Substrate dependent terahertz magneto-optical properties of monolayer WS_2

Reference:
Dong H.M., Tao Zehua, Duan Y.F., Li L.L., Huang F., Peeters François.- Substrate dependent terahertz magneto-optical properties of monolayer WS2
Optics letters / Optical Society of America - ISSN 1539-4794 - 46:19(2021), p. 4892-4895
Full text (Publisher's DOI): https://doi.org/10.1364/OL.435055
To cite this reference: https://hdl.handle.net/10067/1825260151162165141

Substrate dependent terahertz magneto-optical properties of monolayer WS_2

H. M. Dong[1], Z. H. Tao[1,2,*], Y.F. Duan[1,*], L. L. Li[3,*], F. Huang[1,4], and F.M. Peeters[2,5]

[1] School of Materials Science and Physics, China University of Mining and Technology, Xuzhou 221116, P. R. China
[2] Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium
[3] Department of Physics and Centre for Nanointegration (CENIDE), University of Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany
[4] Low Carbon Energy Institute, China University of Mining and Technology, Xuzhou 221116, P. R. China
[5] School of Physics and Astronomy and Yunnan Key Laboratory for Quantum Information, Yunnan University, Kunming 650091, P. R. China
[*] Corresponding authors: zehua.tao@uantwerpen.be, yifeng@cumt.edu.cn, and longlong.li@uni-due.de

Compiled August 20, 2021

Terahertz (THz) magneto-optical (MO) properties of monolayer (ML) tungsten disulfide (WS_2), placed on different substrates and subjected to external magnetic fields, are studied using THz time-domain spectroscopy (TDS). We find that the THz MO conductivity exhibits a nearly linear response in a weak magnetic field, while a distinctly nonlinear/oscillating behavior is found in strong magnetic fields owing to strong substrate-induced random impurity scattering and interactions. The THz MO response of ML WS_2 depends sensitively on the choice of the substrates which we trace back to electronic localization and the impact of the substrates on the Landau level (LL) spectrum. Our results provide an in-depth understanding of the THz MO properties of ML WS_2/substrate systems, especially the effect of substrates, which can be utilized to realize atomically thin THz MO nano-devices.

http://dx.doi.org/10.1364/ao.XX.XXXXXX

1. INTRODUCTION

Two-dimensional (2D) materials have been widely investigated due to their unique electronic and optoelectronic properties that are relevant to important practical applications in nanodevices [1]. Recently, it was reported that the valley-selective optical Stark effect in ML WS_2 can be achieved by breaking time-reversal symmetry via intense circularly polarized light [2]. Sattar et al. found theoretically that the proximity effect in F-doped ML WS_2 on silicene and germanene substrates can lead to spin/valley polarizations and sizable band gaps due to broken inversion symmetry [3]. Moreover, it was shown that the proximity coupling to an insulating antiferromagnetic substrate can result in large valley splitting in ML WS_2 [4]. The inversion symmetry breaking together with spin-orbit coupling gives rise to coupled spin and valley physics in ML MoS_2, WS_2 etc, which can be used to control spin and valley degrees of freedom in these 2D materials [5]. Therefore, ML WS_2 is expected to have promising applications in spintronics and valleytronics due to its tunable band gap, strong spin-orbital coupling, and spin/valley polarizations [6].

The electronic and optoelectronic properties of ML WS_2 can further be tuned by external fields breaking space inversion or time reversal symmetry. For instance, in the presence of a magnetic field, the motion of electrons in ML WS_2 is quantized into discrete Landau levels (LLs), which can lead to fascinating spin/valley-dependent magneto-optical (MO) properties. Recently, the Zeeman splitting and inverted polarization of biexciton emission in ML WS_2 were observed by using polarization-resolved photoluminescence (PL) spectroscopy in a magnetic field up to 30 T [7]. Most recently, valley polarization of singlet and triplet trions in ML WS_2 was achieved by applying an external magnetic field [8]. These important experimental studies indicate that the optoelectronic properties, in particular, the MO properties of ML WS_2/substrate systems, are worth further investigation for their promising optoelectronic applications in the absence or presence of an external magnetic field.

THz time-domain spectroscopy (TDS) is a very powerful no-contact technique for the investigation of optically ultrafast dynamic properties of carriers [9, 10]. Both the amplitude and phase of the THz radiation field transmitted through the samples can be measured from the obtained diagonal and off-diagonal components of the complex dielectric tensor [11]. THz TDS combined with magnetic field at low temperature provides a well-established method to further investigate and understand the dynamical properties of carriers in 2D electronic systems. Recently, it has been found that the cyclotron resonance frequency exhibits a nonlinear dependence on the applied magnetic field using THz MO spectroscopy in a 2D hole gas [12]. Most recently, it was reported that the LLs of electrons and MO transport properties in a 2D material can be significantly modulated by placing it onto a substrate, and the electron-impurity scatterings should not be neglected [13–15]. This motivated us to investigate THz MO properties of ML WS_2 placed on different substrates, in order to understand how the THz response of ML WS_2/substrate systems can be altered by applying a magnetic field. We find that the THz MO reponse is almost linear with photon frequency in weak magnetic fields independent of the photon frequency, whereas it is nonlinear and oscillating as a function of the photon frequency in strong magnetic fields. Moreover, the THz MO response of ML WS_2 turns out to be very distinct for different substrates.

2. EXPERIMENT

The n-type ML WS_2 films with area size of 10 mm × 10 mm were synthesized on a sapphire wafer using the standard CVD method as reported in our previous work [16]. The WS_2 films were transferred from the sapphire wafer to other substrates (i.e., quartz and SiO_2/Si) by using a combination of polymethylmethacrylate (PMMA) transfer method and wet etching process, which has been widely used to fabricate 2D materials and electronic devices, such as ML MoS_2, WS_2, and other transition metal dichalcogenides [6, 17]. The Raman spectroscopy, the optical microscope images with 1 mm × 1mm area size and the PL spectroscopy (three-point measured) were used to identify the continuous, uniform and single layer film on all the substrates (see S1 in Supplement 1).

The experiment was set up in the Faraday geometry in the presence of a perpendicular magnetic field (B) at liquid nitrogen temperature ($T = 80$ K). The magnetic field and the incident THz light beam are precisely designed and applied perpendicular to the 2D surface of the used sample, as shown in Fig. S4 in Supplement 1. The time-dependent electric field strength transmitted through the sample was measured as a function of the radiation frequency f from 0.2 THz to 1.0 THz. In order to determine the transmission coefficient of the ML WS_2 film, the measurement was performed for both the ML WS_2/substrate system and the bare substrate sample, as documented previously [16] (see S2 in Supplement 1). The corresponding frequency-dependent electric field strength was obtained from a Fourier transformation of the measured experimental data. After that, the complex longitudinal MO conductivity $\sigma_L(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ for ML WS_2 on different substrates was calculated by using the Tinkham relation [16] with $\omega = 2\pi f$ the angular frequency of the radiation field. The real part $\sigma_1(\omega)$, reflects the THz MO response of ML WS_2 to the THz radiation field, corresponding to the energy dissipation or the optical absorption, while the imaginary part $\sigma_2(\omega)$, represents the energy exchange between the electrons and the radiation field.

3. RESULTS AND DISCUSSION

In Figs. 1 (a), (b) and (c), we show the real part of the longitudinal THz MO conductivity, $\sigma_1(\omega)$, as a function of the THz radiation frequency f, for ML WS_2 on three different substrates (Sapphire, Si/SiO_2 and Quartz) for different magnetic fields B at $T = 80$ K. As can be seen, in the absence of magnetic field ($B = 0$ T) and in the presence of a weak field ($B = 2$ T), the THz MO conductivity $\sigma_1(\omega)$ of ML WS_2 exhibits an almost linear dependence on the radiation frequency f for all three substrates. In particular, $\sigma_1(\omega)$ for $B = 0$, describing the THz optical absorption by free electrons in WS_2, gradually increases with the radiation frequency f, which is in agreement with our previous results [16]. However, with increasing field strength $B = 4, 6, 8$ T, the THz MO conductivity $\sigma_1(\omega)$ displays a distinct nonlinear/oscillating behavior as a function of the radiation frequency f. Moreover, the oscillating behavior of THz MO conductivities depends on the choice of the substrates.

To further understand the different THz MO responses of ML WS_2 to relatively weak and strong magnetic fields, we cal-

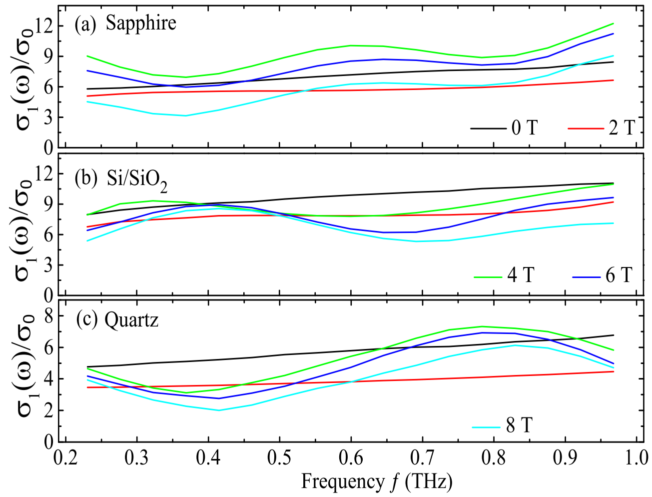

Fig. 1. The real part of the complex longitudinal MO conductivity, σ_1, for ML WS_2 as a function of the radiation frequency f on (a) sapphire, (b) Si/SiO_2 and (c) quartz substrate at temperature $T = 80$ K for different magnetic fields B as indicated.

culated the LLs spectrum E_N and the corresponding Fermi energy E_F as a function of the magnetic field B using an effective mass model with the parabolic energy dispersion. The Fermi level E_F is obtained from the electron density n_e given by $n_e = (2eB/\pi\hbar)\sum_N f(E_N)$ with f(x) the Fermi-Dirac function. $E_N = (N + 1/2)\hbar\omega_c$ are the LLs with $N(= 0, 1, 2, \cdots)$ the Landau Level index. The calculated results are shown in Fig. 2. We find that the B-dependence of E_F exhibits a nearly linear behavior for weak magnetic fields $B < 3$ T but a clearly oscillating feature for strong magnetic fields $B > 3$ T. This is because the LLs are quasi-continuous for relatively weak B (e.g. $B < 3$ T) but are well defined for relatively strong B (e.g. $B > 3$ T) due to magnetic quantization, as shown in Fig. 2. As the photon frequency increases, the energy gained by the electrons in quasi continuous states by optical absorption increases, resulting in more electronic transitions. The longitudinal MO conductivity induced by optical absorption increases with the radiation frequency increasing at relatively weak magnetic fields B. The high magnetic field B leads to strong electron-impurity interactions owing to the strong quantum confinement effect. The oscillating behaviors of the THz MO absorption as function of frequency f is due to random impurity and disorder scatterings from the substrate via both inter- and intra-LL transitions when $\hbar\omega_c = E_{N+1} - E_N = \hbar\omega$ can be achieved with $\omega_c = eB/m_e^*$ the cyclotron frequency [14, 15]. m_e^* is the effective mass of electrons. Furthermore, the LLs spectrum in ML WS_2 can exhibit a quasi-linear dependence on the magnetic field B within an effective Dirac model [15], which also leads to the weak nonlinear behaviors of MO conductivity at relatively strong magnetic fields B. However, the quasi-linear effect induced from pristine WS_2 is very weak and is not sensitive to the substrates. Here we observed substrate dependent THz MO conductivities. Therefore, we confirm that the oscillating behaviors of the THz MO conductivities primarily result from the strong electron-impurity interactions under strong magnetic fields.

Moreover, by fitting the experimental results to the longitudinal MO Drude-Smith formula which we derived self-consistently [18], we are able to obtain the key parameters for ML

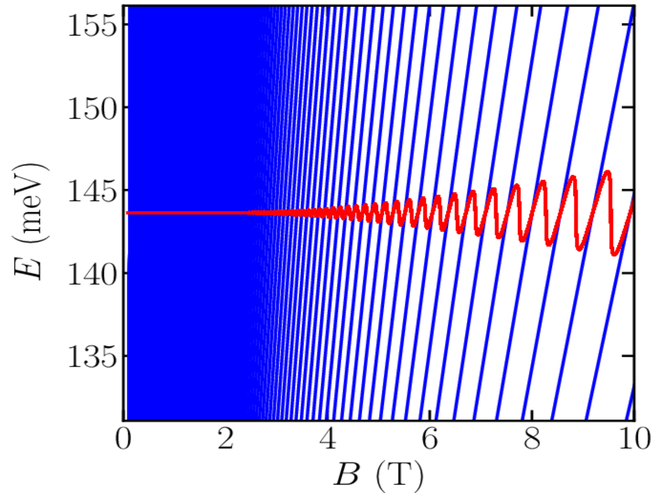

Fig. 2. The LL structure (blue lines) and the electron Fermi energy E_F (red line) as function of magnetic field B. The corresponding electron density is $n_e = 3 \times 10^{12}$ cm^{-2}.

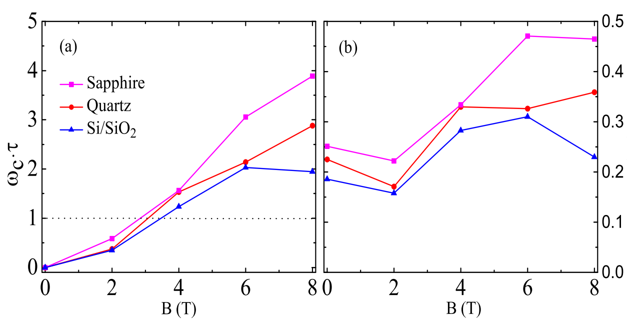

Fig. 3. (a) The $\omega_c\tau$ and (b) the electronic relaxation time τ as a function of magnetic fields B for ML WS_2 on different substrates at temperature $T = 80$ K.

WS_2 on different substrates, such as the free electron density n_e, the electronic relaxation time τ, and the electronic localization (EL) factor C by using [18]

$$\sigma_L(\omega) = \frac{\sigma_0 \cdot \kappa_c(\omega,\tau)}{(1 - i\omega\tau)^2 + (\omega_c\tau)^2}, \quad (1)$$

with

$$\kappa_c(\omega,\tau) = 1 + C - i\omega\tau - \frac{2C(\omega_c\tau)^2}{(1 - i\omega\tau)^2 + (\omega_c\tau)^2}. \quad (2)$$

Here $\sigma_0 = e^2 n_e \tau / m_e^*$ is the dc conductivity in the absence of a magnetic field ($B = 0$) with e the elementary charge. m_e^* is the effective mass of electrons [15, 19], which is the only input parameter when fitting the experimental results shown in Fig. 1. Furthermore, the EL factor C, varying between 0 and -1, describes the degree of EL induced by the localization effect of a magnetic field. The large $|C|$, reveals the strong EL effect of electrons. Our fitting results shows that the theoretically calculated THz MO conductivities can reproduce the experimental results (see S3 in Supplement 1). Thus we are able to obtain more fruitful and more important information of the electronic properties of materials utilizing THz TDS measurements by using magnetic fields and cryogenic technology, as compared with other spectroscopic techniques.

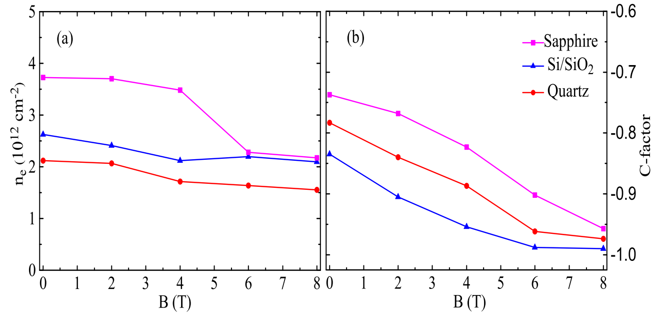

Fig. 4. The electron density n_e in (a), and the electronic localization factor C in (b) for ML WS_2 on three substrates as a function of magnetic field B.

As shown in Fig. 3 (a), it is found that the condition $\omega_c\tau > 1$ is satisfied when $B > 3$ T which signals well separated LLs. The electronic relaxation time τ is given in Fig. 3 (b). The strong magnetic field condition is satisfied, when $\hbar/\tau < \hbar\omega_c$, namely $\omega_c\tau > 1$, and the natural broadening of LLs is smaller than the energy interval between LLs. This agrees well with the theoretical findings in Fig. 2 where Landau quantization effect is significant for $B > 3$ T, and oscillations in the electronic density of states (DOS) and the Fermi energy E_F is evident. Notice nonlinear behavior in the electronic relaxation time τ with varying magnetic fields in Fig. 3 (b).

The electron density n_e and the EL factor C for ML WS_2 on the three substrates are presented in Fig. 4 as a function of magnetic field B. As can be seen, the EL factor C quasi-linearly approaches -1 as the magnetic field B increases, revealing that the EL effect is enhanced by the magnetic field. Meanwhile, the electron density n_e decreases with increasing magnetic field, e.g., from $n_e \sim 2 - 3.7 \times 10^{12}$ cm^{-2} at $B = 0$ T to $n_e \sim 1.5 - 2.2 \times 10^{12}$ cm^{-2} at $B = 8$ T. More remarkably, the electron density n_e, and the EL factor C are found to depend sensitively on the substrates. This dependence also applies to the THz MO conductivity $\sigma_1(\omega)$ and the electronic relaxation time τ, as shown in Figs. 1 and 3. The physical reasons for the substrate dependence of MO properties are as follows. The substrates have an impact on the LL spectrum due to an effective Zeeman field introduced by van der Waals force between substrates and ML WS_2 [3, 20]. It has been demonstrated that the exchange interaction induced by substrates can affect the THz optoelectronic properties of ML MoS_2 [20]. The different substrates can induce the different effective Zeeman fields that have an impact on the LL spectrum of ML WS_2. The effective Zeeman field is usually weak, but it can change the THz MO conductivity because the THz energy (1 THz $\sim$ 4.2 meV) is very small, which is sensitive to the small substrate-induced interactions. Furthermore, the strong magnetic field gives rise to a strong quantum confinement effect, which results in the strong electron-impurity scatterings and an electron localization effect [15]. Therefore, the effective free electron density n_e decreases with increasing of the magnetic field B as shown in Fig. 4 (a). As a result, we find the substrate-dependent electron-localization factor C increases with the magnetic field B enhances as shown in Fig. 4 (b). The substrate dependent behavior is consistent with the recent experimental findings [17]. Very recently, it was found that the impact of the substrate on the band structure and LLs of 2D materials are of significant importance for interpreting their electronic and optoelectronic properties [13, 15]. Our experimental results indicate that substrates can have profound effects on the electronic and optoelectronic properties of 2D materials in the presence of a magnetic field. The fabrication technology of 2D materials and devices, such as CVD method, distinctly dependent on the choice and quality of substrates [17]. Spintronic and valleytronic polarization in 2D electronic systems, such as ML WS_2, are realized by the breaking of the inversion symmetry from the substrates. Therefore, our research is of important for the development of novel 2D optoelectronic nano-devices.

4. CONCLUSION

In conclusion, the THz MO properties in ML WS_2 placed on different substrates are investigated using THz TDS technology in the presence of an external magnetic field. The THz MO conductivity shows an oscillating dependence on the photon frequency at strong magnetic field, in contrast to the linear dependence on the photon frequency in a weak magnetic field. The free electron density decreases and the EL effect increases as the magnetic field increases. The THz MO conductivity, and the electronic relaxation time depend sensitively on the choice of the substrate. Our study shows that THz TDS technology with tunable magnetic fields can not only obtain vital material parameters, but also be used to investigate the impact of substrates on the optoelectronic properties of 2D materials, such as the EL effect. We hope that our experimental results can provide additional useful information to expand the horizon of applications for ML WS_2 in novel spintronic and valleytronic THz nano-devices.

FUNDING.

This work was supported by the National Natural Science foundation of China (Grant Nos. 11604380 and 11774416).

DISCLOSURES.

The authors declare no conflicts of interest.

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. G. Fiori, F. Bonaccorso, G. Iannaccone, T. Palacios, D. Neumaier, A. Seabaugh, S. K. Banerjee and L. Colombo, "Electronics based on two-dimensional materials", Nature Nanotechnology **9**, 768 (2014).
2. E. J. Sie, J. W. McIver, Y. H. Lee, L. Fu, J. Kong and N. Gedik, "Valley-selective optical Stark effect in monolayer WS_2", Nature Materials **14**, 290 (2015).
3. S. Sattar, N. Singh, and U. Schwingenschlögl, "Proximity-induced spin-valley polarization in silicene or germanene on F-doped WS_2", Phys. Rev. B **94**, 205415 (2016).
4. L. Xu, M. Yang, L. Shen, J. Zhou, T. Zhu, and Y. P. Feng, "Large valley splitting in monolayer WS_2 by proximity coupling to an insulating antiferromagnetic substrate", Phys. Rev. B **97**, 041405(R) (2018).
5. D. Xiao, G. B. Liu, W. X. Feng, X. D. Xu, and W. Yao, "Coupled spin and valley physics in monolayers of MoS_2 and other group-VI dichalcogenides", Physical Review Letters **108**, 196802 (2012).
6. C. Mai, Y. G. Semenov, A. Barrette, Y. F. Yu, Z. H. Jin, L. Y. Cao, K. W. Kim, and K. Gundogdu, "Exciton valley relaxation in a single layer of WS_2 measured by ultrafast spectroscopy", Phys. Rev. B **90**, 041414(R) (2014).
7. P. Nagler, M. V. Ballottin, A. A. Mitioglu, M. V. Durnev, T. Taniguchi, K. Watanabe, A. Chernikov, C. Schüller, M. M. Glazov, Peter. C. M. Christianen, and T. Korn, "Zeeman Splitting and Inverted Polarization of Biexciton Emission in Monolayer WS_2", Physical Review Letters **121**, 057402 (2018).
8. P. Kapuściński, D. Vaclavkova, M. Grzeszczyk, A. O. Slobodeniuk, K. Nogajewski, M. Bartos, K. Watanabe, T. Taniguchi, C. Faugeras, A. Babiński, M. Potemski and M. R. Molas, "Valley polarization of singlet and triplet trions in a WS_2 monolayer in magnetic fields", Phys. Chem. Chem. Phys. **22**, 19155 (2020).
9. R. Ulbricht, E. Hendry, J. Shan, T. F. Heinz, and M. Bonn, "Carrier dynamics in semiconductors studied with time-resolved terahertz spectroscopy", Rev. Mod. Phys. **83**, 543 (2011).
10. A. M. Shuvaev, G. V. Astakhov, C. Brüne, H. Buhmann, L. W. Molenkamp and A. Pimenov, "Terahertz magneto-optical spectroscopy in HgTe thin films", Semicond. Sci. Technol. **27**, 124004 (2012).
11. A. M. Shuvaev, G. V. Astakhov, A. Pimenov, C. Brüne, H. Buhmann, and L. W. Molenkamp, "Giant Magneto-Optical Faraday Effect in HgTe Thin Films in the Terahertz Spectral Range", Physical Review Letters **106**, 107404 (2011).
12. N. Kamaraju, W. Pan, U. Ekenberg, D. M. Gvozdić, S. Boubanga-Tombet, P. C. Upadhya, J. Reno, A. J. Taylor, and R. P. Prasankumar, "Terahertz magneto-optical spectroscopy of a two-dimensional hole gas", Applied Physics Letters **106**, 031902 (2015).
13. S. Che, P. Stepanov, S. P. Ge, M. L. Zhu, D. Y. Wang, Y. J. Lee, K. Myhro, Y. M. Shi, R. Y. Chen, Z. Q. Pi, C. Pan, B. Cheng, T. Taniguchi, K. Watanabe, Y. Barlas, R. K. Lake, M. Bockrath, J. Hwang, and C. N. Lau, "Substrate-Dependent Band Structures in Trilayer Graphene/h-BN Heterostructures", Physical Review Letters **125**, 246401 (2020).
14. D. Muoi, N. N. Hieu, C. V. Nguyen, B. D. Hoi, H. V. Nguyen, N. D. Hien, N. A. Poklonski, S. S. Kubakaddi, and H. V. Phuc, "Magneto-optical absorption in silicene and germanene induced by electric and Zeeman fields", Phys. Rev. B **101**, 205408 (2020).
15. N. D. Hien, C. V. Nguyen, N. N. Hieu, S. S. Kubakaddi, C. A. Duque, M. E. Mora-Ramos, L. Dinh, T. N. Bich, and H. V. Phuc, "Magneto-optical transport properties of monolayer transition metal dichalcogenides", Phys. Rev. B **101**, 045424 (2020).
16. H. M. Dong, Z. H. Tao, L. L. Li, F. Huang, W. Xu, and F. M. Peeters, "Substrate dependent terahertz response of monolayer WS_2", Appl. Phys. Lett. **116**, 203108 (2020).
17. H. Yin, X. D. Zhang, J. W. Lu, X. M. Geng, Y. F. Wan, M. Z. Wu, and P. Yang, "Substrate effects on the CVD growth of MoS_2 and WS_2", J. Mater. Sci. **55**, 990 (2020).
18. F. W. Han, W. Xu, L. L. Li, and C. Zhang, "A generalization of the Drude-Smith formula for magneto-optical conductivities in Faraday geometry", J. Appl. Phys. **119**, 245706 (2016).
19. A. Kormányos, V. Zólyomi, N. D. Drummond, and G. Burkard, "Spin-orbit coupling, quantum dots, and qubits in monolayer transition metal dichalcogenides", Phys. Rev. X **4**, 011034 (2014).
20. X. N. Zhao ,W. Xu, Y. M. Xiao, J. Liu, B. Van Duppen, and F. M. Peeters, "Terahertz optical Hall effect in monolayer MoS_2 in the presence of proximity-induced interactions", Phys. Rev. B **101**, 245412 (2020).