit high crystallinity, which allows for the distinct identification of the interface between the amorphous and crystalline components of Al_2O_3 and ZnO and accurate measurements of the amorphous shell thickness. TEM and high-resolution micrographs are presented for representative $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures with 7 and 18 nm of Al_2O_3 in Figure 2a,b before and after thermal treatment at 620 °C for 40 min, showing the (0001) lattice planes of ZnO covered by the amorphous Al_2O_3 layer. Chemical analysis by an EDXS line scan recorded across one $\text{Al}_2\text{O}_3/\text{ZnO}$ nanowire heterostructure (see Figure 2c) confirms the homogeneity of the aluminum oxide coating around the nanostructure. The HRTEM analyses as well as extended selected-area electron diffraction experiments (see Figure 2d) show crystallization resistance of the amorphous oxide at temperatures as high as 620 °C given the absence of reflections from a second nanocrystalline phase. In addition, we observed no significant changes in the thickness or homogeneity of the layers after annealing. To determine the reliability of the ALD process targeting 3–18 nm of Al_2O_3 , the measured shell thicknesses are statistically evaluated and compared against the ZnO nanowire diameter in Figure 2e and the targeted thickness in Figure 2f. As expected, the scatter plots demonstrate little variation of Al_2O_3 thicknesses versus the ZnO diameter. In addition, the scatter measurements are summarized in box plots showing the average layer thickness, the standard variation, and the 25–75 percentile intervals (colored boxes), which attest to the reliability of the ALD process, even when targeting small thicknesses, concluding identical deposition characteristics on columnar ZnO thin films. For example, when targeting 3 or 7 nm, this results in an average deposited layer thicknesses of 2.9 ± 0.1 and 6.7 ± 0.5 nm, respectively.

X-ray diffraction (XRD) analysis was performed to investigate the crystalline film texture of the columnar $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures grown by combining the SCS and ALD approaches. The 2θ angle of the XRD patterns ranges between 20° and 80° for ZnO, based on the PDF card #36-

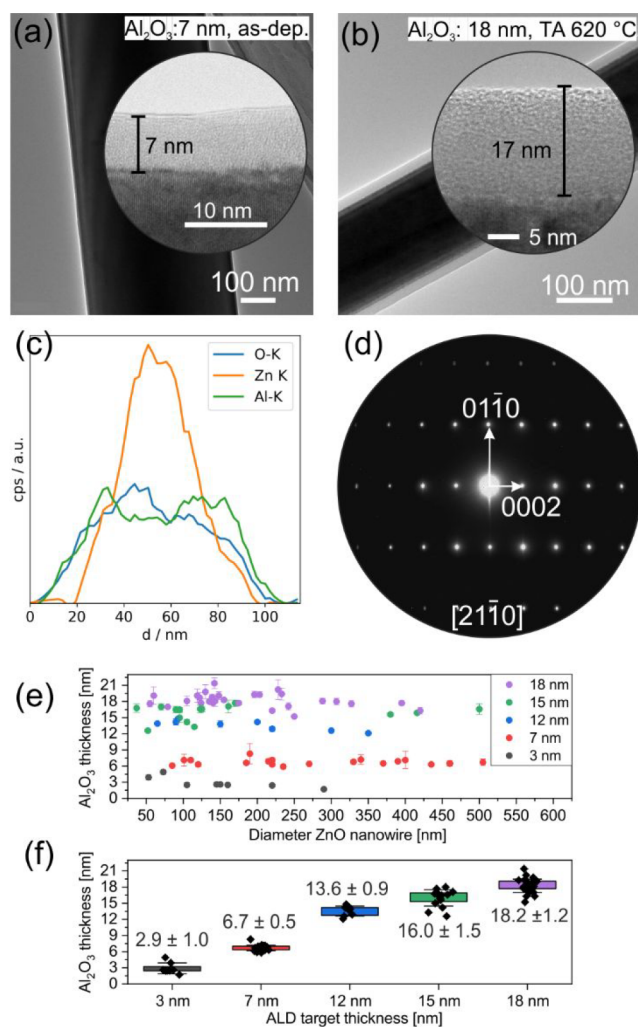


Figure 2. (a, b) TEM images of the ZnO nanowire model systems of the $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures coated with 7 and 18 nm of aluminum oxide. The HRTEM micrographs show the $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures before (a) and after (b) annealing at 620 °C. (c) Chemical analysis by EDXS line scan across one nanowire heterostructure. (d) Electron diffraction pattern of the $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructure showing only reflections assigned to ZnO. (e) Scatter plot of the measured coating thickness vs the ZnO diameter for various ALD processes and (f) box plots summarizing average values of Al_2O_3 thickness vs the targeted thickness.

1451, for both the ZnO films and $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructure samples with a film thickness of 15 nm after thermal annealing at 620 °C for 40 min (see Figure 3). Significant hkl reflections correspond to the $(10\bar{1}0)$, (0002) , $(10\bar{1}1)$, $(10\bar{1}2)$, $(11\bar{2}0)$, $(10\bar{1}3)$, $(11\bar{2}2)$, and $(20\bar{2}1)$ lattice planes of ZnO (pdf #36-1452, Zincite syn) at the 2θ values of 31.7°, 34.3°, 36.2°, 47.5°, 56.6°, 62.65°, 67.9°, and 69.1°, respectively. No reflections associated with crystalline Al_2O_3 phases were detected in our experiments. By comparing the intensity distribution of the ZnO reflections in our samples with reference to XRD powder patterns of ZnO, we found that the increased intensity of the 0002 reflections indicates a certain crystalline texture in the film, suggesting that a high fraction of columnar ZnO grows along the c -axis direction parallel to the film surfaces. Assuming that longitudinal columnar growth always takes place along the c -axis in the wurtzite-type crystal structure, the powderlike intensity distribution further supports a large out-of-plane

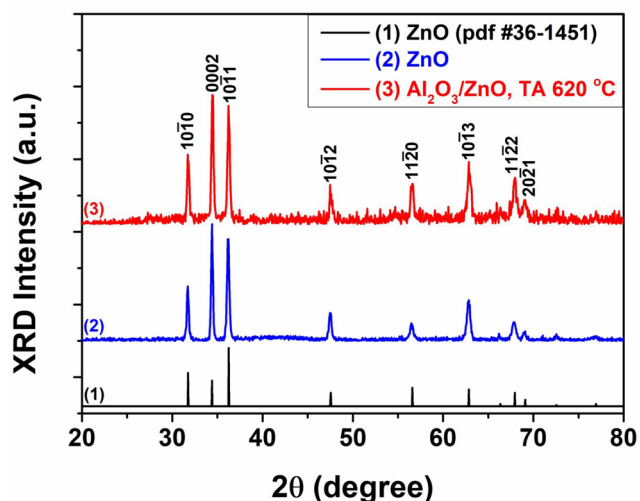


Figure 3. XRD patterns of the ZnO based on PDF card #36-1451 (curve 1), pure ZnO (curve 2), and $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures containing a nanolayer of Al_2O_3 with a thickness of 15 nm (curve 3).

mistilt of the ZnO columns, which exposes the nonpolar ($10\bar{1}0$) surface to the environment, which is useful for gas detecting properties, as we will demonstrate later.

The room temperature micro-Raman spectrum of the $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures with an Al_2O_3 thickness of 15 nm after thermal annealing at 620 °C for 40 min is shown in Figure 4. The high-intensity peaks at 100 and 437 cm^{-1} can be

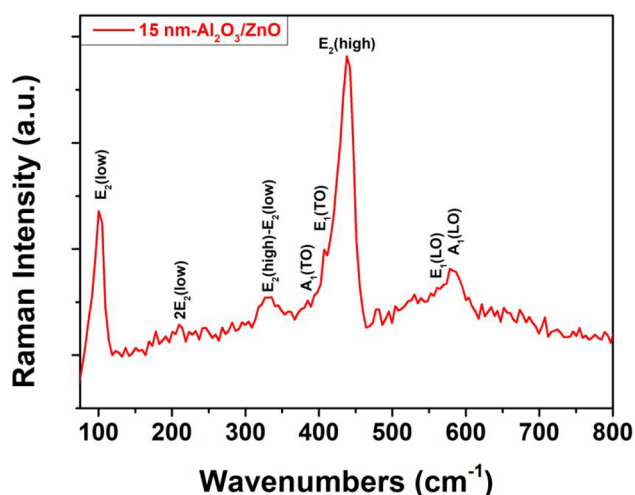


Figure 4. Room temperature micro-Raman spectrum of the annealed $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures containing a nanolayer of Al_2O_3 with a thickness of 15 nm.

assigned to the $E_2(\text{low})$ and $E_2(\text{high})$ modes of zinc oxide, respectively.^{50,51} Additional peaks at 210, 331, 384, 407, 570, and 580 cm^{-1} can be assigned to $2E_2(\text{low})$, second-order mode $E_2(\text{high}) - E_2(\text{low})$, and multiphonon scattering $A_1(\text{TO})$, $E_1(\text{TO})$, $A_1(\text{LO})$, and $E_1(\text{LO})$ (superposition) modes of zinc oxide, respectively.^{51–53} The Raman spectrum of the $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures after thermally annealing the columnar ZnO samples at 550 and 650 °C and coating them with a nanolayer of Al_2O_3 with a thickness of 7 nm followed by further thermal annealing at 620 °C for 40 min is shown in Figure S2. No peaks associated with crystalline Al_2O_3 phases

were detected, indicating that the exposed nanomaterial is an amorphous aluminum oxide layer.

The ZnO and $\text{Al}_2\text{O}_3/\text{ZnO}$ thin films deposited over two different types of substrates, namely conventional microscope glass and quartz glass substrates, were also investigated by XPS. We observed a significant signal corresponding to sodium, in agreement with previous studies of samples grown on conventional glass slides by using a similar deposition technique to the one used here after thermal annealing (see the Supporting Information Text S1 and Figure S3). The presence of Na is typically attributed to migration from the glass substrate to the sensor surface due to the elevated temperatures required to prepare the samples during post-growth thermal annealing.¹⁴ Given our choice of quartz glass as an alternative substrate, the presence of Na can be neglected to obtain a cleaner spectrum. In the investigated XPS spectrum (see Figure 5), the observed signals can be assigned to the elements Zn, O, C, and Al. It is important to point out that no signal of Zn was detected in the untreated $\text{Al}_2\text{O}_3/\text{ZnO}$ thin films deposited on quartz glass, which is explained by a continuous and complete coating of the ZnO thin film by an overlayer of Al_2O_3 , similar to the samples used for the TEM studies. Furthermore, in the spectra of both samples, namely ZnO and $\text{Al}_2\text{O}_3/\text{ZnO}$, the signal of C originates from environmental carbon compounds and was used to correct for potential charging. The high-resolution spectra of the O-1s, C-1s, Al-2p, and Zn-2p lines are shown in Figure 5.

The Zn-2p_{3/2} signal, with its peak position around 1022.0 eV, correlates well with Zn²⁺ in ZnO, which is usually reported between 1021.4 and 1022.5 eV. Furthermore, the peak separation of the Zn-2p_{3/2} and Zn-2p_{1/2} signals is 23.15 eV, which is within the expected range.³² XPS analysis indicates that the presence of ZnO rather than metallic Zn, given the characteristic shape of the O-1s peak and the presence of the additional component around 530.0 eV.^{32,54}

The Al-2p line has its main peak at 73.7 eV, which corresponds well with Al³⁺ in Al_2O_3 that is frequently reported between 73.7 and 74.8 eV.^{32,54} The obtained data are in good compliance with previous reports and confirm the high-quality nature of the nanomaterials used in our sensor studies.

3.2. Morphology of the $\text{Al}_2\text{O}_3/\text{ZnO}$ Heterostructures.

Figure 6 shows the SEM images of the $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures coated by using aluminum oxide with a thickness of 15 nm and subsequently thermally treated at 620 °C for 40 min in ambient air. For comparison purposes, Figure S4 shows the $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures with an aluminum oxide overlayer of 15 nm in thickness. Lower magnification SEM images (Figure 6a) show that nanocrystallites have grown to cover completely the glass substrate. Figure 6b shows films formed by interconnected columns that are merged over the entire surface, where they form favorable pathways for the flow of electricity through such samples. From Figure 6c,d, we measured the average diameter (D) of the nanocrystallites, which is about 300 nm. The standard deviation of the grain diameter distribution was reported in our previous works.^{8,53} Our current SEM measurements display the columnar shape of the nanostructures (see Figure 6), which compares well with the cross-section micrographs of the columnar films reported previously.⁸ Because of the highly tilted columns, which form a very rough surface structure, the nonpolar side facets are exposed to a large extent, acting as adsorption centers/sites for the VOC molecules during the sensor investigations. One of those active facets is the nonpolar ($10\bar{1}0$) surface, which has

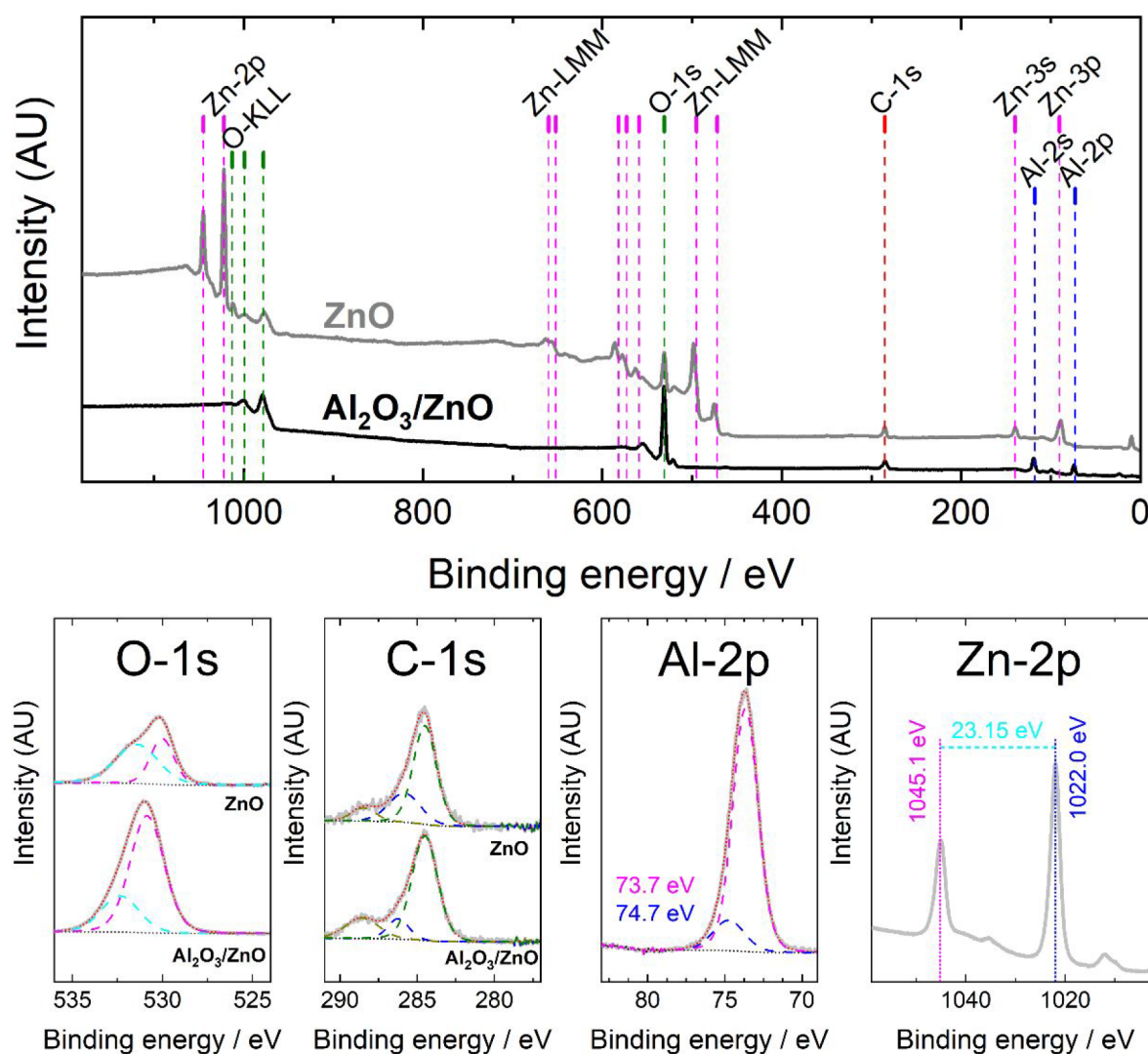


Figure 5. XPS survey (top) and high-resolution (bottom) spectra of ZnO and Al₂O₃/ZnO thin films on quartz glass substrates. The presence of the elements Zn, O, C, and Al is indicated by dashed lines in the survey spectrum. Deconvolution of the O-1s, C-1s, and Al-2p lines is indicated by dashed lines in the high-resolution spectra.

been extensively studied for gas sensing applications^{55,56} (see Figure S5).

3.3. Gas Sensing Properties of the Al₂O₃/ZnO Heterostructures. The sensing performances of the Al₂O₃/ZnO heterostructures with varying thicknesses of the Al₂O₃ layer ranging from 5 to 18 nm were investigated for several gases, including hydrogen, *n*-butanol, 2-propanol, ethanol, acetone, and ammonia, at a working temperature of 350 °C, as reported in Figure 7a. The measured gas response values indicate that 12–15 nm of Al₂O₃ in the top layer leads to the highest response and largest selectivity toward 2-propanol vapor. The lowest response value to 2-propanol is 284%, which was measured for the sensor containing an Al₂O₃ coating layer with a thickness of just 5 nm, whereas the extraordinary response to 2-propanol, on the order of 2000%, is achieved for the sensor containing an aluminum oxide layer with a thickness of 15 nm. The gas response of the Al₂O₃/ZnO heterostructures with a thickness of 15 nm was measured several times over a period of two years. Figure S6 shows that the response is essentially the same even after such a long period of time, which is very important for the use of gas sensors in safety applications. For thicker coatings, the gas response values

decrease drastically, since 15 nm is the maximum thickness of the top Al₂O₃ layer which still allows the ZnO underlayer of the heterojunction to participate in the sensing mechanism to 2-propanol. The influence of the thickness of the Al₂O₃ layer on the gas response value can be explained by the initial electrical resistance of the Al₂O₃/ZnO heterostructure, which depends proportionally on the thickness of the Al₂O₃ top layer. Figure S7 shows that as the thickness of the aluminum oxide layer increases, the initial electrical resistance of the heterostructure also increases. The lowest resistance value was obtained for the heterostructure with a top layer of only 5 nm thickness, and the highest resistance was obtained for the layer with a thickness of 18 nm. When exposed to 2-propanol vapor, different responses were observed depending on the thickness of the Al₂O₃ films deposited over the ZnO columns. The largest gas response was obtained for an optimum thickness of 15 nm. Sensors with a smaller or larger thickness of the Al₂O₃ layer have smaller responses. Sensors with thinner or thicker Al₂O₃ layers have lesser responses. From the experimental data, the gas reaction exhibits n-type semiconductor behavior, which means that the resistance to

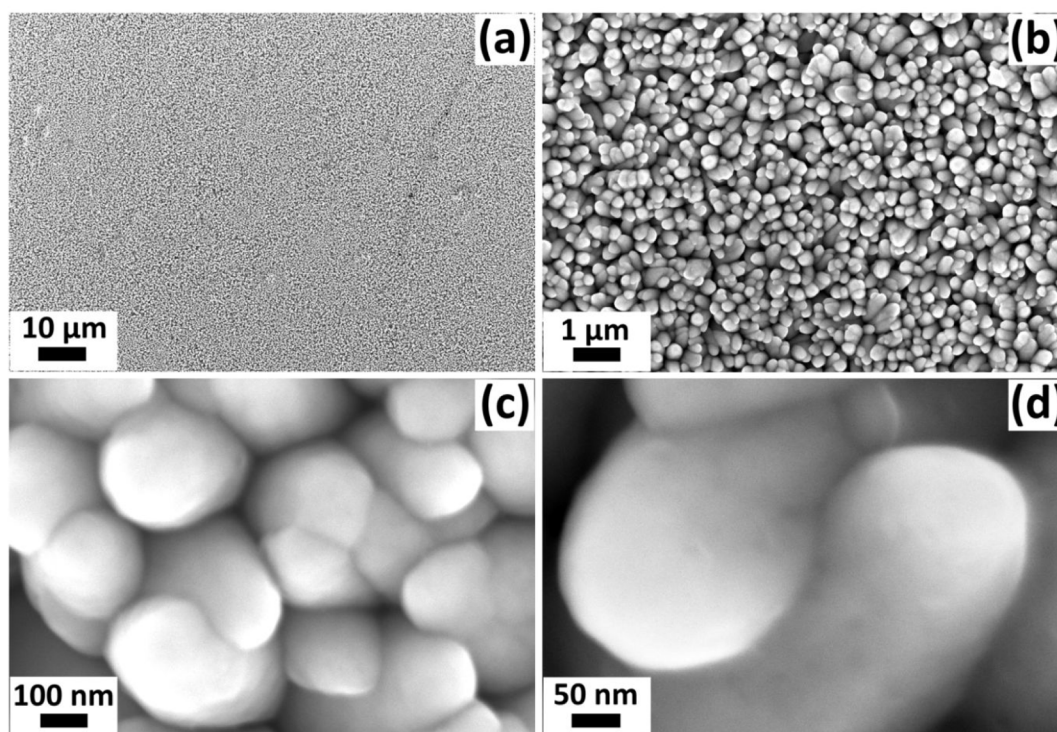


Figure 6. (a, b) Low-magnification and (c, d) high-magnification SEM images of the $\text{Al}_2\text{O}_3/\text{ZnO}$ thin films containing a nanolayer of Al_2O_3 with a thickness of 15 nm following postdeposition thermal treatment at 620°C for 40 min. The rough surface morphology is characterized by protruding columnar grains with a large degree of mistilt from the vertical growth direction and interpenetration of the grains.

gas action decreases.¹⁷ At a thickness of 5 nm, the electrical resistance of the aluminum oxide/zinc oxide heterojunction is the lowest, which means that the sensor only has a small number of electrons available to participate in the detection of 2-propanol vapors.¹⁷ As the thickness of the aluminum oxide increases, so does the number of electrons involved in detecting 2-propanol vapor. Despite measuring the highest resistance for samples with a thickness of 18 nm for the Al_2O_3 layer deposited over ZnO columns, the gas response was lower, which is related to the tunneling lifetime of the charge carriers, which is longer for the samples with smaller thickness.¹⁷ This can be justified based on the higher number of charge carriers and the shorter tunneling times, resulting in a thickness of 15 nm of the Al_2O_3 layer as optimal for the detection of 2-propanol vapors.¹⁷ To provide more insight, we have performed computer simulations to rationalize the contribution of each component of the columnar interface, that is, the ZnO underlayer and the Al_2O_3 overlayer to the sensing mechanism, with the results reported in section 3.4.

To provide further insights into the properties of the sensor structure with a 15 nm thick layer of Al_2O_3 deposited over the columnar ZnO and to compare its performance to the untreated ZnO films, we also studied the response to the gases with a concentration of 100 ppm at diverse operating/working temperatures. Figure 7b displays the response to 2-propanol vapors, which takes place at operating temperatures (OPT) equal to and above 200°C , where the response value is the lowest at about 20%. Increasing the operating temperature leads to a rise in the gas response, which reaches the value of $\sim 2000\%$ at the operating temperature of 350°C . In addition, the effect of the relative humidity on the 2-propanol response at an operating temperature of 350°C was investigated for the ZnO films and $\text{Al}_2\text{O}_3/\text{ZnO}$ heterostructures with a thickness of

15 nm for the Al_2O_3 nanolayer (see Figure S8). The gas response of the coated sensor drastically decreases by a factor of 10 at 40% of relative humidity. Compared to pure ZnO, it is evident that the Al_2O_3 overlayer protects the ZnO films against the effects of humidity, ensuring a high gas response. Figure 7b also shows the response to other gases, such as hydrogen and ethanol, which can be detected at an OPT temperature as low as 200°C , whereas the response to acetone vapors appears only at an OPT temperature of 250°C . Figure 7c provides evidence that the dynamic response curves of the sensor recover completely at the operating temperature of 350°C after stopping the flow of each of the tested gases, i.e., hydrogen, ethanol, 2-propanol, *n*-butanol, and acetone, with a concentration each of 100 ppm. The gas response was determined as

$$S = \frac{\Delta G}{G_{\text{air}}} \times 100\% = \frac{G_{\text{gas}} - G_{\text{air}}}{G_{\text{air}}} \times 100\% \quad (1)$$

where G_{air} is the conductance of the sample in air and G_{gas} is the conductance of the sample in the tested gases.⁵⁷ The response and recovery times for 2-propanol, which are shown in Table S1, have been defined in previous works^{51,58} as the time required to achieve or recover 90% of the complete response. A comparison of parameters published in the literature for other sensors for 2-propanol is shown in Table S1. The proposed gas sensing mechanism is described in Supporting Information Text S2. On the basis of this investigation, the decreasing order of stability for the adsorption of the VOCs on the exposed sites is 2-propanol > *n*-butanol \approx ethanol > acetone. Figure S9 shows that the current–voltage characteristics show ohmic character at room temperature and operating temperatures of 150 and 200°C .

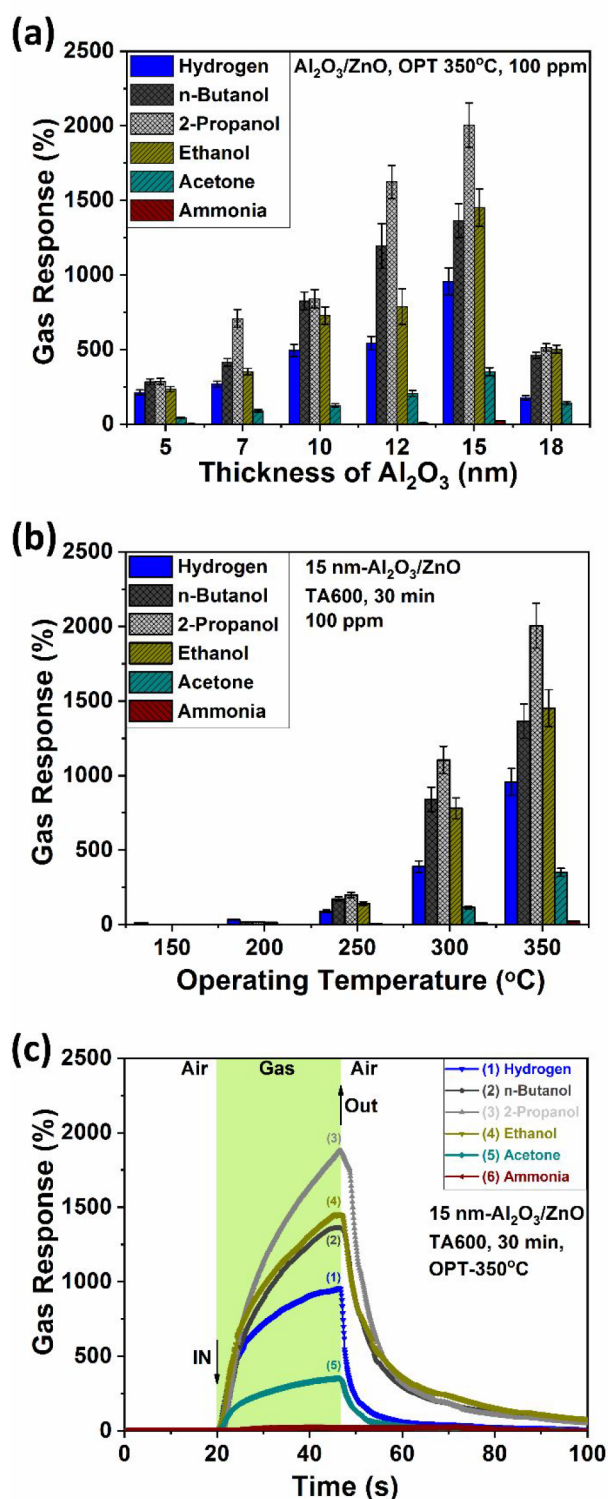


Figure 7. (a) Gas response vs thickness of Al₂O₃ overlayer (5, 7, 10, 12, 15, and 18 nm). (b) Gas response vs operating temperatures. (c) Dynamic response of the Al₂O₃/ZnO sample set containing a nanolayer of Al₂O₃ with a thickness of 15 nm.

The *I*–*V* electrical curve changes at elevated operating temperatures between 250 and 350 °C, demonstrating the nonlinear behavior of the sensor due to an increase of its conductivity.^{59–61} It was also observed that the electrical current values are quite small, on the order of microamperes, up to the operating temperature of 200 °C. However, the value

of the electrical current increases in the order of milliamperes after raising the operating temperature from 250 to 350 °C because of the increase in electrical conductivity.^{24,51,62}

3.4. Adsorption of Molecules on the Al₂O₃/ZnO Heterostructures. Ab Initio Calculations of the Sensor Surface and Interface. To rationalize the experimental observations, we have performed comprehensive DFT calculations of our model of the sensor surface and interface, where we have considered the special surface morphology characterized by a large proportion of grains that expose nonpolar side facets. An explanation for performing the calculations using the particular Al₂O₃/ZnO(10 $\bar{1}0$) interface is presented in Supporting Information Text S3. The XRD and SEM measurements suggest that the columnar zinc oxide film is *c*-textured and exhibits an “irregular”/rough surface structure, where the ZnO columns do not grow perpendicular to the surface normal and have conical shapes at the top.⁸ This surface structure allows ZnO to expose a large fraction of side facets, which act as adsorption sites upon exposure to the test gas. To provide further insight into the surface chemistry of the Al₂O₃/ZnO(10 $\bar{1}0$) interface, we simulated the adsorption of a selection of VOCs comprising 2-propanol (2-C₃H₇OH), *n*-butanol (*n*-C₄H₉OH), ethanol (C₂H₅OH), and acetone (CH₃COCH₃), as well as hydrogen (H₂). Given the structure of the Al₂O₃/ZnO(10 $\bar{1}0$) interface, we explored the interaction of the VOCs via coordination of their O atom with the exposed Zn and Al species, while the adsorption of H₂ was calculated on the surface O atoms. For the binding configurations, the atoms forming the coordinate bond at the interface were initially placed at a distance of ~1.5 Å, and the entire systems were afterward permitted to relax to their equilibrium adsorption geometries and energies, in line with our previous works.^{41–43,63}

The adsorption energies for the interactions of the molecules with the Al₂O₃/ZnO(10 $\bar{1}0$) interface are listed in Table 1. Our

Table 1. Adsorption Energies (E_{ads}) and Charge Transfers (Δq) for 2-C₃H₇OH, *n*-C₄H₉OH, C₂H₅OH, CH₃COCH₃, and H₂ on the Al₂O₃/ZnO(10 $\bar{1}0$) Interface^a

adsorbate	site	E_{ads} (eV)	Δq (e ⁻)
2-C ₃ H ₇ OH	Al	-0.697	-0.019
	Zn	-1.330	0.054
<i>n</i> -C ₄ H ₉ OH	Al	-0.450	-0.021
	Zn	-1.329	0.047
C ₂ H ₅ OH	Al	-0.642	-0.013
	Zn	-1.245	0.043
CH ₃ COCH ₃	Al	-0.622	-0.019
	Zn	-0.959	0.034
H ₂	molecular	-0.118	-0.011
	dissociated	-0.434	1.181

^aThe adsorption site of the adsorbate on the nanoparticles is also indicated. A negative value of Δq denotes that the adsorbate gains electron charge.

calculations suggest that the VOCs release the largest adsorption energies upon interaction with the surface Zn atoms, which are on average 0.3–0.8 eV more reactive than the Al dopant site. We found that the adsorption energies for the less favorable Al sites follow almost the same trends simulated for the Zn atoms. The H₂ molecule shows a preference by 0.316 eV for dissociative rather than molecular adsorption. Although still releasing slightly larger adsorption energy than

the dissociative binding mode of H_2 , the interaction of n - C_4H_9OH with the Al site displays the smallest adsorption energy of all VOCs at -0.450 eV. The calculated binding energies, at the most stable adsorption sites, reveal that the decreasing order of molecular preference for the $Al_2O_3/ZnO(10\bar{1}0)$ interface is 2-propanol ($2-C_3H_7OH$) \approx n -butanol ($n-C_4H_9OH$) $>$ ethanol (C_2H_5OH) $>$ acetone (CH_3COCH_3) \gg hydrogen (H_2). These binding strengths for the organic molecules on the Zn site agree with our gas response experiments. However, our molecular adsorption simulations are unable to capture the larger selectivity observed for H_2 with respect to acetone (CH_3COCH_3) in our gas sensing tests, which may be the result of other surfaces present in small proportions in the experimental morphology, which are not considered in our simulations. Figure S10 shows the unit cell of the ZnO wurtzite-type structure.

We have also simulated the adsorption energies and charge transfers of the adsorbates on the pristine α - $Al_2O_3(0001)$ and ZnO ($10\bar{1}0$) surfaces, which are listed in Table 2. We found

Table 2. Adsorption Energies (E_{ads}) and Charge Transfers (Δq) for $2-C_3H_7OH$, $n-C_4H_9OH$, C_2H_5OH , and CH_3COCH_3 as Well as Molecular and Dissociated H_2 on the α - $Al_2O_3(0001)$ and ZnO($10\bar{1}0$) Surfaces^a

adsorbate	α - $Al_2O_3(0001)$		ZnO($10\bar{1}0$)	
	E_{ads} (eV)	Δq (e^-)	E_{ads} (eV)	Δq (e^-)
$2-C_3H_7OH$	-1.523	0.017	-1.126	0.041
$n-C_4H_9OH$	-1.501	0.011	-1.043	0.036
C_2H_5OH	-1.509	0.013	-1.071	0.033
CH_3COCH_3	-1.545	0.019	-0.926	0.044
H_2 molecular	-0.378	-0.197	-0.327	-0.012
H_2 dissociated	-0.862	1.172	-0.357	-0.018

^aA negative value of Δq denotes that the adsorbate gains electron charge.

that the adsorption energies on the $Al_2O_3/ZnO(10\bar{1}0)$ interface have intermediate values with respect to the parent

materials. This explains that the vapor molecules do not bind too strongly, poisoning the interface and preventing the interaction and detection of other molecules. On the other hand, the largest charge transfers were obtained for the interaction with the $Al_2O_3/ZnO(10\bar{1}0)$ interface, supporting the strong signal measured during the gas sensing experiments.

Figure 8 illustrates the most stable binding modes for the adsorption of the molecules investigated here, that is, the VOCs and H_2 , on the surface of the $Al_2O_3/ZnO(10\bar{1}0)$ interface. As discussed previously, the alcohols and the ketone show the largest preference for the Zn site, where the Zn–O coordinate bond distances formed range from 2.08 to 2.12 Å. We also found evidence that the alcohols form a hydrogen bond with a nearby surface O atom in a secondary interaction. The longest hydrogen bond distance of 2.30 Å was calculated for the most stable adsorption mode of 2-propanol ($2-C_3H_7OH$), while the shortest hydrogen bond of 1.99 Å was predicted for ethanol (C_2H_5OH). Our simulations suggest that there is an inverse correlation between the adsorption energy of the alcohols and the distance of the hydrogen bond formed with the surface. By comparing the average adsorption energies of the alcohols with the value for the ketone, we estimate that the formation of the hydrogen bonds accounts for around 0.3 eV. The alkyl radical of the alcohols containing up to three C atoms lies almost parallel to the surface, but it accommodates itself perpendicularly to the surface for n -butanol ($n-C_4H_9OH$). The H_2 molecule dissociates upon adsorption, with the H atoms forming OH groups with the surface O ions. The mean O–H bond distance is 0.99 Å, which is typical of hydroxyl groups, while the separation between the dissociated H atoms was computed at 6.82 Å.

We next performed a Bader charge analysis to rationalize the trends obtained for the adsorption energies. Table 1 lists the charges transferred upon the interaction between the adsorbates and the surface. For the least favorable adsorption modes on the Al sites, we found that the VOCs gain electron density from the surface and become negatively charged. The charge density donated by the surface in the least stable

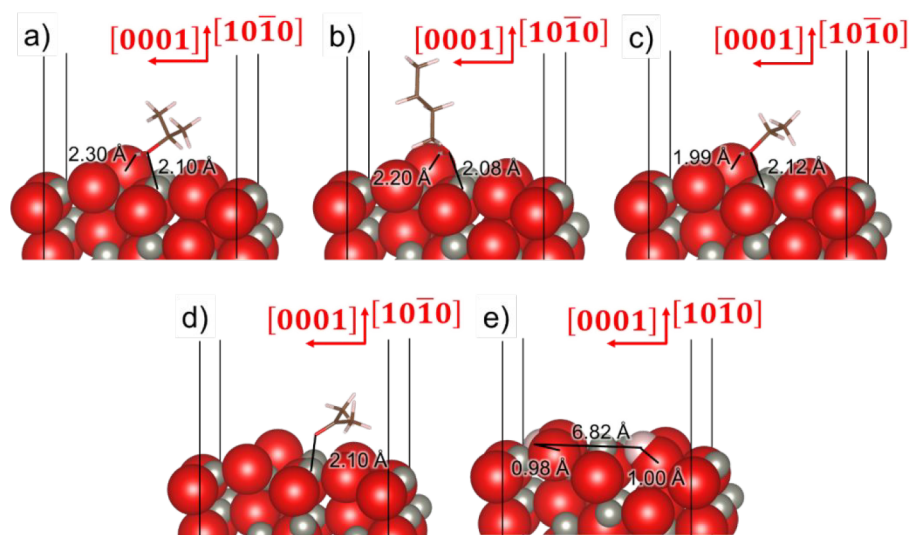


Figure 8. Adsorption of (a) $2-C_3H_7OH$, (b) $n-C_4H_9OH$, (c) C_2H_5OH , (d) CH_3COCH_3 , and (e) H_2 on the $Al_2O_3/ZnO(10\bar{1}0)$ interface. Interatomic distances are indicated, and crystallographic directions are shown with respect to the ZnO($10\bar{1}0$) layer. The $Al_2O_3/ZnO(10\bar{1}0)$ interfaces are displayed by using the space-filling representation, whereas the adsorbates are indicated by using the stick representation. O atoms are in red, H atoms are in white, C atoms are in brown, Zn atoms are in gray, and Al atoms are in blue.

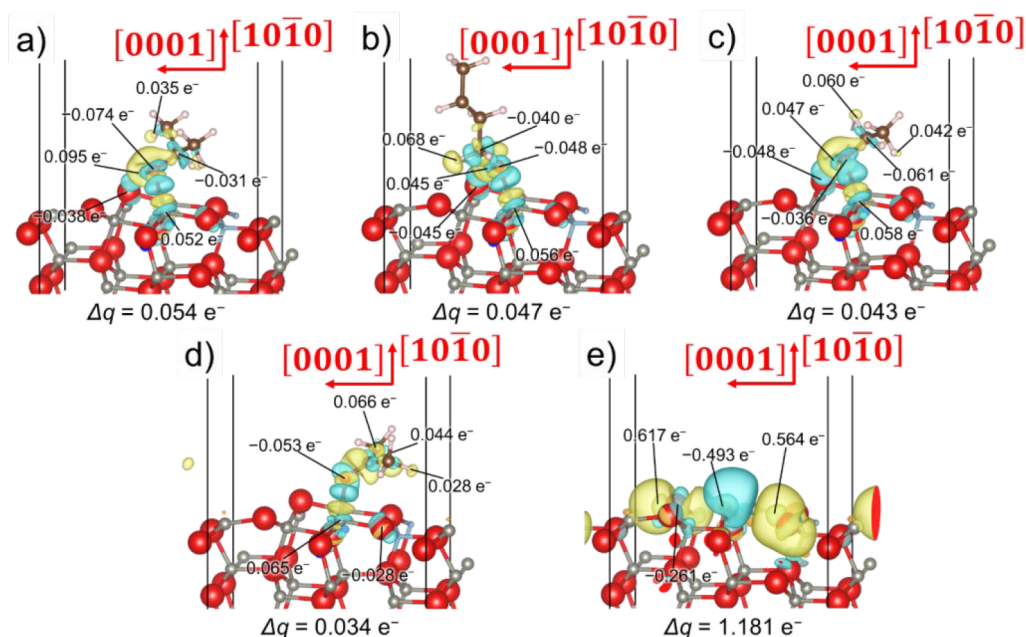


Figure 9. Charge density flow ($\Delta\rho$) for the adsorption of (a) 2- $\text{C}_3\text{H}_7\text{OH}$, (b) $n\text{-C}_4\text{H}_9\text{OH}$, (c) $\text{C}_2\text{H}_5\text{OH}$, (d) CH_3COCH_3 and (e) H_2 on the $\text{Al}_2\text{O}_3/\text{ZnO}(1010)$ interface. Crystallographic directions are indicated with respect to the $\text{ZnO}(1010)$ substrate. The $\text{Al}_2\text{O}_3/\text{ZnO}(1010)$ interfaces and the adsorbates are displayed by using the ball-and-stick representation. Electron density gain and depletion surfaces are in green and yellow, respectively. Isosurfaces display a value of $\pm 0.002 \text{ e}^- \text{ \AA}^{-3}$. The atomic charge density differences for the atoms that suffered the largest change are also indicated. A negative value of charge transfer denotes that the species gains electron charge. O atoms are in red, H atoms are in white, C atoms are in brown, Zn atoms are in gray, and Al atoms are in blue.

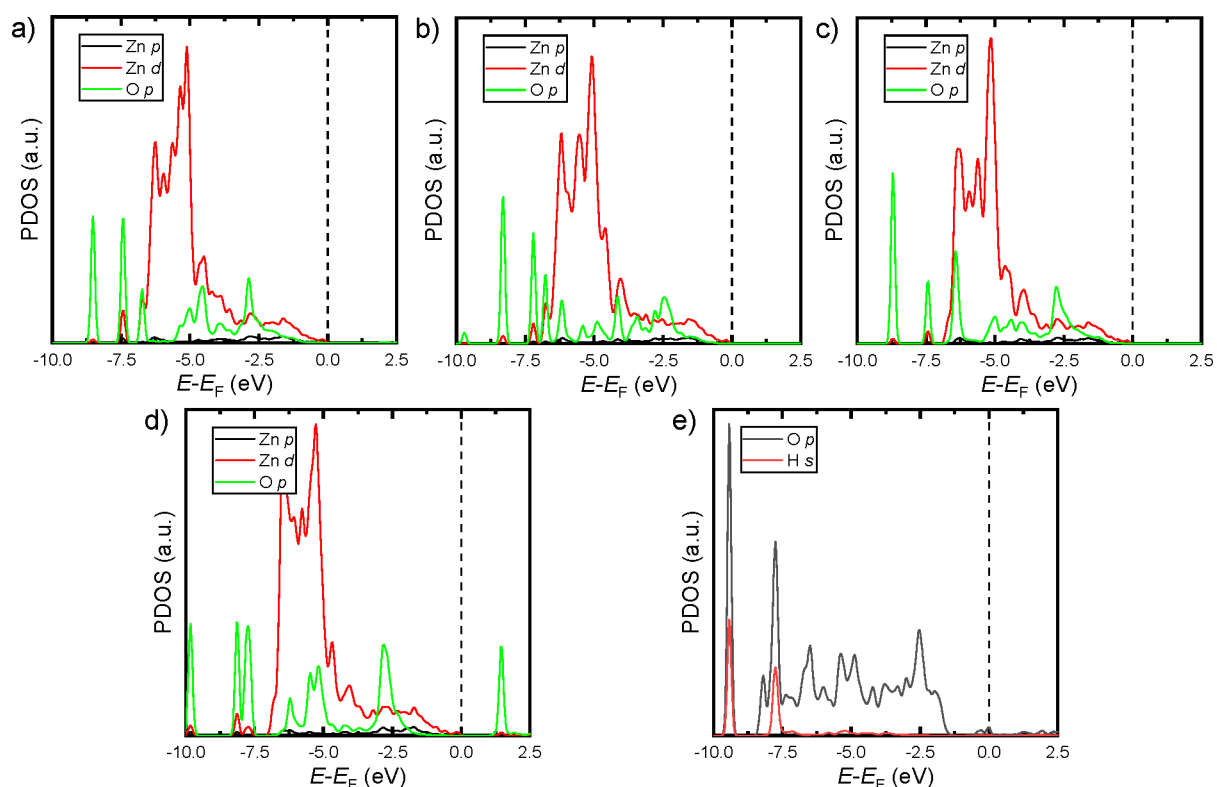


Figure 10. Atomic projections of the density of states (PDOS) for the p and d electrons of the surface Zn ions and for the p states of the molecular O atoms directly interacting for the most stable adsorption modes of (a) 2- $\text{C}_3\text{H}_7\text{OH}$, (b) $n\text{-C}_4\text{H}_9\text{OH}$, (c) $\text{C}_2\text{H}_5\text{OH}$, and (d) CH_3COCH_3 on the $\text{Al}_2\text{O}_3/\text{ZnO}(1010)$ interface. The p states of the surface O anions are plotted alongside the s orbitals of the interacting H species for the adsorption of the (e) H_2 molecule. The vertical dashed lines represent the Fermi level.

binding configurations was calculated between -0.019 and -0.021 e^- for the VOCs, apart from ethanol ($\text{C}_2\text{H}_5\text{OH}$),

which gained a more modest value of -0.013 e^- . We also found evidence of charge density migration of -0.011 e^- from

the surface to the adsorbed H₂ molecule. In contrast, the VOCs and H₂ lost electron density to the surface in the interactions with the most sensitive Zn site and when H₂ is adsorbed dissociatively, respectively. Our calculations reveal that in the adsorption of the alcohols at the Zn atoms they donated more than twice the charge gained from the surface in the interactions with the Al sites. In particular, the H₂ molecule transferred 1.181 e⁻ during its dissociative adsorption, which is the largest charge flow observed in this work. Our DFT-calculated charges show that the electron densities donated by the VOCs at the Zn sites follow the same trend as the adsorption energies, validating the coordinate nature of the bond formed at the molecule/surface interface. Figure 9 displays the charge density difference ($\Delta\rho$) for the most exothermic binding configurations and for the atoms that experienced the largest electron density change. Note that the charge density differences were calculated as $\Delta\rho = \rho_{\text{ads}} - \rho_{\text{mol}} - \rho_{\text{surf}}$, where ρ_{ads} , ρ_{mol} , and ρ_{surf} represent the charge density of the adsorption, the isolated molecule, and the isolated surface, respectively, with identical structure. Figure 9a–c illustrates that the alcohols lost between 0.043 and 0.054 e⁻ of charge during adsorption, whereas the hydroxyl O received -0.036 to -0.074 e⁻ from the coordinated Zn atom, which donated 0.052 to 0.058 e⁻. Moreover, the hydroxyl H, which is involved in the hydrogen bond between the alcohols and the surface, saw its electron charge reduced by 0.047 to 0.095 e⁻, which was incorporated by a nearby surface O atom, which increased its charge by -0.036 to -0.045 e⁻. The O atom from the acetone (CH₃COCH₃) molecule accepted -0.053 e⁻ to reach a total charge of -1.127 e⁻, whereas the coordinated Zn atom depleted its electron density by 0.065 e⁻ (see Figure 9d). The atoms from the alkyl chain of the VOCs containing fewer than four C atoms, which adsorb parallel to the surface, also experienced significant charge transfers, indicating the existence of weak Coulomb attraction forces between the adsorbate and the sensor. Figure 9e shows that each of the H atoms donated over 0.5 e⁻ of charge, in one case to the O atom forming the structural OH group and in the other case to a nearby surface anion that establishes a hydrogen bond, which gained between -0.261 and -0.493 e⁻ of electron density.

To provide further insight into the electronic properties of the most exothermic adsorption configurations, we have calculated the projection of the density of states (PDOS) onto the interacting atoms, as shown in Figure 10. The PDOS of the p states of the Zn atoms are negligible and are therefore not discussed. Figure 10a–d shows that the Zn valence d states appear between the Fermi level and -7.0 eV, with the center of the largest PDOS calculated at around -5.5 eV. The Zn d states do not display any virtual band below 2.5 eV, indicating that the surfaces are large bandgap insulators. Despite the minor differences observed on the d states of Zn, the O p orbitals of the adsorbates show discrete peaks with their positions slightly shifted for the different molecular adsorptions. For example, the alcohols have three bands at approximately -9.75, -7.5, and -6.25 eV as well as a shoulder within the range of -2.0 to -5.5 eV. However, the ketone displays mostly isolated bands that are away from the Fermi level with respect to the alcohols. Our PDOS for the interaction of the VOCs with the sensor shows minimal hybridization between the d and p states of the Zn and O atoms, respectively, confirming that these atoms form a coordinate bond with moderate charge transfers. For the dissociative adsorption of H₂, the surface O atoms forming the

structural hydroxyl groups have a broad band between -1.25 and -9.75 eV and two distinctive bands at -9.5 and -7.7 eV (see Figure 10e). The dissociated H atoms have an s band each, which are strongly hybridized with the isolated bands of the surface O atoms, providing further evidence for the covalent bond formed between these atoms and explaining the large charge transfer calculated for this adsorption configuration.

To summarize our DFT calculations of the adsorption of VOCs, which are in excellent agreement with the gas response investigations, we predict that 2-C₃H₇OH releases the largest adsorption energy when it interacts with the Al₂O₃/ZnO-(10 $\bar{1}$ 0) surface. The interaction between our model of the nanostructured sensor and the secondary alcohol is characterized by one interfacial Zn–O coordination bond and a secondary interaction in the form of a hydrogen bond between the adsorbate and the surface. The alkyl radical of 2-C₃H₇OH lies parallel to the surface due to weak Coulomb attractive forces. The O atom of 2-C₃H₇OH donates electronic charge to the coordinated Zn cation, as confirmed by the Bader analysis and projection of the density of states, which is typical of coordinative covalent bonds.

4. CONCLUSIONS

The Al₂O₃/ZnO heterostructure-based sensors deposited on different substrates were successfully obtained by using an SCS approach in combination with a new high-aspect-ratio ALD method, in which coatings of Al₂O₃ ultrathin films with a thickness of between 3 and 18 nm were deposited on top of columnar ZnO films. The reliability of this process was demonstrated by TEM studies on suitable model systems. The morphological, microtopological, nanostructural, electrical, and gas sensing performances of these sensors were fully characterized. The analysis of the morphology of the sensors revealed that as-grown, interconnected, and interpenetrated nanocrystallites of the columnar ZnO underlayer were covered by a thin overlayer of Al₂O₃. The structural studies confirmed the formation of the Al₂O₃/ZnO heterostructures, whereas the TEM measurements validated the thickness of the Al₂O₃ layers between 3 and 18 nm. The morphological and structural characterization of the ZnO film revealed a rough surface composed of protruding and interpenetrating columnar grains grown with a distinct 0002 texture and a large out-of-plane tilt, suggesting a dominant fraction of exposed (10 $\bar{1}$ 0) side facets in the total surface area of the sensor.

We found that the best response is obtained at a nominal thickness of the aluminum oxide overlayer of 15 nm deposited on top of the columnar ZnO underlayer. By gradually increasing the thicknesses of Al₂O₃ to 15 nm, we improved the response to 2-propanol to the highest selectivity of ~2000% at the OPT of 350 °C.

We also calculated the adsorption modes, structures, and electronic properties of the interaction of a series of VOC molecules and H₂ with the Al₂O₃/ZnO(10 $\bar{1}$ 0) interface using DFT-D2 methods to identify the contribution of this junction to the sensing mechanism. We first obtained the relevant Al₂O₃/ZnO(10 $\bar{1}$ 0) interface structure by replacing three Zn atoms with two Al atoms and identified the most stable structure where two subsurface Zn atoms had been replaced by Al atoms, while removing a nearby subsurface Zn atom to keep the system electrically neutral. We calculated negative adsorption energies for the interaction of all the molecules studied here with the interface, indicating that these are

spontaneous processes. The Zn sites are more reactive than the Al dopant atoms, indicated by the relative exothermicity of the molecular adsorptions at the two sites. The adsorbates acquired electron charge upon binding to the Al sites but donated electron densities in their interactions with the Zn site, supporting the coordinative nature of the bond formed between the adsorbate and the sensor. The decreasing order of stability for the adsorption of the VOCs on the Zn site is $E_{\text{ads}}(2\text{-C}_3\text{H}_7\text{OH}) \approx E_{\text{ads}}(n\text{-C}_4\text{H}_9\text{OH}) > E_{\text{ads}}(\text{C}_2\text{H}_5\text{OH}) > E_{\text{ads}}(\text{CH}_3\text{COCH}_3)$. The alkyl radical chain of the VOCs with up to three C atoms becomes flat after adsorption to facilitate small charge transfers with the surface. On the basis of the local density of states analysis, we have determined the fundamental role of the Zn d states and molecular O p orbitals in the interaction between the adsorbates and the sensor. The strong hybridization of the H s electron and the interacting surface O p states evidences the covalent character of the bond formed during the dissociative adsorption of H₂.

To conclude, this study confirmed the successful synthesis of Al₂O₃/ZnO heterostructures and their suitability as a new sensor device for the detection of VOCs. We have demonstrated that a thorough optimization of technological approaches, especially by combining different methods like SCS and ALD, and enhancement of surface properties, by creating heterostructured nanomaterials, improve the gas response to 2-propanol and *n*-butanol in real applications. The results obtained are highly important for practical applications as well as for further fundamental studies of the junction effects on the sensing mechanism of VOC sensors based on semiconducting metal oxides.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.2c03704>.

Structure of the 2 × 2 supercell of the ZnO (10 $\bar{1}$ 0) surface simulated by using DFT calculations; micro-Raman spectra of the ZnO films and Al₂O₃/ZnO heterostructures with thermal annealing of ZnO at 550 and 650 °C and with a nanolayer of Al₂O₃ with a thickness of 7 nm treated with thermal annealing/treatment at 620 °C for 40 min; XPS spectra and related discussion of the Al₂O₃/ZnO heterostructures deposited over glass substrates; SEM results of the Al₂O₃/ZnO heterostructures with a thickness of 15 nm of Al₂O₃; crystallographic structure of ZnO showing the shape of a hexagonal prism and the planes (0001), (000 $\bar{1}$), and (10 $\bar{1}$ 0); variation of the gas response to 2-propanol vapors over time for the Al₂O₃/ZnO heterostructures with a thickness of 15 nm for the Al₂O₃ overlayer; the initial electrical resistance of the Al₂O₃/ZnO heterostructure depends on the thickness of the Al₂O₃ film; the influence of relative humidity in the response to 2-propanol at different relative humidity values of the ZnO films and Al₂O₃/ZnO heterostructures; comparison of the reported 2-propanol sensors with high gas response values; scheme of the suggested gas detection/sensing mechanism; current–voltage characteristics and related discussion of a ZnO/Al₂O₃ heterostructure sensor with 15 nm Al₂O₃ layer thickness at different operating temperatures; the unit cell of the ZnO wurtzite-type structure (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Oleg Lupan – Department of Materials Science, Chair for Functional Nanomaterials, Faculty of Engineering, Christian-Albrechts Universität zu Kiel, D-24143 Kiel, Germany; Center for Nanotechnology and Nanosensors, Department of Microelectronics and Biomedical Engineering, Faculty of Computers, Informatics and Microelectronics, Technical University of Moldova, MD-2004 Chisinau, Republic of Moldova; Department of Physics, University of Central Florida, Orlando, Florida 32816-2385, United States; orcid.org/0000-0002-7913-9712; Email: ollu@tf.uni-kiel.de, oleg.lupan@mib.utm.md

David Santos-Carballal – School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom; orcid.org/0000-0002-3199-9588; Email: d.santos-carballal@leeds.ac.uk

Lorenz Kienle – Department of Materials Science, Chair for Synthesis and Real Structure, Faculty of Engineering, Christian-Albrechts Universität zu Kiel, D-24143 Kiel, Germany; Email: lk@tf.uni-kiel.de

Rainer Adlung – Department of Materials Science, Chair for Functional Nanomaterials, Faculty of Engineering, Christian-Albrechts Universität zu Kiel, D-24143 Kiel, Germany; orcid.org/0000-0002-2617-678X; Email: ra@tf.uni-kiel.de

Alexander Vahl – Department of Materials Science, Chair for Multicomponent Materials, Faculty of Engineering, Christian-Albrechts Universität zu Kiel, D-24143 Kiel, Germany; Email: alva@tf.uni-kiel.de

Sandra Hansen – Department of Materials Science, Chair for Functional Nanomaterials, Faculty of Engineering, Christian-Albrechts Universität zu Kiel, D-24143 Kiel, Germany; orcid.org/0000-0002-3529-8367; Email: sn@tf.uni-kiel.de

Authors

Nicolae Magariu – Center for Nanotechnology and Nanosensors, Department of Microelectronics and Biomedical Engineering, Faculty of Computers, Informatics and Microelectronics, Technical University of Moldova, MD-2004 Chisinau, Republic of Moldova

Abhishek Kumar Mishra – Department of Physics, School of Engineering, University of Petroleum and Energy Studies (UPES), Dehradun 248007 Uttarakhand, India

Nicolai Ababii – Center for Nanotechnology and Nanosensors, Department of Microelectronics and Biomedical Engineering, Faculty of Computers, Informatics and Microelectronics, Technical University of Moldova, MD-2004 Chisinau, Republic of Moldova

Helge Krüger – Department of Materials Science, Chair for Functional Nanomaterials, Faculty of Engineering, Christian-Albrechts Universität zu Kiel, D-24143 Kiel, Germany; orcid.org/0000-0002-9638-8753

Niklas Wolff – Department of Materials Science, Chair for Synthesis and Real Structure, Faculty of Engineering, Christian-Albrechts Universität zu Kiel, D-24143 Kiel, Germany

Mani Teja Bodduluri – Fraunhofer Institute for Silicon Technology (ISIT), Itzehoe D-25524, Germany

Niklas Kohlmann – Department of Materials Science, Chair for Synthesis and Real Structure, Faculty of Engineering, Christian-Albrechts Universität zu Kiel, D-24143 Kiel, Germany; orcid.org/0000-0001-8494-118X

Nora H. de Leeuw – School of Chemistry, University of Leeds, Leeds LS2 9JT, United Kingdom; Department of Earth Sciences, Utrecht University, 3584 CB Utrecht, The Netherlands; orcid.org/0000-0002-8271-0545

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsami.2c03704>

Author Contributions

O.L., N.M., M.T.B., and S.H. have prepared the materials and developed the deposition approach. A.V. performed all XPS experiments, analyzed the XPS data, and drafted part of the article. O.L., N.M., R.A., and S.N. fitted a technological strategy and experiments for material incorporation into the devices for detecting VOCs. N.M., N.A., H.K., and O.L. performed the characterization of the materials, analyzed the data, and wrote part of the draft of the article. M.T.B. performed laboratory research of the alumina ALD. O.L., N.M., D.S.-C., A.K.M., N.A., A.V., N.H.d.L., R.A., H.K., and S.H. analyzed the data from experiments and contributed to writing the manuscript. D.S.-C., A.K.M., and N.H.d.L. performed the DFT simulations and drafted the computational part of the manuscript. O.L., N.M., S.N., R.A., L.K., N.H.d.L., and D.S.-C. conceived and designed the study and gave the final approval of the draft to be submitted and published. N.K., N.W., and L.K. performed TEM laboratory research and investigations, analyzed the TEM results, and drafted part for the article. O.L., S.H., L.K., and R.A. performed the design and conception of the studies. The work was written based on contributions by all authors, who all reviewed the manuscript.

Funding

Project “SuSiBaBy”-SulfurSilicon Batteries by the EUSH and EFRE in SH (LPW-E/3.1.1/1801). Federal Ministry of Education and Research - “PorSSi” project (03XP0126 A & B). German Research Foundation (DFG, Deutsche Forschungsgemeinschaft) under the schemes SFB1261, SFB 1461 & AD 183/16-1. Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), Project-ID 434434223, SFB 1461. Grant G5634 “Advanced Electro-Optical Chemical Sensors” AMOXES, NATO Science for Peace and Security Programme (SPS). Additionally, the authors thank the WTSH and the EUSH for partially funding this project BAEW with (LPW-E/1.1.2/1486). A.K.M. acknowledges the UPES SEED grant (year 2022) for computations.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge funding within the project “SuSiBaBy”-SulfurSilicon Batteries by the EUSH and EFRE in SH (LPW-E/3.1.1/1801). We are especially grateful to the Federal Ministry of Education and Research by funding the former “PorSSi” project (03XP0126 A & B). The membership of D.S.C. and N.H.d.L. of the UK’s HEC Materials Chemistry Consortium was funded by EPSRC (EP/L000202 and EP/R029431). This work used the ARCHER2 UK National Supercomputing Service (<http://www.archer2.ac.uk>). This work also used ARC4 resources, part of the High-Performance Computing facilities at the University of Leeds, United Kingdom. This work was in part funded by the German Research Foundation (DFG) under Grant KI 1263/17-1. This work was also funded by the Deutsche Forschungsgemein-

schaft (DFG, German Research Foundation), Project-ID 434434223, SFB 1461 and SFB 1261. A.K.M. acknowledges the SEED computational support from University of Petroleum and Energy Studies (UPES), Dehradun. All data created during this research are presented in this paper and in the [Supporting Information](#). This research was sponsored in part by the NATO Science for Peace and Security Programme (SPS) within Grant G5634 “Advanced Electro-Optical Chemical Sensors” AMOXES.

REFERENCES

- (1) Lin, T.; Lv, X.; Hu, Z.; Xu, A.; Feng, C. Semiconductor Metal Oxides as Chemoresistive Sensors for Detecting Volatile Organic Compounds. *Sensors (Switzerland)* **2019**, *19* (2), 233.
- (2) Zappa, D.; Galstyan, V.; Kaur, N.; Munasinghe Arachchige, H. M. M.; Sisman, O.; Comini, E. Metal Oxide -Based Heterostructures for Gas Sensors”- A Review. *Anal. Chim. Acta* **2018**, *1039*, 1–23.
- (3) Li, T.; Zeng, W.; Wang, Z. Quasi-One-Dimensional Metal-Oxide-Based Heterostructural Gas-Sensing Materials: A Review. *Sensors Actuators, B Chem.* **2015**, *221*, 1570–1585.
- (4) Choi, S. J.; Kim, I. D. Recent Developments in 2D Nanomaterials for Chemiresistive-Type Gas Sensors. *Electron. Mater. Lett.* **2018**, *14* (3), 221–260.
- (5) Lupan, O.; Ababii, N.; Mishra, A. K.; Bodduluri, M. T.; Magariu, N.; Vahl, A.; Krüger, H.; Wagner, B.; Faupel, F.; Adelung, R.; de Leeuw, N. H.; Hansen, S. Heterostructure-Based Devices with Enhanced Humidity Stability for H₂ Gas Sensing Applications in Breath Tests and Portable Batteries. *Sensors Actuators, A Phys.* **2021**, *329*, 112804.
- (6) Galstyan, V.; Kaur, N.; Zappa, D.; Núñez-Carmona, E.; Sberveglieri, V.; Comini, E. Chemical Gas Sensors Studied at SENSOR Lab, Brescia (Italy): From Conventional to Energy-Efficient and Biocompatible Composite Structures. *Sensors (Switzerland)* **2020**, *20* (3), 579.
- (7) Cretu, V.; Postica, V.; Mishra, A. K.; Hoppe, M.; Tiginyanu, I.; Mishra, Y. K.; Chow, L.; De Leeuw, N. H.; Adelung, R.; Lupan, O. Synthesis, Characterization and DFT Studies of Zinc-Doped Copper Oxide Nanocrystals for Gas Sensing Applications. *J. Mater. Chem. A* **2016**, *4* (17), 6527–6539.
- (8) Lupan, C.; Khaledialidusti, R.; Mishra, A. K.; Postica, V.; Terasa, M. I.; Magariu, N.; Pauporté, T.; Viana, B.; Drewes, J.; Vahl, A.; Faupel, F.; Adelung, R. Pd-Functionalized ZnO:Eu Columnar Films for Room-Temperature Hydrogen Gas Sensing: A Combined Experimental and Computational Approach. *ACS Appl. Mater. Interfaces* **2020**, *12* (22), 24951–24964.
- (9) Hübner, M.; Simion, C. E.; Tomescu-Stănoiu, A.; Pokhrel, S.; Bârsan, N.; Weimar, U. Influence of Humidity on CO Sensing with P-Type CuO Thick Film Gas Sensors. *Sensors Actuators, B Chem.* **2011**, *153* (2), 347–353.
- (10) Kohlmann, N.; Hansen, L.; Lupan, C.; Schürmann, U.; Reimers, A.; Schütt, F.; Adelung, R.; Kersten, H.; Kienle, L. Fabrication of ZnO Nanobrushes by H₂-C₂H₂ Plasma Etching for H₂ Sensing Applications. *ACS Appl. Mater. Interfaces* **2021**, *13* (51), 61758–61769.
- (11) Kwon, J. H.; Jeong, E. G.; Jeon, Y.; Kim, D.-G.; Lee, S.; Choi, K. C. Design of Highly Water Resistant, Impermeable, and Flexible Thin-Film Encapsulation Based on Inorganic/Organic Hybrid Layers. *ACS Appl. Mater. Interfaces* **2019**, *11* (3), 3251–3261.
- (12) LIU, X.-P.; PENG, B.; ZHANG, W.-L.; ZHU, J. Al₂O₃ Coating Layer on the High Temperature Conductive Stability of Pt/ZnO/Al₂O₃ Film Electrode. *J. Inorg. Mater.* **2019**, *34* (6), 605.
- (13) French, P.; Krijnen, G.; Roozeboom, F. Precision in Harsh Environments. *Microsystems Nanoeng.* **2016**, *2* (1), 16048.
- (14) Ababii, N.; Hoppe, M.; Shree, S.; Vahl, A.; Ulfa, M.; Pauporté, T.; Viana, B.; Cretu, V.; Magariu, N.; Postica, V.; Sontea, V.; Terasa, M. I.; Polonskyi, O.; Faupel, F.; Adelung, R.; Lupan, O. Effect of Noble Metal Functionalization and Film Thickness on Sensing

Properties of Sprayed TiO₂ Ultra-Thin Films. *Sensors Actuators, A Phys.* **2019**, *293*, 242–258.

(15) Das, A.; Patra, M.; Hazarika, M.; Nair, R. G. ZnO-In₂O₃ Nanocomposite: An Efficient Solar Photocatalyst. *AIP Conf. Proc.* **2018**, *2100*, 020033.

(16) Bigiani, L.; Zappa, D.; Maccato, C.; Gasparotto, A.; Sada, C.; Comini, E.; Barreca, D. Mn₃O₄ Nanomaterials Functionalized with Fe₂O₃ and ZnO: Fabrication, Characterization, and Ammonia Sensing Properties. *Adv. Mater. Interfaces* **2019**, *6* (24), 1901239.

(17) Kim, J.-H.; Mirzaei, A.; Kim, H. W.; Kim, S. S. Variation of Shell Thickness in ZnO-SnO₂ Core-Shell Nanowires for Optimizing Sensing Behaviors to CO, C₆H₆, and C₇H₈ Gases. *Sensors Actuators B Chem.* **2020**, *302*, 127150.

(18) Kim, J.-H.; Lee, J.-H.; Park, Y.; Kim, J.-Y.; Mirzaei, A.; Kim, H. W.; Kim, S. S. Toluene- and Benzene-Selective Gas Sensors Based on Pt- and Pd-Functionalized ZnO Nanowires in Self-Heating Mode. *Sensors Actuators B Chem.* **2019**, *294*, 78–88.

(19) Kim, J.-H.; Wu, P.; Kim, H. W.; Kim, S. S. Highly Selective Sensing of CO, C₆H₆, and C₇H₈ Gases by Catalytic Functionalization with Metal Nanoparticles. *ACS Appl. Mater. Interfaces* **2016**, *8* (11), 7173–7183.

(20) Liu, Z.; Yang, P. Optoelectronic Performances on Different Structures of Al-Doped ZnO. *J. Am. Ceram. Soc.* **2018**, *101* (12), 5615–5626.

(21) Li, C.; Han, C.; Zhang, Y.; Zang, Z.; Wang, M.; Tang, X.; Du, J. Enhanced Photoresponse of Self-Powered Perovskite Photodetector Based on ZnO Nanoparticles Decorated CsPbBr₃ Films. *Sol. Energy Mater. Sol. Cells* **2017**, *172*, 341–346.

(22) Kuo, T. J.; Lin, C. N.; Kuo, C. L.; Huang, M. H. Growth of Ultralong ZnO Nanowires on Silicon Substrates by Vapor Transport and Their Use as Recyclable Photocatalysts. *Chem. Mater.* **2007**, *19* (21), 5143–5147.

(23) Saito, N.; Haneda, H.; Sekiguchi, T.; Ohashi, N.; Sakaguchi, I.; Koumoto, K. Low-Temperature Fabrication of Light-Emitting Zinc Oxide Micropatterns Using Self-Assembled Monolayers. *Adv. Mater.* **2002**, *14* (6), 418–421.

(24) Lupan, O.; Chow, L.; Shishiyanu, S.; Monaico, E.; Shishiyanu, T.; Şontea, V.; Roldan Cuenya, B.; Naitabdi, A.; Park, S.; Schulte, A. Nanostructured Zinc Oxide Films Synthesized by Successive Chemical Solution Deposition for Gas Sensor Applications. *Mater. Res. Bull.* **2009**, *44* (1), 63–69.

(25) Lupan, O.; Shishiyanu, S.; Chow, L.; Shishiyanu, T. Nanostructured Zinc Oxide Gas Sensors by Successive Ionic Layer Adsorption and Reaction Method and Rapid Photothermal Processing. *Thin Solid Films* **2008**, *516* (10), 3338–3345.

(26) Shishiyanu, S. T.; Lupan, O. I.; Monaico, E. V.; Ursaki, V. V.; Shishiyanu, T. S.; Tiginyanu, I. M. Photoluminescence of Chemical Bath Deposited ZnO:Al Films Treated by Rapid Thermal Annealing. *Thin Solid Films* **2005**, *488* (1–2), 15–19.

(27) Lupan, O. I.; Shishiyanu, S. T.; Shishiyanu, T. S. Nitrogen Oxides and Ammonia Sensing Characteristics of SILAR Deposited ZnO Thin Film. *Superlattices Microstruct.* **2007**, *42* (1–6), 375–378.

(28) Shishiyanu, S. T.; Shishiyanu, T. S.; Lupan, O. I. Sensing Characteristics of Tin-Doped ZnO Thin Films as NO₂ Gas Sensor. *Sensors Actuators, B Chem.* **2005**, *107* (1), 379–386.

(29) Shishiyanu, S. T.; Shishiyanu, T. S.; Lupan, O. I. Novel NO₂ Gas Sensor Based on Cuprous Oxide Thin Films. *Sensors Actuators, B Chem.* **2006**, *113* (1), 468–476.

(30) Paulowicz, I.; Postica, V.; Lupan, O.; Wolff, N.; Shree, S.; Cojocar, A.; Deng, M.; Mishra, Y. K.; Tiginyanu, I.; Kienle, L.; Adelung, R. Zinc Oxide Nanotetrapods with Four Different Arm Morphologies for Versatile Nanosensors. *Sensors Actuators B Chem.* **2018**, *262*, 425–435.

(31) Gapeeva, A.; Bodduluri, M. T.; Kaps, S.; Rasch, F.; Wagner, B.; Adelung, R.; Lupan, O. Mechanical and Wetting Properties of Three-Dimensional Flexible Tetrapodal ZnO Networks ALD-Coated with Al₂O₃. In *IFMBE Proceedings*; Tiginyanu, I., Şontea, V.; Railean, S., Eds.; Springer International Publishing: Cham, 2020; Vol. 77, pp 263–267.

(32) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-Ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation: Eden Prairie, MN, 1992; pp 52–53.

(33) Lupan, O.; Magariu, N.; Khaledialidusti, R.; Mishra, A. K.; Hansen, S.; Krüger, H.; Postica, V.; Heinrich, H.; Viana, B.; Ono, L. K.; Cuenya, B. R.; Chow, L.; Adelung, R.; Pauporté, T. Comparison of Thermal Annealing versus Hydrothermal Treatment Effects on the Detection Performances of ZnO Nanowires. *ACS Appl. Mater. Interfaces* **2021**, *13* (8), 10537–10552.

(34) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.

(35) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50* (24), 17953–17979.

(36) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B - Condens. Matter Mater. Phys.* **1999**, *59* (3), 1758–1775.

(37) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47* (1), 558–561.

(38) Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metamorphous-Semiconductor Transition in Germanium. *Phys. Rev. B* **1994**, *49* (20), 14251–14269.

(39) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6* (1), 15–50.

(40) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B - Condens. Matter Mater. Phys.* **1996**, *54* (16), 11169–11186.

(41) Postica, V.; Vahl, A.; Strobel, J.; Santos-Carballal, D.; Lupan, O.; Cadi-Essadek, A.; De Leeuw, N. H.; Schütt, F.; Polonskyi, O.; Strunskus, T.; Baum, M.; Kienle, L.; Adelung, R.; Faupel, F. Tuning Doping and Surface Functionalization of Columnar Oxide Films for Volatile Organic Compound Sensing: Experiments and Theory. *J. Mater. Chem. A* **2018**, *6* (46), 23669–23682.

(42) Vahl, A.; Lupan, O.; Santos-Carballal, D.; Postica, V.; Hansen, S.; Cavers, H.; Wolff, N.; Terasa, M. I.; Hoppe, M.; Cadi-Essadek, A.; Dankwort, T.; Kienle, L.; De Leeuw, N. H.; Adelung, R.; Faupel, F. Surface Functionalization of ZnO:Ag Columnar Thin Films with AgAu and AgPt Bimetallic Alloy Nanoparticles as an Efficient Pathway for Highly Sensitive Gas Discrimination and Early Hazard Detection in Batteries. *J. Mater. Chem. A* **2020**, *8* (32), 16246–16264.

(43) Postica, V.; Vahl, A.; Santos-Carballal, D.; Dankwort, T.; Kienle, L.; Hoppe, M.; Cadi-Essadek, A.; De Leeuw, N. H.; Terasa, M. I.; Adelung, R.; Faupel, F.; Lupan, O. Tuning ZnO Sensors Reactivity toward Volatile Organic Compounds via Ag Doping and Nanoparticle Functionalization. *ACS Appl. Mater. Interfaces* **2019**, *11* (34), 31452–31466.

(44) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13* (12), 5188–5192.

(45) Cooke, D. J.; Marmier, A.; Parker, S. C. Surface Structure of (1010) and (1120) Surfaces of ZnO with Density Functional Theory and Atomistic Simulation. *J. Phys. Chem. B* **2006**, *110* (15), 7985–7991.

(46) Wander, A.; Harrison, N. M. Ab-Initio Study of ZnO(1120). *Surf. Sci.* **2000**, *468* (1–3), L851–L855.

(47) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem.* **2006**, *27* (15), 1787–1799.

(48) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A Fast and Robust Algorithm for Bader Decomposition of Charge Density. *Comput. Mater. Sci.* **2006**, *36* (3), 354–360.

(49) Orville-Thomas, W. J. Atoms in Molecules — a Quantum Theory. *J. Mol. Struct. THEOCHEM* **1996**, *360* (1–3), 175.

(50) Decremps, F.; Pellicer-Porres, J.; Saitta, A. M.; Chervin, J.-C.; Polian, A. High-Pressure Raman Spectroscopy Study of Wurtzite ZnO. *Phys. Rev. B* **2002**, *65* (9), 092101.

(51) Hoppe, M.; Lupan, O.; Postica, V.; Wolff, N.; Duppel, V.; Kienle, L.; Tiginyanu, I.; Adelung, R. ZnAl₂O₄-Functionalized Zinc

Oxide Microstructures for Highly Selective Hydrogen Gas Sensing Applications. *Phys. status solidi* **2018**, *215* (7), 1700772.

(52) Cuscó, R.; Alarcón-Lladó, E.; Ibáñez, J.; Artús, L.; Jiménez, J.; Wang, B.; Callahan, M. J. Temperature Dependence of Raman Scattering in ZnO. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2007**, *75* (16), 165202.

(53) Postica, V.; Hölken, I.; Schneider, V.; Kaidas, V.; Polonskyi, O.; Cretu, V.; Tiginyanu, I.; Faupel, F.; Adelung, R.; Lupan, O. Multifunctional Device Based on ZnO:Fe Nanostructured Films with Enhanced UV and Ultra-Fast Ethanol Vapour Sensing. *Mater. Sci. Semicond. Process.* **2016**, *49*, 20–33.

(54) Naumkin, A. V.; Kraust-Vass, A.; Gaarenstroom, S. W.; Powell, C. J. NIST X-ray Photoelectron Spectroscopy Database, National Institute of Standards and Technology.

(55) Patolsky, F.; Timko, B. P.; Zheng, G.; Lieber, C. M. Nanowire-Based Nanoelectronic Devices in the Life Sciences. *MRS Bull.* **2007**, *32* (2), 142–149.

(56) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. Nanobelts of Semiconducting Oxides. *Science* (80-). **2001**, *291* (5510), 1947–1949.

(57) Kutukov, P.; Rummyantseva, M.; Krivetskiy, V.; Filatova, D.; Batuk, M.; Hadermann, J.; Khmelevsky, N.; Aksenenko, A.; Gaskov, A. Influence of Mono- and Bimetallic PtO_x, PdO_x, PtPdO_x Clusters on CO Sensing by SnO₂ Based Gas Sensors. *Nanomaterials* **2018**, *8* (11), 917.

(58) Lupan, O.; Postica, V.; Gröttrup, J.; Mishra, A. K.; de Leeuw, N. H.; Adelung, R. Enhanced UV and Ethanol Vapour Sensing of a Single 3-D ZnO Tetrapod Alloyed with Fe₂O₃ Nanoparticles. *Sensors Actuators B Chem.* **2017**, *245*, 448–461.

(59) Vahl, A.; Dittmann, J.; Jetter, J.; Veziroglu, S.; Shree, S.; Ababii, N.; Lupan, O.; Aktas, O. C.; Strunskus, T.; Quandt, E.; Adelung, R.; Sharma, S. K.; Faupel, F. The Impact of O₂/Ar Ratio on Morphology and Functional Properties in Reactive Sputtering of Metal Oxide Thin Films. *Nanotechnology* **2019**, *30* (23), 235603.

(60) Lupan, O.; Cretu, V.; Postica, V.; Ababii, N.; Polonskyi, O.; Kaidas, V.; Schütt, F.; Mishra, Y. K.; Monaco, E.; Tiginyanu, I.; Sontea, V.; Strunskus, T.; Faupel, F.; Adelung, R. Enhanced Ethanol Vapour Sensing Performances of Copper Oxide Nanocrystals with Mixed Phases. *Sensors Actuators, B Chem.* **2016**, *224*, 434–448.

(61) Postica, V.; Lupan, O.; Gapeeva, A.; Hansen, L.; Khaledialidusti, R.; Mishra, A. K.; Drewes, J.; Kersten, H.; Faupel, F.; Adelung, R.; Hansen, S. Improved Long-Term Stability and Reduced Humidity Effect in Gas Sensing: SiO₂ Ultra-Thin Layered ZnO Columnar Films. *Adv. Mater. Technol.* **2021**, *6* (5), 2001137.

(62) Gröttrup, J.; Paulowicz, I.; Schuchardt, A.; Kaidas, V.; Kaps, S.; Lupan, O.; Adelung, R.; Mishra, Y. K. Three-Dimensional Flexible Ceramics Based on Interconnected Network of Highly Porous Pure and Metal Alloyed ZnO Tetrapods. *Ceram. Int.* **2016**, *42* (7), 8664–8676.

(63) Lupan, O.; Ababii, N.; Santos-Carballal, D.; Terasa, M. I.; Magariu, N.; Zappa, D.; Comini, E.; Pauporté, T.; Siebert, L.; Faupel, F.; Vahl, A.; Hansen, S.; de Leeuw, N. H.; Adelung, R. Tailoring the Selectivity of Ultralow-Power Heterojunction Gas Sensors by Noble Metal Nanoparticle Functionalization. *Nano Energy* **2021**, *88*, 106241.

Recommended by ACS

Ethanol Gas Sensing by a Zn-Terminated ZnO(0001) Bulk Single-Crystalline Substrate

Taku T. Suzuki, Kenjiro Fujimoto, *et al.*

AUGUST 11, 2020
ACS OMEGA

READ 

ZnO Nanorods with Doubly Positive Oxygen Vacancies for Efficient Xylene Sensing

Hui Yang, Le-Xi Zhang, *et al.*

FEBRUARY 19, 2022
ACS APPLIED NANO MATERIALS

READ 

TiO₂ Nanowires for Humidity-Stable Gas Sensors for Toluene and Xylene

Zamaswazi P. Tshabalala, David E. Motaung, *et al.*

DECEMBER 29, 2020
ACS APPLIED NANO MATERIALS

READ 

Low-Concentration NO_x Gas Analysis Using Single Bimodular ZnO Nanorod Sensor

Bo Zhang, Pu-Xian Gao, *et al.*

JULY 18, 2021
ACS SENSORS

READ 

Get More Suggestions >