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# Active-matrix monolithic gas sensor array based on MoS<sub>2</sub> thin-film transistors

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Highly sensitive and system integrable gas sensors play a significant role in industry and daily life, and MoS<sub>2</sub> has emerged as one of the most promising two-dimensional nanomaterials for gas sensor technology. In this study, we demonstrate a scalable and monolithically integrated active-matrix gas sensor array based on large-area bilayer MoS<sub>2</sub> films synthesized via two-successive steps: radio-frequency magnetron sputtering and thermal sulfurization. The fabricated thin-film transistors exhibit consistent electrical performance over a few centimeters area and resulting gas sensors detect NO<sub>2</sub> with ultra-high sensitivity across a wide detection range, from 1 to 256 ppm. This is due to the abundant grain boundaries of the sputtered MoS<sub>2</sub> channel, which perform as active sites for absorption of NO<sub>2</sub> gas molecules. The demonstrated active-matrix gas sensor arrays display good switching capabilities and are anticipated to be readily integrated with additional circuitry for different gas sensing and monitoring applications.

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as sensors, which allow ubiquitous and personal airquality monitoring, pollution tracking, and preventive health care via point-of-care breath analysis, are in great demand and will become one of indispensable internet of things sensors toward the hyper-connected<sup>1-5</sup>. To achieve this agenda, development of low-power and monolithically integrated gas sensors without sacrificing their sensitivity is crucial, and thus various gas-sensing methods have been proposed based on electrochemical, resistive, and nanomechanical system<sup>6-12</sup>. In particular, chemiresistors made of semiconducting metal oxides have been extensively explored and are now the most common gassensing devices. These gas sensors operate in resistance modulation resulting from gas-oxide charge transfer at an elevated temperature, but they are typically bulky and require high-power consumption. In recent years, field-effect transistors (FETs) have emerged and shown a potential for overcoming the aforementioned drawbacks13-15.

The FET-based gas sensor works on a principle of carrier transport modulation on the channel induced by gas molecules. Various nanomaterials, such as silicon nanowires, carbon nanotubes, and organic semiconductors, have been used as channel materials of the FET-based gas sensors to realize high sensitivity<sup>16–24</sup>. Especially, two-dimensional (2D) nanomaterials including transition metal dichalcogenides have attracted a significant attention as a promising candidate for ultrasensitive gas sensors because of a high surface-to-volume ratio and excellent charge sensitivity<sup>25–29</sup>.

In particular, ultrahigh sensitive gas sensors based on molybdenum disulfide ( $MoS_2$ ) have been successfully fabricated with mechanical and chemical exfoliation methods<sup>30–32</sup>. However, poor reproducibility and uniformity of exfoliated  $MoS_2$  flakes significantly limit their practical applications. In this regard, massive efforts to grow large-area and high-crystalline  $MoS_2$  films have been devoted, and a feasibility of diverse growth methods has been demonstrated, including chemical vapor deposition (CVD)<sup>33,34</sup>, atomic layer deposition (ALD)<sup>35,36</sup>, and physical vapor deposition (PVD)<sup>37,38</sup>. Nonetheless, the poor reliability and reproducibility of CVD owing to the unstable gas flow dynamic in the chamber as well as high-cost and low throughput of ALD reduce the availability of rather efficient and scalable growth techniques. Thus, a sputtering for large-area uniform MoS<sub>2</sub> films has been developed, because sputtering is a widely commercialized technique in the industry to facilitate mass-production of thin films. The sputtered MoS<sub>2</sub> shows large-area uniformity and good electrical properties<sup>39,40</sup>. However, no reports have been conducted on MoS<sub>2</sub> gas sensor arrays driven by large-area active-matrix.

Here, we demonstrate a scalable, highly sensitive, and monolithically integrable gas sensor active-matrix array based on bilayer MoS<sub>2</sub> films synthesized via a two-step method, that is, through subsequent radio-frequency (RF) magnetron sputtering and thermal sulfurization. The fabricated MoS<sub>2</sub> thin-film transistor (TFT)-based gas sensor exhibits a reduction of field-effect mobility ( $\mu_{\rm FE}$ ) and a positive threshold voltage ( $V_{\rm TH}$ ) shift upon the exposure to nitrogen dioxide (NO<sub>2</sub>) at room temperature, which are dissimilar to the change of exfoliated MoS<sub>2</sub>-based gas sensors. We found that two-step-grown MoS<sub>2</sub> film has a polycrystalline structure and its abundant grain boundaries activate the adsorption of NO<sub>2</sub> molecules, resulting in the increment of potential barriers to inhibit the carrier transport in the channel. Monolithic integration of the active-matrix gas sensor array comprising switching and sensing TFTs is presented with transient gas-sensing characteristics.

#### **Results and discussion**

**Characterizations of two-step-grown MoS**<sub>2</sub>. The schematic image of Fig. 1a shows the synthesis of  $MOS_2$  film on a silicon (Si)/silicon dioxide (SiO<sub>2</sub>) substrate, where molybdenum (Mo) metal was pre-deposited by RF magnetron sputtering at room temperature with RF power of 150 W, and then sulfurized at 750 °C in a CVD chamber with a gas mixture of hydrogen sulfide (H<sub>2</sub>S), hydrogen (H<sub>2</sub>), and argon (Ar). The sulfurization induced a transition from the Mo film into a layered MoS<sub>2</sub> structure (bottom of Fig. 1a). The thickness of Mo film, which



Fig. 1 MoS<sub>2</sub> synthesized by two-step method. a Schematic image of two-step growth of bilayer MoS<sub>2</sub>. b Optical image of MoS<sub>2</sub> film and Si/SiO<sub>2</sub> substrate, and thickness profile of MoS<sub>2</sub> film. c Raman and d XPS spectra of MoS<sub>2</sub> films.

determines the thickness of the final MoS<sub>2</sub> film, is controlled by the sputtering parameters and the deposition time<sup>41</sup>. However, in case of thick Mo film (>5 nm), it could not be completely sulfurized due to the limited diffusion length of sulfur (S) atoms, resulting in multiphase film with MoS<sub>2</sub> on top and Mo underneath<sup>41,42</sup>. To obtain fully sulfurized MoS<sub>2</sub> films, we deposited ultra-thin Mo film with the thickness of 2 nm by optimizing the deposition time to 180 s. In the optical image of Fig. 1b, the fabricated MoS<sub>2</sub> film showed a blue color, which is completely different from the purple color of Si/SiO<sub>2</sub> substrate, with a highly uniform distribution over a centimeter scale, denoting its continuity and connectivity of the large-area MoS2 film. The thickness of the MoS<sub>2</sub> film was measured as 1.64 nm using atomic force microscopy (AFM), which may suggest two MoS<sub>2</sub> layers (insets of Fig. 1b). Raman spectrum of the MoS<sub>2</sub> film (Fig. 1c) showed two typical peaks of in-plane (E12g) and out-of-plane  $(A_{1g})$  modes at 383.52 cm<sup>-1</sup> and 405.69 cm<sup>-1</sup>, respectively. The peak difference ( $\Delta k$ ) between the E<sup>1</sup><sub>2g</sub> and A<sub>1g</sub> modes was calculated to be  $22.17 \text{ cm}^{-1}$ , corresponding to bilayer MoS<sub>2</sub><sup>43</sup>, consistently with the AFM result. The average values of the  $E^{1}_{2g}$ and  $A_{1g}$  peaks from randomly distributed nine points on the 2 ×  $2 \text{ cm}^2 \text{ MoS}_2$  film were estimated to 383.32 and 405.49 cm<sup>-1</sup>, respectively, with  $\Delta k$  of 22.17 cm<sup>-1</sup> (Inset of Fig. 1c), indicating high homogeneity of bilayer MoS<sub>2</sub> on large-area.

X-ray photoelectron spectroscopy (XPS) was employed to identify chemical binding states of Mo and S atoms in the MoS<sub>2</sub> film. XPS spectra of Mo 3*d* and S 2*p* core levels of the MoS<sub>2</sub> film including deconvolution curves were depicted in Fig. 1d. In Mo 3*d* spectrum, two strong doublet peaks were observed at 229.75 (Mo<sup>4+</sup> 3*d*<sub>5/2</sub>) and 232.88 eV (Mo<sup>4+</sup> 3*d*<sub>3/2</sub>), respectively, corresponding to MoS<sub>2</sub> bonding<sup>44</sup>. In addition, two small doublets peaks of Mo<sup>6+</sup> 3*d*<sub>5/2</sub> and Mo<sup>6+</sup> 3*d*<sub>3/2</sub> were confirmed at 232.93 and 236.06 eV, respectively, which were attributed to the existence of residual MoO<sub>3</sub><sup>44</sup>. However, the atomic fractions of the Mo<sup>6+</sup>, which was estimated to be 13% (<20% of the total Mo species), is reasonable for air-exposed MoS<sub>2</sub> films<sup>45</sup>. In the S 2*p* spectrum, only two doublet peaks belonging to MoS<sub>2</sub> bonding appeared at 162.44 (S<sup>2-</sup> 2*p*<sub>3/2</sub>) and 163.62 eV (S<sup>2-</sup> 2*p*<sub>1/2</sub>), respectively. The quantitative ratio between S<sup>2-</sup> 2*p* and Mo<sup>4+</sup> 3*d* was ~1.96, which indicates a perfect MoS<sub>2</sub> configuration.

Transmission electron microscopy observations of MoS<sub>2</sub> film. The atomic structure of the MoS<sub>2</sub> film was explored through transmission electron microscopy (TEM). The cross-sectional TEM image of the MoS<sub>2</sub> film shows its 2D bilayer structure as shown in Fig. 2a. A plan-view TEM image of the MoS<sub>2</sub> over an area of  $41 \times 41$  nm<sup>2</sup> exhibits its large-area continuous lattice (Fig. 2b). In addition, several kinds of Moirè patterns were observed, indicating a lattice mismatch between two layers. A layered structure is formed by the van der Waals (vdW) interactions between the different layers. The relatively weak vdW forces can induce variations in strain response between adjacent layers, resulting in the lattice mismatch by sliding the layer or nucleating ripples<sup>46</sup>. The MoS<sub>2</sub> films with Moirè fringes exhibit a ring-shape of fast Fourier transform (FFT) pattern (Inset of Fig. 2b), suggesting a polycrystalline structure of the films. The high-resolution TEM image of Fig. 2c shows partially wellorganized hexagonal lattice structures along with grain boundaries. In Fig. 2d, two MoS<sub>2</sub> grains of (100) plane meet each other with a relative misorientation of 30°, and the corresponding FFT patterns of the high-resolution TEM image (Inset of Fig. 2d) reveal their diffraction spots indicated with different colors. Despite the insufficient statistical data to identify the size of the MoS<sub>2</sub> grain, we can anticipate that many grain boundaries were possessed in the polycrystalline MoS<sub>2</sub> films.

Electrical properties of MoS2 TFTs. To investigate electrical characteristics of the large-area synthesized MoS<sub>2</sub> films, we fabricated MoS<sub>2</sub> TFTs as shown in Fig. 3a. The MoS<sub>2</sub> films on Si/ SiO<sub>2</sub> substrate were patterned by photolithography combined with dry etching to obtain active channels for transistors. Titanium (Ti) and gold (Au) electrodes were placed for source and drain contacts. Figure 3b illustrates bottom gate voltage  $(V_{GS})$ -drain current  $(I_{DS})$  curves of the MoS<sub>2</sub> TFT in logarithmic (red circle line) and linear (blue square line) scales with  $V_{GS}$  range from -40 to 40 V and drain voltage  $(V_{DS})$  of 1 V, where a channel width (W) and length (L) were 20 and 7 µm, respectively. We observed an excellent n-type semiconducting property with a very high on-off ratio  $(I_{on}/I_{off})$  over  $2 \times 10^6$ .  $V_{DS}$ - $I_{DS}$  curves of the  $MoS_2$  TFT obtained in the  $V_{GS}$  range from -40 to 40 V at intervals of 10 V (Fig. 3c) also exhibited typical n-type characteristics. Here, the top-down approach of the sputtered MoS<sub>2</sub> facilitated a large-volume integrated 2D MoS<sub>2</sub> sensor arrays on a substrate. Figure 3d shows statistics on the electrical parameters of maximum transconductance (gm) and VTH obtained by randomly distributed 24 MoS<sub>2</sub> TFTs on a substrate (Supplementary Fig. 1), revealing very narrow distributions and small standard deviations of 9% for  $g_{\rm m}$  and 17% for  $V_{\rm TH}$ , respectively. These statistical distribution of as-fabricated transistors shows superior electrical uniformity.

NO<sub>2</sub> gas-sensing behavior. NO<sub>2</sub> gas not only has a huge impact on the environment but can also be a diagnostic tool for breath analysis<sup>47</sup>. To confirm sensing responses of the MoS<sub>2</sub> TFT to NO<sub>2</sub> gas, the device was mounted on a stage in a gas chamber equipped with a semiconductor characterization system. An optical image of the MoS<sub>2</sub> gas-sensing TFT was shown in Fig. 4a, where W/L of the device was 20/7 µm. Figure 4b shows V<sub>GS</sub>-I<sub>DS</sub> curves of the MoS<sub>2</sub> gas sensor measured under various concentrations of NO2 gas from 0 to 256 ppm. Increasing the  $NO_2$  concentration resulted in the significant decrease of  $I_{DS}$ over the whole range of  $V_{GS}$ , which denotes that the NO<sub>2</sub> adsorption on the MoS<sub>2</sub> surface reduces the conductivity of the MoS<sub>2</sub> channel. We also measured a time-resolved sensing response of the device to confirm its real-time current behavior when NO<sub>2</sub> gas was injected into the chamber for 5 min, and then the sensor was recovered via pure N<sub>2</sub> purging for 5 min (Fig. 4c). The concentration of NO<sub>2</sub> gas was ranged from 8 to 256 ppm, and 1 V of  $V_{\rm DS}$  was applied. The response is calculated as  $(R_{gas}-R_0)/R_0$ , where  $R_{gas}$  represents a resistance of the device under the NO<sub>2</sub> gas environment and  $R_0$  is its initial resistance without NO<sub>2</sub> gas exposure.  $V_{GS}$  was fixed at 0 V since most MoS<sub>2</sub> TFTs exhibited higher response values at V<sub>GS</sub> near 0 V (Supplementary Figs. 2a-d). Considering that the average  $V_{\rm TH}$  of the MoS<sub>2</sub> TFTs was evaluated as 13.5 V (Fig. 3d),  $V_{\rm GS}$ range near 0 V is considered as a subthreshold regime. The high response in subthreshold region has been proposed earlier in many TFT-based sensors<sup>48-50</sup>. In Fig. 4c, as the NO<sub>2</sub> concentration increased, R<sub>gas</sub> also increased, resulting in positive values of response. However, the response value was not saturated within 5 min owing to a continuous condensation of gas molecules on the  $MoS_2$  surface<sup>51,52</sup>. When we measured the electrical response longer than 5 min (Supplementary Fig. 3), the saturation in sensing response was observed. In addition, rapid recovery was observed when the NO<sub>2</sub> gas was removed (Fig. 4c), indicating great suitability of MoS<sub>2</sub> TFTs for gassensing applications. To confirm a limit of detection of the MoS<sub>2</sub> gas sensor, we tried to measure the sensing response of the device at lower ppm level from 1 to 4 ppm. The sensor presented the response value of 0.5% for 1 ppm of NO<sub>2</sub> concentration (Supplementary Fig. 4).



Fig. 2 TEM images of MoS<sub>2</sub> film. a Cross-sectional and b plan-view TEM images. c Basal plane and d grain boundary (Inset of FFT patterns extracted from each figure).



Fig. 3 Electrical properties of MoS<sub>2</sub> TFTs. a Schematic image of MoS<sub>2</sub> TFTs. b Transfer characteristics and c output characteristics of MoS<sub>2</sub> TFT. d Plot of  $g_m$  and  $V_{TH}$  of 24 different MoS<sub>2</sub> TFTs.



**Fig. 4**  $NO_2$  gas-sensing performances of  $MOS_2$  TFTs. a Optical microscopic image of  $MOS_2$  TFT. b Transfer characteristics of  $MOS_2$  TFT upon  $NO_2$  exposure with different concentrations ranging from 0 to 256 ppm. c Real-time sensing response of gas sensor with  $NO_2$  exposure from 8 to 256 ppm concentration. d Response of nine different gas sensors measured at  $NO_2$  concentrations of 8, 32, and 128 ppm and average response at each concentration.

To evaluate a sensing uniformity of the  $MoS_2$  gas sensors, the sensing responses of nine different devices were examined under the injection of various  $NO_2$  concentrations. The response of each TFT was presented by different colors depending on different concentrations of  $NO_2$ ; red for 8 ppm, green for 32 ppm and blue for 128 ppm, and the average values of nine TFTs were marked as dotted lines. The response of each device did not deviate significantly from the mean value, which was supported by low standard errors of 1.36, 1.34, and 2.65, respectively.

For in-depth study of the sensing mechanism of the twostep-grown MoS<sub>2</sub> gas sensor, we examined variations of device electrical parameters of the device under increasing NO2 gas concentrations. The  $V_{\rm TH}$  and  $\mu_{\rm FE}$  values were extracted from each  $V_{GS}$ - $I_{DS}$  curves in Fig. 4b. In Fig. 5a, the variation of  $V_{TH}$  $(\Delta V_{\rm TH})$  is plotted as a function of NO<sub>2</sub> concentration, indicating continuous positive shift of V<sub>TH</sub>, especially, with rapid changes in low concentrations. Moreover,  $\mu_{FE}$  gradually degraded when the NO<sub>2</sub> concentrations increased (blue circle in Fig. 5b). These electrical behaviors are unequivocally different from the previously reported exfoliated MoS<sub>2</sub> TFT gas sensors<sup>29,53</sup>. As shown in Supplementary Fig. 5a, for comparison purposes, we also measured the sensing responses of exfoliated MoS<sub>2</sub> TFT having a channel area similar to that of the two-step-grown MoS<sub>2</sub> TFT. In the exfoliated MoS<sub>2</sub> gas sensors, NO<sub>2</sub> gas molecules are physically adsorbed on the basal surface of the MoS<sub>2</sub> by vdW interactions<sup>32,54-56</sup>, which generates in-gap states in bandgap region close to the valence band and thus, increases the tunneling of hole carriers<sup>29,53</sup>. As a result, Ioff for the transistor gradually increased along with NO<sub>2</sub> concentrations (Supplementary Fig. 5b). However, these devices showed no change in  $\mu_{\rm FE}$  according to NO<sub>2</sub> concentrations, as shown in an orange square in Fig. 5b, unlike the two-step-grown MoS<sub>2</sub> TFT. The major difference between two MoS<sub>2</sub> FETs is the crystalline structure of MoS<sub>2</sub>

films, i.e., the two-step-grown MoS<sub>2</sub> film is polycrystalline, whereas the exfoliated MoS<sub>2</sub> flake is single-crystal. On the polycrystalline MoS<sub>2</sub> surface, the abundant grain boundaries are expected to serve as active binding sites for NO<sub>2</sub> molecules, so that the adsorption of NO<sub>2</sub> on grain boundaries is more dominant than that on basal plane<sup>57–59</sup>, as shown in schematic illumination of an inset of Fig. 5a. This can be further understood by the fact that the shifts of  $V_{\rm TH}$  and  $\mu_{\rm FE}$  variation were gradually diminished as the grain boundaries became saturated.

There are many reports on organic TFT-based chemical sensors, having many grain boundaries in their channels, like the two-step-grown MoS<sub>2</sub><sup>59-61</sup>. In organic TFT sensors, the adsorption of gas analytes on the grain boundaries induces local electric fields through polarization of the semiconductor, leading to the trapping of mobile carriers, and consequently, to variations in current behaviors. To establish the relationship between the NO<sub>2</sub> adsorption on the MoS<sub>2</sub> grain boundaries and the  $I_{\rm DS}$  decrease involving the variations of  $V_{\rm TH}$  and  $\mu_{\rm FE}$ , the temperature-dependent current behavior measurements were conducted on two-step-grown MoS2 TFT with and without NO<sub>2</sub> gas exposure. We measured  $V_{GS}$ - $I_{DS}$  curves at different temperatures from 350 to 400 K at intervals of 10 K under pure N<sub>2</sub> (Supplementary Fig. 6a) and NO<sub>2</sub> environments with the concentration of 256 ppm (Supplementary Fig. 6b). In both cases, two devices exhibited thermally activated I<sub>DS</sub> when the temperature increased. We extracted a carrier activation energy  $(E_A)$  from experimentally measured results by using the following equation:

#### $I_{DS} = I_{D0} exp(-E_A/k_B T)$

where  $I_{D0}$  is the prefactor,  $k_B$  is the Boltzmann constant, and T is temperature<sup>62–64</sup>. Supplementary Figs. 7a and b plot  $I_{DS}$  as a function of  $1/k_BT$  derived from Supplementary Figs. 6a and b,



**Fig. 5 Atomic structure-dependent NO**<sub>2</sub> **sensing behavior. a**  $\Delta V_{TH}$  according to NO<sub>2</sub> exposure and schematic image of NO<sub>2</sub> adsorption on MoS<sub>2</sub> grain boundaries (inset). **b** Comparison of  $\mu_{FE}$  between exfoliated and two-step-grown MoS<sub>2</sub> TFTs under different concentrations of NO<sub>2</sub>. **c** Calculated activation energy ( $E_A$ ) as a function of  $V_{GS}$  and **d** density of states for MoS<sub>2</sub> TFT with and without NO<sub>2</sub> gas exposure.

respectively, and Supplementary Figs. 7c and d are  $I_{D0}$  according to  $V_{GS}$ . The calculated  $E_A$  curves according to  $V_{GS}$  are presented in Fig. 5c, which show a higher  $E_A$  values under NO<sub>2</sub> environment than only N<sub>2</sub> environment in the whole range of  $V_{GS}$ . This indicates that the absorption of NO<sub>2</sub> gas molecules induced a higher potential barrier for electron carriers to hop to the next grain. Furthermore, we can estimate the density of sub-gap states as follows:

$$N(E) = C_{ox}q^{-1} \left(\partial E_A \partial V_{GS}^{-1}\right)^{-1}$$

where  $C_{ox}$  is oxide capacitance and q is electron charge. Figure 5d shows the calculated density of states near conduction band ( $E_c$ ). A new sub-state was observed near  $E_c$ -0.2 eV under NO<sub>2</sub> environment, providing direct evidence of the formation of trap state. These results indicate that the NO<sub>2</sub> adsorption on the grain boundaries generates trap states in the forbidden band, inducing charge trapping and increment in the potential barrier, which inhibits the carrier transport in the channel and induces the decrease of  $I_{DS}$  and  $\mu_{FE}$ .

Active-matrix of gas sensors based on  $MoS_2$  TFT. Large-area and uniform  $MoS_2$  films enable to manufacture a monolithically integrated circuit of active-matrix gas sensor array. Figure 6a shows an optical image of the  $NO_2$  gas-sensing active-matrix consisting of  $7 \times 6$  pixels; each pixel contains both one switching TFT and one sensing TFT based on largearea synthesized  $MoS_2$  film as shown in Fig. 6b. Switching TFTs were operated by local bottom gate separated from back gate and an 80 nm thick aluminum oxide ( $Al_2O_3$ ) was used as gate dielectric. To prevent the reaction between  $NO_2$  gas molecules and  $MoS_2$  of switching transistors, their  $MoS_2$  channels were encapsulated by a 20 nm thick  $SiO_2$  insulator. Figure 6c shows the transfer curve of a switching MoS<sub>2</sub> TFT at a supplied voltage  $(V_{DD})$  of 1 V under switching gate bias  $(V_{SW})$  from -10 to 10 V. The switching states of the MoS<sub>2</sub> TFT were determined to be ON when  $V_{SW}$  is 10 V and OFF when  $V_{SW}$  is -10 V, respectively. Based on the electrical property of the switching TFT, we operated the integrated gas-sensing circuit under different NO<sub>2</sub> gas concentrations from 8 to 64 ppm at  $V_{DD}$  of 1 V (Fig. 6d). Here, back gate voltage ( $V_{\text{Back}}$ ) was fixed at 0 V so that the sensing TFTs can operate in subthreshold regime.  $V_{SW}$ was applied to 10 and -10 V periodically for 5 min. When the device is on the ON state (V<sub>SW</sub> of 10 V), the channel of switching TFT was opened and the drain current flowed through the channel of sensing TFT. Under NO<sub>2</sub> environment, the device current (I<sub>DD</sub>) gradually decreased in a good agreement with the sensing behavior of the single MoS<sub>2</sub> TFT as shown in Fig. 4c. However, the OFF state ( $V_{SW}$  of -10 V) limits the current flow in the channel of sensing TFT, resulting in current values independent of NO<sub>2</sub> concentrations. As a result, both the great sensing and switching performances of the twostep-grown MoS<sub>2</sub> gas sensor active-matrix were confirmed in Fig. 6d. In addition, statistical distributions of the switching and gas-sensing properties of active matrix were presented in the mapping images that present the  $I_{DD}$  level of each MoS<sub>2</sub> pixel before and after the exposure of NO<sub>2</sub> gas when the devices were on the OFF (Supplementary Fig. 8a) and ON (Supplementary Fig. 8b) states, respectively. V<sub>DD</sub> of 1 V and  $V_{\text{Back}}$  of 0 V were fixed, respectively. All 42 MoS<sub>2</sub> gas sensors exhibited no noticeable variation in IDD values when the devices were OFF state. However, at ON state, the IDD values of all gas sensors were reduced when the NO<sub>2</sub> gas was added. However, the differences in the electrical properties were existed for each pixel. Therefore, device calibration is required for practical use.



**Fig. 6** MoS<sub>2</sub> **TFTs-based gas sensor active-matrix. a** Image of MoS<sub>2</sub> gas sensor active-matrix consisting of  $7 \times 6$  pixels. **b** Schematic image, circuit diagram, and optical image of integrated single pixel containing a switching TFT and a sensing TFT. **c** Transfer characteristic of switching TFT. **d** NO<sub>2</sub> gas-sensing behavior of MoS<sub>2</sub> gas sensor active device under dynamic switching.

#### Conclusion

In summary, we have demonstrated active-matrix gas sensor array with pixel circuits comprising gas-sensing TFT and switching TFT based on two-step-grown large-area  $MoS_2$  films. Consistent  $g_m$  as well as  $I_{\rm on}/I_{\rm off}$  ratio of ~ 2 × 10<sup>6</sup> were obtained across a few centimeters of the grown film. The MoS<sub>2</sub> TFT-based gas sensors can detect as low as 1 ppm of NO2 level with a wide detection range of up to 256 ppm, and the decent gas-sensing performance are attributed to the abundant grain boundaries of the sputtered polycrystalline MoS<sub>2</sub> channel as investigated via structural TEM analysis as well as temperature-dependent current measurements with corresponding sub-gap states analysis. Furthermore, the pixel circuit of the demonstrated  $7 \times 6$  active-matrix gas sensor array is capable of NO<sub>2</sub> gas sensing as well as electrical switching depending on operation regimes. The proposed two-step-grown MoS<sub>2</sub> TFTbased gas sensors with highly sensitive detection of gas molecules and scalability into integrated systems have enormous potential as a standard gas-sensing platform.

#### Methods

**MoS<sub>2</sub> growth**. Mo was deposited on P-type boron-doped Si/SiO<sub>2</sub> (300 nm) substrates, which were preliminarily cleaned in an ultrasonic bath for 10 min by sequentially using acetone, isopropyl alcohol, and deionized water. Both a Mo target (99.99%) with a 101.6 mm diameter and these substrates were placed in the sputtering chamber under high-vacuum conditions ( $<3 \times 10^{-6}$  Torr). The working pressure was maintained at 10 mTorr with an Ar flow of 100 sccm. Prior to the deposition, the Mo target was pre-sputtered for 10 min to remove its oxidized surface and enhance the plasma stability. The Mo deposition was conducted with RF power of 150 W for 180 s at room temperature. The as-deposited Mo films were then placed in a CVD chamber for the sulfurization. The chamber temperature was raised to 750 °C for 30 min. Only Ar gas (50 sccm) was injected until 300 °C. At the higher temperatures, Ar/H<sub>2</sub>/H<sub>2</sub>S (50:5:1) gas mixture was added for 15 min. After the sulfurization process, the high temperature of 950 °C was maintained for 1 h to improve the crystallinity of synthesized MoS<sub>2</sub> films. **Characterizations**. The thickness of MoS<sub>2</sub> film was measured with AFM (XE7 Atomic Force Microscope, Park Systems). Raman spectra was obtained by Micro-Raman spectrometer system (ALPHA300, WITec Co.) at the MEMS · Sensor Platform Center of Sungkyunkwan University (SKKU) with an excitation laser at 532 nm with a power of 0.5 mW. XPS analysis was also conducted using AR-XPS system (Theta Probe AR-XPS System, ThermoFisher Scientific) with monochromated Al Ka radiation (1486.6 eV). For TEM measurments, the MoS<sub>2</sub> film was transferred onto copper (Cu) grids with a lacey carbon support film. Cross-sectional and plan-view TEM images were obtained by aberration corrected TEM(JEM-ARM200F, JEOL Ltd.) with an accelerating voltage of 80 kV. The electrical properties of the MoS<sub>2</sub> TFTs were investigated using a semiconductor characterization system (Keithley 4200 SCS, Keithley) and dark box under ambient condition.

**Fabrications of MoS<sub>2</sub> TFT**. The synthesized MoS<sub>2</sub> films were patterned via photolithography using mask aligner (MA6, SUSS MicroTec) and oxygen plasma reactive ion etching at 30 sccm and 50 W for 1 min to obtain TFT channels. For the lift-off process, the source and drain were pre-patterned through photolithography and, then, Ti/Au (20 nm/100 nm) were deposited by an electron beam evaporator. After the removal of the unnecessary Ti/Au part, the samples were annealed at 200 °C for 2 h in a vacuum chamber to improve the electrical junctions.

 $NO_2$  gas-sensing measurement. The fabricated MoS<sub>2</sub> FET-based gas sensors were inserted in a sensing chamber designed to evaluate the electrical properties under a gas flow. Before the gas injection, the vacuum condition (10 mTorr) was applied to remove unnecessary gases. NO<sub>2</sub> gas was diluted with N<sub>2</sub> gas; the flow rate of the injected gases was controlled by mass flow controllers and the total flow rate was maintained at 1000 sccm for the whole time. Before measuring the electrical properties of the sensors, each sample device was exposed to NO<sub>2</sub> gas for 10 min at room temperature.

#### Data availability

The data supporting the findings of this study are included in this paper and its supplementary information.

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## ARTICLE

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#### Author contributions

Sunkook Kim and G. Yoo conceived the project. Sehwan Kim and H. Park, and J.Y. Yang fabricated the TFT-based gas sensor using the MoS2 synthesized by S. Choo and S. Baek. Y. Kwon, N. Liu, and C.-W. Yang contributed to structural and chemical characterizations of the MoS<sub>2</sub> using TEM and XPS. All authors wrote and contributed to the manuscript.

#### **Competing interests**

The authors declare no competing financial or non-financial interests.

#### Additional information

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