High responsivity in MoS₂ phototransistors based on charge trapping HfO₂ dielectrics

Roda Nur, Takashi Tsuchiya, Kasidit Toprasertpong, Kazuya Terabe, Shinichi Takagi & Mitsuru Takenaka

2D Transition Metal Dichalcogenides hold a promising potential in future optoelectronic applications due to their high photoresponsivity and tunable band structure for broadband photodetection. In imaging applications, the detection of weak light signals is crucial for creating a better contrast between bright and dark pixels in order to achieve high resolution images. The photogating effect has been previously shown to offer high light sensitivities; however, the key features required to create this as a dominating photoresponse has yet to be discussed. Here, we report high responsivity and high photogain MoS₂ phototransistors based on the dual function of HfO₂ as a dielectric and charge trapping layer to enhance the photogating effect. As a result, these devices offered a very large responsivity of $1.1 \times 10^6 \text{ AW}^{-1}$, a photogain $>10^9$, and a detectivity of $5.6 \times 10^{13}$ Jones under low light illumination. This work offers a CMOS compatible process and technique to develop highly photosensitive phototransistors for future low-powered imaging applications.
Transition metal dichalcogenides (TMDCs) have been recently studied with great interest due to their unique electronic and optoelectronic properties. Unlike graphene, these materials have an intrinsic bandgap that makes them a promising candidate for developing future electronic devices, including transistors, integrated circuits, and non-volatile memory devices. Although MoS₂ has been extensively studied, other TMDC materials such as molybdenum diselenide (MoSe₂), tungsten diselenide (WSe₂), tungsten disulfide (WS₂), and palladium diselenide (PdSe₂) have been investigated to explore interesting properties, such as interface charge transport mechanisms, controlling doping carrier type by field emission, developing high mobility transistors using two-dimensional (2D) hexagonal boron nitride (h-BN) dielectrics, and understanding the influence of external stimuli on charge transport properties.

For 2D photodetection applications, graphene as a photoactive material has been pursued for its broadband detection ability and fast time response speeds, however, its short carrier lifetime in the picoseconds range and small optical absorption (~2%) limits its light detection sensitivity. On the other hand, TMDCs such as MoS₂ hold a promising role in future photodetectors, since they offer attractive features such as high photosensitivity, low dark currents, and tunable bandgaps via layer thickness for wider optical absorption.

Many techniques proposed to explore its photodetection ability and to enhance its photosresponse like combining MoS₂ to form hybrid materials, heterostructures, PN junctions, intrinsic photogating, and three-dimensional device structures. Enhancing the photosensitivity with intrinsic MoS₂ is highly attractive, because it can offer a simple fabrication process and complementary metal–oxide–semiconductor (CMOS) compatibility. However, to achieve simultaneously a high light sensitivity under low power operation is challenging, yet highly desirable for its use in future image sensors.

The ability to design a dominating photocurrent generation mechanism can enable the opportunity to develop application-specific performance for photodetectors. MoS₂ has been known to display in visible light a combination of two photocurrent generation mechanisms: the photoconductive and photogating effect. Overall, the photogating effect can provide higher light sensitivity, since the built-in electric field from trapped photocarriers can induce more majority free carriers. Although there has been an exploration of different kinds of applications of photogating such as the use of environmental gases to provide molecular gating and dual photogating with optical absorbing insulators, there is still a lack of understanding how to control this effect with TMDC materials. In addition, previous reported works using TMDCs as photoactive channels have claimed to observe a dominant photogating effect in the on-state (accumulation); however, in the off-state (depletion) the photoconductive effect dominates. One important parameter to consider is the influence of the dielectric layer properties on the photoresponse. To enable a dominating photogating effect for all operation modes (on- and off-state), a dielectric layer with an intrinsic affinity for charge trapping would be required to generate very large photocurrents.

Here we report a low-powered highly photosensitive MoS₂ phototransistor through employing high-k HfO₂ dielectrics. In this device structure, HfO₂ serves as both a dielectric and charge-trapping layer. The intrinsic charge-trapping property of HfO₂ via oxygen vacancies helps to enhance the photoresponse by trapping the photogenerated hole carriers. As a result, the photogating effect is strongly enhanced resulting in providing simultaneously a very large responsivity of $1.1 \times 10^8$ A/W⁻¹, detectivity of $5.6 \times 10^{13}$ Jones, and photogain of $1.6 \times 10^9$ under weak light detection and low power operation.

**Results and discussion**

**Multi-layered MoS₂ and device characterization.** The device schematic of the HfO₂-based multi-layered MoS₂ phototransistor can be seen in Fig. 1a and a close-up optical microscopic image of the channel region in Fig. 1b. A back-gated device configuration was selected, since it allows for direct light illumination onto the MoS₂ channel region for better optical absorption. Heavily doped n⁺⁺ silicon was used as a back-gate where 10 nm of atomic layer deposition (ALD) HfO₂ was deposited as the dielectric layer. Next, the multi-layered MoS₂ flake was mechanically exfoliated from a bulk crystal and transferred onto HfO₂. Finally, top contacts of Ti (5 nm)/Au (50 nm) with channel length of 5 µm were deposited by e-beam evaporation. Details of the device fabrication process can be found in the “Methods” section. To characterize the exfoliated multi-layered MoS₂, a Raman spectroscopic and atomic force microscopic (AFM) measurements were performed. The Raman spectrum in Fig. 1c shows the in-plane $E_g$ and out-of-plane $A_{1g}$ vibrational modes from the Mo-S bond in MoS₂ where the two peaks were located at 382.9 and 407.7 cm⁻¹, respectively. The wavenumber difference between the peaks was 24.8 cm⁻¹, which is close to bulk MoS₂ that has 25 cm⁻¹. AFM height profile measurements were performed to obtain the film thickness of the multi-layered MoS₂ flake as seen in Fig. 1d. Typical MoS₂ flake thicknesses used in this study were in the range of 3–20 nm due to the result of our exfoliation/transferring method and in addition to evaluate near-infrared (NIR) wavelengths. Additionally, an AFM surface topographic scan of the channel region can be found in Supplementary Fig. 1.

Next, a performance evaluation of the HfO₂-based MoS₂ phototransistor was analyzed under the dark condition (no light illumination). The dark transfer characteristics of the phototransistor under different drain–source voltages ($V_{DS}$) of 150, 250, and 500 mV can be seen in Fig. 1e. Under $V_{DS}$ bias of 150 mV, the $I_{DS}/V_{DS}$ ratio was 2.92 × 10⁷, the subthreshold swing (SS) was determined to be 142 mV/dec, the threshold voltage ($V_{TH}$) was −0.71 V from the linear extrapolation method, and the field-effect mobility of 5.07 cm² V⁻¹ s⁻¹ was extracted from the linear region of the $I_{DS}$−$V_{G}$ plot using the equation $\mu = \frac{dI_{DS}}{dV_{G}} \frac{L}{W \times V_{TH}}$, where $W$ is the width, $L$ is the channel length, $V_{DS}$ is the drain–source voltage, and $C_{ox}$ is the oxide capacitance per unit area. One aspect to point out is the large SS and low field-effect mobility that was obtained. In this structure, as-deposited ALD HfO₂ is used with no surface pretreatments or post-deposition annealing to preserve an amorphous defect-rich interface. Back-gated MoS₂ field-effect transistors have been reported to show lower mobilities compared to top-gate structures. Some of the reasons include the exposure of the channel region to environmental gaseous absorbates like O₂ and H₂O that deplete electrons from MoS₂ via electron transfering and the reduction in gate capacitance density due to the contribution of non-gapless contact of transferred MoS₂, which is known as the van der Waals gap. However, an improved electrical performance for back-gated devices can be achieved by channel encapsulation. Lastly, the dark output characteristics are seen in Fig. 1f. A close-up of the $I_{DS}$−$V_{D}$ plot at lower drain voltages can be seen in Supplementary Fig. 2. The linear relationship between the drain current and drain voltage under lower voltages indicates that our metal contacts have ohmic-type behavior.

**Photoresponse performance.** The general light detection process starts with the absorption of incident light by the photoactive channel when the energy condition of $E_{photon} > E_{g,MoS₂}$ is satisfied. Next, the photogenerated electron/hole pairs are separated by the applied electric field from $V_{DS}$ in the depletion region
where the electrons and holes are collected at the electrodes. Generally, MoS$_2$ has two dominant photocurrent generation mechanisms in visible light, which are the photoconductive and photogating effect$^{27,28}$. Typically, when observing the photoresponse of MoS$_2$ phototransistors, its transfer characteristics will display a combination of these effects. The photoconductive effect is the increase in conductivity of the semiconductor from illumination resulting in the generation of electron/hole pairs. These photogenerated carriers get collected by the electrodes and produce an increase in the current that adds to the dark current. The photogating effect is when one of the photogenerated carriers gets trapped and acts as a built-in local electric field. For n-type semiconductors, these trapped holes induce more majority carrier electrons and causes a horizontal shift in the $I_D$–$V_G$ curve.

An evaluation of the photoresponse with the HfO$_2$-based MoS$_2$ phototransistor under the illumination of blue light (λ = 460 nm) was studied. In addition, we compared its performance with the conventional SiO$_2$-based MoS$_2$ phototransistor with the same dielectric thickness. The effects of light illumination at different optical power densities can be seen in Fig. 2a, b for the HfO$_2$ and SiO$_2$ devices, respectively. As expected for both cases, there is an increase in $I_D$ as the optical power was increased. For the HfO$_2$ device, the $I_{PH}$–$V_G$ illumination curves are strongly shifted toward the left indicating a strong photogating effect. Since this device without illumination displays hysteresis, we found that its hysteresis window became larger with increasing optical powers (Supplementary Fig. 9). Its optical detection under red (λ = 630 nm) and NIR (λ = 850 nm) wavelengths were also measured and displayed the same photogating behavior (Supplementary Figs. 3 and 8). In addition, a measurement under vacuum conditions (2 × 10$^{-3}$ Pa) was also performed with the HfO$_2$ device and can be seen in Supplementary Figs. 10 and 11. We found that the multi-layered MoS$_2$ channel region could not become fully depleted due to the poor gate control (back-gate structure) and absence of gaseous absorbates (O$_2$ and H$_2$O) that help to deplete the channel.

Also, its output characteristics under constant illumination in comparison to the dark condition can be found in Supplementary Fig. 4. On the other hand, the SiO$_2$ device showed a stronger photoconductive effect where its $I_{PH}$–$V_G$ illumination curves increased in the vertical direction. There has been a large variation in the reported responsivities$^{29,30}$ and even in the dominant photoresponse behavior in SiO$_2$-based MoS$_2$ phototransistors. Some have reported to observing a dominating photogating effect$^{31}$ or photoconductive effect$^{32}$. This discrepancy comes from the interface between MoS$_2$/SiO$_2$ where SiO$_2$ is well known for dangling bonds, which can act as trap sites. Also, the presence of moisture and surface absorbates at the interface have been shown to cause variations in hysteresis due to polar molecules like water$^{33}$, which can act to screen the electric field in the channel region. In addition, due to the dielectric scaling down to 10 nm, the gate bias sweep has been reduced for both devices to 2 V in comparison to other works that requires much larger gate voltages between 20 and 40 V.

Next, the photocurrent ($I_{PH} = I_{LIGHT} − I_{DARK}$) generation between the two devices was compared by plotting the photocurrent ($I_{PH}$) versus gate voltage ($V_G$) at $V_{DS} = 150$ mV and $P_{opt} = 1.5$ mW cm$^{-2}$ in Fig. 2c. The HfO$_2$ device displayed a much larger peak $I_{PH}$ of 2.1 μA compared to the SiO$_2$ device whose peak $I_{PH}$ was 62.3 nA. Here the HfO$_2$ device provided a 33 times higher photocurrent generation compared to the SiO$_2$ device under the same biasing and illumination conditions. After the peak photogenerated current was reached, the SiO$_2$ device showed a decline; however, the HfO$_2$ device still displayed detection of photocurrent even into accumulation mode. A close-up of the illumination curves from Fig. 2a, b can be seen in Fig. 2c, d. For the HfO$_2$ device, due to the strong $I_D$–$V_G$ parallel shifting under illumination, there is an increase in the on-state
Fig. 2 Photoresponse of MoS2 phototransistors. Effects of light illumination with blue LED at different optical power densities at $V_{DS} = 150$ mV for a HfO2 phototransistor and b SiO2 phototransistor. Close-up of the illumination curves in the accumulation mode region of c the HfO2 phototransistor and d the SiO2 phototransistor. e Photocurrent generation comparison of HfO2 and SiO2 phototransistors under illumination at 1.5 mW cm$^{-2}$. f Photocurrent ($I_{PH}$) versus optical power density under varying gate voltages and constant $V_{DS} = 150$ mV.

current in comparison to the dark state on-current. As a result, this device is still able to detect photocurrent in both depletion and accumulation mode operation. Conversely, the SiO2 device did not show this behavior as the illumination on-current is roughly the same as the dark condition. Lastly, the dependence of the photocurrent on the incident optical power density was plotted in a log scale in Fig. 2f. The gate voltages of $-1.52$ and $-1$ V were evaluated under depletion mode for the phototransistors and $V_{DS}$ was 150 mV. The photocurrent as a function of the optical power can be fitted using a power-law relationship: $I_{PH} \propto P^{\alpha}$, where the exponent $\alpha$ can range from 0 < $\alpha$ ≤ 1. A value of 1 represents a linear relationship where the increase in photocurrent is solely due to the photogenerated carriers (photoconductive effect). For the case of $\alpha < 1$, it indicates a sub-linear relationship due to the presence of traps, defects, and other complicated photogeneration/recombination processes. From the data fitting, the HfO2 device had $\alpha = 0.82$ for $V_G = -1.52$ V and $\alpha = 0.29$ for $V_G = -1$ V. On the other hand, the SiO2 device had $\alpha = 0.94$ for $V_G = -1.52$ V and $\alpha = 1.39$ for $V_G = -1$ V. The HfO2 device maintained the expected sub-linear relationship; however, the SiO2 device showed a close to linear photocurrent relationship with increasing optical powers. As a result of the photogating effect, the HfO2 device is capable of producing $10^3$–$10^5$ order of magnitude larger photocurrents under depletion mode versus SiO2 whose photoresponse is photoconductive in this regime.

High-temperature annealing and dielectric hole trapping. HfO2 is currently used in CMOS technology. In comparison to silicon dioxide, its use in TMDC-based transistors offers benefits, such as higher carrier densities, dielectric screening effects, and lower operating voltages. For silicon-based transistors, these types of metal oxide dielectrics have been found to have an inherent charge-trapping property, which has been shown to have reliability issues such as degraded mobility from Coulomb and phonon scattering and threshold voltage shifts from charge injection into pre-existing traps in the high-k material. One technique to improve the dielectric interface quality by reducing the interface trap density between the oxide and semiconductor layer is to perform a high-temperature anneal. Here we explored the effects of thermal annealing to HfO2 and explore its impact on the photoresponse. After ALD deposition of HfO2, a rapid thermal annealing was performed at 1000 °C for 1 min before transferring MoS2. As-deposited HfO2 is amorphous; however, by applying a high-temperature anneal, it can introduce some crystalline domains to produce a polycrystalline film. An X-ray diffraction of both the amorphous and 1000 °C annealed HfO2 films can be seen in Supplementary Fig. 5. The 1000 °C HfO2 displayed some monoclinic phase peaks in its spectrum in comparison to the no-anneal HfO2, which had none. The photoresponse of the 1000 °C annealed HfO2 device under the same biasing ($V_{DS} = 150$ mV) and illumination conditions from before can be seen in Fig. 3a. It also displays the photogating effect; however, its illumination curves did not display strong parallel shifting like the no-anneal device. The photocurrent generation of the 1000 °C HfO2 device was also measured and plotted in Fig. 3b. Under a constant illumination of 1.5 mW cm$^{-2}$, it generated a lower peak $I_{PH}$ of 46.7 nA.

To test the intrinsic potential of hole trapping with HfO2, a “stress and sense” $I$–$V$ measurement was performed under the dark condition. In this measurement, a negative gate pulse of $-2$ V was applied under varying stress time durations of 100 ms, 1 s, 10 s, and 100 s. After each gate pulse stress, an $I$–$V$ sweep around the threshold voltage was measured and plotted in Fig. 3c. The threshold voltage shift was measured with respect to the before stress threshold voltage ($V_{THO}$). As the stress time was increased, the $I_D$–$V_G$ curves moved toward the left as a parallel shift. This
negative threshold voltage shift indicates the presence of trapped hole charges. Figure 3d shows the threshold voltage shift and effective density of defects ($\Delta N_{\text{eff}}$) generated from the negative bias with respect to stress time. In negative bias temperature instability, $\Delta N_{\text{eff}}$ is a term that contains the total contribution of fast and slow defect states that are generated from the applied stressing conditions. It can be determined from $\Delta N_{\text{eff}} = \Delta V_{\text{TH}} \cdot C_{\text{ox}} / q$, where $\Delta V_{\text{TH}}$ is the threshold voltage shift, $C_{\text{ox}}$ is the oxide capacitance, and $q$ is the electronic charge. The same measurement was also performed with the SiO$_2$ device where the negative bias stress $I_D$–$V_G$ plot can be found in Supplementary Fig. 6. Comparing the two devices, the HfO$_2$ device showed a larger threshold voltage shift and a larger defect density in ~10$^{12}$ cm$^{-2}$ with increasing bias stress time. Overall, these results show that a longer negative bias stress time leads to more defects generated in the oxide layer leading to larger threshold voltage shifting.

Mechanism of photogating with HfO$_2$. As previously discussed, the photogating mechanism relies on the charge trapping of the photogenerated holes. One method to confirm the photogating effect is to look at the amount of threshold voltage shifting under increasing optical powers. The threshold voltage shift is defined as: $\Delta V_{\text{TH}} = V_{\text{TH}, \text{DARK}} - V_{\text{TH}, \text{DARK}}$. In Fig. 4a, it shows a comparison of the threshold voltage shift versus optical power density for all three devices: no anneal HfO$_2$, SiO$_2$, and 1000 °C HfO$_2$. The negative sign in $\Delta V_{\text{TH}}$ indicates the presence of trapped hole charges. The no anneal HfO$_2$ device overall displayed a stronger threshold voltage shift compared to the other devices indicating its higher sensitivity to the photogating effect. Another method to confirm the presence of photogating is to look at the relationship between the photocurrent and transconductance. Since the photogating effect produces a shift in the threshold voltage resulting in an increase to the drain current, the photocurrent should have a proportional relationship with the transconductance based on the following approximation: $I_{\text{PH}} \approx g_m \cdot \Delta V_{\text{TH}}^2$, where $g_m = \frac{dI_D}{dV_G}$. Based on the results from Fig. 2c, we plotted the photocurrent at 1.5 mW cm$^{-2}$ and the device’s transconductance as a function of the gate voltage up until the peak photocurrent in Fig. 4b, c for the HfO$_2$ and SiO$_2$ devices, respectively. Both devices displayed a similar trend for the photocurrent and transconductance; however, the HfO$_2$ device showed a closer proportional relationship, thus further confirming a stronger photogating effect.

Light detection occurs in depletion mode where the bands near the surface of the channel bend upwards. A model of the charge-trapping process with the HfO$_2$ dielectric can be found in Fig. 4f. The photogeneration process of free e$^-$/h$^+$ occurs in the depletion region of MoS$_2$ where the electric field from $V_{DS}$ assists to separate the charges. According to our proposed model, the photogenerated holes tunnel into HfO$_2$ to occupy oxide trap levels near the valence band edge of MoS$_2$. As a result of this hole accumulation process in HfO$_2$, the trapped holes act as a local built-in electric field, which shifts the Fermi level in MoS$_2$ to induce more electrons. Evidence of the presence of oxide traps can be seen from the strong horizontal $I_D$–$V_G$ shifting under light illumination. In order to suppress the photogenerated hole
trapping in HfO$_2$, the insertion of 3.4 nm of deposited SiO$_2$ was inserted between the MoS$_2$ channel and HfO$_2$ to function as an insulating tunneling barrier layer (Fig. 4d). Next, the same blue light illumination measurement as before was performed in Fig. 4e. This device now showed a more dominant photoconductive behavior, thus indicating the successful separation of the oxide traps in HfO$_2$ with the valence band edge of MoS$_2$.

Next, the photoresponse of a different TMDC material WSe$_2$ was analyzed utilizing the same device structure and metal contacts. Although higher optical powers were needed to clearly observe its light detection, its photoresponse to blue light can be seen in Fig. 4g where its flake thickness was close to 5 nm. Interestingly, the WSe$_2$ device with the same HfO$_2$ dielectric showed a strong photoconductive behavior. To understand this discrepancy with MoS$_2$, an energy band diagram of multi-layered MoS$_2$, multi-layered WSe$_2$, and HfO$_2$ with respect to the vacuum level can be seen in Fig. 4h. The valence band maximum (VBM) of WSe$_2$ lies at a higher energy level in comparison to MoS$_2$ and their VBM difference was determined to be 0.4 eV. HfO$_2$ is known to have intrinsic defects such as oxygen vacancies and interstitials located within the bandgap where they can serve as electron and hole traps. According to a simulation study with monoclinic HfO$_2$, there is a distribution of oxygen vacancies of different charged states (positive $V^+$, negative $V^-$, and neutral $V^0$) located slightly below the mid bandgap region of HfO$_2$. In particular, the oxygen vacancies of type $V^+$ at 2.71 eV and $V^0$ at 2.91 eV with respect to the valence band of HfO$_2$ correspond to energy levels with respect to the vacuum level of 5.89 eV for $V^+$ and 5.69 eV for $V^0$, which lie close in energy to the VBM of multi-layer MoS$_2$ at $-5.6$ eV (monolayer MoS$_2$ has VBM at $-5.8$ eV). The phenomenon of charge tunneling relies on the potential of the barrier height and effective mass of the carrier. Although the
effective hole mass for MoS$_2$ (0.54 $m_e$) is heavier than WSe$_2$ (0.36 $m_e$), the observed tunneling behavior for MoS$_2$ most likely arises from the defect energy levels of the oxygen vacancies in HfO$_2$ having good band alignment with the low-lying valence band edge of MoS$_2$. We found the photogating effect for MoS$_2$ to be reproducible and present in all devices made (Supplementary Table 1—all devices show high responsivity); therefore, this contributing defect state in HfO$_2$ must be an intrinsic defect. As for the photoconductive behavior observed with WSe$_2$, its valance band offset with these oxygen vacancies provides a trap energy-level misalignment resulting in no hole trapping and instead allows for the collection of the photogenerated hole carriers at the electrode.

Photodetection metrics. Some of the figures of merit for photodetectors such as responsivity, detectivity, photogain, and time response were evaluated for the HfO$_2$ phototransistor. The responsivity ($R$) represents the conversion efficiency of the incident photon flux (input signal) into photogenerated free carriers (output signal). It is defined as $R = \frac{I_{ph}}{P_{in}}$, where $I_{ph}$ is the photocurrent, $P_{in}$ is the incident optical power density, and $A$ is the area of the channel. Under a negative gate bias and $V_{DS} = 150$ mV, the responsivity with respect to optical power density can be seen in Fig. 5a. The peak responsivity of $1.1 \times 10^6$ A W$^{-1}$ was obtained under the lowest optical power of 0.33 pW. The detectivity describes the response to light (sensitivity) and the noise floor of a photodetector. The dark noise current was measured based on a previously reported technique$^{46}$ where we obtained 10.6 pA Hz$^{-1/2}$ at a frequency of 2 Hz, which was the lowest frequency we could experimentally obtain. Due to the low dark current of this device (avg $I_{dark} \sim 5$ pA), the shot noise limit was determined to be 1.3 fA Hz$^{-1/2}$ from $I_{shot} = \sqrt{2qI_{dark}}$, where $q$ is electronic charge. Next, the noise equivalent power (NEP) was calculated from $\text{NEP} = \frac{I_{shot}}{A}$, where $R$ is the responsivity. The specific detectivity ($D^*$) was obtained from $D^* = \frac{\sqrt{A}}{\text{NEP}}$, where $A$ is the area of the channel region. Figure 5b shows the specific detectivity as a function of the optical power density at different $V_G$ biasing where the highest detectivity achieved was $5.62 \times 10^{13}$ Jones. A more accurate measure of the detectivity of this phototransistor can be obtained by performing a dark noise current measurement at the intrinsic bandwidth of this detector at around 3 mHz (narrow bandwidth is due to its long carrier lifetime).

The photoswitching behavior was investigated to determine its time response. The device was biased under depletion mode with $V_G$ at $-1.5$ V and $V_{DS}$ at 150 and 500 mV in Fig. 5c. The blue region indicates the on-state where the light source was turned on for a duration of 30 s. Within the first few seconds the light source is turned on, there is a rapid increase in the current due to band-to-band transitions. Next, the current transitions into a slow increase where the peak current value occurs at the moment when the light source is cut off. This slow current generation is due to the photogenerated electrons that are induced from the photogenerated hole-trapping process. After the light source is turned off, the current first decays rapidly but then transitions into a slow decay, which is called persistent photocurrent effect (PPC)$^{47,48}$. The PPC effect is the sustained conductivity after illumination and is attributed to the presence of trapped charges at the interface between the semiconductor and dielectric. The relaxation time constant can be extracted from the slowly decaying drain current ($I_D$) by using a stretched exponential decay function: $I_{PPC}(t) = I_p e^{-\left(\frac{t}{\tau}\right)^\beta}$ where $\tau$ is the relaxation time constant and $\beta$ is the decay exponent that ranges from 0 to 1. Figure 5d shows the PPC model fitted to the decaying $I_D$ after illumination. The fitting parameters of $\tau$ and $\beta$ were determined to be 312 s and 0.395 for $V_{DS} = 150$ mV and 272 s and 0.326 for $V_{DS} = 500$ mV, respectively. For both drain voltages, the time constants were large due to the slow de-trapping time of the oxide-trapped charges. On the other hand, the SiO$_2$ phototransistor displayed a much faster photoswitching behavior as seen in Supplementary Fig. 7. The rise and fall times were 408 and 682 ms for $V_{DS}$ bias of 150 mV. The faster switching speeds and
stable illumination current of the SiO2 device indicates the absence of slow deep-level traps.

Photogain is the ratio between the generated photocarrier lifetime and carrier transit time. For the case where \( \mu_C < \mu_h \), more electrons are collected, so the photogain can be determined by

\[
G = \frac{\tau}{L/V_{DS}},
\]

where \( \tau \) is lifetime of photogenerated carriers, \( \mu \) is the carrier mobility, \( V_{DS} \) is the drain–source voltage, and \( L \) is the channel length. For \( V_{DS} = 150 \) and 500 mV, the photogain was determined to be \( 9.49 \times 10^8 \) and \( 2.76 \times 10^9 \), respectively. In general, there is a tradeoff between a fast time response and high photogain, since a higher photosensitivity relies on having longer carrier lifetimes. The large photogain obtained with this device can be attributed to the slow de-trapping process of the trapped hole carriers. As previously mentioned, MoS2-based phototransistors have been demonstrated to offer very large responsivities. A benchmark of previously reported MoS2 phototransistors responsibilities based on monolayer and multilayer MoS2 are summarized in Fig. 5e. This study offers the highest responsivity in visible light at blue and red wavelengths \((1.3 \times 10^4 \text{ A W}^{-1})\). The responsivity for the NIR wavelength at 850 nm was 13.2 A W\(^{-1}\).

**Conclusion**

In summary, we developed a highly photosensitive MoS2 phototransistor using high-k metal oxide HfO2 dielectrics. Due to the valence band edge alignment of MoS2 with oxygen vacancies in HfO2, it enabled hole-trapping behavior in HfO2 resulting in generating a stronger photogating effect. By providing a valence band offset with the oxygen vacancies, a strong photoconductive behavior can be observed as in the WS2 device case. In addition, we found providing a charge-tunneling blocking layer can help to suppress the hole-tunneling into HfO2 for MoS2 and the use of SiO2 dielectrics can also show photoconductive behavior for MoS2. For the MoS2/HfO2 device, it provided a very high responsivity of approximately \(10^6 \text{ A W}^{-1}\) and photogains in ~10^9. By scaling the dielectric thickness down to 10 nm, it enabled lower power operation and the ability to still optically detect thin flakes. Overall, this enhancement in the photosensitivity allows for better photodetection of weak light signals under low power operation.

**Methods**

**Device fabrication.** A bulk crystal of MoS2 was purchased from 2D semiconductors and the bulk crystal of WS2 was purchased from GrapheneHQ. Heavily doped n-type silicon was used as the substrate and was cleaned by RCA pre-cleaning followed by HF etching. Deposition of the dielectric layer, 10 nm of ALD HfO2 (Picosun) from pre-cursors of tetraisopropyl(methylamino)hafnium and H2O was deposited at 250 °C or 10 nm of SiO2 was thermally grown by 850 °C. A bulk crystal of MoS2 was purchased from 2D semiconductors and the bulk crystal of WS2 was purchased from GrapheneHQ. Aluminum was deposited on the backside of silicon to provide better electrical contact for the back-gate. The final step was lift-off.

**Device characterization.** All measurements were performed at room temperature and under ambient conditions. For the vacuum measurements, Nagano Techno Engineering Co., Ltd Grain 408-32-B was used as the probe station and Keithley 4200 SCS was used for device measurements. A commercial blue (460 nm) and red (630 nm) 0.5 W Mid-Power Flux light-emitting diode (LED) from LED Paradise (LP-5FCIBHC) and NTR (850 nm) from Optosupply (OSIX5NE3EE1) was used as a light source with an LED lens where the distance between the LED and sample was ~6.5 cm. Ambient condition measurements were performed using Cascade probe system (Form Factor) and Agilent 4156C Precision Semiconductor Parameter Analyzer. In order to obtain a steady-state condition for illumination measurements, the LED was turned on for 1 min before the measurement was taken and was turned off for 3–5 min before subsequent measurements were made. Time response/noise measurements were made using Agilent 33500B series waveform generator to provide the light pulse waveforms. Ametek 7270 lock-in amplifier and Femto variable-gain low-noise current amplifier (DLPCA-200) was used for the noise current measurement.

**Data availability**

The data supporting the findings of this study can be available from the corresponding author upon reasonable request.

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