Research Article | Vol. 31, No. 12 / 5 Jun 2023 / Optics Express 19746
Optics EXPRESS

Check for updates

Interference tunable second harmonic generation for two-dimensional materials in layered structures

YING SONG,[1,2] WEIMING WANG,[1,2] YANCHAO WANG,[2,3] YUWEI SHAN,[1,2,5] JIN LUO CHENG,[1,2,*] AND J. E. SIPE[4]

[1] *GPL Photonics Laboratory, State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, Jilin 130033, China*
[2] *University of Chinese Academy of Science, Beijing 100049, China*
[3] *Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, Jilin 130033, China*
[4] *Department of Physics, University of Toronto, Toronto, Ontario M5S 1A7, Canada*
[5] *yuweis@ciomp.ac.cn*
[*] *jlcheng@ciomp.ac.cn*

Abstract: We experimentally study the tunability of second harmonic generation (SHG) from a two-dimensional (2D) material in a 2D material/dielectric film/substrate layered structure. Such tunability arises from two interferences: one is between the incident fundamental light and its reflected light, and the other is between the upward second harmonic (SH) light and the reflected downward SH light. When both interferences are constructive, the SHG is maximally enhanced; it becomes attenuated if either of them is destructive. The maximal signal can be obtained when both interferences are perfectly constructive, which can be realized by choosing a highly reflective substrate and an appropriate thickness for a dielectric film that has a large difference in its refractive indices at the fundamental and the SH wavelengths. Our experiments demonstrate variations of three orders of magnitude in the SHG signals from a monolayer $MoS_2/TiO_2/Ag$ layered structure.

© 2023 Optica Publishing Group under the terms of the Optica Open Access Publishing Agreement

1. Introduction

Interference effects in layered structures play an important role in realizing specific optical functionality [1,2]. Examples range from traditional anti-reflective coatings to the recently reported tunability of the Raman intensity of graphene, and of the photoluminescence (PL) intensity of monolayer MoS_2, that can be achieved by varying the thickness of an SiO_2 capping layer [3,4]. The interference from a layered structure can also have strong effects on nonlinear optical signals. Nonlinear photoluminescence and transient absorption in graphene [5] can be significantly affected by the thickness of SiO_2 in an SiO_2/Si structure on which the graphene resides. Savostianova and Mikhailov [6] theoretically proposed that the third harmonic generation (THG) of graphene could be enhanced two orders of magnitude by placing it in a graphene/dielectric film/metal layered structure. Experimentally, a 117-fold enhancement for THG from graphene was observed by integrating with a planar cavity [7], but the SHG from monolayer MoS_2 [5] or other transition metal dichalcogenide materials [8,9] is enhanced only a few times as the thickness of the SiO_2 layer in underlying SiO_2/Si structures is varied. The reason for this is still not clear.

Based on a recent theory [10] in this paper we experimentally verify the conditions for maximizing or minimizing the SHG signal of a monolayer MoS_2 on a layered structure. Our results show that the output SHG intensity can be tuned over a range of three orders of magnitude by choosing an appropriate material and thickness for the layer in the structure. We organize the paper as follows: in the section "Theoretical model" we briefly discuss how the layered structure affects the intensity of SHG, and identify the conditions for achieving the strongest

#486719 https://doi.org/10.1364/OE.486719
Journal © 2023 Received 2 Feb 2023; revised 8 Apr 2023; accepted 9 May 2023; published 30 May 2023

Optics EXPRESS

or weakest SHG signal. In the section "Experiment" we discuss the sample preparation and characterization by optical spectroscopy. Finally, in the section "Results and discussion" we report the experimental results for layered structures of different designs, and compare theory and experiment.

2. Theorical model

In Fig. 1 we illustrate the layered structure of interest, which consists of monolayer MoS_2, a dielectric film with thickness d, and a substrate. For a normally incident plane wave with wavelength λ and intensity I_λ, the intensity of SH field $I_{\lambda/2}$ can be written as [11],

$$I_{\lambda/2} = \frac{1}{2\epsilon_0 c} \cdot |\beta_\lambda|^2 \cdot \left| \frac{2\pi\chi^{(2)}}{\lambda\epsilon_0} \right|^2 \cdot I_\lambda^2 \tag{1}$$

Here $\chi^{(2)}$ is the effective sheet susceptibility for SHG, and all effects from the layered structure are summarized in the structure factor β_λ,

$$\beta_\lambda = (1 + R_\lambda)^2 \cdot (1 + R_{\lambda/2}), \tag{2}$$

with R_λ and $R_{\lambda/2}$ the reflection coefficients of the whole structure at wavelength λ and $\lambda/2$, respectively. The reflection coefficients can be obtained using the standard transfer matrix method [11]. The expression of R_λ at normal incidence is given as

$$R_\lambda = r + \frac{R_{s,\lambda} t^2}{1 - R_{s,\lambda} r}, \tag{3}$$

$$R_{s,\lambda} = \frac{r_{01} + r_{12} e^{2i\tilde{\omega} n_1 d}}{1 + r_{01} r_{12} e^{2i\tilde{\omega} n_1 d}}, \tag{4}$$

Here $r = -\eta/(1 + \eta)$ and $t = 1/(1 + \eta)$ represent the reflection and transmission coefficients of a monolayer MoS_2 layer, respectively; the parameter η is calculated from the effective bulk refractive index n_{2D} through $\eta = -ih\tilde{\omega}(n_{2D}^2 - 1)/2$ with the effective thickness $h = 0.65$ nm of monolayer MoS_2 and $\tilde{\omega} = 2\pi/\lambda$; $R_{s,\lambda}$ represents the reflection coefficient of the structure without MoS_2 layer, $r_{ij} = (n_i - n_j)/(n_i + n_j)$ gives the reflection coefficient at interface between two layers i, j with n_i the refractive index of the layer i, where the index i is taken as 0, 1 and 2 for air, dielectric layer, and substrate, respectively. For a layered structure, the reflection coefficient varies between -1 to 1; thus the structure factor $|\beta_\lambda|^2$ can reach the maximal value 64 for perfectly constructive interferences at $R_\lambda = R_{\lambda/2} = 1$ or $|1 + R_\lambda| = |1 + R_{\lambda/2}| = 2$, and the minimal value 0 for perfectly destructive interference at $R_\lambda = -1$ or $R_{\lambda/2} = -1$. When there exists absorption from 2D material or substrate, $|\beta_\lambda|^2$ cannot reach its maximal value 64 or minimal value 0.

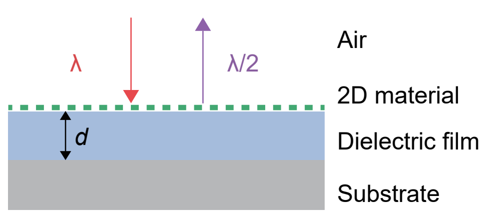

Fig. 1. Schematic of a layered structure.

Equations (1) and (2) give the results for a monochromatic plane wave at normal incidence. However, most nonlinear optical experiments use tightly focused femtosecond laser pulses, which consists of plane wave amplitudes incident from a range of directions. For obliquely incident plane wave light, the structure factor in Eq. (2) becomes incident angle dependent. With increasing incident angle, the structure factor at a given wavelength oscillates between constructive and the destructive interference, and the variation with angle becomes stronger for thicker films. Therefore, the interference effects are suppressed for a focused beam, which can be clearly seen from Fig. 2. Wang et al. [10] argued that for focused laser beam excitation two conditions must hold for the SHG intensity to be tunable over a large range: (1) the substrate has to be a highly reflective material, such as a noble metal, so that as much light as possible can be reflected; (2) the dielectric layer has to have significantly different indices of refraction at fundamental and SH wavelengths. With respect to the pulses that make up the incident light, our experiments use a pulse duration of 120 fs, giving a fairly narrow spectra broadening, and the changes in the structure factor in Eq. (2) over the range of wavelengths involved are very small; thus a continuous wave analysis suffices. Here we experimentally study the effect of the layered structure on the SHG of monolayer MoS_2 for the following structures: MoS_2/Si, MoS_2/Fused silica, MoS_2/Sapphire, MoS_2/SiO_2(d nm)/Si, and MoS_2/TiO_2(d nm)/Ag, where several thicknesses of the dielectric film are used. Although there are important consequences of the incident light being focused, much of the physics can be captured by a description based on normally incident plane waves.

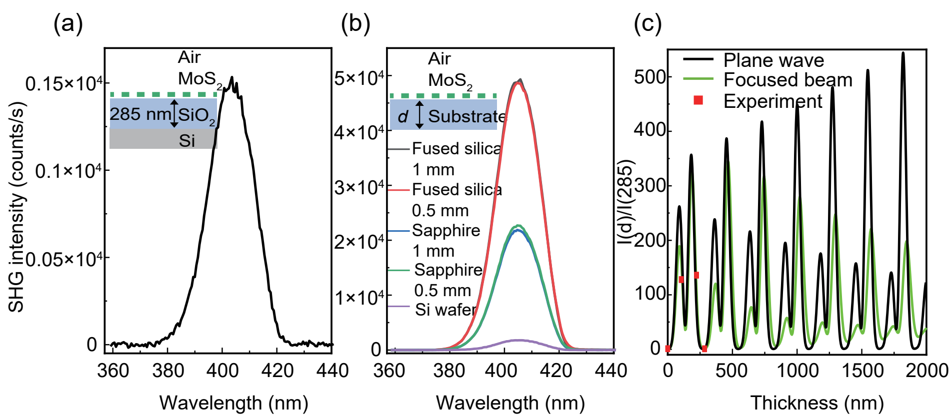

Fig. 2. (a) SHG spectra for a monolayer MoS_2 on top of 285 nm SiO_2/Si substrate. Inset: schematic diagram of structure. (b) SHG spectra for a monolayer MoS_2 on top of different substrates, choosing as fused silica, sapphire, and silicon. Inset: schematic diagram of structures. (c) The normalized SHG intensity for the MoS_2/SiO_2(d nm)/Si substrate structure as a function of the film thickness d. The dots are experimental values and the lines are the theoretical results (black for plane wave light and green for focused beam). The average power of incident light is about 3×10^{-4} W.

3. Experiment

Monolayer MoS_2 samples were fabricated on polydimethylsiloxane (PDMS) substrates by mechanical exfoliation of bulk MoS_2 crystals (HQ graphene), and were transferred to SiO_2/Si, fused silica, sapphire and TiO_2/Ag substrates by the dry transfer technique. The MoS_2 layer number is characterized by PL spectra, performed using an objective (100×, NA = 0.9) in micro-Raman instrument (HORIBA Scientific) under normal incidence. The incident laser is linearly polarized with wavelength 532 nm and power 54 µW. As show in Supplement 1, Fig. S1, the PL spectra exhibit a single prominent maximum at about 660 nm, agreeing with the band gap of monolayer MoS_2. The thickness of the SiO_2 and TiO_2 films were identified by a spectroscopic ellipsometry analyzer (Semilab), with linearly polarized light obliquely incident on the surface of a thin film at an angle of 70.09°.

We performed SHG measurements with a home-built, confocal microscope at room temperature and under ambient conditions. Lineally polarized femtosecond laser pulses (Maitai HP, Spectra Physics), centered at 800 nm, were focused on the monolayer MoS_2 by a 60× objective (NA = 0.7, Nikon) at normal incidence. The repetition rate was 80 MHz, and the pulse duration was 120 fs. The diameter of the laser beam on the sample surface was 2 μm. The SHG signal was collected by the same objective in the back scattering configuration, and was directed to a spectrometer (Princeton Instruments) for spectroscopy, or to a CCD camera for imaging. After passing through a dichroic beam splitter and a short-pass filter in the collection path, the SHG signal was detected by a liquid nitrogen-cooled spectrometer equipped with a 150 grooves/mm grating. Note that no polarization analyser is placed in detection optical path, and the collected SH signal becomes independent of pump polarization direction, which is also consistent with Eq. (1).

4. Results and discussion

A silicon wafer with a 285 nm oxide layer is a widely used substrate in monolayer MoS_2 fabrication because of the easy sample identification under optical microscopy [12,13]. The SHG signal of MoS_2/SiO_2(285 nm)/Si was first measured, and the SHG spectra is shown in Fig. 2(a); the spectra peak locates around 400 nm. In the measurement, the average power of incident light and SH signal are about 3×10^{-4} W and 2.3×10^{-14} W, the effective bulk susceptibility $|\chi^{(2)}/h|$ is extracted as about 403 pm/V based on Eqs. (1)–(4). In the following, the signal from this structure is taken as a reference to discuss how the dielectric film and substrate affect SHG in a layered structure of MoS_2/dielectric film(d nm)/substrate.

We first take the thickness of the dielectric film to zero and investigate the effects of the substrate, which is chosen to be either silicon [14], fused silica, or sapphire; a metal substrate without a dielectric film is not considered, because the possible charge transfer and quench process [15,16] from MoS_2 to metal can change the intrinsic second order susceptibility of 2D materials and obscure any interference effects. The SHG spectra are shown in Fig. 2(b), and the normalized intensity with respect to the reference is listed in Table 1. The order of the intensities of SHG signal from large to small is fused silica > sapphire > silicon. This result can be well understood from Eqs. (1) and (2). Usually the reflection from MoS_2 can be neglected; under that approximation the total reflection comes from the air/substrate interface, and the reflection coefficient is $R_\lambda = (1 - n_{2,\lambda})/(1 + n_{2,\lambda})$, with $n_{2,\lambda}$ the refractive index of substrate at wavelength λ. Table 2 lists the refractive index at both the fundamental and SH wavelengths; the real parts of the reflection coefficients of the structure are negative for our samples. For example, the reflection coefficients for an air/silicon interface are about -0.57 at 800 nm and -0.70-0.02i at 400 nm. Thus both the incident electric fields and generated SH fields interfere destructively with their associated reflected light, and the structure factor of an air/silicon interface is about $|\beta_\lambda|^2 = 0.003$; such a substrate greatly reduces the detectable SHG. In fact, it is easy to show that the structure factor is always less than 1 for a dielectric substrate, due to the destructive interference from the negative reflection coefficients R_λ.

To obtain a structure factor larger than 1, the reflection coefficients should become positive, which can be realized by inserting a dielectric film to tune the phase. As an example, we insert SiO_2 films with different thickness d=105, 233 and 285 nm between monolayer MoS_2 layer and the silicon substrate. The normalized intensity with respect to the reference is listed in Table 1. It is clear that the intensity of the SHG signal can range over a factor of about 150 as the thickness of the SiO_2 film varies, which confirms the tunability of the SHG signals by a dielectric film. The experimental results agree very well with theoretical results calculated for a focused beam, as shown in Fig. 2(c).

Optics EXPRESS

Table 1. The SHG intensity for different layered structures normalized to the value of MoS_2/SiO_2 (285 nm)/Si substrate. For the cases of fused silica and sapphire, the film thickness refers to the thickness of the substrate material used in experiments.

Structure	Film thickness	Experimental results	Theoretical results
SiO_2 film/Si	285 nm	1	1
	105 nm	127	160
		128	
	223 nm	147	106
		137	
Si wafer	0.5 mm	1	0.5
Fused silica	1 mm	31	37
		30	
	0.5 mm	30	
Sapphire	1 mm	14	20
		13	
	0.5 mm	14	
TiO_2/Ag	80 nm	594	809
	280 nm	4004	4589
	445 nm	1529	2089
		1484	
	488 nm	25	49

Table 2. The refractive index of each material used in our experiment [17].

Material	Refractive index (800 nm)	Refractive index (400 nm)
Monolayer MoS_2	3.2828	2.7226 + 2.6765i
SiO_2 (Fused silica)	1.453	1.470
Si	3.669 + 0.005266i	5.623 + 0.3263i
Sapphire	1.760	1.787
TiO_2	2.095	2.338
Ag	0.03676 + 5.57i	0.05 + 2.104i

Physically, the effects of the dielectric film can be understood from the phase change of the reflected light, which can be estimated as $\phi_\lambda = 2\pi \cdot n_{1,\lambda} \cdot 2d/\lambda$ at wavelength λ. For the refractive indexes listed in Table 1, a d=285 nm SiO_2 film can cause approximately $2\pi \times 1.03$ ($2\pi \times 2.10$) phase change for 800 nm (400 nm) light, and thus SHG intensity is approximately the same as that without a dielectric film. Because the refractive index is weakly dispersive at both the fundamental and SH wavelengths, their phase changes can reach even multiples of π simultaneously with a period $d_0 \approx \lambda/(2n_{1,\lambda}) = 275$ nm. The existence of such approximate periodicity ensures that local maxima for SHG exist in any period, and they occur at film thicknesses for which phase changes of reflected light are odd multiples of π. For a SiO_2 film with a thickness d=105 or 233 nm, the destructive interference present without the film is broken and the SHG signal is enhanced, although the phase changes are only partially constructive. To obtain the largest local maximum, the film should give a phase change of an odd multiple of π for both wavelengths simultaneously, and such thicknesses can be estimated as following: For the fundamental wavelength, the thickness required is $D = (m + 1/2)\lambda/(2n_{1,\lambda})$, at which the phase change for the SH wavelength can be written as $\phi/2\pi = (2m + 1) + (4D\delta_n/\lambda)$, with

Optics EXPRESS

$\delta_n = n_{1,\lambda/2} - n_{1,\lambda}$. For the phase change of the SH wavelength also to be an odd multiple of π requires $4D\delta_n/\lambda$ equal to $l + 1/2$ for any integer l, which leads to $D = (2l + 1)\lambda/(8n_{1,\lambda})$. It is obvious that this cannot be achieved for a dispersionless medium ($\delta_n = 0$). For SiO_2 films, which are weakly dispersive, the smallest thickness is 5.8 µm, about 7 times of the wavelength. Note that the thickness identified is for plane wave light incidence, and for a tightly focused laser beam the enhancement is greatly suppressed, as shown in Fig. 2(c). The thicker the film, the more significant the suppression, until the thick film behaves like a dielectric substrate, which does not lead to SHG enhancement. Therefore, a large SHG enhancement requires a phase change that is an odd multiple of π phase for a thin dielectric film, which requires a large δ_n.

From the discussion above, we can find that the enhancement of SHG from the layered structure of $MoS_2/SiO_2/Si$ has not been maximized due to two reasons: (1) the reflection coefficients of an air/silicon structure are not high enough, (2) the simultaneous phase change of an odd multiple of π at both fundamental and SH wavelengths requires the thickness of the dielectric film to be about 7 times larger than the wavelength, and for such thick films the interference effects of light amplitudes at difference incident angles lead to their cancellation for a tightly focused laser beam. To overcome these two limitations, we choose the monolayer $MoS_2/TiO_2/Ag$ layered structure, where TiO_2 is more dispersive than SiO_2, and the air/Ag interface has a very high reflectivity. Figure 3 shows the dependence of the normalized SHG intensity on the TiO_2 thickness. The theoretical results predict a maximal intensity about ~5000 times larger than the reference, which can be achieved for a film thickness of 275 nm. Two other local extremes occur at film thickness of around 95 and 455 nm. All these thicknesses are smaller than the wavelength. We experimentally fabricated structures with TiO_2 thickness of 80, 280, 445 and 488 nm; the experimental results are in good agreement with our theory.

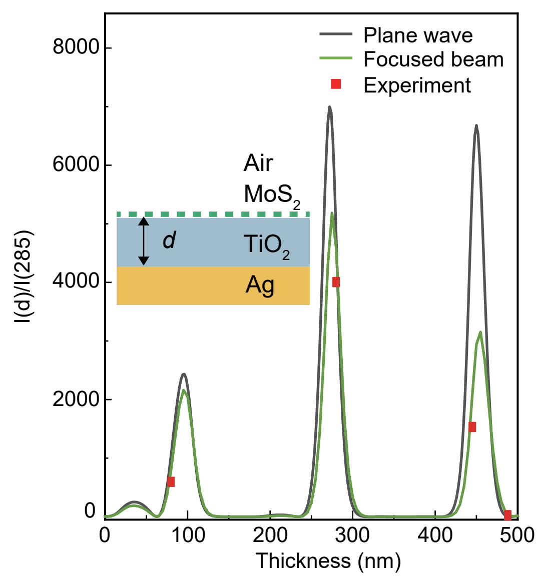

Fig. 3. Normalized SHG intensity for a $MoS_2/TiO_2/Ag$ layered structure (inset) as a function of TiO_2 film thickness d. The dots are experimental values and the lines are the theoretical results (black for plane wave light and green for focused beam).

5. Conclusion

In conclusion, we have experimentally demonstrated that the second harmonic generation from a monolayer MoS_2 can be significantly modulated by MoS_2/dielectric film/substrate layered structures. We discussed and demonstrated the conditions for obtaining the strongest or weakest second harmonic signals: one is the substrate should be very reflective, and the other is the dielectric film has to have large different indices of refraction at fundamental and SH wavelengths. By choosing the monolayer MoS_2/TiO_2 film/Ag layered structure, the second harmonic intensity generated by light at a fundamental wavelength 800 nm can vary over three orders of magnitude, depending on the TiO_2 film thickness, and theoretically the maximal values are obtained for a 275 nm thickness. Our results clearly demonstrate the significant effect of a layered structure on the second harmonic generation of 2D materials, and this effect should be carefully considered in extracting the nonlinear susceptibility from experimental data.

Funding. National Natural Science Foundation of China (12034003, 12004379, 62005272); Natural Sciences and Engineering Research Council of Canada; "Shu Guang" Talent Program of CIOMP; Scientific Research Projects of the Chinese Academy of Sciences(QYZDB-SSW-SYS038).

Disclosures. The authors declare no conflicts of interests.

Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

Supplemental document. See Supplement 1 for supporting content.

References

1. W. Liu and Y. S. Kivshar, "Multipolar interference effects in nanophotonics," Phil. Trans. R. Soc. A **375**(2090), 20160317 (2017).
2. G. Roberts, "Interference effects in femtosecond spectroscopy," Philos. Trans. R. Soc., A **360**(1794), 987–1021 (2002).
3. D. Yoon, H. Moon, Y.-W. Son, J. S. Choi, B. H. Park, Y. H. Cha, Y. D. Kim, and H. Cheong, "Interference effect on Raman spectrum of graphene on SiO_2/Si," Phys. Rev. B **80**(12), 125422 (2009).
4. H. Zhang, Y. Wan, Y. Ma, W. Wang, Y. Wang, and L. Dai, "Interference effect on optical signals of monolayer MoS_2," Appl. Phys. Lett. **107**(10), 101904 (2015).
5. X. Miao, N. Xuan, Q. Liu, W. Wu, H. Liu, Z. Sun, and M. Ji, "Optimizing Nonlinear Optical Visibility of Two-Dimensional Materials," ACS Appl. Mater. Interfaces **9**(39), 34448–34455 (2017).
6. N. A. Savostianova and S. A. Mikhailov, "Giant enhancement of the third harmonic in graphene integrated in a layered structure," Appl. Phys. Lett. **107**(18), 181104 (2015).
7. C. Beckerleg, T. J. Constant, I. Zeimpekis, S. M. Hornett, C. Craig, D. W. Hewak, and E. Hendry, "Cavity enhanced third harmonic generation in graphene," Appl. Phys. Lett. **112**(1), 011102 (2018).
8. S. D. Lavrov, A. V. Kudryavtsev, A. P. Shestakova, L. Kulyuk, and E. D. Mishina, "Second Harmonic Generation in Nanoscale Films of Transition Metal Chalcogenides: Taking into Account Multibeam Interference," Opt. Spectrosc. **120**(5), 808–814 (2016).
9. A. V. Kudryavtsev, S. D. Lavrov, A. P. Shestakova, L. L. Kulyuk, and E. D. Mishina, "Second harmonic generation in nanoscale films of transition metal dichalcogenide: Accounting for multipath interference," AIP Adv. **6**(9), 095306 (2016).
10. W. M. Wang, Y. Song, Y. W. Shan, J. L. Cheng, and J. E. Sipe, is preparing a manuscript.
11. J. L. Cheng, J. E. Sipe, N. Vermeulen, and C. Guo, "Nonlinear optics of graphene and other 2D materials in layered structures," JPhys Photonics **1**(1), 015002 (2018).
12. P. Blake, E. W. Hill, A. H. Castro Neto, K. S. Novoselov, D. Jiang, R. Yang, T. J. Booth, and A. K. Geim, "Making graphene visible," Appl. Phys. Lett. **91**(6), 063124 (2007).
13. A. M. van der Zande, P. Y. Huang, D. A. Chenet, T. C. Berkelbach, Y. You, G.-H. Lee, T. F. Heinz, D. R. Reichman, D. A. Muller, and J. C. Hone, "Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide," Nat. Mater. **12**(6), 554–561 (2013).
14. For pure silicon substrate, it usually includes a few nanometers SiO_2 film on the surface, which almost does not change the results. The thicknesses of other dielectric films are measured values, which are a bit different from the designed ones.
15. U. Bhanu, M. R. Islam, L. Tetard, and S. I. Khondaker, "Photoluminescence quenching in gold-MoS_2 hybrid nanoflakes," Sci. Rep. **4**(1), 5575 (2014).
16. I. Abid, P. Benzo, B. Pecassou, S. Jia, J. Zhang, J. Yuan, J. B. Dory, O. G. Lafaye, R. Pechou, A. Mlayah, and J. Lou, "Plasmon damping and charge transfer pathways in Au@$MoSe_2$ nanostructures," Mater. Today Nano **15**, 100131 (2021).

Optics EXPRESS

17. The refractive indexes are taken from https://refractiveindex.info.

159.226.165.13 {ts '2024-04-29 01:56:23'}