Indirect Band Gap Emission by Hot Electron Injection in Metal/MoS$_2$ and Metal/WSe$_2$ Heterojunctions

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ABSTRACT: Transition metal dichalcogenides (TMDCs), such as MoS$_2$ and WSe$_2$, are free of dangling bonds and therefore make more “ideal” Schottky junctions than bulk semiconductors, which produce Fermi energy pinning and recombination centers at the interface with bulk metals, inhibiting charge transfer. Here, we observe a more than 10× enhancement in the indirect band gap photoluminescence of transition metal dichalcogenides (TMDCs) deposited on various metals (e.g., Cu, Au, Ag), while the direct band gap emission remains unchanged. We believe the main mechanism of light emission arises from photoexcited hot electrons in the metal that are injected into the conduction band of MoS$_2$ and WSe$_2$ and subsequently recombine radiatively with minority holes in the TMDC. Since the conduction band at the K-point is 0.5 eV higher than at the Σ-point, a lower Schottky barrier exists for the Σ-point band, making electron injection more favorable. Also, the Σ band consists of the sulfur $p_z$ orbital, which overlaps more significantly with the electron wave functions in the metal. This enhancement in the indirect emission only occurs for thick flakes of MoS$_2$ and WSe$_2$ (≥100 nm) and is completely absent in monolayer and few-layer (∼10 nm) flakes. Here, the flake thickness must exceed the depletion width of the Schottky junction, in order for efficient radiative recombination to occur in the TMDC. The intensity of this indirect peak decreases at low temperatures, which is consistent with the hot electron injection model.

KEYWORDS: Dichalcogenide, MoS$_2$, WSe$_2$, photoluminescence, hot electron

Recently, 2D layered metal dichalcogenides (TMDCs), such as MoS$_2$ and WSe$_2$, have drawn attention from a wide research community due to their intriguing optoelectronic properties. Bulk MoS$_2$ is an indirect band gap semiconductor with a band gap of 1.3 eV between the valence band at the Γ-point and the conduction band at the Σ-point in the Brillouin zone. The band structure evolution from bulk to monolayer TMDCs has been extensively studied by optical absorption, photoreflection, and photoluminescence spectroscopies. Various methods are currently being developed to improve the optoelectronic performance of TMDC devices. Different heterostructures, including graphene/TMDCs, monolayer TMDC stacks, and monolayer TMDCs/metal junctions have been fabricated in order to explore their material properties and device performances. For the monolayer TMDC/metal heterolayers, the A$_{1g}$ (i.e., out of plane) Raman mode shifts due to the presence of the metal substrate, and the A' and A'' PL peak intensities change due to substrate doping. The two-dimensional nature of TMDCs enables the possibility of building layer-by-layer vertically stacked heteromaterials with atomically clean and sharp interfaces, leading to unique physics, such as split excitons, interlayer charge transfer, and plasmonic-exciton interactions.

While a vast majority of research on these materials has focused on the indirect-to-direct band gap transition that occurs in monolayer TMDCs, thicker MoS$_2$ and WSe$_2$ films also provide an interesting semiconductor system, which is free of dangling bonds. Thicker TMDC films (>100 nm) provide substantially larger optical densities than monolayers and can withstand substantially higher injection currents, which are advantageous for solar energy conversion and light-emitting diodes applications. The absence of chemical interactions at the interface make the Schottky junction between metals and MoS$_2$ more “ideal” than 3D semiconductors like Si or III–V compounds. Lince et al. have found that in MoS$_2$/metal Schottky junctions, unlike other covalent semiconductors, the Fermi level is not strongly pinned at the interface.

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essential advantage of TMDCs, which has not yet been fully exploited.

In the work presented here, we explore the optoelectronic properties of heterojuctions formed between relatively thick MoS$_2$ (and WSe$_2$) flakes and metal contacts. We characterize these heterojuctions using photoluminescence spectroscopy and photorelectance spectroscopy. We systematically study the effects caused by the Schottky junction with different metals spanning a wide range of work functions and different MoS$_2$ thicknesses.

**Fabrication of MoS$_2$ Devices.** We exfoliate MoS$_2$ flakes from bulk material (SPI Supplies, Inc.) using the Scotch tape method. MoS$_2$/metal junctions were obtained by two methods. In the first, we exfoliate MoS$_2$ onto Si/SiO$_2$ substrates containing lithographically defined grid markers and measured PL from flakes on the Si/SiO$_2$. The thickness of the flakes are characterized by atomic force microscopy and optical microscopy, as shown in Figure S2 of the Supporting Information. We then transferred the same flake from the Si/SiO$_2$ substrate to a metal film and took another PL spectrum from the same flake. In the MoS$_2$ transfer process, PMMA is spun on the substrate from which it will be transferred. A 1 mol/L NaOH solution enables the PMMA/MoS$_2$ stack to be removed from the Si/SiO$_2$ substrate. Raman spectra taken before and after the transfer process (shown in Figure S3 of the Supporting Information) indicate that the properties of the TMDC layers remain unchanged, ruling out the possibility of chemical modification or strain/tension induced during the transfer process. In the alternative approach, we directly exfoliate MoS$_2$ or WSe$_2$ flakes on Si/SiO$_2$ substrates with prepatterned metal pads (50 nm metal deposited by electron beam evaporation). Atomic force microscopy imaging of the metal films show an RMS surface roughness of 4 nm. Before the exfoliation, the substrate is cleaned by using O$_2$ plasma. We then select TMDC flakes that lie partially across the metal pad and collect PL spectra from regions of the flake on top of the metal and on top of Si/SiO$_2$. Both of these approaches produce the same effect in the PL spectra when the MoS$_2$ or WSe$_2$ flakes are in contact with a bulk metal. PL spectra are collected on a Renishaw InVia spectrometer using a 532 nm laser (0.1 mW) focused through a 100× objective lens (room temperature measurement) and a 40× objective lens (low temperature measurement).

Figure 1a–c shows optical microscope images of a thick (>200 nm) MoS$_2$ flake exfoliated on a Si/SiO$_2$ substrate and subsequently transferred onto copper foil. The PL intensity in panels c and f are normalized using the Raman intensity measured from the MoS$_2$ flakes, in order to accurately depict the 1.3 eV PL enhancement of MoS$_2$ on metal. The scale bar is 10 μm.
Figure 1d and e shows optical micrographs of a few-layer MoS2 flake (<10 nm) on a Si/SiO2 substrate and then subsequently transferred to a copper foil, respectively. Unlike the 200-nm-thick sample, the PL spectrum of the few-layer flake is not affected significantly after the transfer. We consistently found these results in more than 30 different MoS2 flakes that were studied. In addition to MoS2, PL spectra were measured from WSe2 flakes on various metal substrates, which showed a similar enhancement of the indirect PL emission for relatively thick flakes, as shown in Figure S1 of the Supporting Information. We have also measured the differential photoreflectance spectra of a many-layer MoS2 flake on Si/SiO2 and on Cu, as shown in Figure S4 of the Supporting Information. These spectra show that MoS2 on Cu has a weaker absorption peak at 1.3 eV than 1.8 eV, as in bare bulk MoS2. These photoreflectance spectra indicate that there is no change in the absorption of the constituent materials either through a change in the band structure or plasmonic effects.

We believe that the main mechanism of enhanced light emission arises from photoexcited hot electrons in the bulk metal that are injected into the conduction band of MoS2, as illustrated in Figure 2a. Since the conduction band at the K-point is 0.5 eV higher than at the Σ-point, a lower Schottky barrier exists for the Σ-point band. The overall transmission probability, however, will not be determined solely by the barrier height, but also by the wave function overlap between the two materials. First-principles calculations have shown that the Σ-point conduction band valley consists primarily of out-of-plane (i.e., Mo 4dz2 and S 3pz) orbitals, whereas the K-point valley consists of in-plane orbitals (i.e., Mo 4dx and Mo 4dxy). In the MoS2 layer, sulfur atoms lie at the surface, so the S 3pz orbitals interact more significantly with the underlying metal, making electron injection into the Σ-point conduction band more favorable. Also, electrons at the K-valleys can decay to the Σ-point before radiative recombination. For these reasons, only the 1.3 eV PL peak is enhanced by hot electron injection, while the 1.8 eV peak remains at roughly the same intensity. The blue shift of the PL spectra taken from MoS2 on copper is caused by the recombination of hot injected electrons before they reach the minimum of the conduction band, which emit photons at a slightly larger energy than 1.3 eV. Also, it is known that the direct PL peak position of MoS2 flakes can red-shift with doping induced either electrically or when in contact with substrates. Usually, the actual Schottky barrier is much more complicated than the simple Schottky model described in most textbooks, due to surface and defect states, metal-induced gap states, and chemical bonds formed at the interface. These interfacial states create a layer with net charge at the interface, preventing electrons from passing through and causing Fermi level pinning at the Schottky junction. Researchers have found that in MoS2/Metal junctions, unlike other covalent semiconductors, the Fermi level is not strongly pinned at the interface. This anomalous behavior of MoS2 results from the inertness of its surface. Thus, the two-dimensional nature of MoS2 makes it possible for hot electrons to pass through the junction and contribute to photoluminescence emission.

Interestingly, this increased indirect photoluminescence emission occurs only for thick MoS2 flakes (>200 nm). This effect decreases with thickness, and it is completely absent in few-layer MoS2 (~10 nm), as shown in Figure 1f. 10 nm MoS2 contains about 16 layers and has the same band structure as 200-nm-thick (i.e., bulk) MoS2. The reason indirect emission is not enhanced in these thinner MoS2 flakes is related to the depletion width of the junction, as illustrated in Figure 2b. For thick MoS2 flakes, the photoexcited (hot) electrons injected into the MoS2 do not recombine in the depletion region, because there are no holes to recombine with. These injected electrons are swept out to the charge neutral region (by the build-in potential of the depletion region) where they recombine with the minority holes. Based on the equation $x_n = (\phi_s/\epsilon N_s)^{1/2}$, where $\phi_s$ is the Schottky barrier height, $\epsilon$ is the permittivity, and $N_s$ is the carrier concentration of MoS2, we can estimate the depletion width $x_n$ of the barrier. The work function of copper is 4.7 eV, and the electron affinity of MoS2 is between 3.7 eV to 4.4 eV, giving a barrier height $\Phi_B$ around 0.5 eV. A similar barrier height has been reported in previous literature. The exfoliated MoS2 from natural mineral is intrinsically n-type due to impurity doping, which is confirmed by the electrical measurement. We estimate the depletion width of the metal/MoS2 junction to be around 100 nm, based on an impurity concentration of $N \approx 10^{16} \text{cm}^{-3}$ to $10^{17} \text{cm}^{-3}$, and $\epsilon$, for bulk MoS2, is approximately 10. However, 100 nm is only a very rough estimation, because all the parameters involved are not measured precisely, and there is flake-to-flake variation. However, we, therefore, can expect the ~10 nm thick MoS2 flakes to be completely depleted, prohibiting radiative recombination of the injected hot electrons. In order to further demonstrate the mechanism of hot electron injection from the metal to the TMDC, we have fabricated MoS2-on-metal devices with an additional top electrode, as shown in Figure 3. Under an applied reverse bias, the PL intensity of the 1.3 eV peak decreases while the 1.8 eV peak remains the same. Here, the reverse bias voltage increases the width of depletion region,
which in turn reduces the thickness of the neutral recombination region thus lowering the PL intensity. A wider charge neutral region makes 250 nm thick flakes have stronger PL intensity than 100 nm, as shown in Figure S1. The bias measurement further confirms the hot electron injection model. The modulation of the PL intensity under applied bias voltages is limited by the uniformity of the bias potential in the plane of the MoS2 flake. In particularly, only the MoS2 that is close to the top metal electrode, within the depletion width of ~100 nm, will exhibit a bias-induced change in PL intensity. Since the laser spot is 0.5 μm, the resulting PL measurement represents an average of biased and unbiased MoS2.

Considering that hot electrons from the bulk metal cause the indirect PL enhancement, we explored several different metals in this metal/MoS2 junction that result in different Schottky barrier heights. In addition to Cu foil, we prepared junctions with Au, Cu, Ag, Al, and Gd pads patterned lithographically. Figure 4 shows the PL spectra acquired from MoS2 on four different metals. While these flakes appear largely opaque in the inset of these images, the optical image under white light illumination is mostly determined by the interference of the flake and SiO2 layer.35 We have found that a substantial amount of the incident light can penetrate 100~200 nm thick MoS2 flakes and reach the underlying metal electrode. To demonstrate this, we measured the silicon Raman spectra through 110 and 50 nm MoS2 flakes, as shown in Figure S5 of the Supporting Information. These spectra indicate that more than 6% of the incident light is able penetrate more than 220 nm of MoS2. For Au and Ag we observe the same selective enhancement of the 1.3 eV indirect PL emission from thick MoS2 flakes seen on Cu foils. On the other hand, Al and Gd junctions provide significantly less enhancement of the indirect PL peak. The work functions of the metals used in the experiment are Au 5.1 eV, Cu 4.7 eV, Ag 4.3~4.7 eV, Al 4.1 eV, and Gd 3.1 eV.36,37 Here, we find that the large work function metals generally give more significant enhancement of the 1.3 eV indirect PL emission. The work functions of Gd and Al are actually less than the electron affinity of MoS2, which results in an accumulation layer of electrons at the metal/MoS2 interface, rather than a depletion region. For these metals, the built-in field at the junction is in the opposite direction from the case of the large work function metals, impeding the injection of electrons from the metal to the semiconductor. Furthermore, these low work function metals tend to oxidize more readily than the noble metals, which can further impede charge injection. The relation between Schottky barrier height (ΦB) and probability (P) of hot electron injection follows the simple formula P ∝ exp(−ΦB).

The temperature dependence of a MoS2-on-Cu heterojunction is shown in Figure 5. Here, the indirect band gap PL enhancement is significantly suppressed as the temperature decreases. This is due to the decrease in minority carrier (hole) concentration in the charge neutral region of the MoS2 at low temperature, which follows the general relation p ∝ exp(−(E_F/2))

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Figure 3. Optical image (a) and PL spectra (b) of MoS2 on Cu with a bias voltage applied. With a increasing reverse bias applied, as the depletion width increasing, the PL intensity of 1.3 eV peak decreases as the 1.8 eV remains the same. The result further proves the hot electron injection model. The scale bar is 10 μm.

Figure 4. Photoluminescence spectra and optical microscope images of MoS2 flakes exfoliated on Si/SiO2 substrates with metal pads. (a) Au, (b) Ag, (c) Al, and (d) Gd. The enhancement in the indirect (1.3~1.4 eV) peak is most significant on Au and Ag, while Al and Gd do not provide as much enhancement. This is related to the Schottky barriers formed between these metals and the MoS2 flake.
While for MoS$_2$ on Si/SiO$_2$, the intensity of the 1.8 eV peak of the direct transition increased, due to the reduced nonradiative recombination as the temperature goes down, as reported in previous studies. The intensity of the 1.3 eV peak remains relatively weak because of its indirect band gap nature.

In conclusion, we observe a strong enhancement in the indirect band gap (1.3 eV) photoluminescence of metal/MoS$_2$ and metal/WSe$_2$ junctions, while the direct band gap emission remains unchanged. Interestingly, this enhancement in the indirect emission only occurs for thick flakes of MoS$_2$ and is completely absent in few-layer flakes. The large thickness is required to exceed the depletion width of the junction, which enables radiative recombination with minority holes in the charge neutral region of the semiconductor. The intensity of this indirect peak decreases at low temperatures, as the concentration of minority carriers decreases. These TMDC materials are free of dangling bonds and surface states, which is essential for the hot electron injection, allowing us to observe this phenomenon. This is the main reason this effect is not seen in Schottky junctions formed with bulk indirect band gap semiconductors, like Si and GaP. These results indicate that it may be possible to build future optoelectronic devices based on these two-dimensional semiconductor/metal junctions, e.g., photodiodes. Hot electrons in bulk TMDCs can also be used in tunneling devices and photocatalysts.

**ASSOCIATED CONTENT**

Supporting Information

Photoluminescence spectra of WSe$_2$/metal heterojunction, AFM images of MoS$_2$ flakes, and Raman and reflectance spectra of MoS$_2$ on Si/SiO$_2$ and on Cu. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b00885.

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Notes

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