DFT-based layered dielectric model of few-layer MoS$_2$

L. Donetti *, C. Navarro, C. Marquez, C. Medina-Bailon, J.L. Padilla, F. Gamiz

Departamento de Electronica and CITIC, Universidad de Granada, Granada, Spain

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**ABSTRACT**

We employ atomistic calculations to study charge distribution in few-layer MoS$_2$ structures with an applied perpendicular electric field. The results suggest a simple continuum model consisting of alternating regions which represent the semiconductor layers and the Van der Waals gaps between them. Such model is a first step towards an accurate simulation of MoS$_2$ in TCAD tools.

**1. Introduction**

Among 2D semiconductors, MoS$_2$ is one of the most extensively studied for its potential electronic, optoelectronic and sensing applications [1]. Ab initio calculations based on Density Functional Theory (DFT) are being successfully employed to analyze its mechanical, electronic, and optical properties. However, to simulate the behavior of devices and sensors, traditional TCAD tools are still very valuable because of their versatility and faster response time. To this aim, 2D materials are not currently well modeled by traditional TCAD tools because of the lack of calibrated material parameters and, more fundamentally, because their 2D nature requires different material models (for example considering the 2D vs. 3D density of states). A promising approach employs a traditional TCAD simulator but models an MoS$_2$ region with a stack of semiconductor layers separated by empty thin layers which represent the Van der Waals (VdW) gaps [2]. Following this idea, we perform a DFT study of mono- and few-layers MoS$_2$ structures with an applied perpendicular electric field. In particular, we analyze the induced charge distribution and dipole moment of the different layers with the aim of obtaining a simple layered model.

In Section 2, we describe the DFT calculations performed for this study. Then, in Section 3, we analyze the results of DFT calculations by computing the 2D charge and dipole moment densities in each layer of the studied structures. The results are analyzed employing a layered model consisting of a stack of alternating materials, allowing us to extract the relative dielectric constant and thickness of the different parts of the structure. Finally, in Section 4, we draw our conclusions and compare our results to previous experimental and theoretical values of MoS$_2$ dielectric constant.

**2. DFT calculations**

DFT calculations are performed with QuantumATK (version S-2021.06) [3], employing its Linear Combination of Atomic Orbitals (LCAO) calculator. We use the Generalized Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional, along with PseudoDojo Medium basis set for Molybdenum and Sulfur. In multi-layer MoS$_2$, the interlayer distance is strongly influenced by the Van der Waals interaction, which is not included in regular DFT calculations: to properly take it into account we add Grimme DFT-D2 correction [4].

First, we perform geometry optimization on a bulk MoS$_2$ cell, obtaining lattice parameters in good agreement with known experimental values [5]: $a = 3.19\AA$ and $C = 12.23\AA$. Then, we consider a mono-layer and a few multi-layer structures, with a number of layers, $N$, between 2 and 10. Numerical accuracy parameters are fixed to a sampling of $12 \times 12 \times 1$ k-points in the Brillouin zone and a density mesh cutoff of 200 Hartree. Relaxation of atomic coordinates is performed until forces get smaller in magnitude than 0.001 eV/Å. In all the relaxed structures, the resulting interlayer spacing, i.e. the distance $d$ between adjacent Mo atoms, is always in the range between 6.11 Å and 6.12 Å, which is consistent with the bulk $c$ lattice constant.

Finally, for each structure, we apply a perpendicular electric field, by forcing a potential difference in the range 0 V to 8 V between the top and the bottom of the structure. Atomic coordinates relaxation is performed for all considered values of the external bias.

**3. Results**

For each configuration, we compute the modifications induced by the applied bias. Some examples are shown in Figs. 1 and 2, where we
plot the induced electron density difference $\Delta n$, the electrostatic potential difference $\Delta V$ and the absolute value of the electric field $E$ taking in-plane averages as a function of the vertical position $z$. We can observe that, in each layer, the electric field is reduced by the dipole formed by charge densities that are generated around the position of the Mo atom. Then, in the VdW gaps between layers, the electric field increases but it is still weaker than the constant value that it takes outside the structure. To allow the extraction of a model for the layered structure, we integrate the excess electron density $\Delta n$ in each layer, $i$, to compute the 2D charge density $\sigma_{2D,i}$. We also compute the partial integrals in the bottom and top part of the layer with respect to the position of Mo atom, $\sigma_{b,i}$ and $\sigma_{t,i}$, respectively, and the dipole moment density $p_{2D,i}$.

For mono-layer MoS$_2$, the total charge density of the only layer, $\sigma_{2D,1}$, vanishes, since $\sigma_{b,1}$ and $\sigma_{t,1}$ cancel each other. If we model the semiconductor as a uniform slab of thickness $t_i$ with relative dielectric constant $\epsilon_r$, the surface charge density induced at the bottom interface can be computed as:

$$\sigma_{b,i} = \epsilon_r (E_i - E_0) = \epsilon_r E_0 \left( \frac{1}{\epsilon_r} - 1 \right),$$

(1)

where $E_i$ is the electric field in the semiconductor layer, $E_0$ is the external electric field and $\epsilon_0$ is the vacuum permittivity. As $\sigma_{b,1}$ and $\sigma_{t,1}$ are of equal magnitude and opposite sign, the dipole density $p_{2D,1}$ can be written as:

$$p_{2D,1} = \sigma_{b,1} t_i = -\sigma_{t,1} t_i.$$  

(2)

Thus, by fitting $\sigma_{b,1}$ and $p_{2D,1}$ as a function of $E_0$ (Fig. 3), we can extract the values of $\epsilon_r$ and $t_i$ shown in the first row of Table 1.

Considering now multi-layer structures, we can observe in Fig. 1(d) that the induced charge densities in the external half-layers ($\sigma_{b,1}$ and $\sigma_{s,N}$) are larger (considering their absolute value) than the internal ones, which are approximately equal to each other. Thus, the layer densities $\sigma_{2D,1}$ and $\sigma_{2D,N}$ are nonzero, while the internal ones vanish, $\sigma_{2D,i} = 0$ for $i = 2, \ldots, N - 1$. This behavior is consistent with a layered model where semiconductor layers alternate with barrier layers representing VdW gaps with a different dielectric constant, $\epsilon_r$, still larger than 1. This is also consistent with the observation that in such gaps the electric field is much smaller than the external electric field $E_0$. With this model in mind, we can still express the bottom charge density in the first layer as in Eq. (1), while the corresponding total 2D density can be written as:

$$\sigma_{2D,1} = \sigma_{b,1} + \sigma_{t,1} = \epsilon_0 E_0 \left( \frac{1}{\epsilon_0} - 1 \right).$$

(3)

Therefore, we represent $\sigma_{b,1}$ and $\sigma_{2D,1}$ as a function of $E_0$ to extract $\epsilon_r$ and $t_i$. As shown in Fig. 4, for $N$-layer structures with $N$ between 2 and 10, a good linear fit of $\alpha_{b,1}$ can be obtained. The extracted value of the relative dielectric constant in the semiconductor layer is $\epsilon_r = 22.1$, close to the mono-layer value. For $\sigma_{2D,1}$, a linear behavior is observed only for small values of $E_0$ and some deviations are present for larger $E_0$.
produced solely by the previous simple dielectric model: MoS biases, the total charge and electric field distribution cannot be repro especially in thicker structures. Indeed, for thick structures and strong-

Fig. 4. Charge density of the first layer, $\sigma_{2D,1}$, and of its bottom region, $\sigma_{b,1}$, as a function of the external electric field $E_0$ for multi-layer structures with different number of layers. Lines show the linear fits performed to extract the dielectric constants.

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Fig. 5. Layered model for MoS$_2$. The interlayer distance, $d = 6.115\,\text{Å}$, is equal to half of bulk MoS$_2$ $c$ lattice constant.

Table 1 Parameters of mono- and few-layer models.

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon_s$</th>
<th>$\varepsilon_b$</th>
<th>$t_i$ (Å)</th>
<th>$t_s$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-layer</td>
<td>21.2</td>
<td>–</td>
<td>5.02</td>
<td>–</td>
</tr>
<tr>
<td>2-10 layers</td>
<td>22.1</td>
<td>2.2</td>
<td>5.08</td>
<td>4.49</td>
</tr>
</tbody>
</table>

$\ell = \frac{1}{2} + \frac{1}{2}$, $\sigma_{2D,b} = \frac{\sigma_{2D,s}}{2} + \frac{\sigma_{2D,b}}{2}$ (7)

Now, linear fits of the data from the DFT calculations give us the values of $t_i$ and $t_s$ shown in the second row of Table 1. The electric field profile obtained with the layered model and the parameters shown in Table 1 is compared to the DFT results in Figs. 1(c) and (f).

4. Discussion and conclusions

The dielectric constant of MoS$_2$ has been the subject of several experimental studies [6–8] and theoretical calculations [9–12] with a wide range of reported values. Even focusing only on the perpendicular (out of plane) dielectric constant we can observe a large variation among published values. In any case, a qualitative agreement seems to exist about the fact that $\varepsilon_r$ is smaller in mono-layer MoS$_2$ than in the bulk material, and that it grows with the number of layers.

In this work, we obtain a value of $\varepsilon_r$ which is larger than all the published values, but we must take into account that this parameter only reflects the properties of a thin layer representing the inner part of the semiconductor. To compute a global effective dielectric constant, in our case we must consider the external empty layers needed to obtain the overall thickness equal to $N \cdot d$ and the alternating semiconductor/gap layers (Fig. 5). With this clarification in mind, it is remarkable that a single set of parameters can fit all the computed structures from $N = 2$ to $N = 10$, and also that the extracted parameter values are close to the corresponding ones for the mono-layer case. Then, we can compute an average dielectric constant $\varepsilon_{eff}$, that would give the same overall capacitance as the structure in Fig. 5, as:

$$\varepsilon_{eff} = \frac{N \cdot d}{\varepsilon_{eff} / C_{eff}} = N d \left( \frac{t_i}{\varepsilon_s} + (N-1) \frac{t_i}{\varepsilon_b} + (N-1) \frac{d-t_i}{\varepsilon_b} + (d-t_i) \right)^{-1}$$

Fig. 6 shows the values obtained by substituting the multi-layer data of Table 1 in this expression. In this way, employing one set of parameters common to all multi-layer structures, we obtain an increase in the value of the dielectric constant for increasing sample thickness, as reported in other experimental or theoretical works [6,10].

Declaration of Competing Interest

The authors declare that they have no known competing financial
interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


Luca Donetti received the Ph.D. degree in physics from the Università degli Studi di Milano, Milan, Italy, in 2002. Since 2005, he has been with the Department of Electronics, University of Granada, Granada, Spain. His current research interests include the simulation of electron and hole transport properties in nanoscale electronic devices, including SOI, multigate devices and 2D materials.