Complementary Dual-Channel Gas Sensor Devices Based on a Role-Allocated ZnO/Graphene Hybrid Heterostructure

Garam Bae, ‡† In Su Jeon, ‡ Moonjeong Jang, ‡ Wooseok Song, ‡‡ Sung Myung, ‡‡ Jongsun Lim, ‡ Sun Sook Lee, ‡ Ha-Kyun Jung, ‡ Chong-Yun Park, ‡ and Ki-Seok An* ‡‡

†Thin Film Materials Research Center, Korea Research Institute of Chemical Technology (KRICT), 141 Gajeong-ro, Yuseong-gu, Daejeon 34114, Republic of Korea
‡Department of Physics, Sungkyunkwan University, 2066 Seobu-ro, Jangan-gu, Suwon 16419, Republic of Korea
§Department of Materials Science and Engineering, Hongik University, 94 Wausan-ro, Mapo-gu, Seoul 04066, Republic of Korea

ABSTRACT: Here, we present a new approach to dual-channel gas sensors on the basis of a role-allocated graphene/ZnO heterostructure, formed by the complementary hybridization of graphene and a ZnO thin film. The method enables cyclic and reproducible gas response as well as high gas response. The role allocation of graphene and ZnO was verified by studying the electrical transport properties of the heterostructure. The results indicated that the ZnO top layer and graphene bottom layer act as a gas adsorption layer and a carrier conducting layer, respectively. The charge interactions of the heterostructures were systematically explored by monitoring changes in transfer characteristics at room temperature and elevated temperature (∼250 °C) after introducing 20 ppm NO2. These results can be understood in terms of the dual-channel effect of the graphene/ZnO heterostructures. Remarkably, an abrupt and reliable gas response under periodic NO2 gas injection was unambiguously achieved by the heterostructure-based gas sensors and as ∼30 times higher than those of a graphene-based gas sensor. These proposed heterostructures represent a fundamental building block of a complementary hybrid gas sensor with highly sensitive and reproducible gas response.

KEYWORDS: graphene, zinc oxide, hybridization, gas sensor

INTRODUCTION

The intriguing physical phenomena associated with the massless Dirac Fermion, namely, the linear dispersion relation near the Fermi level at the K point, originating from the inherent low-dimensional nature of graphene corroborate a great potential for applications in a wide variety of graphene-based next-generation nanoelectronics.1–4 Especially, the extraordinary electrical and structural properties of graphene render it attractive for high-performance, flexible graphene-based gas sensor applications.5–7 The reasons for the inclusion of graphene as an adequate candidate for gas sensor applications are as follows: (i) excellent gas sensitivity in terms of a variation in its electrical conductivity stimulated by the gas adsorption can be gained because of its structural and electrical features including two-dimensional geometry and facile manipulation of the Fermi level by charge interaction with adsorbed gas molecules due to the low density of states near the Fermi level. (ii) Since graphene possesses a high crystalline structure, it enables to allow inherently low electrical noise, and also the charge fluctuation can be effectively suppressed.8,9 However, owing to its chemical inertness, the target gas is preferentially adsorbed on the structurally unstable sites, such as grain boundaries and inevitably occurring oxygen-related functional groups. This leads to the lack of the cyclic and reliable gas response because of the relatively poor gas desorption. To overcome this insurmountable hurdle, various attempts have been undertaken to fabricate a gas-sensing channel using heterostructures or hybrid materials based on randomly distributed heterojunctions and particle-decorated structures.10 For instance, reduced graphene oxide (r-GO) decorated with tin oxide nanocrystals showed enhanced NO2 gas-sensing performance compared with bare r-GO.11 Graphene nanoribbons hybridized with Pd were reported to facilitate improved H2-sensing properties, specifically enhanced gas sensitivity, response and recovery time, and repeatability.12 However, in spite of extensive efforts to improve gas sensing performance, a crucial issue for cyclic and reproducible gas response as well as high gas sensitivity of hybrid nanomaterial-based gas sensors still remains elusive. To address this prerequisite for practical applications, it is noted that an in-depth understanding of the variation in interfacial effects and electrical interactions between the two heteromaterials under various circumstances. These conditions can be categorized into stages: at the first stage, after the formation of the hybrid...
structure; at the 2nd stage, at the elevated temperature for gas-sensing measurement; and at the 3rd stage, after the adsorption of target gases. Meanwhile, we previously demonstrated the hybridization of ZnO thin films with synthesized graphene using thermal chemical vapor deposition (TCVD) for field effect transistors (FETs) applications, which exhibited a high on/off current ratio and excellent carrier mobility via the complementary hybridization.13,14 The excellent performance of these FETs can be explained by the dual-channel effect, which is a conclusion supported by an applicable circuit model. The mechanism involves a superimposed density of states related to the donor states of the band gap of ZnO and the linear dispersion of graphene. Along these lines, we intend to extend the ZnO/graphene hybrid system for use in gas sensor applications. This is a new concept, to our knowledge, for gas sensor applications. The approach exploits the complementary hybridization of a ZnO thin film for cyclic and reproducible gas response governed by the oxygen-mediated gas-sensing mechanism with the graphene for high gas sensitivity correlated with the linear dispersion relation near the Fermi level. Moreover, the TCVD-based large-area compatible approach enables the synthesis of continuous graphene with spatial homogeneity, which allows compatibility with conventional top–down lithographic fabrication techniques for the realization of gas sensor arrays. It is worth noting that the ZnO thin film and graphene are employed as role-allocated hybrid heterostructures for the dual-channel gas sensors where the ZnO top layer and graphene bottom layer act as a gas adsorption layer and a carrier conducting layer, respectively. Moreover, to explore the correlation between the electrical interactions of the hybrid materials and their gas-sensing performance under various circumstances, including those occurring in the 1st, 2nd, and 3rd stages, we systematically studied the structural, chemical, and electrical transport properties of the ZnO/graphene heterostructures.

**RESULTS AND DISCUSSION**

We rationally designed a conceptually new complementary dual-channel gas sensor based on role-allocated hybridized ZnO and graphene, as depicted in Figure 1a. The ZnO top layer and graphene act as the gas adsorption/desorption channel and the carrier conducting channel, respectively. The variation in the carrier concentration of the ZnO channels is associated with the formation of a depletion layer, which is determined by gas adsorption/desorption. This allows the current of the graphene conducting channel with the linear bands to be effectively modulated by charge interactions, including the donation and withdrawal of electrons. We also studied how the thickness of the ZnO top layers affected the electrical and gas-sensing properties of the hybrid heterostructures. A structural characterization of the fabricated role-allocated heterostructure was performed using high-resolution transmission electron microscopy (HR-TEM) and atomic force microscopy (AFM). Figure 1b–d shows representative cross-sectional HR-TEM images of thickness-controlled ZnO/graphene heterostructures. The thickness of the ZnO top layer was effectively manipulated by repeated ALD cycles. On the basis of the TEM observation, the thicknesses of the ZnO thin films were 30, 50, and 100 nm, which correspond to 164, 225, and 550 ALD cycles, respectively. These results confirmed that highly uniform,
The formation of ZnO nanocrystals. To validate the substrate during the growth procedure or due to external factors, as displayed in Figure 1e. The evolution of the surface morphologies of the thickness-controlled ZnO/graphene heterostructures was then examined using AFM, as seen in Figure 1f. Wrinkles of graphene were observed to coexist with ZnO nanograins, regardless of the samples. It has been well-established that wrinkles occur in graphene because of differences in thermal expansion coefficient with the Cu substrate during the growth procedure or due to external strain during the PMMA-assisted wet transfer process. The high-density ZnO nanograins that are observed adjacent to the graphene wrinkles reflect the fact that structural defects in graphene preferentially serve as nucleation sites for ZnO nanograins. The root mean square (RMS) roughness of the heterostructures with thicknesses of 15, 30, 50, and 100 nm were 1.40, 2.07, 2.63, and 3.29 nm, respectively, as presented in Figure 1i. This structural evolution can also be seen in the top-view FE-SEM images of ZnO thin films on graphene and SiO2/Si substrate (Figure S1). Interestingly, there was a discernible discrepancy between the surface morphology of the ZnO thin films on graphene, also on SiO2/Si, revealing that aggregated and crystallized ZnO nanograins can be formed on graphene after hybridization. In previous studies, the size of the ZnO nanograins on graphene/SiO2/Si was greater than for ZnO on SiO2/Si, and crystallinity was also enhanced, as confirmed by an increase in the intensity of XRD diffraction patterns after hybridization.16,17 These results mean that the atomically thin carbon layer with hexagonal lattice acts as an efficient buffer layer for the formation of ZnO nanocrystals. To validate the effect of the ZnO and graphene role allocation, the main conduction path was identified by evaluating the current–voltage (I–V) characteristics of the thickness-controlled ZnO/graphene heterostructures at room temperature, and at gas sensor measurement conditions (T = 250 °C; most of oxide semiconductor-based gas sensors require relative high temperature for operation, at least >150 °C), as shown in Figure 1j–l. Figure 1j reveals the I–V curves of various heterostructure-based two-terminal devices with ZnO top-layer thicknesses of 5, 30, 50, and 100 nm acquired at room temperature (1st stage: after the formation of the heterostructure). All devices had a fixed channel length and width of 500 and 50 μm, respectively. On the basis of these results, the current of the devices was determined to be inversely proportional to the thickness of the ZnO top layer. Figure 1k presents the I–V characteristics of devices measured at 250 °C. This measurement was conducted to identify the main conducting path of the heterostructures under gas sensor measurement conditions (2nd stage). They revealed a similar trend of changing current with increasing ZnO thickness, and the current level for all devices decreased ecumenically. The resistances of the devices with controlled ZnO thicknesses at RT and 250 °C are summarized in Figure 1l. In general, the electrical conductivity of the semiconducting ZnO thin films was found to be proportional to their thickness (R = ρl/wt, where R, resistance, ρ, resistivity, l, channel length, w, channel width, and t, thickness of the film), while the resistance of the films decreased with increasing temperature because of contributing thermally excited electrons (\( n \propto T^{4.5} \exp (-E_g/2k_B T) \)), where \( n \) charge carrier density, \( E_g \) donor level, \( k_B \) Boltzmann constant, and \( T \) temperature. This discrepancy in the temperature-dependent electrical resistance behavior indicates that the main conducting path of the heterostructures...
is graphene. In addition, the current level at 1 V extracted from the $I−V$ curves is similar results for pristine graphene, which is a clear manifestation of our suggestion. The increase in resistance with increasing temperature can be understood as the degradation of electrical conductivity by phonon scattering in graphene. In a previous study with a ZnO/graphene hybrid system, the conducting path of electrons that formed in the heterostructure was ZnO/graphene/ZnO.13 Our observation of a decrease in electrical conductivity with increasing thickness of the ZnO top layers is explained by the fact that as the ZnO content in the dual-channel increases, total resistance consequently increases significantly in the whole channel section.

As mentioned before, we confirmed the role allocation in the laminated dual-channel devices based on ZnO/graphene hybrid heterostructures by examining the temperature-dependent $I−V$ characterization. We first explored the electrical interaction between the two heteromaterials in the 1st stage. Figure 2a provides a schematic representation of the ZnO/graphene heterostructure-based FET with a bottom-gate configuration, which was used to examine the electrical transport properties of the heterostructure. Three hundred nanometer-thick SiO$_2$ and highly doped Si were adopted as gate dielectric and the gate electrode, respectively, and 100 nm-thick Au was deposited as the source/drain electrodes using thermal evaporation with a shadow mask. The channel length and width were fixed at 500 and 50 $\mu$m, respectively. Because we had already established that the main conduction path corresponds to graphene using the $I−V$ characteristics of the heterostructures, it is reasonable to expect that the transfer characteristics of the heterostructures-based FETs also reflect the electronic structure of graphene. Hence, we studied the charge interactions between the two heteromaterials by monitoring variations in the transfer curves, which were found to be strongly correlated with the electronic structure of graphene. Figure 2b–e presents representative transfer curves ($I_{DS}$ vs $V_G$) at $V_{DS} = 0.1$ V of the ZnO/graphene heterostructures-based FETs with 15, 30, 50, and 100 nm-thick ZnO top layers, respectively. The charge-neutral Dirac point (CNDP) of graphene, as defined by the minimum point $I_{DS}$, can generally be observed in the transfer curves because of the low density of states near the Fermi level. For the FETs based on ZnO/graphene heterostructures with a 5 nm-thick ZnO top layer, as displayed in Figure 2b, the CNDP was found at $>150$ V, indicating the presence of highly p-type doped graphene due to the inevitable adsorption of water molecules during the wet transfer process.21 As the thickness of the ZnO top-layers increased from 5 to 50 nm, the CNDP shifted to negative gate voltage, consistent with the fact that hole and electron conduction exhibit symmetrical ambipolar behavior, which means that the charge neutralization of the initially p-type doped graphene occurs via n-type doping, as seen in Figure 2c,d. n-Type unipolar behavior with suppressed hole conduction was observed for the FETs with a 100 nm-thick ZnO top layer, as shown in Figure 2e. This can be understood to originate with the dual-channel effect caused by the superimposed density of states involving the donor states of ZnO and the linear dispersion near the Fermi level in graphene. The change in the carrier concentration of graphene
as a function of the thickness of the ZnO top layer is summarized in Figure 2g.

The carrier concentration \( n \) was calculated by utilizing a simple capacitor model,

\[
    n = \frac{C_G(V_G - V_{\text{CNDP}})}{e}
\]

where \( C_G \), \( e \), \( V_G \), and \( V_{\text{CNDP}} \) are the gate capacitance, electron charge, an applied back gate voltage, and charge-neutral Dirac voltage, respectively. The extracted carrier concentration of graphene was \( 8.2 \times 10^{11}, 2.9 \times 10^{11}, \) and \( -1.5 \times 10^{11} \) cm\(^{-1}\), which corresponds to 15, 30, and 50 nm-thick ZnO top layers, respectively.

In general, ZnO exhibits \( n \)-type semiconducting behavior due to the presence of oxygen vacancies or common native point defects in the hexagonal wurtzite structure. We investigated the evolution of chemical states in the thickness-controlled ZnO top layer on graphene to elucidate the effect of \( n \)-type doping on the ZnO top layers on graphene. The two elements Zn and O in the ZnO thin films were observed in the survey spectra (Figure S2). The Zn 2p core level spectra for the heterostructures with 30, 50, and 100 nm-thick ZnO top layers...
are presented in Figure 3a–c. They reveal that the resultant Zn $P_{\text{Zn}}$ and $P_{\text{O}}$ bonding states located at binding energies ($E_b$) of 1021.7 and 1044.8 eV correspond to stoichiometric ZnO, regardless of the samples. Figure 3d–f presents O 1s core level spectra obtained from the heterostructures with thickness-controlled ZnO top layers. O 1s spectra for the heterostructures were deconvoluted into three components: loosely bound oxygen on the surface of the ZnO (A, $E_b = 533.38$ eV), $O^2-$ ions in the vicinity of oxygen vacancies (B, $E_b = 531.88$ eV), and $O^2-$ ions surrounded by Zn atoms in the hexagonal wurtzite structure (C, $E_b = 530.18$ eV). It is worth noting that an increase in the thickness of the ZnO top layers leads to an increase in the oxygen vacancy-related chemical states at $531.88$ eV. Because the electronic structure of ZnO can be modulated by the density of oxygen vacancies in the crystal structure, it can strongly affect the charge interaction with graphene. In fact, the formation of defect-induced donor states in the ZnO band gap, caused by an increase in the density of oxygen vacancies, allows a decrease in the work function of ZnO because of the Fermi level upshift. Accordingly, $n$-type doping of graphene can occur by electron transfer from ZnO to graphene. This phenomenon of $n$-type doping of graphene by the thickness-controlled ZnO was confirmed using resonant Raman spectroscopy. Figure 3g exhibits the Raman overview spectra recorded at an excitation wavelength of $514$ nm of the thickness-controlled ZnO/graphene heterostructures, representing the graphene Raman fingerprints: the D-, G-, and 2D-bands were observed for all samples. The G-band is associated with normal first-order Raman scattering, involving an electron and the doubly degenerated phonons (iTO and iLO) at the Brillouin zone center. The 2D-band is originated from an intervalley double resonance Raman process, involving an electron and two iTO phonons at the K point. In general, the structural deformation of graphene by the hybridization of hetero-materials is more pronounced in the D-band. After the formation of heterostructure, a variation in the intensity of D-band for graphene is the marginal, irrespective of the thickness of the ZnO top layers, which signals that inherent structural properties of graphene were well-preserved. We further studied an evolution of the XPS spectra of the ZnO (30 nm)/graphene heterostructures as a function of Ar$^+$ etching for depth profiling to identify the chemical state of graphene after the formation of heterostructure, as seen in Figure S3. The sp$^2$ C=C bond and a small amount of C=O and C=O bonding states for graphene were observed after etching for $220$ s, which are nearly identical with the C 1s spectrum of graphene on SiO$_2$/Si. Figure 3h shows the G-band spectra (1510–1670 cm$^{-1}$) of the thickness-controlled ZnO/graphene heterostructures. The G-band experiences a significant redshift from 1596.2 to 1588.0 cm$^{-1}$ as the thickness of the ZnO top layers increases. The relationship between the G-band position and thickness of the ZnO top layers is plotted in Figure 3i. This phonon softening phenomenon in graphene corroborates the $n$-type doping effect of graphene induced by hybridizing the ZnO thin films.

To explore the electrical interaction between the ZnO and graphene when NO$_2$ gases are adsorbed on the surface of the ZnO top layers at $250$ °C (the 3rd stage), we investigated the transfer characteristics of the FETs based on the heterostructures, reflecting the electronic structure of graphene as a main conducting path in the dual channel. Figure 4a shows the transfer curves at $V_{DS} = 10$ mV and $250$ °C of FETs based on heterostructures with a 30 nm-thick ZnO top layer, before (blue line) and after (red line) introducing 20 ppm NO$_2$. The results indicate that the CNDP shifts toward a higher gate voltage from 47 to $53$ V, after 20 ppm NO$_2$ is injected. Figure 4b depicts a proposed band diagram for the ZnO/graphene heterostructures before and after NO$_2$ adsorptions on the ZnO surface. When oxidizing NO$_2$ molecules are adsorbed on the ZnO surface, electron transfer occurs from ZnO to NO$_2$, resulting in an increase in the work function due to lowering of the Fermi level of the ZnO. Consequently, the $p$-type doping of graphene occurs via charge compensation due to electron transfer from graphene to ZnO. On the basis of these understandings, we studied the effect of the ZnO top-layer thickness on the gas response (20 ppm, NO$_2$) of the heterostructure-based gas sensors. Figure 4c–e displays the change in the resistance recorded at 1 V (applied voltage) for the ZnO (15 nm)/graphene, ZnO (30 nm)/graphene, and ZnO (50 nm)/graphene heterostructures-based gas sensor after introducing 20 ppm NO$_2$. The results reveal a significant decrease in resistance with abrupt switching behavior after periodic gas injection. This behavior is attributed to the additional $p$-type doping of graphene, as mentioned above. Astonishingly, in the case of the 100 nm-thick of ZnO top-layer, the resistance of the heterostructures-based gas sensor increased when NO$_2$ gas was introduced, as seen in Figure 4f. This was presumably due to the pronounced contribution of the ZnO thin films in terms of their conducting path in the dual channel, as depicted in Figure 4g. This conclusion is also supported by the transfer curve for the 100 nm-thick ZnO/graphene FET, which showed $n$-type behavior with the suppression of hole conduction, as confirmed by Figure 2e. It should be noted that the ZnO/graphene heterostructure-based gas sensors exhibit an abrupt and reliable gas response under periodic NO$_2$ gas injection, irrespective of the thickness of the ZnO top layers. On the basis of these results, the gas response (response (%) = ($R_{	ext{gas}} - R_0$) / $R_0$, where $R_{	ext{gas}}$ is resistance when exposed with target gas, $R_0$ is resistance at the initial stage) of the ZnO (15, 30, 50, and 100 nm)/graphene-based gas sensor was estimated to be 12.4, 18.8, 19.7, and 17.5%, respectively, as represented in Figure 4h. This performance is distinctly different from that of graphene-based gas sensors, as shown in Figure S4. As we mentioned earlier, graphene-based gas sensors are capable of effective detection of a few of gas molecules because of the graphene’s two-dimensional structure; however, it also suffers from poor recovery properties because the gas molecules are preferentially absorbed at defect sites. Figure 4i,j reveals the cyclic gas response of the ZnO (30 nm)/graphene and ZnO (100 nm)/graphene for various NO$_2$ concentrations (1, 10, and 20 ppm), measured at $250$ °C. On the basis of these results, the gas response of the ZnO (30 nm)/graphene-based gas sensor was estimated to be 3.9, 11.6, and 16.9% correspondingly to 1, 10, and 20 ppm NO$_2$ concentration, respectively, and that of the ZnO (100 nm)/graphene sensor was 3.7, 13.4, and 18.5% corresponding to 1, 10, and 20 ppm NO$_2$ concentration, respectively, as summarized in Figure 4k. These extracted gas responses for the heterostructures are ~30 times higher than those of the graphene-based gas sensor, as shown in the Figure S4, which implies that our device has a competitive advantage over rival heteromaterials. In addition, we examined the gas response of the gas sensors on the basis of ZnO (30 nm)/graphene under the injection of various gas species (NO$_2$, NH$_3$, CH$_4$, and H$_2$) to evaluate the selectivity of gas sensors, as presented in Figure S5. The resulting gas responses of the gas
sensor were estimated to be 108.6% (100 ppm NO₂), 65.3% (100 ppm NH₃), 5.6% (1000 ppm H₂), and 3.2% (1000 ppm CH₄), which mean that the gas responses of the ZnO/graphene gas sensor for NO₂ and NH₃ were higher than those for H₂ and CH₄.

**CONCLUSION**

In summary, we rationally designed conceptually new complementary dual-channel gas sensors on the basis of role-allocated graphene/ZnO heterostructures. This role allocation of the graphene as the carrier conducting channel was verified by examining the temperature-dependent electrical resistance of the heterostructures. We further studied the changes in the electrical interaction between the two heteromaterials under various circumstances. The charge interaction of the heterostructures was explored by monitoring the changes in the transfer curves at RT and elevated temperature (250 °C) after introducing 20 ppm NO₂. After the formation of the heterostructures at RT, the CNDP was shifted to a negative gate voltage, which reflects the charge neutralization of the initially p-type doped graphene via n-type doping. After introducing 20 ppm NO₂ at 250 °C, the CNDP shifted toward a higher gate voltage, from 47 to 53 V. These results can be understood using the proposed band diagram for the hybrid system. Notably, the heterostructure-based gas sensors exhibited an abrupt and reliable gas response under the periodic NO₂ gas injection, irrespective of the thickness of the ZnO top layers, which is unlike the performance of graphene-based gas sensors. The NO₂ gas response for the heterostructures was ~30 times higher than those of a graphene-based gas sensor, as confirmed by the cyclic gas response analysis. These findings provide a facile method of fabricating a complementary hybrid system with highly response and reproducible gas response for gas sensor applications.

**METHODS**

**Synthesis of ZnO/Graphene Heterostructure.** First, graphene was synthesized using a conventional thermal chemical vapor deposition (TCVD) system. A 25 μm-thick Cu foil (Alfa Aesar, 99.8% purity) was utilized as a catalytic substrate for the graphene synthesis. The Cu foil was loaded into the TCVD chamber and preannealed at 1050 °C by introducing H₂ (200 sccm) under a pressure of ~3.6 Torr for 2 h to initiate chemical reduction and surface flattening of the Cu catalytic substrate. After the preannealing process, the graphene was immediately synthesized by the introduction of CH₄ (2 sccm) and H₂ (200 sccm) for 80 min. Structural and chemical characterizations of synthesized graphene were conducted, as presented in the Figure S6. After the graphene was grown, the TCVD reactor was cooled down to room temperature with H₂. The graphene was then transferred onto a 300 nm-thick SiO₂/Si(001) substrate by introducing H₂O under a pressure of ~1 Torr to form a CNDP. The CNDP was shifted to a negative gate voltage, which reflects the charge neutralization of the initially p-type doped graphene via n-type doping. After introducing 20 ppm NO₂ at 250 °C, the CNDP shifted toward a higher gate voltage, from 47 to 53 V. These results can be understood using the proposed band diagram for the hybrid system. Notably, the heterostructure-based gas sensors exhibited an abrupt and reliable gas response under the periodic NO₂ gas injection, irrespective of the thickness of the ZnO top layers, which is unlike the performance of graphene-based gas sensors. The NO₂ gas response for the heterostructures was ~30 times higher than those of a graphene-based gas sensor, as confirmed by the cyclic gas response analysis. These findings provide a facile method of fabricating a complementary hybrid system with highly response and reproducible gas response for gas sensor applications.

**Electrical Transport Properties.** Heterostructures-based TFTs with the bottom-gate configuration were fabricated to examine their electrical transport properties. The ZnO/graphene hybrid films were used as a channel material. Al source/drain electrodes (80 nm-thick) were patterned by thermal evaporation through a shadow mask without the need for any lithographic processing. Heavily p-type doped Si and a thermally grown 300 nm-thick SiO₂ layer were employed as the gate electrode and dielectric layer, respectively.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b01596.

Additional characterization and figures including XPS survey spectra, core level spectrum, cyclic gas response of individual graphene-based gas sensor, and the gas response of the heterostructure-based gas sensor with various gas species (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

E-mail: wssong@krict.re.kr (W.S.).
E-mail: ksan@krict.re.kr (K.-S.A.).

**ORCID**

Wooseok Song: 0000-0002-0487-2055
Sung Myung: 0000-0003-2030-2391
Sun Sook Lee: 0000-0002-3518-5952
Ki-Seok An: 0000-0001-8250-7347

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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