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Improved Gas Sensing Performance of ALD AZO 3-D Coated ZnO Nanorods

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This paper reports an enhancement on the sensing performance of ZnO nanorod ethanol sensors with a new approach by utilizing nested coatings of Aluminum doped ZnO (AZO) thin films by Atomic Layer Deposition (ALD) technology. ZnO nanorods were grown by the hydrothermal method with the ZnO seed layer synthesized on Silicon wafers by ALD. To enhance the sensing performance of ZnO nanorod ethanol sensors, multiple coated AZO thin film 3-D coatings were deposited on the surface of the intrinsic ZnO nanorods by ALD. To investigate the sensing performance of the ZnO nanorods sensor for the detection of ethanol vapor, a gas sensor testing system was designed and built with a sealed reaction chamber and a temperature controller. The demonstrated sensing performance results include the sensing response comparison between ZnO nanorods before and after ALD coatings with AZO films at different temperatures and with various concentrations of input ethanol vapor. The response times and recovery times of ZnO nanorods before and after ALD coatings with AZO thin films were analyzed to investigate the sensing enhancement. The sensing response improvement peaks at 25°C room temperature with approximately 200% enhancement. However, the sensing response improvement decreases as a function of increasing operating temperature.

Metal Oxide Semiconductor (MOS) gas sensors have received considerable attention as electronic devices for the specific identification and concentration detection of combustible and hazardous gases. Among various semiconductor materials used in MOS gas sensors, ZnO has been widely introduced into gas sensor applications due to its good electrical conductivity, wide band gap of 3.37 eV, ~60 meV exciton binding energy, low cost, and high mechanical stability. Currently ZnO ethanol sensors based on nanorod structures have been widely investigated due to their high electrochemical stability, suitable doping, nontoxicity, and high surface-to-volume ratio. ZnO gas sensors based on one-dimensional nanostructures have good performance in terms of their sensing response, response time and recovery time. Various methods and technologies have been applied to synthesize ZnO nanorods, such as thermal evaporation, laser ablation, chemical vapor deposition, arc plasma reaction, and solution methods. Moreover, to achieve an enhanced sensing performance of ZnO nanorods, numerous materials have been applied as coatings on the surface of ZnO nanorod gas sensors, like Pd, InSb, Ni, etc.

In this paper, the hydrothermal growth method was utilized for intrinsic ZnO nanorod synthesis. To enhance the sensing performance of ZnO nanorod gas sensors to ethanol vapor, a new approach was adopted by utilizing the unique conformal 3-D wrap-around coating capability of ALD technology. In this way ALD coatings of multiple Al doped ZnO thin films can be achieved, which completely cover the surface of the intrinsic ZnO nanorods with precisely controlled thickness. To synthesize 25 nm 2% Al doped ZnO thin films, only 2 ALD deposition cycles of Al2O3 thin films were deposited by ALD interspersed by 56 ALD deposition cycles of ZnO. Little work exists in the context of ZnO nanorod gas sensors. For our study Atomic Layer Deposition technology was chosen to synthesize Al delta doped ZnO thin coatings surrounding the intrinsic ZnO nanorod core, due to its advantage of precise thickness control at Angstrom level and the unique capability of absolutely conformal 3-D wrap-around coatings. ALD AZO thin films have been well characterized exhibiting desirable features such as non-toxicity, low material cost, good thermal stability, and good electrical conductivity. The conductivity of ZnO nanorods will be significantly increased with Al donor dopants provided for the reactive surface region, which provides additional carriers to the conduction band. Furthermore, the additional oxygen vacancies generated by the Al donors also increase the sensing response of the ZnO nanorod gas sensor to ethanol vapor. The resulting improvement of the sensing performance of synthesized ZnO nanorod gas sensor to ethanol vapor was demonstrated by careful sensing investigation before and after the conformal coating with AZO thin films.

Figure 1 provides a schematic overview of the process flow of the experimental approach adopted to achieve sensing performance enhancement for ZnO nanostructure gas sensor. Due to their high surface-to-volume ratio, ZnO nanorod configurations are a preferred approach for the detection of various reducing gases in numerous gas sensor applications. This paper documents an enhancement of the sensing performance of ZnO nanorod gas sensors by equipping them with conformal ALD 3-D wrap-around coatings of multiple additional Al doped ZnO thin films. For this study the sensing performance of ZnO nanorod gas sensors, we have investigated ethanol vapor concentrations before and after AZO coatings by ALD to elucidate the potential beneficial effect. Furthermore, the temperature of the sensing performance has also been considered for the analysis.

**Experimental**

**Sample preparation.**—Three process steps were applied to synthesize ZnO nanorod gas sensors with enhanced performance. To grow ZnO nanorods by hydrothermal growth, for the initial first process step fine grained ZnO seed layers have to be deposited on Silicon substrates by ALD. After establishing the baseline with sensing performance testing for different volumes of ethanol vapor at different temperatures, these initial results were benchmarked in a second process step, where ZnO nanorods received 3-D wrap-around coatings with AZO thin films by ALD for further testing.

At the start, a fine grain ZnO seed layer was deposited on Si substrates by ALD technology at a deposition temperature of 200°C. The two ALD precursors for the ZnO ALD seed layer were diethylzinc (Zn(C2H5)2) and DI water, which were alternatively introduced into the ALD reaction chamber by high purity N2 serving as a carrier gas. The regular ZnO seed layer thickness target is 30 nm. After ALD deposition, the ZnO samples was annealed at a temperature of 350°C for 30 minutes in the furnace. Subsequently, hydrothermal method was used to grow the ZnO nanorods on the fine grain ZnO seed layer prepared by ALD. All the samples were kept in a sealed glass autoclave bottle at 75°C for 16 hours in an aqueous solution prepared with 0.03756 g zinc nitrate hexahydrate (Zn(NO3)2·6H2O).
and 0.0176 g hexamethylenetetramine \((\text{(CH}_2\text{)}_6\text{N}_4)\) dissolved in DI water.\(^\text{13}\) The molar concentration of each chemical was 20.8 mM when dissolved in 60 ml DI water.\(^\text{15}\)

The sensing performance of the synthesized ZnO nanorod gas detectors for ethanol vapors was measured and recorded by an in-house built gas sensor testing system. After the initial testing, the hydrothermal synthesized intrinsic ZnO nanorods were further processed and received added 3-D wrap-around coatings with AZO thin films. The ALD precursors used for AZO coating include diethylzinc \((\text{Zn(C}_2\text{H}_5)_2)\), trimethylamine \((\text{Al}(\text{CH}_3)_3)\) and DI water. The percentage of aluminum dopant was 2% and the final coating thickness was around 25 nm. Based on the recipe of ALD AZO deposition, the thickness of one cycle of 2% Al doped ZnO thin films is 25 nm. Therefore, to get a thicker AZO coating, one more cycle of ALD AZO thin films is coated on the surface of ZnO nanorods, which thickness is 50 nm. However, thicker AZO thin film might cause nanorods to stick to each other and change the sensing properties based on the Field emission scanning electron microscope (FESEM) results. In addition, if the added AZO film coating thickness is too thick, this will cause a reduction of the surface-to-volume ratio. The 3-D wrap-around AZO nanolaminate coating is using a delta doping approach, where each 56 monolayers of ALD ZnO is followed by one monolayer of ALD Al\(_2\text{O}_3\). To evenly diffuse the Al donors throughout the ALD coating, one monolayer of ALD Al\(_2\text{O}_3\) is followed by one monolayer of ALD AZO thin films. The ALD AZO process is followed by a final furnace annealing step at 300 °C for 30 minutes, which simultaneously serves to electrically activate the Al donors on substitutional Zn sites.

Characterization.—FE-SEM microscopy was utilized for the investigation of the morphology of ZnO nanorod gas sensors before and after ALD AZO coating. The compositions of AZO thin films were analyzed by energy dispersive X-ray spectroscopy (EDS). The I-V characteristics of the ZnO nanorods before and after AZO coating were measured at room temperature. X-ray diffraction (XRD) was performed to determine the crystal structure of the ZnO nanorod gas sensors before and after ALD AZO coating.

Sensing response testing system.—A gas sensor testing system was designed and assembled to investigate the sensing performance of the synthesized ZnO nanorod assembly to ethanol vapor at different temperatures. The in-house built testing system incorporates four basic design features: a sealed reaction chamber, a simple resistance monitoring circuit, mass flow controllers (MFCs) for adjustable ethanol vapor concentrations, and a stable temperature control. The sensing performance of the fully processed and assembled ZnO nanorod gas sensors was tested in a sealed reaction chamber, which could maintain a stable concentration of ethanol vapor and eliminate all outside influence, for example water vapor in air. It is well established and typical for MOS sensors, that the sensing response of the ZnO nanorod gas sensors is based on its physical resistance change in response to the redox reactions on the surface of the nanorods with various concentrations of ethanol vapor. Therefore, a resistance monitoring circuit was designed and built to measure the resistance change of the assembled ZnO nanorod gas detectors. One objective of the testing system was to render the concentration of input ethanol vapor precisely adjustable. The other design objective was to enable a stable control of the temperature of the reaction chamber, which can be modified by the controller.

The in-house developed testing system contains two main parts: the testing hardware and the controller. The testing hardware includes the reaction chamber and the resistance monitoring circuit. The prepared ZnO nanorod gas sensor attached with two wires is sealed in a glass flask which is used as the reaction chamber. The concentration of the input ethanol vapor was controlled by the injected ethanol volume from a syringe. A resistance Temperature Detector (RTD) was used to monitor the temperature in the chamber. Figure 2 shows the schematic of gas sensor testing circuit which contains the power source, the reference resistor, and the ZnO nanorod samples. The voltage of the reference resistor was detected by the designed controller. Therefore, the voltage of the ZnO nanorods sample and resistance change could be calculated with known values of power source voltage and reference resistor based on Ohm’s law as shown in the equations below.

\[
V_{\text{Sample}} = V_{\text{Source}} - V_{\text{Reference}} \tag{1}
\]

\[
I = \frac{V_{\text{Reference}}}{R_{\text{Reference}}} \tag{2}
\]

\[
R_{\text{Sample}} = \frac{V_{\text{Sample}}}{I} = \frac{V_{\text{Source}} - V_{\text{Reference}}}{V_{\text{Reference}} / R_{\text{Reference}}} \tag{3}
\]

To detect the sample resistance change and control the reaction chamber temperature, a controller was designed and programmed based on the Compact Rio 9068 and corresponding modules from National Instrument and LabVIEW. For temperature control, NI 9217 was used to collect the temperature signal from the RTD and the NI 9269 was used to send a power signal to the Relay, which provides power to the heating belts wrapping the quartz test chamber. A closed-loop control circuit was formed with the feedback signal from the RTD and the power signal from the controller, which accurately controls the temperature on the quartz reaction chamber. The NI 9381 was used to provide the power source to the testing circuit and to indicate the voltage on the reference resistor. Therefore, the resistance change on the ZnO nanorod samples can be calculated based on the Equation 3.

![Figure 1. Schematic process flow of experimental approach to achieve enhanced performance ZnO nanorod gas sensors with 3-D wrap-around ALD AZO coating.](image1)

![Figure 2. Schematic of gas sensor testing circuit.](image2)
Results and Discussion

N-type mechanism of metal oxide semiconductor (MOS) gas sensor.—As a n-type MOS gas sensor, the fundamental mechanism of ZnO gas sensor is based on the change of conductivity of semiconducting metal oxide during the interaction process with reducing gases. The mechanism of MOS gas sensor involves the chemical composition of the semiconductor, the surface structure and morphology, and the interaction between gas particles and surface atoms of semiconductors. N-type MOS gas sensor detection contains two basic processes: the sensor preparation and the gas detection following the general pattern of gas adsorption, charge transfer and gas desorption. During the sensor preparation step, an oxidation reaction occurs on the surface. Oxygen molecules adsorb electrons from the conduction band of the semiconductor and form one layer of oxygen negative ions on the surface. At higher temperature, more electrons adsorbed from conduction band to the surface eventually lead to a decrease of the majority carrier density of n-type MOS material, forming $O_2^-$ (<100°C),

![Graphs](image-url)

Figure 3. I-V curves of a) as grown intrinsic single crystal ZnO nanorods, b) intrinsic ZnO nanorod-core structure with ALD AZO wrap-around coating, and c) comparison.
O\(^{-}\) (100–300 \(^{\circ}\)C), or \(\text{O}_2^{-}\) (>300 \(^{\circ}\)C).\(^{16,17}\) After the reducing gas was input into the test quartz chamber, gas molecules react with oxygen negative ions and release electrons back to the conduction band which leads to an increase of its majority carrier density. The reaction equations of the MOS gas detection processes are shown below.\(^{18}\) \(X\) is the target gas and \(X'\) is the out gas, \(\delta\) is the number of electrons, which depends on the temperature during sensor preparation.

Sensor Preparation:

\[
\text{O}_2 + e^- \leftrightarrow \text{O}_2^- \quad \text{(adsorb)} \quad [4]
\]

\[
\frac{1}{2} \text{O}_2 + e^- \leftrightarrow \text{O}^- \quad \text{(adsorb)} \quad [5]
\]

\[
\frac{1}{2} \text{O}_2 + 2e^- \leftrightarrow \text{O}_2^- \quad \text{(adsorb)} \quad [6]
\]

Gas Detection:

\[
X \quad (\text{gas}) + \text{O}_2^- \leftrightarrow X' + 2e^- \quad [7]
\]

The total depletion layer width:\(^{18}\)

\[
W = \sqrt{\frac{2\epsilon N_s + N_D}{N_A + N_D}} V_{bi} \quad [8]
\]

The Barrier potential equation as derived from the equation of Poisson states:\(^{18}\)

\[
V_s = \frac{q N_s^2}{2\epsilon \epsilon_0 Ni} \quad [9]
\]

where \(N_s\) is the net density of ions in the space-charge region (depletion region), \(N_i\) is the density of charged surface states, \(\epsilon\) is the dielectric constant of the semiconductor, and \(\epsilon_0\) is the permittivity of free space.\(^{18}\)

The energy \(q V_s\) is the energy that electrons obtain to move through grains. Based on Equation 9, the barrier potential \(V_s\) increases with decreasing majority carrier density which are electrons in n-type MOS material like ZnO. When the semiconductor sensors are exposed to oxygen, oxygen molecules adsorb electrons from conduction band. A layer of oxygen negative ions is formed on the surface, which leads to a decrease on its majority carrier density. Therefore, the width of depletion region and built-in potential increase. As a result, the resistance of MOS material increases. After the reducing gas is introduced, gas molecules interact with oxygen negative ions and release electrons back to the conduction band. According to Equation 9, the width of depletion layer and barrier potential decrease with increasing majority carrier density. The lowered barrier results in a convenient percolation path for electrons to move through different grains of polycrystalline semiconductor material.\(^{18}\) The resistance of the MOS sensing material decreases after the reducing gas has been introduced.

Al doped ZnO coating by ALD technology was explicitly introduced to enhance the sensing performance of the surface of the nominally intrinsic ZnO nanorods to ethanol vapor. Aluminum donor dopants can generate more oxygen vacancies and act as preferential adsorption sites for ethanol molecules.\(^{20}\) Compared to undoped intrinsic ZnO, Al doped ZnO (AZO) is characterized by a greater increase of its majority carrier density (electrons) after introducing the reducing gas, which leads to a significant decrease of its depletion layer width and potential barrier. Therefore, the sensing response of Al doped ZnO to reducing gas is much more pronounced than the response of undoped intrinsic ZnO.

Characteristics of prepared ZnO nanorods.—The EDS results shown in Table I demonstrate the composition of the Aluminum doped ZnO thin films synthesized by ALD technology. To investigate the percentage of Al dopant, an additional Si test wafer was placed in the ALD reaction chamber during the coating process of AZO thin films on the surface of the ZnO nanorod gas sensor. The EDS testing was operated on the AZO coating film synthesized on a flat Si test wafer. Based on the EDS result, the percentage of Aluminum atoms was 2.57\% which achieved the expected percentage of about 2\%. Figure 3 shows I-V curves of ZnO nanorods before and after coating with AZO thin films deposited by ALD technology. From Figure 3c, the plots clearly demonstrate the enormous improvement on the conductivity of ZnO nanorods after coating with AZO thin films due to effect of the Al surface doping.

The XRD results of ZnO nanorods before and after coating with AZO thin films are shown in Figure 4. The three peaks at 31.92\°, 34.64\°, and 36.44\° are indexed to the (100), (002), and (101) directions of the ZnO hexagonal wurtzite structure.\(^{20}\) After the ALD AZO annealing process, which diffuses uniformly the Al dopant through the ALD ZnO coating, the increased intensities of the three peaks indicate the ZnO nanorods were oriented in all of the directions based on ZnO nanorod’s structure.\(^{21}\) It should be pointed out that the hydrothermal growth of the undoped intrinsic ZnO nanorods produces single crystal nanorods with a hexagonal cross-section as seen by the FE-SEM micrographs. While the intrinsic ZnO nanorod core is a single crystal, the subsequent ALD coatings of ZnO and Al\(_2\)O\(_3\) films are polycrystalline. The ALD deposition temperature is too low to enable epitaxial growth of ALD films. Consequently, the final structure results in single crystal hexagonal intrinsic ZnO nanorods cores surrounded by polycrystalline ALD AZO coatings. There was a significantly increased intensity at (002) direction of the ZnO nanorods after coating with ALD AZO thin films and subsequent annealing. The Aluminum diffusion annealing and electrical activation of the Al donors following right after the AZO coating step (2500 °C) at the higher annealing temperature of 300 °C causes some solid state growth of the core nanorod and also grain growth of the polycrystalline ZnO coating along the preferred c-axis orientation, as indicated in the XRD measurements in Figure 4.\(^{22}\)

Figure 5 shows the FE-SEM micrographs of ZnO nanorods synthesized by hydrothermal growth on an annealed polycrystalline ZnO seed layer before (left) and after (right) coating with an ALD 3-D wrap-around coating with AZO thin films. The crystallographic
hexagonal cross-sectional shape of the original intrinsic nanorods grown by hydrothermal growth indicates single crystal ZnO nanorods. The granular surface of the ZnO nanorods in the right two figures demonstrate that polycrystalline AZO thin films were coated on the surface of the initially single crystal ZnO nanorods.

**Sensing performance of assembled ZnO nanorods gas sensors and testing results.**—There are several key parameters used to evaluate the sensing performance of MOS gas sensors, which include sensitivity, selectivity, stability, response time, recovery time etc. To study the performance enhancement resulting from AZO coating, the sensitivity, the response time, and the recovery time of ZnO nanorod gas sensors before and after coatings with AZO thin films by ALD were investigated.

The directly observable physical change of ZnO nanorods to exposure to ethanol vapors is resistance and conductivity change. However, the sensing performance of ZnO nanorod gas sensors is based on their sensing response. Therefore, the resistance change of ZnO nanorods exposed to ethanol vapors was converted into a sensing response based on Equation 10.

Sensing response as a function of time:  
\[
\text{Response} = \frac{R_{\text{air}} - R_{\text{gas}}}{R_{\text{gas}}} \times 100\% \quad [10]
\]

**Sensing response analysis with various temperatures.**—To investigate the relationship between temperature and the sensing response of ZnO nanorods to ethanol vapor, ZnO nanorod samples before and after coatings with AZO thin films were tested with 800 ppm ethanol vapor at different temperatures ranging from 25°C to 340°C, as shown in Figure 6. Both sensing responses of ZnO nanorods before and after being coated with AZO thin films demonstrate the sensitivity increases with increasing temperature until reaching a maximum value at 320°C. After reaching the optimum temperature the response started to decrease when the testing temperature continued to increase further. This is attributed to the fact that more electrons are adsorbed on the ZnO surface at higher temperature. After the reducing gas (ethanol vapor) was put into the quartz test chamber system, more electrons were released back to the conduction band at higher temperature compared to the number of electrons at lower temperature, which means there was a significant drop in the potential barrier height and the depletion layer width. However, the sensing response decreases at higher temperature. This may be caused by the oxidation (desorption) rate, which was faster than the reduction (chemisorption) speed, as shown in the Equations 4 to 7. Based on the results, 320°C can be considered as the optimum working temperature of ZnO nanorods to ethanol vapor.

Figure 7 shows the sensing response comparison between ZnO nanorod gas detectors before and after receiving a conformal ALD 3-D wrap-around coatings of multiple Al doped ZnO thin films to 800 ppm ethanol vapor at different temperatures. The response of ZnO nanorod gas detectors without AZO coatings to ethanol vapor at low temperature (lower than 150°C) is weak and unstable. However, after coating with AZO by ALD, the ZnO nanorod gas detectors show a significantly higher sensing response compared with the original non-coated intrinsic ZnO nanorod samples. This test result comparison benchmark shows a good agreement with the theory that AZO coatings with thinner depletion layers during gas detection can be used to improve the sensing response of ZnO nanorods. The theoretical concept leading to a decrease of the depletion width upon exposure to a reducing gas was described earlier based on Equation 9.
Furthermore, there is a very significant improvement on the response at lower operating temperatures, for example at room temperature (25°C) and human body temperature (37°C). The sensing response improvement peaks at 25°C room temperature with approximately 200% performance enhancement and around 100% enhancement at 37°C human body temperature. The sensing response improvement decreases as a function of increasing operating temperature. This is attributed to the faster oxidation ratio of AZO at elevated temperatures compared to the ZnO surface oxidation at lower temperature.

**Sensing response analysis with various ethanol vapor concentrations.**—After elucidating the optimum working temperature of ZnO nanostructures, ZnO nanorod sensor samples were tested at 320°C before and after coating with AZO thin films. For testing purpose, the sealed quartz reaction chamber was filled in a controlled manner with ethanol vapor with various concentrations ranging from 200 ppm to 1000 ppm. Figure 8 shows the sensing responses of ZnO nanorods to ethanol vapor as a function of various ethanol concentrations at 320°C. The sensing responses of both ZnO nanorods before and after being coated with AZO thin films increase with increasing ethanol vapor concentration and reach saturation when the concentration is increased to about 800 ppm. The saturation status is limited by the adsorption sites on the surface of ZnO nanorods which can be improved with further increasing the surface-to-volume ratio.

Figure 9 shows the sensing response comparison between ZnO nanorods before and after being coated with AZO. This graph documents the enhancement on the sensing response of ZnO nanorods to ethanol vapor after being coated with AZO films, especially at lower concentration.

**Response time and recovery time analysis.**—Response time and recovery time are two significant features to evaluate the sensing performance of gas sensors. Figure 10 shows the sensing response of ZnO nanorod samples before and after being coated with AZO thin films to 800 ppm ethanol vapor at 320°C. The response time can be determined as the time range starting from the moment when the target gas is introduced to the moment when the response reaches 90% (known as T90). The recovery time can be considered as the time range from gas-out moment (considered as 100% of the response) to the moment when the response decreases to 10% of the response (known as T10). The response time of intrinsic ZnO nanorods without any AZO coatings was 29 seconds and the recovery time was 207 seconds. After having been coated with AZO thin films, the ZnO nanorod sensor samples showed significant improvements on their response time and recovery time, which were measured as 17 seconds and 120 seconds respectively. These two results demonstrate that the response time and recovery time of ZnO nanorod sensors after being coated with AZO thin films are measurably shorter than the ZnO samples before AZO coatings. After having been coated with ALD polycrystalline granular AZO nanolaminates, the initially smooth single crystal ZnO nanorods experience an increase in the surface-to-volume ratio due to surface roughening. This is a crucial factor that causes a decrease of response time and recovery time to ethanol vapor exposure.

**Conclusions**

A high-density assembly of single crystal ZnO nanorods were successfully grown by the hydrothermal method utilizing fine grain ALD ZnO seed layers deposited on a silicon substrate. A novel approach of ALD 3-D wrap-around nanolaminate coatings of delta doped AZO films was employed to enhance the sensing performance of ZnO nanorod gas detectors in terms of their sensing response, response time, and recovery time. The sensing response of the ZnO nanorods to ethanol vapor decreased at increasingly higher temperatures beyond the optimum temperature, which was caused by a faster oxidation rate compared to the reducing reaction. The optimum operating temperature of the synthesized ZnO nanorod gas detector for ethanol vapor was determined to be at 320°C. The sensing response of the same ZnO nanorods before and after ALD coating with AZO increases as a function of increasing ethanol vapor concentration and reached saturation when the concentration was increased to about 800 ppm. As a tangible improvement, the response time and recovery time of ZnO nanorod gas detector for ethanol detection were shortened by the new approach of ALD AZO coatings. The ZnO nanorods coated with ALD AZO demonstrated superior sensing performance on ethanol vapor detection when compared and benchmarked again to the ZnO nanorods without AZO coating. The sensing response improvement peaks at 25°C room temperature with approximately 200% performance enhancement. However, the sensing response improvement decreases as a function of increasing operating temperature.
Figure 10. Sensing response to 800 ppm ethanol vapor at 320°C of intrinsic ZnO nanorods before (left) and after (right) having been coated with AZO.

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