

# Direct Observation of Charge Transfer between NO<sub>x</sub> and Monolayer MoS<sub>2</sub> by Operando Scanning Photoelectron Microscopy

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Cite This: *ACS Appl. Nano Mater.* 2021, 4, 3319–3324

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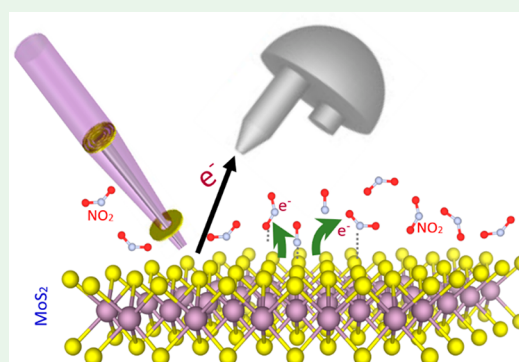
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**ABSTRACT:** Atomically thin transition-metal dichalcogenides (MoS<sub>2</sub>, WSe<sub>2</sub>, etc.) have long been touted as promising materials for gas detection because of their tunable band gaps; however, the sensing mechanism, based on a charge-transfer process, has not been fully explored. Here, we directly observe the effect of this charge transfer on the doping levels in MoS<sub>2</sub> upon exposure to NO<sub>x</sub> by performing scanning photoelectron microscopy (SPEM) on a monolayer MoS<sub>2</sub> transistor under bias conditions in a gas environment. By a comparison of the operando SPEM maps of the transistor with and without exposure to NO<sub>x</sub> gas, a downward shift in the Fermi level position could be detected, consistent with NO<sub>x</sub> gas making the MoS<sub>2</sub> channel less n-type.



**KEYWORDS:** molybdenum disulfide (MoS<sub>2</sub>), *in situ*, field-effect transistor (FET), gas sensor, scanning photoelectron microscopy (SPEM), X-ray photoelectron microscopy (XPS), NO<sub>x</sub>

Global urbanization and industrialization have led to significant increases in the levels of air pollutants.<sup>1</sup> These air pollutants, such as NO and NO<sub>2</sub>, are detrimental to human health and must therefore be closely monitored.<sup>2</sup> Currently, gas sensors based on metal oxide films are the predominant technology used in environmental monitoring systems. They do, however, require elevated temperatures and exhibit sensitivities limited to the low parts per million range.<sup>3</sup> Two-dimensional (2D)-layered nanomaterials and their heterostructures have shown promising results in the development of ultrasensitive gas sensors because of their high surface-to-volume ratios, high carrier mobilities, and tunable band gaps.<sup>4</sup> Graphene-based gas sensors have even shown single-gas-molecule detection at room temperature.<sup>5</sup> Among the various 2D-layered nanomaterials, molybdenum disulfide (MoS<sub>2</sub>) has been widely used in gas sensor research because of its layer-dependent tunable band gap (2.8–1.9 eV),<sup>6</sup> wafer-scale fabrication<sup>7</sup> with various active sites (sulfur defects, vacancy defects, and edge sites), and relatively high mobilities.<sup>8</sup> Sensitivities down to parts per billion toward NO and NO<sub>2</sub> have been demonstrated,<sup>4,9</sup> which makes it clear that MoS<sub>2</sub> field-effect transistors (FETs) can be used as highly sensitive gas sensors.

The sensing mechanism of n-type MoS<sub>2</sub> is believed to be based on a charge-transfer process,<sup>10,11</sup> where oxidizing and reducing gases accept or donate electrons from the channel during adsorption, thereby increasing or reducing the

resistance, respectively. To validate the charge-transfer mechanism in the presence of a gas environment, various techniques have been used, such as Kelvin probe force microscopy,<sup>12</sup> *in situ* Raman spectroscopy,<sup>13</sup> photoluminescence,<sup>11</sup> and ultraviolet photoemission spectroscopy.<sup>14</sup> Notwithstanding, experiments that directly probe the interaction between the gas and MoS<sub>2</sub> at the interface are still lacking.

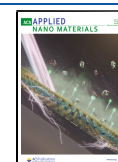
Here, for the first time, the electrical and chemical interactions between gas molecules and monolayer MoS<sub>2</sub> are probed simultaneously by employing scanning photoelectron microscopy (SPEM) at the Elettra synchrotron's ESCA microscopy beamline.<sup>15,16</sup> By performing spatially resolved operando photoelectron spectroscopy on a monolayer MoS<sub>2</sub> transistor under different bias conditions in a gas environment, we demonstrate that charge transfer is the main sensing mechanism of MoS<sub>2</sub> toward NO<sub>x</sub>.

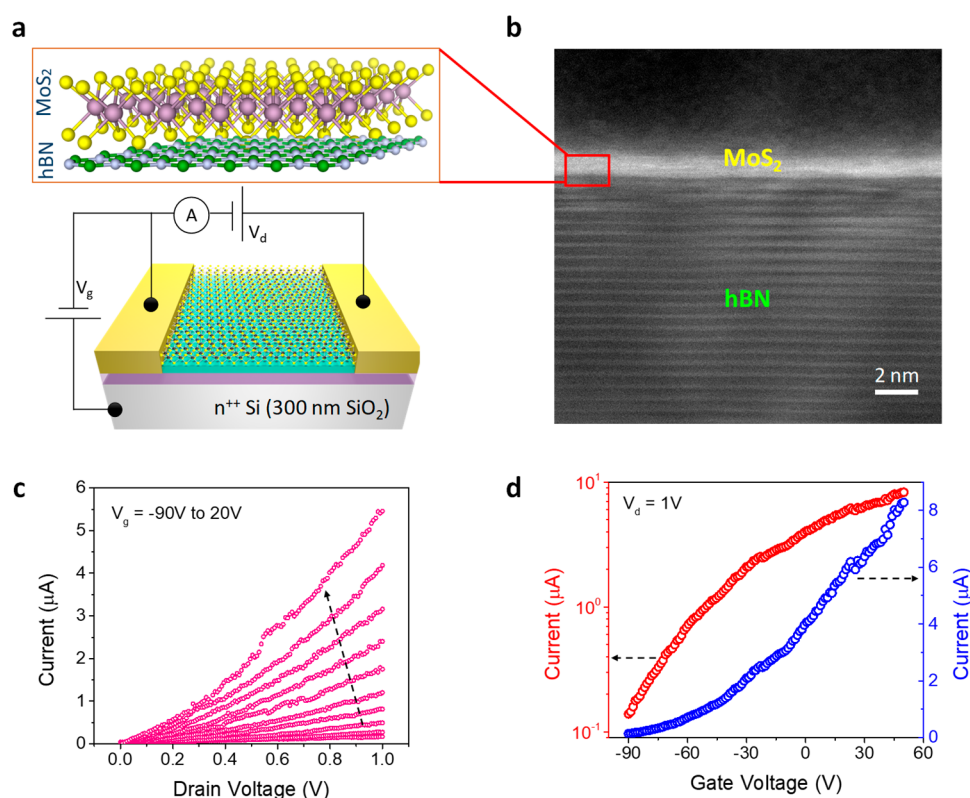
MoS<sub>2</sub>/hexagonal boron nitride (hBN) FETs, as illustrated in Figure 1a, were fabricated on highly doped oxidized (300 nm) silicon wafers using a dry transfer technique,<sup>17</sup> followed by

Received: January 15, 2021

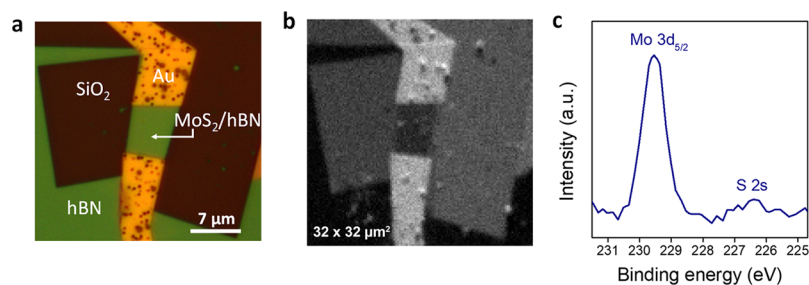
Accepted: February 24, 2021

Published: March 2, 2021





**Figure 1.** (a) Device schematic of a monolayer MoS<sub>2</sub>/hBN transistor. (b) Cross-sectional LAADF STEM image of the MoS<sub>2</sub>/hBN heterostructure. (c) Output characteristics ( $V_d$ - $I_d$ ) curves at different gate voltages ( $V_g = -90$  to  $+20$  V). (d) Transfer characteristics ( $V_g$ - $I_d$ ) at a drain voltage ( $V_d$ ) of 1 V shown in linear (blue curve) and logarithmic (red curve) scale.



**Figure 2.** (a) Optical image of a MoS<sub>2</sub>/hBN device. (b) Corresponding SPEM map of the same device acquired at the Mo 3d<sub>5/2</sub>/S 2s signal at a BE of 228.3 eV, with contacts grounded and in UHV. (c) Averaged Mo 3d spectrum extracted from the MoS<sub>2</sub> channel area in the SPEM map shown in part b.

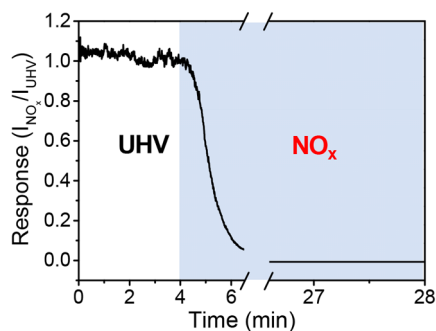
standard electron-beam lithography (EBL), the details of which are given in Figure S1. The interface of the MoS<sub>2</sub>/hBN heterojunction was characterized by cross-sectional high-resolution low-angle annular dark field scanning transmission electron microscopy (LAADF STEM), as shown in Figure 1b, confirming that our devices are indeed monolayer with clean interfaces. The devices were annealed in ultrahigh vacuum (UHV) at 300 °C for several hours prior to measurements to desorb adsorbates from the fabrication process. Figure 1c shows typical current ( $I$ )-voltage ( $V$ ) curves between the source and drain. The observed nonlinearity of the  $I$ - $V$  curves indicate a non-ohmic, slightly rectifying character of the metallic contacts, also visible in our SPEM maps discussed later. The transfer curves shown in Figure 1d demonstrate that the device is n-type with a mobility of  $4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

The FETs were mounted onto the SPEM with three independent electrical contacts for gate ( $V_g$ ), source ( $V_s$ ), and

drain ( $V_d$ ). SPEM maps were acquired to characterize the device in different states of operation. Figure 2a shows an optical image of one such device, while Figure 2b shows the corresponding SPEM map acquired at the Mo 3d<sub>5/2</sub>/S 2s signal, showing excellent agreement. The intensity of the MoS<sub>2</sub> channel is not the brightest in the maps shown in Figures 2b and S5a-d because the grayscale is based on the total intensity in the acquired spectrum. An increase in the background caused by strong peaks at lower binding energy (BE), e.g., from Au 4f, will make the pixel appear bright. Each pixel of the SPEM map contains an X-ray photoelectron spectroscopy (XPS) spectrum and shows the integral intensity of the spectrum (see the experimental section for details). Figure 2c shows an extracted spectrum averaged over the area of the MoS<sub>2</sub> channel.

A mixture of argon and NO<sub>x</sub> (1.7 ppm of NO and 1.9 ppm of NO<sub>2</sub>) was dosed into the chamber at a total pressure of 4.1

$\times 10^{-6}$  mbar, while operando XPS and electrical data were measured. Figure 3 shows the device response to  $\text{NO}_x$  for the



**Figure 3.** Electrical response to  $\text{NO}_x$  measured in situ just before the operando measurements.

device shown in Figure 4a. The current in the device decreases upon exposure to  $\text{NO}_x$ , which is expected given the oxidizing nature of the gas, and equilibrates below the instrumental resolution of the sourcemeter (10 nA) within a few minutes.

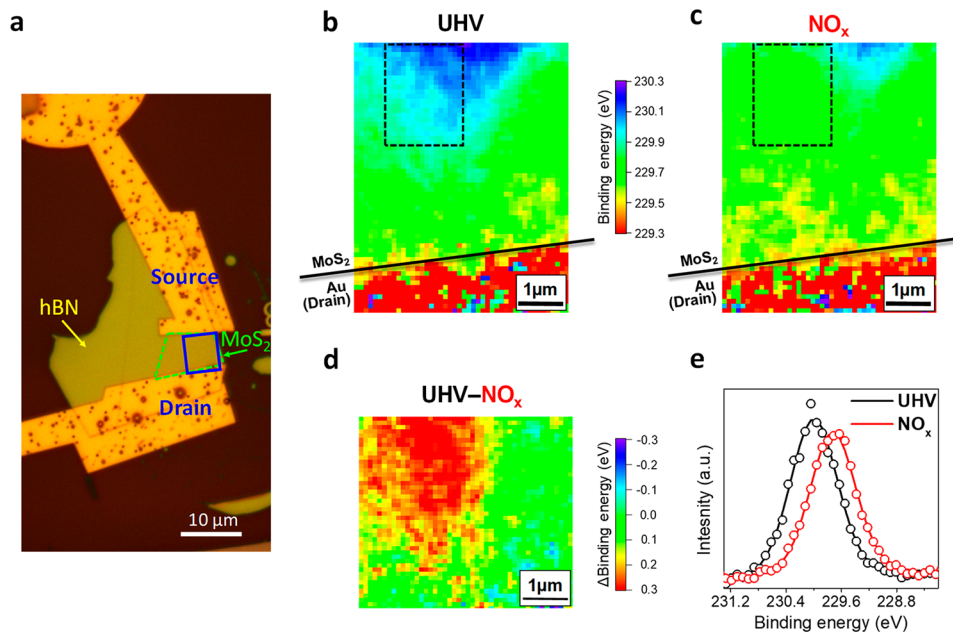
This fast decrease in the current is remarkable given the low partial pressure of  $\text{NO}_x$  of  $\sim 10^{-11}$  mbar inside the chamber. We rationalize this observation as the combined effect of two processes with different time constants, as had been observed earlier for  $\text{NO}_x$  adsorption on  $\text{MoS}_2$ :<sup>13,18</sup> (i) a rapid decrease of the carrier mobility (cf. Figure S3) and (ii) a slower decrease of the charge-carrier concentration due to charge transfer between adsorbed gas species and  $\text{MoS}_2$ . When these two effects are combined, the experimental response curve can be quantitatively described (Figure S4).

The low pressure in the chamber raises questions regarding the type of interaction between  $\text{MoS}_2$  and adsorbed  $\text{NO}_x$

molecules. For comparison, physisorbed  $\text{O}_2$  is only weakly bound to  $\text{MoS}_2$  and can be removed by exposing the sample to mild vacuum pressures of  $10^{-3}$  mbar.<sup>19</sup> In contrast, for recovery after  $\text{NO}_x$  exposure,  $\text{MoS}_2$  samples need to be annealed or illuminated,<sup>20</sup> indicating a much stronger binding. Indeed, the BE for physisorbed  $\text{NO}_2$  is significantly higher than that for  $\text{O}_2$ .<sup>21</sup> Moreover, oxidizing gas species can bind strongly to the surface of  $\text{MoS}_2$  in the vicinity of sulfur vacancies by forming chemical bonds.<sup>22</sup>

Operando high-resolution SPEM maps of the same sample area (Figure 4a) with and without  $\text{NO}_x$  gas in the analysis chamber are presented in Figure 4b,c. In both cases,  $V_d$  was set to 1 V, and the two maps correspond to the device operated in the two steady states of the response curve in Figure 3. The maps in Figure 4b,c show the position of the Mo  $3d_{5/2}$  peak maximum, which was obtained by peak fitting each spectrum (see the experimental section for details). The local BE of the core levels is a direct probe of the potential distribution of electrons between the source and drain. The maps in Figure 4b,c show shifts in the Mo 3d peak position along the channel, from 230.3 eV at the source contact at the top (located just outside the frame of the maps) to 229.3 eV at the drain contact at the bottom, within the range set by the applied  $V_d = 1$  V. Most of the potential drop is known to occur in the regions close to the metallic contacts.<sup>23</sup>

Spatial inhomogeneity in the direction perpendicular to the applied bias can be observed in the maps. In the region close to the source contact, the lateral injection region formed by the Schottky contact between Ti/Au and  $\text{MoS}_2$  is easily observed as a blue V-shaped region of high BE peak positions.<sup>24</sup> Small-scale inhomogeneities in the channel could be the result of trapped impurities. Although our dry transfer process in the assembly of  $\text{MoS}_2/\text{hBN}$  stacks results in clean interfaces, as demonstrated in Figure 1b, it is well-known that pockets of



**Figure 4.** (a) Optical microscopy image of a single-layer  $\text{MoS}_2/\text{hBN}$  device. The blue square indicates the area investigated by SPEM. Operando SPEM maps from the Mo  $3d_{5/2}/S\ 2s$  energy region of the same  $\text{MoS}_2/\text{hBN}$  device acquired in UHV (b) and in  $\text{NO}_x$  (c), with an applied bias  $V_d = 1$  V. The color refers to the Mo  $3d_{5/2}$  BE position. The grounded gold contact is seen in red at the bottom of the maps, while the positive contact is located slightly above the top of the image not in view. (d) Difference between the Mo  $3d_{5/2}$  peak position in UHV and  $\text{NO}_x$ . (e) Extracted Mo  $3d_{5/2}$  spectra averaged over the area indicated by the dark dotted box in parts b and c.

hydrocarbons and water can become trapped between the individual layers during the transfer process. These pockets of contamination could create small areas of strain, leading to variations in the band gap, which are then visible as changes in the BE.<sup>25</sup>

In Figure 4d, the difference in the Mo 3d<sub>5/2</sub> peak position before and during gas exposure has been quantified by subtracting the UHV and NO<sub>x</sub> maps in Figure 4b,c. This difference map is dominated by a red area in the top-left corner with a homogeneous relative shift in the BE of 0.3 eV, extending far into the channel away from the contacts. Lower changes in the BE are observed in the region close to the drain contact. In this region, the surface is covered by carbon deposited during the initial focused-beam exposure (visible as a dark area of subdued intensity in the maps in Figure S5), possibly preventing gas adsorption and thus causing this area of the channel to be less active in gas sensing.

The small difference in the BE with and without gas along the edge on the right-hand side of the map is less understood. This is the physical edge of the MoS<sub>2</sub> channel, while the left side of the maps in Figure 4 corresponds to the middle of the MoS<sub>2</sub> channel (Figure 4a). We note that inhomogeneities perpendicular to the applied field have been observed in similar devices<sup>24</sup> and could be an edge effect related to nonideal electrical contacts. Given the many sources of local variation in the BE, from inhomogeneous potential distribution to contaminations of various kinds, the analysis of spatial maps is found to be more reliable than individual peak shifts from discrete point measurements.

Figure 4e shows XPS spectra averaged over the channel area indicated by the dotted box in Figure 4b,c. The Mo 3d<sub>5/2</sub> peak maximum is at 230.0 eV in UHV and 229.7 eV in NO<sub>x</sub>. A lower BE of the Mo 3d<sub>5/2</sub> state corresponds to a downward shift in the Fermi level ( $E_F$ ), consistent with NO<sub>x</sub> gas making the MoS<sub>2</sub> channel less n-type. To explore the correspondence between the operando SPEM results and the in situ electrical measurements, the shift in  $E_F$  was estimated from the transfer characteristics of the device (Figure S3). In UHV, the charge-carrier density ( $n$ ) was calculated using the parallel-plate capacitor model (eq 1)

$$n = C_t \frac{V_g - V_{th}}{e} \quad (1)$$

where  $C_t$  is the total capacitance of the hBN and SiO<sub>2</sub> substrate layers,  $e$  is the electron charge, and  $V_{th}$  is the threshold voltage. The charge-carrier concentration of  $n_{UHV} = 3.43 \times 10^{12} \text{ cm}^{-2}$  can be translated into a Fermi level position of 23 meV above the conduction-band edge via eq 2

$$E_F = \hbar^2 \pi n / m_e \quad (2)$$

where  $m_e = 0.4m_0$  is the effective electron mass in monolayer MoS<sub>2</sub>.<sup>26</sup> In NO<sub>x</sub> gas, the current (and thus the charge-carrier concentration) through the device drops to virtually zero (Figure 3), meaning that the corresponding  $E_F$  must be inside the band gap of MoS<sub>2</sub>. Our transport data do not allow us to quantify the  $E_F$  position in NO<sub>x</sub>; however, we note that the observed change in the SPEM experiment corresponds well with the energetic position of sulfur vacancies in MoS<sub>2</sub>, located 0.2–0.3 eV below the conduction band.<sup>27</sup> In this scenario, sulfur vacancies act as pinning sites, preventing the Fermi level from moving even deeper into the band gap. The changes in the BE observed in Figure 4d are thus qualitatively and

quantitatively consistent with charge transfer between MoS<sub>2</sub> and adsorbed NO<sub>x</sub> gas species.

Finally, we note that we could not detect an additional component in the Mo 3d<sub>5/2</sub> peak signal, indicative for device oxidation by chemisorbed gas species during several rounds of NO<sub>x</sub> dosing and annealing (Section S7). Our experiments show that our devices are fully recoverable by annealing in UHV (Figure S3). It is reasonable to expect that if significant defects are created by the removal of sulfur atoms with the subsequent replacement by oxygen atoms, removal of the oxidant species by UHV annealing should not lead to a full recovery of mobility due to the increased number of vacancies left in the basal plane, which would then act as scattering sites.<sup>28</sup>

However, it is plausible to assume chemisorption of NO<sub>x</sub> molecules at preexisting sulfur vacancies. Such a process would have a 2-fold impact on the SPEM results: (i) a reduction in the BE related to a decrease in  $E_F$  due to the depletion of charge carriers, as was indeed observed experimentally, and (ii) an additional component in the Mo 3d<sub>5/2</sub> peak signal, reflecting the chemical environment of molybdenum atoms, which we do not observe (Figure 4e). However, reported values for the intrinsic sulfur vacancy concentration in MoS<sub>2</sub> range from  $10^{11}$  to  $10^{13} \text{ cm}^{-2}$ ,<sup>29,30</sup> so that even if each sulfur vacancy was decorated with an adsorbed gas molecule, the gas coverage of the MoS<sub>2</sub> surface would only correspond to  $10^{-4}$ – $10^{-2}$  monolayers, which is below the detection limit of this SPEM technique.

In summary, we have performed concurrent operando SPEM and in situ electrical transport measurements to study the interaction of a monolayer MoS<sub>2</sub> gas sensor with NO<sub>x</sub> gas molecules. Charge transfer between adsorbed gas species and MoS<sub>2</sub> does indeed result in a less n-type MoS<sub>2</sub> channel. The changes in the BE observed by SPEM are related to electrical transport, and the characteristics of the spatial distribution and gas–solid interaction are discussed. We believe that this study further demonstrates the sensitivity and efficacy of MoS<sub>2</sub> as a gas-sensing nanomaterial.

**Materials and Methods.** Mechanically exfoliated monolayers MoS<sub>2</sub> were transferred on preprepared 70-nm-thick hBN flakes by a dry transfer technique (Figure S1). The MoS<sub>2</sub> channel was patterned using EBL, followed by reactive ion etching. Finally, electrodes were realized by EBL and electron-beam evaporation and lift-off of titanium/gold (5 nm/110 nm) metals.

The cross-sectional transmission electron microscopy (TEM) sample was prepared by a Helios G4 UX dual-beam focused ion beam–scanning electron microscopy (FIB–SEM) from FEI. A thin layer of gold ( $\approx 30$  nm thick) was sputter-coated on top of the sample prior to FIB preparation. A 2–3- $\mu\text{m}$ -thick platinum protection layer was deposited on top of the region of interest. The first part of this platinum layer was deposited by electron-beam-assisted deposition to avoid any Ga<sup>+</sup>-ion-beam damage to the MoS<sub>2</sub>/hBN. The TEM lamella was transferred to a dedicated copper TEM grid by a standard lift-out technique. Coarse thinning was performed with a 30 kV ion-beam acceleration voltage. Final thinning was performed at 5 and 2 kV on either side of the lamella to minimize surface damage. TEM was performed with a JEOL ARM 200F double-cesium aberration-corrected cold field emission gun, operated at 200 kV. The ARM is equipped with a large solid angle (0.98 sr) Centurio detector for energy-dispersive X-ray spectroscopy (EDS) and a GIF Quantum ER for fast dual electron energy loss spectroscopy (EELS).

SPEM was performed at the ESCA microscopy beamline at the Elettra synchrotron in Trieste, Italy. Technical details of the SPEM setup can be found in refs 15 and 16. The X-ray beam energy was 701.3 eV. The maps were acquired using a multichannel delay line detector, which allows one to obtain a small spectrum in the snapshot

mode at every pixel of the map and thus allows one to extract the local BE peak position. To extract local BE peak positions, the data were first filtered by applying a  $3 \times 3$  averaging filter to reduce the noise. Using an automated routine, a peak fitting was performed at every pixel. New maps were created containing the obtained peak position for every pixel. To make sure the analysis area is the same with and without gas, the maps in Figure 3 have been adjusted for sample drift (for details, see Figure S5). The effect of beam damage was limited by using a defocused beam and by taking SPEM maps where the beam was rastered across the sample instead of high-energy resolution spectra in a fixed spot (see details in Section S6).

The electrical transport properties of the device were characterized using a two-point configuration with a Keithley 2440 sourcemeter. The gate voltage was applied by a Keithley 2450 instrument, and all data were recorded by a customized LabVIEW program.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnm.1c00137>.

Heterostructure assembly process, STEM image of the heterostructure combined with EDS and EELS maps, transfer characteristic curves before and after NO<sub>x</sub> exposure, quantitative analysis of the sensor response, SPEM intensity maps, effects of beam damage, and evaluation of molybdenum oxidation (PDF)

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<https://pubs.acs.org/doi/10.1021/acsnm.1c00137>

## Author Contributions

I.J.T.J. and B.D.B. conceived the study, T.T. and K.W. prepared materials, and A.A. and B.D.B. fabricated devices. Near-ambient-pressure SPEM investigation and data analysis were carried out by I.J.T.J., B.D.B., A.A., P.Z., M.A., L.G., M.B.M., P.B., B.R.M., and M.S. TEM investigations were carried out by P.E.V. The manuscript was prepared by I.J.T.J., M.S., A.A., and B.D.B. with contributions of all authors.

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors thank D. C. Elias for insightful discussions. This work was supported by the Research Council of Norway (Project 280788). The Research Council of Norway is also acknowledged for support of the Norwegian Micro- and Nano-Fabrication Facility, NorFab (Project 245963/F50), and of the NORTEM infrastructure (Grant 197405), TEM Gemini Centre, Norwegian University of Science and Technology, Trondheim, Norway. K.W. and T.T. acknowledge support from the Elemental Strategy Initiative conducted by the MEXT, Japan (Grant JPMXP0112101001), the JSPS KAKENHI (Grant JP20H00354), and the CREST, JST (Grant JPMJCR15F3).

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