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Broadband dielectric spectroscopic detection of volatile organic compounds with ZnO nanorod gas sensors*

Papa K Amoah^{1,2}, Pengtao Lin^{1,2}, Helmut Baumgart^{1,2}, Rhonda R Franklin³ and Yaw S Obeng⁴

¹ Department of Electrical and Computer Engineering, Old Dominion University, Norfolk VA 23529, United States of America

² Applied Research Center at Thomas Jefferson National Accelerator Laboratories, 12050 Jefferson Avenue, Suite 721, Newport News, VA 23606, United States of America

³ Department of Electrical and Computer Engineering, University of Minnesota, 200 Union Street SE, Minneapolis, MN 55455, United States of America

⁴ Physical Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, United States of America

E-mail: yaw.obeng@nist.gov

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Abstract

Metal-oxide (MO) semiconductor gas sensors based on chemical resistivity necessarily involve making electrical contacts to the sensing materials. These contacts are imperfect and introduce errors into the measurements. In this paper, we demonstrate the feasibility of using contactless broadband dielectric spectroscopy (BDS)-based metrology in gas monitoring that avoids distortions in the reported resistivity values due to probe use, and parasitic errors (i.e. tool-measurand interactions). Specifically, we show how radio frequency propagation characteristics can be applied to study discrete processes on MO sensing material, such as zinc oxide (i.e. ZnO) surfaces, when exposed to a redox-active gas. Specifically, we have used BDS to investigate the initial oxidization of ZnO gas sensing material in air at temperatures below 200 °C, and to show that the technique affords new mechanistic insights that are inaccessible with the traditional resistance-based measurements.

Keywords: VOC, ZnO, nanorods, broadband dielectric spectroscopy, microwaves

(Some figures may appear in colour only in the online journal)

1. Introduction

Metal-oxide (MO) nanostructures are used in multiple fields, including optoelectronics, microelectronics and gas sensing.

In gas sensing applications, most of the MO tend to be II–VI semiconducting MO materials due to their low cost, simple design and ease of production, short response time, wide detection range, and resistance to harsh working environments [1, 2]. We have developed and demonstrated the utility of ZnO and ZnO/Al₂O₃ MO nanorods for ethanol detection [3]. However, the intrinsic properties of these MO and their complex point defect physics are not well understood, partly due to tool–measurand interactions because of the electrical techniques used in the characterization. The electrical contacts to the metal oxide devices invariably introduce parasitic artifacts that distort the measurands. Thus, we need non-contact metrology that will enable an unbiased understanding of how

^{*} Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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these metal oxide devices work; broadband dielectric spectroscopy (BDS) has the potential for probing the intrinsic properties material systems [4, 5].

ZnO is well-known in gas sensing due to its good inherent electrical properties, wide band gap of 3.37 eV, $\approx 60 \text{ meV}$ exciton binding energy at room temperature, high electrochemical and mechanical stabilities [6]. However, the ZnO properties can be tuned by extrinsic modulation such as substitutional doping, mechanically induced stress, and by significantly decreasing the size of the ZnO crystallites towards quantum dots [7]. Defects have been implicated in gas sensing with ZnO nanostructures [8-10]. These defects in ZnO could have chemical [6], as well as mechanical origins [7, 11]. In general, ZnO based gas sensors tend to work well for ethanol detection with high sensitivity, short response time, and fast recovery time. However, the state-of-the-art thin-film ZnO gas sensors suffer from insufficient sensitivity, long response times, and long recovery times. To address this shortcoming, we synthesized ZnO nanorods (see figure 1) to increase the surface-to-volume ratio offering significantly increased sensing surfaces [3]. While other ZnO nanostructures besides nanorod may have higher surface-to-volume ratios [12], but they are not the focus of the current work. Furthermore, besides the "surface-to-volume ratio" advantage, the densely packed ZnO nanorod grown on a dense compact atomic layer deposition (ALD) ZnO seed layer used in the current work improves the electrical conductivity and the reliability of the gas sensors [3].

Mechanistically, when n-type MO semiconductor material, such as ZnO, are exposed to oxygen-rich ambient, oxygen molecules adsorb on the metal oxide moieties, and withdraw electrons from the conduction band, resulting in a layer of oxygen-negative ions being formed on the surface. This leads to a decrease in its majority carrier density, an increase in the width of the depletion region, and the built-in potential barrier on the MO–air interface. This causes the resistance of a MO gas sensor material to increase.

As a standard volatile organic compound (VOC) sensor activation step, the MO solid-state gas sensors need to be heated to their operating temperature. This MO sensor preparation step is typically conducted in ambient air, with oxygen ionic species adsorbing and oxidizing the n-type ZnO surface. In this chemical oxidation reaction, electrons transfer from the conduction band of the semiconducting ZnO nanorod surface into the adsorbed oxygen species, causing a negative charge build-up on the nanorod surface. This, in turn, causes an increase in the depletion width and results in the initial increase of resistance during the sensor preparation step. In the subsequent sensing step, upon exposure to a reducing target gas (in our case ethanol), electrons are injected back into the conduction band, thus restoring the depletion layer with increasing majority carrier density and decreasing the electrical resistance of the MO solid-state sensor device.

Microwave signals are absorbed when inserted into such materials due to the interactions with the intrinsic electrical and magnetic properties of the material, in addition to the changes in the polarizability of the MO–adsorbate interface. In general, the electromagnetic signal–material interactions



Figure 1. Planar view and cross-sectional FE-SEM images of intrinsic ZnO nanorods highlighting the fine grain polycrystalline ALD ZnO seed layer and the resulting morphology of a dense array of ZnO nanorods (adapted from [3]).

result in changes in the signal's characteristics such as attenuation constant and phase constant, used to define the propagation constant, which can be monitored with a two-port vector network analyzer. Contactless BDS is most advantageous for monitoring reactions involving some degree of charge transfer regardless of the nature of the charge carriers, i.e. electrons and holes [13]. This makes BDS an ideal method for monitoring gas-sensing reactions, especially VOCs interactions with MOs, since they involve reversible charge transfer reactions that result in measurable changes in the electrical properties of the sensing element [14, 15]. In this paper, we demonstrate the initial feasibility of the BDS, as an alternative technique, and use it to investigate the sensor activation step for VOC detection with our ZnO nanorod materials.

We emphasize that this paper is primarily a report on the demonstration of the feasibility of using BDS to monitor VOC gas sensing with ZnO. We have already studied in detail the sensing performance, response- and recovery times for these ZnO nanorod samples with dc resistance measurement (see [3] and [15]). In contrast, the present manuscript investigates ac characteristics by the contactless BDS technique which enables the investigation of aspects of target gas sensing that are not accessible with conventional dc measurements, and to avoid the technical challenges of electrical contacts to a ZnO nanorod array. For example, in this manuscript, we used the technique to instigate the initial oxidation ZnO in preparation for gas sensing.

2. Experimental

2.1. ZnO sensing material preparation

For this study, the MOS solid-state gas sensor device consisted of hydrothermally synthesized ZnO nanorods grown on a fine grain ZnO seed layer fabricated by ALD on a native oxidized doped p-type silicon substrate [3, 15]. In the device structure, the native silicon oxide layer served as an isolation dielectric layer that separates the electrically conductive seed ZnO from the host Si substrate. The XRD peaks of the hydrothermally ZnO nanorod grown on the seed ZnO, indexed with the JCPDS database of the Intl. Center for Diffraction Data, show that our ZnO nanorods were comprised of (002) and (100) preferentially oriented near-perfect single crystals with hexagonal shape characterized by distinct crystallographic facets. The intrinsic (undoped) single crystals ZnO nanorods (500 nm tall by 50 nm physical diameter) were too large to invoke sizedependent properties. In the direct current electrical measurements, surface contacts were only made to the seed ZnO; thus, the Si substrate was never part of the measurement circuit. The ZnO samples were used as received for the BDS measurements.

Figure 1 shows a plan view and cross-sectional FE-SEM images of intrinsic ZnO nanorods used in this work, highlighting the fine grain polycrystalline ALD ZnO seed layer and the resulting morphology of a dense array of ZnO nanorods [3]. In our hands, the average ZnO nanorod was ${\sim}500~\text{nm}$ tall and \sim 50 nm in diameter. We note that the ZnO nanorods do not appear to align perfectly with the grains of the seed ZnO layer; a perfectly normally aligned array of nanorods is only possible with a top-down approach via photolithography and a mask and dry etching. On the other hand, hydrothermal growth of ZnO nanorods on ALD fine grain ZnO seed layers is a bottom-up technique where the nanorods grow primarily orthogonal on the ZnO seed layer, but not all nanorods grow perfectly normal on the sample surface. A statistical distribution of small angular deviations occurs from perfect orthogonal nanorod growth depending on the morphology of the seed layer [16].

2.2. BDS setup and measurements

Figure 2 shows a schematic representation of the experimental setup used in this study showing the ZnO sample on a ground-signal-ground (GSG) coplanar waveguide (CPW) situated in a controlled environment (Pyrex tube). The CPW was fabricated from a tin-covered printed circuit board (RF4, 61 mm long, with 5 mm wide ground lines separated from the 1.5 mm wide signal line by 1.2 mm gaps). The cables to the VNA were connected to the CPW with edge mount connectors (Amphenol RF SMA). This configuration effectively converts the coaxial mode signal into microstrip mode propagating towards the device under test (DUT). The cables connecting the CPW were de-embedded, with a two-port short-open-load-through calibration in which the calibration standards were attached to the end of the feed cables, i.e. the reference plane of the measurement was moved from the port faces of the VNA

to the connector/cable interface. Thus, the launch connectors and CPW itself were part of the DUT, and the reported S-parameters are those resulting from experimental perturbations to the DUT. In this configuration, the ZnO gas sensing element perturbs the electric fields emanating from the signal and terminating on ground lines in the CPW. While the system response in a broadband (0.1–20 GHz) range was monitored, a reporting frequency of 6 GHz was chosen based on the sample dimensions and the fact that it provided data free of resonances and minimized signal reflections due to the experimental setup [17].

Because of the relatively low resistivity of the silicon substrate, the sample chip (4.5 mm wide by 9 mm length) was insulated from the 50 Ω GSG CPW by a 0.2 mm thick precleaned glass microscope slide coverslip (24 mm by 24 mm) to prevent shorting the signal lines. The sample-CPW assembly was situated in a thermally heated Pyrex tube, with porous endcaps, that allowed us to independently control the environment around the ZnO nanorods, as shown in figure 2. The temperature of the assembly was manually controlled with a power supply from room temperature to approximately 120 °C; the heater was turned off after about 26 min. Both the S-parameters in the 0.1 GHz to 20 GHz range and the temperature were measured every 30 s.

In an effort to explore the capabilities of the BDS system, 1 ml of analytical grade ethanol was injected into the reactor via a long-needled hypodermic syringe as needed. This amount of ethanol was more than enough to saturate the test chamber to over 1000 ppm in the temperature window used in this study. However, the temperatures were too low for optimal VOC sensing by ZnO³. Furthermore, because of the thermal limitations of the waveguide, we were unable to conduct a side-by-side comparison of the resistive and BDS sensing metrologies.

3. Results and discussion

In the following discussion of the results, elapsed time and reactor temperature are the independent variables. Figure 3 shows the time evolution of the reactor temperature, measured with a thermocouple attached to the RF cable from the VNA port-1 and hovering over the GSG waveguide, as shown in figure 2. Thus, the changes we observe in the S-parameters are both temperature and time-dependent. The data from the 10–24 min time window represent the steady temperature state, any observed changes in that time window is time-dependent.

Figures 4 and 5 show a phenological and an electrical equivalent circuit model without the host silicon substrate, respectively, of the ZnO nanorods under microwave interrogation in a gaseous ambient during the oxidative sensor preparation step as used in this study. In figure 4 we distinguish three electrically distinct zones: the residual core ZnO nanorod (ϕ_{bulk}), the depletion layer (ϕ_d) around the core ZnO due to the adsorption of polarizable electroactive gaseous species from the ambient onto nanorods, and the adsorption layer (ϕ_{ads}) comprised of a complex mix of negatively charged species confined to the surface of the nanorods. Figure 5 is a



Figure 2. A schematic representation of experimental setup used in this study showing the ZnO sample on a GSG waveguide situated in a controlled environment (Pyrex tube).



Figure 3. The time evolution of the reactor temperature during the experiments described in this work.

resistance-capacitance (RC) equivalent circuit model of all the electrically distinct interaction layers as a segment of the microwave (E) travels through a typical ZnO nanorod from point A to point B. The figure does not consider the inductance from the seed layer. In figure 5 the quantities R_{bulk} , C_{bulk} , and the ϕ_{bulk} are the residual resistance, capacitance, and diameter, respectively, of the bulk ZnO nanorod after the depletion layer formation, while R_d , C_d , and ϕ_d are the resistance, capacitance and diameter (strictly, the arc length because of radial length of the electric fields associated with the GSG waveguide), respectively, of the depletion layer, while the R_{ads} , C_{ads} and ϕ_{ads} are the characteristics of the adsorption layer formed due to the adsorption of



Figure 4. A phenological model of a ZnO nanorod under microwave interrogation in a gaseous ambient during sensor preparation step. The adsorbed oxygen species cause a negative charge build-up layer (Φ_{abs}) on the nanorod surface. The adsorbed layer induces a carrier depleted region (Φ_d) around the core ZnO nanorod (Φ_{bulk}). E is an electric field fringe from the microwave emanating from the signal line and terminating on the ground line of the GSG CPW. Position A-B corresponds to the RC network model per nanorod on the ZnO seed layer.

electroactive gaseous species on the ZnO nanorods. The electrical elements in figure 5 are related to features in figure 4 by equations (1) and (2) below. C_{ads} , C_{bulk} , are to be determined experimentally.

$$R_{\text{bulk}} = K\phi_{\text{bulk}}$$
, where K is a constant. (1)

Note that R_{bulk} is not constant; it is only a constant before the start of the oxidative sensor preparation step. As soon as negative charge accumulates on the surface, the ZnO nanorods surface become depleted. Instead, the growing depletion width is restricting the available conducting bulk cross-section



Figure 5. An electrical equivalent circuit model of the ZnO nanorod configuration described in figure 4 as used in this study. Position A-B corresponds to the RC network model per nanorod on the ZnO seed layer. The total RC response for the entire layer will be the summation of these nanorod circuits in parallel. Note the inductance of the seed layer is expected to be small relative to the nanorods and has been excluded.

and causing an increase in the dc resistance. As we modulate the depletion width, we automatically increase R_{bulk} by progressively reducing the bulk ZnO nanorod cross-section.

The negative oxide charge on the surface following the preparation step can be regarded as a wrap-around gate charge surrounding the semiconducting ZnO nanorod cylinder. Thus, the depletion capacitance in a semiconductor cylinder is given. Using the standard formula for the capacitance of coaxial cylinders gives:

$$C_{\rm d} = 2p \,\varepsilon_r \varepsilon_{\rm o} / \ln \left(r_2 / r_1 \right) \tag{2}$$

where ε is the relative dielectric constant of silicon, ε_0 is the vacuum permittivity and r_1 , r_2 are the inner and outer radii of the depletion region, respectively [18].

It is important to note that the seed ZnO layer thickness is exaggerated for illustrative purposes in figure 4; it is very small compared to the length of the ZnO nanorods. Furthermore, despite the areal density of nanorods in the ZnO sensing film, the average distance between nanorods was in the range of 150–200 nm, while the diameter of the ZnO nanorods was \sim 50 nm. Thus, Coulombic forces were assumed to be negligible and were not considered in the simple approximation.

In the experimental configuration we used, the ZnO nanorods were interrogated by the interaction of the electric fields emanating from the signal line and terminating on the ground lines of the CPW. Given the thicknesses of the glass coverslip, silicon substrate and the ZnO seed layer, the electric fields reaching the nanorods can be approximated as a planar (although, it is actually an arc length/segment). With this approximation, the microwave insertion loss (i.e. S21) measures the fraction of energy that is transmitted from the source to the detector through the DUT (i.e. ZnO sample). With proper calibration, the S21 amplitude can be correlated to the total impedance of the GSG waveguide, the glass coverslip and ZnO/Si device. Thus, we can use the S21 magnitude as an index to the changes in the DUT in response to an external perturbation.



Figure 6. Temperature dependence of microwave insertion loss (S21 amplitude) of ZnO on Si in various gaseous environments, monitored at 6 GHz.

With reference to figure 5, the total impedance is the sum of the bulk ZnO resistance and reactance of the interfaces. The latter is mostly due to the variable capacitances of all the interfaces, as identified in figure 4, as described by equation (3). Analysis of the BDS data (at specific frequencies) provides electrical information that can be correlated to elementary processes, such as charge-transfer reactions involving the point defects in the ZnO material, and adsorbed molecules from the gaseous environment [19].

$$X = \frac{1}{2}\Pi f C_{\rm s} \sim \frac{L}{A} \left[\frac{1}{2} f \varepsilon_0 \varepsilon' p^2 \right]. \tag{3}$$

X is the reactance, where C_s is the total series capacitance of the interfaces between the bulk-ZnO and the depletion layer, the interface between the depleted area and the adsorbed ambient species interface, and the interfaces between the overlayers of ambient species within the adsorbed layer, ρ is the resistivity of the interfacial layer (assuming the layer is mechanically very thin), ε' is the effective permittivity of all the interfacial layers, as shown in figures 4 and 5, and ε is the permittivity of free space. We note that the Si host substrate contributed a finite temperature independent impedance to the DUT within the temperature (20 °C–120 °C) range [20].

Figure 6 shows the time evolution of temperature at 6 GHz in our experimental setup. The S21 amplitude was stable below 100 °C, while the system became less resistive at above that temperature. This suggests that, in air, the impedance was relatively high at temperatures below 100 °C and decreased with temperature in a series of discrete steps within the temperature range of 100 °C-120 °C, as shown in figure 6. These changes could be attributed to the temperature dependence of the intrinsic semiconductor resistivity of the ZnO-silicon substrate combination, at temperatures above 100 °C. Indeed, the observed reduction of system impedance with increasing temperature is consistent with the well-characterized ZnO resistance decrease with increasing temperature at temperatures below 200 °C due to the temperature dependence of the resistive MO semiconductor such as ZnO in the 100 °C-200 °C temperature regime [21–23]. However, the discrete nature of the impedance transitions indicates contributions from other phenomena besides resistivity changes due to the mobility of carriers in the ZnO nanorods. The stepped impedance change with increasing temperature could be due to differences in the temperature dependence of resistivity in the ZnO seed layer and the nanorods, due to the differences in crystallography and defect densities in the two ZnO allotropes [24]. The interface capacitances, as shown in figure 4, could also contribute to the observed impedance changes. This is supported by the impact of ethanol vapor on the impedance change in figure 6. The ethanol molecules could adsorb on, and react with, the preexisting adsorbed layer on the ZnO nanorod surface to alter the electronic structure of the adsorbed layer in figure 4. We suggest that the stepped impedance changes with increasing temperature have contributions from events at the interfaces, possibly involving the adsorption/desorption and speciation of molecules from the ambient on the ZnO rods. The system became more resistive when ethanol was injected into the reactor at the 24 min timestamp, i.e. the impedance of the ZnO was relatively higher in the ethanol environment than in air. In our experiment, the introduction of ethanol resulted in a reactor temperature drop, due to energy consumed in the analyte's evaporation that could not be compensated for due to equipment constraints. The changes in the insertion loss may not be due to ethanol's interaction with the ZnO, as the reactor temperature may be too low.

Alternatively, the steps in the microwave insertion loss (S21 amplitude) response may be simply due to the thermal characteristics of the GSG waveguide as shown in figure 7. The FR4 PCB substrate used for GSG waveguide fabrication has a glass transition temperature (T_g) in the 115 °C–200 °C range and may undergo structural deformation at the temperatures used in this work. This limited the highest temperature we could access in this work to about 120 °C. These alternative explanations for the observed impedance changes with temperature and ambience will be fully resolved in future work.

We quantified energy dissipation into the ZnO material by calculating the microwave attenuation constant (i.e. the real part of the microwave propagation constant) by numerical RLCG modeling using a custom MATLAB (MathWorks, Natick, MA) code [25]. The attenuation represents the total microwave signal losses probably due to the reorientation of electric dipoles of the charge transfer adducts on the MO surface. The changes in attenuation constant give us indications of changes in the chemical and electrical properties of the MO material matrix, especially when polar defects are generated during the experiments. As shown in figure 8, the attenuation constant depends on the reactor temperature and the gaseous environment; the attenuation constant was higher in the ethanol environment but converged to that of the air at temperatures below 100 °C. In any event, the attenuation data clearly indicates that the impedance changes on the ZnO samples are reversible within the temperature range of our current experiments, and that the impedance modulates in response to interfacial events, including possible redox reactions occurring on the ZnO nanorod surfaces [19]. It is remarkable, that we observe these impedance changes in the 100 °C-120 °C temperature range, associated with the sample



Figure 7. Comparison of the temperature dependence of microwave insertion loss (S21 amplitude) of the waveguide-cover glass slide stack with (CPW–CS–ZnO Sample) and without (CPW–CS) the ZnO sample in air monitored at 6 GHz. We note that the experimental setup becomes thermally unstable above 120 °C.



Figure 8. A comparison of the temperature dependence of microwave attenuation constant of ZnO on Si in air only and with air–ethanol vapor mixture present in the reactor environments, monitored at 6 GHz. The data suggest that the attenuation constant is independent of the gaseous environment in the temperature regime used in this work.

activation step, well below the optimum direct current resistance sensing temperature of around 320 °C [3, 15].

In air at least two competing processes impact the resistance of the ZnO sample. Atmospheric water chemisorbs and dissociates on the ZnO surface to form hydroxyl (OH⁻) ions on the surface, and directly introduce electrons into the conduction band to increase the conductivity of the n-type sensor. Ambient oxygen also adsorbs on the MO surface initially as O⁻ and slowly transforms into O²⁻, at temperatures around 100 °C, through the acquisition of electrons from the ZnO surface, thereby removing electrons on the conduction band of n-type semiconductor [26]. There is ample evidence in the literature to suggest that the homolytic dissociation of water and the subsequent electron transfer reactions on the surface dominate in air ambient leading to the net reduction of the ZnO resistance [27]. Such changes in surface polarization are readily detected by BDS. The ZnO nanorod samples used in this work have very large surface areas relative to their volume and can adsorb large quantities of gaseous species to form polarons on the surface [24, 25]. When exposed to microwaves, at temperatures above 100 °C, the polarons appear to fluctuate, thus dissipating the microwave energy through dipolar relaxation [28, 29]. In the temperature regime of this work, the resistance increase from the depletion of the carriers from the ZnO surface can be neglected, so the energy dissipation from the polarons on the ZnO surfaces dominates the observed impedance change. Thus, the impedance we measured by BDS on the ZnO nanorods is probably predominantly due to dielectric relaxation, with a small contribution from the conductivity due to carrier concentration. The observed impedance changes are attributable to the discrete charge transfer events occurring in the ZnO sensing surface in response to various environmental conditions at temperatures above 100 °C.

In this report, we did not study the conditions for optimal BDS detection of ethanol nor the limits of the technique due to the thermal stability limitations of the waveguide. However, the BDS data provide very detailed insights into the elementary events associated with the initial oxidation of ZnO nanorod sensing elements for ethanol detection. To the best of our knowledge, such a detailed description of the events that occur in the MO sensing material cannot be obtained with the traditional electrical direct current resistivity measurements. Using this technique, we hope to be able to distinguish between charge transfer reactions on the ZnO-nanorods and on the surface of the bulk ZnO [7, 30, 31], identify point defects, and characterize reaction intermediates and products.

4. Conclusions

Using microwave signal attenuation, we have demonstrated physics consistent with increasing conductivity of the semiconductor ZnO with increasing temperature during the sensor activation step in the 100 °C–120 °C range. However, the semiconductor behavior is perturbed by depletion layer thickness modulation and charge transfer to the gaseous species adsorbed on the ZnO nanorod sensing element. The charge transfer reactions create polarized species on the ZnO nanorod, and fluctuations of the polarons dominate the impedance of the ZnO. Thus, the BDS technique affords new mechanistic insights into the elementary events that occur on the ZnO surface during the initial activation step for ethanol detection.

ORCID iDs

Papa K Amoah (b) https://orcid.org/0000-0003-3328-2692 Yaw S Obeng (b) https://orcid.org/0000-0002-4880-1689

References

- Mirzaei A, Leonardi S G and Neri G 2016 Detection of hazardous volatile organic compounds (VOCs) by metal oxide nanostructures-based gas sensors: a review *Ceram. Int.* 42 15119–41
- [2] Umar A and Hahn Y B (eds) 2010 Metal Oxide Nanostructures and Their Applications (Valencia, CA: American Scientific Publishers)
- [3] Lin P 2019 Enhanced sensing performance of novel nanostructured ZnO gas sensors in ethanol vapor concentration detection applications *PhD Disseration* Old Dominion University (https://doi.org/10.25777/j9r7-vs61)
- [4] Orji N G et al 2018 Metrology for the next generation of semiconductor devices Nat. Electron. 1 532–47
- [5] Obeng Y S *et al* 2016 Low frequency radio wave detection of electrically active defects in dielectrics *ECS J. Solid State Sci. Technol.* 5 P3025
- [6] Anantachaisilp S, Smith S M, Ton-That C, Osotchan T, Moon A R and Phillips M R 2014 Tailoring deep level surface defects in ZnO nanorods for high sensitivity ammonia gas sensing J. Phys. Chem. C 118 27150–6
- [7] Kaftelen H, Ocakoglu K, Thomann R, Tu S, Weber S and Erdem E 2012 EPR and photoluminescence spectroscopy studies on the defect structure of ZnO nanocrystals *Phys. Rev.* B 86 014113
- [8] Ahn M-W, Park K-S, Heo J-H, Park J-G, Kim D-W, Choi K J, Lee J-H and Hong S-H 2008 Gas sensing properties of defect-controlled ZnO-nanowire gas sensor *Appl. Phys. Lett.* 93 263103
- [9] Tam K H et al 2006 J. Phys. Chem. B 110 20865-71
- [10] Zhao L, Shu C, Jia Z and Wang C 2016 Surface defects control for ZnO nanorods synthesized through a gas-assisted hydrothermal process J. Electron. Mater. 46 432–8
- [11] Wu T, Wang A, Zheng L, Wang G, Tu Q, Lv B, Liu Z, Wu Z and Wang Y 2019 Evolution of native defects in ZnO nanorods irradiated with hydrogen ion *Sci. Rep.* **9** 17393
- [12] Gurav K et al 2014 Gas sensing properties of hydrothermally grown ZnO nanorods with different aspect ratios Sensors Actuators B 190 439–45
- [13] Wernbacher A M *et al* 2019 Operando electrical conductivity and complex permittivity study on vanadia oxidation catalysts J. Phys. Chem. C 123 8005–17
- [14] Kim H-J and Lee J-H 2014 Highly sensitive and selective gas sensors using p-type oxide semiconductors: overview Sensors Actuators B 192 607–27
- [15] Lin P, Chen X, Zhang K and Baumgart H 2018 Improved gas sensing performance of ALD AZO 3D coated ZnO nanorods ECS J. Solid State Sci. Technol. 7 Q246–Q252
- [16] Song J and Lim S 2007 Effect of seed layer on the growth of ZnO nanorods J. Phys. Chem. C 111 596–600
- [17] Amoah P K *et al* 2018 Microwave monitoring of atmospheric corrosion of interconnects *ECS J. Solid State Sci. Technol.* 7 N143–9
- [18] Garnett E et al 2009 Dopant profiling and surface analysis of silicon nanowires using capacitance–voltage measurements. *Nat. Nanotech.* 4 311–4
- [19] Heine C, Girgsdies F, Trunschke A, Schlögl R and Eichelbaum M 2013 The model oxidation catalyst α-V₂O₅: insights from contactless *in situ* microwave permittivity and conductivity measurements *Appl. Phys.* A **112** 289–96
- [20] Lederer D and Raskin J-P 2005 Temperature dependence of RF losses in high-resistivity SOI substrates Science and Technology of Semiconductor-On-Insulator Structures and Devices Operating in a Harsh Environment NATO Science Series II: Mathematics, Physics and Chemistry Flandre D, Nazarov A. N. and Hemment P. L. (Berlin: Springer) 6 pp 191–6

- [21] Mosely P T and Tofield B C 1987 Solid State Gas Sensor (Bristol: Adam Hilger)
- [22] Min Y 2003 Properties and sensor performance of zinc oxide thin films *PhD Thesis* Massachusetts Institute of Technology
- [23] Zhang S, Byun H, Lim J, Huh J and Lee W 2012 Controlled synthesis of ZnO nanostructures for sub-ppm-level VOC detection *IEEE Sens. J.* 12 3149–3155
- [24] Wisz G et al 2017 Structural, optical and electrical properties of zinc oxide layers produced by pulsed laser deposition method Nanoscale Res. Lett. 12 253
- [25] Sunday C E *et al* 2017 Broadband dielectric spectroscopic characterization of thermal stability of low-k dielectric thin films for micro- and nanoelectronic applications *ECS J. Solid State Sci. Technol.* 6 N155–N162
- [26] Barry T I and Stone F S 1960 The reactions of oxygen at dark and irradiated zinc oxide surface *Proc. R. Soc.* A 255 124–44
- [27] Bai Z, Xie C, Hu M, Zhang S and Zeng D 2008 Effect of humidity on the gas sensing property of the tetrapod-shaped ZnO nanopowder sensor *Mater. Sci. Eng.* B 149 12–17
- [28] Maglione M 2016 Free charge localization and effective dielectric permittivity in oxides *J. Adv. Dielectr.* 6 1630006
- [29] Maglione M 2016 Free charge localization and effective dielectric permittivity in oxides J. Adv. Dielectrics 6 1630006
- [30] Toufani M, Kasap S, Tufani A, Bakan F, Weber S and Erdem E 2020 Nanoscale 12 12790–800
- [31] Erdem E 2014 J. Alloys Compd. 605 34–44