

Piezophotonics of the heterostructures and optoelectronic devices from layered III-VI semiconductors

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Abstract: Piezophotonic effect can be dynamically tuned in real time. Additionally, my group has demonstrated phototransistors based on wafer-scale 2D III-VI thin-films. These studies offer an opportunity to develop optoelectronic and energy devices. © 2019 The Author(s)
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1. Introduction

The piezophotonic effect is the coupling between piezoelectric properties and photoexcitation, where strain-induced piezopotential modulates and controls the relevant optical process. Many emerging photonics and optoelectronics applications require them to be directly triggered or tuned by mechanical inputs from their environment. For this purpose, metal ions as activators are capable of responding to photoexcitation and subsequent emission of light. Wang coined the field of piezophotonics in semiconductors, regarded as a two-way coupling of piezoelectric-photoexcitation [1,2]. Therefore, metal ions as activators may serve for demonstrating the piezophotonic effect since they are capable of responding to photoexcitation and subsequently emitting light [3]. Typically, photoluminescence (PL) is stimulated by photon energy while electroluminescence (EL) is triggered by an electric field. PL- and EL-based materials have been extensively applied in display systems, light-emitting diodes (LEDs), solid state lighting, and biomedicine [4-7]. It is noted that the progress in this field combined with the assembly and characterization of nanostructural materials based hybrid structures leads to exciting opportunities ranging from fundamental studies of piezoelectric semiconductors at nanoscale to improving conventional optoelectronic devices and conceiving novel nanoopto-electro-mechanical systems. Specifically, 2D III-VI compounds in the two main categories of MX (e.g., InSe, InS, GaSe, and GaS) and M_2X_3 (e.g., In_2Se_3 and In_2S_3) have recently attracted much attention due to their remarkable properties and promises in optoelectronic device applications [8]. III-VI compounds have also been predicted to show strong piezoelectric responses because of their non-centrosymmetrical crystal structure. Therefore, it is anticipated to demonstrate novel opto-electro-mechanical devices towards adaptive and active optoelectronics based on 2D III-VI compound heterostructures.

2. Results and discussion

1.1. Temporal Piezophotonics

In our design, poly(dimethylsiloxane) (PDMS) is chosen as a matrix for packaging a flexible laminated composite, and also functions as delivering the generated strain. The composite was fabricated with integration of one layer embedding soft ferromagnetic particles into PDMS, generating magnetostrictive strain under a magnetic field. This magnetostrictive strain then triggers the adjacent PDMS layer embedded in the ZnS piezophosphor doped with various metal ions (e.g., Al, Cu) to produce light emission.

We have provided an evidence of tuning emission peak wavelength and color of various composites by modulating the frequency of the excitation [9,10]. Some proof-of concept devices, including red-green-blue (RGB) full-color displays and tunable white-light sources are demonstrated simply by frequency modulation based on the temporal piezophotonic effect. Obviously, such a temporal tuning of emission wavelength differs greatly from conventional methods where *ex situ* ways (e.g., changes in chemical compositions of hosts and/or metal-ion dopants of phosphors) are routinely employed for tuning emission wavelength. The result suggests that the rise time for both blue and green components becomes longer with the accretion of excitation frequency. Apart from the changes in rise time with the modulation frequency, the relative intensity of blue and green emissions can be adjusted by the modulation frequency. The overall luminescent intensity is varied with the modulation frequency. Moreover, RGB full-color and white light with tunable color temperature are achieved via photon energy coupling with persistence phosphor. The study provides a new insight and understanding on the piezophotonic emission mechanism. Our new finding of the luminescent materials with ability to be accessed and modulated remotely will offer opportunities for

applications in the fields of magnetic optical sensing, piezophotonics, energy harvester, nondestructive environmental surveillance and novel light sources.

1.2 Optoelectronic Devices Based on 2D III-VI Compounds

The 2D layered materials not only share many excellent properties from their bulk counterparts, but also show some unique physical characteristics owing to the quantum confinement effect [11-15]. III-VI layered materials are significant group of 2D semiconductors, which has gain renewed interests for optoelectronic applications in recent years thanks to their tunable bandgaps, efficient light absorption, and large carrier mobility. Particularly, the optical bandgap of III – VI layered semiconductors ranges from 1.25 (IR) to 3.05 eV (UV), showing a large optical window in 2D limit, which makes them potential candidates for different functional optoelectronic devices, such as LEDs, phototransistors, and solar cells. In general, 2D heterostructures based on III-VI semiconductors usually exhibit type-II band alignment, which could boost the separation efficiency of electron-hole pairs for optoelectronic applications.

Firstly a strong second harmonic generation (SHG) in bilayer and multilayer III-VI GaSe sheets was found [16]. Importantly, the SHG of multilayer GaSe above five layers shows a quadratic dependence on the thickness; while that of a sheet thinner than five layers shows a cubic dependence, which is attributed to the weakened stability of non-centrosymmetric GaSe in the atomically thin flakes where a layer-layer stacking order tends to favor centrosymmetric modification.

Secondly, our group has demonstrated phototransistors based on centimeter-scale highly crystalline 2D III-VI InSe thin films by pulsed laser deposition [8]. The high responsivity could be explained by high absorption of InSe nanosheets due to the direct band gap and the photogating effect. Interestingly, 2D III-VI compounds such as In₂Se₃ are capable of holding both superior optoelectronic properties and remarkable piezoelectric response. These characteristics in 2D III-VI semiconductors are attractive to make piezo-phototronics particularly helpful for understanding fundamental physics and developing novel optoelectronic devices based on 2D III-VI compound and heterostructure. The research was supported by the grant Research Grants Council of Hong Kong (GRF No. PolyU 153023/18P).

3. References

- [1] Z.L. Wang, *Piezotronics and Piezo-Phototronics* (Springer, Berlin, 2013).
- [2] W. Wu and Z. L. Wang, "Piezotronics and piezo-phototronics for adaptive electronics and optoelectronics" *Nat. Rev. Mater.* **1**, 16031 (2016).
- [3] J. Hao and C.-N. Xu, "Piezophotonics: From fundamentals and materials to applications", *MRS Bulletin*, **43**, 965 (2018).
- [4] J. Hao, J. Gao, and M. Cocivera, "Tuning of the blue emission from europium-doped alkaline earth chloroborate thin films activated in air", *Appl. Phys. Lett.* **82**, 2778 (2003).
- [5] J. H. Hao and J. Gao, "Abnormal reduction of Eu ions and luminescence from CaB₂O₄: Eu thin films", *Appl. Phys. Lett.* **85**, 3720 (2004).
- [6] Z. Yi, S. Zeng, W. Lu, H. Wang, L. Rao, H. Liu, and J. Hao, "Synergistic dual-modality in vivo upconversion fluorescent/X-ray imaging and tracking of amine-functionalized NaYbF₄:Er nanoprobe", *ACS Appl. Mater. Interfaces*, **6**, 3839 (2014).
- [7] L. Chen, M.-C. Wong, G. Bai, W. Jie, and J. Hao, "White and green light emissions of flexible polymer composites under electric field and multiple strains", *Nano Energy*, **14**, 372 (2015).
- [8] Z. Yang, W. Jie, C.-H. Mak, S. Lin, H. Lin, X. Yang, F. Yan, S. P. Lau, and J. Hao, "Wafer-scale synthesis of high-quality semiconducting two-dimensional layered InSe with broadband photoresponse", *ACS Nano* **11**, 4225 (2017).
- [9] M.-C. Wong, L. Chen, M.-K. Tsang, Y. Zhang, and J. Hao, "Magnetic-induced luminescence from flexible composite laminates by coupling magnetic field to piezophotonic effect", *Adv. Mater.* **27**, 4488 (2015).
- [10] M.-C. Wong, L. Chen, G. Bai, L.-B. Huang, and J. Hao, "Temporal and remote tuning of piezophotonic effect induced luminescence and color gamut via modulating magnetic field", *Adv. Mater.* **29**, 1701945 (2017).
- [11] W. Jie, Z. Yang, G. Bai, and J. Hao, "Luminescence in 2D materials and van der Waals heterostructures", *Adv. Opt. Mater.* **6**, 1701296 (2018).
- [12] Z. Yang, Z. Wu, Y. Lyu, and J. Hao, "Centimeter-scale growth of 2D layered high-mobility bismuth films by pulsed laser deposition", *InfoMat*, **1**, 98 (2019).
- [13] Z. Yang and J. Hao, "Progress in pulsed laser deposited two-dimensional layered materials for device applications", *J. Mater. Chem. C* **4**, 8859 (2016).
- [14] S. Yuan, X. Luo, H. L. Chan, C. Xiao, Y. Dai, M. Xie, and J. Hao, "Room-temperature ferroelectricity in MoTe₂ down to the atomic monolayer limit", *Nature Commun.*, **10**, 1775 (2019).
- [15] S.-Y. Pang, Y.-T. Wong, S. Yuan, Y. Liu, M.-K. Tsang, Z. Yang, H. Huang, W.-T. Wong, and J. Hao, "Universal strategy for HF-free facile and rapid synthesis of two-dimensional MXenes as multifunctional energy materials", *J. Am. Chem. Soc.*, **141**, 9610 (2019).
- [16] W. Jie, X. Chen, D. Li, L. Xie, Y. Y. Hui, S. P. Lau, X. Cui, and J. Hao, "Layer-dependent nonlinear optical properties and stability of non-centrosymmetric modification in few-layer GaSe sheets", *Angew. Chem. Int. Ed.* **54**, 1185 (2015).