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DFT-based layered dielectric model of few-layer MoS_2

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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 multilayer 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]: $a = 3.19$Å and $C = 12.23$Å. 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

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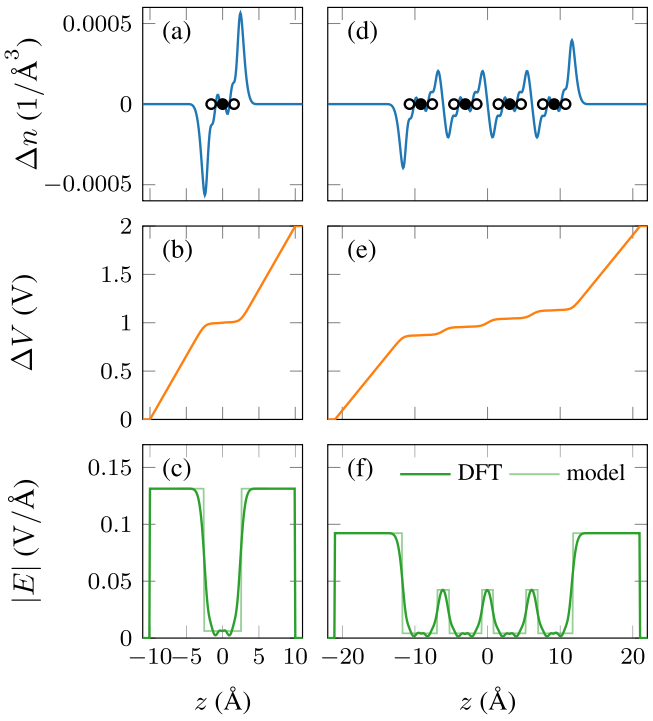

Fig. 1. Excess electron density Δn (a, d), electrostatic difference potential ΔV (b, e) and electric field E (c, f) for mono-layer (a–c) and 4-layer (d–f) MoS_2 with 2 V bias. In subfigures (a) and (d), closed and open circles represent the z positions of Mo and S atoms, respectively.

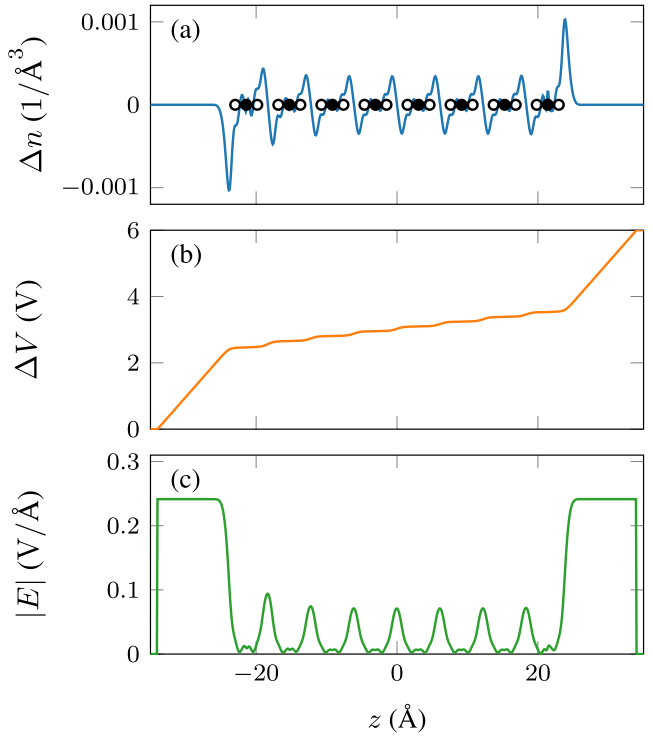

Fig. 2. Excess electron density Δn (a) electrostatic difference potential ΔV (b) and electric field E (c) for the 8-layer MoS_2 structure with 6 V bias.

plot the induced electron density difference Δn, the electrostatic potential difference ΔV 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 Δn 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 MoS2, 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_s with relative dielectric constant ϵ_s, the surface charge density induced at the bottom interface can be computed as:

$$\sigma_{b,i} = \epsilon_0(E_s - E_0) = \epsilon_0 E_0\left(\frac{1}{\epsilon_s} - 1\right), \tag{1}$$

where E_s is the electric field in the semiconductor layer, E_0 is the external electric field and ϵ_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:

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

Thus, by fitting $\sigma_{b,1}$ and $p_{2D,1}$ as a function of E_0 (Fig. 3), we can extract the values of ϵ_s and t_s 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 $\sigma_{t,N}$) 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 $i = 2, \cdots, N-1$. This behavior is consistent with a layered model where semiconductor layers alternate with barrier layers representing VdW gaps with a different dielectric constant, ϵ_b, 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:

$$\sigma_{2D,1} = \sigma_{b,1} + \sigma_{t,1} = \epsilon_0 E_0\left(\frac{1}{\epsilon_b} - 1\right). \tag{3}$$

Therefore, we represent $\sigma_{b,1}$ and $\sigma_{2D,1}$ as a function of E_0 to extract ϵ_s and ϵ_b. As shown in Fig. 4, for N-layer structures with N between 2 and 10, a good linear fit of $\sigma_{b,1}$ can be obtained. The extracted value of the relative dielectric constant in the semiconductor layer is $\epsilon_s = 22.1$, 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,

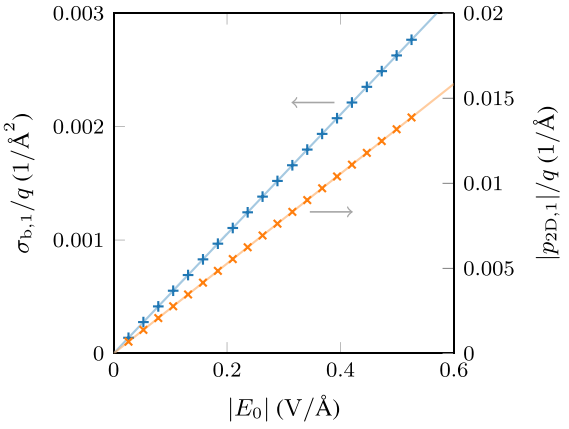

Fig. 3. Charge density in the bottom half of the layer, $\sigma_{b,1}$, and dipole moment density, $p_{2D,1}$, in mono-layer MoS_2 as a function of the external electric field E_0. The lines show linear fits of the data.

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

	ϵ_s	ϵ_b	t_s (Å)	t_i (Å)
Mono-layer	21.2	–	5.02	–
2–10 layers	22.1	2.2	5.08	4.49

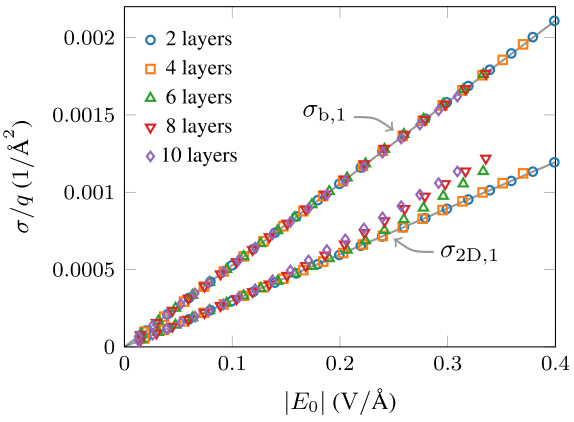

Fig. 4. Charge density of the first layer, $\sigma_{2D,1}$, and of its bottom region, $\sigma_{b,1}$, as a function of the external electric field E_0 for multi-layer structures with different number of layers. Lines show the linear fits performed to extract the dielectric constants.

especially in thicker structures. Indeed, for thick structures and strong biases, the total charge and electric field distribution cannot be reproduced solely by the previous simple dielectric model: MoS_2 is a semiconductor, not an insulator, and charges induced by band bending are also present. As an example, Fig. 2 shows the case of 8 layers with an applied bias of 6 V: here, we can observe a large potential difference between the bottom and top layers, so that the induced band bending generates additional charges. Therefore, the electric field in the different VdW gaps is not the same anymore and the charge density $\sigma_{2D,i}$ does not vanish for $i = 2,\cdots,N-1$. However, if we restrict ourselves to a small bias range (different for each MoS_2 thickness) such that this extra charge can be neglected, a good linear behavior is achieved and a value of $\epsilon_b = 2.2$ for the VdW relative dielectric constant is obtained. To fit the dipole moment densities $p_{2D,i}$ in the first and following layers, we must assume that the thickness of the external and internal semiconductor layers are different: these are modeled through parameters t_s and t_i, as shown in Fig. 5. Therefore, in the dielectric response regime (i.e. for small E_0), we can write:

$$p_{2D,1} = \sigma_{t,1}\frac{t_i}{2} - \sigma_{b,1}\frac{t_s}{2} = \frac{E_0}{2}\left(t_s\left(1-\frac{1}{\epsilon_s}\right) + t_i\left(\frac{1}{\epsilon_b}-\frac{1}{\epsilon_s}\right)\right) \tag{4}$$

and

$$p_{2D,2} = \sigma_{t,2}\frac{t_i}{2} - \sigma_{b,2}\frac{t_i}{2} = E_0 t_i\left(\frac{1}{\epsilon_b}-\frac{1}{\epsilon_s}\right). \tag{5}$$

Now, linear fits of the data from the DFT calculations give us the values of t_s and t_i 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).

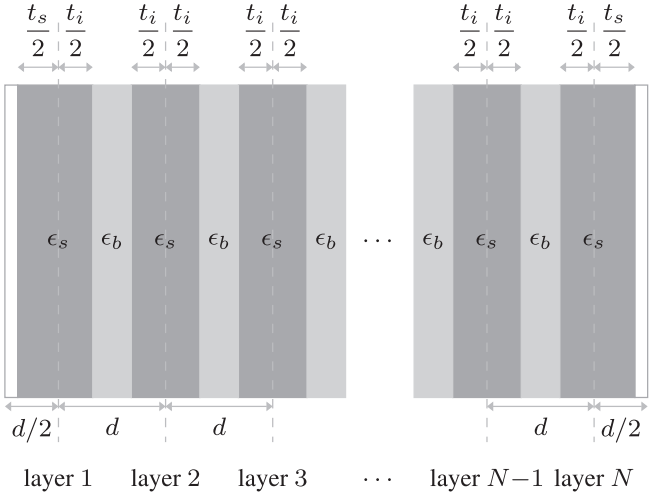

Fig. 5. Layered model for MoS_2. The interlayer distance, $d = 6.115\text{Å}$, is equal to half of bulk MoS_2 c lattice constant.

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 ϵ_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 ϵ_s 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 ϵ_{eff}, that would give the same overall capacitance as the structure in Fig. 5, as:

$$\epsilon_{\text{eff}} = \frac{Nd}{\epsilon_0 C_{\text{eff}}} = Nd\left(\frac{t_s}{\epsilon_s} + (N-1)\frac{t_i}{\epsilon_s} + (N-1)\frac{d-t_i}{\epsilon_b} + (d-t_s)\right)^{-1} \tag{6}$$

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

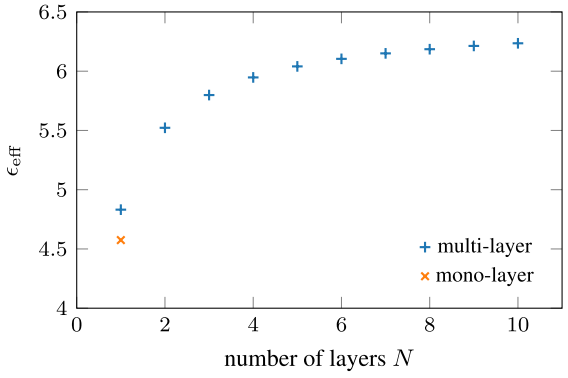

Fig. 6. Average relative dielectric constant of few-layer MoS_2 as a function of the number of layers obtained with the multi-layer parameters of Table 1. For $N = 1$, we also show the value obtained with mono-l.ayer parameters.

interests or personal relationships that could have appeared to influence the work reported in this paper.

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Luca Donetti received the Ph.D. degree in physics from the Universit? 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, multi-gate devices and 2D materials.