Investigation of Optical Properties of layered MoS_2

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ABSTRACT

Few atomic layers of molybdenum disulphide (MoS_2) have been prepared using chemical exfoliation techniques. Optical properties of few atomic layers of MoS_2 were investigated experimentally using Raman and Photoluminescence spectroscopy. Ab-initio density functional theory has been used to understand the electronic structure and lattice dynamics of monolayered and bilayered MoS_2.

Keywords: layered dichalcogenides, raman spectroscopy, photoluminescence, density functional theory, phonons

1 INTRODUCTION

Three dimensional transition metal dichalcogenides have been investigated for a long time now. These materials form two types of stable structures namely the 3R-MoS_2 polytype[1] and layered 2H MoS_2. The recent discovery of mono-layered sheets of elements such as carbon [2] and boron [3] has rejuvenated the interest of the research community into investigations of mono- and few atomic layers of layered materials. Nano crystals of MoS_2 have found several interesting applications such as hydrogen production [4, 5], removing sulphur components from oil during purification [6, 7], solar cells [8] and photocatalysis. Recent studies have also indicated that mono- or multilayer sheets of MoS_2 could have interesting optoelectronic applications. Raman spectroscopy has been used to investigate the optical properties of these materials [9], however there is a great need to further understand the optical properties of these layered MoS_2.

In this manuscript we investigate the Raman and Photoluminescence spectrum of few atomic layers of molybdenum disulphide in light of phonon density of states and electronic structure obtained using ab-initio density functional theory.

2 MATERIALS AND METHODS

2.1 Experimental methods

Ultra thin layered MoS_2 samples were prepared using chemical exfoliation method. Simgle crystal wafers of MoS_2 obtained from SPI inc. (specific gravity 4.8) were dissolved in acetonitrile by stirring the solution on magnetic stirrer at room temperature. A highly concentrated solution of atomic layers of MoS_2 suspended in acetonitrile is shown in Figure 1 below. The solution so obtained appeared dull greenish - grey in color.

Figure 1 – Atomic layers of MoS_2 suspended in acetonitrile

Atomic layers of MoS_2 so exfoliated in the acetonitrile solution were deposited on TEM grids and SiO_2/Si substrate for further characterization. This method is very simple to perform as compared to scotch tape and other methods. Raman and photoluminescence measurements (Reinshaw) were performed using a continuous He-Ne laser with wavelength of 633 nm.

2.2 Computational Methods

Density functional calculations have been performed using Vienna Ab-initio Simulation Package (VASP)[9, 10]. First principle spin restricted calculations within the local density approximation (LDA) with plane wave basis set were carried out using highly efficient ultra soft pseudo potentials (USPP) employing the exchange correlation form of Ceperley and Alder[11] as parameterized by Perdew and Zunger[12] were used. A large planewave cutoff of ~450 eV was used. The geometry was relaxed using the conjugate gradient algorithm and K – points sampling was done using the Monkhorst Pack scheme. K-point mesh of 16x16x8 was taken to optimize the structure. The convergence of energy was chosen as 10^{-7} between two consecutive steps and the maximum Hellmann-Feynman force acting on each atom is less than .005eV/Å for electronic structure calculations. The electronic band structure was calculated by sampling the reciprocal space along the high symmetry lines using 54 divisions. The phonon dispersion curves are calculated using the supercell approach. The Hessian matrix was

calculated using finite difference method as implemented in VASP.

3. RESULTS AND DISCUSSION

The sample prepared as discussed above was deposited on holey carbon TEM grids. TEM images of the sample along with selected area electron diffraction (SAED) pattern are shown in Figure 2.

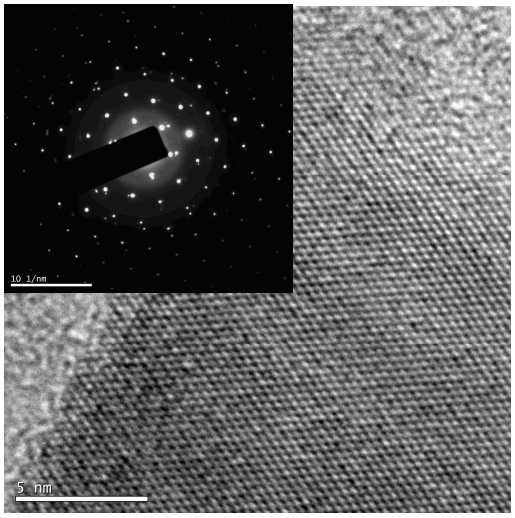

Figure 2 – TEM image (scale 5 nm) of the sample on holey carbon TEM grid. The inset shows the SAED pattern (scale 10 nm)

The TEM images along with the SAED pattern confirm the hexagonal symmetry of the prepared sample. The diffraction pattern shows a bright and two faint spots indicating the basis of molybdenum and sulphur atoms as shown in Figure 4.

Figure 3 shows the representative Raman spectrum for few atomic layers of MoS_2 samples as deposited on TEM grids.

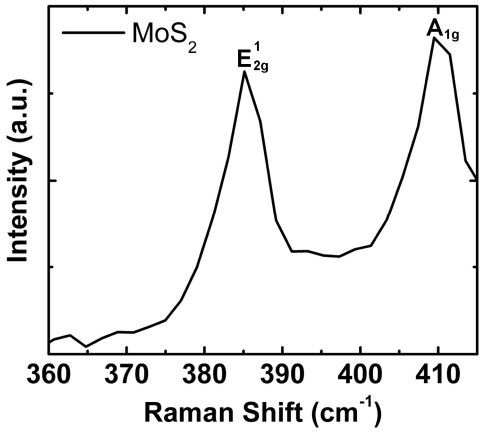

Figure 3 – Raman spectrum of bulk MoS2 sample using λ=633nm from 75mW He-Ne Laser.

We observe the E^1_{2g} and A_{1g} vibrational modes at around 400 cm^{-1}. The E^1_{2g} modes are occur due to inplane movement of the molybdenum and sulphur atoms while the A_{1g} correspond to the out of plane motion of the sulphur atoms as shown in Figure 4. The two sulphur atoms in adjacent layers move towards each other and hence in monolayered samples these vibrational or phonon modes are expected to soften due to no interactions with other layers.

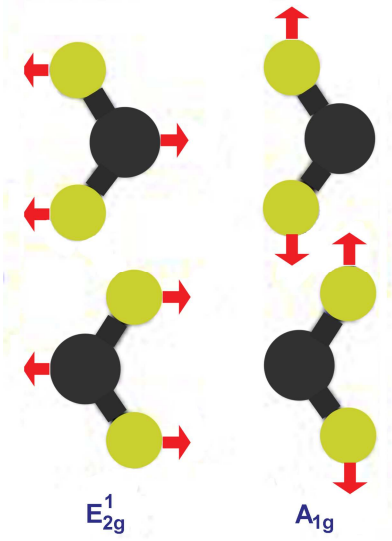

Figure 4 – Atomic arrangement in MoS_2 along with the E^1_{2g} and A_{1g} Raman active vibrations

The photoluminescence measurements were performed by using excitation wavelength of 633 nm. The photoluminescence spectrum shows a broadened peak around 710 nm and a very sharp peak at about 650 nm as shown in Figure 5. The intensity of the peak at ~650 nm increases in as the no. of monolayers in the sample increase.

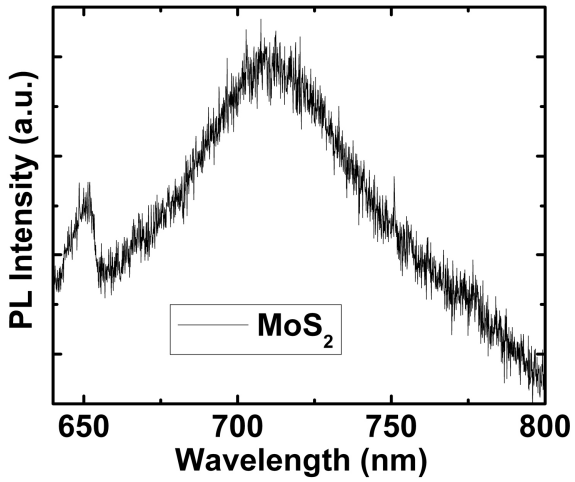

Figure 5 – Photoluminescence spectrum of MoS_2 obtained using excitation wavelength of 633 nm.

Density function calculation as described above were performed to determine the electronic band structure and electronic density of states to to investigate the electronic structure and phonon dispersion of mono-layered, bi-layered, tri-layered and bulk MoS_2. The unit cell for the mono-layered, bilayered and tri-layered MoS_2 were chosen such that the interaction between the MoS_2 layers could be minimized due to periodic boundary conditions. The density of states is plotted in Figure 6 below.

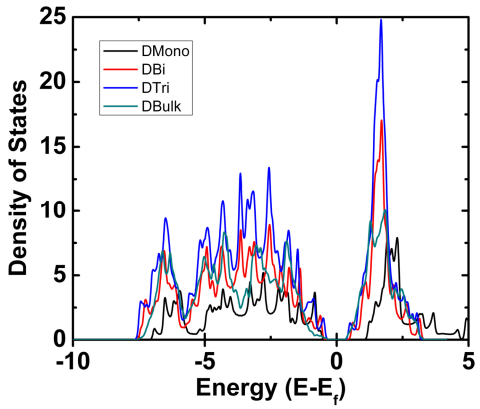

Figure 6 – Comparative plot of the density of states for few atomic layers and bulk MoS_2. The fermi level is adjusted to 0 eV.

The comparative density of states suggest that as the no. of layers increase from mono to bulk the band gap decreases. The plot of also indicates the possibilities of emission wavelengths of ~650 nm as also observed in our measurements in Figure 5. The electronic structure was further probed by plotting the electronic band structure along high symmetry lines along the Γ-M-K-Γ directions in the reciprocal space. These plots indicate that as the no. of layers of MoS_2 are increased, the direct band gap in monolayer MoS_2 becomes an indirect band gap semiconductor in bulk form. These observations are found to be in agreement to the previously published electronic band structure data [13].

The Phonon density of states for the mono-, bi-layered and bulk MoS_2 is shown in Figure 7 below.

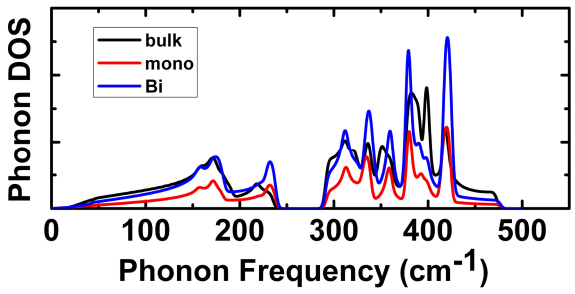

Figure 7 – Phonon density of states for monolayered, bilayered and bulk MoS_2.

The phonon density of states indicate no phonon branches beyond ~450 nm. The comparative plot of the phonon density of states indicate the dimensionality effects shows up between 2D and 3D MoS_2 structures.

3 CONCLUSIONS

Few atomic layers of MoS_2 were prepared using chemical exfoliation method in solution. The optical properties were investigated using Raman and photoluminescence spectroscopy and were found to be excellent agreement with the calculated values. Further investigation of these properties in under progress and will help in exploiting the potential of MoS_2 as an optical material.

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