Excitonic luminescence of the I$_2$-intercalated HfS$_2$

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Photoluminescence from bulk HfS$_2$ grown by the chemical vapor transport (CVT) method is reported. A series of emission lines is apparent at low temperature in the energy range of 1.4 - 1.5 eV. Two groups of the observed excitonic transitions followed by their replicas involving acoustic and optical phonons are distinguished using classical intensity correlation analysis. The emission is attributed to the recombinant states bound to iodine (I$_2$) molecules intercalated between layers of HfS$_2$. The I$_2$ molecules are introduced to the crystal during the growth as hydrogen transport agents in the CVT growth process. Their presence in the crystal is confirmed by secondary ion mass spectroscopy.

Although layered transition metal dichalcogenides (TMDs) have been well known and broadly investigated for more than a century,$^1$ they emerged in the spotlight of material scientists for only over a decade. The interest is motivated by a variety of properties, which characterize TMDs and the unique dependence of their properties on their thickness in the few-layer limit. Although about 60 layered TMDs have been recognized to date, researchers have focused mainly their attention on Mo- and W-based semiconducting compounds.$^{1,2}$ Properties of other TMDs have been less investigated, which opens up new avenues for research. Recently, it has been shown that hafnium disulfide (HfS$_2$), a member of group IVB TMDs with octahedral coordination (hexagonal 1T, space group: $P\bar{3}m1$), a member of group IVB TMDs with octahedral coordination (hexagonal 1T, space group: $P\bar{3}m1$), has a very effective electrical response,$^3$ which justifies a need to uncover its fundamental properties.

In this work, optical properties of HfS$_2$ grown by chemical vapor transport (CVT) are investigated using photoluminescence (PL) spectroscopy. It is shown that the low-temperature optical emission consists of a series of well-resolved lines apparent in the energy range of 1.4 - 1.5 eV. The observed emission is attributed to the recombinant states bound to iodine (I$_2$) molecules intercalated between layers of the TMD crystal. The I$_2$ molecules are introduced to the crystal during the growth as halogen transport agents in the CVT growth process. Their presence in the crystal is confirmed by secondary ion mass spectroscopy (SIMS). We claim that the presence of intercalated halogen molecules in the CVT-grown HfS$_2$ crystals is more general, as similar PL spectra were also observed in other HfS$_2$ samples including commercially available crystals from Ossila and 2D Semiconductors.

Bulk HfS$_2$ crystals, studied in this work, were synthesized by the CVT method with iodine as a transport agent.$^6$ Single crystals of HfS$_2$ of 0.8-1 cm$^2$ size were grown. Their high quality was confirmed by powder X-Ray diffraction (XRD) measurements found to be in perfect agreement with that of the octahedral 1T phase of HfS$_2$.\(^7\)

The PL spectra were measured under laser excitation of $\lambda = 561$ nm (2.21 eV) on samples placed on a cold finger of a continuous flow cryostat. The excitation light was focused by means of a 50x long-working distance objective with a 0.55 numerical aperture (NA) producing a spot of about 1 $\mu$m diameter. The signal was collected via a liquid nitrogen cooled charge-coupled device (CCD) camera. The excitation power focused on measured samples was kept at 100 $\mu$W during all measurements to avoid local heating.

Density functional theory (DFT) calculations were conducted in Vienna Ab initio Simulation Package\(^8\) with Projector Augmented Wave method,\(^9\) Perdew–Burke–Ernzerhof parametrization\(^10\) of general gradients approximation to the exchange-correlation functional was used. The plane waves basis cutoff energy was set to 550 eV and a 9×9×6 $\Gamma$-centered Monkhorst-Pack $k$-grid sampling was applied. Geometrical structure was optimized with $10^{-5}$ eV/Å and 0.01 kbar criteria for the interatomic forces and stress tensor components, respectively. Grimme’s D3 correction was applied to describe the interlayer vdW interactions.$^{11}$ Spin-orbit interaction was taken into account during geometry optimization. Phonon calculations were performed within Parlinski-Kawazoe method,\(^12\) as implemented in Phonopy software.$^{13}$ The 3×3×2 supercells were found sufficient to converge the interatomic force constants within the harmonic approximation. The phonon density of the states (and band structure) was obtained from integration over full Brillouin zone (BZ) on a 27×27×18 grid.

The in-depth composition of the sample was probed using SIMS. As received, the samples were transferred without special pre-treatment to the analytical chamber where the pressure was 9×10$^{-10}$ mbar. The distribution of elements was obtained with a time-of-flight SIMS apparatus (TOF SIMS 5, ION-TOF GmbH, Germany) operating in dual beam mode.
The samples were sputtered by cesium ions (operating conditions: 1 keV, 76 nA), rastered over 200 µm × 200 µm area. Exposed this way, internal layers of the sample were analysed with a Bi⁺ ion beam (operating conditions: 50 µm × 50 µm raster size, 30 keV, 1.12 pA). The internal mass calibration was performed using mass of ions always present: $^{34}\text{S}^-$, $^{32}\text{S}^-$, $^{33}\text{S}^-$, $^{34}\text{S}^-$. The PL spectrum of the investigated bulk HfS$_2$ sample measured at $T=5K$ comprises several emission lines apparent in the energy range 1.4 - 1.5 eV (see. Fig.1(a)). The general lineshape of the spectrum does not change over a whole sample. Two characteristic peaks: $X_1$ and $X_2$, which will be analyzed in more detail in the following, appear in the spectrum at $E_{X_1} = 1.5184$ eV and $E_{X_2} = 1.5021$ eV. Spectrum of a similar lineshape, although blue-shifted by 5 meV was also measured on the HfS$_2$ flake of approx. 5 nm thickness, which can be appreciated in Fig. 1(b). Although the spectra are similar, the absence of the $X_1$ peak from the flake’s spectrum can be noticed. Missing are also two other features, denoted in Fig. 1(a) with arrows. These lines are red-shifted from $X_1$ by 10.2 meV and 25.7 meV, respectively. Note that similar PL spectra were also observed from other CVT-grown HfS$_2$ samples, including commercially available from Ossila and 2D Semiconductors.

The lineshape of the PL spectra suggests their relation to excitonic recombination followed by a series of phonon replicas. To study the spectra in more detail and profit from their general resemblance over the sample of millimeter size, we collected 920 spectra from the sample area of 4 mm by 4 mm. The set of spectra were analyzed and a classical coefficient of the intensity correlation was determined. The coefficient $\Gamma$ of the intensity correlation between intensities at different energies $\alpha$ and $\beta$ in the PL spectrum can be expressed by the formula:

$$\Gamma = \frac{\sum (I^\alpha_i - \bar{I}^\alpha)(I^\beta_i - \bar{I}^\beta)}{\sqrt{\sum (I^\alpha_i - \bar{I}^\alpha)^2 \sum (I^\beta_i - \bar{I}^\beta)^2}},$$

where $I^\alpha_i$ and $I^\beta_i$ are the intensities of the signal in the spectrum at energies $\alpha$ and $\beta$, respectively. The $\bar{I}^\alpha$ and $\bar{I}^\beta$ are the intensities averaged over all spectra at energies $\alpha$ and $\beta$, respectively. The false color map of the correlation coefficient $\Gamma$ for the measured PL spectra (lower panel) together with the typical PL spectrum (upper panel) is shown in Fig. 2. The correlation coefficient exhibits values from -1 to 1, which correspond to deep blue and dark red in the Figure. The correlation coefficient equal to 1, apparent on the diagonal of the map, is related to the auto-correlation, i.e. correlation of a given emission line in the spectrum with itself. Three energy regions can be distinguished in the map with different color patterns. Most central region is limited by the energies of the $X_2$ emission line at $E_{X_2} = 1.5021$ eV and $E=1.464$ eV. A set of emission lines of high correlation parallel to the diagonal of the map is apparent in the region. The energy separations between the diagonal and those lines are equal to 10.4 meV, 17.9 meV, 28.1 meV, and 35.3 meV. For the reason explained later in the text, we refer to them as LA, TA, LA+TA, and 2TA, respectively. The apparent correlation pattern at energies higher...
than $E_{X2}$ is different. Lines of high correlation in that energy region are vertical. Finally, the region of the map with $E<1.455$ eV corresponds to much weaker, low-energy emission, which is most likely related to intrinsic defects in the crystal lattice.\(^{15}\) This low-energy emission is not addressed in this work.

The distinctive properties of the $X_1$ and $X_2$ emission lines and their phonon replicas can be determined from the correlation matrix. To see the effect in more detail, we plot the correlation spectra $\Gamma(E)$ calculated at the energies of the $X_1$(panel (a)) and $X_2$(panel (c)) emission lines, see Fig. 3. The PL spectrum (with both $X_1$and $X_2$ lines) from a selected spot on the sample is also shown in Fig. 3(b). As expected, $\Gamma=1$ for the energies of the respective $X_1$ and $X_2$ emission lines, which corresponds to auto-correlation previously highlighted as a diagonal of the map shown in Fig. 2. Notably, $\Gamma=1$ for $X_1(X_2)$ is accompanied by $\Gamma=0$ for $X_2(X_1)$. This confirms the lack of correlation between the presence of $X_1$ and $X_2$ emission lines and can be compared with results shown in Fig. 1. It means that both peaks appear in the spectrum independently. The correlation spectra also reflect a rich structure of replicas that follow the $X_1$ and $X_2$ emission lines. There are two local maxima in the spectrum for $X_1$(Fig. 3(a), which correspond to peaks previously attributed to the phonon replicas of the $X_1$ line. The are referred to $X_1$-LA and $X_1$-E$_S$(TO), and their origin will be addressed later in the text. Similarly, some maxima in the correlation spectrum for $X_2$(Fig. 3(c), correspond to peaks apparent in the PL spectra. This allows to trace the origin of the lines to the $X_2$ line. The emission lines are referred to as: $X_2$-TA, $X_2$-E$_S$(TO), $X_2$-(LA+TA), and $X_2$-2TA. There are more local maxima in the correlation spectra (mainly for the $X_1$ line), which cannot be directly correlated with the emission lines in the PL spectra. The absence of emission features related to those maxima is most likely due to their weak intensity and substantial broadening, which prevents their observation in the spectra. One may also appreciate the local maxima of the correlation spectra at energies higher than those of the respective emission line. These two lines are referred to as $X_1^*$ and $X_2^*$ in Fig.3(b). As we associate the $X_1$ and $X_2$ lines with the recombination processes within the ground states, therefore, the $X_1^*$ and $X_2^*$ emission lines can be ascribed to the corresponding excited states.

To support our attribution of the observed phonon replicas of the $X_1$ and $X_2$ emission lines to particular phonons in HfS$_2$, we performed DFT calculations. The resulting phonon dispersion is shown in Fig.4(a). There are three branches of acoustic vibrations: longitudinal (LA), transverse (TA), and out-of-plane (ZA) in HfS$_2$, as expected. Optical modes can be appreciated at energies higher than 150 cm$^{-1}$. The characteristic LO-TO splitting of the infrared-active $E_u$ and $A_2g$ modes can be appreciated. Note that the former vibrations are active for light’s electric field $E \bot c$, while the latter ones are active for $E || c$, in which $c$ is normal to layer planes. The corresponding total density of phonon states (DOS) is presented in Fig.4(b).

Three DOS maxima corresponding to acoustic vibrations, which are referred to as ZA (54 cm$^{-1}$), LA (80 cm$^{-1}$), and TA (148 cm$^{-1}$) after modes that mainly contribute to the DOS at particular energies, see Fig. 4(b). The maximum of the DOS at 202 cm$^{-1}$ can be attributed to the flat regions of the $E_u$(TO) vibration dispersion near M and L points of the BZ in bulk HfS$_2$. The DOS maximum at 250 cm$^{-1}$ corresponds to the practically dispersion-less Raman-active $E_g$. The peaks at even higher energy can be related to other infrared- or Raman-active vibrational modes.

The PL from bulk HfS$_2$ was also examined at higher temperatures. The corresponding spectra at selected temperatures are shown in Fig. 5. The emission lines broaden with increasing temperature and eventually quench, leaving the broad-band low-energy emission attributed to intrinsic defects in HfS$_2$. The temperature evolution measurements provide yet another proof of the independent origin of the $X_1$ and $X_2$ lines, since...
the X₁ line and its phonon replicas quench at temperatures lower than those of the X₂ line and its phonon replicas. Moreover, two high-energy features, blue-shifted from the X₁ line, emerge at elevated temperature, which can be seen in the inset in Fig. 5. The X₁⁺ line (apparent in the correlation spectrum, see Fig. 3) can be associated with the X₁⁺ emission line. The X₁⁺ emission line gains its relative intensity with respect to the X₁ line with increasing temperature. An another emission line, denoted X₁⁺∗, can be distinguished in the Figure, whose attribution to the X₁ line is confirmed by correlation analysis at elevated temperature (not shown here).

The expected energy position of the X₂⁺ emission line is also marked in the inset of Fig. 5. It is most likely that at elevated temperature the X₂⁺ line gives rise to the low-energy side-band of the X₁⁺ peak.

The observation of the excitonic PL at approx. 1.5 eV in bulk HfS₂, the material which is characterized by indirect band gap of approx. 2 eV, might seem surprising. However, we note that similar low temperature excitonic PL has previously been observed in 2D polytypes of molybdenum/tungsten sulfides/selenides: MoS₂:Cl₂, WS₂:Br₂, WSe₂:I₂, or WS₂:I₂. The emission spectra reported in the literature were attributed to excitons bound to intercalated halogen molecules and their phonon replicas with local phonons. The ability of TMDs to serve as hosts for intercalating molecules in TMDs originates from their van der Waals (vdW) gaps. Each TMD unit cell (layer) comprises planes of covalently bond transition metal atoms “encapsulated” between two chalcogenide atom planes. The layers are kept together by weaker vdW interactions and separated one from another by the vdW gap. The large electron affinity of halogen molecules results in a short range potential attracting electrons from HfS₂ layers. The localized electrons interact with optically-excited holes giving rise to bound excitons. Our results unambiguously point to two distinct excitonic complexes present in the structure: X₁ and X₂. Their independent characteristics were confirmed by the accidental absence of the X₁ line in the spectrum of the HfS₂:flake as well as the intensity correlation analysis (see Figs. 1 and 3). Moreover, our attribution is supported by the temperature dependence of the spectra with simultaneous quenching of the X₁ line and its X₁-LA and X₁-E₂g(TO) replicas. In our opinion, the X₁ and X₂ emission lines correspond to neutral and charged excitons, respectively. They combine conduction and valence band carriers in HfS₂, which are bound by the iodine molecule. Microscopic-scale fluctuations in the unintentional sample doping may be responsible for the observed quenching of the X₁ emission line in particular spots of the sample. Notably, while the intensity of the X₁ line fluctuates strongly over the sample area and quenches at some spots, the X₂ line is present in all measured spectra. This may reflect generally intermediate doping of the investigated sample (allowing for the creation of both neutral and charged complexes) with some more heavily doped spots with trions only. Assuming the attribution of the observed excitonic lines to the neutral exciton and trion, one can approximate the binding energy of the latter as Δ=16.3 meV. The attribution of the investigated PL emission to bound excitons comprising band carriers also explains the apparent effect of the sample thinning on their energy. Thinning the TMD structure results in the energy increase of the conduction band minimum at the Q point of the BZ, which in 2H-TMDs eventually leads to the direct bandgap in the monolayer limit. A similar shift can be expected in the bulk HfS₂, which explains the observed evolution of the spectrum with sample thickness. The attribution of the X₁ and X₂ lines to bound excitons also facilitates the analysis of their phonon replicas. The spatial location of such excitons leads to their delocalization in the momentum space. Therefore, the exciton can be coupled with phonons of the whole BZ, which explains the rich structure of the phonon replicas in the PL spectrum of the iodine-intercalated HfS₂, see Fig. 1. If one assumes the coupling of the bound excitons with phonons from the whole BZ, the phonon replica energy structure of the excitonic line should reflect the phonon DOS. In particular, the PL features corresponding to the phonon replicas of the X₁ and X₂ emission lines should be expected at the energies of the phonon DOS maxima. In fact, the PL peaks related to LA, and E₂g(TO) replica of the X₁ line as well as the TA, E₂g(TO), LA+TA, and 2TA replica of the X₂ line (denoted in Fig. 3 with red arrows) can be clearly identified in the PL spectra. One can appreciate very good agreement of the expected energies with the actual energies of the low-energy satellites of the excitonic features, which supports their attribution to phonon replicas of the excitonic lines. It must also be noted that most of the observed peaks can be related to the DOS maxima of HfS₂ phonons and not to local vibrations as observed in Refs. 15–17.

To support the attribution of the observed PL to the recombination of excitons bound to I₂ molecules, SIMS was performed on the investigated crystal. Figure 6 presents the evolution of the HfS₂, sulfur (S), and iodine (I) concentration as a function of the sputter time, which can be interpreted as a depth profile of sample. The results confirm the presence of iodine in the crystal. Furthermore, it can be seen that while the HfS₂ and S atoms are evenly distributed throughout the crys-
tal, iodine exhibits a higher concentration close to the sample surface and its density is lower in the deeper parts of the sample. As in previously investigated TMD materials, it is most likely that the iodine is present in our samples in the form of I₂ molecules, which reside in the vdW gaps between HfS₂ layers.

In conclusion, the optical emission from the bulk HfS₂ is reported. A series of well-resolved emission lines, observed at low temperature in the energy range of 1.4 - 1.5 eV, has been ascribed to bound excitons in HfS₂. Two independent series of excitonic lines followed by acoustic and optical phonon replicas have been identified using a classical analysis of the PL intensity correlations. It has been proposed that the excitonic lines are due to neutral and charged bound excitons in HfS₂. The excitons are bound by the electron-attractive potential introduced by the I₂ molecules intercalated between layers of the crystal. The I₂ molecules are introduced to the crystal during the growth as halogen transport agents in CVT process and their presence in the crystal is confirmed by SIMS. According to our knowledge, our report is the first observation of the excitonic emission in HfS₂. We believe that further investigation of the emission will provide important insight in properties of that material and our report would trigger more theoretical studies on possible configurations of I₂ molecules in the vdW gaps of HfS₂. More experimental efforts are also necessary to explain the structure of the excited states of the excitonic complexes. This may shine new light on the properties of HfS₂. Moreover, it may be of fundamental importance as similar PL spectra were also observed from other CVT-grown HfS₂ samples, including those commercially available.

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CONFLICT OF INTEREST

The authors have no conflicts to disclose.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

1. A. Wilson and A. D. Yoffe, Advances in Physics 18, 193 (1969).
2. M. Koperski, M. R. Molas, A. Arora, K. Nogajewski, A. O. Slobodenik, C. Faugeras, and P. M., Nanophotonics 6, 1289 (2017).
3. G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie, T. Amand, and B. Urbaszek, Rev. Mod. Phys. 90, 021001 (2018).
4. K. Xu, Z. Wang, F. Wang, Y. Huang, F. Wang, L. Yin, C. Jiang, and J. He, Advanced Materials 27, 7881 (2015).
5. T. Kanazawa, T. Amemiya, A. Ishikawa, V. Upadhyaya, K. Tsuruta, T. Tanaka, and Y. Miyamoto, Scientific reports 6, 22277 (2016).
6. M. Grzeszczyk, K. Olkowska-Pucko, K. Nogajewski, K. Watanabe, T. Taniguchi, P. Kossacki, A. Babinski, and M. R. Molas, Nanoscale 13, 18726 (2021).
7. G. Luzovskiy, R. M. White, J. A. Benda, and J. F. Revelli, Phys. Rev. B 7, 3859 (1973).
8. G. Kresse and J. Furthmüller, Physical Review B 54, 11169 (1996).
9. G. Kresse and D. Joubert, Physical Review B 59, 1758 (1999).
10. J. P. Perdew, K. Burke, and M. Ernzerhof, Physical Review Letters 77, 3865 (1996).
11. S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, The Journal of Chemical Physics 132, 154104 (2010).
12. K. Parlinski, Z. Q. Li, and Y. Kawazoe, Physical Review Letters 78, 4063 (1997).
13. A. Togo and I. Tanaka, Scripta Materialia 108, 1 (2015), 1506.08498.
14. B. Pierta, J. Saffczyński, M. Goryca, T. Kazimierczuk, A. Golnik, P. Kossacki, A. Wysmolek, J. A. Gaj, R. Stępniewski, and M. Potemski, Phys. Rev. B 87, 035310 (2013).
15. L. Kulyuk, L. Charron, and E. Fortin, Phys. Rev. B 68, 075314 (2003).
16. L. Kulyuk, D. Dumchenko, E. Bucher, K. Friemelt, O. Schenker, L. Char- ron, E. Fortin, and T. Dumouchel, Phys. Rev. B 72, 075336 (2005).
17. D. Dumchenko, C. Gherman, L. Kulyuk, E. Fortin, and E. Bucher, Thin Solid Films 495, 82 (2006).