ATOMIC PROPERTIES OF HEXAGONAL BORON NITRIDE FROM FIRST PRINCIPLES

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ABSTRACT

Density functional theory calculations were performed on hexagonal Boron Nitride (h-BN) in both bulk and nanosheet forms. We find good agreement between experimental lattice parameters and theoretical results. However, we are unable to reproduce trends found by Zhou [Andrew F. Zhou, PARADIM Proposal 220 (2020)] regarding the increase in interlayer distance with decreasing layers. We find that the interlayer distance shows minimal change with changing the number of layers. We also report the band structure of bilayer nanosheets.

INTRODUCTION

Hexagonal Boron Nitride (h-BN) has encountered much attention in recent times due to its incredible electrical, thermal, and mechanical properties. Its chemical composition leads to its chemical inertness and non-toxicity, which puts it in a different class than graphitic materials (1). In the past, h-BN has been used as a ceramic due to its tribological properties i.e. friction, lubrication, surface interactions. For example these properties have been theorized to be effective as a coating on spacecraft for its ability to hold its structure at high temperature (2, 3). Analysis of h-BN on a smaller scale as Hexagonal Boron Nitride Nanosheets (BNNS) is also of interest. Just as graphitic materials have been found to have wide reaching applications, BNNS is no different. BNNS could be used as a method of cancer drug delivery since it is more biocompatible and less toxic than graphene based materials but retains many of the same properties (4). Motivations have also been found for use of h-BN in quantum information and quantum communication science as 'single photon emitters' (5). Our specific interest in h-BN stems from its theorized use as a UV photodetector at high temperatures (6).

METHODS

First-principles calculations were performed using QUANTUM ESPRESSO software package. Testing was done into different pseudopotentials including Ultrasoft, PAW, Ultrasoft GBRV, and Non-Conserving across both the PBE and PBEsol exchange correlation functionals. We found no variation in lattice parameters across choice of pseudopotential. These levels of theory were also cross tested with and without the vdW-DFT-D3 scheme proposed by Grimme *et al.* Our findings indicate that the PBEsol exchange-correlation functional with a DFT-D3 van der Waals correction term agrees most with experimental findings. The kinetic energy cutoff for wavefunctions was set as 80 Ry and the kinetic energy cutoff for charge density and potential was set at 800 Ry.

The electronic momentum k-point mesh was set as 12 x 12 x 4. Lattice parameters and internal coordinates have been relaxed.

Nanosheet calculations were carried out by using the relaxed cell parameters of the corresponding bulk system in a large supercell to mimic an isolated nanosheet system. The supercell was defined as taking the interlayer distance from the bulk system and stretching it by a factor of 7 , 8 , 9, and 10 for 2, 3, 4, and 5 layers respectively. This results in a vacuum layer of about 20 Å for every system. We also held the movement of the system along the x-y plane constant by using cell_dofree='2DXY', thus allowing the interlayer distance to relax for the nanosheets.

RESULTS

Experiment agrees well with theory results for bulk h-BN systems. h-BN can exist in one of five stacking orders. AA is most straightforward where each atom perfectly aligns, AA' is where every other layer is rotated 60° clockwise, and AB is derived from translating every other layer along the plane of the *a* lattice parameter. Note here AA' AB' and A'B are also constructed using the same definitions. Ref. 10 shows that the experimental stacking order is AA'. Measured results on the lattice parameters of bulk h-BN report that the a lattice parameter is 2.502 Å and the c lattice parameter is 6.660 Å (10). Table 1 shows these agreements between experimental lattice parameters and our calculated results. The calculated a lattice parameter varies from 2.504 Å to 2.5025 Å with different stacking orders. These modulations are on the order of thousandth of an Ångstrom difference from experimental results and thus agree well. The calculated c lattice parameter varies from 6.49 Å to 7.19 Å. Here the difference between experimental and theoretical results is about 0.2 Å with regards to AA' stacking.

	a	c
AA	2.503	7.194
AA'	2.503	6.539
AB	2.503	6.493
AB'	2.504	6.488
A'B	2.503	7.070
Experimental	2.502	6.66

Table 1: Bulk lattice constants a & c in Ångstroms as compared with the different stacking orders of hBN and experimental data.

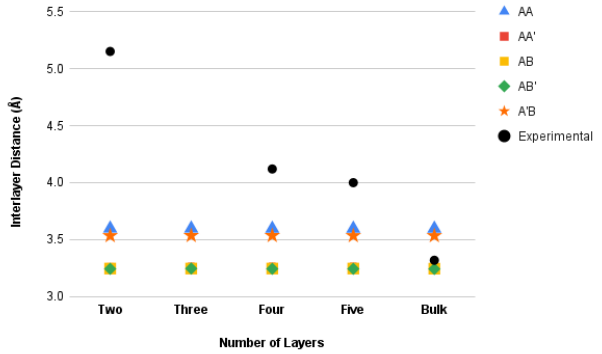

Figure 1: The measured and calculated interlayer distances as a function of the total number of layers.

In addition to bulk systems, Figure 1 shows the c lattice parameter results from nanosheet systems. We attempted to recreate experimental findings by Zhou *et. al*. (6) by using nanosheets simulated with the vacuum system described in the Methods section. Ref. 6 reports a steady decrease in interlayer spacing as a function of increasing layers. This trend should be brought upon by the increasing vdW interactions as one increases the number of layers. However, our theoretical results are unable to reproduce experimental findings. DFT finds non-varying interlayer distances across all five stacking orders when decreasing the number from bulk to two layers on the order of a hundredth or thousandth of an Ångstroms.

Despite an inability for the system to recover experimental results, band structure calculations were done to further elucidate the h-BN nanosheet electronic structure in Figure 2. Each plot for different stacking orders has been translated so that the valence band maximum (VBM) is set to zero and the fundamental band gap is reported in Figure 2. AA' and AB are of similar band gap energy and higher in magnitude than AA, AB', and A'B who are all also similar in magnitude. Our bilayer band structure results also find that AA and AB' has direct band gap while AA', AB, and A'B has indirect band gap. The experimental reported band gap is 4.02 eV (11). These overall trends in band structures are also reported by Gilbert *et al.* (12).

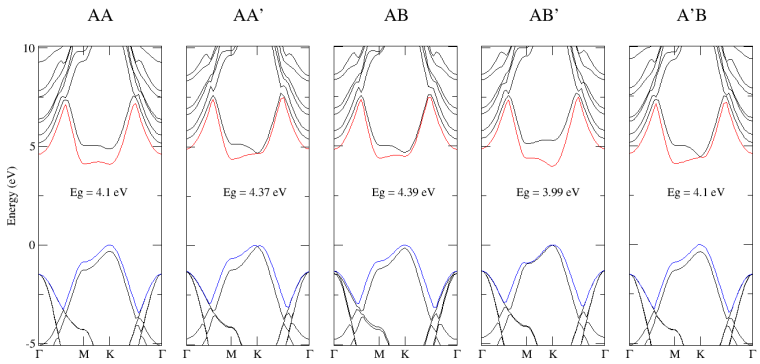

Figure 2: The electronic band structure of bilayer h-BN: AA, AA', AB, AB', and A'B, from left to right. The red (blue) coloring of a band indicates the conduction (valence) band.

FUTURE WORK

Future work includes investigating the discrepancies between calculated interlayer spacing and experimental findings. This could be due to experimental distance measured at the edge of the sample. Creating this experimental setup would require more complex simulations with vacuum layers in all three dimensions. Aside from different systems, the uses of other functionals of DFT are also remaining to be explored.

ACKNOWLEDGEMENTS

Special thanks to Dr. Pamuk and Dr. Zhou for their assistance in this project. This work is supported by the National Science Foundation, Platform for the Accelerated Realization, Analysis and Discovery of Interface Materials (PARADIM) under Cooperative Agreement No. DMR-2039380. Calculations were performed at Maryland Advanced Research Computing Centre (MARCC). Questions can be directed to nimitmishra@ucla.edu

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