

Electronic and Optical Properties of Hydrogen-Terminated Diamond Doped by Molybdenum Oxide: A Density Functional Theory Study

Joseph McGhee, Vihar P. Georgiev,

Device Modelling Group
James Watt School of Engineering
University of Glasgow, Glasgow G12 8QQ, United Kingdom
E-mail: vihar.georgiev@glasgow.ac.uk

ABSTRACT

In this work we investigate the surface transfer doping process induced between a hydrogen-terminated (100) diamond and a metal oxide MoO_3 , using the Density Functional Theory (DFT) method. Using DFT, we have calculated the electronic and optical properties of the hydrogen-terminated diamond and established a link between the underlying electronic structure and the charge transfer between the oxide materials and the hydrogen-terminated diamond. Our results show that the metal oxide can be described as an electron acceptor and extracts the electrons from the diamond creating 2D hole gas in the diamond surface. Hence, this metal oxide acts as a p-type doping material for the diamond.

INTRODUCTION

Diamond is a compound semiconductor material with many electronic applications such as microwave electronic devices [1], bipolar junction transistors [2] and Schottky diodes [3]. However, one of the most promising areas for diamond industrial application is in high-performance field effect transistors (FETs) used in the production of high frequency and high-power electronic devices [4]. Its properties potentially enable devices that are beyond the scope of current systems in terms of operating frequency, power handling capacity, operating voltage, thermal robustness and operating environment. This is due to the fact that diamond has a wide band-gap of 5.5eV, a thermal conductivity 5 times greater than 4H-SiC of 24 W/cm²*K (for CVD diamond), a high breakdown field of 20Wcm⁻¹ and high hole and electron carrier velocities of 0.8x10⁷cm/s and 2.0x10⁷cm/s respectively. As a result, diamond is a superior new candidate for high frequency and high-power devices [5]. However, the primary issue that has inhibited the application of diamond is the lack of a suitably efficient and stable doping mechanism. The most promising way to dope diamond is by surface transfer doping (STD), which is achieved by depositing materials on the surface of diamond. In this paper, we would like to explore the possibility of metal oxide materials, such as molybdenum oxide (MoO_3), as a material for achieving such STD in diamond. Our work is based on performing numerical semi-empirical DFT.

SIMULATION METHODOLOGY

All calculations were carried out with the Quantumwise Atomistix ToolKit (ATK) software using DFT [5]. Generalised Gradient Approximation (GGA) exchange

correlation was used for the geometry optimisations of the

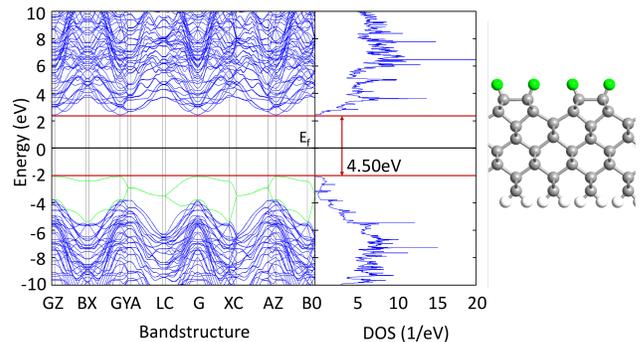


Figure 1. Hydrogen terminated (100) diamond band structure and Density of States (DOS). Grey atoms are the carbon; white and green atoms are hydrogen.

system and to obtain the total energies of the interfaced systems and the individual component parts, i.e. H-diamond and the oxide layer in question. For all geometry optimisations a force tolerance of 0.01eV/Å was used. GGA-1/2 exchange correlation was used for all electronic structure calculations. To obtain a more accurate electronic description of the systems, DFT-1/2 method was used [6]. However, DFT-1/2 method is not suitable for calculating total energies, hence, we used GGA for the geometry optimisations and calculating adsorption energies.

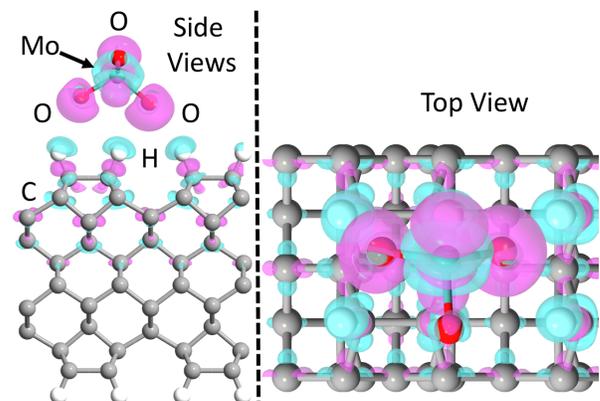


Figure 2. The (left hand side) side view and (right hand side) top view of charge density different for the most stable MoO_3 -doped diamond surface. The purple regions represent electron accumulation and the green regions represent electron depletion (hole accumulation). The isosurface values are $\pm 0.001 \text{ Bohr}^{-3}$.

RESULTS AND DISCUSSION

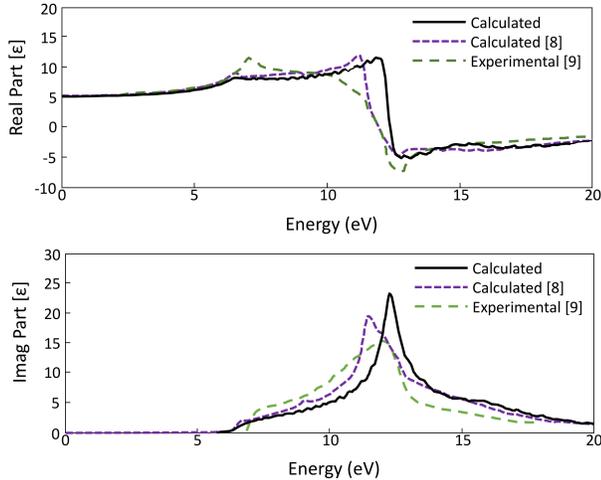


Figure 3. Dielectric constant plots for a bulk diamond comparing our calculated results with calculated results by Xiang *et al.* [8] and experimental results by Philipp and Taft [9].

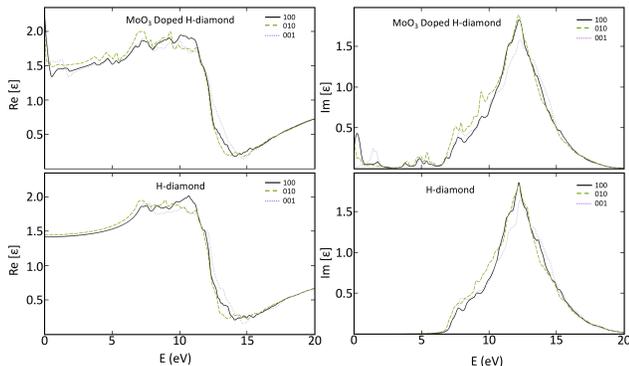


Figure 4. The dielectric function of the real ($\text{Re}[\epsilon]$) and imaginary ($\text{Im}[\epsilon]$) parts for the clean hydrogenated diamond surface and the most preferred MoO_3 -doped diamond surface.

Fig. 1 shows the hydrogen terminated diamond band structure and Density of States (DOS) obtained from the DFT simulations. The data presented shows that when the diamond is hydrogen terminated, the band gap is slightly reduced at the surface due to surface gap states at the valance band maximum (VBM) because of the presence of hydrogen atoms. This is due to bonding and antibonding C-H states at VBM and CBM. Although the band gap of the system has been reduced to 4.50eV, the projected DOS plot for the carbon atoms in the bulk of the structure shows their band gap remains $\sim 5.5\text{eV}$. The first two valance sub-bands in Fig. 1, which have higher energies in comparison to the other sub-bands, arise from the interaction of the first layer of carbon with the adjacent hydrogen atoms. If these two sub-bands are disregarded, the band gap for the diamond remains $\sim 5.5\text{eV}$.

Fig. 2 shows the electron density change for the MoO_3 :H-diamond interface. The blue regions show where a loss of electron density occurs and thus the accumulations of holes, while the purple regions show where there is an increase in electron density. Hence, from the data it can be concluded that there is a hole accumulation that occurs near the surface of the diamond, while most of the electron density gained by MoO_3 clearly migrates to the oxygen atoms. Therefore, MoO_3 acts as a p-type doping for the H-diamond substrate.

To further validate the reliability of our calculation parameters, we calculated the optical spectrum of a bulk diamond and plotted the dielectric constant to compare our results to a recent theoretical study by Xiang *et al.* [8] and experimental data published by Philipp and Taft [9]. The comparison plots for the real ($\text{Re}[\epsilon]$) and imaginary ($\text{Im}[\epsilon]$) parts of the dielectric constant in Fig. 3 show that our DFT method produces results in agreement with other published theoretical work and experimental data. For the bulk diamond, the spectrums of [100, 010, 001] crystallography orientation are degenerate and hence only one result for [100] orientation is presented. The small discrepancies between the calculated and the experimental curves are due to the inter-band transitions and neglected excitonic effects in the simulations. It should be pointed out that the absorption edge corresponding to the bulk gap of diamond of 5.5 eV is suppressed in the experimental spectre due to its indirect transition nature.

Fig. 4 shows the calculated $\text{Re}[\epsilon]$ and $\text{Im}[\epsilon]$ parts of the dielectric function of the H-diamond and the MoO_3 -doped H-diamond. For both systems the spectra of [100, 010, 001] crystallography orientations are degenerate due to inherent structural anisotropy. The most significant difference between the two systems is at below 5 eV where, due to the MoO_3 molecule, there are additional absorption features such as peaks. This shows that the adsorption of the MoO_3 molecule on the H-diamond surface introduces empty states within the band gap which enhances the optical absorption of the MoO_3 -doped H-diamond near the infrared (IR) region. Similar behaviour is observed for a thin layer of metal oxides [10].

In conclusion, our results suggest that the MoO_3 molecule acts as a p-type doping material to the H-diamond surface and that the MoO_3 -doped H-diamond may have great potential in application of opto-electronic devices for IR and near IR light detection.

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