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SYNTHESIS AND PROCESSINGOPTICAL MATERIALS AND
STRUCTURESMeasuring the Refractive Index of Highly Crystalline Monolayer MoS₂ with High ConfidenceHui Zhang^{1,2}, Yaoguang Ma¹, Yi Wan¹, Xin Rong¹, Ziang Xie¹, Wei Wang¹ & Lun Dai^{1,2}¹State Key Lab for Mesoscopic Physics and School of Physics, Peking University, Beijing 100871, China, ²Collaborative Innovation Center of Quantum Matter, Beijing 100871, China.Received
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Monolayer molybdenum disulphide (MoS₂) has attracted much attention, due to its attractive properties, such as two-dimensional properties, direct bandgap, valley-selective circular dichroism, and valley Hall effect. However, some of its fundamental physical parameters, *e.g.* refractive index, have not been studied in detail because of measurement difficulties. In this work, we have synthesized highly crystalline monolayer MoS₂ on SiO₂/Si substrates via chemical vapor deposition (CVD) method and devised a method to measure their optical contrast spectra. Using these contrast spectra, we extracted the complex refractive index spectrum of monolayer MoS₂ in the wavelength range of 400 nm to 750 nm. We have analyzed the pronounced difference between the obtained complex refractive index spectrum and that of bulk MoS₂. The method presented here is effective for two-dimensional materials of small size. Furthermore, we have calculated the color contour plots of the contrast as a function of both SiO₂ thickness and incident light wavelength for monolayer MoS₂ using the obtained refractive index spectrum. These plots are useful for both fundamental study and device application.

In recent years, the discovery of various kinds of two-dimensional (2D) materials^{1–4} has promoted low-dimensional physics research. Among these materials, monolayer MoS₂, a stable atomically thin structure with honeycomb lattice, has attracted much attention, because of its remarkable physical properties and novel applications, such as direct bandgap², strong spin-orbit coupling^{5,6}, valley-selective circular dichroism^{7–10}, valley Hall effect^{11,12}, nonlinear optical effect¹³, and two-dimensional heterostructures^{14–17}. Recent progress in the synthesis of highly crystalline monolayer MoS₂ with chemical vapor deposition (CVD) method^{18–20} has made it a promising candidate for novel electronic and optoelectronic devices. Its complex refractive index in visible range is important, because many of its novel properties are closely related to this wavelength range. Beal *et al.* measured the complex refractive index of bulk MoS₂²¹ in 1979. However, physical properties of a 2D material are usually very different from those of bulk material, especially for MoS₂, which has an indirect bandgap in bulk form and a direct bandgap in monolayer form². Recently several groups have measured the optical constants of large-area CVD grown thin films of MoS₂ or other transition metal dichalcogenides using spectroscopic ellipsometry technique^{22–24}. However, so far, it is still difficult to measure the refractive index of highly crystalline monolayer MoS₂ directly, because the highly crystalline monolayer MoS₂ flakes obtained by present methods (mechanical exfoliation, CVD *etc.*), are usually too small in size (~ tens of microns). In 2007, Blake *et al.* successfully visualized graphene under an optical microscope by utilizing the contrast of graphene on a SiO₂/Si substrate. Given the refractive index of graphene, the contrast can further be calculated based on the Fresnel law²⁵. In our work, by improving the spatial resolution of a reflectance spectrum system via spatial filtering, we managed to obtain the optical contrast spectra of highly crystalline monolayer MoS₂. Then by curve fitting the relations between the contrast and SiO₂ thickness based on the Fresnel law, we obtained the complex refractive index spectrum of monolayer MoS₂ in the wavelength range of 400 nm to 750 nm, together with the confidence interval, which reflects the accuracy of the obtained refractive index. We have analyzed the pronounced difference between the obtained complex refractive index spectrum and that of bulk MoS₂. Furthermore, we have calculated the color contour plots of the contrast as a function of both SiO₂ thickness and incident light wavelength for monolayer MoS₂ using the obtained refractive index spectrum. These plots are useful for both fundamental study and device application.

Figure 1 | Synthesis and characterization of monolayer MoS₂. (a) and (b) Optical images of typical MoS₂ on 280 nm SiO₂/Si substrates synthesized by CVD method. The growth durations are 10 min and 20 min, respectively. In (b), some monolayer MoS₂ islands overlapped with one another because of the longer growth time, as indicated with arrows. The scale bars correspond to 10 μ m. (c) AFM image of two neighbored MoS₂ triangular islands. The white curve shows the thickness along the red dashed line. The scale bar corresponds to 0.5 μ m. (d) Room-temperature PL spectra from monolayer MoS₂ (red) and bilayer MoS₂ (black). Peak height is normalized to the silicon Raman peak. Raman signals also appear in the PL spectra at the higher energy, details of which are shown in the inset. (e) HRTEM image of freely suspended monolayer MoS₂. The inset is the corresponding SAED pattern recorded along the [001] zone axis. The scale bar corresponds to 2 nm.

Results

Synthesis and characterization of highly crystalline monolayer MoS₂. In this work, we synthesized monolayer MoS₂ on various SiO₂/Si substrates by CVD method. Figures 1a, b show two typical optical images of the material grown on 280 nm SiO₂/Si substrates. The monolayer MoS₂ tend to form isolated triangular islands, with grain sizes ranging from a few microns to tens of microns. With increased growth time, some monolayer MoS₂ islands overlap with one another to form bilayer or multi-layer structures as indicated with the arrows in Fig. 1b. The thickness of a MoS₂ triangular island depicted in Fig. 1c, measured by an atomic force microscope (AFM), is about 0.79 nm, consistent with data from literatures^{18,26}.

The photoluminescence (PL) spectra of both monolayer and bilayer MoS₂ are shown in Figure 1d. Raman signals also appear in the PL spectra at higher energy, details of which are shown in the inset. For monolayer MoS₂, the PL spectrum is dominated by two peaks around 1.85 eV and 2.00 eV, which come from the A and B exciton transitions, respectively. The A and B excitons form at the K-point of the Brillouin zone, where strong spin-orbit coupling induces a splitting in the opposite spin valence bands by about 150 meV^{2,10,27}. For bilayer MoS₂, the corresponding two exciton transition peaks are much weaker and exhibit a small red shift^{27,28}. The Raman spectrum of monolayer MoS₂ consists of the E_{2g}^1 (384.3 cm⁻¹) and A_{1g} (404.6 cm⁻¹) modes. Peak distance (Δ) of them is about 20.3 cm⁻¹. The E_{2g}^1 and A_{1g} Raman modes of bilayer MoS₂ peak at 382.9 cm⁻¹ and 404.8 cm⁻¹ respectively, with a Δ of about 21.9 cm⁻¹. Peak distance between these two modes has been used to identify the number of layers of MoS₂²⁹. For monolayer and bilayer MoS₂, the Δ values are about 18~20 cm⁻¹ and 21~22 cm⁻¹, respectively^{19,29}. Our results are consistent with these criteria.

We characterized crystal structure of the monolayer MoS₂ with a high-resolution transmission electron microscope (HRTEM), as shown in Fig. 1e. We can see clearly the {100} planes of MoS₂, with a lattice spacing of about 0.270 nm¹⁸. The HRTEM image, together with the corresponding selected area electron diffraction (SAED) shown in the inset, demonstrates that the monolayer MoS₂ is a single crystal with a hexagonal lattice structure.

Measuring the contrast spectra of monolayer MoS₂ on SiO₂/Si substrates. The schematic diagram of the experimental set-up for measuring the contrast spectrum of monolayer MoS₂ on a SiO₂/Si substrate is shown in Fig. 2a. An optical microscope equipped with a white light source was used to collect the reflected light signal from the sample. An optical fiber was used to selectively couple part of the reflected light signal into a spectrometer. In our case, the spatial resolution of the reflectance spectrum, which depends on both the objective lens magnification and the fiber diameter, is about 1 μ m under 50 $\times$ objective lens, smaller than the size of the monolayer MoS₂ islands. Figure 2b shows the reflectance spectra measured on monolayer MoS₂ grown on a 280 nm SiO₂/Si substrate and a bare 280 nm SiO₂/Si substrate respectively, for wavelengths ranging from 400 nm to 750 nm. Corresponding measured sites are labeled as A and B in the inset. The contrast of monolayer MoS₂ on a SiO₂/Si substrate can be defined as:

$$C = \frac{I_{\text{substrate}} - I_{\text{MoS}_2}}{I_{\text{substrate}} + I_{\text{MoS}_2}}, \quad (1)$$

where I_{MoS_2} and $I_{\text{substrate}}$ are the reflected light intensities from MoS₂ and the substrate, respectively. From the two reflectance spectra, we can calculate the contrast spectrum, which is also shown in Fig. 2b.

Figure 2 | Measurement of Spatially Resolved Contrast Spectrum. (a) The schematic diagram of the experimental set-up for measuring the contrast spectrum of monolayer MoS_2 on a SiO_2/Si substrate. Inset: The geometric structure of our sample. (b) The reflectance spectra measured on monolayer MoS_2 (red line) and $280\text{ nm SiO}_2/\text{Si}$ substrate (black line), respectively. Corresponding measured sites are labeled as A and B in the inset. The scale bar corresponds to $10\text{ }\mu\text{m}$. The contrast spectrum extracted from the reflectance spectra is shown by the cyan line. (c) The contrast spectra of monolayer MoS_2 on a $281\text{ nm SiO}_2/\text{Si}$ substrate collected by using three objective lenses with different N. A. (0.2 ($10\times$), 0.55 ($50\times$), and 0.75 ($100\times$)).

We assume normal incidence in the analysis of this work. We need to select a proper objective lens in order to minimize the error caused by the spatial Fourier components of the beam away from normal incidence³⁰. On one hand, this requires the numerical aperture (N. A.) to be as small as possible. On the other hand, the lens with a smaller N. A. usually has smaller magnification, which in return reduces spatial resolution. Figures 2c shows three contrast spectra of monolayer MoS_2 on a $280\text{ nm SiO}_2/\text{Si}$ substrate, which were obtained by using objective lenses with N. A. of 0.2 ($10\times$), 0.55

($50\times$), and 0.75 ($100\times$), respectively. We can see that, apart from the spectrum collected by the lens with N. A. of 0.75 , the contrast spectra collected by the other two lenses are similar, which means that the error caused by the beam away from normal incidence can be ignored when the N. A. is less than 0.55 . Therefore, we used the $50\times$ objective lens in our experiment to achieve optimal results.

Fitting the complex refractive index of monolayer MoS_2 . For normal light incidence, the reflected light intensity from a sample

with the geometric structure shown in the inset of Fig. 2a can be written as²⁵:

$$I = \frac{|r_1 e^{i(\Phi_1 + \Phi_2)} + r_2 e^{-i(\Phi_1 - \Phi_2)} + r_3 e^{-i(\Phi_1 + \Phi_2)} + r_1 r_2 r_3 e^{i(\Phi_1 - \Phi_2)}|^2}{|e^{i(\Phi_1 + \Phi_2)} + r_1 r_2 e^{-i(\Phi_1 - \Phi_2)} + r_1 r_3 e^{-i(\Phi_1 + \Phi_2)} + r_2 r_3 e^{i(\Phi_1 - \Phi_2)}|^2}, \quad (2)$$

where

$$r_1 = \frac{\tilde{n}_0 - \tilde{n}_1}{\tilde{n}_0 + \tilde{n}_1},$$

$$r_2 = \frac{\tilde{n}_1 - \tilde{n}_2}{\tilde{n}_1 + \tilde{n}_2},$$

$$r_3 = \frac{\tilde{n}_2 - \tilde{n}_3}{\tilde{n}_2 + \tilde{n}_3},$$

are the relative indices of refraction. $\Phi_i = \frac{2\pi\tilde{n}_i d_i}{\lambda}$ is the phase shift due to the variation of the optical path, in which λ is the wavelength, d_i is thickness of related layer, and $\tilde{n}_i = n_i - ik_i$ is the complex refractive index of related material. The reflected light intensity from bare SiO₂/Si substrate can be obtained by setting $\tilde{n}_i = \tilde{n}_0 \equiv 1$. Given the theoretical thickness for monolayer MoS₂ ($d_1 = 0.63 \text{ nm}^{31}$), the incident light wavelength, and the complex refractive indices of both SiO₂ and Si, we can obtain, from equations (1) and (2), the contrast of monolayer MoS₂ on a SiO₂/Si substrate as a function of both SiO₂ thickness (d_2) and complex refractive index of monolayer MoS₂ (n_1, k_1):

$$C = \frac{I_{\text{substrate}} - I_{\text{MoS}_2}}{I_{\text{substrate}} + I_{\text{MoS}_2}} = C(\tilde{n}_1, d_2) = C(n_1, k_1, d_2), \quad (3)$$

In order to obtain the complex refractive index spectrum of monolayer MoS₂, we measured contrast spectra of 26 monolayer MoS₂ samples on SiO₂/Si substrates with SiO₂ thickness ranging from ~130 nm to ~370 nm (Supplementary Fig. S1). From these contrast spectra, we extracted the relation between the contrast (C) and SiO₂ thickness (d_2) under a specific incident light wavelength, e.g. 651 nm, as shown in Fig. 3a (scattered open circles). The standard deviation of each point, indicated by its error bar, was obtained by multiple measurements. By curve fitting these data with equation (3) (the solid line), we obtained the complex refractive index of monolayer MoS₂ (n_1, k_1) at 651 nm. Similarly, we can obtain the C - d_2 relations under different incident light wavelength (from 400 nm to 750 nm). The resulting complex refractive index spectrum of monolayer MoS₂ is shown in Fig. 3b (scattered red circles), together with the confidence interval (red shadow), which corresponds to a 95% confidence level. The overall confidence interval is narrow, especially in the wavelength range from 550 nm to 700 nm, indicating that the result is with high confidence. We expect uniformity in sample properties, such as MoS₂ thickness, crystalline quality, and surface flatness, to contribute to the confidence interval. Therefore the narrow confidence interval in the wavelength range from 550 nm to 700 nm indicates good sample uniformity, which can be attributed to the stable double-temperature-zone CVD synthesis method employed in this work as well as the fundamental thickness uniformity of the layered 2D material (the thickness can only be one, two, or more mono-layers). The observed gradually broadened confidence interval at wavelengths below 450 nm and above 700 nm may result mainly from the poor signal-noise ratio of the measuring system in those wavelength ranges. The broadened confidence interval at the wavelength range of 450–525 nm may result from the poor signal-noise ratio of the measured optical contrast, which is related to the SiO₂ thickness employed. We can see in Fig. S1 that the absolute optical contrast of most of our samples are weaker in the wavelength range of 450–525 nm.

Figure 3 | Curve Fitting results of complex refractive index for monolayer MoS₂. (a) The contrast of monolayer MoS₂ as a function of the SiO₂ thickness under incident light wavelength of 651 nm (scattered open circles). The standard deviation of each point is shown by the error bar. The curve fitting result of the complex refractive index of monolayer MoS₂ at 651 nm is shown in the table in the inset. (b) The complex refractive index spectrum (scattered red circles) of monolayer MoS₂, obtained by curving fitting the relation between contrast and SiO₂ thickness relation with equation (3) under different incident light wavelength (from 400 nm to 750 nm). The red shadow shows the confidence interval, corresponding to a 95% confidence level. The black dashed lines show the complex refractive index spectrum of bulk MoS₂²¹.

For comparison, we also plotted the complex refractive index spectrum of bulk MoS₂²¹ in this figure with the black dashed lines. We can see that, for most wavelengths, the real and imaginary parts of the refractive index of monolayer MoS₂ are both lower than their bulk counterparts. In addition, for monolayer MoS₂, two peaks of the real part of the refractive index spectrum, located at 663 nm and 621 nm, exhibit a blue shift compared to their bulk counterparts (at 684 nm and 626 nm, respectively). Similarly, two peaks of the imaginary part (at 651 nm and 603 nm) also show a blue shift compared to their bulk counterparts (at 671 nm and 611 nm, respectively). Given that the imaginary part represents the electromagnetic wave absorption in a material, we attribute the two peaks of the imaginary part of the refractive index spectra to A and B exciton absorptions, respectively. The observed blue shifts of exciton absorption of monolayer MoS₂ compared to their bulk counterparts may be due to the difference of A and B excitons energy in bulk and monolayer MoS₂^{2,27}. It is worth noting that, compared to the exciton emission peaks (located at 1.85 eV and 2.00 eV) shown in Fig. 1d, the observed A and B exciton absorption peaks of monolayer MoS₂ (located at 651 nm and 603 nm, i.e. 1.90 eV and 2.06 eV) also show a blue shift. This phenomenon results from the well-known Stokes shift between absorption and emission³². There also exists a peak near 400 nm for the imaginary part spectrum of monolayer MoS₂, which may be related to the convoluted C and D excitons^{28,33}. The

Figure 4 | Comparison of the optical contrasts of monolayer MoS₂ on SiO₂/Si substrates calculated with the refractive index of monolayer MoS₂ and that of bulk MoS₂. (a) Three representative contrast spectra of monolayer MoS₂ on different substrates, calculated with the refractive index of monolayer MoS₂ (solid lines), together with those calculated with the refractive index of bulk MoS₂ (dashed lines). The samples (1)–(3) correspond to SiO₂ thicknesses of 262, 281, and 150 nm, respectively. The scattered open circles are the contrast data obtained directly from the monochromatic images of the three samples. (b) The optical images of samples (1)–(3). (c) The monochromatic (blue, green, and red) images of sample (1) under 445 nm, 526 nm, and 672 nm light illumination, respectively. (d) The upper and lower ones are the color contour plots of the contrast as a function of both SiO₂ thickness and incident light wavelength calculated using the refractive index of monolayer MoS₂ and that of bulk MoS₂, respectively. (e) The redrawing of the upper one in (d) using a different color bar. All the scale bars in Fig. 4 correspond to 10 μ m.

reason why the peak located around 480 nm of the real part of refractive index spectrum for the bulk MoS₂ splits into two peaks for monolayer case is still unknown, and needs further study.

In order to demonstrate the difference of the refractive indices for monolayer and bulk MoS₂ from another point of view, we calculated three representative contrast spectra of monolayer MoS₂ on SiO₂/Si

substrates, with SiO₂ thicknesses of 262, 281, and 150 nm, respectively, labeled as samples (1)–(3). The results are plotted (solid lines) together with those calculated using the refractive index of bulk MoS₂ (dashed lines) in Fig. 4a. Figure 4b shows the optical images of samples (1)–(3), respectively. The optical images show different colors as a result of the different reflectance spectra of the three samples.

We also took the monochromatic images of the samples by inserting narrow-band filters into the illuminating optical path. As an example, three monochromatic images of sample (1) are shown in Fig. 4c. The images show quite different contrast, the blue one having the worst contrast, and the green one having the best. From the converted grayscale images, we obtained the contrast data directly. The obtained contrast data for all the three samples are plotted in Fig. 4a (scattered open circles). We can see that the measured contrast data agree well with those calculated with the refractive index of monolayer MoS₂ (solid lines).

Using refractive indices of monolayer and bulk MoS₂, we calculated the color contour plots of the contrast as a function of both SiO₂ thickness and incident light wavelength for monolayer MoS₂ on SiO₂/Si substrate. The results were plotted in Fig. 4d under the same color bar. The clear difference between these two plots confirms again that the difference between the refractive indices of monolayer and bulk MoS₂ cannot be ignored. For both fundamental study and device application, it is useful to make the sample visible under an optical microscope. It is common to use 280 nm–300 nm SiO₂/Si substrates for monolayer MoS₂ in order to visualize it. In principle, with this color contour plot, one can make the monolayer MoS₂ visible on any SiO₂/Si substrate by selecting the proper incident light wavelength, and vice versa. For convenient to use, we replotted the color contour plot in Fig. 4e using a more appropriate color bar.

Discussion

In this work, we have synthesized highly crystalline monolayer MoS₂ on 26 different SiO₂/Si substrates with SiO₂ thickness ranging from ~130 nm to ~370 nm, and have devised a method to measure the contrast spectra of monolayer MoS₂ on these substrates. Using these contrast spectra, we extracted the complex refractive index spectrum of monolayer MoS₂ in the wavelength range of 400 nm to 750 nm. We have analyzed the pronounced difference between the obtained complex refractive index spectrum and that of bulk MoS₂. Furthermore, we have calculated the color contour plots of the contrast as a function of both SiO₂ thickness and incident light wavelength for monolayer MoS₂ using the obtained refractive index spectrum. These plots are useful for both fundamental study and device application. The measurement method presented here, with the advantage over conventional methods for 2D materials with small size, can be applied to other 2D materials which can be synthesized with good repeatability.

Methods

Preparation of SiO₂/Si substrates. We chemically etched the thermally oxidized SiO₂ capping layers on the Si substrates to various thicknesses (from 130 nm to 370 nm) using buffered hydrogen fluoride (HF) (HF (40%): NH₄F (8 M) = 1:10). The original thickness of the SiO₂ capping layer was 600 nm. The whole etching process was carried out in ice-bath with magnetic stirring. The thickness of the SiO₂ layer was measured by a thin film thickness measurement system (SpectraThick Series, ST2000-DLXn) with repeatability of 0.5 nm. The refractive index of the *p*-Si substrate (resistivity: 8–12 Ω·cm) was measured by an ellipsometer (Horiba Jobin Yvon Uvisel) (shown in Fig. S2).

Synthesis of monolayer MoS₂. We synthesized monolayer MoS₂ on SiO₂/Si substrates with a double-temperature-zone CVD method at ambient pressure. The MoO₃ (99.99%) and S (99.999%) powders, serving as the source, were loaded onto two quartz boats, respectively, which were later inserted into a 1-inch diameter quartz tube placed in a tubular furnace. The MoO₃ located at the downstream of high-purity argon (Ar) carrier gas. SiO₂/Si substrates were placed with faces down above MoO₃. During the synthesis process, the temperatures at MoO₃ and S sources were first raised to 100 °C and kept there for 1 h with Ar gas flow rate of 120 sccm to exhaust water and air. Then the temperatures at MoO₃ and S were ramped to 650 °C and 220 °C, respectively, in 40 min, and kept there for 10 min, with Ar gas flow rate of 10 sccm. After that, the furnace was cooled down to room temperature without feedback with Ar gas flow rate of 10 sccm.

Characterization of monolayer MoS₂. The thickness and crystal structure of monolayer MoS₂ were characterized by AFM (Bruker Dimension Icon-PT) and TEM (Tecnai F30), respectively. For TEM sample preparation, we first spun a layer of poly(methyl methacrylate) (PMMA) onto a MoS₂/SiO₂/Si sample. Then we etched off the

SiO₂ layer by KOH aqueous solution (2 M) and cleaned the floating PMMA/MoS₂ membrane several times with deionized water. Finally the membrane was scooped onto a TEM grid and dried. The PMMA was removed by annealing the TEM sample at 400 °C for 3 h in an Ar/H₂ ambient. The PL and Raman spectra of monolayer MoS₂ were measured by a confocal Raman microscopic system (Horiba Labram HR800) at room temperature. The excitation laser wavelength was 488 nm.

Spatially resolved spectrum system. The spatially resolved reflectance spectrum was measured by using an optical microscopic spectrum system, which included an optical microscope (Zeiss Axio Imager. A2m) equipped with a halogen lamp (Zeiss Hal 100, 12 V, and 100 W), and a spectrometer (Horiba Jobin Yvon Triax 320). One end of an optical fiber was placed at the image plane of the microscope to selectively couple part of the light signal there to the spectrometer. The diameter of the optical fiber is 9 μm.

Obtaining Monochromatic Images. Monochromatic image was obtained by inserting a color filter with bandwidth of ~10 nm into the illuminating optical path of the optical microscope. The central wavelengths of the three filters used in Fig. 4 are 445 nm, 526 nm, and 672 nm, respectively.

- Novoselov, K. S. *et al.* Electric field effect in atomically thin carbon films. *Science* **306**, 666–669 (2004).
- Mak, K. F., Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically thin MoS₂: A new direct-gap semiconductor. *Phys. Rev. Lett.* **105**, 136805 (2010).
- Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N. & Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nat. Nanotechnol.* **7**, 699–712 (2012).
- Ezawa, M. Spin-valley optical selection rule and strong circular dichroism in silicene. *Phys. Rev. B* **86**, 161407 (2012).
- Xiao, D., Liu, G. B., Feng, W. X., Xu, X. D. & Yao, W. Coupled spin and valley physics in monolayers of MoS₂ and other group-vi dichalcogenides. *Phys. Rev. Lett.* **108**, 196802 (2012).
- Zhu, Z. Y., Cheng, Y. C. & Schwingenschlogl, U. Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors. *Phys. Rev. B* **84**, 153402 (2011).
- Cao, T. *et al.* Valley-selective circular dichroism of monolayer molybdenum disulphide. *Nat. Commun.* **3**, 887 (2012).
- Mak, K. F., He, K. L., Shan, J. & Heinz, T. F. Control of valley polarization in monolayer MoS₂ by optical helicity. *Nat. Nanotechnol.* **7**, 494–498 (2012).
- Zeng, H. L., Dai, J. F., Yao, W., Xiao, D. & Cui, X. D. Valley polarization in MoS₂ monolayers by optical pumping. *Nat. Nanotechnol.* **7**, 490–493 (2012).
- Sallen, G. *et al.* Robust optical emission polarization in mos2 monolayers through selective valley excitation. *Phys. Rev. B* **86**, 081301 (2012).
- Shan, W. Y., Lu, H. Z. & Xiao, D. Spin hall effect in spin-valley coupled monolayers of transition metal dichalcogenides. *Phys. Rev. B* **88**, 125301 (2013).
- Li, Z. & Carbotte, J. P. Longitudinal and spin-valley hall optical conductivity in single layer MoS₂. *Phys. Rev. B* **86**, 205425 (2012).
- Yin, X. B. *et al.* Edge nonlinear optics on a MoS₂ atomic monolayer. *Science* **344**, 488–490 (2014).
- Hong, X. P. *et al.* Ultrafast charge transfer in atomically thin mos2/ws2 heterostructures. *Nat. Nanotechnol.* **9**, 682–686 (2014).
- Lee, C. H. *et al.* Atomically thin p-n junctions with van der waals heterointerfaces. *Nat. Nanotechnol.* **9**, 676–681 (2014).
- Furchi, M. M., Pospischil, A., Libisch, F., Burgdorfer, J. & Mueller, T. Photovoltaic effect in an electrically tunable van der waals heterojunction. *Nano Lett.* **14**, 4785–4791 (2014).
- Cheng, R. *et al.* Electroluminescence and photocurrent generation from atomically sharp wse2/mos2 heterojunction p-n diodes. *Nano Lett.* **14**, 5590–5597 (2014).
- Lee, Y. H. *et al.* Synthesis of large-area MoS₂ atomic layers with chemical vapor deposition. *Adv. Mater.* **24**, 2320–2325 (2012).
- Najmaei, S. *et al.* Vapour phase growth and grain boundary structure of molybdenum disulphide atomic layers. *Nat. Mater.* **12**, 754–759 (2013).
- Van Der Zande, A. M. *et al.* Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide. *Nat. Mater.* **12**, 554–561 (2013).
- Beal, A. R. & Hughes, H. P. Kramers-Kronig analysis of the reflectivity spectra of 2h-MoS₂, 2h-MoSe₂ and 2h-MoTe₂. *J. Phys. C: Solid State Phys.* **12**, 881–890 (1979).
- Yim, C. Y. *et al.* Investigation of the optical properties of mos2 thin films using spectroscopic ellipsometry. *Appl. Phys. Lett.* **104**, 103114 (2014).
- Eichfeld, S. M., Eichfeld, C. M., Lin, Y. C., Hossain, L. & Robinson, J. A. Rapid, non-destructive evaluation of ultrathin wse2 using spectroscopic ellipsometry. *APL Mat.* **2**, 092508 (2014).
- Liu, H. L. *et al.* Optical properties of monolayer transition metal dichalcogenides probed by spectroscopic ellipsometry. *Appl. Phys. Lett.* **105**, 201905 (2014).
- Blake, P. *et al.* Making graphene visible. *Appl. Phys. Lett.* **91**, 063124 (2007).
- Benamer, M. M. *et al.* Visibility of dichalcogenide nanolayers. *Nanotechnology* **22**, 125706 (2011).
- Splendiani, A. *et al.* Emerging photoluminescence in monolayer MoS₂. *Nano Lett.* **10**, 1271–1275 (2010).

28. Eda, G. *et al.* Photoluminescence from chemically exfoliated MoS₂. *Nano Lett.* **11**, 5111–5116 (2011).
29. Li, S. L. *et al.* Quantitative raman spectrum and reliable thickness identification for atomic layers on insulating substrates. *ACS Nano* **6**, 7381–7388 (2012).
30. Mak, K. F. *et al.* Measurement of the optical conductivity of graphene. *Phys. Rev. Lett.* **101**, 196405 (2008).
31. Rydberg, H. *et al.* Van der waals density functional for layered structures. *Phys. Rev. Lett.* **91**, 126402 (2003).
32. Zhao, W. J. *et al.* Evolution of electronic structure in atomically thin sheets of WS₂ and WSe₂. *ACS Nano* **7**, 791–797 (2013).
33. Evans, B. & Young, P. Optical absorption and dispersion in molybdenum disulphide. *Proc. R. Soc. Lond. A* **284**, 402–422 (1965).

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Author contributions

L.D. and H.Z. conceived the research, analyzed the data, and wrote the manuscript. Y.M. and H.Z. devised the optical contrast spectra measurement method. H.Z. and Y.W. synthesized the samples, did the PL, Raman, and optical contrast spectra measurements. X.R. did the AFM measurement. Z.X. measured the refractive index of silicon. H.Z. did the TEM characterization and the numerical calculation (assisted by W.W.). L.D. supervised the study. All authors discussed the results.

Additional information

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