Wide-Range Controllable n-Doping of Molybdenum Disulfide (MoS\textsubscript{2}) through Thermal and Optical Activation

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Molybdenum disulfide (MoS\textsubscript{2}), a transition metal dichalcogenide (TMD) with layered structure, has recently been considered a promising candidate for next-generation flexible electronic and optoelectronic devices because of its superior electrical,\textsuperscript{1–4} optical,\textsuperscript{5–7} and mechanical properties.\textsuperscript{8} Thickness scalability down to a monolayer and van der Waals exfoliation without surface dangling bonds (consequently, native oxides) make MoS\textsubscript{2}-based thin film transistors (TFTs) immune to the short channel effect (SCE) and provides very high field-effect mobility (\textasciitilde 200 cm\textsuperscript{2}/V s), which is comparable to the universal mobility of Si,\textsuperscript{9} respectively. In addition, an excellent photodetector with a wide spectral range from ultraviolet (UV) to near-infrared (IR) is achievable using MoS\textsubscript{2}, since its energy band gap varies between 1.2 eV (bulk) and 1.8 eV (monolayer), depending on layer thickness.\textsuperscript{6,7,9–12} It also has potential for use in chemical sensors,\textsuperscript{13,14} memory,\textsuperscript{15,16} and valleytronic devices.\textsuperscript{4,5,17}

However, one of the critical issues that hinder the successful integration of such MoS\textsubscript{2} electronic and optoelectronic devices is the lack of a reliable and controllable doping method. Such a component is essential for inducing a shift in the Fermi level, which subsequently enables wide modulations of its electrical and optical properties.\textsuperscript{18,19}

Fang et al. reported a potassium-based degenerate n-doping method on a 2D TMD material (exfoliated trilayer and bulk MoS\textsubscript{2}) with the assistance of a phosphorus silicate glass (PSG) insulating layer, which has the broadest doping range among the results reported to date (between $3.6 \times 10^{10}$ and $8.3 \times 10^{12}$ cm\textsuperscript{2}) and is also applicable to other 2D semiconductors. This is achieved through (1) a three-step process consisting of, first, dopant out-diffusion between 700 and 900 °C, second, thermal activation at 500 °C, and, third, optical activation above 5 μW steps and (2) weight percentage adjustment of P atoms in PSG (2 and 5 wt %). We anticipate our widely controllable n-doping method to be a starting point for the successful integration of future layered semiconductor devices.

**KEYWORDS:** MoS\textsubscript{2} · wide-range · controllable doping · thermal activation · optical activation

**ABSTRACT** Despite growing interest in doping two-dimensional (2D) transition metal dichalcogenides (TMDs) for future layered semiconductor devices, controllability is currently limited to only heavy doping (degenerate regime). This causes 2D materials to act as metallic layers, and an ion implantation technique with precise doping controllability is not available for these materials (e.g., MoS\textsubscript{2}, MoSe\textsubscript{2}, WS\textsubscript{2}, WSe\textsubscript{2}, graphene). Since adjustment of the electrical and optical properties of 2D materials is possible within a light (nondegenerate) doping regime, a wide-range doping capability including nondegenerate and degenerate regimes is a critical aspect of the design and fabrication of 2D TMD-based electronic and optoelectronic devices. Here, we demonstrate a wide-range controllable n-doping method on a 2D TMD material (exfoliated trilayer and bulk MoS\textsubscript{2}) with the assistance of a phosphorus silicate glass (PSG) insulating layer, which has the broadest doping range among the results reported to date (between $3.6 \times 10^{10}$ and $8.3 \times 10^{12}$ cm\textsuperscript{2}) and is also applicable to other 2D semiconductors. This is achieved through (1) a three-step process consisting of, first, dopant out-diffusion between 700 and 900 °C, second, thermal activation at 500 °C, and, third, optical activation above 5 μW steps and (2) weight percentage adjustment of P atoms in PSG (2 and 5 wt %). We anticipate our widely controllable n-doping method to be a starting point for the successful integration of future layered semiconductor devices.

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charge transfer mechanism and then used it to form highly n-doped source/drain (S/D) regions in TMD-based TFTs. Sreeprasad et al. observed n- and p-doping phenomena on MoS2 through different functionalization methods of Au nanoparticles. In addition, n- and p-doping techniques based on polymers such as polyethylenimine (PEI) and functional self-assembled monolayers (SAMs) with different dipole moments were reported by Du et al. and Li et al. Chen et al. also presented a p-doping method on MoS2 by using selected-area plasma treatment with fluorine (F) or oxygen (O). Although Fang et al. controlled the doping level by adjusting the exposure time to potassium, the range of doping was limited within the heavily doped (degenerate) regime, where MoS2 works as a near-metallic layer. Since adjusting the electrical and optical properties of MoS2 is possible within a nondegenerate doping regime, wide-range doping capability including nondegenerate and degenerate regimes is a critical point in the design and fabrication of MoS2-based electronic and optoelectronic devices. However, it is very challenging to achieve nondegenerate doping on 2D semiconductors and secure its wide-range doping controllability because a method such as ion implantation cannot be applied to the doping process. Recently, Lin et al. reported nondegenerate n-doping of MoS2 using cesium carbonate (Cs2CO3). In this work, we first demonstrate a wide-range controllable n-doping method for MoS2 on a phosphorus silicate glass (PSG) insulating layer, which (1) activates the doping phenomenon via a thermal/optical process and (2) adjusts the doping level of MoS2 by controlling the thermal/optical process conditions or weight percentage of P atoms during the in situ doped PSG growth step. This controllable n-doping process is also demonstrated on exfoliated trilayer and bulk MoS2 films. In addition, the proposed doping method is investigated in detail through Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), electrical measurements (\(I_{D}/C_0V_G\) and \(I_{D}/C_0V_D\)), and atomic force microscopy (AFM).

### RESULTS AND DISCUSSION

#### Characterization of n-Doped MoS2

First, Raman spectroscopy analysis was performed on the MoS2/SiO2 and MoS2/PSG samples to investigate the effects of (1) the thermal annealing process on MoS2 and (2) P atoms (these atoms exist in the form of phosphorus pentoxide, a chemical compound with the molecular formula P2O5) in the PSG layer on MoS2, respectively, during second-step annealing. Figure 1a and b show the Raman spectra measured on MoS2/SiO2 and MoS2/PSG samples with or without annealing. Here, two conventional peaks (E\(^1\)\(_{2g}\) and A\(_{1g}\)) indicating the in-plane and out-of-plane vibrations for bulk MoS2 were respectively observed at \(\sim 380\) and \(\sim 406\) cm\(^{-1}\). Then, the peak position shifts in E\(^1\)\(_{2g}\) and A\(_{1g}\) peaks for the MoS2 flake before/after the n-doping process through 500 °C annealing.

#### Raman mapping images in E\(^1\)\(_{2g}\) and A\(_{1g}\) peaks for the MoS2 flake before/after the n-doping process through 500 °C annealing.

Figure 1. Raman spectrum analysis of MoS2 on SiO2 and PSG. Raman spectra of MoS2 on (a) SiO2 and (b) PSG, which were nonannealed (NA) and annealed at different temperatures (300, 400, and 500 °C). E\(^1\)\(_{2g}\) and A\(_{1g}\) peak shift data as a function of annealing temperature, which were extracted from the Raman spectra of (c) MoS2/SiO2 and (d) MoS2/PSG samples. (e) Raman mapping images in E\(^1\)\(_{2g}\) and A\(_{1g}\) peaks for the MoS2 flake before/after the n-doping process through 500 °C annealing.
in $E_{1g}$ and $A_{1g}$ mode vibrations caused by thermal expansion of MoS$_2$ after 400 °C annealing. Similar red-shift phenomenon in the $E_{1g}$ peak was previously reported by Tongay et al. after 450 °C annealing for 40 min, and this was possibly attributed to the desorption of contaminants or the stress-releasing effect on MoS$_2$. However, for higher temperature annealing (500 °C), the peaks in the MoS$_2$/PSG sample are pushed further to the left ($\Delta E_{1g} = \sim 3.7$ cm$^{-1}$ and $\Delta A_{1g} = \sim 2.46$ cm$^{-1}$) when compared with the peak shifts ($\Delta E_{1g} = \sim 2.47$ cm$^{-1}$ and $\Delta A_{1g} = \sim 1.23$ cm$^{-1}$) in a MoS$_2$/SiO$_2$ sample. P$_2$O$_5$ molecules in the surface region of the PSG layer are thought to electrically affect MoS$_2$ after 500 °C annealing, which consequently provides more electrons to MoS$_2$. Sreeprasad et al. previously reported the red-shift of $E_{1g}$ and $A_{1g}$ peaks after the n-doping process on MoS$_2$, which induced functionalization of Au nanoparticles on MoS$_2$ through instantaneous reaction using microwave. In addition, Li et al. observed the red-shift of the $A_{1g}$ peak by 1.6 cm$^{-1}$ in MoS$_2$ flakes on a 3-(trimethoxysilyl)-1-propanamine (APTMS)-treated substrate and confirmed the n-doping phenomenon through electrical measurements. The distance between $E_{1g}$ and $A_{1g}$ peaks obtained in all of the samples in the present study was larger than 24 cm$^{-1}$, since measurement was done on thick MoS$_2$ flakes, considered bulk MoS$_2$. Figure 1e shows the Raman mapping images corresponding to $E_{1g}$ and $A_{1g}$ peaks before/after the n-doping process through 500 °C annealing. Darker MoS$_2$ images were observed after the annealing process, indicating that the MoS$_2$ flake was uniformly n-doped by the P atoms in PSG. Although there are color differences in each Raman mapping image, which seem to be caused by thickness variation in the exfoliated MoS$_2$ flake, this does not indicate nonuniformity of the n-doping concentration, because $E_{1g}$ and $A_{1g}$ peak shift values are constant at all positions despite thickness variation.

Figure 2a shows the schematics of the back-gated transistor fabricated on MoS$_2$ and explains the n-doping mechanism. Since the P$_2$O$_5$ molecule in the PSG layer is asymmetric in structure with nonzero dipole moment (having a positive pole in P atoms and a negative pole in O atoms), the n-doping effect is thought to originate from another dipole induction at the MoS$_2$/PSG interface. The O atoms with a negative pole on the PSG surface seem to attract holes from the MoS$_2$ layer and hold them at the interface region, thereby n-doping the MoS$_2$ layer. In addition, the increased amount of P$_2$O$_5$ molecules on the PSG surface and the annealing-related surface smoothing are predicted to strengthen the dipole moment and, consequently, the degree of n-doping. As shown in Figure 2b, the XPS spectra of O 1s peaks, the intensity of the P$_2$O$_5$ signal (at 533.4 eV) increased slightly as the annealing temperature rose to 500 °C, consequently indicating the larger amount of P$_2$O$_5$ in the surface region. Figure 2c presents AFM images and surface roughness on the PSG samples, which were nonannealed and annealed at 300, 400, and 500 °C. Although it was confirmed that P$_2$O$_5$ molecules were out-diffused from PSG film via annealing, the root-mean-square (RMS) roughness of the annealed PSG film was reduced from 0.65 nm to 0.55 nm as the annealing temperature increased to 500 °C due to the
high reflowing property of the PSG film. As a result, a shorter distance between P₂O₅ (particularly the negatively charged O atoms) and MoS₂ is expected in the 500 °C annealed sample when compared to other samples annealed at lower temperatures. In order to reconfirm the n-doping phenomenon on MoS₂ verified by Raman spectroscopy analysis in Figure 1, the I₂–V₆ characteristics of MoS₂ transistors were measured and compared in Figures 2d and e, where the lateral electric field (E_lateral) between the source and drain electrodes was fixed at 1 V/µm. Although shifts in E₁₂₋₉ and A₁₉ peaks were observed on MoS₂/PSG samples that were annealed at 400 and 500 °C, no changes were observed in the I₂–V₆ curves of Figure 2d, indicating that the peak shifts did not originate from the n-doping effect. However, for the case of MoS₂/PSG samples, a rising trend in off-current (2 × 10⁻¹² A/µm → 6 × 10⁻¹¹ A/µm → 2 × 10⁻⁸ A/µm at V_GS = −55 V) and a negative shift in threshold voltage (−25 V → −40 V → −42 V) were confirmed as the annealing temperature increased from 300 °C to 500 °C. Additional electrons are thought to be supplied to the MoS₂ after annealing above 400 °C because the n-doping phenomenon associated with the formation of dipoles eventually influences the tunneling of electron carriers from the source metal to MoS₂. The MoS₂ energy band is down-shifted due to n-doping, which increases the electric field at the source–MoS₂ junction, thereby enhancing the tunneling of electrons and causing a negative V_th shift. The increase in off-current can be explained by the interfacial charge layer caused by the dipoles, which consists of hole carriers. Although the injection of hole carriers from drain to MoS₂ is not significant even under negative V_GS, this conductive interfacial hole layer is expected to induce the transport of hole carriers and a subsequent increase in off-currents. This n-doping phenomenon is also present in the I₂–V₀ characteristic curves (Supporting Information Figure S1) obtained for the nonannealed (NA) and the 500 °C annealed MoS₂/PSG samples. For the 500 °C annealed MoS₂/PSG device, the drain current (I₀) did not saturate as drain voltage (V_DG) increased, because a higher n-type carrier concentration is formed in the nonaccumulated region (between the drain electrode edge and the channel edge) after the pinch-off regime (V_DG > V_GS – V_th). The 2D sheet doping concentration (n₂₋₀) extracted from n₂₋₀ = I₀DV_GS/W is also consistent with the rising trend in off-current as a function of second-step annealing temperature, showing a significant increase from 3.6 × 10¹⁰ cm⁻² to 4.5 × 10¹¹ cm⁻² (Supporting Information Figure S2a). In the doping concentration equation, L and W refer to the length and width of the MoS₂ channel, respectively, q is the electron charge, μ is the field-effect mobility at V_GS = 0 V, I₀ is the drain current at V_GS = 0 V, and V_DG is the drain–source voltage. The obtained n₂₋₀ values are much lower than the concentrations (1.0 × 10¹¹ and 7.2 × 10¹² cm⁻²) achieved by the potassium²₀ and APTMS²³ doping processes, which were performed on three- and one-layer MoS₂, respectively. In addition, on-currents in MoS₂/PSG devices were dramatically changed as a function of annealing temperature, unlike MoS₂/SiO₂ samples, as shown in Figure 2e. The on-current was first reduced when the annealing temperature was increased up to 400 °C, but was increased again after going through 500 °C annealing. Compared to the control and 300 °C annealed samples, more P₂O₅ molecules were expected to gather at the surface region of the PSG layer and cause a slightly stronger reaction with MoS₂. The negative poles of O atoms in P₂O₅ molecules influence the MoS₂ channel region and consequently seem to cause more severe interfacial carrier scattering, eventually decreasing on-current level and field-effect mobility in the n-channel MoS₂/PSG transistor. According to the maximum field-effect mobility extracted at V_DG = 5 V in Supporting Information Figure S2b, the initial value (10.5 cm² V⁻¹ s⁻¹) of the control device was severely decreased down to 0.01 cm² V⁻¹ s⁻¹ when the second-step annealing temperature increased to 400 °C. However, on-current was recovered to a similar level to the control sample after 500 °C annealing, and we also confirmed that the mobility was increased up to 3.9 cm² V⁻¹ s⁻¹ in Figure S2b. It is thought that MoS₂ reacts more strongly with P₂O₅ molecules in PSG at this temperature and the large amount of electrons provided to MoS₂ consequently increase the on-current. As shown in Figure 2f, we also note that the carrier concentrations (3.6 × 10¹⁰ cm⁻² for NA–NA and 4.5 × 10¹¹ cm⁻² for NA–500 °C) obtained from the formula were slightly overestimated when compared to those (9.8 × 10⁹ cm⁻² for NA–NA and 2.1 × 10¹⁰ cm⁻² for NA–500 °C) obtained from Hall-effect measurement.

Two-Step n-Doping Process through Thermal Activation. To adjust the amount of P₂O₅ molecules in the surface region through out-diffusion, additional annealing steps (first annealing step) between 700 and 900 °C were performed on the PSG films in a N₂ ambient, as shown in Figure 3a. Comparing the XPS spectra for O 1s peaks between the as-deposited PSG film and the PSG films mentioned above (Figure 3b), the intensity of the P₂O₅ signal (at 533.4 eV) increased after annealing at higher temperatures. In addition, the atomic percentage of the P 2p XPS peak (at 134.58 eV) gradually increased as a function of annealing temperature (0.7% at NA, 0.77% at 700 °C, 1.74% at 800 °C, and 2.02% at 900 °C in Supporting Information Figure 3a). These indirectly indicate a higher surface concentration of P atoms and, consequently, a larger number of P₂O₅ molecules after higher temperature first-step annealing. Since it was confirmed that 500 °C annealing is the minimum requirement to activate the surface doping phenomenon, all second-step annealing after MoS₂ exfoliation was done at 500 °C. Figure 3c shows the E₁₋₂ and A₁₋₉ peak shifts in MoS₂ after the first and second annealing steps, which were extracted from
of P atoms in the interfacial region, inducing extensive carrier scattering. On the basis of AFM analysis performed on the PSG samples (Supporting Information Figure S3c), the RMS surface roughness was reduced as the process temperature rose, owing to the high reflowing property of the PSG film. Through this, it can be predicted that interfacial scattering was mainly dominated by the Columbic effect due to P atoms at the interface, not by physical scattering due to the surface roughness of the PSG. The n-doping levels that were achieved using a one- or two-step doping process were confirmed once again with XPS analysis in Supporting Information Figure S4. These upshifts observed in the 900–500 °C annealed sample (compared to NA–NA) were ∼0.2 eV (Mo 3d5/2), ∼0.3 eV (Mo 3d3/2), ∼0.2 eV (S 2p1/2), and ∼0.1 eV (S 2p3/2), directly indicating successful n-doping on MoS2 because the Fermi level shifted toward the conduction band edge because n-doping results in a lower binding energy. Although this shift is coincident with previously reported XPS data on potassium-doped MoS2, the degree of shift obtained by this work is smaller than that in the previous report (∼0.7 eV in the Mo 3d peak and ∼0.6 eV in the S 2p peak), which was degenerately doped by potassium.20 This also indicates that the n-doping levels of our one- or two-step thermal process on PSG are in the nondegenerate regime. In addition, the achieved nondegenerate n-doping phenomenon was stable even after exposure in air for 4 days, based on the $I_{DSS} - V_{GS}$ characteristic of the 900–500 °C annealed device sample (Supporting Information Figure S5). As seen in the control sample (NA–NA), a small reduction in drain current also occurred in the doped device (900–500 °C).

As shown in Figure 4a, another PSG film with a lower P weight percentage (2 wt %) than the previous film (5 wt %) was used to adjust the concentration of P atoms on the surface of the PSG film and eventually the n-doping level. In this doping control experiment, first- and second-step annealing process temperatures were fixed at 900 and 500 °C, respectively, to clearly observe differences in the level of n-doping. According to XPS analysis performed on 5 and 2 wt % samples in Figure 4b and Supporting Information Figure S6a, where the intensity of $P_{2O_{5}}$ and P in the 2 wt % sample was lower than that in 5 wt %, a slightly lower surface concentration of P atoms (thereby, $P_{2O_{5}}$ molecules) in the 2 wt % sample was confirmed after first-step annealing at 900 °C. As a result, after performing second-step annealing at 500 °C to activate the n-doping phenomenon, smaller peak shifts ($\Delta E_{2g} = -2.96 \text{ cm}^{-1}$ and $\Delta A_{1g} = -1.72 \text{ cm}^{-1}$) were observed in the 2 wt % sample than seen in the 5 wt % sample ($\Delta E_{2g} = -3.7 \text{ cm}^{-1}$ and $\Delta A_{1g} = -2.46 \text{ cm}^{-1}$) in Figure 4c. Since the peak shifts in the 2 wt % sample were slightly larger than those ($\Delta E_{2g} = -2.47 \text{ cm}^{-1}$ and $\Delta A_{1g} = -1.23 \text{ cm}^{-1}$) of the 500 °C annealed MoS2/SiO2 sample, MoS2 on...
2 wt % PSG film is expected to be successfully n-doped at a much lower doping level. Back-gated MoS2 transistors fabricated on the 5 and 2 wt % PSG films also demonstrate a significant difference in off-currents at $V_{GS} = -50$ V ($\sim 1.2 \times 10^{-7}$ A/μm in 5 wt % and $\sim 4.5 \times 10^{-10}$ A/μm in 2 wt %) in Figure 4d, which provide evidence of the lower n-doping level of MoS2 on 2 wt % PSG film. Although a decreasing trend was previously observed in the on-current due to the interfacial scattering effect in the high doping level regime (Figure 2), in this study, higher on-current was obtained in the 5 wt % sample with a higher surface concentration of P$_2$O$_5$. The dramatically increased number of electrons transferred from source metal to MoS2 as the P$_2$O$_5$ concentration of PSG rose from 2 to 5 wt % has an ascendency over the scattering effect.

Three-Step n-Doping Process via Thermal and Optical Activation. Additional laser exposure was performed on the 900–500 °C sample to enhance the activation of the n-doping phenomenon. Here, we also note that the second-step thermal anneal above 500 °C cannot be used to achieve higher n-doping concentration because it decomposes MoS2 flakes even in H$_2$ ambient. Figure 5a shows a schematic diagram briefly explaining the optical n-doping process. When considering the energy band gap ($\sim 1.2$ eV) of thick MoS2 flakes, higher photon energy incident lasers are predicted to cause extra energy loss ($h\nu - E_g$) to reach thermal equilibrium, consequently providing heat energy to the MoS2/PSG interface and enhancing n-doping activation. Because MoS2 exhibits different light absorption properties as the wavelength varies, three laser sources with wavelengths of 520, 655, and 785 nm were used in this experiment. Figure 5b shows the $I_D$–$V_G$ characteristics of back-gated MoS2 transistors that were exposed to the 655 nm wavelength laser with power varying from 0.5 to 1000 μW. Although no change in the $I_D$–$V_G$ curves was observed below 1 μW, the current level was increased about 70-fold when the power rose from 5 μW to 50 μW, indicating that the additional n-doping effect occurred above 5 μW for the 655 nm laser. In particular, the n-doping concentration increased from $1.0 \times 10^{12}$ cm$^{-2}$ (900–500 °C sample) to $8.3 \times 10^{12}$ cm$^{-2}$ after exposure to the 10 μW laser, and the doped MoS2 eventually exhibited metallic properties at 50 μW. This means that the n-doping level of MoS2 can be successfully controlled in the degenerate doping regime by adjusting the laser power. We then plotted the off-current values (at $V_{GS} = -65$ V) extracted from the $I_D$–$V_G$ curves as a function of the laser power in Figure 5c after exposing the transistors to lasers at three different wavelengths ($\lambda = 520, 655,$ and 785 nm).
dark current level when the laser was turned off in devices on SiO$_2$, the current of the device on PSG was not altered before or after laser illumination.

**Three-Step Thermal and Optical Doping on Trilayer and Bulk MoS$_2$**

The thermal and optical doping process was performed again on trilayer MoS$_2$ films to determine whether a thickness effect influences n-doping. As shown in Figure 6a, the thickness of MoS$_2$ flakes was reduced down to ~2.3 nm (trilayer) from ~30 nm (bulk). $\Delta E_{2g}^T$ and $\Delta A_{1g}^T$ values extracted from Raman peaks before/after the doping process are plotted and compared with those of bulk MoS$_2$ in Figure 6b. The $\Delta E_{2g}^T$ and $\Delta A_{1g}^T$ values of trilayer MoS$_2$ respectively decreased to $-5.1$ cm$^{-1}$ and $-4.2$ cm$^{-1}$ after first-step annealing (at 900 °C) and laser treatment ($\lambda = 655$ nm) and $P = 1000 \mu W$; trilayer MoS$_2$ showed similar behavior to bulk MoS$_2$ (gray dotted lines). In addition, the MoS$_2$ transistors fabricated under four different doping conditions (NA—NA, NA—500 °C, NA—900 °C, 900–500 °C) demonstrated significantly different off-currents ($\sim 1.67 \times 10^{-12}$, $\sim 1.25 \times 10^{-8}$, $\sim 5.75 \times 10^{-7}$, and $\sim 4.41 \times 10^{-6}$ A/μm, respectively, at $V_{GS} = -55$ V) in Figure 6c and d. However, the increasing trend in the off-current (black solid line) is similar to that observed in the bulk MoS$_2$ transistors (gray dotted line). In particular, the $n_{2D}$ values of NA—500 °C, 900—500 °C, and 900–500 °C + laser samples (trilayer MoS$_2$ transistors) are $6.1 \times 10^{11}$, $1.1 \times 10^{12}$, and $1.0 \times 10^{13}$ cm$^{-2}$, which are comparable to those obtained for bulk MoS$_2$ transistors ($4.5 \times 10^{11}$, $1.0 \times 10^{12}$, and $1.2 \times 10^{13}$ cm$^{-2}$). These results indicate that the doping range is very broad from nondegenerate to degenerate and also the thickness of MoS$_2$ does not have an influence on the n-doping phenomenon.

In previous cases of degenerate n-doping of MoS$_2$ via potassium$^{20}$, and APTMS$^{23}$-doping processes, the n-doping concentrations were $1.0 \times 10^{13}$ and $7.2 \times 10^{12}$ cm$^{-2}$, which were very similar to that of our 900–500 °C + laser sample. The doping concentration of nondegenerate n-doped MoS$_2$ by cesium carbonate (Cs$_2$CO$_3$) was between $1 \times 10^{11}$ and $3.5 \times 10^{11}$ cm$^{-2}$, which is also close to that of the NA—500 °C sample.

**CONCLUSIONS**

In summary, a widely controllable n-doping process for MoS$_2$ on a PSG insulating substrate was demonstrated by adjusting the thermal and optical process conditions ($T = 300–500$ °C for the thermal process and $P = 0.5–1000 \mu W$ for the optical process) or the concentration of P atoms in the PSG (5 and 2 wt %). Via the self-controlled n-doping method, the doping range is very broad from degenerate to nondegenerate and also the doping level is highly uniform. In addition, the doping range is very broad from degenerate to nondegenerate and also the doping level is highly uniform. Therefore, the n-doping effect can be properly engineered. The doping range is broadest among the results reported up to now, and also, this method is applicable to other 2D semiconductors (e.g., MoSe$_2$, MoSe$_2$, WS$_2$, WSe$_2$, graphene). This was achieved by (1) a three-step process consisting of (i) dopant out-diffusion between 700 and 900 °C, (ii) thermal activation at 500 °C, and (iii) optical activation above $5 \mu W$ steps and (2) weight percentage adjustment of P atoms (thereby, $P_2O_5$ molecules) in PSG. This controllable n-doping effect was also demonstrated on exfoliated trilayer and bulk MoS$_2$, where it was confirmed that the thickness of MoS$_2$ does not influence the n-doping phenomenon. We expect our wide-range controllable n-doping method to be a starting point for the successful integration of future layered semiconductor devices.

**EXPERIMENTAL METHODS**

**Preparation of PSG Films and Surface Doping Control.** First, 300 nm thick PSG layers with a 5 or 2 wt % P doping concentration were deposited on a heavily doped p-type Si substrate (resistivity <0.005 Ω·m) at 480 °C in a low-pressure chemical vapor deposition (LPCVD) system. In order to control the amount of P atoms in the surface region, we performed a first-step annealing process in N$_2$ ambient from 700 to 900 °C.
Thermal and Optical Doping of MoS2 on PSG Films. After transferring MoS2 films on the annealed and nonannealed PSG samples using adhesive tape, an acetone wash was done on the samples for 1 h to remove tape residue. Then, a second-step thermal activation process was carried out in N2/H2 ambient from 300 to 500 °C, or optical activation (refer to Supporting Information Figure S7) was performed with laser sources at wavelengths of 520, 655, and 785 nm, in order to cause a reaction between the P atoms in the surface region of the PSG and MoS2, eventually doping MoS2. The doping level of MoS2 was controlled by adjusting the second-step thermal/optical process conditions as well as regulating the weight percentage of P atoms during the in situ doped PSG growth step.

Characterization of Doped MoS2 Films. The prepared MoS2/PSG/Si samples were investigated and compared with control samples (MoS2/SiO2/Si) by PL/Raman spectroscopy (Alpha300 M+ Witec). XPS (ESCA200, VG Microtech Inc.), and AFM (SPA-300, Seiko Instrument) measurements. Raman spectroscopy with an excitation wavelength of 532 nm was used; its laser beam size was 0.7–0.9 μm, and the instrumental spectral resolution was below 0.9 cm⁻¹. An integration time of 5 s and spectrometry at 1800 grooves/mm were employed for the test. A Mg Kα twin-anode source and 0° of X-ray incident angle were used for XPS measurement.

Fabrication and Electrical Measurements of Undoped and Doped MoS2 Devices. For the fabrication of back-gated MoS2 devices (transistors and photodetectors), source/drain electrode regions were patterned on the MoS2/PSG/Si and MoS2/SiO2/Si samples using optical lithography to achieve a 1 μm (or 5 μm) channel length and 1 μm (or 5 μm) channel width, followed by Ti (10 nm) and Au (50 nm) deposition via e-beam evaporator. For the fabrication of trilayer MoS2 transistors, an e-beam lithography process was used instead of optical lithography. The fabricated devices were analyzed through electrical measurements (Ids–Vds and Id–Vgs) by an HP 4155B semiconductor parameter analyzer, and we subsequently calculated the carrier concentration and field-effect mobility at the fabricated MoS2/SiO2/Si samples (NA, NA, 900–3700). Air-stability analysis of undoped and doped MoS2 devices. XPS and Raman spectrum analysis of PSG films with different P concentrations. Experimental setup for the laser annealing process and Id–Vgs characteristics of MoS2 transistors on SiO2 and PSG for a number of cycles of laser illumination. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES
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