

Tuning the Bandgap of Bulk Molybdenum Disulphide using Defects

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Abstract. This report highlights the use of defects to change the electronic properties of bulk molybdenum disulphide (MoS₂). The defects introduced also have significant effects on the thermal properties. We further demonstrate the effects of altering the atom arrangement or introducing other atoms in the lattice, has on the electronic properties of MoS₂ and other metal dichalcogenides. Pristine MoS₂ is p-type semiconductor and it can also be turned into an n-type semiconductor, depending on the choice of impurity introduced. We have demonstrate this by using plots of Seebeck coefficient against chemical potential. The high Seebeck coefficients observed suggest that defect modified MoS₂ is a potential candidate for thermoelectric applications. The anisotropic nature of the electronic properties of MoS₂ is demonstrated for the thermal conductivity and electronic conductivity as a function of chemical potential. The induced defects lead to bandgap reductions ranging between 10.7% and 100%, relative to the pristine MoS₂.

1. Introduction

Bulk MoS₂ is a quasi-2D Material. Subject to the coordination of Mo atoms within a single layer and the stacking order of single layers, there are three known polytypes: 1T, 2H, and 3R of MoS₂. The 2H polytype is reported to be abundant in the earth's crust [1, 2] and with the discovery of direct bandgap in 2D MoS₂, there was a shift in research, away from the traditional applications like dry lubricants, hydrodesulphurisation catalysts, and cathode materials for lithium ion batteries towards possible applications in electronics [3]. The indirect bandgap in multi-layered MoS₂ still finds utility in electronic devices, and it can also be utilised in chemical applications such as hydrogen evolution reaction and chemical sensing [4, 5, 6].

The properties of monolayer MoS₂ have been studied both theoretically and experimentally [7, 8]. Reports on field effect transistors and phototransistors based on monolayer MoS₂ have suggested monolayer MoS₂ as a promising candidate materials for novel electronics and photonics devices [9]. First-principles calculations demonstrated a bandgap tuning in bilayer MoS₂ sheets by applying a perpendicular external electric field and they predicted that the electronic properties of armchair MoS₂ weakly dependent on width of the ribbon, whereas the zigzag MoS₂ exhibits metallic behavior [10]. The electronic properties of monolayer and multilayer MoS₂ have also been engineered by imposing compressive and tensile strains and they have shown to lead to a reduction in bandgap [11, 12]. The introduction of functional

defects in MoS₂ could be the key for new applications of MoS₂ [21]. A similar drop in κ was noted with a W interstitial, which amounts to 20.67 W·m⁻¹·K⁻¹. The electronic conductivities (σ) dropped from $5.1 \times 10^6 \Omega^{-1}\cdot\text{m}^{-1}$ to $3.5 \times 10^6 \Omega^{-1}\cdot\text{m}^{-1}$, for MoS₂ with Mo interstitial; and to $2.9 \times 10^6 \Omega^{-1}\cdot\text{m}^{-1}$, for MoS₂ with W interstitial. Introduction of defects in MoS₂ could be the key for new applications of MoS₂ [21]. The ability to change MoS₂ energy conversion devices, like solar cells from its usual p-type semiconductor to an n-type behaviour which could have applications in semiconductor junctions where higher conductivity is desired [22].

4. Conclusion

We have shown how the MoS₂ energy bandgap could be tuned, by defect creation. A reduction of the bandgap between 10.7% and 100% has been achieved where metal interstitials (Mo and W) show the highest reductions of 74.5% and 100% for tungsten and molybdenum atoms, respectively. Thermal conductivities (κ) after introduction of Mo and W interstitial into MoS₂ dropped by about 36% and 44 %, respectively. Similarly, a reduction of the electronic conductivities (σ) was noted as 31 % for Mo interstitial and 43 % in the case of MoS₂ with W interstitial. From the Seebeck coefficient results, the ability to change MoS₂ semiconductor type has the potential of being used in a wider range of energy conversion devices. Based on our results, the technique we used could be extended to other transition metal dichalcogenides (TMD) as well.

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