Control of excitons in multi-layer van der Waals heterostructures

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We report an experimental study of excitons in a double quantum well van der Waals heterostructure made of atomically thin layers of MoS₂ and hexagonal boron nitride. The emission of neutral and charged excitons is controlled by gate voltage, temperature, and both the helicity and the power of optical excitation. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4943204]

van der Waals heterostructures composed of ultrathin layers of transition metal dichalcogenides (TMD), such as MoS₂, WSe₂, etc., offer an opportunity to realize artificial materials with designable properties, forming a new platform for studying basic phenomena and developing optoelectronic devices.¹ In the TMD structures, excitons have high binding energies and are prominent in the optical response. The energy, intensity, and polarization of exciton emission give information about the electronic, spin, and valley properties of TMD materials.²–⁵

The exciton phenomena are expected to become even richer in structures that contain two 2D layers. The energy-band diagram of such a coupled quantum well (CQW) structure is shown schematically in Figure 1(b). Previous studies of GaAs,²⁴ AlAs,²⁵ and InGaAs²⁶ CQWs showed that excitons in these structures can be effectively controlled by voltage and light. Two types of excitons are possible in a CQW structure. The spatially direct excitons (DXs) are composed of electrons and holes in the same layer, while the indirect excitons (IXs) are bound states of electrons and holes in the different layers separated by a distance d (Figure 1(b)). IXs can form quantum degenerate Bose gases.²⁷,²⁸ The realization and control of quantum IX gases was demonstrated²⁹,³⁰ in GaAs CQW structures at temperatures T below a few degrees Kelvin. In a recent theoretical work,³¹ it was predicted that the large exciton binding energies in TMD CQW structures may bring the domain of these phenomena to high temperatures. On the other hand, DXs in TMD CQW structures have high oscillator strength, making these structures good emitters.²–⁵ The CQW structures allow the control of the exciton emission by voltage. These properties make the CQW structures an interesting new system for studying exciton phenomena in the TMD materials.

The DX binding energy E_DX is larger³¹ than E_IX of the IXs, and so, in the absence of an external field, the DXs are lower in energy. The electric field F normal to the layers induces the energy shift eFd of IXs. The transition between the direct regime where DXs are lower in energy to the indirect regime where IXs are lower in energy occurs when eFd > E_DX - E_IX.²⁶ Both the direct and indirect regimes show interesting exciton phenomena. The indirect regime was considered in earlier studies of GaAs,²⁴ AlAs,²⁵ InGaAs,²⁶ and TMD,¹⁸,²¹ CQW structures. The direct regime in the TMD CQW structures is considered in this work. Exploring the direct regime is essential for understanding both the universal properties of complex exciton systems in the CQW structures and the specific properties of direct excitons in the TMD layers. We found that the exciton spectra in the direct regime have three exciton emission lines. The ability to control the CQW structure by voltage provides an important tool for understanding the complex exciton emission in the TMD structures. The measured dependence of exciton spectra on the voltage, temperature, and excitation indicated that the lines correspond to the emission to neutral and charged excitons.

The structure studied here was assembled by stacking mechanically exfoliated layers on a Si/SiO₂ substrate, which acts as a global backgate (Figure 1(a)). The top view of the device showing the contours of different layers is presented in Figure 1(c). The CQW is formed where the two MoS₂ monolayers, separated by a hexagonal boron nitride (hBN)
bilayer, overlap. The upper 20–30 nm thick hBN served as a dielectric cladding layer for a top graphene electrode. The voltage $V_g$ applied between the top graphene layer and a backgate was used to create the bias across the CQW structure.

The excitons were generated by continuous wave (cw) semiconductor lasers with excitation energies $E_{\text{ex}} = 3.1$, 2.3, or 1.96 eV focused to a spot of diameter $\sim 5 \mu m$ (the circle in Figure 1(c)). The photoluminescence (PL) spectra were measured using a spectrometer with a resolution of 0.2 meV and a CCD. In the time-resolved PL measurements, the excitons were generated by a pulsed semiconductor laser with $E_{\text{ex}} = 3.1$ eV, and the emitted light was diffracted by the spectrometer and detected by a photomultiplier tube and time correlated photon counting system. The measurements were performed in a $^4$He cryostat.

Figure 2 shows the PL spectra at different temperatures $T$. At the lowest $T$, the spectrum consists of two high-energy emission lines with the linewidth of $\sim 20$ meV and a broader low-energy line. Additional data and analysis presented below suggest that the high-energy lines correspond to the emission of neutral DXs while the low-energy line to the emission of charged DXs also known as trions.

The energy splitting of 25 meV between the high-energy emission lines constitutes only 5% of the MoS$_2$ exciton binding energy$^{7,8,12-16,20,22}$ of about 0.5 eV. It is also much smaller than 0.2 eV energy difference of the A and B excitons$^3$ caused by the spin-orbit splitting of the valence band (see Figure 4(c)). These data indicate that the high-energy lines represent different species of A excitons. They can be A excitons with different electron spin states. The calculated 10% difference$^{32}$ in the masses, 0.44 vs. 0.49$m_0$, of the conduction band spin states results in a 5% difference in the reduced electron-hole masses and, in turn, exciton binding energies. This leads to the energy splitting $\sim 25$ meV consistent with the experiment.

It is worth noting that the two MoS$_2$ layers in the structure have inequivalent dielectric environment (Figure 1). This may lead to the difference in the binding energy of excitons in these layers in the effective mass approximation.$^{33}$ However, experimental and theoretical studies show that the TMD excitonic states with large binding energy are robust to environmental perturbations,$^{15}$ meaning the exciton energy is the same for the two MoS$_2$ layers in the structure. Although dielectric environment changes the exciton binding energy,$^{33}$ it also changes the self-energies of the electron and the hole. For the excitons in GaAs-based$^{34}$ systems, these two contributions to the total exciton energy partially cancel one another. A similar cancellation presumably occurs in van der Waals heterostructures.

The lower-energy emission line is shifted by about 50 meV from the first two (Figure 2). This shift is in the range, 20–50 meV, of trion binding energies reported$^{5,10-12}$ for monolayer MoS$_2$. The relative intensity of the high-energy exciton lines increases with $T$ (Figure 2), which is consistent with the thermal dissociation of trions. The observed red shift of the lines with increasing temperature originates from the band gap reduction, which is typical in semiconductors,$^{35}$ the TMDs included.$^{11,20,36,37}$

Figure 3 shows the dependence of the exciton PL on the excitation power $P_{\text{ex}}$. The relative intensity of the trion line increases with $P_{\text{ex}}$ (Figure 3). This effect may be due to an enhanced probability of trion formation at larger carrier density. A similar increase in the trion PL intensity relative to the exciton was observed in earlier studies of GaAs CQW structures.$^{38}$

**FIG. 2.** Temperature dependence. (a) Emission spectra at different $T$. The energy (b) and relative intensity (c) of the emission lines marked in (a) vs. $T$. The curves are guides to the eye. $P_{\text{ex}} = 0.8$ mW, $E_{\text{ex}} = 3.1$ eV, and $V_g = 0$.

**FIG. 3.** Excitation power dependence. (a) Emission spectra at different $P_{\text{ex}}$. The energy (b) and relative intensity (c) of the emission lines marked in (a) vs. $P_{\text{ex}}$. The curves are guides to the eye. $T = 2$ K, $V_g = 0$, and $E_{\text{ex}} = 2.3$ eV.
Figure 4 shows that the polarization of exciton emission can be controlled by the helicity of optical excitation. For a circularly polarized excitation nearly resonant with the exciton line, a high degree of circular polarization $\sim 30\%$ of exciton PL is observed (Figures 4(a) and 4(b)), which is consistent with studies of monolayer TMD.\textsuperscript{4–6,9,17} This observation indicates that the spin relaxation time is long compared to the exciton recombination and energy relaxation times.\textsuperscript{39} The conventional explanation for the slow spin relaxation requires inter-valley scattering (Figure 4(c)). If this scattering is weak, the spin relaxation can be long. Virtually, no circular polarization is observed for the nonresonant optical excitation (Figure 4(b)), indicating that the appearance of the aforementioned A and B exciton states.

FIG. 4. Emission polarization. (a) Emission spectra in $\sigma^+$ and $\sigma^-$ polarizations. The laser excitation is $\sigma^+$ polarized, $P_{\text{exc}} = 0.8 \text{ mW}$, $T = 2 \text{K}$, $V = 0$, and $E_{\text{exc}} = 1.96 \text{ eV}$. An unpolarized spectrum at $P_{\text{exc}} = 1 \text{ mW}$, $T = 2 \text{K}$, $V = 0$, and $E_{\text{exc}} = 3.1 \text{ eV}$ is shown for comparison. (b) The emission polarization for low-energy excitation [indicated by an arrow in (a)] $E_{\text{exc}} = 1.96 \text{ eV}$ and high-energy excitation $E_{\text{exc}} = 3.1 \text{ eV}$. (c) Schematic illustrating the bands, coupling of valley and spin degrees of freedom, and optical transitions.

The B excitons are $\sim 0.2 \text{ eV}$ higher in energy, and their contribution to the PL is negligible. The A excitons can come from either K or K$'$ valley. It is important however that the spin and valley indices are coupled, so that exciton spin relaxation requires inter-valley scattering (Figure 4(c)). If this scattering is weak, the spin relaxation can be long. Virtually, no circular polarization is observed for the nonresonant optical excitation (Figure 4(b)), indicating that the high-energy photoexcited carriers loose their spin polarization during energy relaxation. Our time-resolved PL measurements revealed that the exciton and trion lifetimes are short, shorter than the $0.25 \text{ ns}$ resolution of the photon counting system. Such small lifetimes facilitate the realization of the regime where the spin relaxation time is long compared to the exciton recombination time, and therefore, the polarization of exciton emission remains high.

FIG. 5. Gate voltage dependence. (a) Emission spectra at different $V_g$. The energy (b) and relative intensity (c) of the emission lines marked in (a) vs. $V_g$. The curves are guides to the eye. The solid (open) symbols correspond to $E_{\text{exc}} = 3.1(2.3) \text{ eV}$, $P_{\text{exc}} = 0.8 \text{ mW}$, and $T = 2 \text{K}$.

Figure 5 shows the gate-voltage dependence of the exciton PL. The small exciton lifetime $<0.25 \text{ ns}$ indicates the direct regime in the studied range of voltage because the IX lifetimes are expected to be in the ns range.\textsuperscript{18,21,23,31} The positions of the exciton lines remain essentially unchanged while the trion line exhibits a red shift with the slope $\sim 0.3 \text{ meV per 1 V of } V_g$. The smallness of the shifts of the lines corroborates the conclusion that the CQW is in the direct regime. Indeed, if we assume that the electric field in the device is uniform, the IX energy shift with voltage should be $\delta E_{\text{IX}}/V_g = eFd/V_g$ $\sim 10 \text{ meV/V}$. The main effect of the gate voltage in the direct regime is the control of the exciton and trion PL intensities: the high-energy exciton emission increased at the negative $V_g$, while the low-energy trion emission increased at the positive $V_g$ (Figure 5). This behavior is attributed by the voltage-dependent electron concentration $n_e$ in the MoS$2$ layers. The initial electron concentration $n_0$ at $V_g = 0$ arises from unintentional dopants typically present in MoS$2$ materials. The change $\Delta n_e = n_e(V_g) - n_0$ of $n_e$ as a function of $V_g$ can be estimated from simple electrostatics. Treating the CQW as a single unit and neglecting a minor contribution from quantum capacitance, we find

\[
\Delta n_e = \frac{C_a R_a - C_b R_b}{R_a + R_b} \frac{V_g}{e},
\]

(1)
where $C_{a,b}$, $R_{a,b}$ are the geometric capacitances and leakage resistances of the dielectrics above (below) this double layer. (Incidentally, the leakage current across the device did not exceed a few µA until an eventual breakdown of the device at $V_g \sim 70$ V.) Since generally $C_a R_a \neq C_b R_b$, the applied voltage changes $n_e$ and, as a result, modifies the concentration of trions relative to the neutral excitons.

In summary, we presented optical studies of excitons in a MoS$_2$ coupled quantum well van der Waals heterostructure. We observed three emission lines. The dependence of these lines on experimental parameters indicates that the two high energy lines correspond to the emission of charged excitons (trions). We demonstrated control of the exciton emission by the gate voltage, temperature, and also by the helicity and power of optical excitation.

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I. EFFECTIVE INTRALAYER INTERACTION AND EXCITON BINDING ENERGY

Here we consider how dielectric environment may affect the binding energy of excitons in a MoS$_2$ layer in the effective mass approximation. For estimating the binding energies of direct excitons residing in a given MoS$_2$ layer, we consider a model [1] in which the system consisting of only three layers, labeled top to bottom as $j = 0, 1, 2$. We treat the MoS$_2$ layer, which is $j = 1$, as a slab of thickness $c = 0.312$ nm. The adjacent layers $j = 0, 2$ are assumed to be semi-infinite, see Figure S1(a).

All these materials are uniaxial dielectrics with principal values $\epsilon^\perp_j$ and $\epsilon^\parallel_j$ of the dielectric tensors in the directions perpendicular and parallel to the $z$-axis, respectively. Our choices for these parameters are listed in the second and third columns of Table 1 (see [1–3] for literature sources). The average permittivity $\bar{\epsilon}_j = (\epsilon^\perp_j \epsilon^\parallel_j)^{1/2}$ and the anisotropy factor $\kappa_j = (\epsilon^\perp_j)^{1/2} / (\epsilon^\parallel_j)^{-1/2}$ are provided in the last two columns.

Within the effective mass approximation the exciton binding energy $E_B$ is obtained by solving for the groundstate of a 2D particle of mass $\mu$ subject to an effective potential $V(r)$.

$$V(r, z, z') = \frac{1}{\epsilon_1 \sqrt{r^2 + (z - z')^2 \kappa_1^2}} + V_i,$$

where the leading term represents the “direct” interaction and $V_i$ is the image contribution:

$$V_i(r, z, z') = \sum_{n=0}^{\infty} (r_0 r_2)^n (r_0 A_n + r_2 B_n),$$

$$A_n = \frac{r_2}{\sqrt{r^2 + [(2n + 1)c + z - z']^2 \kappa_1^2}} - 1,$$

$$B_n = \frac{r_0}{\sqrt{r^2 + [(2n + 1)c + z + z']^2 \kappa_1^2}} - 1,$$

with

$$r_0 = \frac{\epsilon_1 - \epsilon_0}{\epsilon_1 + \epsilon_0}, \quad r_2 = \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2}.$$
correlation corrections to the electron-hole Coulomb interaction. We arrive at the effective potential in the form

$$V(r) = -\frac{e^2}{\epsilon_1 \sqrt{r^2 + (\alpha \kappa c)}^2} - e^2 V_i(r),$$

(6)

$$V_i(r) = \sum_{n=0}^{\infty} (r_0 r_2)^n \left[ \frac{2r_0 r_2}{\sqrt{r^2 + [(2n + 2)\kappa c]^2]} \right] + \frac{r_0 + r_2}{\sqrt{r^2 + [(2n + 1)\kappa c]^2}}. \quad (7)$$

The term $V_i(r)$ can be evaluated analytically in two limits. At $r = 0$, it is given by

$$V_i(0) = \sum_{s=\pm 1} s \left( \frac{\sqrt{r_0} - s \sqrt{r_2}}{2\epsilon_1 c \sqrt{r_0} \sqrt{r_2}} \right)^2 \ln(1 + s \sqrt{r_0} \sqrt{r_2}). \quad (8)$$

At large $r$, it becomes Coulomnic:

$$V_i(r) \simeq \left( \frac{2}{\epsilon_0 + 2} - \frac{1}{\epsilon_1} \right) \frac{1}{r}, \quad r \gg c. \quad (9)$$

At intermediate $r$ the series for $V_i(r)$ has to be summed numerically but it poses no difficulty. The results are shown in Figure S1(b) for hBN/MoS$_2$/hBN and hBN/MoS$_2$/SiO$_2$ structures by the thin and thick lines, respectively. In the latter case the electron-hole attraction is stronger, which is consistent with smaller $\epsilon$ (weaker screening) of SiO$_2$ compared to hBN, see Table 1.

We find the exciton binding energy $E_B$ and internal wavefunction $\psi(r)$ from a numerical solution of the Schrödinger equation

$$\left( -\frac{\hbar^2}{2\mu r} \frac{d}{dr} r \frac{d}{dr} + V(r) + E_B \right) \psi(r) = 0 \quad (10)$$

discretized on a 300 × 300 real-space grid. Note that the reduced electron-hole mass $\mu$ is still not accurately known for MoS$_2$. We use a representative value $\mu = 0.25 m_0$ in these calculations [2, 5]. The obtained wavefunctions $\psi(r)$ are shown in Figure S1(b) for the case $\alpha = 0.5$. Due to the stronger binding potential, $\psi(r)$ for hBN/MoS$_2$/SiO$_2$ system is slightly more localized than that for hBN/MoS$_2$/hBN; otherwise, these wavefunctions are nearly identical, having a characteristic spread of 1 nm each. Note that the asymptotic Coulomb law (9) becomes quantitatively accurate only at $r \gtrsim 2$ nm, which is yet another reason why the Rydberg-like formula for $E_B$ cannot be used [2] here (the first reason being a finite $\alpha$). From our numerical simulations we found that the absolute exciton binding energies do depend
on $\alpha$: $E_B = 216$ meV and 243 meV for $\alpha = 0.1$ vs. $E_B = 267$ meV and 297 meV for $\alpha = 0.5$. The first number in each pair is for hBN/MoS$_2$/hBN and the second is for hBN/MoS$_2$/SiO$_2$. However, the difference of $E_B$ between hBN/MoS$_2$/hBN and hBN/MoS$_2$/SiO$_2$ is approximately the same for both values of $\alpha$. It is equal to $27 \pm 3$ meV, with the larger binding energy occurring in the hBN/MoS$_2$/SiO$_2$ system.

The presented theoretical analysis is obviously very crude. A more careful calculation could be warranted once accurate values of the basic electronic parameters of the materials in hand are available. One interesting theoretical problem we did not address here at all is a potentially large effect of the frequency and momentum dispersion of the dielectric tensors. Furthermore, accurate estimates require approaches beyond the effective mass approximation considered here. These challenging problems are left for future work.
