Thermally Strained Band Gap Engineering of Transition-Metal Dichalcogenide Bilayers with Enhanced Light–Matter Interaction toward Excellent Photodetectors

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Supporting Information

ABSTRACT: Integration of strain engineering of two-dimensional (2D) materials in order to enhance device performance is still a challenge. Here, we successfully demonstrated the thermally strained band gap engineering of transition-metal dichalcogenide bilayers by different thermal expansion coefficients between 2D materials and patterned sapphire structures, where MoS2 bilayers were chosen as the demonstrated materials. In particular, a blue shift in the band gap of the MoS2 bilayers can be tunable, displaying an extraordinary capability to drive electrons toward the electrode under the smaller driven bias, and the results were confirmed by simulation. A model to explain the thermal strain in the MoS2 bilayers during the synthesis was proposed, which enables us to precisely predict the band gap-shifted behaviors on patterned sapphire structures with different angles. Furthermore, photodetectors with enhancement of 286% and 897% based on the strained MoS2 on cone- and pyramid-patterned sapphire substrates were demonstrated, respectively.

KEYWORDS: chemical vapor deposition, transition-metal dichalcogenide, molybdenum disulfide, thermal strain, patterned sapphire substrate, photodetector

Continuously tuning band gap in optoelectronic materials is highly desirable for enhancing the performance of electro-optical applications, such as light-emitting diodes, solar cells, and photodetectors. By combining with two single two-dimensional (2D) materials into a junction, a tunable band gap behavior with a great advantage of electro-optical devices can be achieved. For example, the ultrafast charge migration within interfaces between the stacking of PN junctions by two 2D semiconductor layers with different band gaps provides extraordinary abilities of optoelectronics and light harvesting in devices. Alloys mixture phases of two transition-metal dichalcogenides (TMDCs) such as MoS2 and MoSe2 result in a wide range of band gap modulation, while this manner is subject to significant challenges of uniformity and industrial production. Although the MoS2 and MoSe2 powders can accomplish growth of larger...
scale MoS$_{2}$($1-x$)Se$_2x$ alloyed layers on substrates, a high barrier of the transferred process into other substrates for the practical applications in large scale is still a major drawback. In addition to the chemical synthesis of TMDCs, a strain-induced process is able to precisely tune not only the electronic band structure but also the electronic transport properties of TMDCs from semiconductor to metal to further achieve the TMDC-based electronic devices without material mismatch because TMDCs have an outstanding capacity of deformation. For example, the experimental results indicate that the MoS$_2$ would not be fractured until a magnitude of strain over 10%, and the breaking strength of MoS$_2$ is indeed better than general semiconducted materials. The extremely high limitation of strain suference creates a possibility for developing a device in a single material.

Several straightforward strain-induced methods have been recently proposed, including directly stretching the flexible substrate with a few layers of 2D materials, utilization of thermal expansion difference by the substrate, and transfer of 2D layered materials on a nonflat substrate. Although these ideas are effective methods to trigger strain into 2D materials, most of them still rely on the transfer process, limiting practical applications. Bending of 2D materials on flexible substrates can directly introduce the uniaxial strain in the 2D materials, while the strain cannot be maintained for further device preparation. Wrinkling can be an alternative to achieve the strained 2D materials, while the nonhomogeneous and uncontrollable strength of the strain will be a key issue. Nonflat substrates provide the localized strains on the transferred 2D materials, while unavoidable issues associated with the transfer process, such as the wrinkles, crumples, and air bubbles, which deteriorate back-end processes and device performance, have to be considered. Although the soaking of MoS$_2$ in an ethylene glycol solution to remove air bubbles between the interface of the nonflat substrate and 2D materials has been proposed and developed, wrinkles and crumples still existed due to the mismatch issue between 2D materials and the nonflat substrate. Therefore, it is much better to introduce the strain during the in situ epitaxial growth of 2D materials on patterned substrates directly. By using differently patterned substrates, the energy band gap of TMDCs can be effectively changed, which is attributed to the substrate-dependent thermal expansion coefficient (TEC) because of the ultrasensitive nature to thermal strain due to the high surface-to-volume ratio characteristic. In addition, it is well-known that bilayers of TMDC materials have been theoretically predicted where the tensile strain can drastically reduce the band gap toward the metallic type, while the compressive strain can increase the energy band gap.

In this regard, we directly demonstrate the band gap tuning utilizing the thermal strain concept on TMDC bilayers epitaxially grown on the different periodic sapphire structures, including cone and pyramid microstructures. Here, MoS$_2$ bilayers were chosen as a material model for the demonstration. Compared with the MoS$_2$ monolayer, we chose the growth of MoS$_2$ bilayers because of distinct physical properties and potential application for the photodetector, including broad absorption in visible spectra, tunable absorption spectra by different stacking orientations, and a lower work function. Besides, from first-principles calculations, the MoS$_2$ bilayers have a higher potential to realize the complete electronic transport property modulation under the same applied strain. The MoS$_2$ bilayers are perfectly formed on patterned substrates, achieving a conformal coating by sulfurizing molybdenum trioxide (MoO$_3$) in a two-step process. Raman and photoluminescence (PL) spectra and mapping images were used to investigate the strain evolution in the MoS$_2$ bilayers. A
specific equation made of the simple thermal expansion model on each patterned structure was built for precisely predicting the different thermal strain in the MoS2 bilayers, leading to the band gap shifts of MoS2 bilayers. Furthermore, based on the simulation of the electron migration behavior on the strained MoS2 bilayers, large numbers of electrons migrated from the conical-shaped pattern to the bottom side occur because of an energy funnel effect, which is capable of collecting a mass of electrons under a low drive voltage for photodetection application. The photodetector results based on the patterned MoS2 bilayers in contrast to the smooth MoS2 bilayers show a higher output photocurrent and photosensitivity. Tunable band gap engineering in TMDC bilayers through a controllable

Figure 2. Raman and PL spectra of MoS2 bilayers on different sapphire substrates. The Raman mapping images of the MoS2-synthesized c-plane sapphire substrate are shown in (a) and (b), which represent in-plane E'\textsubscript{2g} and out-of-plane A\textsubscript{1g} modes, respectively. (c) The PL mapping image of MoS2 bilayers grown on the c-plane sapphire substrate. All of above results exhibit the uniform MoS2 bilayers grown on the flat sapphire substrate. (d) In-plane E'\textsubscript{2g} mode and (e) out-of-plane A\textsubscript{1g} mode display the Raman mapping images of MoS2 bilayers grown on the cone-patterned sapphire substrate, which has a circle-like distribution. (f) The PL mapping image of MoS2 bilayers grown on the cone-patterned sapphire substrate. (g) In-plane E'\textsubscript{2g} mode and (h) out-of-plane A\textsubscript{1g} mode are the Raman mapping images of MoS2 bilayers grown on the pyramid-patterned sapphire substrate. (i) The PL mapping image of MoS2 bilayers grown on the pyramid-patterned sapphire substrate. (j, k) Detailed comparison of Raman spectra, which represent cone- and pyramid-patterned sapphire substrates, respectively. (l) The PL spectra of each MoS2 bilayers grown on different patterned-sapphire substrates.
thermal strain on patterned structures opens the next generation in the electro-optical application.

RESULTS AND DISCUSSION

Although chemical vapor deposition (CVD) and vapor–solid process have been proven to be able to synthesize wafer-scale TMDs on growing substrates, the variation of TMDs in morphologies at different locations of the substrate is still a specific challenge because of spatially-dependent growth parameters. Lin et al. have demonstrated the two-step method to grow continuous and smooth, a few, MoS2 layers on a c-plane sapphire substrate on a larger scale. Note that thermally evaporated molybdenum trioxide (MoO3) was reduced to MoO2 in hydrogen environment at 500 °C, followed by sulfurization of MoO2 into MoS2 at 1000 °C. Therefore, to achieve a uniform growth of MoS2 bilayers without the surface roughness effect in a large area, we, here, apply the two-step process to proceed with our study. Figure 1a–c shows schematics of the growth of MoS2 bilayers on the periodically patterned sapphire substrates via two-step sulfurization processes. MoO3 was first deposited as a starting material on the top of the periodically patterned sapphire substrate (Figure 1a). Subsequently, sulfur powders were placed upstream of the gas source in a heating zone (Figure 1b), resulting in the formation of MoS2 bilayers on the surfaces of patterned substrates (Figure 1c). During the sulfurization process, the furnace tube will keep a pressure of approximately ~550 Torr with a 25 vol % H2/75 vol % N2 mixed gas of 50 sccm. Figure 1d illustrates a low-magnification transmission electron microscope (TEM) image of a cone-shaped patterned sapphire substrate with MoS2 bilayers. Figure 1e–g shows high-resolution TEM (HRTEM) images of three locations in Figure 1d from the top to bottom areas of the cone-patterned structure. Clearly, the growth MoS2 bilayers with the uniform coverage along the different surfaces of the cone-patterned sapphire substrate, including the nonflat areas, can be confirmed. Besides, the number of MoS2 layers can be precisely achieved by controlling the accurately 1 nm-thick predoped MoO3 to achieve MoS2 monolayer through the two-step sulfurization processes on the c-plane sapphire substrate. However, once the thickness of the MoO3 is smaller than 1 nm, the island-like and nonuniform MoO3 film was formed on the cone-patterned structure, resulting in the broken MoS2 layers on the surface of the cone-patterned structure after the sulfurization process (Supplementary Figure S1).

According to previous strain engineering calculation on MoS2, the growth of MoS2 bilayers is preferred because of its technological importance, which has a variety of band gap modification from semiconducting toward metallic behaviors compared with the MoS2 monolayer under the same strain condition. With an increase in numbers of MoS2 layers, the transition from direct to indirect band gap happens, leading to the shift of the band gap being less sensitive to strain. Therefore, the thickness of MoO3 is set to achieve approximately 2 nm thickness, corresponding to MoS2 bilayers after the two-step sulfurization process. To shed light on the band gap engineering induced by the strain from the patterned sapphire structures in the MoS2 bilayers, two kinds of periodic patterned structure, including cone and pyramid patterns were fabricated through a chemical etching process (Figures S2 and S3) on the c-plane sapphire substrates, as shown in Figure 1h,i with angles of cone and pyramid corresponding to 0.27π and 0.34π (more SEM images in Figures S4 and S5). A particularity of the sapphire substrate is that the thermal expansion coefficient of the c-plane is smaller than that of the plane perpendicular to the c-axis. To simplify the analysis, we refer to the different angles of each pattern related to the flat surface of the sapphire substrate.

Raman spectra were used to understand the strain evolution on the band gap engineering of MoS2 bilayers on cone- and pyramid-patterned sapphire substrates. In addition, Raman mapping images are used to shed light on the uniformity of the strain field on MoS2 bilayers in a large area. The corresponding Raman and PL mapping images taken from two kinds of regions, namely top and flat regions of the cone- and pyramid-patterned sapphire substrates, are shown in Figure 2a–i, respectively. Note that Raman spectra and mapping images of the MoS2 bilayers on the flat sapphire substrate were also measured as a standard reference (Figure 2a–c). It is obvious that the in-plane Raman mode (E1g) allocated at 384.6 cm⁻¹ and the out-of-plane Raman mode (A1g) allocated at 406.5 cm⁻¹ were measured on the flat sapphire substrate, indicating of characteristic peaks of MoS2 bilayers. In addition, the center peak of PL spectra was located at 676.26 nm. Uniform contrast in Raman mapping images taken from two modes of A1g shown in Figure 2e provides a distinct evidence of the uniform growth of the MoS2 bilayers on the cone-patterned sapphire substrate. Blue shifts from 406.5 to 407.2 cm⁻¹ in Raman spectra at the A1g mode on the core-patterned sapphire substrates can be distinctly obtained. In addition, blue shift behaviors in the A1g and E1g modes from 406.3 to 407.0 cm⁻¹ and from 384.2 to 385.2 cm⁻¹ on the pyramid-patterned sapphire substrates were found, respectively, as shown in Figure 2g,h, respectively. Raman mapping images confirm the uniform distribution of the blue shift behaviors in the top region of the MoS2 bilayers grown on both cones- and pyramid-patterned sapphire substrates, respectively.

According to previous observation in addition to the thickness effect on TMDs, the Raman shift can be corroborated to the strain induced into the TMDs due to different changes in the lattice constant. Normally, the tensile strain in TMDs leads to a red-shifted tendency in Raman spectra, while the compressive strain in TMDs leads to a blue-shifted tendency in the Raman spectrum. As a result, the Raman blue-shift found in MoS2 bilayers grown on both cone- and pyramid-patterned sapphire substrates can be attributed to a larger compressive strain compared to that grown on the flat region due to the different thermal expansion coefficients along the c-axis. Besides, theoretical studies are also consistent with our assumption. Lu et al. have predicted that the strain induced a band gap-shifted behavior of MoS2 mono- and bilayers through the first-principle calculation. Their simulation results also confirm that tensile and compressive strain on the MoS2 bilayers would lead to a band gap red- and blue-shift, respectively. Band gap changes from the compressive strain in the MoS2 bilayers from both cone- and pyramid-patterned sapphire substrates can be confirmed by PL mapping images, as shown in Figure 2f,i. PL mapping images again reveal the uniform growth of MoS2 bilayers on the flat sapphire substrate. Different contrast due to the blue shift of the band gap on top regions with respect to the flat region of the patterned sapphire substrate was found, confirming the blue shift of the band gap caused by the compressive strain on the top regions of both patterned sapphire substrates. The blue shifts of 10.0 and 13.5 nm for the MoS2...
bilayers grown on the cone- and pyramid-patterned sapphire substrates can be found in PL spectra as shown in Figure 2l. A simple mathematical model based on a linear thermal expansion theory can be used to further explain the band gap-shifted behavior induced by the thermal compressive strain on MoS₂ bilayers grown on the patterned sapphire substrates as shown in Figure 3a. It can be expected that the substrate temperature was basically maintained at 1000 °C during the sulfurization process. Therefore, the temperature of 1000 °C is assumed to be the natural and released state of the MoS₂ bilayers on the sapphire substrates with free of strain. To build a simple mathematical model, a triangle profile of a cone was constructed as shown in Figure 3a, where we defined \( x \) and \( \theta \) as a length of a hypotenuse and an inclination angle at room temperature (25 °C) and the length of the hypotenuse at a synthesized temperature (1000 °C in this case). The lengths of the opposite and adjacent sides increase with the increased temperature. The volume of the cone-patterned sapphire substrate shrinks to the original volume at room temperature during the cooling process. Based on the Pythagorean theorem, the length of hypotenuse at room temperature can be expressed by

\[
x = y\sqrt{\sin^2 \theta (1 + A)^2 + \cos^2 \theta (1 + B)^2}
\]  
(1)

where \( A \) and \( B \) are the variation of opposite and adjacent sides, respectively (Supporting Information Note 2). Then, the strain along the hypotenuse side in the MoS₂ bilayers can be exactly predicted by

\[
\varepsilon(\theta) = \sqrt{\sin^2 \theta (1 + A)^2 + \cos^2 \theta (1 + B)^2} - 1
\]  
(2)

where \( \varepsilon(\theta) \) is the relative thermal strain and the amount of thermal strain is related to the inclination angle of a patterned substrate (Supporting Information Note 2). The thermal strain is just decided by a specific angle between the flat and hypotenuse sides of the pattern surface.

According to previous observations, the thermal strain on TMDCs would be decided by the value of the thermal expansion coefficient (TEC). After the sulfurization process, the larger TEC of the sapphire substrate will lead to the thermal shrinkage during the cooling process, which can introduce the compressive strain into the MoS₂ bilayers.35–37,41 As a result, the thermal strain of MoS₂/sapphire can be plotted as a dash line by inputting the physical properties of the sapphire substrate (Figure S7). Interestingly, if we normalize the angle of the flat sapphire substrate at a zero angle, experimental results of the band gap shift in MoS₂ bilayers grown on different patterned sapphire substrates can completely match up with the theoretical calculation of our current case, as shown in Figure 3b. This result further confirms our assumption of the strain induced by the thermal expansion during the sulfurization process and can be applied to any TMDCs on any patterned substrates. The resolution of our confocal Raman mapping system is approximately 1 μm (laser beam size). However, the diameter of the flat area on the top pyramid is approximately 630 nm, a half of laser beam size. Therefore, even the pyramid structure has a flat area on the top, and the system is still difficult to distinguish the signal.

By taking advantage of this particular band gap shift in the MoS₂ bilayers caused by either tensile or compressive strain at the patterned sapphire substrates, it can provide an important aspect to enhance electron transportation behaviors to boost the device performance in electro-optical applications. To understand the influence of the electron migration behaviors by the localized strain-induced band gap, two different band gap...
regions on the same 2D material are simulated and proposed. As our description above, the thermal strain might introduce tensile and compressive strain into 2D materials, which depend on TEC values. Therefore, two different systems, namely types A and B, were taken into account where the band gap at the top region is smaller or larger than that of the surrounding matrix (flat region). Carrier distributions of 2D a cone with MoS$_2$ bilayers were calculated by using the finite element method. At the beginning, carriers are generated during the irradiation of light, as shown in Figure 3c. By increasing the driven bias to 0.1 V (high potential energy (+) and low potential energy (−) display the electric potential energy), the simulation results indicate that the type A with the smaller band gap on the cone will lead to a “quantum well” region to confine electrons as shown in Figure 3d, resulting in most of the electrons confined inside the cone regions. Therefore, this characteristic is much suitable for light-emitting device application, such as light-emitting diodes and lasers. Additionally, the type B with the larger band gap on the cone forms a “barrier height” region where electrons have a tendency migrating toward the flat area from the cone region, since a funneling effect dominates the electron transport as shown in Figure 3e. This naturally occurring characteristic is undoubtedly able to drive electrons to the metal electrode easier, which is beneficial for absorbing photon devices, such as a photodetector, phototransistor, and solar cells. The natural tendency of the electron flow caused by the strain engineering can largely reduce the photoelectrically driven bias with low power consumption. As a result, it is no doubt that the particular band gap opening in the MoS$_2$ bilayers under the compressive strain caused by patterned sapphire substrates can be suitable for applications of light absorption in optoelectronics. The microstructures from the patterned substrates also enhance light interaction with the MoS$_2$.

According to simulation results, the growth of MoS$_2$ bilayers on patterned sapphire substrates is suitable for applications of light absorption in optoelectronics, and the MoS$_2$ bilayers-based with periodically patterned sapphire substrates, including
cone- and pyramid-patterned structures were fabricated as the photodetector and measured as shown in Figure 4. Three kinds of patterned sapphire substrates were used as the channel materials for photodetector application where finger-type electrodes were prepared using the metal mask (Figure 4a–c). Besides, the corresponding optical images are shown in Figure S8a–c, respectively. The absorption spectra of each patterned structure are shown in Figure 4d. The growth of MoS₂ bilayers on the periodically patterned structures has a larger absorption in contrast to the flat wafer due to the light-scattering effect, and both absorption spectra of patterned sapphire structures have blue shift behavior since the strain affects the band gap shift behavior, as the discussed above. Figure 4e shows the photocurrent of MoS₂ bilayers on the patterned sapphire substrates, respectively (Figure S8d–f). Clearly, the significantly larger photocurrent can be indeed found for the MoS₂ bilayers on the patterned sapphire substrate compared to those on the flat substrate, and the highest enhancement of the photocurrent can be achieved for the MoS₂ bilayers grown on a pyramid-patterned sapphire substrate with the enhancement of 897%. For photodetector measurements, the responsivity is the major index of performance. Larger responsivity indicates a larger electrical output signal (Supplementary Note 3). Therefore, the responsivity of MoS₂ bilayers grown on different sapphire substrates was calculated as plotted in Figure S9. The responsivity of the MoS₂ bilayers grown on the flat sapphire substrate can be calculated to be 2.3 (μA/W), while MoS₂ bilayers grown on the patterned sapphire substrate exhibits the enhanced responsivity. Especially, the highest responsivity of 24.3 (μA/W) can be achieved for MoS₂ bilayers grown on the pyramid-patterned sapphire substrate. To understand the electric field distribution of incident illumination source, the three-dimensional (3D) models have been built by the COMSOL software to investigate the photon (wave-length is 638 nm) propagation in different patterned sapphire substrates. Figure S10 presents the 3D electric field distribution, and the color represents the intensity of light. Additionally, we have taken the cross-section (x–z plane) profiles of single pattern to further investigate the electric field intensity distribution on different substrates (flat, cone and pyramid) as shown in Figure 4f–h. When the light illuminates the substrate, most of the photon pass through the flat sapphire substrate, resulting in the lowest absorption behavior, which is similar to the other experimental results of monolayer or bilayers 2D materials.43–45 However, the specific periodic pattern structure is capable of confining the photon on the certain region through resonance behaviors. As can be seen in Figure 4g,h, the cone can confine the photon inside the structure, while most of the photons surround the pyramid, on which the MoS₂ bilayers grow and the electrical power flows, where white arrows also display the resonance behaviors (Figure S9). The 3D current-migrating behavior also demonstrates both of the patterned substrates with the MoS₂ bilayers have an ability to drive photon-generated electrons toward the bottom, as shown in the bottom insets of Figure 4f–h. This is why the strongest light interaction between MoS₂ bilayers grown on the pyramid-patterned sapphire substrate exhibits the highest performance. We eventually compare area enhancement ratio with absorption and photocurrent enhancement ratios in Supporting Information Table 3 while assuming the flat sample as a baseline. Theoretically, the absorption and the photocurrent will be enhanced as the absorbed material (MoS₂ bilayer) area increases, and the amount of their enhancement ratio will follow the same ratio with respect to total area. However, the absorption enhancement ratio at 638 nm is different from the area enhancement ratio. We think that the structure array may influence the absorption ability, resulting in both patterned structures with the higher absorption. In addition, we also observe a larger photocurrent output on both patterned substrates, where the photocurrent enhancement ratio still does not match the absorption or area enhancement ratios. The amount of photocurrent is dominated by the localized strain, and the pyramid structure has a larger localized strain in our explanation and experiment. Therefore, it can be easier to collect the electron on the same driven bias.

CONCLUSION

In summary, we demonstrated an approach using the different thermal expansion properties of the patterned sapphire substrates to induce strain in 2D materials. An epitaxial growth of MoS₂ bilayers on the periodic sapphire substrates through a two-step sulfurization process method was chosen as the model for the demonstration of band gap engineering by the thermal strain. After the sulfurization process, the band gap changes of MoS₂ bilayers were also measured by Raman and PL spectra and images. Interestingly, by using a simple mathematical model, how the thermal strain affects the band gap-shift behavior of the MoS₂ bilayers on different patterned sapphire substrates can be precisely predicted. From the electron migrating simulation, the strained MoS₂ bilayers on the patterned sapphire structure were indexed as the type B interface, which has an excellent capability to drive electrons toward the flat region, allowing the electrode to collect electrons easily and to save energy. The simulation results of the FEM simulation indicate that both periodic patterned substrates have the strongest resonant regions within each single structure while localizing on the different positions. For the pyramid-patterned substrate, the strongest resonant region appears on the surrounding pyramid region of MoS₂ bilayers. Compared with a flat substrate, the photocurrent enhancements of the cone- and pyramid-patterned substrates are 286% and 897%, respectively. We profoundly believe that this approach is of great importance for understanding strain effects induced by the substrate and how to control them in order to optimize the device performance as an important step to pursuing for the future development of TMDC technology.

METHODS

MoS₂ Synthesis from Two-Step Process. Molybdenum oxide (MoO₃) films as a precursor layer with a thickness of 2 nm were deposited on sapphire substrates by E-gun system with a deposition rate of 0.01 nm/s. The sulfur powder was placed upstream of the gas source, and MoO₃-deposited sapphire substrates were put inside the furnace tube of the heating zone. Then, the heating tape was wrapped outside the quartz tube and totally covered the region of sulfur powder. During the sulfurization process, the pressure of approximately 550 Torr with an H₂/N mixture gas of 50 sccm (ratio is 25% in H₂) was kept in the furnace tube. Heating up of the heating tape and furnace tube reached 180 °C at a rate of 5 °C/min and 1000 °C at a rate of 18 °C/min, respectively. After both targeted temperatures were achieved, the heating tape and furnace tube maintained temperatures of 180 and 1000 °C for 30 min. At the same time, MoO₃, hydrogen, and sulfur vapor would react with each other, and MoS₂ is eventually synthesized on the sapphire surface.

Raman and Photoluminescence Measurements. For Raman and PL mapping, we used a 532 nm laser with the beam spot size of ~1 μm in diameter in a confocal microscope spectrometer to focus the
A Patterned Sapphire Substrates. A finite element package (COMSOL) was used to build 3D cone- and pyramid-shaped unit cell structures with MoS₂ bilayers. Electric field distributions of 3D hexagonal unit cell structures with cone- and pyramid-shaped islands covered with a 2 nm MoS₂ layer were calculated by using the finite element method. The unit cell of flat sapphire with 2 nm MoS₂ layer was used as the reference case. The geometries of the cone- and pyramid-shaped islands including the top width, base width, and height are taken from corresponding SEM images (Figures S4 and S5). For simplifying calculations, the periodic boundary conditions are specified in three principal directions of the hexagonal unit cell. Top and bottom surfaces of those unit cells were set to be the wave excitation and detection ports, respectively. The light with a wavelength of 638 nm is normally incident on the patterned islands and MoS₂ layer. The refractive indices of sapphire and MoS₂ refer to refs 1 and 42, respectively. The absorption of the hexagonal unit cell was deduced from corresponding SEM images (Figures S4 and S5). For simplifying calculations, the periodic boundary conditions are specified in three principal directions of the hexagonal unit cell. To make the tunneling barrier height between the metal and MoS₂ in re
devices.

The research is supported by Ministry of Science and Technology through grant nos. 105-3113-E-007-003-CC2, 105-2119-M-009-009, 104-2628-M-007-004-MY3, 104-2221-E-007-048-MY3, and 105-2633-M-007-003 and the National Tsing Hua University through grant no. 105A0088J4. Y.L.C. greatly appreciates the use of the facility at CNMM. F.C.C. acknowledges support from the National Center for Theoretical Sciences and the Ministry of Science and Technology of Taiwan under grant no. MOST-104-2112-M-110-002-MY3 and is also grateful to the National Center for High-performance Computing for computer time and facilities.

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