Single crystal flake parameters of MoS\textsubscript{2} and MoSe\textsubscript{2} exfoliated using anodic bonding technique and its potential in rapid prototyping

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Abstract
Rapid prototyping of devices using exfoliated Molybdenum di-Sulphide (MoS\textsubscript{2}) and Molybdenum di-Selenide (MoSe\textsubscript{2}) requires an experimental protocol for maximizing the probability of realizing flakes with desired physical dimension and properties. In this work, we analyzed the size and thickness distribution of MoS\textsubscript{2} and MoSe\textsubscript{2} single crystalline flakes exfoliated using anodic bonding technique and established a correlation between physical dimension of the flakes and the bonding parameters. Anodic bonding was carried out by applying a fixed voltage of 200 V with a set temperature of 150 °C for four different bonding time intervals. On analyzing the flake parameters from the four anodic bonded substrates using the optical and atomic force microscopy, it is found that the probability of getting flakes with large lateral size (>200 μm) increases as the bonding time interval is increased. Most of these large sized flakes have thickness of more than one hundred mono-layers and a tiny fraction of them have thickness of the order of few monolayers. A similar trend was also observed for MoSe\textsubscript{2} single crystals. To demonstrate the feasibility of this technique in rapid prototyping, ultra thin MoS\textsubscript{2} flakes was directly bridged between two ITO electrodes and their transport properties was investigated. Micro-Raman and photoluminescence studies were taken on selected regions of the thicker and thinner exfoliated flakes and their physical properties are compared.

1. Introduction

Two dimensional (2D) transitional metal dichalcogenides (TMDCs) are an emerging class of materials for fabricating nano-scale devices as it has non-zero tunable band gap, strong spin–orbit coupling, high electron mobility and large optical absorption window [1]. The most simplest method to realize highly crystalline, pure and atomically thin nanosheets of TMDCs is by mechanical exfoliation [2]. Even though this technique is not scalable unlike other growth techniques such as molecular beam epitaxy, chemical vapour deposition and chemical exfoliation, it offers the advantage of realizing high quality films for rapid prototyping [3–5]. Over the years, such mechanically exfoliated ultra thin films have greatly contributed towards understanding many of the fundamental properties and potential device application of TMDCs and other layered materials [6, 7].

The main bottleneck in the conventional exfoliation process is the smaller flake size and low yield of single layers. Typical size of the exfoliated flakes are often less than 200 nm and requires electron beam lithography for device fabrication. One possible route to increase the size of the flakes is by exfoliating on gold coated substrates [8]. Even though the technique produced larger flakes, the necessity to pre-deposit the substrate with gold requires post-exfoliation chemical treatement which affects the quality of the flakes. Considering the fact that mechanical exfoliation is very cost effective, it would be a great advantage, if one could use this method for rapid prototyping of devices without using expensive lithographic techniques. To realize this objective and overcome the size limitation of the convetional exfoliation process, the best alternative will be anodic bonding technique [9]. In this method, exfoliation is carried out on a sodium rich pyrex glass by applying high voltage and
Optical microscope images of very thin single crystals of MoS$_2$ and MoSe$_2$ flakes. (a) Mechanically exfoliated TMDC flakes on scotch tape is put into contact with a clean glass surface. (b) Experimental schematics for anodic bonding process. (c) Exfoliating TMDC flakes from the glass substrate after anodic bonding. (d) Exfoliated thin TMDC flake on the glass substrate.

Figure 1. Illustration of the anodic bonding process to get few layer MoS$_2$ and MoSe$_2$ flakes. (a) Mechanically exfoliated TMDC flakes on scotch tape is put into contact with a clean glass surface. (b) Experimental schematics for anodic bonding process. (c) Exfoliating TMDC flakes from the glass substrate after anodic bonding. (d) Exfoliated thin TMDC flake on the glass substrate.

temperature [10]. The applied voltage triggers the movement of ions inside the glass substrate to create a space charge region at the boundary. The resultant electrostatic force pull the flakes towards the substrate and an ionic type bonding is established between the flake and the substrate [11]. On separating the scotch tape with the precursor TMDCs from the substrate, high quality large single layer flakes with fewer grain boundaries are obtained [12]. Such exfoliated flakes are easily dispersible in any solution by ultrasonication and subsequently can be transferred to any substrate or pre-patterned electrodes for experimental investigations.

Even though most of the works on anodic bonding and other exfoliation technique report the presence of large area flakes, it seldom highlights the fact that such large flakes are found among the debri of hundreds of other exfoliated flakes with varying size and thickness. The primary objective of this work is to provide a realistic analysis about the size and thickness distribution of TMDC flakes exfoliated using anodic bonding technique with different bonding parameters. The analysis is then used to correlate the likelihood of getting flakes of particular size and thickness with the bonding parameter. Furthermore, by using the bonding parameter that favourably yielded flakes with sizes $> 200 \mu m$, the TMDC flake was directly bridged between two ITO electrodes which are about $200 \mu m$ apart and their transport properties were investigated.

2. Experimental details

Figure 1 illustrates the process flow for obtaining very thin flakes of MoS$_2$ and MoSe$_2$ on a glass substrate using anodic bonding technique. A detailed explanation about the physics of anodizing bonding technique can be found elsewhere [9]. Single crystalline flakes of MoS$_2$ and MoSe$_2$ (size of around 1–2 mm) were carefully cleaved off from the bulk crystal using a scotch tape. The thickness of the freshly cleaved precursor flake is further reduced by exfoliating three to four times before using it for anodic bonding (figure 1(a)). For each of the different bonding trials freshly cleaved TMDC precursors were used and the same tape was never used more than once.

The scotch tape with the 2D precursor flakes is then stuck onto the glass substrate and placed on a heating platform. Two copper electrodes were attached, one on the top of the scotch tape and the other at the bottom of the glass substrate and the two contacts were connected to the Keithely source-meter (figure 1(b)). Anodic bonding procedure was carried out in four different substrates by applying a voltage of 200 V at 150 °C for time intervals 15, 30, 45 and 60 min. A small mechanical pressure was exerted using a 100 gm weight on the top of the scotch tape to improve the adhesion between the glass substrate and the scotch tape. Once the bonding time is completed, the scotch tape was peeled gently leaving behind flakes of different geometry on the glass substrate (figures 1(c) and (d)). The exfoliated flakes were then investigated using optical and atomic force microscope (AFM) to study its size and thickness distribution. Raman and photoluminescence (PL) studies were carried out to ascertain the active phonon modes and the optical band gap of the exfoliated flakes. A simple two terminal device was fabricated without using any lithographic technique by directly exfoliating the flakes between the two Indium Tin Oxide (ITO) electrodes on the glass substrate. The transport properties was then investigated by measuring its resistance as a function of temperature in a variable range closed cycle cryostat.

3. Results and discussion

Optical microscope images of very thin single crystals of MoS$_2$ and MoSe$_2$ flakes exfoliated under four different bonding parameters are shown in figures 2 and 3. The images were taken by illuminating white light from the back of the substrate.

Most of the flakes appear either blue or greenish in colour due to the difference in their optical absorption characteristics. When the flakes are thicker, it absorbs lights with longer wavelength and transmits mostly the shorter wavelength (blue) radiation. As the thickness of the flakes decreases, the intensity maxima of the
transmitted light is red-shifted giving rise to greenish tinge. The thicker bluish flakes are predominantly larger, with lateral size greater than 60 μm whereas the thin greenish ones have lateral sizes varying between 10 and 60 μm. Furthermore it can also be observed that the number of flakes with larger lateral size increases with the bonding time. This is because, on initial contact, many tiny air gaps are formed between the precursor flakes and

Figure 2. Optical images of exfoliated MoS2 using anodic bonding technique for bonding time intervals (a) 15, (b) 30, (c) 45 and (d) 60 min.

Figure 3. Optical images of exfoliated MoSe2 using anodic bonding technique for bonding time intervals (a) 15, (b) 30, (c) 45 and (d) 60 min.
the glass substrate. As the time progresses, the flakes are gradually pulled towards the substrate due to the force exerted by the applied electrostatic field. With the area of physical contact increasing with the bonding time, the probability of getting flakes with large lateral size increases [13].

Figure 4 shows the lateral size distribution for both the MoS₂ and MoSe₂ flakes for all the bonding time intervals. The analysis of the size distribution revealed that for all the bonding time intervals, flakes with sizes between 10–30 \( \mu \)m dominate the distribution (figure 4). The second dominant distribution lie in the 30–50 \( \mu \)m range. Flakes with size above 70 \( \mu \)m are less in number for 15 and 30 min bonding intervals. It is clear from the distribution chart that for realizing larger flakes, bonding time has to be greater than 30 min. Extremely large flakes with size greater than 200 \( \mu \)m start to show up only when the bonding time was increased to 45 min. Further increasing the bonding time resulted in larger and thicker flakes. Similar trend is also observed when the bonding temperature is increased beyond 150 °C (figure 5(a)).

Table 1 shows that, as the bonding time interval is increased from 15 to 60 min, the average flake size increases. Therefore, to get a reasonable number of flakes with size greater than 200 \( \mu \)m, ideal bonding time will be 45 min and more.

For ascertaining the thickness distribution of the flakes, we carried out AFM measurement on all the four anodic bonded substrates. We focused our measurement only on the flakes whose lateral size is 50 \( \mu \)m and more. This 50 \( \mu \)m limit was fixed for two reasons; One, it will give us a rough estimate of thickness distribution of larger flakes which is the focus of this study. Secondly, the AFM measurements are very time consuming and it is not practically feasible to study the thickness distribution of all the exfoliated flakes. The results of our AFM measurements are shown in table 1. From the thickness distribution data across all the four bonding intervals, we found that in MoS₂, the maximum flake thickness varied between 730–840 nm and the range of minimum thickness was between 80–300 nm. In comparison to MoS₂, the flakes are significantly thicker in MoSe₂ for all the four bonding time intervals with maximum flake thickness varying between 1–0.6 \( \mu \)m. This was expected as

![Figure 4](image1.png)

Figure 4. Statistical flake size distribution of (a) MoS₂ and (b) MoSe₂ flakes.

![Figure 5](image2.png)

Figure 5. (a) Size and thickness variation as a function of temperature and time. (b) Room temperature micro Raman spectrum of a monolayer MoSe₂ flake. Inset: optical microscope image of a monolayer flake.
the energy cost of peeling off the layers is lesser for MoSe\textsubscript{2} \cite{14}. Unlike the lateral size distribution, there is a lack of correlation between bonding time interval and the flake thickness. This is due to the small number of samples taken for the study. However the thickness distribution data roughly indicates that the most expected thickness for flakes larger than 50 $\mu$m is around 250 nm. The AFM images taken across the surface of those flakes indicates that the flake surfaces are relatively smooth without any visible cracks (supplementary information (figure S1 is available online at stacks.iop.org/JPCO/4/105015/mmedia)). Large mono-layer flakes (size $>50\mu m$) are obtained in the bonding trails but the likelihood of getting it was highly random. To elaborate, the number of bonding trials (with same bonding parameters) one should carry out to realize such large monolayer and bilayered flakes still remains unpredictable. A monolayer flake of MoSe\textsubscript{2} which was observed in one of the bonding trials is shown in figure 5(b) along with its Raman spectrum.

Optical bandgap and active phonon modes of the exfoliated MoS\textsubscript{2} and MoSe\textsubscript{2} flakes were investigated using PL and Raman spectroscopy respectively. Both these studies were performed on a large number of flakes for all the bonding parameters. However the spectra corresponding to only the thickest and the thinnest flakes were shown as it gives the lower and upper bound for the optical band gap and phonon mode distribution (figures 6 and 7). For the sake of clarity, detailed analysis was limited to 60 min bonding time and the data for all the other bonding parameters are provided in the supplementary information (figures S2–S5).

The thinnest and thickest MoS\textsubscript{2} and MoSe\textsubscript{2} flakes used in this study have their lateral sizes around 7 and 200 $\mu$m respectively. At room temperature, the exciton binding energy for MoS\textsubscript{2} and MoSe\textsubscript{2} is very weak and therefore the excitons will be mostly free \cite{15, 16}. Unlike ‘bound’ excitons, the PL peak due to the recombination of free excitons will be more or less equal to the optical band gap. We use this fact to estimate the band gap of the flakes directly through PL peak wavelength. The thinnest flake has an optical bandgap of 1.7 eV whereas the thicker one is around 1.3 eV (figure 6(a)) \cite{17}. The higher bandgap for the thinner flakes is due to the strong coupling between the adjacent layers. As thickness decreases, the inter-layer coupling becomes stronger and the energy separation between the top of the valence band and the bottom of the conduction band increases \cite{18}. In the case of MoSe\textsubscript{2}, PL shift between the thickest and thinnest flakes is much lesser and is around 0.12 eV. This is
due to the fact that the weak inter-layer interaction in MoSe$_2$ makes the bandgap vary very slowly with layer thickness. The optical bandgap of the thinnest MoSe$_2$ flake is 1.45 eV which is about 0.1 eV less than the monolayer bandgap [19]. The optical band gap of exfoliated flakes for all the other bonding parameters are tabulated and shown in the supplementary information (table ST1).

Micro-Raman spectrum were taken in the back scattering geometry with a 532 nm laser by focusing it at the edges of the same MoS$_2$ and MoSe$_2$ flakes that were used for PL studies. Raman spectrum revealed phonon modes that are very similar to a monolayer flake indicating that the thickness at the edges of both thick and thin layer flakes are almost few monolayer thick. For instance, in MoS$_2$, both in-plane mode ($E_{12g}$) and out-of-plane mode ($A_{1g}$), had a raman shift of less than 25 cm$^{-1}$ which is a typical feature of monolayer flake [20]. Similarly, for MoSe$_2$ a sharp peak at 243 cm$^{-1}$ corresponding to out-of-plane vibration mode of a few layer flake was observed ($A_{1g}$). This study indicate that the exfoliated flakes are thicker at the center and gradually thin down to few monolayer thickness as we move towards the edges. This is also observed in the form of color contrast in the optical microscope images and also in the Raman spectra taken at the center and edge of few layer MoSe$_2$ flake which is shown in the supplementary information (figures S6 and S7).

Finally to demonstrate the feasibility of this bonding technique in rapid prototyping of devices, two and four terminal devices were fabricated by directly exfoliating n-MoS$_2$ flakes between the pre-patterned ITO electrodes (figures 8 and S8). The flakes were exfoliated using 60 min bonding time. The experimental procedure for realizing 200 μm gap pre-patterned ITO electrode was provided elsewhere [21]. Since the optical contrast between the etched and the unetched segments of the ITO portion was very poor, a solid line demarcating the boundary had been drawn as a guide to the eye. In figure 8, one can notice that the exfoliated MoS$_2$ flakes bridges the electrodes in two ways. One is by inter-connected flakes (figure 8(a)) and other is through a large single MoS$_2$ flake directly bridging the electrodes (figure 8(b)).

For the two terminal measurement, the bridged sample was loaded in a closed cycle cryostat and the current-voltage (I-V) measurement was taken at different selected temperatures as the sample was cooled down to 10 K.
The linearity of the I-V curves all the way up to 10 K indicates that the contacts are ohmic. On reaching 10 K, the sample was allowed to warm up naturally and the current was recorded as a function of temperature (T) by applying a constant bias of 3 V. To determine the effect of contact resistance, four terminal measurement was carried out by injecting a constant current of 100 nA and the voltage was measured as a function of temperature (figure S8). The resultant resistance (R) versus temperature (T) plot shows identical characteristics for both two and four terminal measurement which is a clear indication that the contact resistance plays no significant role in our measurement (figure 9). Two distinct conduction regimes are seen in the transport measurement [22]. A regime below 70 K dominated by phonons and the other above 70 K dominated by thermal activation of charge carriers. In the phonon dominated regime, the current increases with decrease in temperature as the number density of phonons decreases. In the thermally activated regime, the current increases with temperature as more and more charge carriers are activated from the donor sites to the conduction band. Given the fact that the Mo interstitials and S vacancy are deep level defects, we speculate that carrier excitations are mostly from the shallow Hydrogen donor sites in MoS2 [23].

4. Summary and conclusion

In summary, we investigated the flake parameters of MoS2 and MoSe2 that were exfoliated using anodic bonding technique. The analysis revealed that the probability of getting flakes with lateral size > 200 μm is high when the bonding time interval is 45 min or more. Larger flakes mostly have a thickness greater than 300 nm and the smaller ones are only a few monolayer thick. The band gap distribution and phonon modes were studied using PL and Raman spectroscopy respectively. The transport properties of the exfoliated flakes were then studied by directly bridging them between the two ITO electrodes. The study revealed two transport regimes, one dominated by phonons and other by thermally activated carriers.

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