Conference materials
UDC 535.015
DOI: https://doi.org/10.18721/JPM.153.221

Phase-change periodic surface structures for engineering of excitonic photoluminescence in WS_2 monolayers

P. I. Trofimov [1]✉, T. Ivanova [1], P.I. Lazarenko [2], M. Fedyanina [2], I.S. Sinev [1]

[1] Department of Physics and Engineering, ITMO University, St. Petersburg, Russia;
[2] National Research University of Electronic Technology, Zelenograd, Moscow, Russia
✉ p.trofimov@metalab.ifmo.ru

Abstract. Due to their two-dimensional nature, transition metal dichalcogenide monolayers exhibit extremely strong sensitivity of their excitonic response to the permittivity of the surrounding medium. Here, we show that the intensity and wavelength of their excitonic photoluminescence can be spatially modulated by periodic structures induced by laser pulses in phase change material films.

Keywords: phase change materials, $Ge_2Sb_2Te_5$, transition metal dichalcogenides, WS_2, laser induced periodic surface structures, phase change gratings, exciton screening

Funding: The reported study was funded by RFBR according to the research project № 20-32-90220.

Citation: Trofimov P. I., Ivanova T. V., Lazarenko P. I., Fedyanina M. E., Sinev I. S., Phase-change periodic surface structures for engineering of excitonic photoluminescence in WS_2 monolayers, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 15 (3.2) (2022) 113–117. DOI: https://doi.org/10.18721/JPM.153.221

Материалы конференции
УДК 535.015
DOI: https://doi.org/10.18721/JPM.153.221

Индуцированные лазером периодические поверхностные структуры с модуляцией фазового состояния для управления экситонной фотолюминесценцией монослоев WS_2

П. И. Трофимов [1] ✉, Т. Иванова [1], П. И. Лазаренко [2],
М. Е. Федянина [2], И. С. Синев [1]

[1] Физико-технический факультет, Университет ИТМО, Санкт-Петербург, Россия;
[2] Московский институт электронной техники, Зеленоград, Москва, Россия
✉ p.trofimov@metalab.ifmo.ru

Аннотация. Из-за своей двумерной природы монослои дихалькогенидов переходных металлов проявляют чрезвычайно сильную чувствительность своего экситонного отклика к диэлектрической проницаемости окружающей среды. В данной работе мы показываем, что интенсивность и длина волны их экситонной фотолюминесценции могут быть пространственно модулированы периодическими структурами, индуцированными лазерными импульсами в пленках материалов с фазовой памятью.

Ключевые слова: материалы с фазовой памятью, $Ge_2Sb_2Te_5$, дихалькогениды переходных металлов, WS_2, индуцированные лазером периодические поверхностные структуры, экранирование экситона

Финансирование: Исследование выполнено при финансовой поддержке РФФИ в рамках научного проекта № 20-32-90220.

Ссылка при цитировании: Трофимов П. И., Иванова Т. В., Лазаренко П. И., Федянина М.

Е., Синев И. С. Индуцированные лазером периодические поверхностные структуры с модуляцией фазового состояния для управления экситонной фотолюминесценцией монослоев WS_2 // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.2. С. 113–117. DOI: https://doi.org/10.18721/ JPM.153.221

Introduction

Two-dimensional transition metal dichalcogenides (TMDC) have attracted a lot of attention in photonics due to their strong excitonic effects, flexibility and tunability. Large exciton binding energy, and high quantum yield found in such materials already established them as a strong candidates for polaritonics, lasing and engineering of single photon emitters [1]. Moreover, the optical response of such systems can be manipulated using various methods such as gate voltage, doping, magnetic field and nonlinear effect which can influence the coupling constants in polariton systems, shift the wavelength of single photon emitters or control the handedness of circularly polarized light emission.

Another way to control the exciton binding energy in TMDC is to tune its dielectric environment, in particular static dielectric constant of the surrounding media which affects the exciton screening. Tuning of refractive index has already been implemented using various methods, such as chemical doping, optical pumping of free carriers in material, electrical or thermal switching of liquid crystals or VO_2 based nanostructures [2]. From this standpoint, the phase switching between crystalline and amorphous phase of chalcogenide phase-change materials (PCM) might be a promising technique, as it provides tuning of both refractive index at optical frequencies and static dielectric permittivity [3]. Heating and subsequent melt-quenching of these materials induced by optical or electrical pulses results in rapid nanosecond-scale reversible switching between its phase states [4]. Furthermore, it was recently shown that the irradiation of PCM thin films with femtosecond laser pulses results in the formation of periodic modulation of the phase state of the film with period and direction defined by wavelength and polarization of the laser radiation [5]. The mechanism of their formation is well described within the concept of laser-induced periodic surface structures (LIPSS) [6].

In this work we studied how phase-change LIPSS formed in $Ge_2Sb_2Te_5$ (GST) thin films and covered by a WS_2 monolayer affect the optical properties of the latter, in particular the wavelength and the intensity of its excitonic photoluminescence.

Results and Discussion

First we fabricated WS_2-GST heterostructures, the details of fabrication could be found in "Experiment Details" section. After that we studied the fabricated heterostructures with optical microscopy which allowed us to observe the reflection image of the sample, as well as the integrated photoluminescence (PL) signal, which was excited with UV range lamp and detected using a longpass filter. In the reflection image of the imprinted GST grating, one can observe the periodic modulation of the refractive index in the visible spectral range (Fig. 1, *a*). Such modulation confirms the formation of the periodic structures of different phase in GST film. In the image of the integral PL from the WS_2 monolayer (Fig. 1, *b*) we observed the suppression of the PL signal in the areas of monolayer above the crystalline GST lines of the grating compared with high PL signal above amorphous ones. We interpret such modulation as the result of enhanced exciton screening in WS_2 monolayer due to higher static dielectric permittivity of the crystalline GST [8], which in turn promotes the PL signal suppression.

To explore in more detail the impact of GST phase state on the WS_2 monolayer optical response we mapped the photoluminescence spectra of the fabricated samples at room and cryogenic temperatures (see for the details of the mapping in Experimental section). The obtained spectra of the monolayer are shown in Figure 1, *c*. We observed the 616 nm exciton peak at 295 K (blue curve) and 593 nm at 6.3 K (red curve). To study how the modulation of the dielectric permittivity induced with GST phase grating affects the position and intensity of the PL signal we

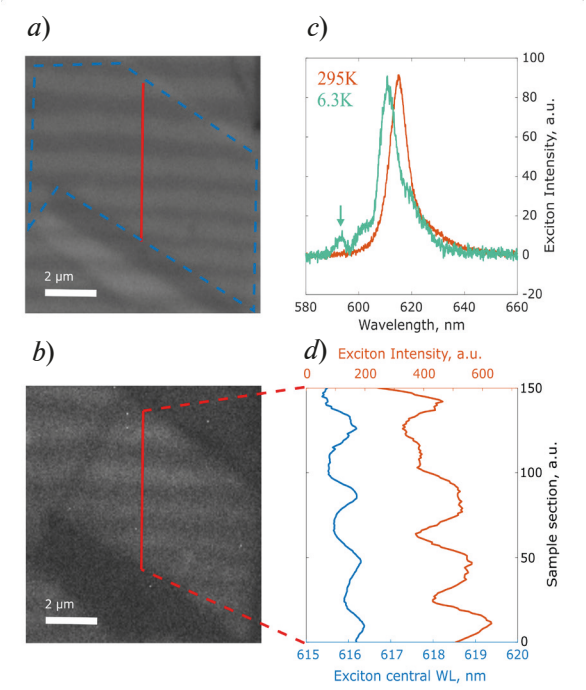

Fig. 1. Reflection (*a*) and integral photoluminescence from WS_2 monolayer on a phase-change GST grating (*b*). Blue dashed line in denotes the area of the grating covered with transferred WS_2 monolayer (*a*). Photoluminescence spectra of the WS_2 monolayer at 295K (red) and 6.3K (green). Green arrow indicates the exciton peak at 6.3K (*c*). Spectral position (blue) and intensity of the exciton (orange) along its section (red line on (*a*, *b*)) at 295K (*d*)

simultaneously excited a large area of the monolayer. After that, using Lorentz fitting of the measured data, we extracted the peak position and intensity of the measured PL signal along a section perpendicular to the grating lines. We observed the suppression of the intensity and an approximately 0.5 nm blue shift of the PL signal above the crystalline lines (Fig. 1, *d*). Such a small change in the exciton spectral position despite the strong exciton intensity modulation is a result of two counteracting effects: renormalization of the band gap of the WS_2 monolayer and a change in the exciton binding energy. We were unable to observe such modulation at cryogenic temperatures due to large aberrations of the optical setup which significantly lowered the spatial resolution of our system.

Finally, to complete the concept of manipulation of the excitonic response of the GST-WS_2 heterostructure, we studied the reversible switching of PL signal of the monolayer transferred onto a non-patterned as-deposited GST film (Fig. 2). During the experiment we switched GST film under the WS_2 monolayer into crystalline state using CW 633 nm laser and observed the suppression of the PL signal (Fig. 2, *b*) along the whole structure in agreement with our previous results for GST phase grating. After that, we restored the initial

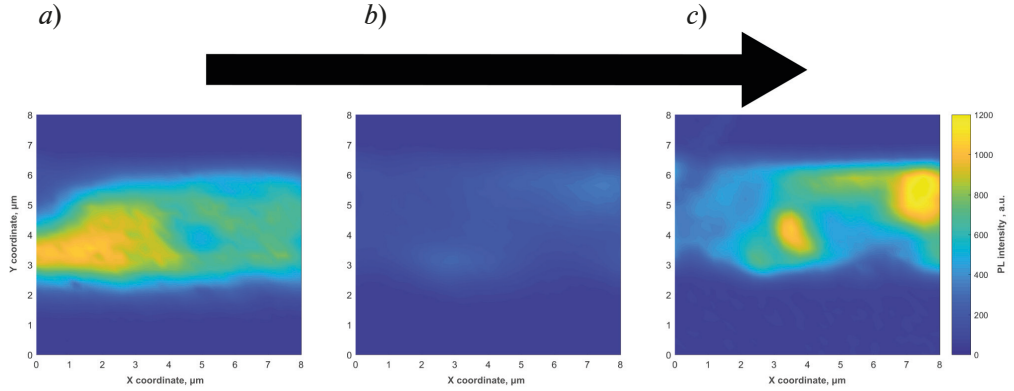

Fig. 2. Photoluminescence maps of the WS_2 monolayer on GST film cycled through different phase states: as deposited amorphous state (*a*); crystalline state (b); reamorphized state (*c*)

amorphous state of the GST film using single femtosecond laser pulses (1047 nm, 20 Hz, 150 fs) which resulted in partial restoration of the exciton signal intensity (Fig. 2, *c*). The heterogeneity of PL signal observed during the experiment could be caused by increase of roughness of the GST film during its phase transformation which in turn resulted in different level of adhesion and local stress of the monolayer that significantly affected its photoluminescence intensity.

Experiment Details

We fabricated WS_2-GST LIPSS heterostructure in three steps. First, we deposited 50 nm film of $Ge_2Sb_2Te_5$ (GST) phase change material on a W substrate using magnetron sputtering. After that we irradiated the sample with femtosecond laser pulses (80 MHz, 290 fs, 700–2000 nm) while scanning it through the laser beam waist at a speed of 10–100 um/s. This process resulted in the formation of periodic surface structures of the amorphous and crystalline GST phases, as described in our previous work [7]. Finally, we exfoliated the high quality monolayer flakes of WS_2 material from commercial bulk crystals and dry-transferred them onto the patterned GST film using scotch and custom-built transfer system.

To obtain maps of photoluminescence spectra of the fabricated samples at room and cryogenic temperatures we used CW laser source with 532 nm wavelength (Torus). The laser was focused onto the back focal plane of the objective to simultaneously excite a large area of the sample. To study the optical properties at cryogenic temperatures the sample was placed into the cell of a closed-cycle He cryostat which maintained a temperature of 6.3 K. The excited photoluminescence was collected with a high numerical aperture objective and focused with a large focal length lens onto the entrance slit of the spectrometer (Princeton Instruments) with a liquid nitrogen cooled CCD camera.

Conclusion

To conclude, we studied the optical properties of the WS_2-GST heterostructure. We showed that the photoluminescence response of the WS2 monolayer, in particular, the spectral position and intensity of the excitonic PL peak can be modulated using LIPSS imprinted in the underlying GST film. We also demonstrated that cycling between crystalline and amorphous phase state of GST film covered with WS_2 monolayer results in suppression and partial restoration of its PL signal. These results shows great potential of phase-change LIPSS – TMD platform for dynamic control the excitonic response, utilizing the process of fast and reversible switching between GST phase states.

Acknowledgments

The reported study was funded by RFBR according to the research project № 20-32-90220.

REFERENCES

1. **Mak K. F., Shan J.,** Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides, Nature Photonics 2016, 10, 216–226.

2. **Cui et al.,** Tunable Metasurfaces Based on Active Materials, Adv. Funct. Mater. 2019, 29, 1806692.

3. **Wuttig M., Taubner T.,** Phase-change materials for non-volatile photonic applications, Nature Photonics 2017, 11, 465–476.

4. **Au Y-Y et al.,** Phase-change devices for simultaneous optical-electrical applications, Sci. Rep. 2017, 7, 9688.

5. **Kozyukhin S. et al.,** Specific Features of Formation of Laser-Induced Periodic Surface Structures on $Ge_2Sb_2Te_5$ Amorphous Thin Films under Illumination by Femtosecond Laser Pulses, Phys. Status Solidi B 2020,257, 1900617.

6. **Bonse J., Gräf S.,** Maxwell Meets Marangoni—A Review of Theories on Laser-Induced Periodic Surface Structures, Laser Photon. Rev. 2020, 14, 10, 2000215.

7. **Trofimov P. et al.,** Rewritable and Tunable Laser-Induced Optical Gratings in Phase-Change Material Films, ACS Appl. Mater. Interfaces 2021, 13, 27, 32031–32036.

8. **Wuttig M., Yamada N.,** Phase-change materials for rewriteable data storage, Nature Mater. 2007, 6, 824–832.

THE AUTHORS

TROFIMOV Pavel I.
p.trofimov@metalab.ifmo.ru
ORCID: 0000-0002-6426-2670

IVANOVA Tatyana V.
tatyana.ivanova@metalab.ifmo.ru
ORCID: 0000-0003-3320-9727

LAZARENKO Petr I.
aka.jum@gmail.com
ORCID: 0000-0003-4309-3481

SINEV Ivan S.
i.sinev@metalab.ifmo.ru
ORCID: 0000-0002-4246-7747

FEDYANINA Maria E.
mfh.miet@gmail.com
ORCID: 0000-0001-9779-2574

Received 14.08.2022. Approved after reviewing 09.09.2022. Accepted 12.09.2022.