Research article

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All-optical dynamic tuning of local excitonic emission of monolayer MoS₂ by integration with Ge₂Sb₂Te₅

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Abstract: Strong quantum confinement and coulomb interactions induce tightly bound quasiparticles such as excitons and trions in an atomically thin layer of transitional metal dichalcogenides (TMDs), which play a dominant role in determining their intriguing optoelectronic properties. Thus, controlling the excitonic properties is essential for the applications of TMD-based devices. Here, we demonstrate the all-optical tuning of the local excitonic emission from a monolayer MoS₂ hybridized with phase-change material Ge₂Sb₂Te₅ (GST) thin film. By applying pulsed laser with different power on the MoS₂/GST heterostructure, the peak energies of the excitonic emission of MoS₂ can be tuned up to 40 meV, and the exciton/trion intensity ratio can be tuned by at least one order of magnitude. Raman spectra and transient pump-probe measurements show that the tunability originated from the laser-induced phase change of the GST thin film with charge transferring from GST to the monolayer MoS₂. The dynamic tuning of the excitonic emission was all done with localized laser pulses and could be scaled readily, which pave a new way of controlling the excitonic

emission in TMDs. Our findings could be potentially used as all-optical modulators or switches in future optical networks.

Keywords: 2D materials; exciton; all-optical; integration; photoluminescence.

1 Introduction

Two-dimensional (2D) materials, such as graphene [1], black phosphorus [2–6], topological insulators [7, 8], and transitional metal dichalcogenides (TMDs) [9–13], with extraordinary optical and electronic properties in fundamental physics and optoelectronic applications [14, 15], have aroused enthusiasm in researchers recently. In particular, the strong excitonic effects that originated from tight quantum confinement and coulomb interactions make the direct-bandgap TMDs stand out from other 2D materials [16, 17], which play an essential role in determining their optical properties, including absorption [18–20], photoluminescence (PL) [21, 22], second harmonic generation [23, 24], spin-orbit coupling [25, 26], and quantum emission [27]. In addition, other exciton complexes, such as charged excitons (trions) [17, 28], biexcitons [29, 30], and dark excitons [31, 32], have also been observed in TMDs. Besides, TMD-based optoelectronic devices, such as atomically thin transistors [33, 34], photodetectors [35, 36], and photodiodes [37, 38], have already been accomplished, and it turns out that their performances are closely related to excitonic properties. Therefore, it is of great significance to control the excitonic properties of TMDs.

The excitons in TMDs are sensitive to the environment. Moreover, various methods have been developed to manipulate the excitonic properties, among which the control of the excitonic emission is the essential part. For instance, the excitonic emission peak can be tuned across tens of meV when changing the ambient temperature from 4 K to room temperature [30, 39]. Electrical doping

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has been shown as a powerful tool to tune the excitonic emission between neutral excitons and charged ones and the exciton binding energy above 100 meV [40, 41]. Strain have also been demonstrated as an effective tool to tune the exciton emission energy peak over tens of meV per 1% strain [11, 12]. Magnetic field was used to tune the emission energy and polarization induced by spin-orbit coupling [42, 43]. Chemical doping [44] and composition engineering [45, 46] also show great power to control the excitonic emission. In addition, integration with photonic nanostructures, including metallic plasmonic structures [47–52] and silicon dielectric structures [53–55], have been demonstrated to tune the excitonic emission from monolayer TMDs effectively. However, the methods that used to control the excitonic emission mentioned above rely on either complicated instruments or sophisticated fabrication procedures, and most of which are not scalable and nonlocal. It is desirable to develop easy and all-optical ways to dynamic tune the excitonic emission of monolayer TMDs locally.

Here, we demonstrate an all-optical localized tuning of the excitonic emission from a monolayer MoS₂, which is hybridized with a phase-change material Ge₂Sb₂Te₅ (GST) thin film. The emission energy peak is tuned over 40 meV dynamically by merely changing the power of the switching laser. The exciton/trion intensity ratio is tuned by at least one order of magnitude. The tuning originates from that the switching laser effectively changes the phase states of GST, causing a change in the dielectric environment for the monolayer MoS₂. Further investigation, including Raman and transient absorption microscopy measurements, show that charge transfer from GST to the monolayer MoS₂ is the primary factor that tunes the excitonic emission. To the best of our knowledge, this is the first time that such a monolayer MoS₂/GST heterostructure is investigated. Our findings provide an all-optical and localized way to engineer the excitonic emission from atomically thin TMDs effectively, and the method is easy to operate. Besides, the tuning we demonstrate here is all done with laser pulses and can be scaled readily, offering new opportunities for all-optical active components such as modulators or switches in future optical networks.

2 Results and discussion

2.1 Sample preparation and characterization

Phase-change materials, the kind that can be switched between their distinct amorphous and crystalline states

upon external stimulus, have been widely used for optical data storage [56, 57] and recently attracted great attention in applications for photonic logic devices [58]. For these applications, a dramatic change in the properties between the amorphous and crystalline states plays the central role, and the broad multilevel tunability of phase-change materials shows great potential in applications in novel photonic devices. Here, we built a heterostructure consisting of a monolayer MoS₂ and a GST thin film. By encoding the states of the GST thin film through optical pulse of different power, we expected to tune the excitonic emission dynamically in an all-optical way. The structure is schematically shown in Figure 1A. Here, an 800 nm femtosecond laser 1 was used as a switching laser to change the state of GST. Another laser 2 was used to probe the transmission of heterostructures or excite the PL/Raman of the monolayer MoS₂.

First, a typical phase-change material GST film was deposited by magnetron sputtering on a sapphire substrate. Then, a monolayer MoS₂ exfoliated from crystals was then dryly transferred onto the GST film. The optical image of the sample is shown in Figure 1B, where we can observe a good contrast between the GST film and MoS₂. The monolayer nature of MoS₂ and the initial amorphous state of the GST film were confirmed by Raman signals as shown in the Figure S1A and B, respectively. To check the quality and tunability of the GST film, we measured the relative change of the transmittance ($\Delta T/T$) under optical pulse excitation of different fluence, as shown in Figure 1C (blue line). Here, we used 800 nm femtosecond laser (65 fs, 500 Hz) as the modulating beam to induce the state change. A 1064 nm laser beam (65 fs, 500 Hz) was used to monitor the change of the transmittance. Note that power of the 1064 nm laser was low enough, which did not induce any phase change in the GST film. As shown in Figure 1C, the transmittance changed dramatically under external laser pulse treatment, indicating a phase transition in the GST film. By carefully tuning the modulation laser pulse fluence, we can successfully tune the GST film into seven distinct states as reflected by the transmittance change, which showed that the GST film was of high quality. After the monolayer MoS₂ transferred, the transmittance change of the heterostructure was measured again upon the same modulating beam, as shown in Figure 1C (pink line). The seven modulated states remained; however, some new features came up. The $\Delta T/T$ overlapped with the pure GST film when the modulating fluence was $<5 \text{ mJ/cm}^2$, whereas it deviated and became smaller compared to the pure GST film for larger fluence, and the deviation got bigger with increasing modulation fluence. The observation indicated

Figure 1: Characterization and schematic diagram of the MoS₂/GST heterostructure.

(A) Principal schematic diagram of dual-light modulating probe experiments. In this system, 800 nm femtosecond laser 1 was used as a switching laser to change the GST state. Another laser 2 was used to probe the transmission of materials or excite the PL. (B) Optical photograph of the MoS₂/GST heterostructure. The height of GST was about 73 nm. (C) Relative transmittance changes of GST and the MoS₂/GST heterostructure under 1064 nm laser probe, in which the state of GST was modulated by 800 nm femtosecond. In this process, the fluence of 800 nm laser varied from 1 to 16 mJ/cm² and the fluence of 1064 nm laser was fixed at 0.2 mJ/cm².

coupling between the monolayer MoS₂ and the GST film, and coupling strength changed with different modulating laser pulses.

2.2 Dynamic tuning of the excitonic emission

As discussed above, external modulating laser beam pulse can encode the MoS₂/GST heterostructure into seven distinct states effectively, implying its capability of dynamically tuning the excitonic emission of the monolayer MoS₂. Indeed, the PL spectra change dramatically when applying an 800 nm external modulating laser, as shown in Figure 2A. Here, a 405 nm continuous-wave laser with constant fluence is used to excite the PL, and controlled measurements show that the PL spectra of the monolayer MoS₂ do not change over time with 405 nm laser excitation in this low-power regime. As the modulating laser energy is below the bandgap of the monolayer MoS₂, it can be inferred that the solely source of spectral change of the MoS₂/GST heterostructure comes from the phase change of GST and their coupling.

To further explore how the spectral tuning works in this heterostructures, the spectra of the PL are fitted into three Gaussian peaks, which can be assigned to originate from the radiative combination of A⁻ trion, A exciton and B exciton consistent with previous reports [17, 44, 59]. As our experiment result, PL spectra of MoS₂/GST heterostructure come from the emission of the monolayer MoS₂. Therefore, the typical spectra of the monolayer MoS₂ and fittings are shown in Figure 2B. All data of fitting results

are given out in Figure S2. As illustrated in Figure 2C, the peak energies of these three components are tuned over 40 meV by changing the modulating laser beam fluence, though they show different trends. The A exciton peak energy increases with increasing modulating laser fluence and starts to saturate when the fluence exceeds 10 mJ/cm². The A⁻ trion and B exciton peak energies show the opposite trend when the fluence is below 10 mJ/cm², then it starts to increase with increasing laser power. The mechanism of this phenomenon is not particularly clear for the time being. We suppose that there are two competing processes ongoing in the heterostructures with increasing incident fluence. On one hand, more neutral excitons are generated with stronger incident light. On the other hand, electrons from GST films combine with neutral excitons to form A⁻ trions. These two processes together determine the ration of proportion of A⁻ trions together. As show in Figure 2D, the intensity ratio of these three components change over one order of magnitude with increasing modulating laser fluence. Both the A⁻/A and A⁻/B intensity ratio increases with increasing fluence, and a sudden change happens at the fluence around 10 mJ/cm².

Raman spectra are also recorded during all the measurements to identify the changes in the MoS₂/GST heterostructure, as shown in Figure 3A, the signals in the region 100 to 200 cm⁻¹ and 350 to 450 cm⁻¹ originate from the GST film and monolayer MoS₂, respectively. The spectra of these two regions are intercepted from Figure 3A, as shown in Figure 3B and C, in order to show the trend clearly. Figure 3B displays changes of the Raman spectra with increasing modulating fluence, indicating the phase

Figure 2: PL signal of the MoS₂/GST heterostructure.

(A) PL of the heterostructure at different modulating fluence ranging from 1 to 20.7 mJ/cm². The PL peak of A exciton, B exciton, and A⁻ trion are indicated by purple, green, and blue solid lines, respectively. (B) Typical Gaussian fitting of the MoS₂ spectra with three peaks under 5 mJ/cm² modulating fluence. The PL peaks of A⁻ trion, A exciton, and B exciton were 1.809, 1.892, and 1.994 eV respectively. The dashed lines are the Gaussian fits, the gray solid line is the measured data, and the green solid line is the sum of the three Gaussian fittings.

(C) Energy peak change of A exciton, B exciton, and A⁻ trion with increasing modulating fluence. (D) Intensity ratio changes of A⁻/B and A⁻/A with increasing modulating fluence.

transition from amorphous to the crystalline states, which are consistent with previous reports [60, 61]. For the monolayer MoS₂, the Raman spectra do not change as much as the GST film with increasing laser fluence, as can be seen from Figure 3C, while the two Raman modes behave differently. To further understand the Raman spectra of the monolayer MoS₂, we fit the two modes E_{2g}^1 and A_{1g} into Gaussian shapes and extract the peak position, and the changes of peak positions with increasing modulating fluence are presented in Figure 3D. The mode A_{1g} downshifts with increasing modulating laser beam fluence, while the mode E_{2g}^1 keeps almost unchanged. There is an abnormal data A_{1g} on the incident laser fluence of 20 mJ/cm². And we give out more details on the upshift A_{1g} in Figure S3. Raman spectroscopy is a powerful tool to detect the coupling mechanism in 2D materials, the observed phenomena indicate that there is net charge transferred

between the GST film and the monolayer MoS₂ [62–64]. Combined with the findings shown in Figure 2D that the proportional of A⁻ trion rises with the increase of modulating laser fluence, it can be inferred that there is net electron transferring from GST film to the monolayer MoS₂, as schematically illustrated in Figure 4A. Combining with the possible energy band as showed in Figure S4, when the GST film is amorphous state in MoS₂/GST heterostructure as show in Figure 4A left, the electron will not transfer to MoS₂ from GST in a large number. However, in the process of GST changing from amorphous to crystalline, a large number of electrons are generated in GST. And then electrons, which in GST film would transfer to MoS₂, will combine with excitons to form trions as Figure 4A right shows.

To further confirm our assumption, transient pump-probe measurements were implemented upon the

Figure 3: Raman spectra of the MoS₂/GST heterostructure.

(A) Raman spectra of the MoS₂/GST heterostructure with different modulating beam fluence. (B and C) Raman spectra of GST (B) and MoS₂ (C) extracted from (A). (D) Change of extracted Raman peaks of A_{1g} and E_{2g}^1 with increasing modulating fluence.

Figure 4: Schematic diagram of the charge transfer in the MoS₂/GST heterostructure and the transient pump-probe measurements.

(A) Schematic diagram of the charge transfer in the MoS₂/GST heterostructure. In the process of GST changing from amorphous to crystalline state, net electron transferred from GST to the monolayer MoS₂, and these electrons combined with neutral excitons in MoS₂ and formed trions. (B) Pump-probe measurements of MoS₂ and the MoS₂/GST heterostructure. Pumping light was 500 nm femtosecond laser, and the probe laser was white laser.

MoS₂/GST heterostructure. The transient pump-probe set up is demonstrated in Figure S6. Figure 4B shows both the relaxation process of the heterostructure and the

monolayer MoS₂ excited by a 500 nm laser of 40 $\mu\text{J}/\text{cm}^2$. The fast and slow fitting relaxation time results of the pump probe are given in Table S7. We focused on the

probe data of 653 nm wavelength, which was the peak of A exciton. From the result, fast relaxation time was 1.74 ps and the slow relaxation time was 34.47 ps in the monolayer MoS₂. In contrast, the fast and slow relaxation times were 1.43 and 11.86 ps, respectively, in the MoS₂/GST heterostructure. The fast relaxation is mainly connected to the relaxing of A exciton generated in the monolayer MoS₂, and the slow relaxation is likely related to the process of electrons combining with A exciton and forming A⁻ trions. Therefore, it is possible that A exciton combines with electrons, making the relaxation time in the heterostructure much quicker than that in the monolayer MoS₂ [65–69]. As such, it can be concluded that the charge transfer from the GST film to the MoS₂ monolayer was the main factor that induced the PL emission change.

3 Conclusion

In summary, a novel heterostructure consisting of a monolayer MoS₂ and a GST thin film was developed, demonstrating the localized all-optical dynamic tuning of the excitonic emission from the monolayer MoS₂, which was realized by laser-induced phase transition in the GST film. The excitonic emission peak can be dynamic tuned up to 40 meV and the exciton/trion intensity ratio can be tuned by one order of magnitude. Raman spectra and transient pump-probe measurements showed that there was a net electron transfer from the GST film to the monolayer MoS₂ when the GST film changed from amorphous to crystallized state, which was the dominant factor that induced the spectral tuning. In our scheme, tunability can be simply implemented by a focused femtosecond laser beam; thus, it can induce local tuning randomly and be readily scalable. Our findings pave a novel way to all-optical dynamic tuning of the excitonic emission of monolayer TMDs, which could be potentially used in all-optical devices such as modulators and switches.

4 Experimental section

4.1 Sample preparation and characterization

The monolayer MoS₂ was mechanically exfoliated from bulk crystal MoS₂ and then dryly transferred onto the GST continuous film, which was magnetron sputtered to sapphire substrate. The thickness and roughness of GST was characterized by atomic force microscopy.

4.2 Confocal dual-beam spectroscopic system

In our measurements, including transmission, PL, and Raman spectra, two laser beams were aligned following the same optical path before reaching the sample, under a home-built confocal spectroscopic system, as schematically shown in Figure S8. A Ti:sapphire laser (Spectra-Physics 800 nm, 1 kHz, Santa Clara, CA, USA) was used as the modulating laser to change the states of GST, and an optical chopper (Thorlabs, MC2000B-EC, Newton, NJ, USA) was used to chop the repetition rate from 1 kHz to 500 Hz. A continuously adjustable neutral density filter (Thorlabs, NDL-10C-4, Newton, NJ, USA) was adopted to adjust the intensity of incident light.

In the transmission measurements, the probing light (1064 nm, 65 fs, 500 Hz, 0.2 mJ/cm²) from an optical parametric amplifier (TOPAS) was used to monitor the relative transmission change of the MoS₂/GST heterostructure. Its intensity was much weaker than the modulating beam and would not induce any change to the sample. To increase the signal-to-noise ratio, the probing light was split into two paths, one went through the sample for measurement and the other one went to a photodetector for reference; dual-channel lock-in amplifiers were used for the measurements. In our experiment, modulating light irradiated onto the MoS₂/GST heterostructure for about 1 min to change GST to a different state, and then probing light took the place of modulating light to measure the transmittance change. After one state was recorded, modulating light was applied again with the next increased fluence.

In the PL measurements, PL spectra were collected by confocal microscopy (Leica DM-2700M, Wetzlar, Germany; objective, ×50) and recorded by a spectrometer (ANDOR SR-500i-B1-R, Belfast, UK) equipped with a CCD and a TCSPC detector. A laser diode ($\lambda = 405$ nm) was used as PL pump laser, and the power was kept low at about 300 nW. The measurements followed the similar procedures as the transmission measurements, except that we took the PL signal instead of the relative transmission change.

Raman spectra were taken in a similar way as the PL, the difference was that the pump laser of Raman spectroscopy was 532 nm continuous-wave laser, and the spectrometer switched to Raman gear.

4.3 Femtosecond pump-probe spectroscopy

The ultrafast transient spectra of MoS₂ and the MoS₂/GST heterostructure was measured by femtosecond pump-probe spectroscopy at room temperature.

In the experimental setup, a strong beam (90%) of the Ti:sapphire laser (Spectra-Physics, 800 nm) with a pulse width of 65 fs and a repetition rate of 1 kHz was delivered to an optical parametric amplifier (TOPAS, Coherent) to generate pump pulse, with a center wavelength of 500 nm. The other small portion (10%) of the Ti:sapphire laser was focused into a sapphire crystal to generate a supercontinuum of white light ranging from 450 to 750 nm, which served as the probe beam. The dynamics of the photoinduced signal were obtained with a computer-controlled delay-line on the pump path. To ensure a good signal-to-noise ratio, the TA signal was acquired by averaging the data from 12,000 samplings.

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