Ab Initio Simulations for Microelectronics: ZnGa₂O₄ and Hexagonal BN

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The computational project IHPms21 provides assistance to the IHP Materials Department in the pursuit for new materials that might be integrated into the existing microelectronic and optoelectronic technologies. We report on the results of *ab initio* calculations pertinent to two distinct subjects: (1) to the surface preparation of $ZnGa_2O_4$ (ZGO), which is an ultra-wide gap transparent semiconductor with properties attractive for high-power electronic devices and deep-UV optoelectronic devices, and (2) to the growth of hexagonal BN (hBN) films, which is a layered 2D material structurally akin to the famous graphene and considered as promising dielectric to be used in graphene devices. With the example of ZGO we illustrate the interpretation of photoemission spectra in the terms of surface structure and composition. With the example of hBN we illustrate the seeking for physicochemical processes, which determine the growth of 2D insulators by industrially viable methods.

1 Introduction

The results reported here have been obtained within the project IHPms21, which uses *ab initio* density functional calculations to interpret and to guide the experiments conducted by the IHP¹. The IHP is a Leibniz institute for basic and applied research and development in the fields of silicon-based microelectronics and technology for wireless and broadband communication. This includes work on new materials and on methods to integrate them into the existing technologies. The *ab initio* theory employed by IHPms21 is the plane wave pseudopotential DFT as implemented in Quantum Espresso^{2–4}, an actively developed open-source package that since decades has been available to the users of the JSC cluster.

The numerical approach is outlined in Sec. 2. The motivation for and the goal of the calculations are given in Sec. 3. Secs. 4 and 5 describe the results for ZGO (completed study)⁵ and for hBN (ongoing research)⁶, respectively. ZGO (ZnGa₂O₄) is a wide-gap transparent semiconductor with properties attractive for high-power electronic and deep-UV optoelectronic devices, and hBN (hexagonal BN) is a layered 2D material structurally akin to graphene and considered as a promising dielectric for graphene devices.

2 Approach

Atomic structures in question are optimised by the Quantum Espresso (QE) plane wave pseudopotential density functional theory (DFT) package², publicly available on JUWELS. Its pw utility constructs and diagonalises the Kohn-Sham Hamiltonian (usually, by the Davidson method)⁷. It solves the Kohn-Sham equations self-consistently and embeds them in a loop, in which the atomic coordinates relax following the Hellmann-Feynman forces. Numerous semilocal and hybrid functionals for exchange-correlation energy are available,

including the libxc library⁸. We mostly use GGA type⁹ of exchange and correlation energy (PBE form)¹⁰. Van der Waals interactions needed for proper description of 2D materials (like hBN) are taken in the non-local meta-GGA form (rVV10)¹¹. For selected cases we adapt hybrid (i.e., with a portion of HF exchange) functionals in the HSE form¹²; this is computationally expensive and therefore used here mostly in the case of doubt, as means to establish the validity limit of less heavy and less accurate GGA calculations.

DFT is designed for efficient computation of atomic structures. The electronic structure it renders corresponds to a fictitious system of non-interacting electrons. It resembles the real electronic structure and in many cases can be used as an informative approximation, but in order to derive the physical quantities which, as photoemission, are closely related to the electronic structure, one must often augment it with other means. One way is to employ the above-mentioned hybrid functionals. A far less expensive, though also less precise, less general and more arbitrary approach is to use the so-called Hubbard U correction¹³. It works well for materials such as ZGO and for this reason it was adapted in this work.

Photoemission spectra were simulated from the projection of the crystal states onto the states of isolated atoms. We used HF atomic photoionisation cross-sections tabulated as a function of the photon energy¹⁴. The inelastic mean free paths of electrons were approximated by the TPP2M formula¹⁵ corrected at low energies E by a $1/E^2$ term¹⁶.

3 Motivation

The path from an idea to its technological realisation may be long, particularly when the confronted roadblocks depend on details evading experimental access. What cannot be seen, must then be computed. Viewed from this perspective, *ab initio* theory becomes just another characterisation tool, with its pros and cons. Being applicable only to smallest dimensions and shortest times, it resembles the experimental tools allowing one to visualise individual atoms, like the scanning tunnelling microscopy (STM) does. And as in the case of STM, when properly applied it can provide understanding helpful in the "debugging" of the concepts and also in the optimisation of the technological process.

The calculations undertaken by IHPms21 and exemplified by the cases reported here are intended to interpret and guide experimental work and to evaluate new ideas by educated guess. In particular, their aim is to infer structure and chemistry of surfaces and to identify the structures, including defective arrangements of atoms, which are responsible for the encountered behaviour of the systems of interest. The main observations, which prompted us to examine ZGO and hBN by *ab initio* means, were:

- X-ray photoemission spectroscopy (XPS) and UV photoemission spectroscopy (UPS) indicate unintended stoichiometry changes of the ZGO surface, apparently induced by the surface preparation process. What is happening on the surface, and does this indicate problems, or new chances, or is just a side effect?
- During the hBN growth by chemical vapour deposition (CVD) from borazine (BZ, $B_3N_3H_6$), the substrate becomes covered by apparently amorphous islands and it is difficult to obtain an ordered, layered film of intended thickness. Why is it so, and what can be changed in the process in order to improve the outcome?



Figure 1. $ZnGa_2O_4$ bulk: a) Band structure. b) Atomic structure: alternating (001) Zn and GaO_2 layers; Zn is blue, Ga is green, O is yellow. c) Top of the valence band. d) Top of the surface-projected valence band, which is the bulk band structure integrated along the Γ -X line, see the Brillouin zone inset in the panel a) of this Figure.

4 The (001) Surface of ZnGa₂O₄ Crystals

ZnGa₂O₄ is a cubic semiconductor with light electrons and heavy holes (Fig. 1a). Its bulk is composed of alternating (001)-oriented, one atom thick layers of two types: (a) positively charged metal layers, Zn, and (b) negatively charged Ge oxide layers, GaO₂ (Fig. 1b). The gap is indirect (Fig. 1c). Because the surface removes the translational symmetry along the surface normal, the band structure measured by techniques which, like angle resolved ultraviolet photoemission spectroscopy (ARUPS) applied by us, feel the presence of the surface, corresponds to the surface projection of the band structure, with states visible on both sides of the Brillouin zone centre at Γ (Fig. 1d). The band structures measured in our experiments by ARUPS are compatible with this simulation.

We have observed significant nominal loss of Zn from the surface of ZGO crystals as the result of treatments needed to prepare the samples for examination: the intensity of the photoelectrons ejected from Zn by Al K α photons decreased with respect to those emitted from Ga and from O atoms, indicating stoichiometry changes and not just creation of isolated defects. On the other hand, the prepared surfaces retain high degree of crystallinity. As direct imaging methods (like STM) provided us with no clue regarding the chemical and structural status of the surface region, we addressed the issue by our *ab initio* tools.

Because the surface preparation is complex, involving removal of atoms by sputtering with Ar^+ ions, the thermodynamical status is unclear and it is not practicable to draw conclusions solely on the basis of computed total energies and entropies. By the selection of the structures for close examination we have thus took a semi-empirical approach, excluding the cases, for which (a) well-ordered arrangements with periodicity higher than the observed 1×1 are favourable, (b) there are empty states at more than about 50 meV below the conduction band minimum (CBM), and/or (c) strong photoemission (PE) from states within the band-gap and/or near the valence band maximum (VBM) is expected.



Figure 2. $ZnGa_2O_4(001)$: left: Zn-terminated, middle: GaO_2 -terminated, right: Ga_2O_3 -terminated. Colours as in Fig. 1b.

Because of the (001) bilayer structuring of the bulk (Fig. 1b), one may have either Znterminated or GaO_2 -terminated ZGO(001) surface. The simplest explanation of the Zn loss would be to assume that as-loaded samples are Zn-terminated (Fig. 2a) and fully prepared samples are GaO_2 -terminated (Fig. 2b). The simulated PE changes are however too small, in agreement with a simple estimate: given the electron escape depth and the measured PE intensity changes, one expects that the loss amounts up to two Zn monolayers. This could be in principle be accounted for by assumption that the as-loaded samples are covered by two Zn monolayers (more precisely, by two ZnO monolayers, because Zn oxidises readily), but the corresponding simulated PE spectra do not fit to those measured.

After having examined numerous structures and stoichiometries and having verified the reliability of the simulations by checking various numerical conditions and approximations (type of pseudopotentials, Hubbard U energies, hybrid functionals) we arrived at the conclusion that the experimental and theoretical data are at the best agreement for the oxide-terminated surface, in which the subsurface Zn atoms are substituted by Ga to form an ultrathin β -Ga₃O₄ film (Fig. 2c). Fig. 3 shows the PE spectra simulated for this case. We also concluded that pseudopotential calculations introduce intrinsic uncertainties to the electron distributions, which cannot be alleviated by Hubbard U or even by HSE. On the other hand, the peak shapes are well assessed, when the position dependence of Hubbard U is accounted for: U must be computed self-consistently, for each surface atom separately.



Figure 3. Measured (points) and simulated (lines) PE spectra: a) XPS: Al Kα, 1486.7 eV. b) UPS: He II, 40.81 eV.



Figure 4. a) HRTEM image of hBN at Ge(001). Ge atoms are visible as big white spots, the blue lines indicate the Ge crystallographic planes. The red lines mark the hBN layers nucleated on Ge, the orange lines mark the other hBN layers, the blue symbols mark the layer connection points. b) Hypothetical structure of a layer interconnection at an antiphase boundary in the bottom layer. Boron atoms are brown, nitrogen atoms are green.

5 Growth of hBN Films from Gaseous Borazine

CVD growth of hBN is achieved by exposing a hot (around 900 °C) Ge(001) sample to gaseous $B_3N_3H_6$ (borazine, BZ). For this purpose, a carrier gas (Ar) is pumped through liquid BZ. The resulting Ar+BZ mixture is ultimately delivered by a stainless steel pipe, which ends about 5 cm away from the sample kept in a vacuum chamber.

We observed that with this approach there is a pronounced tendency for 3D growth: there are high hBN islands (aspect ratio close to 1) surrounded by flat hBN areas. Depending on the technical details, one obtains films, which in high-resolution transmission electron microscopy (HRTEM) images appear to be amorphous with nanocrystalline hBN inclusions, or films built predominantly of nanocrystalline hBN. In the latter case one can see that the deepest layers nucleate at Ge(001) surface steps (Fig. 4a, red lines) and that some layers are interconnected (Fig. 4a, blue symbols). The observed nucleation at Ge(001) steps is in accordance with the computed energy differences and, given the outcome of the calculations, the growth on Ge can be understood as promoted by catalytic activity of the Ge substrate, which is able to decompose BZ down to single atoms. The occurrence of interlayer connections can be readily associated with the natural presence of antiphase boundaries in the nanocrystalline film: we find that such boundaries are the only place at which a new layer may nucleate on an intrinsic layer and remain connected to it. Other plausible nucleation sites on hBN are boron substitutionals (nitrogen vacancies filled with boron), but the layers nucleated there are expected to eventually become detached.

In contrast to the growth directly on Ge, the relatively high hBN growth rate achieved by CVD from BZ on hBN is however not easy to explain. Namely, as soon as the whole Ge surface becomes covered by hBN, the catalytic activity of the substrate is expected to go down practically to zero. Indeed, calculations show that no BZ decomposition can take place on perfect, intrinsic hBN. It follows that from the second hBN layer on, the only BZ molecules contributing to the hBN growth should be those arriving at the layer *edge* undamaged, either directly from the gas or from a narrow collection zone along the edge¹⁷. The computed desorption energy of BZ (0.4 eV) is however too small and the computed energy barriers for attachment of undamaged BZ at the hBN edge (2.0 eV) are too high to allow for noticeable growth of this type, at least at the temperatures and pressures used in the experiment: the frequency of collisions between the molecules and the step edges and the probability that the impinging or diffusing molecule goes then over the energy barrier to make a bond with the edge atom are then much too small. We estimate that pressures in the atmospheric range would be needed for such a process to be efficient, but the actual pres-



Figure 5. a) $B_3N_3H_6$ adsorbed on a Cr atom of stainless steel. Cr atoms are violet, Fe atoms are red, O atoms are yellow. Dehydrogenation occurs by proton jump from between B and Cr onto one of the surface O atoms. b) $B_3N_3H_5$ is physisorbed on intrinsic hBN with the adsorption energy 0.7 eV. c) $B_3N_3H_5$ is chemisorbed on p-type hBN, with the DFT-CGA adsorption energy of 3.2 eV.

sures in the reaction chamber are at least six *orders of magnitude* below the atmospheric pressure. Even though the DFT-GGA barrier heights are not precise, the required corrections to the barrier heights (from 2.0 eV down to at most 1.6 eV) are significant. Moreover, the critical reaction step is here the reordering of H: the moment when two H atoms – one from the hBN edge and the other one from the incoming molecule – leave the B and N atoms to combine into H₂. The barriers computed by us for this process are comparable to those obtained in similar BN systems by other authors using more precise methods¹⁸.

In order to solve this puzzle, we considered a number of alternative reaction schemes. First, the readings from the mass spectrometer suggest that the gas pumped out of the chamber contains considerable amount of BH₃ of unclear origin, possibly already dissolved in liquid BZ, and also some NH₃. A hBN film can in principle be assembled also from such a BZ + BH₃ + NH₃ mixture. However, although the barriers for BH₃ attachment appear be low enough, the barriers for NH₃ attachments, while lower than those for BZ attachments, may be still too high. Second, the mass spectrometer reveals the presence of water; however, according to the calculations, even if water would take part in the reactions on the edge, it tends to stabilise H there (in the form of OH), instead of destabilising it. Third, we considered the possibility that some of the BZ molecules lose a H atom before reaching the sample. We verified that such B3N3H5 molecules would indeed facilitate the growth by abstracting single H atoms from the edge. Some BZ molecules would dehydrogenate to $B_3N_3H_5$ if they come in contact with hot stainless steel (Fig. 5a). Given the computed barrier heights, we estimate that dehydrogenation requires the temperature of the steel to exceed 500 °C. It is unclear if the gas injector heats up to temperatures needed to achieve sufficient partial pressure of B₃N₃H₅. A more realistic source of B₃N₃H₅ radicals could be the heater or the hot sample holder. Furthermore, the conditions for BZ to lose H are similar for those for H₂ dissociate, so that the reaction H(g) + H(ads) \Leftrightarrow H₂(g) may be responsible for partial dehydrogenation of the edge. Finally, we found that those hBN surface regions, where multiple positive charge carriers (holes) are present in the valence band, are able to dehydrogenate BZ to $B_3N_3H_5$ (Fig. 5b-c) and that this $B_3N_3H_5$ may remain on the surface even for about a second at 900 °C and diffuse on it far enough to assure that sufficiently high amount of the radicals take place in the reactions at the step. Such doping with holes may be associated with the formation of defects during growth, nevertheless the doping levels (in the range of several 10^{13} cm⁻²) needed for this mechanism to be efficient may be too high to be realistic. The hypotheses involving $B_3N_3H_5$ and/or H radicals formed on hot parts in the chamber appear to be the most promising. We are now exploring them, attempting to find more theoretical support and seeking for ways of experimental verification.

6 Concluding Remarks

We have presented two examples from our research on new materials for microelectronics and optoelectronics, in which we used *ab initio* calculations treated as characterisation tools in parallel to experimental characterisation techniques. For the case of zinc gallate (ZnGa₂O₄ZGO), a wide gap semiconductor of potential interest to high power microelectronics and deep UV optoelectronics, we have provided interpretation of photoemission spectra in order to strengthen the evidence for the formation of ultrathin β -Ga₃O₃ film on top of ZGO in the course of a standard surface preparation procedure. For the case of hexagonal boron nitride (hBN), we have analysed various film growth mechanisms in order to explain the observed growth rate and morphology of the film.

Acknowledgements

The authors gratefully acknowledge the Gauss Centre for Supercomputing e.V. (www.gauss-centre.eu) for funding this project by providing computing time through the John von Neumann Institute for Computing (NIC) on the GCS Supercomputer JUWELS at Jülich Supercomputing Centre (JSC)¹⁹. JD, MF and ML gratefully acknowledge the support from the EU FLAG-ERA project 2DHetero⁶.

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