Spectroscopic correlation of chalcogen defects in atomically thin MoS$_2$(1–x)Se$_{2x}$ alloys

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Abstract

Engineering of atomically thin transition metal dichalcogenides (TMDs) is highly sought after for novel optoelectronic and spintronic devices. With the limited number of naturally existing TMDs, chalcogen based alloying has become a viable solution for developing TMDs for optical modulators and photovoltaics. Here, we report on detailed optical and microscopic studies of ternary TMD alloys of molybdenum, sulfur, and selenium grown via a single step method. The developed material has tunable band gaps in a broad range 1.5–1.9 eV with the variation in sulfur compositions. Further, the existence of trions, bi-excitons, and defect bound excitons are shown using temperature dependent (4 K–300 K) photoluminescence spectroscopy. A detailed analysis on MoS$_{1.34}$Se$_{0.66}$ alloy system shows the evidence of new types of defect bound excitons originating at low temperatures along with the presence of bi-excitons having a binding energy of $\sim$41 meV. The prospects of defect induced quasiparticles are observed in scanning transmission electron microscope assisted analyses and verified using density functional theory calculations. The thermal conductivity values, calculated using micro-Raman studies, of MoS$_2$, MoSe$_2$, and MoS$_{1.34}$Se$_{0.66}$ are found to be 69(±2) W m$^{-1}$ K$^{-1}$, 33(±2) W m$^{-1}$ K$^{-1}$ and 17(±2) W m$^{-1}$ K$^{-1}$ respectively, in agreement with the theoretical predictions. Tunable optical properties of these ternary atomic layers along with moderate thermal conductivity reveal the potential of these layers in modern opto-electronic devices and sensors.

1. Introduction

Transition metal dichalcogenides (TMDs) are one of the most explored semiconducting two-dimensional (2D) materials because of their intriguing interactions with light [1–3]. Further, interesting magnetic, superconducting, and topological properties are being reported in different TMD monolayers and their heterostructures [4–8]. Many of the TMDs also show layer dependent variations in their optical bandgap, where some of them show indirect to direct while others direct to indirect type bandgap, when isolated in monolayers [9]. For example, bulk MoS$_2$ crystal has an indirect band gap of $\sim$1.2 eV while the monolayer of MoSe$_2$ has a direct band gap of 1.9 eV, resulting in an order higher photoluminescence (PL) and quantum efficiency than bulk [2, 10]. Further, the direct bandgap atomic layers can find applications in modern optoelectronic devices and bio-sensors [1, 2]. The limited number of naturally existing TMDs constrains their applications in broadband photodetectors and solar cells [1]. In this scenario, alloying of atomically thin TMDs with other transition metals or chalcogens (S, Se, Te) can bring controllability in their optical absorption [11–13].
Different attempts were made in the recent past to control the optical properties of TMDs via controlling their structure as well as stoichiometry [11, 12, 14], and alloying with other chalcogens or metals has emerged as one of the possibilities. For example, Song et al have reported the growth of a ternary system $W_xMo_{1−x}Se_2$ alloys, using a two-step process consisting of an atomic layer deposition followed by post sulfuration method [14]. Further, Li et al have shown that isoelectronic atoms such as tungsten (W) substitution in monolayer MoSe$_2$ can suppress the Se vacancy effects and hence enhance the PL due to the decrease in the Se defects mediated recombination in such ternary alloys [15]. But it is found that both MoSe$_2$ and Mo$_{1−x}W_xSe_2$ have similar electronic band structure, and both experimentally and theoretically no variation in band gap is observed [15]. In the similar lines, Susarla et al have reported quaternary Mo$_xW_{1−x}S_2Se_{1−y}S_{2y}$ alloys having bandgap tunability in the range of 1.61–1.85 eV only by varying both $x$ and $y$ [16]. It is theoretically shown that compared to the pseudo-binary alloys, varying both $x$ and $y$ in such a quaternary system provides greater flexibility in tuning the bandgap [17]. Recently Zhang et al have proposed a reverse-flow chemical vapor epitaxy for bilayer single crystals of ternary and quaternary alloys tunable electronic and optical properties [18]. Controlling the metals doping in TMDs requires higher reaction temperatures (>800 °C) and hence it may lead to more defective structures. Thus, chalcogen controlled large band gap tunable structures grown at relatively low temperatures are highly important to be developed.

The optical properties of 2D TMDs are different from 3D direct bandgap materials because of strong quantum confinement effects [2]. Hence, the Wannier-Mott excitons in these TMDs have high Coulombic interactions due to the reduced dielectric screening effect [1, 2]. The reported binding energies of the excitons in these TMDs are in the range of 400–600 μeV, hence the existence of such quasi particles can be realized using room temperature measurements [1, 2, 19]. Apart from the excitons, other quasiparticles like trions (charged excitons), bi-excitons and defect bound excitons are also found to be observable in certain TMDs at low temperatures [20]. Engineering these quasiparticles via external electric or magnetic field play a vital role in TMDs futuristic usage in different opto-electronic and spintronic devices [1, 2]. Though different types of quasiparticles can be present in atomically thin TMDs and their alloys grown via chemical vapor deposition (CVD), a detailed study on their spectroscopic investigation along with theoretical and microscopic correlation is still lacking. For example, though there are a few reports on the observation of bi-excitations in TMD alloys, almost no reports give evidence for defects bound exciton in these TMD alloys [14, 21, 22]. Hence the above review shows that a detailed study on an atomically thin ternary alloy of Mo, S, and Se is still lacking in literature and such a study will be insightful to understand the band-structure and excitations of opto-electronically important class of TMDs.

Chalcogen vacancy, makes TMDs as ‘n-type’ semiconductors, is a common type defect in TMDs, particularly those grown via CVD or physical vapor transport assisted techniques [23, 24]. Here spectroscopic evidence is given for the existence of different types of defects in an atomically thin ternary alloy system, namely MoS$_{(1−x)}$Se$_{2x}$, where the defects are microscopically verified using high angle annular dark-field imaging (HAADF) technique followed by the spectroscopic verification using temperature and power dependent PL spectroscopic analyses. Density functional theory (DFT) based calculations are performed to get further insight into the origin of the different types of excitons, including the novel defect bound excitons reporting here. A single step two zone furnace based CVD synthesis technique is used for the growth of large area alloys on SiO$_2$/Si. The phonon part of the thermal conductivity of MoS$_2$, MoSe$_2$, and the alloy is extracted using Raman studies and correlated with the theoretical predictions. Evaluation of the thermal conductivity of atomic layers is important to explore their potential in miniaturized devices [25]. Though there are recent theoretical predictions on the possibilities to reduce thermal conductivity of atomically thin alloys, yet experimental studies on their validation is still lacking.

2. Result and discussion

Atomic layers and the doped structures were grown over SiO$_2$/Si substrate via a CVD assisted growth technique and the details are given in section 4 and supporting information, figures S1 and S2 (available online at stacks.iop.org/JPMATER/3/045001/mmedia) [26]. The following nomenclature is adopted here for the alloys: MoS$_{(1−x)}$Se$_{2x}$, where the $x = 0$ represents pure MoS$_2$ atomic layer, where the growth temperature was set to 650 °C. To introduce Se into the MoS$_2$ lattice, the temperature of the MoO$_3$ zone was increased almost linearly with $x$ (see figure S2 in the supporting information). The $x = 1$ denotes pure MoSe$_2$ where the furnace temperature was set to 820 °C.

Figure 1(a) shows the optical image of one of the as grown MoS$_{(1−x)}$Se$_{2x}$ over SiO$_2$/Si substrate showing typical triangular morphology of monolayer TMD having large lateral width. Figure 1(b) shows the systematic variations in the PL peak positions of the samples with the variations in the Se ($x$) amount, where the $E_g$ varies from 1.5 eV (MoSe$_2$) to 1.89 eV (MoS$_2$). The amount ‘$x$’ in certain samples has been calculated using x-ray photoelectron spectroscopy (XPS) and the details are discussed later and also in supporting
Figure 1. (a) Optical image of monolayer triangles of MoS$_{2(1-x)}$Se$_x$ grown on SiO$_2$/Si substrates. (b) Tuneable PL from MoS$_{2(1-x)}$Se$_x$ alloys. (c) Micro-Raman signatures of MoS$_{2(1-x)}$Se$_x$ alloys for variable optical band gaps ($E_g$) varying from 1.5 eV (MoSe$_2$) to 1.89 eV (MoS$_2$). (d) Variations in A$_{1g}$, E$_{2g}$ and A$_{1g}$ Raman modes (peaks) of MoS$_2$ and MoSe$_2$ respectively, as a function of S/Se composition in MoS$_{2(1-x)}$Se$_x$ alloys.

information (figure S4). Figure 1(c) shows Raman spectra of all the alloy samples, where they are differentiated with the optical bandgap (calculated from the PL measurement, peak of the emission spectrum (excitation 532 nm)) mentioned over each spectrum. The Raman spectra of pure MoS$_2$ shows E$_{2g}$ and A$_{1g}$ modes $\sim$384 cm$^{-1}$ and $\sim$404 cm$^{-1}$ respectively, with the difference of 20 cm$^{-1}$ among the two modes confirming the monolayer thickness [26]. The Raman spectrum of the alloys depicts strong Se and S composition dependence. Alloys having higher content of S compared to Se demonstrate dominant MoS$_2$like Raman signatures. However, with gradual increase in Se content, several new Raman features appear at $\sim$220 cm$^{-1}$ and 265 cm$^{-1}$ associated with doublet A$_{1g}$ modes of MoSe$_2$. Pure MoSe$_2$ shows its typical Raman spectra with E$_{2g}$ ($\sim$287 cm$^{-1}$) and A$_{1g}$ modes ($\sim$243 cm$^{-1}$) having no traces of defects as well as impurities [27]. The doublet present in the Raman spectrum of the alloys near 220 cm$^{-1}$ and 265 cm$^{-1}$ is due to the different S/Se environment around Mo atoms [11, 12] in the system which is later proven via scanning transmission electron microscope (STEM) assisted high resolution imaging. The variation in the Raman spectrum with different S/Se composition is shown in figure 1(d). Figure 1(d) clearly shows that the MoS$_2$like E$_{2g}$ peak is more prone to the environment around the Mo atoms compared to MoS$_2$like A$_{1g}$ peak. The large atomic radius of Se compared to S develops lattice distortion and strain, which result in increase in the separation between E$_{2g}$ and A$_{1g}$ modes associated with MoS$_2$ feature [11]. The signature of strain and lattice distortion are also strongly demonstrated through the broadening of the Raman features associated with MoS$_2$ as the Se content increases. On the other hand MoSe$_2$like A$_{1g}$ peak shows doublet which comes closer to each other as the amount of Se increases in the MoS$_{2(1-x)}$Se$_x$ alloys.

One of the above alloy samples ($x \sim 0.33$, confirmed by XPS) has the PL centered at $\sim$747 $\pm$ 4 nm, and it is used for further analyses. The XPS analysis of this alloy was carried out to confirm the presence of selenium in the alloy and the results were compared with that of pristine MoS$_2$ (see supporting information, figure S3). The high resolution spectrum of Mo 3d, Se 3d, and S 2p were deconvoluted into Mo 3d$_{5/2}$, 3d$_{3/2}$ at 229.7, 232.9, Se 3d$_{5/2}$, 3d$_{3/2}$ at 55.1, 55.94 eV and S 2p$_{3/2}$, 2p$_{1/2}$ peaks at 162.6, 163.8 eV, respectively [26]. The spin-orbit splitting in Mo 3d is 3.2 eV while it is 1.2 eV and 0.84 eV for S and Se, respectively. The binding energy of Mo 3d $\sim$ 0.18 eV and S 2p $\sim$ 0.17 eV is red shifted which confirm the presence of Se atom having less electronegativity compared to sulfur itself. The aerial (area under the curve) analysis of the peaks shows that the alloy has $x = 0.33$, thus we rewrite the alloy as MoS$_{1.34}$Se$_{0.66}$. 

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The origin of the broad room temperature PL spectra of MoS$_2$ and MoS$_{1.34}$Se$_{0.66}$ was studied by deconvoluting them (see supporting information figure S4). The MoS$_2$ is centered at ~670 nm while that of MoS$_{1.34}$Se$_{0.66}$ is at ~747 nm. The temperature dependent (300 K to 4 K) PL of these samples are shown in figures 2(a) and (b). A schematic of the electronic energy dispersion in TMDs is shown in figure 2(c). The schematic shows all the possible excitation from valence band to higher states, including the defect states [28]. A large spin-orbit splitting ($\Delta_{SO}$) in valence band of these TMDs cause two dominating peaks corresponding to A and B excitons. This schematic showing the possible transitions has been modified for MoS$_{2(1-x)Se_{2x}}$ in the later part, after a detailed spectroscopic analysis carried out here. The deconvolution of room temperature PL (supporting information figure S4) of both MoS$_2$ and MoS$_{1.34}$Se$_{0.66}$ show the possibilities of four major emission correspond to B − exciton, A − exciton, A ′-trion, and a D peak which may related to bi-exciton formation in these TMDs [20].

The temperature dependent PL for both MoS$_2$ and MoS$_{1.34}$Se$_{0.66}$ show a systematic blue shift with lowering of temperature [28]. The figures 2(a) and (b) show some stark contrasts. For example, in MoS$_2$, a new peak starts (marked with dotted cyan line) emerging at 1.77 eV while cooling from 100 K onwards, which may correspond to that due to S vacancy defects where those are very common in CVD grown MoS$_2$, as discussed before [20, 24]. In MoS$_{1.34}$Se$_{0.66}$, two distinct peaks are observed at low temperatures (marked with dotted blue and red lines), where one starts emerging around 120 K while the other emerges around 70 K while cooling the sample. These two new peaks in alloys were not reported by others and hence need further study to understand the origin. The deconvoluted PL spectra of these two samples at all the temperatures are shown in supplementary figure S6 and that at 4 K is shown in figures 2(d) and (e).

The PL spectra of both the samples were fitted using five and six Lorentzian peaks at 4 K temperature, as shown in figures 2(d) and (e), respectively. The MoS$_2$ PL can be fitted with five peaks centered at 1.795 eV,
Figure 3. The individual peak position variations in PL spectra as a function of temperature for: (a) MoS$_2$ and (b) MoS$_{1.34}$Se$_{0.66}$. (c) Power dependent PL evolution in MoS$_{1.34}$Se$_{0.66}$ at 4 K for different laser powers. (d) Relative integrated PL (RIPL) intensity of sub-bands as a function of laser power at 4 K for MoS$_{1.34}$Se$_{0.66}$ alloy. (e) FWHM of A$^-$ exciton, A$^-$ trion and D$^1$ peak of MoS$_{1.34}$Se$_{0.66}$ alloy. (f) Super linear dependence of I$_{D^1}$ with I$_{A^-}$ exciton.

1.871 eV, 1.893 eV, 1.917 eV, and 2.061 eV and the peak can be assigned as D$_2$, D$_1$, A$^-$ trion, A$^-$ exciton and B$^-$ exciton, respectively [20]. Among all the peaks, D$_1$, A$^-$ trion, A$^-$ exciton and B$^-$ exciton peaks are also observable at room temperature, while the D$_2$ peak can be observed at low temperatures only. This is known as due to the excitons bound to S vacancies [20]. The MoS$_{1.34}$Se$_{0.66}$ has six Lorentzian peaks in its PL fitting centered at 1.662 eV, 1.703 eV, 1.740 eV, 1.765 eV, 1.781 eV, and 1.939 eV and they can be named as D$'$_3, D$'$_2, D$'$_1, A$^-$ trion, A$^-$ exciton, and B$^-$ exciton, respectively. In these emissions, D$'$_3, A$^-$ trion, A$^-$ exciton, and B$^-$ exciton are also visible at room temperature, as shown in supplementary figure S5. The D$'$_3 and D$'$_2 start emerging at 150 K and 70 K onwards while cooling, respectively. These two peaks can be related to the excitons bound to vacancy defects of either S or Se and/or both. To investigate these peaks further, their peak positions are recorded with temperature in the range 4 K–300 K as shown in figures 3(a) and (b) for MoS$_2$ and MoS$_{1.34}$Se$_{0.66}$, respectively and the variations are found to be exactly fitted with the equation proposed by O’Donnell et al [29]:

$$E_g(T) = E_g(0) - E_{ph}S \left(\coth\left(\frac{E_{ph}}{2K_bT}\right) - 1\right)$$

where $E_g$, $E_{ph}$, $S$, and $K_b$ are band gap at any temperature $T$, average phonon energy, coupling constant, and Boltzmann constant, respectively. The fitted curves give the $E_{ph}$ for D$_1$, A trion, A$^-$ exciton, and B$^-$ exciton peaks of MoS$_2$ and D$'$_1, A trion, A$^-$ exciton and B$^-$ exciton of MoS$_{1.34}$Se$_{0.66}$ to be around ~28–40 meV, which is comparable to the reported phonon energy of A$_{1g}$, E$_{2g}$ of MoS$_2$ and MoSe$_2$ [20, 30]. The D$_2$ peaks of MoS$_2$ and D$'$_3, D$'$_2 peaks of MoS$_{1.34}$Se$_{0.66}$ show $E_{ph}$ of around 10–14 meV which is much lower than the $E_{ph}$ of A$_{1g}$ and E$_{2g}$, and also equivalent to S vacancy defects in case of MoS$_2$ [20, 31]. All this information suggests that D$_2$ peak of MoS$_2$ and D$'$_3, D$'$_2 Peaks of MoS$_{1.34}$Se$_{0.66}$ can be related to the excitons bound to defects. Although the origin of D$_3$ in MoS$_2$ has already been reported for MoS$_2$ but the two peaks D$'$_3 and D$'$_2 in MoS$_{1.34}$Se$_{0.66}$ are not known before and their origins are still not completely understood.
To further confirm that $D'_1$ and $D'_2$ are originated from defect bound excitons, power dependent PL analysis was performed. The PL of MoS$_{1.34}$Se$_{0.66}$ can be broadly divided into two parts one having $D'_3$, $D'_2$ peaks and second $D'_1$, $A'$-trion and $A$ exciton (figure 3(c)). The power range ($50$–$1000$ $\mu$W) used for the power dependent PL was small enough so that no new defects are created in the lattice. The intensity ratio of the peak B to A is directly related to the defects present in the MoS$_2$ and can vary from 0.001 to 1 [32]. Thus, the ratio of the intensities of B to A is plotted with respect to the power in Figure S5, which further confirms that no new defects are being formed during the laser exposure. Assuming the number of defects to be constant, the increase in laser power is expected to increase the intensity of $D'_1$, $A'$-trion and $A$ exciton peaks while lowering the power is expected to increase in the intensity of $D'_3$ and $D'_2$ peaks [20]. Figure 3(c) shows the same as expected above and thus clearly shows that $D'_3$ and $D'_2$ peaks can be related to the defect bound excitons. To study these emissions individually, we have calculated the intensity ratio of individual peaks with the total intensity of the PL and called it relative integrated PL intensity (RIPL). The effect of laser power used on RIPL of individual peaks is shown in figure 3(d). The RIPL of $D'_3$ and $D'_2$ are found to be decreasing, indicating the number of defects is constant and get saturated at low laser power. While the $D'_1$, $A'$-trion, $A$- exciton, and $B$- exciton RIPL show increase with laser power. This further confirms that the $D'_3$ and $D'_2$ are defect bound exciton related peaks. Out of $D'_1$, $A$ trion, $A$- exciton, and $B$- exciton, the origin of $D'_1$ showed a significant change in RIPL with laser power, which may show its origin from bi-excitons. To confirm this further, the full width at half maxima (FWHM) of $D'_1$, $A'$-trion, and $A$- excitation are plotted with respect to laser power, as shown in figure 3(e), and found that the FWHM of $D'_1$ shows a significant enhancement compared to $A'$-trion and $A$ exciton above 600 $\mu$W. As the power increases, the populations of excitons increases linearly in the system and thus their spatial distance goes down which force them to form bound bi-excitons. The exciton formation shows a linear response with laser power ($I_{\text{exciton}} \propto I_{\text{laser}}$) while the bi-excitons are usually non-linear with laser power ($I_{\text{exciton}} \propto I_{\text{laser}}^\alpha$) where $\alpha > 1$ [20]. The fitted intensity of A exciton is plotted with intensity of $D'_1$ and shows an $\alpha = 1.5$, which is well in agreement with the reported values for bi-excitons [20, 33]. Thus, it can be concluded from the above discussion that the $D'_3$ and $D'_2$ peaks are defect bound excitons while the $D'_1$ is a bi-exciton formed in MoS$_{1.34}$Se$_{0.66}$.

The binding energy of these bi-excitons and bound exciton can be calculated by the relation $E = E_{\text{Di}} - E_{\text{A}}$, where $E_{\text{Di}}$ and $E_{\text{A}}$ are the position of neutral $A$ exciton and position of $D'_i$ peak, respectively and the $i = 1, 2$ and $3$. $E_{\text{A}}$ is the binding energy for these quasiparticles [28, 31]. The observed binding energy of bi-exciton in MoS$_{1.34}$Se$_{0.66}$ is $\sim 41$ meV, while that of $D'_2$ and $D'_3$ are $\sim 80$ meV and $\sim 120$ meV, respectively.

In order to verify the existence of such defects microscopically, a detailed HAADF-STEM analysis (shown in figure 4 and supporting information, figure S7) shows the monolayers of MoS$_{1.34}$Se$_{0.66}$. Figure 4(a) represents the low resolution HAADF-STEM image of a triangular MoS$_{1.34}$Se$_{0.66}$ layer on the quantifoil TEM grid. Figure 4(b) is a high resolution HAADF image, which shows the successful insertion of Se in MoS$_2$ to make MoS$_{1.34}$Se$_{0.66}$. Further, it clearly depicts the presence of Mo, S$_2$, Se$_2$, S + Se, and Se$_3$ sites in MoS$_{1.34}$Se$_{0.66}$ monolayers. Note that alloy sites, such as S + Se, Se$_2$, and Se$_3$ are labelled with green and aqua dashed rings, respectively, while white and gray dashed rings represent the chalcogen defect sites such as $V_{\text{SSe}}$, $V_{\text{S/Se}}$ (discussed later), respectively. Based on the previous reports [26, 34], Mo atoms display brighter intensity than the S$_2$ sites in pristine MoS$_2$ hexagonal lattice, whereas, in the case of Se-doped MoS$_2$, some S$_2$ sites become much brighter and display intensity close to or even higher than the Mo sites with the intensities of the Mo sites remaining unchanged. In the current work, we have quantitatively evaluated that higher image intensity at the S$_2$ sites arises from Se substitution (S + S) and Se$_2$, which are brighter than Mo (see supporting information, Figure S7) [26, 34]. Similar characteristics HAADF intensity variations corresponding to S + Se, Se$_2$, V$_{\text{S/Se}}$, and V$_{\text{S/Se}}$ are found to be in MoS$_{1.34}$Se$_{0.66}$ too, as shown in figure 4(b) [23–35]. It has been shown from the STEM analyses on MoS$_2$ atomic layers that is different types of point defects can be observed in CVD grown layers, where those include monosulfur vacancy ($V_S$), disulfur vacancy ($V_{\text{S2}}$), vacancy complex of Mo and nearby three sulfur ($V_{\text{Mo3S}}$), vacancy complex of Mo nearby three sulfur ($V_{\text{Mo5S}}$), and antisite defects where an Mo atom substituting an S$_2$ column (Mo$_{S2}$) or an S$_2$ column substituting an Mo atom (S$_2$Mo) [35]. However, the structural stability and formation energy of these various point defects are different and it is found that the $V_S$ is found to have the lowest formation energy, while Mo$_{S2}$ and S$_{2Mo}$ antisite defects have the highest formation energies under S-rich and Mo rich environments, respectively. Further, it has been shown that $V_S$, $V_{\text{S2}}$, and S$_2$Mo defects show effect on the electronic properties of MoS$_2$ [23, 36]. S$_2$Mo with relatively low formation energy under S-rich conditions will occupy deep levels, while both $V_S$ and $V_{\text{S2}}$ introduce two unoccupied deep levels about 0.6 eV below the conduction band minimum (CBM). The deep levels below the CBM for the $V_S$ and $V_{\text{S2}}$ vacancies might make them act as compensation centers in n-type MoS$_2$ [35]. Interestingly, HAADF-STEM analysis is in good agreement with our PL studies that are discussed in the previous section. We assign the single chalcogen vacancies of S and Se ($V_{\text{SSe}}$) responsible for $D'_2$ peak while double chalcogen vacancies of S and Se
Figure 4. HAADF-STEM images of MoS$_{1.34}$Se$_{0.66}$ showing: (a) low resolution image of a freestanding monolayer triangle on the TEM grid. (b) High resolution HAADF image showing Mo, S$_2$, S + Se (green dashed circle), Se$_2$ (aqua dashed circle), $V_{S+Se}$ (white dashed circle), and $V_{S2/Se2}$ (gray dashed circles). Note that an orange dashed boundary denotes a high density region of S + Se $&$ Se$_2$ on the MoS$_2$ plane. (c) The false color schematic image of (b) showing various atomic sites and chalcogenide defects in MoS$_{1.34}$Se$_{0.66}$ and corresponding (d) histogram extracted from (c) manually counted to estimate various atomic sites and defects present in MoS$_{1.34}$Se$_{0.66}$ alloy. 

Figure 4(b) also shows that the alloy has lateral heterostructures of MoS$_2$ and MoSe$_2$ with the size of around a few nanometers where it has a large density of S + Se and Se$_2$ sites, which is marked with an orange colored boundary line. In order to estimate the statistical distribution of alloy elements in MoS$_{1.34}$Se$_{0.66}$, we extracted a false color schematic image (see figure 4(c)) from the HAADF image figure 4(b), Corresponding histogram of atomic sites, chalcogen defects was plotted and shown in figure 4(d). Note that more detailed analysis of HAADF-STEM on S + Se, Se$_2$, $V_{S/Se}$ and $V_{S2/Se2}$ sites was performed and included in the supporting information, figure S7.

The concentration of vacancies ($C_i$) formed at a temperature $T$ depends on the formation energy of a particular vacancy [31]. To calculate the formation energy, $E_{form}$, for different kinds of vacancies, the information obtained from the STEM analyses was correlated with DFT-based analyses of the alloy structure. The STEM images confirm that the alloy has lateral heterostructure regions with a few nanometer sized MoS$_2$, MoSe$_2$, and MoSSe clusters. Hence a lateral heterostructure of MoSe$_2$ and MoS$_2$ is taken for the DFT-based analysis (more details in section 4). A $3 \times 6$ superlattice of each MoS$_2$ and MoSe$_2$ were used to make a lateral heterostructure $6 \times 6$, namely: pure heterostructure (named M) (see figure 5(a)). Other structures include heterostructure with a sulfur vacancy (named MS) (see figure S6a), heterostructure with Se vacancy (named MSe) (see figure S6b), a heterostructure with both S and Se vacancies (named MSSe) (see figure S6c) and a heterostructure with two sulfur vacancy (named MS2) (see Figure S6d).

The formation energy $E_{form}$ of $V_S$, $V_{Se}$, $V_{S2}$, $V_{Se2}$, and $V_{Mo}$ vacancies in the lateral heterostructure was calculated using the equation, $E_{form} = \frac{1}{2}(E_{V-M} - E_M + nE_S)$, where $E_{V-M}$ is the total energy of the structure with $n$ vacancies, $E_M$ is the total energy of pristine lateral heterostructure and $E_S$, the total energy of a single chalcogen atom in its stable form, $S_8$ and $Se_8$ respectively. The calculated values of $E_{form}$ for $V_S$, $V_{Se}$, $V_{S2}$,
V_{Se2}, V_{Mo} are found to be 2.32 eV, 2.54 eV, 4.03 eV, 4.21 eV, and 5.12 eV, respectively. The $E_{\text{form}}$ value for $V_{S}$, $V_{Se}$ found to be comparable and thus their concentration in the heterostructure could be almost the same assuming the partial vapor pressure of S and Se is nearly the same during growth of the alloy. While $E_{\text{form}}$ for $V_{S2}$, $V_{Se2}$, $V_{Mo}$ are found to be almost twice of the $E_{\text{form}}$ for $V_{S}$ and $V_{Se}$, and thus the concentrations of $V_{S2}$, $V_{Se2}$, and $V_{Mo}$ in the lattice are expected to be lower compared to $V_{S}$ and $V_{Se}$. The same is observed in the STEM images of MoS$_{1.34}$Se$_{0.66}$ in figure 4(d) where the number of $V_{S}/Se$ is $\sim 130$ while the number of $V_{S2}/Se2$ is only $\sim 13$. The probability of the presence of $V_{Mo}$ in thermodynamically favored growth is reportedly very low and the defect bound excitons for $V_{Mo}$ can be studied by artificially making the vacancies by He ion bombardments or plasma techniques [30, 37]. These artificially formed $V_{Mo}$ shows quantum emitter behavior which has not been seen in our PL studies and thus the possibility of $V_{Mo}$ can be neglected [28, 30].

Thus, the origin of $D'_2$ and $D'_3$ peaks can be related to $V_{S}$ or $V_{Se}$ or $V_{S2}$ or $V_{Se2}$.

Further, density of states (DOS) for the M, MS, MSe, and MSSe are calculated and given in figures 5(b)–(d). The DOS of M shows a band gap of $\sim 1.58$ eV having d orbital of Mo at both valence band maxima and conduction band minima, as shown in figure 5(b). An introduction of a chalcogen vacancy in the structure leads to some mid gap states $\sim 0.16$ eV below the conduction band shown in figure 5(c). In the mid gap states major contribution comes from the Mo 3d orbitals and S orbital. Although the Se atoms are present in the structure, the contribution from the Se is almost zero which shows that the states majorly depend on the neighboring atoms (Mo atoms) and next neighbors of the vacancy (S atoms). But in the MoSe structure, where we have both S and Se vacancies, the DOS shows almost equal contributions from both the S and Se atoms (figure5(d)). The states from S and Se atoms have maxima at almost same energies having an energy difference of around 10 meV which is very close and hard to distinguish in spectroscopy. The DOS of MS also shows the midgap states 0.2 eV below the conduction band. The $V_{S2}$ or $V_{Se2}$ vacancies create mid gap states more deeper in the band gap compared to $V_{S}$ or $V_{Se}$ and the difference between them is $\sim 40$ meV which is similar to the difference between the transitions of $D'_3$ and $D'_2$ peaks at 4 K. Hence the DFT studies suggest that the $D'_3$ and $D'_2$ peaks in PL of MoS$_{1.34}$Se$_{0.66}$ may originate from double chalcogen vacancy ($V_{S2}$ or $V_{Se2}$) and single chalcogen vacancy ($V_{S}$ or $V_{Se}$).

But the number difference between the $V_{S2/Se2}$ and $V_{S/Se}$ is not reflected in the PL originated from the two as the intensity of $D'_3$ and $D'_2$ peaks are comparable. To understand this inconsistency, the intensities of
D’2 and D’3 are fitted with the equation [31]:

\[ I_{PL} = \frac{I_0}{1 + \exp\left(\frac{\gamma E_{ph}}{K_B T}\right)} \]  

(2)

where \( I_0 \) is the intensity at lowest temperature, \( E_{ph} \) and \( K_B \) are the relevant phonon energy and Boltzmann constant, respectively. \( \gamma \) is the non-radiative exciton decay rate for a particular peak. The fitted peaks for D’2 and D’3 are shown in figure 6(a). The \( E_{ph} \) for both the peaks is set to be \( \sim 28 \) meV, which is close to the energy of A1g peak of the MoS2 and the the values of \( \gamma \) are found to be 362 and 83 for D’2 and D’3, respectively. A bound exciton usually has more probability of interaction with phonon and thus more non-radiative decay paths are possible for bound excitons as in the case of V_S/Se. But in V_{S2}, larger lattice distortion around a double chalcogen vacancy may lead to less exciton-phonon interaction and thus \( \gamma_{D’2} > \gamma_{D’3} \) is possible [31]. This shows that the V_{S2} or V_{Se2} is associated with more radiative defect bound exciton than V_S or V_{Se} and thus the intensities of D’3 and D’2 are comparable. Thus, the possibility is that the D’2 is expected to be coming from V_S or V_{Se} and D’3 is coming from V_{S2} or V_{Se2}. Thus, on the basis of all the information from above analysis an energy band diagram is presented schematically in figure 6(a) showing all six possible transitions i.e. B – exciton, A – exciton, A’ trion, Bi-exciton, and two defect bands D’2, D’3 at 1.939, 1.781, 1.765, 1.740 and 1.703, 1.662 eV respectively.

Large band gap tunability of these MoS_{1.34}Se_{0.66} alloys make them suitable for future optoelectronics. But the performance of electronic devices can also largely depend on the thermal conductivity of the samples [38, 39] and electron-phonon coupling present in these materials. Hence it is important to study the thermal coefficients and thermal conductivity of these alloys and here these values of MoS_{1.34}Se_{0.66} are calculated. Temperature and power dependent Raman scattering information can be used as an indirect method to find the thermal conductivity of samples [25, 38]. The temperature dependent and power dependent Raman scattering studies were performed on the SiO2/Si supported and free standing MoS_{1.34}Se_{0.66}, MoS2 and MoSe2 samples and the data is shown in figures 6, 9 and 10 respectively. The temperature dependent Raman scattering is performed on SiO2 supported MoS_{1.34}Se_{0.66} as it is reported that no significant
differences are there in the thermal coefficient values of suspended and supported MoS₂ layers [38]. The temperature range used here is in between 300 K and 600 K. The A₁₄ and E₂₈ modes of MoS₁₃₄Se₀₆₆ showed red shifts with increasing temperature, similar to that reported for pure MoS₂ [38, 39]. The peak shifts with temperature were fitted linearly with equation [37], \( \omega = \omega_0 + \chi_t \), where \( \chi_t \) is the first order thermal coefficient of a Raman peak as shown in figure 6(c). Both the peaks showed different thermal coefficients in this temperature range because E₂₈ peak largely depends on the strain of the lattice which can be present in the MoS₁₃₄Se₀₆₆ alloys due to lattice mismatch of these alloys with the substrate. Thus, for calculating the thermal conductivity of the material, the thermal coefficient of A₁₄ was considered. The \( \chi_t \) for A₁₄ was found to be 1.8 \( \times \) 10⁻² cm⁻¹ K⁻¹, which is higher than the supported monolayer MoS₂ and MoSe₂ having values \( \sim 1.5 \times 10^{-2} \) cm⁻¹ K⁻¹ and \( \sim 1.3 \times 10^{-2} \), respectively (see figures S9c and S10C) [38, 40].

Faster dissipation rate of heat is a problem for studying the power dependent Raman studies [38]. Thus a monolayer of MoS₁₃₄Se₀₆₆, MoS₂ and MoSe₂ are transferred to a TEM grid, using 2 M KOH solution assisted chemical etching of SiO₂, as shown in the figure 6(b). These freestanding monolayers are used for the power dependent Raman spectra analyses. The shift in MoS₁₃₄like A₁₄ peak of MoS₁₃₄Se₀₆₆ is measured and fitted linearly to measure first order power coefficient \( \chi_t \) of MoS₁₃₄Se₀₆₆, as shown in figure 6(d). Increase in the power can lead to the local heating of the sample which results in the phonon softening in these MoS₁₃₄Se₀₆₆ and shows red shift in both A₁₄ and E₂₈ modes. Due to the reason discussed above, the \( \chi_t \) measured for A₁₄ mode of MoS₁₃₄Se₀₆₆, MoS₂ and MoSe₂ are found to be 42.6 cm⁻¹ mW⁻¹, 8.8 cm⁻¹ mW⁻¹ and 16.3 cm⁻¹ mW⁻¹ [38, 40]. Hence, with the values of first order temperature and power coefficients and thickness of the layer as 0.7 nm, the thermal conductivity of the MoS₁₃₄Se₀₆₆, MoS₂ and MoSe₂ is calculated using the formula as [38, 41],

\[
\kappa = f \frac{\chi_t}{2\pi h \chi_p}
\]

where \( \kappa \) is the thermal conductivity of the alloy and \( h \) is the height of the alloy which is taken as 0.7 nm for monolayer MoS₁₃₄Se₀₆₆ [42]. The value of \( f = 1 - \exp (\alpha h) \) where \( \alpha = 2.8 \times 10^8 \) cm⁻¹ [43]. The calculated value of thermal conductivity of MoS₁₃₄Se₀₆₆, MoS₂ and MoSe₂ is found to be \( \sim 17.10 \pm 2 \) W mK⁻¹, 69.01 \( \pm \) 2 W mK⁻¹ and 32.83 \( \pm \) 2 W mK⁻¹ respectively which is in the well range of reported values [39, 40]. The thermal conductivity values are very well matched with the reported theoretical values as shown in figure S11 [44]. The lower thermal conductivity of MoS₁₃₄Se₀₆₆ in comparison to that of MoS₂ is because of mass disorder and local force field disorder which result in enhanced phonon localization [44]. Thus, the moderate thermal conductivity of these alloys supports their future optoelectronic applicability, especially in miniaturized devices for thermal stability of devices, and such possibilities will be explored in the near future.

3. Conclusions

Atomically thin engineered ternary TMDs having Mo, S, and Se atoms are developed and the variations in the chalcogen content is found to be leading to a range of TMDs having bandgap in a large range of 1.5 eV–1.9 eV. A detailed temperature dependent (4 K–300 K) PL study identified the existence of different quasiparticles in the alloys and origins of two different defect bound excitons (centered at 1.662 eV and 1.703 eV) and a biexciton having binding energy \( \sim 41 \) meV are identified in MoS₁₃₄Se₀₆₆ alloy. The existence of defects is verified using STEM-HAADF analyses and the possibilities of such defect bound excitons are calculated using DFT assisted analyses. Hence this study explores the plausible band structure of large lateral area atomically thin Mo, S, and Se containing ternary TMD alloys developed using vapor transport assisted method and showed its possible potential as a tunable opto-electronic material.

Further, the thermal conductivity, an important parameter for the use of TMDs in micro-/nano-electronics, of MoS₂, MoSe₂, and MoS₁₃₄Se₀₆₆ are measured using temperature and laser power dependent Raman analyses and the values are found to be 69(±2) W m⁻¹ K⁻¹, 33(±2) W m⁻¹ K⁻¹, and 17(±2) W m⁻¹ K⁻¹, respectively. A good thermal conductivity with tunable optical properties makes these atomically thin ternary alloys as potential candidates for opto-electronic applications, and simplicity of the experimental method makes this method of development as a large scale expandable one for the future applications.

4. Experimental

4.1. Atomic layer growth

Atomically thin MoS₂ and MoSe₂ were grown using a CVD assisted technique, similar to that reported in our previous work [26]. In order to synthesize the ternary system of Mo, S and Se, both sulfur and selenium
powders were used as precursors and the growth is optimized by fixing the position of sulfur and selenium. The selenium was kept at a temperature of 350 °C and sulfur was placed 6 cm away from the selenium source as shown in the figure S1a. To get the alloys with different atomic percentages of selenium, the temperature of the precursor (MoO$_3$) was varied linearly from 650 °C to 820 °C, as shown in figure S2. During the whole growth process, ultra-pure Ar/H$_2$ gas is flown through the chamber at a flow rate of 200 sccm. The temperature-time profile of the growth is shown in figure S1b where it can be inferred that the sudden cooling after the growth prevents the layer by layer growth of atomic layers and restricts to monolayers.

4.2. Cryogenic PL spectroscopy and micro-Raman spectroscopy

The micro-Raman spectroscopy and low temperature PL measurements were conducted in back scattering geometry using Horiba Jobin-YvonLabRAM HR evolution Raman spectrometer with 1800 g mm$^{-1}$ grating (600 g mm$^{-1}$ grating for PL) and Peltier cooled CCD detector. Temperature dependent PL was performed using closed cycle cryostat in the range of 4–300 K, using 532 nm non-resonant excitation laser. Temperature dependent and power dependent Raman spectroscopy for thermal conductivity measurements were done using Renishaw Invia Raman spectrometer equipped with Linkam cell TS1500. The samples were focused with an L50x objective lens and exposed with 532 nm laser excitation wavelength.

4.3. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)

STEM images were recorded with an 80 keV spherical aberration-corrected STEM (JEOL 2100F) equipped with a probe corrector (CEOS GmbH) in the HAADF mode, and the aperture semi-convergence angle was 19 mrad. The inner and outer collection angles of the annular detector used for Z-contrast imaging were 62 and 164 mrad, respectively. Each STEM image was obtained in a frame of $512 \times 512$ pixels with a dwell time of 38 $\mu$s per pixel.

4.4. X-ray photoelectron spectroscopy (XPS)

XPS was performed to estimate chemical composition and atomic percentage of Se in MoS$_2$(1−x)Se$_x$ alloy using Thermo Fisher scientific K-Alpha using A1 K$\alpha$ monochromatic source.

4.5. Theoretical calculations

DFT calculations were undertaken with the SIESTA 4.0 package. The lateral heterostructures of MoS$_2$ and MoSe$_2$ with a super cell of $3 \times 6 \times 1$ each with periodic boundary conditions in the xy plane were used for DOS calculation of the heterostructure. The interaction between adjacent layers was eliminated by introducing 18 Å distance between them in z direction. The pseudo potentials for electron exchange correlation were generated using generalized gradient approximation–Perdew–Burke–Ernzerhof parameterization. An energy cut off of 500 Ry and $8 \times 8 \times 1$ k-point mesh were used for DOS calculations.

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