

The Role of Transport Agents in MoS₂ Single Crystals

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Abstract

We report resistivity, thermoelectric power and thermal conductivity of MoS₂ single crystals prepared by chemical vapour transport (CVT) method using I₂, Br₂ and TeCl₄ as transport agents. The material presents low-lying donor and acceptor levels, which dominate the in-plane charge transport. Intercalates into the Van der Waals gap strongly influence the inter-plane resistivity. Thermoelectric power displays the characteristics of strong electron-phonon interaction. Detailed theoretical model of thermal conductivity reveals the presence of high number of defects in the MoS₂ structure. We show that these defects are inherent to CVT growth method, coming mostly from the transport agent molecules inclusion as identified by Total Reflection X-ray Fluorescence analysis (TXRF) and in-beam activation analysis (IBAA).

Molybdenum disulfide, MoS₂, has been known for a long time as a mineral but the first detailed studies were performed in the seventies, during the vivid interest for transition metal dichalcogenides¹. This class of materials possesses a variety of electronic ground states, such as superconductivity, periodic lattice deformation (charge density waves), Mott transition, exciton formation etc²⁻⁴. Within this cavalcade of fascinating properties, MoS₂ was left aside, since it had turned out to be a simple, indirect band gap (Δ) semiconductor⁵ of $\Delta = 1.2$ eV.

The revival of interest in this material has come with the isolation of graphene from graphite. Mechanical exfoliation of MoS₂ is also possible, and it still remains the preferred technique for obtaining single or few-layers of this material⁶⁻⁷. MoS₂ single layers achieved by chemical or mechanical exfoliation have been extensively studied for both scientific and applicative purposes⁸⁻¹¹. Chemical vapour transport (CVT) is the most used method to grow large area single crystals of transition metal dichalcogenides¹²⁻¹³. In order to obtain high quality MoS₂ few layers by exfoliation of single crystals, the good quality of the starting CVT-grown material must be ensured. Although other authors have already reported a dependence of the doping sign of WSe₂, MoSe₂ and WS₂ at room temperature on the transport agent used during the CVT growth¹²⁻¹³ a deeper and systematic study on how transport agents influence the electrical and thermal properties of MoS₂ single crystals is still missing. Moreover, a recent work has shown that chlorine doping can drastically reduce the width of the Schottky barrier between few layers of MoS₂ and metallic contacts allowing high performances in few layers MoS₂ field-effect transistors⁹. This observation demonstrates that inclusion of external atoms in MoS₂ can also be advantageous for applications.

We measured resistivity of single crystals grown by CVT method using I_2 , $TeCl_4$ and Br_2 as transport agents. Resistivity was measured parallel to the MoS_2 planes (ρ_{ab}) and out of planes (ρ_c). The possibility to measure ρ_{ab} down to 4 K is already strong evidence that charge transport is not dominated by the charge transfer gap. In fact, in the case of a pristine sample with $\Delta=1.2$ eV the resistivity would be so high that no measurable current would be able to pass through the sample even at room temperature. Both, the in-plane and the out-of-plane ρ , follow a $\rho_0 \exp(E_b/k_B T)$ temperature dependence (k_B is the Boltzmann constant, E_b is the impurity level activation energy and ρ_0 is a temperature independent constant). Figure 1 presents the Arrhenius plot of ρ_{ab} for a sample grown using I_2 as transport agent. The comparison between resistivities measured for different crystals obtained by the same CVT grown with iodine transport agent results in a scattering of ρ_0 and E_b values as shown in the inset of Fig. 1. E_b is found in the 20-90 meV range. Due to the high level of doping, in some cases already at 100 K a conduction channel opens in the impurity band, and one observes very weak activation energy (4-5 meV). The low temperature flat part is presumably due to hopping conduction within the impurity band¹⁴.

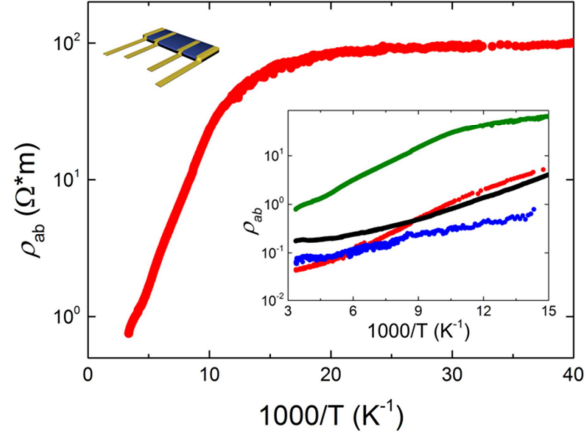


Figure 1. Arrhenius plot of the temperature dependence of the in-plane resistivity of a MoS₂ single crystal grown using I₂ as transport agent. The high temperature slope corresponds to a donor level at 50 meV below the conduction band. The different colour lines in the inset correspond to resistivities measured for four different crystals obtained by the same CVT growth using I₂ transport agent.

Figure 2 shows a comparison between the measured ρ_c and ρ_{ab} for the same MoS₂ single crystal presented in figure 1. The ratio $\rho_c/\rho_{ab}=100$ at 300 K further increases on cooling. The extracted $E_b=0.3$ eV for ρ_c is ~ 6 times higher than for ρ_{ab} . In the high temperature regime, the temperature dependent resistivity ratio suggests that the mechanism of conduction is different along the two directions. The higher activation energy for the inter-plane charge transport can be ascribed to intercalated atoms between the MoS₂ layers. In fact, ρ_c can be well described by $\rho_0 \exp(E_{int} + E_b/k_b T)$, where the additional energy barrier E_{int} is due to hopping process between nearest neighbours¹⁴. The charge carriers need phonon assisted hopping to get to the neighbouring layer and this phenomenon manifests itself as an additional activation term in resistivity¹⁴. Since the phonon assistance is diminishing with the lowering temperature, one observes a strongly increasing resistivity anisotropy.

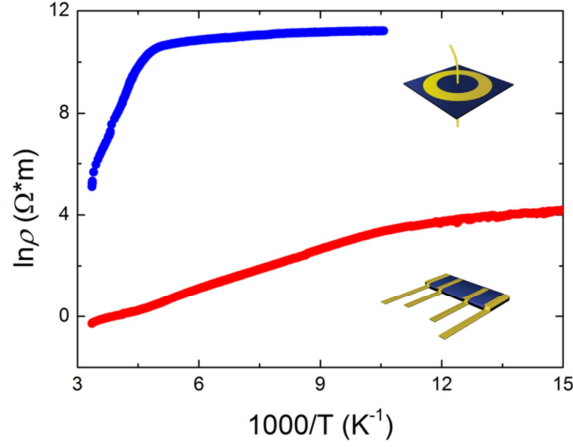


Figure 2. Arrhenius plot of the temperature dependence of the in-plane (red curve) and out-of-plane (blue curve) resistivities for a MoS₂ single crystal grown using I₂ as transport agent.

Whether one deals with a donor or an acceptor impurity level may be deduced from the Seebeck coefficient (S). Figure 3 presents the Seebeck coefficient measured parallel to the MoS₂ planes for a sample prepared using I₂ as transport agent. The sign of S suggests that at high temperature the dominant type of charge carriers are hole-like (coming from an acceptor level), while at low temperatures the electron like charge carriers dominate (donor level). Furthermore, at room temperature S has a large value of 400 $\mu\text{V/K}$, typical for non-degenerated semiconductors¹⁵. In the latter case, S is given by

$$S = \frac{k_B}{e} \left(\frac{E_b}{k_B T} + \text{const} \right) \quad , \quad (1)$$

where e is the electronic charge. This expression gives an increase of $|S|$ with decreasing temperature. However, we find that S is temperature independent down to 180 K. Such behaviour is characteristic of polaronic charge carriers¹⁶, which have been observed in other

materials like boron carbide¹⁷ and TiO₂ anatase¹⁸. In a simplified picture, the charge carrier excited to the conduction band polarizes the lattice and propagates along the lattice surrounded by this polarization. The energy involved in the creation of this new quasi-particle results with large values of S .

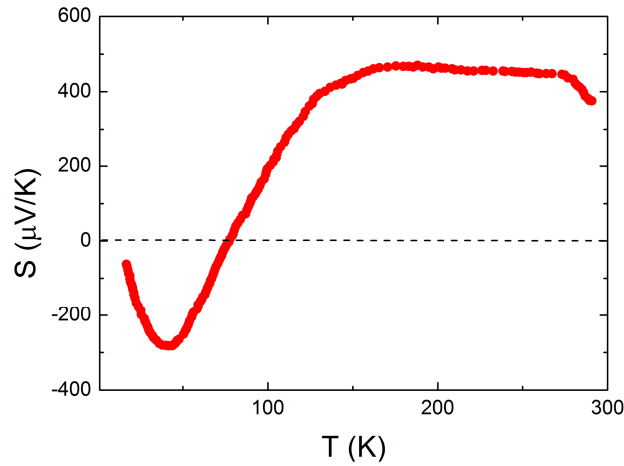


Figure 3. Temperature dependence of thermoelectric power measured along the MoS₂ planes for the sample grown by I₂ transport agent. Electron-like transport at low temperatures and hole-dominated one at high temperatures can be identified.

Thermal conductivity was measured for the MoS₂ sample prepared by I₂ transport agent. The results are presented in Figure 4. As for other poorly conducting materials, one may expect that the dominant contribution to the thermal conductivity (κ) is of phononic origin. Indeed, assuming an electron density that justifies the usage of the Wiedemann–Franz law, one obtains a very low estimation for the value of the thermal conductivity due to charge carriers, being much less than 1 W/(Km). Therefore, one can safely neglect such term and analyse κ behaviour in terms of purely phonon contribution. At room temperature we measured $\kappa=15$ W/Km, a value that is

much lower than in other layered materials like graphite ($\kappa=2000$ W/Km)¹⁹. Room temperature thermal conductivity in a few and single layer MoS₂ was measured by a few authors. The measured data span between $\kappa= 30$ W/Km and 55 W/Km, depending on the layer thickness and the way in which the samples were grown²⁰⁻²². This is a clear indication that impurities and/or strong anharmonicities play a significant role. In particular, from 10 to 300 K, κ reveals three different temperature intervals: i) the low temperature regime, below 40 K, where κ quickly diminishes as temperature decreases, ii) the intermediate temperature regime, from 40 to 70 K, in which κ exhibits a maximum, and iii) the high temperature part, from 70 to 300 K, in which κ becomes suppressed by temperature. This behaviour has strong resemblances to other semiconducting materials and may be investigated in more details in terms of three independent mechanisms (relaxation times) for phonon scattering: Umklapp phonon scattering, impurity scattering and sample boundary scattering²³. With these three scattering contributions, in the context of the Callaway formalism, the integral expression for thermal conductivity due to the phonons is given by²³

$$\kappa = CT^3 \int_0^{\theta_D/T} \frac{1}{a_1 + a_2 T^4 x^4 + a_3 T^3 x^2 \exp[-w_u/T]} \left[\frac{x^4 e^x}{(e^x - 1)^2} \right] dx \quad (2)$$

with $C = \left(\frac{k_B}{2\pi^2 v_s}\right) \left(\frac{k_B}{\hbar}\right)^3$, $x = \hbar\omega/k_B T$, θ_D is Debye temperature, k_b Boltzmann constant, \hbar Planck constant, and v_s the average speed of sound. a_1 , a_2 , a_3 and w_u are parameters that should be determined from experiments, by using a fitting procedure.

All of the scattering mechanisms in equation (2) are active in the entire temperature range shown in Figure 4, however, not with equal importance. Phonon-phonon interaction is dominant at high temperatures, where, thanks to the thermal excitations, the phonon thermal occupation is high for

almost all wavelengths and accompanied with strong anharmonicities. By lowering T , the phonon thermal occupation decreases and Umklapp scattering becomes less significant, which results in an overall rise of thermal conductivity. Yet, by further lowering the temperature, other scattering processes become more efficient. That is, effects of impurities start to dominate at about 1/5 of Debye temperature ($\theta_D = 500$ K for MoS_2 ²⁴). At very low temperatures, only the long-wave phonons remain in the system, with a mean free path being constrained by sample dimensions.

The values found for a_1 , a_2 , a_3 and w_u of equation (2) are given in Table 1. The corresponding fitting curve is shown in blue in Fig. 4, nicely reproducing the experimental data in the entire temperature range. While the Umklapp scattering seems less efficient in comparison to results obtained for a semiconductor with similar values of Debye frequency and κ at room temperature (rutile TiO_2)²⁵, the scattering due to impurities is significantly enhanced for the MoS_2 sample. For the latter, a_2 is two orders of magnitude higher than for rutile TiO_2 . This effect is additionally depicted by a low value of κ at the maximum with respect to the room temperature value, i.e., only a factor of 4, compared to a factor 100 observed in pure rutile TiO_2 ²⁵. The expected low-temperature T^3 behaviour is suppressed up to very low temperature, well below 15 K, which is the lowest temperature investigated in our experiment in Figure 4. All these findings show that our MoS_2 sample involves very strong scattering due to impurities. In particular, we believe that this effect should be ascribed to iodine contamination.

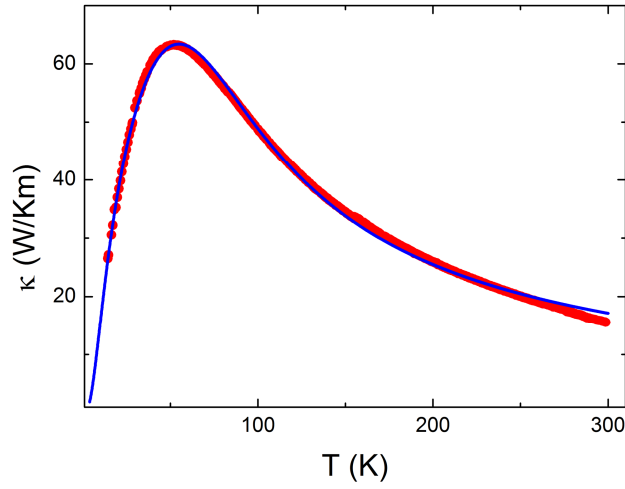


Figure 4. Temperature dependence of basal thermal conductivity of MoS₂ single crystal obtained using I₂ as transport agent. The blue curve represents the fit obtained by using equation (2).

Table 1. Fitting parameters by using Callaway's approach

a_1/C	a_2/C	a_3/C	w_u/C
1.8×10^6	0.69	2.09×10^2	200

The results presented so far indicate that the iodine transport agent causes an unintentional doping of the CVT grown MoS₂ and that the charge carriers have a polaronic character. The presence of transport agents into the bulk of MoS₂ single crystals was confirmed by IBAA and TRXF analysis (see Supporting Information). In the particular case of samples grown using I₂, TRXF reveals iodine contents up to 0.48 molar percent. In order to investigate the effect of different transport agents on the electrical properties of MoS₂ we studied single crystals

produced by TeCl_4 and Br_2 transport agents. Figure 5 shows the comparison between Arrhenius plots of the in-plane resistivity of MoS_2 single crystals grown by the different transport agents. Similarly to the iodine case we measured resistivity of different samples obtained by the same CVT growth using TeCl_4 and Br_2 as transport agents. The results (not shown here) present the same scattering in ρ_0 and E_b as displayed in the inset of Fig. 1. In all the cases resistivity is measurable down to low temperatures and the temperature dependence is very similar, only the absolute value of ρ appears to be transport agent dependent. This could be due to different ways in which transport agents are incorporated into the crystal structure. In fact the layered structure of MoS_2 offers interstitial sites²⁶ and transport agents can intercalates between the MoS_2 layers. Iodine incorporation between planes of metal dichalcogenides has already been observed by scanning tunnelling spectroscopy in other compounds grown by CVT method in our laboratories²⁷. Iodine can enter into the lattice by substituting S (forming $\text{MoS}_{2-x}\text{I}_x$) introducing one electron per formula unit. However iodine can also be intercalated in between the MoS_2 layers. In this case the chemical formula is MoS_2I_x and iodine induces one hole per formula unit. Although iodine can easily be desorbed from the surface by extensive washing, the removal of substituted or intercalated I_2 is more demanding. Probably, high temperature annealing in vacuum or in H_2S vapours would reduce its doping effect.

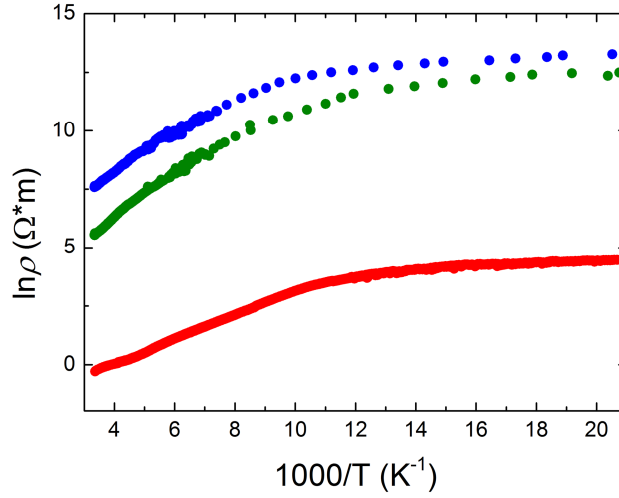


Figure 5. Arrhenius plot of the temperature dependence of the in-plane resistivity of MoS₂ single crystals grown by I₂ (red), TeCl₄ (green) and Br₂ (blue) as transport agents.

Contrary to the positive sign of Seebeck coefficient of MoS₂ grown with I₂, single crystals grown with TeCl₄ and Br₂ transport agents show values of $S(300\text{K}) = -460 \mu\text{V/K}$ and $S(300\text{K}) = -293 \mu\text{V/K}$ respectively. Other authors previously reported that CVT growth employing TeCl₄ and Br₂ transport agents cause n-doping also in WSe₂ and MoSe₂ crystals¹². However WSe₂ and MoSe₂ samples grown with I₂ transport agent display p and n-doping at room temperature respectively¹². Positive Seebeck coefficients were also observed in naturally grown MoS₂ crystal²⁸. However, none of these samples displayed a change in S at low temperatures. The smooth transition from holes dominated transport to electrons dominated transport in our MoS₂ sample grown by I₂ indicate that both, p and n type of charge carriers are present in the material. We showed before that iodine intercalation could give extra holes. Sulphur vacancies could be instead the cause of extra electrons, as it was observed in WS₂¹³.

In conclusion, we have shown that MoS₂ single crystals grown by the chemical vapour transport method suffer from an unintentional doping by the transport agent molecules. Temperature dependent electrical and thermal transport measurements clearly reveal the presence of defect and inclusions inside the material, as confirmed by our IBAA and TXRF studies. This shortcoming of CVT grown MoS₂ should be always taken into account in the discussion of its physical properties, especially when exfoliated MoS₂ single layers are foreseen for applications.

Experimental Methods

First, MoS₂ powder was synthesized by heating a mixture containing stoichiometric amounts of molybdenum (99.9% pure, Alfa Aesar) and sulphur (99.999% pure, Alfa Aesar) at 1000°C for 7 days in an evacuated and sealed quartz ampoule. The mixture was slowly heated from room temperature to 1000°C for 12 hours, in order to avoid any explosion due to the strong exothermic reaction and the high volatility of sulphur. From this powder, MoS₂ crystals were grown using chemical vapour transport (CVT) with iodine, bromine and tellurium tetrachloride as transport agent at ca. 5mg/cm³. All quartz tubes used for vapour transport typically have an inner diameter of 16 mm and a length of 20 cm. The total powder charge is 5 g. A very slight excess of sulphur is always included (typically 0.5 wt% of the charge) to ensure the stoichiometry in the resulting crystals. The excess of sulphur is not incorporated into the dichalcogenide crystals, but condenses as elemental sulphur onto the wall of the quartz tube at the end of the CVT process. The source and growth zones were kept at 1060°C and 1010°C, respectively for 7 days in evacuated and sealed quartz ampoules. After this time the furnace is turned off, a small fraction of the charge is transported towards the colder end of the tube, forming crystals with diameters

of about 2—8 mm and thick tens of microns, with exception of TeCl_4 , where even 400 μm thicknesses were observed. The resulting crystals were washed with acetone and dried in vacuum. X-ray diffraction study has shown that MoS_2 obtained in this way belongs to the 2H polymorphism (see supporting information).

Resistivity measurements in the ab plane and along the c -axis were performed in a conventional four probe configuration after evaporation of chromium/gold contacts. Sketches are shown as insets in Figure 1 and Figure 2. For the ρ_c configuration the outer large circle is the current lead and the point-like contact in the middle is the voltage electrode. For the thermoelectric power measurement the sample was anchored to a ceramic bar on which a temperature gradient (ΔT) was generated by a small heater at one end. The ΔT across the sample was measured by a differential Chromel-Constantan thermocouple attached to the sample (the details are described elsewhere²⁹). Thermal conductivity (κ) was measured by the steady state method, using a reference sample to measure the heat current through the MoS_2 single crystal as described elsewhere³⁰.

Notes

A. Pisoni and J. Jacimovic contributed equally to this work. The authors declare no competing financial interests.

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