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Layered Nanostructures – Electronic and Mechanical Properties

Gotthard Seifert[1], Tommy Lorenz[1] and Jan-Ole Joswig[1]
[1]Physical Chemistry, Technical University Dresden, 01062 Dresden, Germany

ABSTRACT

In addition to graphene, 2D transition-metal chalcogenides as, e.g., MoS_2 and WS_2 nanostructures are promising materials for applications in electronics and mechanical engineering. Though the structure of these materials causes a highly inert surface with a low defect concentration, defects and edge effects can strongly influence the properties of these nanostructured materials. Therefore, a basic understanding of the interplay between electronic and mechanical properties and the influence of defects, edge states and doping is needed. We demonstrate on the basis of atomistic quantum-chemical simulations of a circular MoS_2 platelet, how the mechanical deformation can vary the electronic properties and other device characteristics of such a system.

INTRODUCTION

The electronic properties of semiconducting transition metal dichalcogenides MX_2 (M: Mo, W; X: S, Se) with hexagonal 2H crystal structure have been studied already in the 1960s, e.g. in the pioneering work of Fivaz and Mooser [1]. Layers of dichalcogenides are characterized by a metal sheet sandwiched between two sheets of chalcogenide atoms; a typical example is MoS_2. The molybdenum atoms are six-fold coordinated in this environment, and in the most common phase the sulfur atoms form a prismatic coordination around each molybdenum atom.

Besides graphene, also other layered materials can be exfoliated down to single sheets. This has been shown for a number transition metal dichalcogenides some time ago [2] and revealed also by Novoselov et al. [3]. As single layers, the dichalcogenides of molybdenum and tungsten are semiconducting. Galli et al. [4] showed that – going from the bulk 2H structure to a single MoS_2 layer (1L-MoS_2) – the system becomes a direct-gap semiconductor. Being semiconducting, single-layer transition metal dichalcogenides are much more attractive candidates for a realization of field-effect transistors than graphene, in which the missing gap creates serious problems for its application in corresponding devices. Consequently, the fabrication of a field-effect transistor based on single-layered MoS_2 has been demonstrated already [5].

Another potential field of applications for MoS_2 is in flexible electronic devices. For such applications the interplay between mechanical stress and the electronic properties has to be understood well. Measurements on MoS_2 and WS_2 nanotubes showed exceptional mechanical properties [6]. Bertolazzi et al. [7] reported on the measurement of the in-plane elastic modulus and breaking strength of single- and bi-layered MoS_2. They used nano-indentation with an atomic force microscope for the measurement of the nanomechanical properties of an ultrathin MoS_2 layer suspended over circular holes.

Here, we demonstrate on the basis of atomistic quantum-chemical simulations of an MoS_2 platelet, how the mechanical deformation can vary the electronic properties. Therefore, we

simulate the nano-indentation experiment as described in the theory section. The simulation experiments were performed in close collaboration with our experimental partners, in order to accompany and explain the experimental findings.

THEORY

The calculations were performed using a density-functional based tight-binding (DFTB) method [8,9,10] as implemented in the deMon software package [11]. In the DFTB approach, the single-particle Kohn-Sham eigenfunctions are expanded in a set of localized atom-centered basis functions, which are determined by self-consistent density-functional calculations on the isolated atoms employing a large set of Slater-type basis functions. The effective one-electron potential in the Kohn-Sham Hamiltonian is approximated as a superposition of atomic potentials, and only one- and two-center integrals are calculated to set up the Hamilton matrix. A minimal valence basis set is used.

The studied system is a circular cutout of a single MoS_2 sheet with a diameter of 60 Å consisting of 912 atoms and a tip consisting of 65 molybdenum atoms as depicted in Figure 1. Perpendicular to the sheet, the molybdenum tip is used to simulate the indentation experiment. The DFTB method including a dispersion correction was used to perform a series subsequent Born-Oppenheimer molecular-dynamics (MD) simulations on this system, whereby the edge atoms of the circular sheet (223 atoms located 4 Å or closer to the edge) were not allowed to move. Each part of the series was started by moving the tip towards the sheet by 0.1 Å compared to the simulation before and fixing it at that position. Then the system was equilibrated at 300 K for 1 ps with an MD timestep of 2 fs, in order to simulate the new adjustment of the sheet to the indentation. The equilibrium criterion was $\langle T \rangle - T = \pm 10\ \mathrm{K}$.

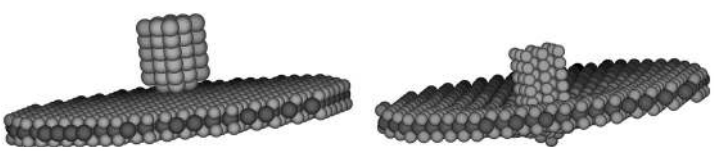

Figure 1: Simulation setup for the nano-indentation simulation experiment with a circular MoS_2 platelet and a molybdenum tip. Left side: initial setup; right side: after indentation. The circular cutout of a single MoS_2 sheet consists of 912 atoms, of which the edge atoms are fixed. The tip consists of 65 molybdenum atoms, which are moved towards the layer successively, but fixed during each MD simulation.

DISCUSSION

Mechanical Properties

The described procedure for the simulation of a nano-indentation experiment by means of molecular dynamics and an electronic-structure method gives access to a number of properties, e.g. the total energy and the electronic states at each step. In Figure 2, the total energy as a function of deflection, i.e. depth of penetration, is monitored. As expected, we find an increase in energy with increasing deflection. The curve progression can be fitted by

$$E = a_0 + a_1 \cdot \delta^2 + a_2 \cdot \delta^4 . \quad (1)$$

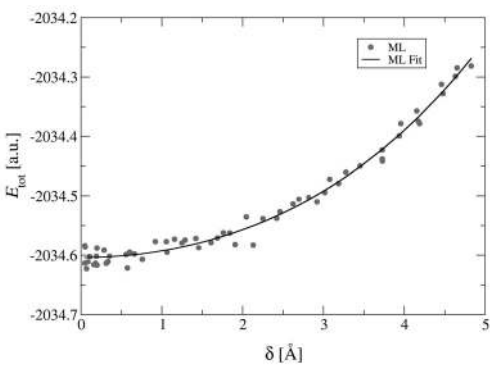

Figure 2: Calculated total energy as a function of the deflection δ resulting from the described simulation setup. Each point results from averaging the total energy over the simulation period of the respective deflection. The fit has been performed according to Equation (1).

From the total energy as function of deflection, we calculated the force F as the first derivative of the energy given in Equation (1) with respect to the deflection δ:

$$F = \frac{dE}{d\delta} = 2a_1 \cdot \delta + 4a_2 \cdot \delta^3 . \quad (2)$$

For a rigidly clamped circular plate with radius r and thickness h ($r \gg h$ and $\delta \ll h$), to which no residual stress is applied, a relation between the applied force F at the center of the plate and the deflection δ can be derived [12,13] as

$$F = E^{2D} \frac{q^3 \delta^3}{r^2}, \quad (3)$$

where r indicates the radius of the plate, E^{2D} its surface-based Young's modulus, and q is connected to its Poisson ratio ν resulting from

$$q = \frac{1}{1.05 - 0.15\nu - 0.16\nu^2}. \quad (4)$$

Equation (4) is valid for large deflections.

For a negligible bending stiffness and small stress the force-deflection behavior follows a linear progress [13] as

$$F = a \cdot \delta. \quad (5)$$

Here, the parameter a is connected to the stress [7] by

$$a = \sigma_0^{2D} \cdot \pi. \quad (6)$$

Therefore, we used the sum of Equations (5) and (6) to calculate the force and the integrated function for the energy fit (cf. Equation (1) and Figure 2). The resulting force as a function of deflection is plotted in Figure 3. For small deflections (negligible bending stiffness and small load), a nearly pure linear dependence can be observed, whereas the cubic term in Equation (2) is dominant for large deflections.

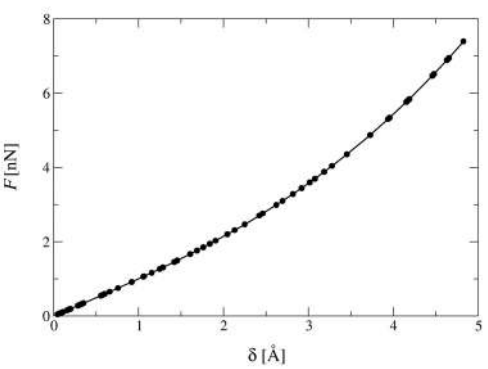

Figure 3: Calculated force as a function of deflection δ. The force is calculated as the first derivative of the total energy (Figure 1) with respect to the deflection according to Equation (2).

From the parameter a_2 in Equation (2), the surface-based Young's modulus E^{2D} can be obtained as $E^{2D} = 4a_2 r^2 / q^3$. We calculated a value of 241 GPa, which is in good agreement with the experimentally observed value of 270 ±100 GPa [7] and the measured Young's modulus of bulk MoS_2 (209 GPa) [14]. Additionally, the maximum stress can be received as

$$\sigma_{\max} = \frac{1}{h} \cdot \sqrt{\frac{F^{\max} E^{2D}}{4\pi r_{tip}}} \tag{7}$$

where F^{max} is the maximum force, r_{tip} the radius of the tip and h is the thickness of the layer. From our simulations, we resulted in a value of 22.14 GPa. This value is approximately 10 % of the Young's modulus calculated before, and it agrees very well with the experimental measurements (22 ± 4 GPa) [7].

Electronic Properties

Figure 4 displays the partial electronic density of states (DOS) for different deflections. For the partial DOS, all atoms of the central part of the circular setup, i.e. lying within a radius of 8 Å around the center, have been considered, in order to avoid influence of edge states and to show the contributions of the atoms that are located in the part that is mostly disturbed by the indentation procedure. It can be seen that the main features of the partial density of states are only weakly influenced by small deflections. However, larger indentation depths lead to an evolution of new features in the partial density of states. The new evolving unoccupied states reduce the original band gap.

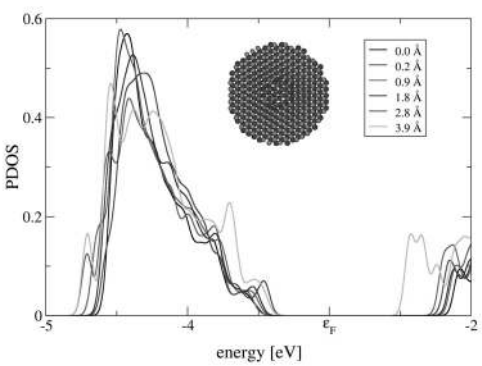

Figure 4: Partial electronic density of states for different deflections. For the partial DOS, all atoms within a radius of 8 Å around the center have been considered.

For comparison, we show in Figure 5 the band gap of an infinite single MoS_2 layer as a function of biaxial strain. The diagram shows a strong influence of the biaxial strain on the gap. The maximum deflection in Figure 4 is 3.9 Å. This results in a local strain of the central molybdenum atoms of up to 3% and a reduction of the bang gap by approximately 0.4 eV. Although the strain in our simulated experiment is locally different, the result can be compared

to the infinite layer (Figure 5), in which the reduction of the band gap is approximately 0.6 eV at applying 3% biaxial strain. However, we point out again that the mechanical stress in the infinite case is similar for all molybdenum atoms, whereas it is locally different in the simulated experiment.

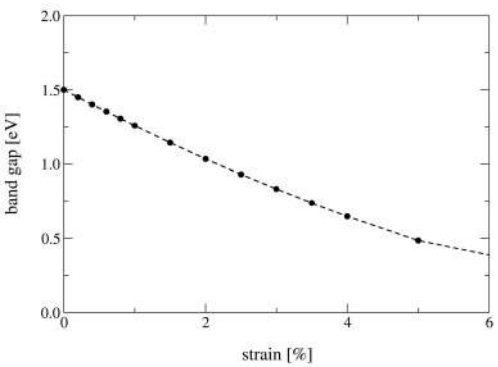

Figure 5: Band gap of an MoS_2 layer as function of biaxial strain. The values result from static DFTB calculations of a single MoS_2 layer with applied periodic boundary conditions.

The presented simulated nano-indentation experiments showed that fixed single MoS_2 layers show a robust behavior of the electronic properties upon deflection. The electronic properties in terms of density of states and band gap do not change abruptly, but vary slightly with increasing deflection. However, in the extreme cases, e.g. at the rupture point, this statement will not be valid.

CONCLUSIONS

In the present study, we have shown that nano-indentation experiments can be simulated very well with molecular-dynamics approaches using a density-functional based tight-binding method. The simulation setup consists of a circular cutout of a single MoS_2 layer with a diameter of 60 Å, which was partly fixed, and a molybdenum tip. Using the described simulation procedure, we were able to study the influence of the deflection on certain mechanical and electronic properties.

From the monitored total energy of the system, we were able to obtain the force acting on the layer as a function of deflection. Both, total energy and force are increasing with increasing deflection, whereby the force shows a linear dependence on the deflection for small deflections. For larger deflections the cubic term in Equation (2) is dominant. The resulting Young's modulus and maximum stress were in very good agreement with experimental findings.

The partial electronic density of states of the most central part of the layer showed that the influence of the deflection initially is only weak. However, larger indentation depths lead to

an evolution of new features in the partial density of states and reduce the band gap. Compared to a single periodic layer, the change of the band gap upon indentation is smaller than for the infinite system. However, the mechanical stress is similar for all molybdenum atoms in the infinite case, whereas it is locally different in the simulated experiment. The gap has been calculated from the partial DOS of the central atoms only.

In summary, the presented simulated indentation experiments showed that fixed single MoS_2 layers show a robust behavior upon deflection for both mechanical and electronic properties. This robustness is a good condition for potential applications, such as flexible electronic devices. However, in the extreme cases, e.g. at the rupture point, this statement will not be valid.

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