Highly sensitive gas sensor based on Al-doped ZnO nanoparticles for detection of dimethyl methylphosphonate as a chemical warfare agent simulant

Ran Yoo\(^a\), Sungmee Cho\(^a\), Min-Jung Song\(^b\),*, Wooyoung Lee\(^a\),*  
\(^a\) Department of Materials Science and Engineering, Yonsei University, 50 Yonsei, Seodaemun-gu, Seoul 120-749, Republic of Korea  
\(^b\) College of Liberal Art & Interdisciplinary Studies, Kyonggi University, 154–42 Gwanggyo-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do 443-760, Republic of Korea

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**A B S T R A C T**  
In this paper, we report a dimethyl methylphosphonate (DMMP) gas sensor using synthesized Al-doped ZnO nanoparticles (NPs) via a hydrothermal method. The average particle size of the Al-doped ZnO NPs is \(\sim 25 \text{ nm} \). The single crystalline phase was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses. The variation in the response of the Al-doped ZnO NP sensors within operating temperatures showed the highest response and recovery at 2 and 96 s, respectively, at 10 ppm in DMMP at 350 °C compared with undoped ZnO NP sensors. Our results showed remarkable sensitivity and selectivity of the Al-doped ZnO NPs sensor toward DMMP. Such increased \(\text{O}_2\) vacancies and surface reactions with small nanocrystals in the Al-doped ZnO NP sensors offer outstanding sensing performance for DMMP detection.

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**1. Introduction**  
Chemical warfare agents (CWA) are lethal chemicals used in warfare and terrorist attacks and are classified as blood, blister, nerve, nettle, and pulmonary agents. Among the nerve agents, sarin gas is an organophosphorus compound in a colorless and odorless liquid that can cause death within 1–10 min by suffocation from lung muscle paralysis. Therefore, it is necessary to detect lower concentration levels of this agent than the immediately dangerous to life and health (IDLH) value of 0.1 mg/m\(^3\) with a fast response time. The dimethyl methylphosphonate (DMMP; \(\text{C}_3\text{H}_9\text{O}_3\text{P}\)) molecule is used in a laboratory as a simulant for sarin (\(\text{C}_4\text{H}_{10}\text{O}_2\text{P}\)) because of safety issues.

Recently, some groups have developed gas sensors based on various metal-oxides for on-site monitoring of DMMP vapor [1–7]. These metal-oxide-based sensors offer advantages such as low cost, fast response time, ease in manufacturing, small size, high efficiency, low power consumption, and portability. In particular, ZnO is an n-type semiconductor with a wurtzite crystal structure. Such a material with various nanostructures has been used widely in gas sensors because of its unique properties including high stability, suitability to doping, high electrical conductivity, wide band gap at approximately 3.37 eV, large binding energy of approximately 60 meV, non-toxicity, and low-cost.

Appropriate doping, an important and effective method used to increase conductivity, enhances the sensing properties of metal-oxide semiconductors by changing the energy-band structure and morphology because dopants can provide electronic defects. This process increases the surface-to-volume ratio and creates more centers on the surface of the metal-oxide semiconductor for gas interaction [8]. Choi et al. reported that an Al dopant exhibited excellent performance among a variety of dopants (e.g., Al, In, Pt, Pd, and Zn) in an \(\text{SnO}_2\)-based gas sensor for DMMP detection [9]. Al doping in ZnO can improve the electrical conductivity caused by the small size of the \(\text{Al}^{3+}\) ion, at 0.53 Å, compared with that of the \(\text{Zn}^{2+}\) ion, at 0.74 Å, thereby decreasing the resistivity of the host ZnO.

In this study, we report the fabrication of an Al-doped ZnO nanoparticle (NP)-based gas sensor for DMMP detection. The Al-doped ZnO NPs are synthesized by a hydrothermal process, and their sensing properties are investigated. The Al-doped ZnO NP sensor with small nanocrystals is shown to introduce further \(\text{O}_2\) vacancies and surface reactions, which offers enhanced sensing performance for DMMP detection.

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\* Corresponding authors.  
E-mail addresses: purejung@yonsei.ac.kr (M.-J. Song), wooyoung@yonsei.ac.kr (W. Lee).  
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2. Experimental

2.1. Fabrication of Al-doped ZnO nanoparticle based sensor

Al-doped ZnO NPs were synthesized by using a hydrothermal method [10] in which 9 g of Zn(CH₃COO)₂·2H₂O (reagent grade ≥98%; Sigma–Aldrich) was first dissolved in 200 mL of methanol to form a solution of 0.205 M. Then, 3.5 g of KOH (reagent grade ≥85%; Sigma–Aldrich) was dissolved in 105 mL of methanol. To prepare the Al-doped ZnO NPs, Al(C₂H₃O₂)₃ (Sigma–Aldrich) was added as an Al source to the Zn(CH₃COO)₂·2H₂O solution under stirring. The dopant concentration, which was controlled to 1 atomic percent, is defined as the Al:Zn atomic ratio (at.) and is shown in percentages. A 0.06 mol KOH solution was mixed with the Zn precursor solution under stirring at 60 °C for 24 h. The synthetic product was collected by centrifugation and was washed with methanol three times. Then, it was dried at 90 °C for 60 min and annealed at 350 °C for 30 min in H₂ atmosphere. The obtained product was then ground uniformly by using a ball mill.

Prior to fabrication of the Al-doped ZnO-based sensor, Ti and Pt layers 5 and 150 nm thick, respectively, were deposited in situ on the patterned SiO₂ substrate through a direct current (DC) sputtering process. Here, the Ti layer was used as an under-layer to enhance the adhesive strength between the Pt thin-film and the SiO₂ substrate. The synthesized Al-doped ZnO NPs were blended with α-terpinolene paste, and this mixture was dispersed onto the interdigitated Pt electrode through a dropping method. This sample was dried at 100 °C for 1 h and at 250 °C for 1 h. To remove the α-terpinolene paste and to enhance the stability of the sensor, it was annealed at 600 °C for 1 h.

2.2. Characterization

The morphology of the Al-doped ZnO NPs was observed by field-emission–scanning electron microscopy (FE–SEM; Hitachi S-4200, Japan). Their chemical compositions were analyzed by energy dispersive spectroscopy (EDS; Hitachi S-4200, Japan). Further, the phase and crystal structures as well as the doping properties were identified by X-ray diffraction (XRD; Rigaku, Ultima IV/ME 200DX, Japan) and Raman spectroscopy (Horriba Jovin Yvon LabRam Aramis, Japan).

2.3. Gas-sensing properties

In order to determine the sensitivity of the sensor to DMMP gas, the sensor’s electrical properties were measured by using a gas-sensing system consisting of a furnace (Korea Vacuum Tech., Korea), mass flow controllers (MFCs), cylinders of the target gas and the balance gas, a current source (Keithley 6220), a nanovoltmeter (Keithley 2182), and a personal computer (PC). The sample was placed on a quartz cylinder in the furnace, and its signals were obtained from two Pt probes connected to the current source and the voltmeter, respectively. The DMMP gas concentration in the synthetic air was achieved by controlling its partial pressure by using MFCs. All of the gas-sensing measurements were conducted at an operating temperature of 300–400 °C. The sensing response (S) for the DMMP gas was estimated using the following equation:

\[ S = \frac{R_{\text{air}} - R_{\text{gas}}}{R_{\text{gas}}} \]  

where \( R_{\text{gas}} \) and \( R_{\text{air}} \) denote the resistances of the sensors when exposed to the target gas and air, respectively. The response time and the recovery time are defined as the times required to reach 90% of total resistance change upon exposure to the test gas and to return to 10% of the original resistance in air after the test gas is released, respectively.

Fig. 1. (a) Schematic illustration of sensor device, (b) scanning electron microscope (SEM) image of an actual Pt electrode, and (c) SEM image of the synthesized Al-doped ZnO nanoparticles (NPs).

3. Results and discussion

3.1. Characterization of Al-doped ZnO-based nanoparticles.

The Al-doped ZnO NPs were synthesized by using a hydrothermal method; the formation mechanism is explained by Eqs. (2)–(5).

\[
\text{Zn(CH}_3\text{COO)}_2\text{(aq)} + 2\text{KOH(aq)} \rightarrow \text{Zn(OH)}_2\text{(aq)} + 2\text{CH}_3\text{COOK(aq)} \tag{2}
\]

\[
\text{Zn(OH)}_2\text{(aq)} + 2\text{OH}^-\text{(aq)} \rightarrow \text{Zn(OH)}_4^{2-}\text{(aq)} \tag{3}
\]

\[
\text{Zn(OH)}_4^{2-}\text{(aq)} \rightarrow \text{ZnO}_2\text{(s)} + 2\text{OH}^-\text{(aq)} + \text{H}_2\text{O(aq)} \tag{4}
\]

\[
\text{Al}_2\text{O}_3 + \text{ZnO} \rightarrow \text{Zn}_2\text{Zn} + 2\text{Al}_2\text{O}_3 + \text{3O}_2\text{O}_x + (1/2)\text{O}_2\text{(g)} + 2\text{e}^- \tag{5}
\]

The Zn source is converted to Zn(OH)_2 precipitate in an aqueous KOH solution [Eq. (2)]. Zn(OH)_4^{2-} ions are produced, which may exist as spherical clusters because of the steric effects and the hydrophilicity of the hydroxyl groups [Eq. (3)]. ZnO was formed together with two hydroxyl ions and one water molecule, and the ZnO nuclei coalesced at a high temperature in order to decrease the total surface energy of the system, resulting in a larger effective surface area. Finally, the Al-doped ZnO NPs were obtained through the replacement of Zn^{2+} by Al^{3+} ions in the ZnO lattice [Eq. (5)]. It is known that Eq. (5) is predominant for a doping of 1 wt.% Al [11].

Fig. 1 shows a schematic illustration of a sensor device with an actual Pt electrode image (inset) and SEM image of the synthesized Al-doped ZnO NPs. The sensor device is composed of Pt interdigitated electrodes on the SiO₂ substrate via a photolithography method, as shown in Fig. 1a. The inset in the figure shows the SEM image of a highly interdigitated array of the Pt electrode in the actual sensor device. As shown the SEM image in Fig. 1b, the Al-doped Zn NPs after annealing on the Pt electrodes appeared in a uniform distribution of highly crystalline particles. The average particle size of the Al-doped ZnO NPs was ~25 nm, which is smaller than that of the un-doped ZnO NPs, at ~40 nm (image not shown).

Fig. 2 a and b, respectively show energy dispersive X-ray (EDX) spectra and SEM images with EDS mapping of Al-doped ZnO
NPs. As shown in Fig. 2a, the EDS spectrum of the Al-doped ZnO NPs exhibited peaks in the presence of Zn, O, and Al signals at ~0.99 at.% of Al. The SEM images with EDS mapping of Al-doped ZnO NPs showed uniform distribution of Zn and O atoms, and the Al atom exhibited a low density, as was expected (Fig. 2b).

Fig. 3 presents the magnified high-resolution TEM (HRTEM) images with a selected-area electron diffraction (SEAD) pattern of the Al-doped ZnO NPs. It was observed that the particles were spherical in the size range of 25 nm and were agglomerated. The SAED pattern in the inset showed the preferred direction of growth of the ZnO particles on the (002) plane with a single crystalline structure.

Fig. 4 shows the XRD patterns of the un-doped ZnO and Al-doped ZnO NPs. All detected patterns on both samples indicate that ZnO (JCPDS: # 36-1451) formed a hexagonal wurtzite phase with no impurity phases. The crystalline state and crystal orientation of these samples exhibited (100), (002), (101), and (110) orientations. The ZnO peak positions with Al were found to shift with slightly larger diffraction angles, indicating that the unit cell size decreased in samples in which Al was substituted for Zn, since the ionic radius of Al³⁺, at 0.53 Å, is smaller than that of Zn²⁺, at 0.74 Å [12], as shown in the inset.

Fig. 5 displays the Raman spectra of the un-doped ZnO and Al-doped ZnO NPs. For both, a dominant peak was observed at 438 cm⁻¹, which corresponds to the $E_g^{\text{high}}$ mode of the wurtzite structure of ZnO. Moreover, the $E_g^{\text{high}}$ mode corresponds to a ZnO hexagonal structure with vibrations of the O sub-lattice as non-polar phonons. The full width at half maximum (FWHM) of the $E_g^{\text{high}}$ peak was broadened, and its intensity decreased according to the increase in doping concentration, showing a lattice disorder due to the ionic radii difference between Al³⁺ and Zn²⁺ [14]. Thus, the ZnO hexagonal structure resulted in an increase in efficiency of the scattering mechanisms including phonon scattering and ionized impurity scattering [12].

3.2. Sensing properties of the Al-doped ZnO sensor to DMMP gas

Fig. 6 shows variation in the response properties of the un-doped and the Al-doped ZnO NPs sensors in the temperature range of 300–400 °C for 10 ppm DMMP in air. The un-doped ZnO NPs sensor showed no change of the response at any temperature. In contrast, the response of the Al-doped ZnO NPs sensor increased up to 350 °C and then decreased from 375 to 400 °C; the best response was observed at 350 °C. The Al-doped ZnO NPs exhibited...
excellent sensing properties to DMMP gas in terms of sensor response and response time, at 4347 and 2 s, respectively. This enhancement might be explained by the adsorption/desorption rates of DMMP or the surface reactivity of DMMP with adsorbed O species along with the operating temperatures. That is, a large amount of DMMP was adsorbed onto the ZnO surface, since the DMMP chemisorption reaction occurred until 350 °C; thus, desorption of DMMP was predominant at temperatures higher than 350 °C. More detailed sensing properties of the un-doped and the Al-doped ZnO NPs sensors investigated with the best temperature of 350 °C in 10 ppm concentration of DMMP, as shown in Fig. 7. In Fig. 7a and b, reproducibility of un-doped ZnO NPs sensor showed a low resistance level with no saturation of the sensor response; however the resistance level of the Al-doped ZnO NPs sensor exhibited a rapid response of 2 s with a relatively short recovery time of 96 s when exposed to 10 ppm DMMP at 350 °C. The dynamic response of the Al-doped ZnO NPs sensor for different concentrations of DMMP in the range of 0.1–10 ppm at 350 °C was also tested, as shown in Fig. 7c. The measured response and recovery times of the Al-doped ZnO NPs sensor as a function of DMMP concentration were 2, 3, 5, 7.6, and 10.2 s and 96, 85, 79, 72, and 65 s for 10, 5, 1, 0.5, and 0.1 ppm, respectively. From these results, the values of the times of highest response, 2 s, and recovery, 96 s, at 10 ppm in the DMMP were fairly comparable or superior to those of existing metal-oxide-based sensors for the DMMP detection. It is obvious that the variation in electrical resistance of the Al-doped ZnO NPs sensor decreased with a reduction in DMMP concentration, indicating that the Al doping retained the n-type semiconducting properties of the un-doped ZnO and that DMMP acted as a reducing gas. Fig. 7d presents the response of the Al-doped ZnO NPs sensor at various DMMP concentrations at 350 °C. A general overview of the data showed a linear increase of the response with an increase in DMMP concentration. The sensitivity of the Al-doped ZnO NPs sensor was approximately 26.55 (correlation coefficient, r = 0.9982) with a linear range from 0.1 to 5 ppm. This enhanced sensing performance can be attributed to the synergistic effect of the smaller crystallite size and the low lattice disorder of the Al-doped ZnO NPs, which led to a rapid response [12,15,16]. For the enhanced DMMP sensing properties, the reactions and response mechanism of the Al-doped ZnO NPs sensor may be explained by the following process. First, O was adsorbed onto the surface of the ZnO upon exposure to air. During chemisorption, atmospheric O formed ionosorption of molecular (O$_2^-$) and atomic (O$^-$ and O$^{2-}$) species at 25–500 °C due to the capture of electrons from the conduction band. Because the O$^-$ species is generally dominant above 150 °C, O$^-$ was frequently chemisorbed onto the surface of the ZnO at the operating temperature of 350 °C in this

![Fig. 3](image1.png) (a) Transmission electron microscopy (TEM) image of Al-doped ZnO nanoparticles (NPs) and (b) high resolution TEM (HRTEM) image of the Al-doped ZnO NP. The inset shows selected-area electron diffraction (SAED) patterns of the particle.

![Fig. 4](image2.png) X-ray diffraction (XRD) patterns of un-doped and Al-doped ZnO nanoparticles (NPs).
work. These O species removed conduction electrons, forming an electron-depletion layer on the ZnO surface. The O adsorption processes can be represented by Eqs. (6) and (7).

\[ O_{2\text{(gas)}} \leftrightarrow O_{2\text{(ads)}} \quad (6) \]

\[ O^{2-} \text{(ads)} + e^{-} \leftrightarrow 2O^{-} \text{(ads)} \quad \text{dominates at } 150-500^\circ C \quad (7) \]

As shown in a schematic reaction in Fig. 8a, DMMP adsorbed, dissociated into ethyl methylphosphonate (MMP) and methylphosphonic acid (MP), and then reacted with the adsorbed oxygen ions on the ZnO surface. Finally, volatile components such as CO₂,
H$_3$PO$_4$, and H$_2$O were produced. The electrons could have been released to the conduction band of the ZnO NPs, which would have led to a decrease of the resistance in the ZnO NPs due to the thinned depletion layer. In the case of the Al-doped ZnO NPs, the Zn$^{2+}$ ions, at 0.74 Å, were partially replaced by Al$^{3+}$, at 0.53 Å, in the ZnO lattice with a smaller ionic size. These Al dopants can generate more oxygen vacancies and act as preferential adsorption sites for DMMP molecules, as shown a schematic illustration of the mechanism in Fig. 8b. Accordingly, an increase in oxygen vacancies by Al doping and surface reactions with small nanocrystals can result in enhanced gas sensing performance [16,17].

To evaluate the selectivity of the Al-doped ZnO NPs sensor with various gases, the selectivity was tested by using NH$_3$, CO, NO, and NO$_2$ gases at the same concentration of 10 ppm at 350 °C, as shown in Fig. 9. The response to DMMP exhibited a remarkably higher selectivity compared with that of the other gases.

As shown in Table 1, we summarized the DMMP gas sensing properties of the Al-doped ZnO NPs sensor from above results. Our results showed an extraordinary response time of 2 s with a low detection limit of 100 ppb compared with the results of several metal-based ZnO or SnO$_2$ sensors. This demonstrates that the Al-doped ZnO NP is a promising material for achieving superior response and sensitivity in DMMP sensor applications.

**4. Conclusions**

In this work, we fabricated a DMMP gas sensor using synthesized Al-doped ZnO NPs via a hydrothermal method. The average particle size of the Al-doped ZnO NPs was ~25 nm, and we confirmed a single crystalline phase through SEM and TEM observations. The
variation in the response of the Al-doped ZnO NPs sensor within operating temperatures showed a rapid response of 2 s and a relatively short recovery time of 96 s, compared with the un-doped ZnO NPs sensor, when exposed to 10 ppm DMMP at 350 °C. The sensitivity exhibited a linear increase of the response with an increase in DMMP concentration, and the selectivity for DMMP showed the fastest response among the gases. Such increased O2 vacancies and surface reactions with small nanocrystals in Al-doped ZnO NP sensors provide enhanced gas sensing performance for DMMP detection.

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References


Biographies

Ran Yoo earned her Master’s Degree in 2013. She is currently studying on the nerve agent gas sensor using carbon nanotubes or metal oxide toward her ME in Nerve Agent Gas sensor at Yonsei University.

Sungmee Cho earned his Ph.D. degree in Electrical Engineering in 2011 from Texas A&M University. She was postdoc researcher at Materials Science & Engineering at Northwestern University in 2011–2012. She has been with Doosan Precision Engineering as a researcher in 2003–2004 and Korea Institute Science Engineering (KIST) as a researcher in 2002–2003 and 2004–2005. Now she is a research professor in Materials Science and Engineering at Yonsei University. Her current research interests include MgZn2-based thermoelectric (TE) energy conversion, TE module joint, thin film hydrogen storage, hydrogen gas sensor, solid oxide fuel cell (SOFC), and Li ion battery.

Min-Jung Song received her Ph.D. in chemical engineering from Korea University (2007). Now, she is working as an assistant professor at Kyonggi University. Her research interests are focused on the electrochemical sensors, electro analysis, diamond based sensors and MEMS.

Wooyoung Lee is a Professor of Department of Materials Science and Engineering at Yonsei University in Korea. He received a BS degree in metallurgical engineering from the Yonsei University in 1986, a MS degree in metallurgical engineering from the Yonsei University in 1988. He received a Ph.D. degree in Physics from University of Cambridge, England in 2000. He is also the Chairman in University Industrial Technology Force (UNITEF), and a Member of the National Council on Science and Technology. In recent years, his research interests have centered on thermoelectric devices, spintronics and hydrogen sensors based on nanowires. He has received a number of awards in nano device-related research areas, including a Service Merit Medal (2008) due to contribution on the development of intellectual properties. He has authored and co-authored over 150 publications, and has edited a few of special books on nano-structured materials and device.