



Atomic-Scale Modeling of Equilibrium and Transport Properties at Metal-Dielectric Interfaces

Wolfgang Windl
OHIO STATE UNIVERSITY

10/10/2019
Final Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ RTB1
Arlington, Virginia 22203
Air Force Materiel Command

DISTRIBUTION A: Distribution approved for public release

REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services, Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.						
1. REPORT DATE (DD-MM-YYYY) 23-10-2019		2. REPORT TYPE Final Performance		3. DATES COVERED (From - To) 15 Sep 2014 to 14 Sep 2017		
4. TITLE AND SUBTITLE Atomic-Scale Modeling of Equilibrium and Transport Properties at Metal-Dielectric Interfaces				5a. CONTRACT NUMBER		
				5b. GRANT NUMBER FA9550-14-1-0322		
				5c. PROGRAM ELEMENT NUMBER 61102F		
6. AUTHOR(S) Wolfgang Windl				5d. PROJECT NUMBER		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) OHIO STATE UNIVERSITY 1960 KENNY RD COUMBUS, OH 43210-1016 US				8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AF Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR RTB1		
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-VA-TR-2019-0294		
12. DISTRIBUTION/AVAILABILITY STATEMENT A DISTRIBUTION UNLIMITED: PB Public Release						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT This project provided DFT modeling work in order to understand defect energetics in dielectrics around conductor/dielectric interfaces and the influence of electric fields on them. The project included two components: First, we identified the correct method to determine point defect energetics along with experimental validation for two systems, Zn1-xMgxO with point defects quantified by cathodoluminescence (collaborator: Brillson, OSU) and two-dimensional BN sheets where defects were directly counted in TEM images (collaborators: Duscher and Gu, UTK). We found that of the different methods in the literature, only stoichiometry balancing agrees with experiment. Second, we investigated the effect of electric fields on point defects in doped Zn-ZnO junctions. Schottky-type band curvature resulted in Zn vacancies having the lowest energy away from the interface while ohmic-type curvature resulted in O vacancies having the lowest energy at the interface. These results indicate that clustering of O and Zn vacancies would occur at the different ends of a metal-oxide-metal structure. The energy difference increased with increasing field.						
15. SUBJECT TERMS atomistic model, conductor/dielectric material interfaces, dielectric, diffusion effect, electronic structure, electric field						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT	b. ABSTRACT	c. THIS PAGE			SAYIR, ALI	
Unclassified	Unclassified	Unclassified	UU		19b. TELEPHONE NUMBER (Include area code) 703-696-7236	

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

DISTRIBUTION A: Distribution approved for public release

Project # FA9550-14-1-0332
Final Report:
Atomic-Scale Modeling of Equilibrium and Transport Properties at
Metal-Dielectric Interfaces

Wolfgang Windl
Materials Science and Engineering, The Ohio State University, Columbus, OH

Executive Summary:

High-density capacitors play a crucial role in US Air Force and DoD technology within electronic devices (e.g. in gate stacks in field-effect transistors) and for energy storage. However, the continuous demand for increasing electric fields and sometimes extreme temperatures imposes challenges in term of fatigue and failure on the device structures. This project focused on modeling of atomic-scale electronic structure methods in order to understand defect energetics and kinetics in dielectrics in bulk and around conductor/dielectric material interfaces, including the influence of strain and electric fields on them. We also developed a new model to predict heat transport on the metal side, called Mott+, which would be important for holistic modeling of the entire system. The core of the project work included two components: First, a new method was developed to determine the most sensible chemical potentials for point defect energetics and validated through experiments by external collaborators. Two model dielectrics were chosen, where experimental defect quantification of point defects was made possible through two different experimental methods. One was $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, where defect concentrations were quantified through cathodoluminescence measurements of the cation and oxygen vacancy level intensity in the band gap. While this method does not allow determining absolute defect concentrations, relative changes with respect to Mg-concentration can be measured, from which the dependence of the formation energies on concentration could be determined. This dependence (which consists in two linear slopes with a kink between them as a function of concentration) needed to be reproduced by calculation, which then identified the most physical method to determine chemical potentials, which were identified as stoichiometry balancing. The material and cathodoluminescence measurements came from Dr. Len Brillson in OSU's ECE Department, and his work was funded through an NSF project. For the second system, we chose two-dimensional BN sheets, for which defects can be directly seen and quantified in scanning transmission electron microscopy. Material and STEM measurements were from Dr. Gong Gu and Dr. Gerd Duscher at UT Knoxville. Finally, we also had the opportunity to apply our point-defect calculation methods to other materials, leading to a paper on the direct observation of vacancies in $\beta\text{-Ga}_2\text{O}_3$ in collaboration with Dr. Jinwoo Hwang from OSU. Papers on point defects in BAs, SiC, and Al_2O_3 are also in preparation.

In order to then include the effects of fields on the point defect energetics, we examined the dependence of vacancies in ZnO in electric and strain fields. Since electric and resulting strain fields are the major influence on defect kinetics around interfaces in high fields, the goal was to develop a validated theory for the relevant energetics, which, if combined with the necessary kinetics, can be applied to predict the behavior and failure mechanisms in dielectric materials.

Publications from Project

1. G. M. Foster, J. Perkins, M. Myer, S. Mehra, J. M. Chauveau, A. Hierro, A. Redondo-Cubero, W. Windl, and L. J. Brillson, *Native point defect energies, densities, and electrostatic repulsion across (Mg, Zn) O alloys*, Physica Status Solidi A **212**, 1448-1454 (2015).
2. J. Perkins, G. M. Foster, M. Myer, S. Mehra, J. M. Chauveau, A. Hierro, A. Redondo-Cubero, W. Windl, and L. J. Brillson, *Impact of Mg content on native point defects in $Mg_xZn_{1-x}O$ ($0 \leq x \leq 0.56$)*, Appl. Phys. Lett. **3**, 062801 (2015).
3. C. Wei, N. Antolin, O. D. Restrepo, W. Windl, and J. C. Zhao, *A general model for thermal and electrical conductivity of binary metallic systems*, Acta Mater. **126**, 272-279 (2017).
4. J. M. Johnson, S. Im, W. Windl, and J. Hwang, *Three-dimensional imaging of individual point defects using selective detection angles in annular dark field scanning transmission electron microscopy*, Ultramicroscopy **172**, 17-29 (2017).
5. Peizhi Liu, Junjie Guo, Lei Liu, Wolfgang Windl, Gong Gu, Gerd Duscher, *Direct Observation of Defects in Hexagonal Boron Nitride Monolayers*, Microscopy and Microanalysis **20**(S3), 1738-1739 (2014).

Publications in preparation:

1. Y. Wang and W. Windl, *Native Point Defects and Evidence of Ultrahigh Thermal Conductivity in BAs*
2. M. Hornak, N. Antolin, O.D. Restrepo, and W. Windl, *Defect Formation Energies in Sapphire from Stoichiometry-Balancing Chemical Potentials*
3. G. Duscher, G. Gong, W. Windl, *Point Defects and Stoichiometry in Two Dimensional BN*
4. A. Kumar, O. D. Restrepo, and W. Windl, *Fermi-Level Dependent Chemical Potentials and Point Defect Formation Energies in Non-Metallic Compounds – Silicon Carbide*
5. W. Windl, M. Ball, O. D. Restrepo, L. J. Brillson, and W. Windl, *Experimentally Measured Chemical Potentials and Point Defect Energies in $Zn_{1-x}Mg_xO$*

Research Output – Table of Contents

- 1. Point-Defect Energetics from Stoichiometry Balancing**
 - a. Point Defects in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ and Experimental Chemical Potentials**
 - b. Point Defects, Dislocations and Edges in 2D-BN**
 - c. Further Systems**
- 2. Thermal transport and point defects in dielectrics around metal-dielectric interfaces**
 - a. Thermal transport on the metal side (alloys)**
 - b. Point Defect Energy at Metal-Oxide Interfaces with Internal Electric Fields**

1. Point-Defect Energetics from Stoichiometry Balancing

Point defects influence the properties in materials to a larger degree than most any other factor, especially when functional materials are considered. However, their experimental examination is usually difficult to impossible, and thus their study is one of the central topics of materials computation. In fact, according to a Google Scholar search, 28% of all papers including the expression “Density Functional Theory” also include “point defects.”

One of the most central questions about point defects is their concentration, which needs to be known before their influence on any property can be assessed. While there is consensus in the community by now about calculation of formation energies of point defects and thus their equilibrium concentration in elemental solids, large discrepancies exist for materials with more than one component, which often leads to unphysical and contradictory results, depending on the method used, as we will show below. The topic under dispute concerns the energy that each single atom contributes to the overall energy, also known as its chemical potential. Without correct chemical potentials, the results are frequently meaningless or even unphysical, and so one of the central tasks in this project was to assess the different methods proposed in the past in comparison to experiment, which led to a novel approach to do that which we argue is physically much more sensible than previous attempts.

a. Point Defects in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ – Experimentally Measured Chemical Potentials

In this first section, we will demonstrate for the first time how computational analysis of cathodoluminescence defect spectroscopy can be used to unambiguously determine the chemical potentials in binary compound semiconductors, specifically ZnO and ZnMgO alloys, which then allows resolving a number of heavily disputed questions. For that, we first measured in collaboration with Dr. Len Brillson’s group at OSU the intensity of the cation and oxygen vacancy emissions in ZnMgO alloys relative to the intensity of the near-band gap emission,

which is proportional to the concentration of the respective vacancies [1, 2]. The resulting intensities are shown in Fig. 1(a).

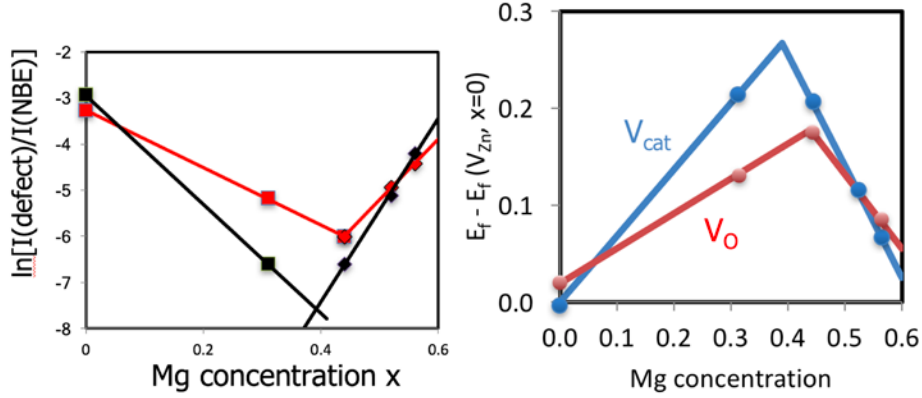


Fig. 1. (a) Intensity of the deep-level emission of cation (V_{cat} , black) and oxygen (V_{O} , red) vacancy concentrations in $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, measured with depth-resolved cathodoluminescence spectroscopy [1, 2]. Two regions are identified, “low” and “high”, which are intensities below and above the change-of-slope points. (b) Difference in formation energy between cation and oxygen vacancies, extracted from Fig. 1(a) using Eq. (2).

In order to analyze the intensities in Fig. 1(a), we assume that the vacancy concentrations are in thermal equilibrium, which means their concentrations can be described by an Arrhenius expression, $C_v(x) = C_0(x) \exp(-E_f(x)/kT)$ which in logarithmic form can be written as

$$\ln[C_v(x)] = \ln(C_0(x)) - E_f(x)/kT, \quad (1)$$

C_0 is the prefactor (formation-entropy term) and E_f is the formation energy. With that, we can look at the ratio of cation and oxygen vacancies, and get (assuming the prefactors are the same)

$$k_B T \cdot \ln[C_{V_{\text{O}}}(x)/C_{V_{\text{cat}}}(x)] = E_f^{\text{V}_{\text{cat}}}(x) - E_f^{\text{V}_{\text{O}}}(x) \equiv \Delta E_f^{\text{expt}}(x). \quad (2)$$

Table III reports the measured $\Delta E_f^{\text{expt}}(x)$ values.

Furthermore, within the O or cation vacancies, the energies between two concentrations x_1 and x_2 can be related in the analogous way,

$$k_B T \cdot \ln[C_v(x_1)/C_v(x_2)] = E_f^{\text{V}}(x_2) - E_f^{\text{V}}(x_1). \quad (2a)$$

Using Eq. (2), we can now determine from Fig. 1(a) the experimentally measured difference in formation energy between cations and vacancies at the various compositions, shown in Fig. 1(b).

The formation energies E_f of cation and oxygen vacancies, V_{cat} and V_{O} , with charge Q were now calculated within Density-Functional Theory (DFT) using the standard formula

$$\begin{aligned} E_f^{\text{cat}}(Q, E_F) &= E\left[\left(\text{Zn}_{1-x}\text{Mg}_x\right)_N \text{O}_N, Q_{\text{cat}}\right] - E\left[\left(\text{Zn}_{1-x}\text{Mg}_x\right)_N \text{O}_N\right] + \mu_{\text{cat}}(x, E_F) + Q[E_v + E_F]; \\ E_f^{\text{O}}(Q, E_F) &= E\left[\left(\text{Zn}_{1-x}\text{Mg}_x\right)_N \text{O}_{N-1}, Q_{\text{O}}\right] - E\left[\left(\text{Zn}_{1-x}\text{Mg}_x\right)_N \text{O}_N\right] + \mu_{\text{O}}(x, E_F) + Q[E_v + E_F]. \end{aligned} \quad (3)$$

E are total energies that will be calculated within DFT; Q is the charge; E_F is the Fermi energy relative to the valence band edge E_v (again from DFT), and μ_{cat} and μ_{O} are the chemical potentials of cations and O. Additionally, we enforce the usual constraint that the sum of the chemical potentials needs to be identical to the energy per cation-oxygen pair in the perfect solid,

$$\mu_{\text{cat}}(x) + \mu_{\text{O}}(x) = E_{\text{Zn}_{1-x}\text{Mg}_x}(x) = E\left[\left(\text{Zn}_{1-x}\text{Mg}_x\right)_N \text{O}_N\right] / N_{\text{cation-O pairs}}^{\text{Zn}_{1-x}\text{Mg}_x}. \quad (4)$$

Using Eqs. (3) and (4), we find for $\Delta E_f(x)$

$$\begin{aligned} \Delta E_f(x) &= E\left[\left(\text{Zn}_{1-x}\text{Mg}_x\right)_N \text{O}_{N-1}, Q_{\text{O}}\right] - E\left[\left(\text{Zn}_{1-x}\text{Mg}_x\right)_N \text{O}_N, Q_{\text{cat}}\right] - E\left[\left(\text{Zn}_{1-x}\text{Mg}_x\right)_N \text{O}_N\right] / N \\ &\quad + 2\mu_{\text{O}}(x, E_F) + \min_Q(Q_{\text{O}} - Q_{\text{cat}})(E_F(x) + E_v(x)) \end{aligned} \quad (5)$$

At this point, the energies of defective and perfect cells are calculated with DFT. In the considered concentration range, the experimental alloy oxides have the wurtzite structure [1, 2], for which we use 72-atom supercells, making $N = 36$. We use VASP [3, 4] with PBE PAW potentials [5, 6] and an HSE06-derived hybrid functional [7] with $\alpha = 0.36$ for ZnO, resulting in a bandgap of $E_g = 3.29$ eV (matching the experimental value of 3.3 eV), $\alpha = 0.43$ for MgO with $E_g = 7.94$ eV (experiment 7.8 eV), and linear interpolation of α for alloys in-between. Cut-off energy was 400 eV, and k-point meshes $3 \times 3 \times 1$. We constructed special quasirandom structures using the ATAT suite [8] for $\text{Mg}_{1-x}\text{Zn}_x\text{O}$ alloys with and without vacancies with 6 alloy concentrations in the relevant range, including charge states up to two electrons, and used monopole and finite size corrections for the energies [9]. All energies can be fitted by second or third-order polynomials with $R^2 > 0.998$, and the resulting coefficients can be found in Table I. For the relevant vacancies and perfect structure, we also performed free-energy calculations at the growth temperature of 400 °C within the quasiharmonic approximation [10] for the vibrational-free energy and the Stirling formula for configurational entropy. From the fit, the alloy cation energy $E\left[\left(\text{Zn}_{1-x}\text{Mg}_x\right)_N \text{O}_N, Q_{\text{cat}}\right]$ can be simply calculated for any composition.

This alloy vacancy model eliminates the ill-defined question if a vacancy with stoichiometry $\text{Zn}_M\text{Mg}_{N-M-1}\text{O}_N$ has been generated in a $\text{Zn}_M\text{Mg}_{N-M}\text{O}_N$ or in a $\text{Zn}_{M+1}\text{Mg}_{N-M-1}\text{O}_N$ alloy, leading to a not uniquely defined chemical potential. Within this alloy vacancy model, no cation ordering

effects noted before [11] are taken into account. We also calculated hcp ZnMn metal alloy energies in 36 atom SQS supercells as well as O₂ energies in a cubic cell with 10 Å side length, where the α was varied between 0.36 and 0.43 to be consistent with the different ZnMgO alloys, to compare the measured chemical potentials to ones calculated with the commonly used heat-of-formation method.

Table I. Second and third-order polynomial fitting coefficients of calculated alloy total energies for Zn _{1-x} Mg _x O, defects in Zn _{1-x} Mg _x O, and Zn _{1-x} Mg _x alloys, also band gaps (E_g), and experimental Fermi level (E_F). The number in brackets in the structure column are charge states. $E(x) = E_0 + E_1x + E_2x^2 + E_3x^3$.				
Structure	E_0	E_1	E_2	E_3
(ZnMg) ₃₆ O ₃₆	-567.245	-114.269	8.314	0.408
E_v (DFT)	-0.738	1.035	1.005	-1.504
E_g (DFT)	3.29	2.88	-0.89	1.59
E_g (expt)	3.33	5.51	-0.88	
E_F (expt)	3.21	1.05	1.17	
(ZnMg) ₃₆	-83.907	6.772	13.085	-2.895
O ₂	-20.266	-2.050	-0.006	0.001
V _O (0)	-552.770	-111.428	7.906	-4.317
V _O (+1)	-552.66	-657.61	-12.60	
V _O (+2)	-551.53	-659.33	-8.94	
V _{cat} (0)	-557.64	-659.67	-9.01	
V _{cat} (-1)	-557.54	-657.14	-9.02	
V _{cat} (-2)	-558.408	-97.324	-26.540	37.978
I _{cat} (-2)	-556.42	-656.04	-11.02	
I _{cat} (-1)	-560.98	-663.06	-13.25	
I _{cat} (0)	-557.64	-659.67	-9.01	
I _{cat} (+1)	-568.82	-675.98	-10.24	
I _{cat} (+2)	-569.92	-680.43	-11.77	
I _O (-2)	-567.74	-666.76	-9.92	
I _O (-1)	-571.88	-674.65	-10.17	
I _O (0)	-575.02	-681.43	-10.52	
I _O (+1)	-574.64	-682.29	-10.29	
I _O (+2)	-573.26	-682.10	-10.37	
O _{cat} (-2)	-562.04	-658.49	-9.93	
O _{cat} (-1)	-566.17	-666.81	-9.90	
O _{cat} (0)	-568.31	-668.50	-10.38	
O _{cat} (+1)	-566.96	-671.87	-10.40	
O _{cat} (+2)	-564.23	-671.94	-9.27	

cat _O (-2)	-543.16	-638.86	-8.21	
cat _O (-1)	-548.45	-645.86	-6.92	
cat _O (0)	-549.56	-656.16	-5.52	
cat _O (+1)	-555.49	-661.08	-1.80	
cat _O (+2)	-553.09	-659.85	-24.15	

Table II. Third-order polynomial fitting coefficients of calculated alloy free energies at 400 °C within the quasi-harmonic approximation. The number in brackets in the structure column are charge states.

Structure	E_0	E_1	E_2	E_3
Perfect	-574.68	-116.69	18.49	-3.25
V _O (0)	-560.26	-116.88	32.43	-25.21
V _{cat} (-2)	-565.10	-100.93	-8.33	23.52

Using the energy fits from Table I, we find that the minimum-charge states for oxygen and cation vacancies throughout the considered concentration range are -2 and 0 , respectively, and Eq. (5) becomes

$$\Delta E_f^{\text{theor}}(x) = 19.92 - 8.86x + 36.23x^2 - 45.32x^3 + 2[\mu_O(x, E_F) + E_F(x)]. \quad (6)$$

Since the minimum-energy charge state for vacancies doesn't change, one unfortunately cannot separate here the chemical potential from the Fermi level, although that should be in general possible. Fortunately, for the alloys considered here, the carrier concentrations have been determined previously with CV measurements [12], from which the Fermi level can be calculated, shown in Fig. 2.

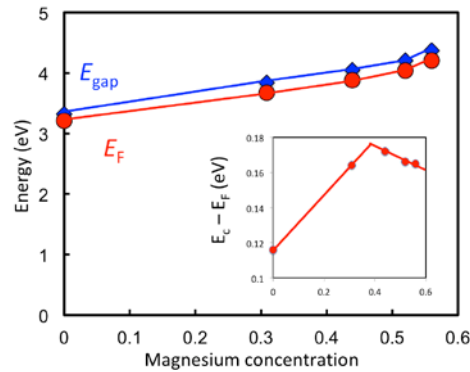


Fig. 2. (a) Experimental Fermi energy in the considered $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloys as a function of Mg concentration calculated from CV-measured carrier concentrations [12], along with the measured gaps [1]. The inset shows the difference between conduction band edge and Fermi level on a more detailed level.

With these Fermi-level measurements and the ΔE_f^{expt} values from Fig. 1(b) and Table III, Eq. 6 becomes with zero temperature energies

$$\Delta E_f^{\text{theor}}(x, 0 \text{ K}) = 26.34 - 6.76x + 38.56x^2 - 45.32x^3 + 2\mu_{\text{O}}(x, E_F, 0 \text{ K}), \quad (7)$$

and with 400 °C free energies

$$\Delta E_f^{\text{theor}}(x, 673 \text{ K}) = 25.75 - 8.54x + 44.60x^2 - 51.65x^3 + 2\mu_{\text{O}}(x, E_F, 673 \text{ K}), \quad (7b)$$

From that, we can now calculate the oxygen chemical potentials, with that from Eq. 4 the cation chemical potentials, and from those determine the absolute formation energies. The calculated chemical potentials are shown in Table III, and the calculated formation energies for all defects in Fig. 3.

Since we have now measured chemical potentials, we want to compare the experimental results to commonly used models to determine chemical potentials purely from theory, which are the heat-of-formation (HoF) approach and the stoichiometry-balancing (SB) approach [13].

For the heat-of-formation approach, we also need the energies of the metal alloy, which are calculated in 36-atom hcp SQS cells, and those of O₂ molecules, both with HSE and with the changing alpha parameter to match the ZnMgO calculation. The results for the fitting parameters are also shown in Table I.

Table III. Chemical potentials in ZnMgO alloys from DFT-analysed cathodoluminescence vacancy concentration measurements using zero temperature energies. All energies in units of eV.

x_{Mg}	Experiment			HoF, cation rich		HoF, O rich		SB, $\delta = 0$	
	ΔE_f^{expt}	μ_{O}	μ_{cat}	μ_{O}	μ_{cat}	μ_{O}	μ_{cat}	μ_{O}	μ_{cat}
0	-0.019	-13.18	-2.58	-13.43	-2.33	-10.13	-5.62	-13.17	-2.59
0.31	0.083	-13.26	-3.46	-14.48	-2.24	-10.45	-6.27	-13.30	-3.42
0.44	0.035	-13.47	-3.64	-14.92	-2.18	-10.58	-6.52	-13.49	-3.62
0.52	0.010	-13.44	-3.90	-15.20	-2.15	-10.67	-6.68	-13.44	-3.90
0.55	-0.013	-13.38	-4.05	-15.30	-2.13	-10.70	-6.73	-13.37	-4.06

Table IIIa. Chemical potentials in ZnMgO alloys from DFT-analysed cathodoluminescence vacancy concentration measurements using zero-T total energies. All energies in units of eV.

x_{Mg}	Experiment			SB, cation rich		SB, O rich		SB, $\delta = 0$	
	ΔE_f^{expt}	μ_{O}	μ_{cat}	μ_{O}	μ_{cat}	μ_{O}	μ_{cat}	μ_{O}	μ_{cat}
0	-0.019	-12.88	-2.87	-14.47	-1.49	-11.33	-4.63	-12.87	-2.88
0.31	0.083	-12.88	-3.84	-15.18	-1.75	-10.81	-6.11	-12.92	-3.79
0.44	0.035	-13.10	-4.01	-15.24	-2.05	-11.07	-6.22	-13.11	-4.00
0.52	0.010	-13.05	-4.29	-15.18	-2.35	-11.12	-6.41	-13.05	-4.29
0.55	-0.013	-12.98	-4.45	-15.11	-2.53	-11.07	-6.56	-12.97	-4.46

Table IIIb. Chemical potentials in ZnMgO alloys from DFT-analysed cathodoluminescence vacancy concentration measurements using 400 °C free energies. All energies in units of eV.

x_{Mg}	Experiment			SB, $\delta = 0$	
	ΔE_f^{expt}	μ_{O}	μ_{cat}	μ_{O}	μ_{cat}
0	-0.019	-12.88	-2.87	-12.87	-2.88
0.31	0.083	-12.88	-3.84	-12.92	-3.79
0.44	0.035	-13.10	-4.01	-13.11	-4.00
0.52	0.010	-13.05	-4.29	-13.05	-4.29
0.55	-0.013	-12.98	-4.45	-12.97	-4.46

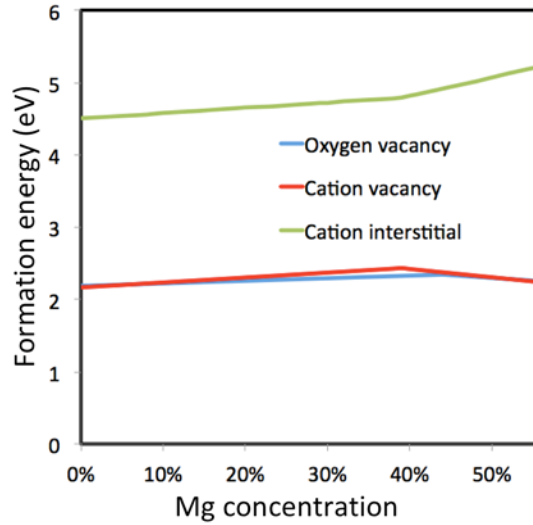


Fig. 3. Formation energies ZnMgO alloys, calculated from Eq. (3) using the measured chemical potentials from Table I and the measured Fermi energies from Fig. 2.

Within HoF, two cases are considered, “cation rich” and “oxygen rich.” For the cation-rich case, it is assumed that the chemical potential of the cations approaches the average atomic energy of the corresponding metal alloy, while for the oxygen-rich case, it is assumed that the O-chemical potential approaches the energy per atom in molecular O_2 .

While it is usually not discussed in publications, the HoF approach has the problem that once the energies are plotted as a function of Fermi level, frequently negative formation energies appear, such as in the example shown in Fig. 4 for ZnO from [14]. However, it is generally argued that the negative energies do not matter, since the only sensible Fermi level within the figures would be the “charge neutrality point,” which is where the lowest intersection point of defects that have the same value of charge with opposite signs (or more general, whose added charges total zero). For both cases in Fig. 4, the respective defects would be V_O and V_{Zn} with charges of +2 and -2, intersecting at ~ 2.25 eV for the Zn-rich case, and at ~ 0.5 eV for O-rich ZnO. The case where extrinsic doping changes the Fermi level, in our case to a value of 3.21 eV, is thus outside of the capabilities of this model, especially since for the O-rich case, the predicted formation energy of V_{Zn} would be negative.

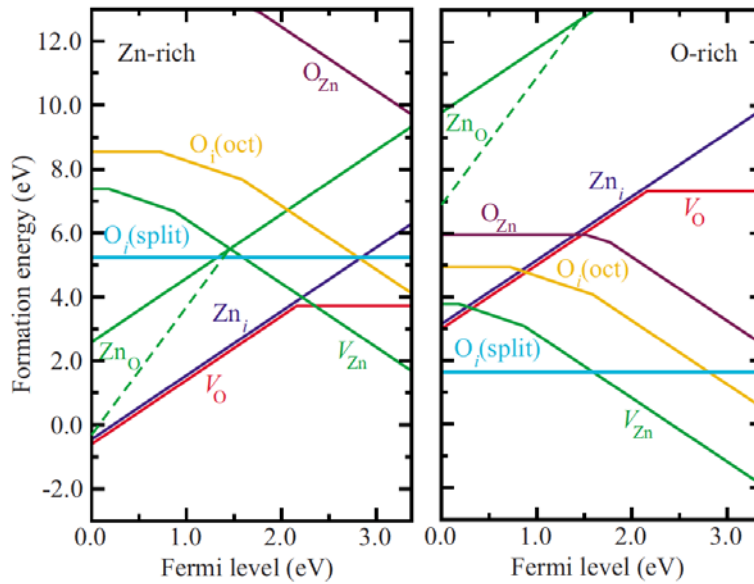


Fig. 4. “Formation energies as a function of Fermi-level position for native point defects in ZnO. Results for Zn-rich and O-rich conditions are shown. The zero of Fermi level corresponds to the valence-band maximum. Only segments corresponding to the lowest-energy charge states are shown. The slope of these segments indicates the charge state. Kinks in the curves indicate transitions between different charge states.” Calculations were performed within the HoF approach. From [14].

Next, we examine the stoichiometry balancing approach, where we start from the realization that non-stoichiometry in alloys has to be due to point defects, whose concentration in turn determine the stoichiometry. For example, O-depleted $Zn_{1-x}Mg_xO$ has to either have O vacancies, cation-O antisites (which however are less than likely), or cation interstitials that result in the non-stoichiometry. The lowest-energy point defect should then dominate in a non-stoichiometric crystal and is non as constitutional defect, but in genera, the (non-)stoichiometry is determined

by the collective of all point defects. As discussed above, in thermal equilibrium the concentration of a certain point defect is given by an Arrhenius equation,

$$C_V(x) = C_0(x) \exp(-E_f(x)/kT). \quad (7)$$

Including all point defects considered above and reported for in Table I, the number of cations and O-atoms in the crystal is then

$$\frac{N_{\text{cat}}}{V} = \frac{N}{V} - C_{\text{O}_{\text{cat}}} - C_{V_{\text{cat}}} + C_{\text{cat}_{\text{O}}} + C_{\text{cat}_I}, \quad \frac{N_{\text{O}}}{V} = \frac{N}{V} - C_{\text{cat}_{\text{O}}} - C_{V_{\text{O}}} + C_{\text{O}_{\text{cat}}} + C_{\text{O}_I}. \quad (8)$$

Now that we have defined total numbers for the two species in the crystal, we can use it to determine chemical potentials for any given stoichiometry in the crystal, which links chemical potential to stoichiometry, which should be the case according to standard thermodynamics, but which is not done in any quantitative way in the HoF approach. Introducing parameter δ which defines the (non-)stoichiometry of the crystal (e.g., for a stoichiometric crystal, $\delta = 0$; for a crystal with 2% O-vacancies, $\delta = 0.02$; or for an O-rich crystal with 1% more O than cations, $\delta = -0.01$),

$$\frac{N_{\text{cat}}}{N_{\text{O}}} = 1 + \delta. \quad (9)$$

Introducing the average volume per atom, $\Omega = V/N$, Eq. (9) combined with Eq. (8) results in

$$\frac{1 - \Omega C_{\text{O}_{\text{cat}}} - \Omega C_{V_{\text{cat}}} + \Omega C_{\text{cat}_{\text{O}}} + \Omega C_{\text{cat}_I}}{1 - \Omega C_{\text{cat}_{\text{O}}} - \Omega C_{V_{\text{O}}} + \Omega C_{\text{O}_{\text{cat}}} + \Omega C_{\text{O}_I}} = 1 + \delta \quad (10)$$

For small off-stoichiometries where all concentration terms are $\ll 1$, this can be linearized with the usual Taylor-series based operations to

$$2C_{\text{cat}_{\text{O}}} - 2C_{\text{O}_{\text{cat}}} + C_{V_{\text{O}}} - C_{V_{\text{cat}}} + C_{\text{cat}_I} - C_{\text{O}_I} = \delta \frac{V}{N}. \quad (11)$$

Assuming all prefactors in Eq. (7) are the same (although they can be calculated through QHA, which we do in some applications), Eqs. (10) or (11) contain DFT band and total energies for cells with and without point defects (see Eq. (3)) plus the two unknown chemical potentials. Thus, Eqs. (4) and (10/11) together are sufficient to determine the chemical potentials.

For non-tiny off-stoichiometries, usually one defect will have lower formation energy than everyone else and thus be the defect that regulates the off-stoichiometry, which makes it the “constitutional defect”. Since the groundstate of non-stoichiometric material thus has to have point defects (otherwise, it would be stoichiometric), and the formation energy of a defect is taken with respect to the groundstate of the crystal at the same stoichiometry, the constitutional defect thus has to have a formation energy of zero, which thus defines the chemical potential and defines the O-rich and cation-rich limits now in a physical way, instead of the HoF ad-hoc assumption of defining those limits by precipitation of the elemental phases, irrespective of the phase diagram.

For stoichiometric materials ($\delta = 0$) at lower temperatures, it is usually one pair of defects that balances each other, which can be the two opposite vacancies, antisites or interstitials, or mixed pairs. Note that Eq. (11) indicates that it takes two antisites to compensate for one vacancy.

Applying this approach now to our measured defect concentrations, we start from the assumption that we have stoichiometric material, and that the dominating balancing point defects are the two opposite vacancies V_{cat} and V_{O} and thus Eq. (11) becomes

$$C_{V_{\text{O}}} - C_{V_{\text{cat}}} = 0. \quad (12)$$

Assuming equal prefactors results in the requirement that both formation energies have to be the same, and Eqs. (3) with (4) then give

$$\begin{aligned} \mu_{\text{O}}(x, E_F) = \frac{1}{2} \Big\{ & E \left[\left(\text{Zn}_{1-x} \text{Mg}_x \right)_{N-1} \text{O}_N, Q_{\text{cat}} \right] - E \left[\left(\text{Zn}_{1-x} \text{Mg}_x \right)_N \text{O}_{N-1}, Q_{\text{O}} \right] \\ & + E \left[\left(\text{Zn}_{1-x} \text{Mg}_x \right)_N \text{O}_N \right] / N + (Q_{\text{cat}} - Q_{\text{O}}) [E_v + E_F] \Big\}. \end{aligned} \quad (13)$$

With the values from Table I, we arrive finally at

$$\mu_{\text{O}}(x, E_F) = 13.17 - 3.38x + 19.28x^2 - 22.66x^3. \quad (14)$$

The resulting values are shown in Table III and agree very well with the experimentally measured chemical potentials, making this approach much more realistic than the HoF limits, of which neither describes the experimental trend even qualitatively.

However, there is one more thing the SB approach can do, which is explaining the unexpected shape of the measured vacancy concentrations in Fig. 1a and resulting formation energies in Fig 1b. Table IIIb has also cation and O rich limits, calculated from constitutional defects. Cation rich chemical potential is outside of the HoF defined range for Mg concentrations up to 44%, so thermodynamically, it seems as if the material cannot be cation rich. That becomes

thermodynamically stable for the two samples with Mg concentrations > 50%, and thus the trend is indeed reversed, and cation vacancy formation energies climb higher than the O vacancy formation energies. Thus, the changing slope with concentration is an expression of thermodynamic stability, and another confirmation of the predictive power of stoichiometry balancing for chemical potentials. This also gives the HoF approach a better defined interpretation as “last frontier” to define utmost, but usually unapproached limits for chemical potentials. However, whenever dilute-limit point defect formation energies fall below zero, another limit of thermodynamics is violated, and such results are not sensible.

Thus, in conclusion, we have shown by experimental validation, that the stoichiometry balancing approach to determine Fermi-level dependent chemical potentials gives much more realistic results to determine point defect energetics in multicomponent compounds.

b. Point Defects, Dislocations and Edges in 2D-BN

Two-dimensional (2D) hexagonal boron nitride (h-BN) has promising applications in nanoelectronics. In order to study the stoichiometry-balancing point-defect energy calculation method described above, we collaborated with the groups of Gerd Duscher and Gong Gu from UT Knoxville (as well as with Dr. Matt Chisholm from ORNL) to see if we can quantify point defects in 2D h-BN by counting from TEM images, and also study the effect of point defects on the optoelectronic properties. Previous to our work, point defects, dislocations (which in 2D, are “point defects” that cause the BN-sheet to warp) and grain boundaries of h-BN, had been studied theoretically but not directly been seen in experiment [15-17]. In addition, with our new point defect theory, we can now relate (off-) stoichiometry to point defect formation in a unique way, since point defects can be directly seen and counted for 2D system when cutting-edge resolution microscopy is employed.

i. DFT Approach

Similar to the work on Zn-MgO alloys, in order to understand what point defects should be stable from a theoretical point of view, we have performed density-functional theory (DFT) calculations using VASP [3, 4] with projector-augmented wave (PAW) potentials [5, 6] within PBE [18] for relaxation, and HSE [7] with a mixing of exact exchange of 0.2 for band structures and final energies. Supercells between 18 (3×3 BN unit cells) and 200 (10×10) were used with 15 Å of vacuum between the sheets. A kinetic cutoff energy of 348 eV was used for the plane-wave expansion along with special k-points ranging between 6×6×1 and 1×1×1 for Brillouin zone integration, respectively. Monopole corrections [9] were added to the total energy for charged cells.

The formation energies E_f of B and N vacancies, V_B and V_N , were again calculated using the formula

$$\begin{aligned} E_f^{V_N}(Q, E_F) &= E_{\text{tot}}^{V_N}(Q) - E_{\text{tot}}^{\text{perf}}(Q) + \mu_N(E_F) + Q[E_v + E_F] \\ E_f^{V_B}(Q, E_F) &= E_{\text{tot}}^{V_B}(Q) - E_{\text{tot}}^{\text{perf}}(Q) + \mu_B(E_F) + Q[E_v + E_F] \end{aligned} \quad (15)$$

while formation energies for antisites, B_N and N_B , are determined with

$$\begin{aligned} E_f^{N_B}(Q, E_F) &= E_{\text{tot}}^{N_B}(Q) - E_{\text{tot}}^{\text{perf}}(Q) - \mu_N(E_F) + \mu_B(E_F) + Q[E_v + E_F]; \\ E_f^{B_N}(Q, E_F) &= E_{\text{tot}}^{B_N}(Q) - E_{\text{tot}}^{\text{perf}}(Q) - \mu_B(E_F) + \mu_N(E_F) + Q[E_v + E_F]. \end{aligned} \quad (16)$$

E_{tot} are total energies calculated with VASP; Q is the charge; E_F is the Fermi energy relative to the valence band edge E_v , and μ_N and μ_B are the chemical potentials of N and B.

Once again, as for ZnMgO alloys, different assumptions can be used for the chemical potential. As stated before, the least amount of thinking effort is required when it is assumed that the chemical potentials have to be below those of their corresponding elemental phases, otherwise, those would start to form. Thus,

$$\mu_B < \mu_B^{\text{bulk}} = E_B \equiv E_{\text{tot}}^{B_{\text{bulk}}} / N_{\text{at}}^{B_{\text{bulk}}} \quad (17)$$

where $N_{\text{at}}^{B_{\text{bulk}}}$ is the number of B atoms in the bulk structure and

$$\mu_N < \mu_N^{N_2} = E_N \equiv E_{\text{tot}}^{N_2} / 2. \quad (18)$$

Together with the condition that the sum of the chemical potentials needs to be identical to the energy per BN pair in a perfect sheet,

$$\mu_B + \mu_N = E_{\text{BN}} = E_{\text{tot}}^{\text{BN}} / N_{\text{BN-molecules}}^{\text{BN}}, \quad (19)$$

this puts upper and lower boundaries on the chemical potentials,

$$E_{\text{BN}} - E_N < \mu_B < E_B. \quad (20)$$

Then, one can simply plot the formation energies as a function of one of the chemical potentials, calls the respective ends B and N-rich limits and never has to worry about how the chemical potentials would be related to the stoichiometry, i.e. how the B or N excess would be accommodated in the structure.

In order to identify how the non-stoichiometry is accommodated in a binary compound, we again turn to the concept introduced for ZnMgO, which is through defects – in the absence of higher-dimensional defects through point defects. Again, the lowest-energy point defect that can change the stoichiometry to a desired value is the “constitutional defect.” Among the four defects discussed here, the presence of both V_B and N_B can result in N-rich BN, and analog for the B-rich case. If a N-rich sheet has an overall lower energy for a given stoichiometry with N_B than with V_B , then N_B will be the dominant and thus “constitutional” defect. All other “thermal” defects which come from entropy effects (the “usual” point defects that we teach in class) then

should have a negligible concentration compared to the constitutional defect for any measurable non-stoichiometry at normal conditions – 1% non-stoichiometry results in 1% constitutional defects, whereas thermal point defect concentrations are several orders of magnitude smaller. In the following, we calculate point defect energies in BN for three different cases, N-rich, B-rich, and stoichiometric. The non-stoichiometric cases are again based on the concept of constitutional defects with zero formation energy, as described in the previous section on ZnMgO. Since our experimental collaborators, Dr. Gerd Duscher and colleagues from the University of Tennessee also observed 2D dislocations and island edge structures, we have then used the chemical potentials determined with this approach to also examine the nature and limits of the observed structures.

ii. Experiment

Our experimental collaborators resolved boron dislocations and single point defects in single layer h-BN atom by atom. A state-of-the-art 5th order aberration-corrected scanning transmission electron microscope (STEM, Nion UltraSTEM100) located at ORNL was used for atomic resolution imaging. Annular dark field (ADF) images from this dedicated STEM have the abilities of resolving light atoms such as boron, carbon, nitrogen, oxygen and so on at an acceleration energy of 60 kV since quite a while [19], a capability that is only slowly starting to enter the STEM capabilities at OSU. A monochromatic TEM (Libra200 MC) with an energy resolution of 0.15 eV was used for electron diffraction and electron energy-loss spectra (EELS) collection. ADF images in Fig.1 (a), (b) and (c) show a boron vacancy (V_B), a V_N and an antisite N_B (where a N atom occupies a B position) defects in h-BN monolayer respectively.

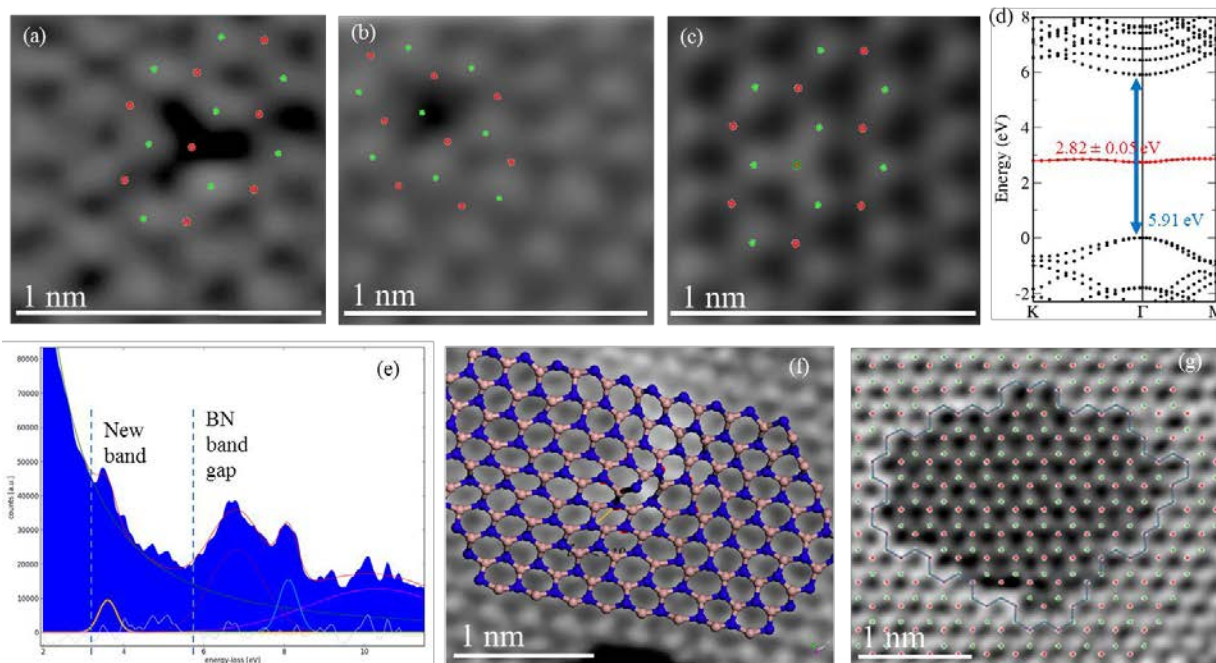


Figure 1. Defects in h-BN. (a), (b) (c) show a V_B , a V_N and a N_B defect, respectively. (d) is the band structure of N-rich BN calculated within DFT with an HSE06 hybrid functional for 3x3 super cells. (e) is a low loss EEL spectrum, which shows a new band prior to the normal band gap. (f) is a dislocation with the burgers vector (1,1) and (g) is a AB stacked h-BN double layer with a monolayer in the center. Edges of the second layer were connected with solid lines. In h-BN atomic model, boron: red dot; nitrogen: green dot.

iii. DFT Results and Analysis

1. Points Defects and Chemical Potentials

As a first step of the calculation, the formation energies of vacancies and antisites in h-BN were calculated and the corresponding chemical potentials were determined. All calculations here were performed within PAW-GGA for computational efficiency, noting that the predicted band gap is nearly 1 eV too small (Fig. 2).

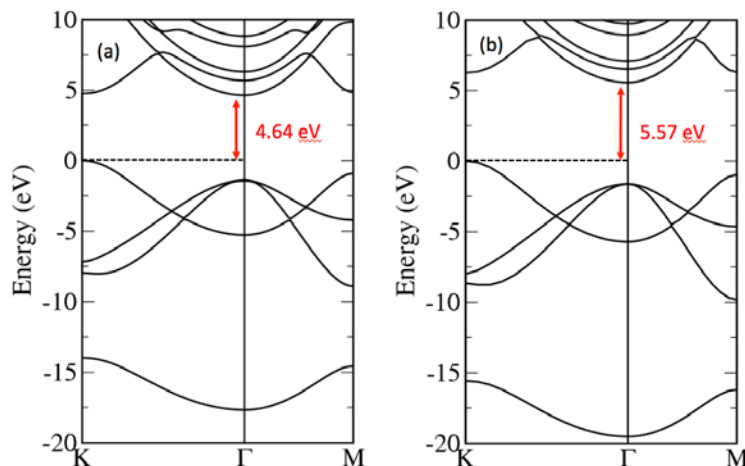


Fig. 2. Band structure of h-BN within (a) GGA and (b) HSE06.

Using the method by Mishra et al. [20] outlined above, we find for stoichiometric h-BN the formation energies, minimum-energy charge states and chemical potentials shown in Fig. 3.

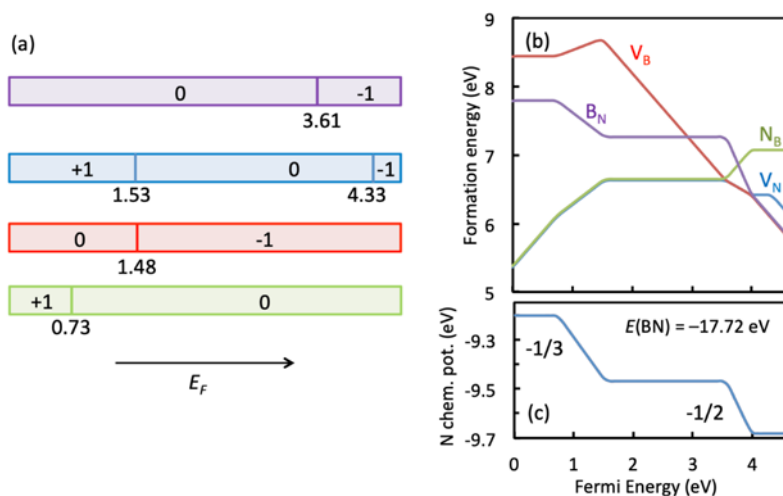


Fig. 3. DFT-GGA results for point defects in a 200-atom 10×10 supercell of stoichiometric h-BN. (a) Minimum-energy charge states of (top to bottom) B_N antisite, nitrogen vacancy V_N , boron vacancy V_B , and N_B antisite. The number in the bars indicates the minimum-energy charge state, the numbers below the vertical separations is the Fermi energy at which the charge state changes. (b) calculated formation energies (color coordination the same as in (a)), and (c) N-chemical potential. $E(BN)$ indicates the energy of a BN formula unit in perfect h-BN, which allows calculation of the B chemical potential from the displayed N chemical potential. Where the chemical potential curve is not flat, the fractional numbers indicate the charge on the “perfect” N atom, which results from the total charge on the energy-balancing point defects and is compensated to zero by the charge on the “perfect” B atom.

At mid-gap, the chemical potential on N from stoichiometry conserving point defects is found to be -9.47 eV, while B has a chemical potential of -8.25 eV. Similarly, Figs. 4 and 5 show the chemical potentials of B and N rich h-BN. Antisites are the respective constitutional defects, and the chemical potentials at mid-gap are $\mu_N = -13.10$ eV and $\mu_B = -4.62$ eV for B-rich, and $\mu_N = -6.14$ eV and $\mu_B = -11.58$ eV for N-rich h-BN, respectively. However, the energies per atom in elemental N_2 and solid boron put tighter limits on the respective elements ($E_{at}(B) = -6.69$ eV, $E_{at}(N_2) = -8.31$ eV), with -11.03 eV $< \mu_N < -8.31$ eV and -6.69 eV $> \mu_B > -9.42$ eV. Thus, elemental precipitation defines the limits, resulting in $\mu_N = -11.03$ eV and $\mu_B = -6.69$ eV for B-rich, and $\mu_N = -8.31$ eV and $\mu_B = -9.42$ eV for N-rich h-BN, respectively. With these chemical potential, the formation energies are far away from zero, with minimum values around 4 eV at midgap (Figs. 4(d) and 5(d)), which indicates the h-BN in thermodynamic equilibrium allows only for very small if any non-stoichiometries. This suggests that the point defects observed in TEM in Figs. 1(a)-(c) are not results from thermodynamic equilibrium, but results from deposition and thus non-equilibrium. In N-rich material, the N_B antisite creates a deep level ~ 2.8 eV above the valence band edge (Fig. 1(d)), which makes N-rich h-BN difficult to use for electronic applications.

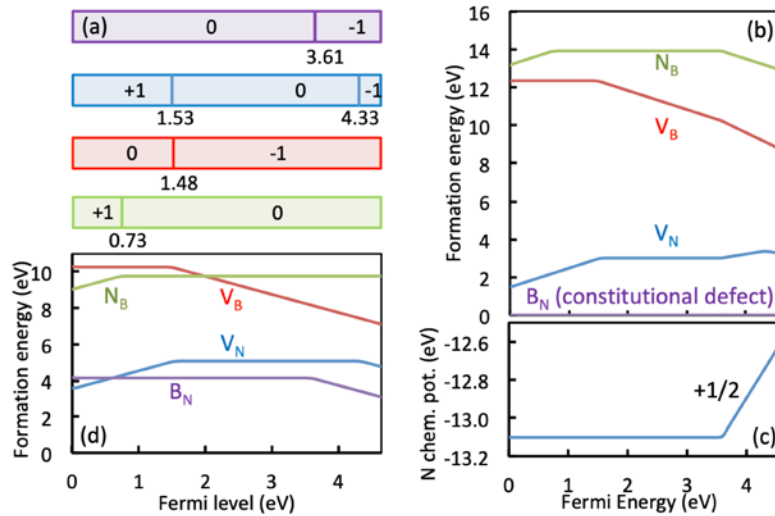


Fig. 4. DFT-GGA results for point defects in a 200-atom 10x10 supercell of B-rich h-BN. (a) Minimum-energy charge states of (top to bottom) B_N antisite, nitrogen vacancy V_N , boron vacancy V_B , and N_B antisite. The number in the bars indicates the minimum-energy charge state, the numbers below the vertical separations is the Fermi energy at which the charge state changes. (b) Formation energies (color coordination the same as in (a)) calculated from the constitutional-defect assumption within the grand thermodynamic potential, and (c) corresponding N-chemical potential. Where the chemical potential curve is not flat, the fractional number indicates the charge on the “perfect” N atom, which results from the total charge on the energy-balancing point defects and is compensated to zero by the charge on the “perfect” B atom. (d) Formation energies calculated within the heat of formation approximation where the energy of elemental boron determines the chemical potential.

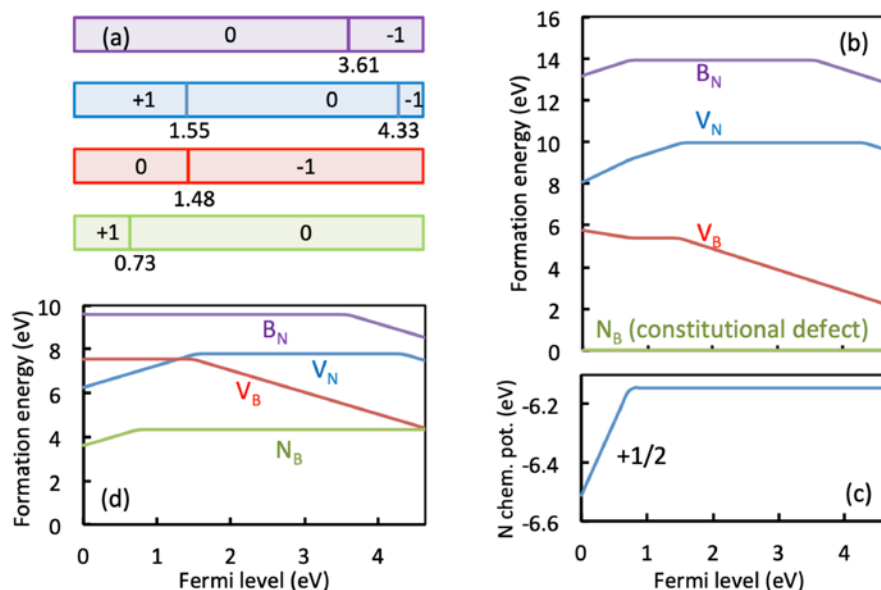


Fig. 5. DFT-GGA results for point defects in a 200-atom 10x10 supercell of N-rich h-BN. (a) Minimum-energy charge states of (top to bottom) B_N antisite, nitrogen vacancy V_N , boron vacancy V_B , and N_B antisite. The number in the bars indicates the minimum-energy charge state, the numbers below the vertical separations is the Fermi energy at which the charge state changes. (b) calculated formation energies (color coordination the same as in (a)), and (c) N-chemical potential. Where the chemical potential curve is not flat, the fractional number indicates the charge on the “perfect” N atom, which results from the total charge on the energy-balancing point defects and is compensated to zero by the charge on the “perfect” B atom. (d) Formation energies calculated within the heat of formation approximation where the energy of elemental N_2 determines the chemical potential.

2. Dislocations

Fig. 1(f) is an ADF image of an observed dislocation in h-BN with a relaxed atomistic model, where the atom positions were chosen using the TEM image as a blueprint. Upon relaxing the sheet, which started off as flat with some apparently strained bonds with no periodic boundary conditions, strong undulations developed, similar to what one gets when cutting a sheet of paper and overlapping the resulting edges. While in this warped sheet, all bonds are similar to the ideal value, while in 2D projection or “top view”, some bonds appear to have extensive compression, which then explains the partially too-close positions of some neighboring atoms in the TEM image, especially around the core.

In order to calculate the structure and core energy of the observed edge-type dislocation, a periodic structure with a 264 atom supercell was created. Due to the hexagonal symmetry of the structure, a dislocation tripole instead of the dipole commonly used in orthogonal cells was used. Since the cell is small and the energetics would be dominated by strain energy away from the dislocations, a Stillinger-Weber type interatomic potential was fitted to a series of elastic in-plane strains applied to a primitive unit cell, and then used to calculate and subtract the strain energies on all atoms in the cell that are not within the dislocation core. For the observed dislocation, the core was chosen to consist of the eight-member ring as well as the neighboring hexagon that contains the protruding N atom from the eight-member ring. For the Stillinger-

Weber fit, 32 strained cells were used overall, where 21 cells had hydrostatic (2D) strain applied between -7% and 10% strain; 7 cells with opposite signs between ε_{11} and ε_{22} with strains between 1% and 9%; and 4 cells with single-component shear strain between 1% and 5%. The Stillinger-Weber potential chosen typically considers only nearest-neighbor interactions, has a Morse potential as two-body term and the usual three-body term, i.e.,

$$E = E_0 + \sum_{i<j} \phi_2(r_{ij}) + \sum_{i<j<k} \phi_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k),$$

$$\phi_2(r_{ij}) = D_e \left\{ \exp[-2\alpha(r_{ij} - r_e)] - 2 \exp[-\alpha(r_{ij} - r_e)] \right\},$$

$$\phi_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}),$$

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda \exp \left[\gamma (r_{ij} - a)^{-1} + \gamma (r_{ik} - a)^{-1} \right] (\cos \theta_{jik} + 0.5)^2.$$

A least-squares fit resulted in the parameters shown in Table I.

Table I. Parameters (units in brackets) for the Stillinger-Weber potential shown in Eq. (1) for h-BN, fitted to DFT results for strained primitive cells.

D_e (eV)	2.9492
α ($\text{\AA}^{-1}$)	2.5771
r_e ($\text{\AA}$)	1.4420
a ($\text{\AA}$)	1.8000
λ (eV)	2.7236
γ ($\text{\AA}$)	-0.2261
E_0 (eV)	-8.8809

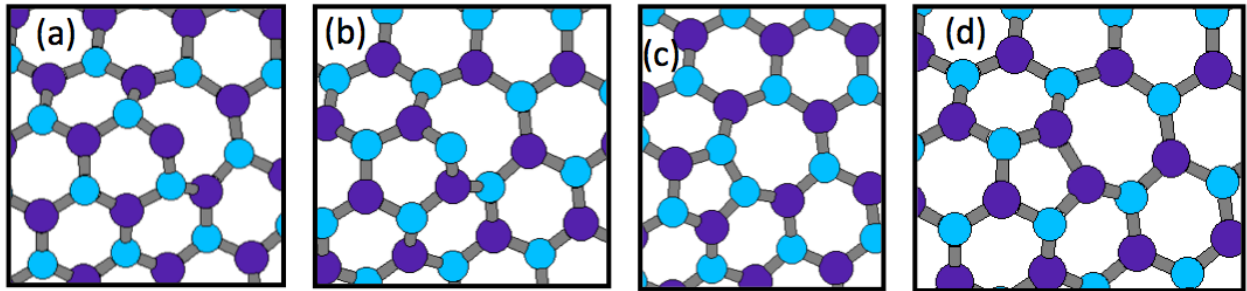


Fig. 6. Considered core structures for dislocations with $[110]$ Burgers vector in h-BN. The panels show the observed structure with 8-6 ring pattern and under-coordinated (a) N atom (N-8-6) and (b) B atom (B-8-6), and a previously proposed structure with 7-5 ring structure and (c) B homopolar bond (B-7-5) or (d) N homopolar bond (N-7-5).

The DFT structure and energetics of the observed dislocation core structure was calculated and compared to three other structures, one of them identical to the observed structure but with opposite elemental composition (i.e. the N atom at the tip of the octagon became B along with all other N atoms, and vice versa), and the other two with a structure previously predicted by DFT in the literature [16]. All these structures represent edge dislocations where the extra rows of atoms are added in zig-zag directions (Burgers vector in [110] direction). Dislocations with other Burgers vectors have been predicted [16], but were not considered here. The calculated core structures are shown in Fig. 6.

The calculations were performed spin resolved, with varying charge states. At midgap, all structures are charge neutral, which is the case we will discuss here. In the 8-6 structures, the tip atom carries a spin of one, which thus makes the dislocation magnetically active. In contrast, the 7-5 structures are found to have zero magnetic moment. Since the 7-5 structure have one atom less in the core than the 8-6 structures, it is important to consider where the extra atom comes from to compare the energies, which means choosing the correct chemical potential. Two scenarios are sensible: First, a sheet of BN is mechanically distorted so that the dislocation forms without adding or losing atoms (i.e. the ensemble is not grand canonical). Here, the chemical potential is determined by the stoichiometry of the sheet. Second, the dislocation is formed during growth, with additional supply of atoms in e.g. the vacuum chamber of an MBE system. Here, the chemical potential is determined by the energy of the supplied atoms in vacuum. For the first case, we use the chemical potentials from above point defect calculations. For the second, atomic energies calculated in their minimum spin state in a 20^3 Å super cell. Finally, the strain outside of the core (which we chose to consist of 5-7 and 8-6 rings for a fair comparison) was subtracted. The resulting core energies for the fixed-atom number case for the three different stoichiometry limits are shown in Table II.

Table II. Core energies from DFT calculations with stoichiometry-balancing chemical potential for the stoichiometric case and the limiting heat-of-formation chemical potentials for B and N-rich material for the four core structures shown in Fig. 2.

Structure	Stoichiometric	B-rich	N-rich
N-8-6	7.83	8.35	7.44
B-8-6	7.39	6.87	7.78
B-7-5	6.58	6.58	6.58
N-7-5	6.32	7.36	5.54

As can be seen, the N-7-5 dislocation has the lowest formation energy for stoichiometric and N-rich case, while B-7-5 has the lowest formation energy for the B-rich case. While for full stoichiometry, N-7-5 and B-7-5 have very similar energies, this is the case also for B-8-6 and B-7-5 for B-rich h-BN. Only for N-rich material, N-7-5 is the clear and unrivaled winner. So, why then does the observed dislocation have N-8-6 structure? The reason for that is that the dislocation was not created by mechanical deformation in a thermodynamically closed system, but during growth. If a B-7-5 structure was initially grown while N-atoms were still available in the vacuum, where they don't have bonds and thus have a much higher energy than in the h-BN compound, the system of B-7-5 plus N atom in vacuum would gain 5.5 eV by capturing the N atom into the N-8-6 tip position, which thus would be thermodynamically favorable.

4. H-BN Islands

Fig. 7(a) is an AB stacked h-BN double layer with a N-rich monolayer in the center consisting of 86 B-atoms and 88 N-atoms, Fig. 7(b) a free standing DFT-relaxed atomistic model of the island.

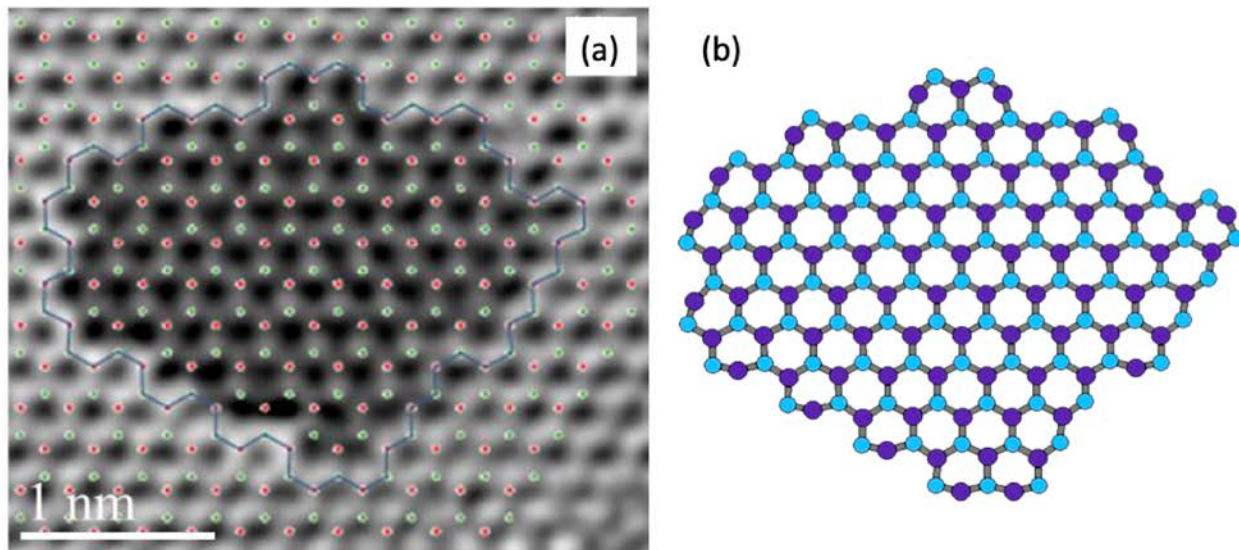


Fig. 7 (a) Z-contrast image of an AB stacked h-BN double layer with a N-rich monolayer in the center consisting of 86 B-atoms and 88 N-atoms (same as in Fig. 1(g)), and (b) a free standing DFT-relaxed atomistic model of the island, zoomed to the same scale.

The entire edge drawn in Fig. 7 has 66 atoms with 33 each of B and N. It has 36 edge atoms with only two neighbors (21 of which are N and 15 B) and 138 fully three-fold coordinated atoms, of which 65 are N, and 73 B-atoms. Of the 2-neighbor atoms, 15 B₂-N₂ armchair-type bonds are formed, involving 14 B and 15 N atoms (the double-B₂-N₂ bond with the B atom in the middle is found at the right end of the observed island). 6 N atoms are in zig-zag tip position (connected to two three-fold coordinated B atoms), while only 1 B atom is in that position.

The island consists overall of 70 hexagons. With a calculated equilibrium bond length of 1.44 Å and using the standard hexagon-area formula, the island has thus an area of 378.2 Å². The entire edge with 66 atoms consists of 66 bonds with a total ideal length of 95.2 Å. Thus, the edge/area ratio is 0.25 Å⁻¹, a lot higher than a circle of the same area (0.18 Å⁻¹) or square (0.21 Å⁻¹), but only slightly less than an equilateral triangle (0.23 Å⁻¹).

In order to understand the underlying energetics, we have calculated BN-bond energies from 25 isolated h-BN patches with different stoichiometries but all stoichiometric or N-rich and sizes between 43 and 204 atoms such as shown in Fig. 8, following the approach proposed in [21] but included edge bonds as separate bonds. The observed patch from Fig. 7(b) was included too. No atoms with only one bond were included in any of the islands. Table III shows the fitted bond energies, which can be fitted with very high fidelity (a slope of 0.999 ± 0.002 where the error bar indicates the 95% confidence interval).

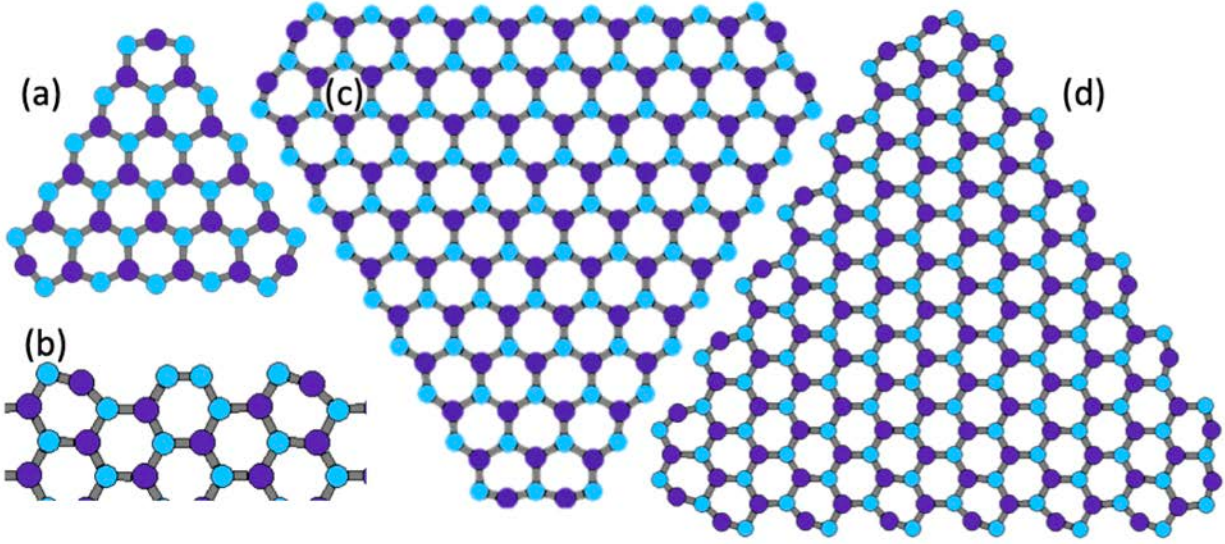


Fig. 8. Island structures used for calculation of bond energies with predominantly zigzag ((a) and (c)) and arm chair ((b) and (d)) edges, selected from ~25 used for the bond fit of Table II. (b) shows the close up of an armchair edge with an N antisite.

Table III. Fitted bond energies (eV) for 25 island structures as shown in Fig. 8.

Bond/At.	B3-N3	B3-N2	B2-N2	B2-N3	N3-N3	N3-N2	N2-N2	B3-B3	B3-B2	B2-B2	B	N
Energy	-4.82	-4.23	-6.17	-5.10	-2.09	-1.70	-6.18	-2.92	-4.25	-2.29	-0.29	-2.99

We will use the values from Table III now to rationalize why the edge of the island in Fig. 1(g) is thermodynamically sensible in its composition of mostly armchair with a bit of zigzag. Since we have found from the high point-defect energies that bulk h-BN cannot accommodate appreciable amounts of point defects within its stability limits, all non-stoichiometry needs to be accommodated at the edges. While a zig-zag edge through its termination can naturally create non-stoichiometry (Figs. 8(a) and (c)), this is not the case for an armchair edge, which maintains stoichiometry (Fig. 8(d)).

From a bond-counting perspective, a zig-zag edge is characterized by B3-N2 bonds for N-rich and N3-B2 bonds for B-rich material, whereas an armchair edge shows B2-N2 bonds in addition to B3-N2 and N3-B2 bonds. The structure in Fig. 8(d), which has as with the exception of the corners only armchair bonds, is perfectly stoichiometric with 102 atoms of each element. In order to make one of its armchair edges N-rich without destroying the overall structure, one would have to swap a B for a N-atom (Fig. 8(b)). Removing an B edge atom would break two bonds and lose their energies, which are a N3-B2 and a B2-N2 bond, totaling a loss of -11.3 eV. Replacing the B now by an N-atom would create two new bonds and regain energy in the form of a N2-N2 and a N3-N2 bond, totaling a gain of -8.3 eV. Thus, overall we would sacrifice 3 eV for this substitution, making non-stoichiometric armchair edges energetically extremely unfavorable.

From the bond count, one now can determine easily the energies of the atoms in the different positions. For example the energies of perfectly 3-coordinated B and N-atoms (and thus their

chemical potentials) are given by $E(B) = [-0.29 + 1.5*(-4.82)] \text{ eV} = -7.49 \text{ eV}$ and $E(N) = -10.23 \text{ eV}$, where the bond energies are distributed equally to the atoms at both ends of the bonds as described in [23]. N (B) in a two-bonded zigzag tip position has two N2-B3 (B2-N3) bonds and thus an energy of -7.24 eV (-5.48 eV). N (B) in a two-bonded armchair position has one N2-B3 (B2-N3) and one B2-N2 bond and thus an energy of -8.18 eV (-5.96 eV). For armchair antisite atoms such as the N atom shown in Fig. 8(b) or its B equivalent, we calculate energies of -7.00 eV and -3.56 eV, respectively, higher than any other 2-bonded position and thus should not likely be observed. Overall, both N and B-atoms are energetically happiest in the armchair position, resulting in the predominance of armchair edges in the observed island. Only where geometrically necessary, or necessary by non-stoichiometry, zigzag edges will be favorable, where atoms have the second-lowest edge energy.

iv. Conclusions

In this part of the project, we have introduced a new way to choose and understand atomic energies and chemical potentials in 2D h-BN based on point-defect balanced stoichiometry and bond-energy analysis. With that, we have calculated the formation energies of point defects, where we have shown for the first time how to calculate energies for stoichiometric h-BN instead of the “B-rich” and “N-rich” limits usually shown in the heat-of-formation approach. For non-stoichiometric material, we have shown that the non-stoichiometry is limited by precipitation of the pure elemental phases rather than by formation of constitutional defects, and have shown that because of that, h-BN should be a very narrow line compound with extremely small solubility. We have further used the chemical potentials and their limits to analyze the energetics of 2D dislocations observed by Z-contrast STEM, where we have corrected for small-cell strains by a Stillinger-Weber empirical potential that we have fitted to DFT energies for strained perfect h-BN cells. We have shown that the 5-7 dislocation core for both N and B-rich cores should have in most cases the lowest energy when a fixed-atom number ensemble is considered (i.e. when the dislocation would form in the material without loss of atoms), while the observed N-rich 8-6 dislocation is energetically favorable under growth conditions, where N is added by deposition. Finally, we have explained why observed h-BN islands have usually large fractions of armchair configurations on their edge over zig-zag or mis-coordinated edges, which is due to the fact that bonds between 2-neighbored B and N atoms has a much lower energy, making armchair positions energetically favorable. Since armchair edges maintain the stoichiometry, non-stoichiometry can make zigzag edges, which can be N- or B-rich, become favorable. Within this work, we also have provided a full set of bond energies in h-BN, which allows within reasonable accuracy to evaluate the enthalpy of h-BN islands including at their edges.

c. Further Systems: β -Ga₂O₃, Al₂O₃, SiC, and BAs

Once the method of Fermi-level dependent chemical potentials for dielectric compounds had been developed, we applied it to a number of other systems, where the work has been done, but publications are still outstanding. Part of the delay was that we hadn’t understood for a long time how to combine the heat-of formation limits, set by chemical potentials where precipitation of a neighboring phase begins, and the stoichiometry-linked point defects into a wholistic picture, which we managed to start to do only recently. Thus, the methods developed in this project were already applied to a number of other materials, including BAs, Al₂O₃, SiC, and β -Ga₂O₃ for

Figure 1 consists of two plots. Plot (a) shows the scattering rate (1/s) on a logarithmic y-axis (from 10^2 to 10^{14}) versus Frequency (THz) on a linear x-axis (from 0 to 10). It compares Bi isotopes (open circles), Bi isotopes + V_{As} (red circles), and Bi isotopes + B_{As} (blue circles). The Bi isotopes + V_{As} and B_{As} curves are higher and broader than the Bi isotopes curve. Plot (b) shows Thermal conductivity ($Wm^{-1}K^{-1}$) on a logarithmic y-axis (from 100 to 2000) versus As deficiency (%) on a logarithmic x-axis (from 10^{-4} to 10^0). It compares the data from Lv et al. (blue line) and This work (red circles). The data from This work shows a much higher thermal conductivity at low As deficiency compared to the data from Lv et al.

Figure 2 consists of three subplots (a), (b), and (c) showing the formation energy (eV) of various defects as a function of Fermi Energy (eV) from 0 to 8. The y-axis for all plots is Formation Energy (eV). A dashed line at 0 eV indicates the reference level.

- (a) Formation energy of V_O , V_{Al} , $V_{2O,b}$, and $V_{2O,c}$:**
 - V_O (blue line) starts at 0 eV at 0 eV Fermi energy, peaks at ~7 eV at 5 eV Fermi energy, and then decreases.
 - V_{Al} (red line) starts at ~5 eV, peaks at ~6 eV at 5 eV Fermi energy, and then decreases.
 - $V_{2O,b}$ (yellow line) starts at ~7 eV, peaks at ~10 eV at 6 eV Fermi energy, and then decreases.
 - $V_{2O,c}$ (purple line) starts at ~9 eV, peaks at ~13 eV at 6 eV Fermi energy, and then decreases.
- (b) Formation energy of O_i and AVOID:**
 - O_i (green line) starts at ~5 eV, peaks at ~9 eV at 6 eV Fermi energy, and then decreases.
 - AVOID (cyan line) starts at ~7 eV, peaks at ~7 eV at 5 eV Fermi energy, and then decreases.
- (c) Formation energy of Al_O :**
 - Al_O (red line) starts at ~18 eV, peaks at ~18 eV at 1 eV Fermi energy, and then decreases.

The legend for all plots is:

- V_O (blue line)
- V_{Al} (red line)
- $V_{2O,b}$ (yellow line)
- $V_{2O,c}$ (purple line)
- O_i (green line)
- AVOID (cyan line)
- Al_O (red line)

DISTRIBUTION A: Distribution approved for public release

valence band maximum, while 8.8 eV represents the conduction band minimum. The considered types of defects can be seen in the legend to the right, where V stands for vacancy, “2O” for double vacancy (two different types are considered), “O_i” denotes an O interstitial, AVOID stands for aluminum vacancy-oxygen interstitial defect, and Al_O is an aluminum antisite. The chemical potentials were determined by (a) the new approach from this project, Fermi energy-dependent stoichiometry-balancing. Notice that all formation energies here are positive, as is thermodynamically sensible. (b) and (c) use van de Walle’s heat of formation method with (b) in the O-rich and (c) in the Al-rich limit. Notice the strongly negative formation energies, indicating that the chosen chemical potentials lay far outside the stability range of the compound. The results in (b) and (c) agree with van de Walle’s previous predictions [24].

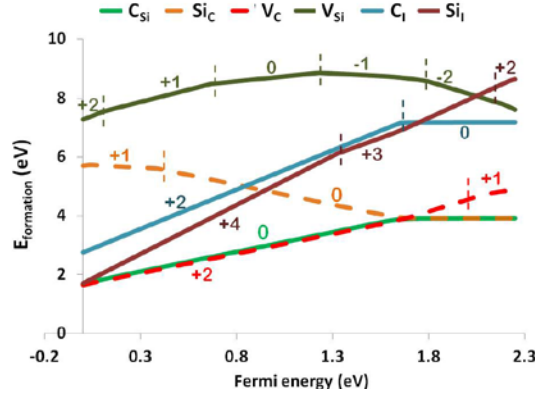


Fig. 12. Fermi level dependent defect formation energies for all six point defects in 3C-SiC, calculated within the HSE06 functional and 64-atom supercells using Fermi-level dependent stoichiometry balancing chemical potentials developed within this project. Defect labeling identical to Fig. 11.

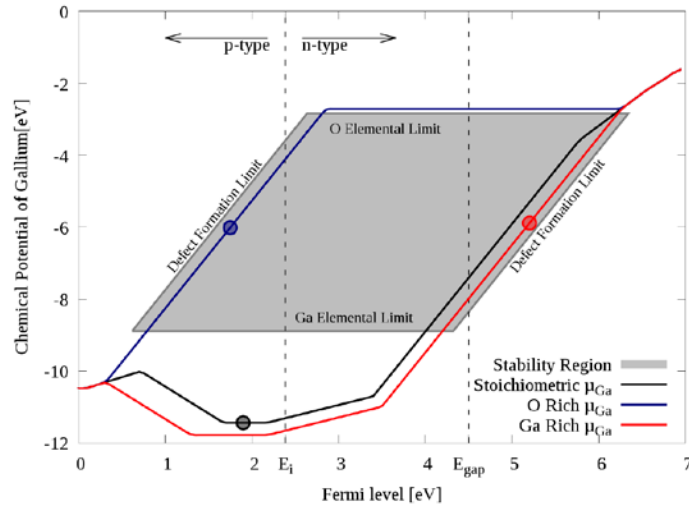


Fig. 13. Central result of the work on point defects in β -Ga₂O₃: Stability space for the chemical potential of gallium in β -Ga₂O₃ at 300 K. Thermodynamic limits are defined by the elemental chemical potentials and negative defect formation energies as we proposed above and discussed in detail for h-BN. The region of stable chemical potentials of gallium are shaded in grey. Calculated values for gallium chemical potential are in black for stoichiometric, red for O-rich, and blue for Ga-rich. Circles indicated computed charge neutrality points using stoichiometry and charge balancing. The figure indicates that stable material for stoichiometric and Ga-rich material can only be grown for Fermi levels close to the gap energy, i.e., n-type material. The plot also suggests that O-rich material should be stable in the p-type regime.

2. Thermal Transport and Point defects in Dielectrics around Metal-Dielectric Interfaces

At the start of the project, the general idea was to understand detrimental processes of point defect formation and motion around metal-dielectric interfaces in high electric field. As it turned out, the main-stream understanding of point defect energetics was not good enough for this purpose, which led to the strong focus on the first part of the project, which was to develop a new fundamental understanding of chemical potentials and the role of point defects for stoichiometry. Nevertheless, we also invested some work into processes around the interface. First, since thermal and electrical conduction on the metal side of the interface happens through electron transport, we noticed that existing models for alloys, using “Nordheim’s” or “Mott’s” rule were insufficient when compared to experiment. Thus, we entered a collaboration with J. C. Zhao’s group at OSU, who did the experiments, to develop a new, fundamental understanding of electron transport in alloys which we called “Mott+” model and which has been published in [25]. Second, we eventually got around to put defects in the oxide of a Pt-ZnO interface and studied its energetics, which is the second part of this section.

a. Thermal and Electrical Transport on the Metal Side (Alloys)

In metals and alloys, free electrons are the main carriers for both thermal and electrical conduction, which make the thermal and electrical conductivities proportionally related by the Wiedemann-Franz relation. There, phonon-induced lattice thermal conductivity only contributes less than 5% to the total thermal conductivity. In alloys, solute atoms result in lattice perturbation and change the electron distribution, and thus significantly alter the electrical conduction behavior of the host materials. As a consequence, residual resistivity (which is the resistivity caused by electron interaction with the defects in the material) is mainly a function of alloy and defect concentration, and is therefore nearly independent of temperature.

Based on these observations, conductivity models have been proposed that model the composition dependence of resistivity in metal alloys based on simple model assumptions, most notably by Nordheim and Mott. However, as we will show, the model assumptions underlying these models do not generally hold for all alloy systems, and not all systems can be described to a satisfactory degree.

For a completely soluble binary materials system (A-B solid-solution with x_A mole fraction of A and x_B mole fraction of B), the Nordheim rule proposes that the residual resistivity can be described by

$$\rho(x_B) = Cx_Ax_B,$$

where ρ is the residual resistivity and C is a constant for all compositions.

The Nordheim rule assumes random distributions of solute atoms in single phase solid solutions, without any phase mixtures. In addition, it is assumed that there is no significant change in

crystal structure, atomic volume, and number of free electrons during alloying. The Nordheim rule has been successfully applied to a number of binary systems to describe the concentration-dependent thermal conductivity or electrical resistivity, such as phonon dominated thermal conductivity of Si-Ge alloy [35] and s-s electron scattering dominated electrical resistivity of noble metal alloys [36]. For alloys or systems containing transition metal elements, the Nordheim rule inadequately describes the electronic interactions.

According to Mott's model, electrical resistivity is controlled by scattering of the itinerant s electrons on impurities/solutes (or more exactly, their electrons) and phonons into vacant s - and d -states. Considering the Pd-Ag system as his driving example, Mott considered the s -DOS as very small compared to the d -DOS and thus ignored it in the model. The d -DOS of Pd was approximated as a simple parabolic function. With this, a satisfactory agreement was achieved between the model and the experimental data. Mott's resistivity model thus consists of

$$\begin{aligned}\rho &= \rho_{ss} + \rho_{sd}, \\ \rho_{ss} &\propto x_{\text{Pd}} x_{\text{Ag}}, \\ \rho_{sd} &\propto x_{\text{Pd}} x_{\text{Ag}}^2 N_{d,\text{Pd}}(E_F), \\ N_{d,\text{Pd}}(E_F) &= \begin{cases} 0 & \text{if } x > p \\ (p - x^2) & \text{if } x \leq p \end{cases}\end{aligned}$$

where x_x is the mole fraction of element X in the alloy, $N_{d,\text{Pd}}(E_F)$ is the parabolic DOS of d -electrons of Pd at the Fermi energy, and p is a parameter describing how many open states are available per atom in the d -band of pure Pd.

Even though Mott's two-band conductivity model agrees reasonably well with the experimental data for Pd-Ag and a number of other alloy systems, it still has flaws. Firstly, it assumes the DOS of d -electrons of pure Ag is zero and thus it is not included in the model. This assumption is incorrect according to the ab initio calculation results below. Moreover, for the transition metal-transition metal alloys, the s-d scattering occurs at both alloy elements sites, and thus a single parabola cannot fit the total d -DOS. Therefore both elements need to be included in the model. Secondly, the assumption that the DOS of d -electrons at the Fermi energy is a parabolic function of alloy composition has limited applicability in real cases where much more complicated forms are found as shown in our results. Thirdly, the carrier concentration in the alloy is assumed to be independent of alloy composition in Mott's model. However, this is not consistent with first-principles results for the total DOS of the s -electrons near the Fermi energy. In order to accurately describe the composition dependence of the thermal conductivity, the discussion needs to include separate functions for both alloy elements, accurately calculated DOS values, and composition dependent carrier densities.

As we show in our detailed derivation of an expanded, Mott+, formula in [25], once partial, orbital-resolved densities of states are calculated for all elements in an alloy, the total alloy resistivity can be described by DFT-calculated partial DOS values at the Fermi level E_F , and four fitting parameters C_{1-4} ,

$$\rho(x_A) = x_A \rho_A + x_B \rho_B + x_A x_B^2 V_A^2 [C_1 g_{s,A}^2(E_F) + C_2 g_{d,A}^2(E_F)] + x_B x_A^2 V_B^2 [C_3 g_{s,B}^2(E_F) + C_4 g_{d,B}^2(E_F)].$$

The scattering potentials V_A and V_B are species specific and proportional to the local average electrostatic potential around atoms of a given species as calculated from first principles. We use the peak potential around each atomic site for the fitting results presented here, but find no significant difference in using an integrated average over the Bader volume for each atom. Thus, by the combination of DFT results with only four fitting parameters, we have created an alloy model that as the results below show can describe all types of binary alloys and is extendable in a straightforward way to multicomponent alloys.

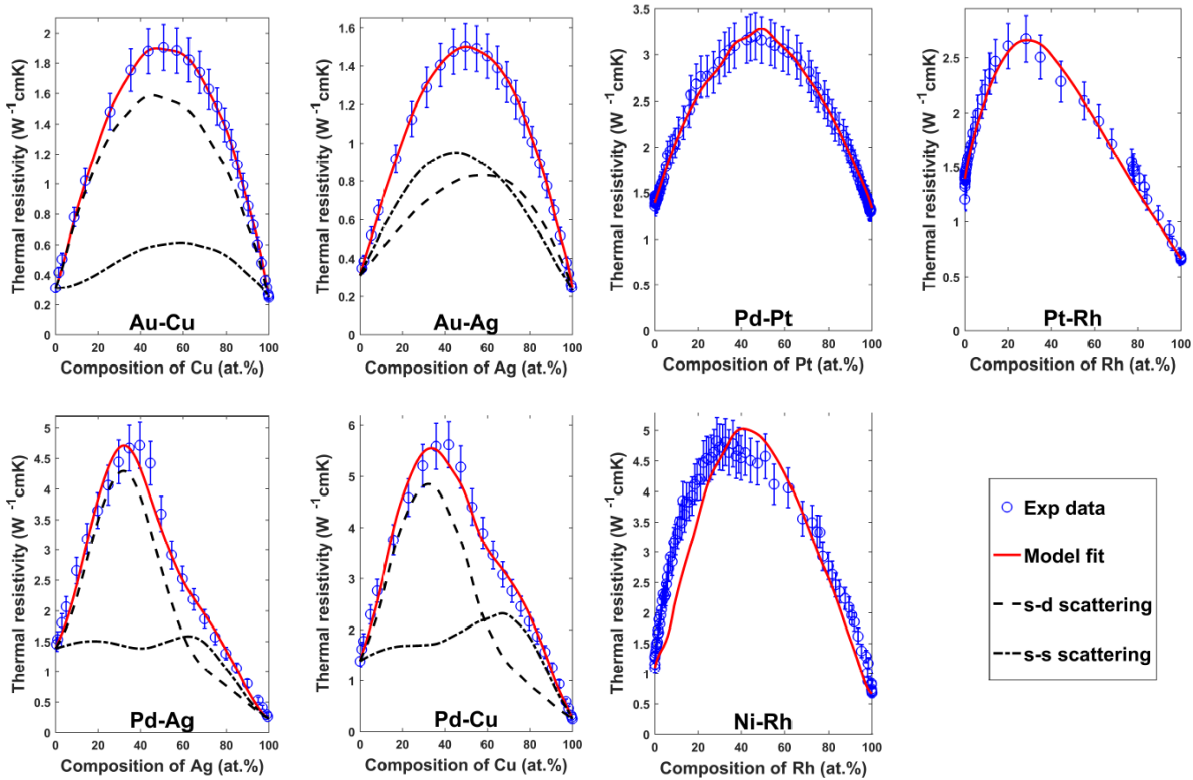


Fig. 14. Mott+ resistivity model fits to NIST recommended data from Refs. [26, 27] for the Au-Cu, Au-Cu, Pd-Ag, and Pd-Cu systems and to experimental data from the Zhao group for the Pd-Pt, Pt-Rh, and Ni-Rh systems. Error bars on NIST recommended data are displayed to be consistent with the experimental data collected by Zhao et al. within our collaboration [28].

b. Point Defect Energy at Metal-Oxide Interfaces with Internal Electric Fields

Summary

In this part of the project, a computational method has been developed to calculate how high electric fields and distance from metal-oxide interface affect point defect energies in the dielectric. It was found that high internal electric fields can be generated and controlled efficiently in Schottky junctions with controlled charge imbalance both in surface and slab geometries for zinc oxide – platinum structures through the addition and removal of electrons. This procedure causes bending of the conduction and valance bands in the dielectric. Addition of

electrons (*n*-doping) causes band bending typical of an *n*-type Schottky contact, while removal of electrons (*p*-type doping) resulted in a *p*-type contact. Internal electric fields generated by band bending affected the energies of single zinc and oxygen vacancy point defects. Schottky-type band curvature resulted in zinc vacancies having the lowest energy away from the interface while ohmic-type curvature resulted in oxygen vacancies having the lowest energy at the interface. These results indicate that clustering of oxygen and zinc vacancies would occur at the different ends of a metal-oxide-metal structure. The energy difference for the defects to be at these locations increases with increasing field.

Background and Motivation

Capacitors that utilize zinc oxide (ZnO) interfaced with two conducting metal plates, show large specific capacitance and operational lifetime compared to other capacitors [29]. However, failure of the ZnO material can occur when an applied voltage causes substantial current to flow between the electrodes, effectively “shorting” the capacitor. This process is known as dielectric breakdown. In solid dielectrics, this breakdown damage is permanent and cannot be reversed [30]. Breakdown can occur when a free electron in the conduction band of the dielectric is accelerated to large energies in the presence of a large electric field [30]. This effect causes the electron to collide with and ionize host atoms in the dielectric, causing defects. Partial discharges that take place in microstructural defects such as voids or cracks also can cause breakdown by creating a conducting path [30]. Also, point defect migration can occur similar to electron-hole drift along the field direction [31]. Thus, understanding how an electric field affects defect formation and migration in the dielectric material in a capacitor is important.

In most ionic oxides of interest, the dominating point defects are vacancies and interstitials of both the metal cation and oxygen anion, as we had discussed in the first section for bulk ZnO and ZnMgO alloys. When they are in a dielectric in proximity to an interface, they experience an electric field, which results in a bending of the band structure in the dielectric. Figure 15 shows the bands in a metal and a semiconductor before and after the junction is formed, for the cases of both *n*- and *p*-type doped semiconductors leading to opposite band bending. The band bending causes a built-in electric field as shown in Figure 16.

Since electric field and charge at the junction are connected through Gauss’s Law,

$$d\mathcal{E}(x) = \int \frac{\rho_{\text{net}}(x)}{\epsilon(x)} dx$$

adding or removing electrons from a system will change the electric field in the dielectric, analogous to applying additional external bias to the system. Thus, charges on defects do not only react to the built-in field in the dielectric, but also “actively” modify the local field felt by the charged defect.

As a result of the electric field, a depletion zone develops at the interface where charge carriers are no longer present. The strength of the depletion zone electric field increases as a reverse-bias voltage is applied. The strength of the depletion zone also affects the drift velocity of electrons where velocity increases linearly with the applied field [30]. Once the electric field intensity increases beyond a critical level, the depletion zone breaks down and current begins to flow, usually by either the Zener or the avalanche breakdown processes. In a very high electric field,

defect migration can occur similar to electron or hole drift along the field direction [31], especially oxygen vacancy migration [32]. If vacancy defect formation and mobility is anisotropic, clustering of vacancies can occur and cause voids in the dielectric, causing breakdown due to internal discharges [30].

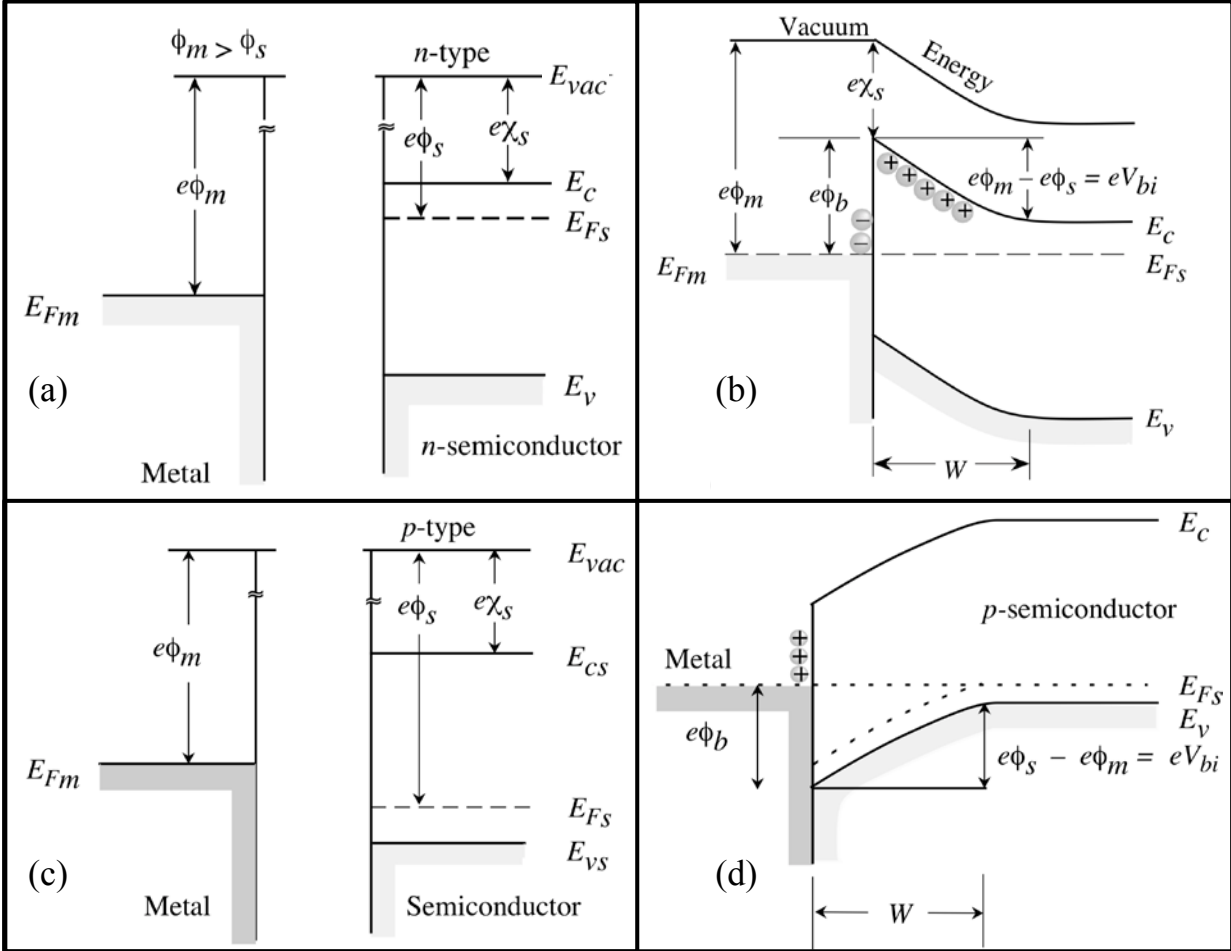


Figure 15: Band profiles of disconnected metal and n - (a) and p - (c) type semiconductors, along with the resulting band structure of the respective Schottky junctions, (b) and (d).

Simulation Methodology

Two different 2x2 simulation cells were modeled in this study and are seen below in Figure 17. Figure 17a shows a ZnO slab interfaced with two times four layers of Pt (111), simulating a capacitor structure. A vacuum of 20 Å was used. The Pt layers were strained to the lattice constant of ZnO (3.25 Å). The ZnO cell was zinc terminated on both ends with 17 oxygen layers and 18 zinc layers. 15 Å of vacuum was put on both ends of the slab. Figure 17b shows the same ZnO slab with only one interface to 4 layers of Pt (111) and a free ZnO surface, where four hydrogen atoms were used to passivate the oxygen atoms and terminate the surface. The ZnO layer has 18 layers of oxygen and zinc atoms. Each structure in Figure 17 is rotated so the c -direction is to the right.

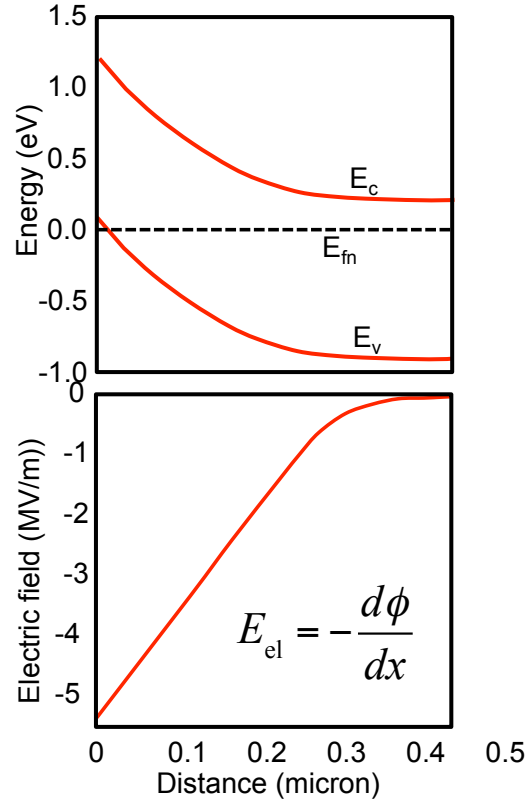


Figure 16: Electric field generation in a Schottky junction due to band bending, numerical simulation for contact between Au and n-doped Si with $N_d = 10^{16} \text{ cm}^{-3}$.

Total cell energies and densities of states (DOS) were determined through density functional theory (DFT) calculations using the Vienna *Ab-initio* Simulation Package (VASP) [3, 4]. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [18] with projector augmented wave (PAW) potentials [5] was used. Energy relaxation calculations were carried out using 6x6x1 k-points. Density of states plots were generated using a finer mesh of 27x27x1 k-points with 4500 density value points using the tetrahedron method with Blöchl corrections. Only ions in the simulation cell were relaxed and cell size and shape were fixed to represent the lattice constant of ZnO.

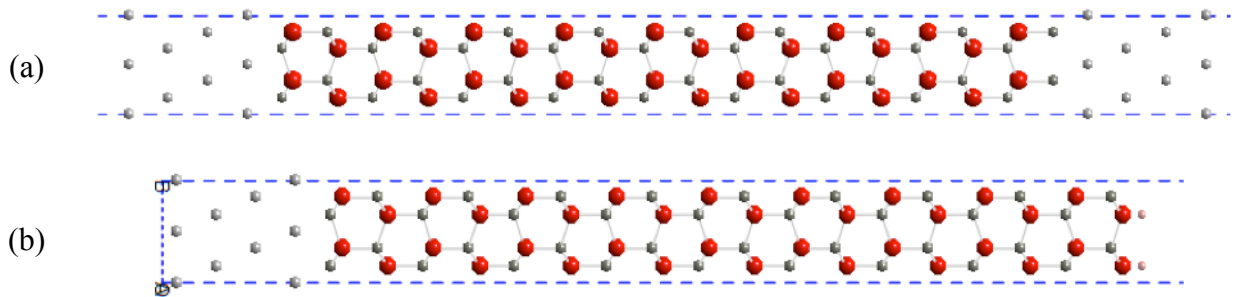


Figure 17: Simulation cells; (a) interface, (b) slab.

Results and Discussion

Color-scale density of states (DOS) plots were generated using a program that plots the DOS by atomic layer in the simulation cell. Figure 18 below shows a DOS plot for bulk ZnO. The darker blue (brighter yellow) regions represent a small (high) DOS. This type of plot facilitates visualizing the valence band, band gap, and conduction band in ZnO, and how they change with distance from the interface. For bulk ZnO, the band edges are flat as expected.

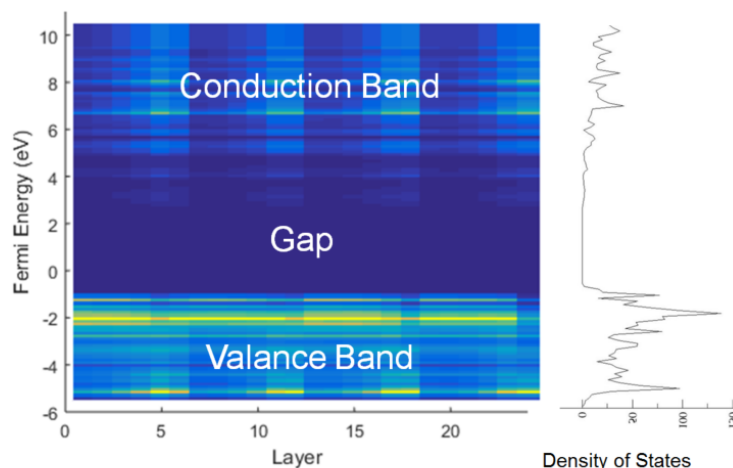


Figure 18: Pure ZnO density of states (DOS) plot by atomic layer and total DOS graph on right y axis. The color scale goes from low/zero DOS (dark/blue) to high values (bright/yellow).

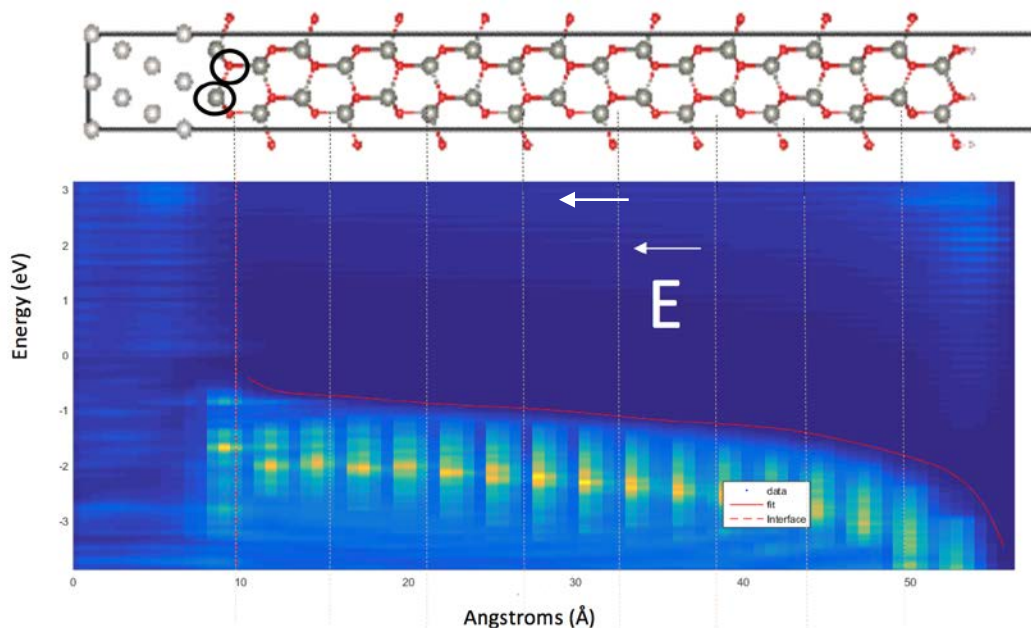


Figure 19: Spatially-resolved DOS by layer for interface structure. Circles and lines indicate vacancy locations for defect cell .

This changes when we go to the interface system. As seen in Figure 15, the interface cell should exhibit band bending as the Fermi level of ZnO shifts and equalizes with that of the metal. The resulting slope of the bands has units of $\text{eV}/\text{\AA}$ which represents the generated electric field times electron charge, or electric-field force. Figure 19 shows the resulting spatially resolved DOS plot for the interface structure seen in Figure 15a. The two black circles and dotted lines indicate where oxygen and zinc vacancies were removed to determine the total cell energy for defects at different locations away from the interface. The red line following the valance band is a polynomial fit that was used to calculate the slope at each point where a defect was removed. The band energies are shown relative to the calculated Fermi energy of the system.

Figures 20 and 21 show the DOS plots for the Pt-ZnO interface structure with a negative two (-2) and positive two (+2) charge respectively. It can be seen that a negative charge induced steeper band bending while the removal of electrons caused the opposite curvature and followed the expectation in Figure 15b for *p*-type band bending.

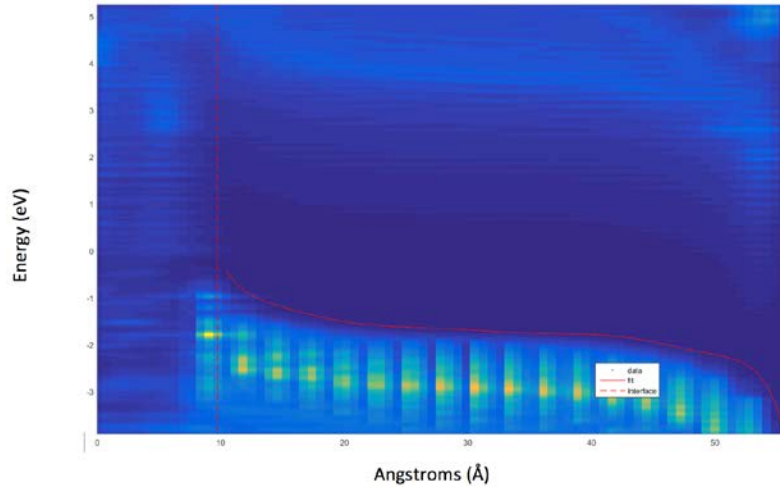


Figure 20: DOS by layer for interface structure with 2 additional electrons (-2 charge).

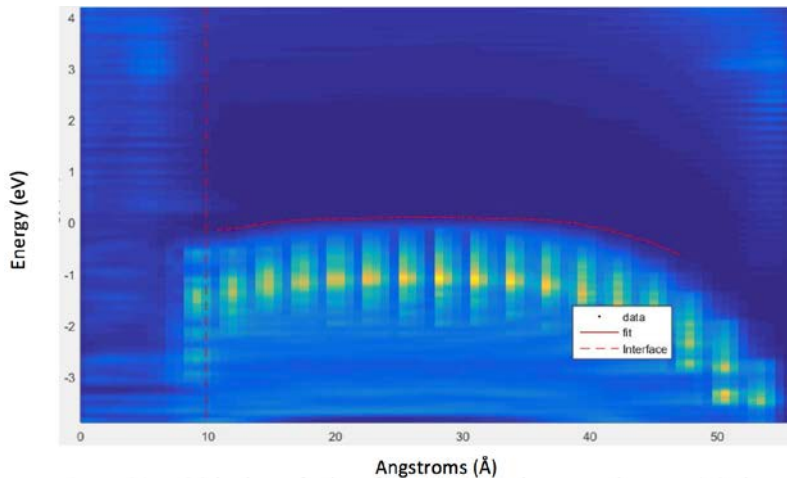


Figure 21: DOS by layer for interface structure minus two electrons (+2 charge).

Figure 22 outlines the total cell energy difference for zinc vacancies at different locations from the interface. The interface location itself was taken as the reference point and assigned zero energy. It can be seen that both neutral and charged zinc defects gained energy as location distance was increased away from the interface. Initially this gain in energy is steep immediately after the interface but drops back down toward the reference total energy value far away from the interface. Figure 23 shows the calculated slope of the polynomial fit to the valance band in Figure 19 and 20. It can be seen that the addition of two electrons causes a steeper slope and higher $\text{eV}/\text{\AA}$ force. The slope has a steep drop off and goes to zero relatively quickly from the interface. The larger slope for the -2 charge simulation cell resulted in a drop in the energy required for a defect to be at different locations away from the interface. This drop ultimately changed where the lowest energy location of a zinc vacancy would be. For the neutral surface the lowest energy state is located at the interface. For the negatively charged surface the lowest energy state is 46 $\text{\AA}$ away from the interface.

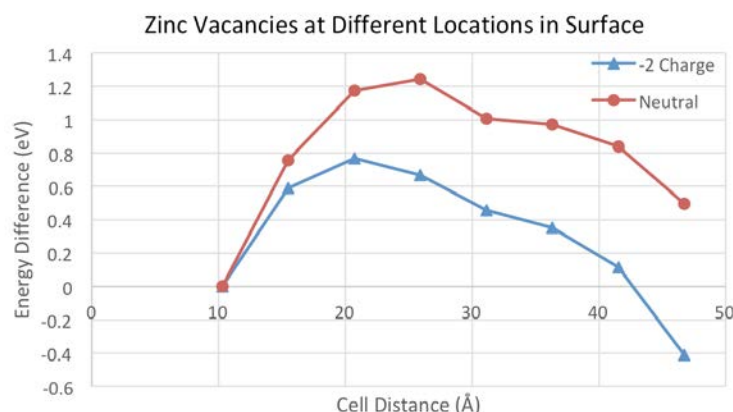


Figure 22: Energy change as a function of distance from interface for zinc vacancies in surface structure

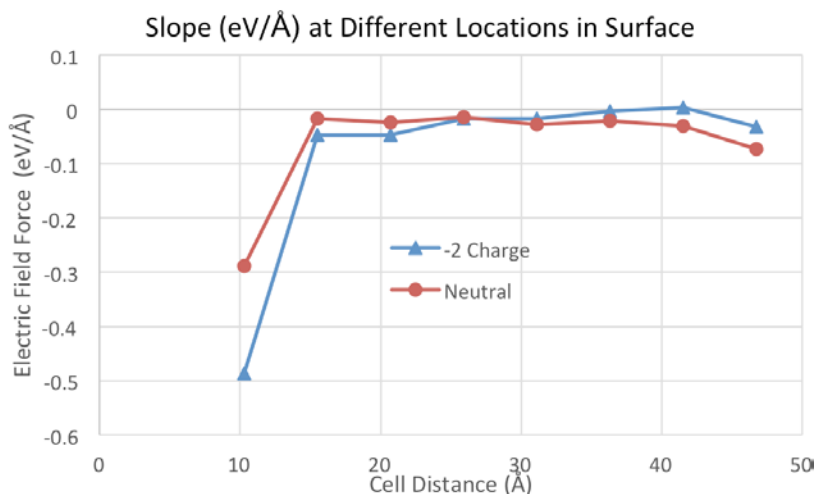


Figure 23: Electric field force ($\text{eV}/\text{\AA}$) for zinc vacancies at different locations in surface structure

Figure 24 below shows the total cell energy difference for oxygen vacancies at different locations from the interface. The interface location itself was again taken as the reference point

and assigned zero energy. It can be seen that both neutral and charged oxygen defects would need to gain energy to be located away from the interface. Compared to the curves seen for the zinc vacancies, this gain in energy is relatively constant regardless of position from interface at about 1.8 and 1.4 eV respectively for the +2 and neutral charge state. Figure 25 shows the calculated slope of the polynomial fit to the valance band in Figure 19 and 21. It can be seen that the removal of two electrons caused a change in curvature following the prediction in Figure 15b for a *p*-type interface. The large electric field force for the neutral cell resulted in a larger energy gain for oxygen vacancies across all positons. The interface location itself was the lowest energy state for the oxygen vacancy.

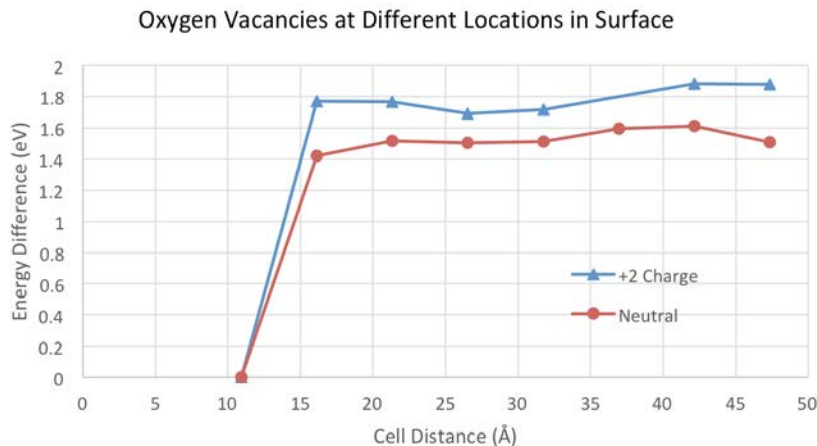


Figure 24: Energy change as function of distance in surface interface for oxygen vacancies.

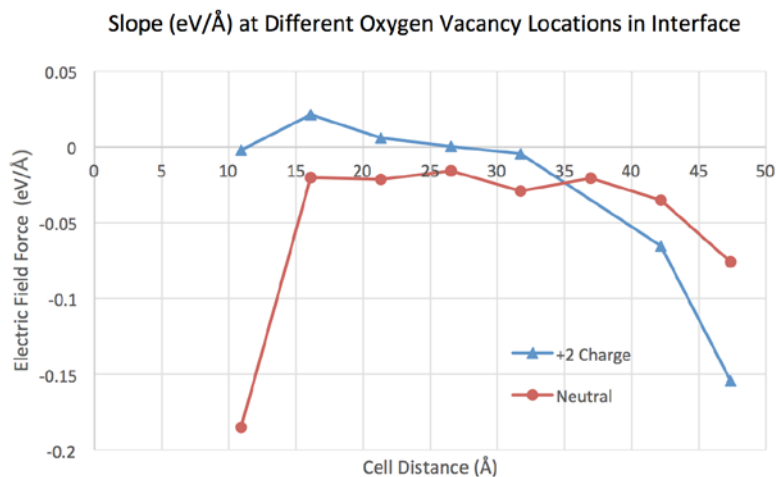


Figure 25: Electric field force (eV/Å) for zinc vacancies at different locations in surface structure

Finally, we would like to note that while the previous results were calculated for a Pt-ZnO cell with vacuum at both ends, similar results can be produced within a periodic Pt-ZnO slab, results for which will be discussed separately in the following conclusion section.

Summary and Conclusions

For both the Pt-ZnO interface and Pt-ZnO-Pt slab simulation cells, bending of the valence and conduction bands was observed relative to the pure ZnO band structure in Figure 5. Both neutral structure types showed slight bending caused by equalization of the Fermi level as electrons in the conduction band transferred into the metal. The addition of additional electrons (-2 charge) resulted in increased bending and a larger electric field force compared to the neutral structure. A positive depletion region was observed in the negatively charged surface and interface cells. The removal of two electrons (+2) charge changed the curvature of bands to follow band bending in a *p*-type interface compared to the negatively charged *n*-type structure.

For the neutral surface cell, the lowest energy state for a zinc vacancy was at the interface. In the negatively charged surface cell the lowest energy state for a zinc vacancy was 46 Å away from the interface. Overall the addition of two electrons lowered the energy gain needed for an zinc vacancy at all distances from the interface compared to the neutral cell. Both neutral and charged oxygen defects would need to gain energy to be located away from the interface in the surface cell. The large electric field force for the neutral surface cell resulted in a larger energy gain for oxygen vacancies across all positions. The interface location itself was the lowest energy state for the oxygen vacancy.

In the slab cell, both neutral and charged oxygen defects had the lowest total energy state at the interface. This gain in energy was relatively constant regardless of position from interface at about 1.8 and 1.45 eV for the charged and neutral cell respectively. However, both the -2 charge and neutral zinc vacancies showed a lowest energy state away from the interface at a location of about 50 Å from the interface. The larger slope (eV/Å) in the -2 charged slab cell resulted in a drop in the energy required for a zinc vacancy to be at different locations away from the interface compared to the neutral structure.

Bibliography

- [1] G.M. Foster, J. Perkins, M. Myer, S. Mehra, J.M. Chauveau, A. Hierro, A. Redondo-Cubero, W. Windl, L.J. Brillson, Native point defect energies, densities, and electrostatic repulsion across (Mg,Zn)O alloys, *physica status solidi (a)* 212(7) (2015) 1448-1454.
- [2] J. Perkins, G.M. Foster, M. Myer, S. Mehra, J.M. Chauveau, A. Hierro, A. Redondo-Cubero, W. Windl, L.J. Brillson, Impact of Mg content on native point defects in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($0 \leq x \leq 0.56$), *APL Materials* 3(6) (2015) 062801.
- [3] G. Kresse, J. Hafner, Ab initio Molecular Dynamics for Liquid Metals, *Phys. Rev. B* 47 (1993) 558–561. .
- [4] G. Kresse, J. Hafner, Ab initio Molecular-Dynamics Simulation of the Liquid-Metal-Amorphous-Semiconductor Transition in Germanium, *Phys. Rev. B* 49 (1994) 14251– 14269.
- [5] P.E. Blöchl, Projector Augmented-Wave Method, *Phys. Rev. B* 50 (1994) 17953–17979.
- [6] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B* 59 (1999) 1758–1775.
- [7] J. Heyd, G.E. Scuseria, M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, *The Journal of chemical physics* 118(18) (2003) 8207.

- [8] A. van de Walle, P. Tiwary, M. de Jong, D.L. Olmsted, M. Asta, A. Dick, D. Shin, Y. Wang, L.Q. Chen, Z.K. Liu, Efficient stochastic generation of special quasirandom structures, *Calphad* 42 (2013) 13-18.
- [9] G. Makov, M.C. Payne, Periodic boundary conditions in ab initio calculations, *Physical Review B* 51(7) (1995) 4014-4022.
- [10] W. Luo, W. Windl, First principles study of the structure and stability of carbynes, *Carbon* 47(2) (2009) 367-383.
- [11] A. Boonchun, W.R.L. Lambrecht, First-principles study of oxygen vacancies in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys, *Physical Review B* 81(2) (2010).
- [12] E. Gür, G. Tabares, A. Arehart, J.M. Chauveau, A. Hierro, S.A. Ringel, Deep levels in a-plane, high Mg-content $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ epitaxial layers grown by molecular beam epitaxy, *Journal of Applied Physics* 112(12) (2012) 123709.
- [13] R. Mishra, O. Restrepo, D. A. Kumar, W. Windl, Native point defects in binary InP semiconductors, *Journal of Materials Science* 47(21) (2012) 7482-7497.
- [14] A. Janotti, C.G. Van de Walle, Native point defects in ZnO, *Physical Review B* 76(16) (2007).
- [15] Y. Liu, S. Bhowmick, B.I. Yakobson, BN white graphene with "colorful" edges: the energies and morphology, *Nano Lett* 11(8) (2011) 3113-6.
- [16] Y. Liu, X. Zou, B.I. Yakobson, Dislocations and grain boundaries in two-dimensional boron nitride, *ACS Nano* 6(8) (2012) 7053-8.
- [17] G.J. Slotman, A. Fasolino, Structure, stability and defects of single layer hexagonal BN in comparison to graphene, *Journal of physics. Condensed matter : an Institute of Physics journal* 25(4) (2013) 045009.
- [18] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, *Physical Review Letters* 77(18) (1996) 3865-3868.
- [19] O.L. Krivanek, M.F. Chisholm, V. Nicolosi, T.J. Pennycook, G.J. Corbin, N. Dellby, M.F. Murfitt, C.S. Own, Z.S. Szilagy, M.P. Oxley, S.T. Pantelides, S.J. Pennycook, Atom-by-atom structural and chemical analysis by annular dark-field electron microscopy, *Nature* 464(7288) (2010) 571-4.
- [20] R. Mishra, O.D. Restrepo, A. Kumar, W. Windl, Native point defects in binary InP semiconductors, *Journal of Materials Science* 47(21) (2012) 7482-7497.
- [21] C. Oberdorfer, W. Windl, Bond-order bond energy model for alloys, *Acta Materialia* 179 (2019) 406-413.
- [22] B. Lv, Y. Lan, X. Wang, Q. Zhang, Y. Hu, A.J. Jacobson, D. Broido, G. Chen, Z. Ren, C.-W. Chu, Experimental study of the proposed super-thermal-conductor: BAs, *Applied Physics Letters* 106(7) (2015).
- [23] Y. Wang, W. Windl, Native Point Defects in Boron Arsenide, *ArXiv*, 2019.
- [24] M. Choi, A. Janotti, C.G. Van de Walle, Native point defects and dangling bonds in $\alpha\text{-Al}_2\text{O}_3$, *Journal of Applied Physics* 113(4) (2013) 044501.
- [25] C. Wei, N. Antolin, O.D. Restrepo, W. Windl, J.-C. Zhao, A general model for thermal and electrical conductivity of binary metallic systems, *Acta Materialia* 126 (2017) 272-279.
- [26] C.Y. Ho, M.W. Ackerman, K.Y. Wu, T.N. Havill, R.H. Bogaard, R.A. Matula, S.G. Oh, H.M. James, Electrical Resistivity of Ten Selected Binary Alloy Systems, *Journal of Physical and Chemical Reference Data* 12(2) (1983) 183-322.

- [27] C.Y. Ho, M.W. Ackerman, K.Y. Wu, S.G. Oh, T.N. Havill, Thermal conductivity of ten selected binary alloy systems, *Journal of Physical and Chemical Reference Data* 7(3) (1978) 959-1178.
- [28] C. Wei, N. Antolin, O.D. Restrepo, W. Windl, J.-C. Zhao, A general model for thermal and electrical conductivity of binary metallic systems, *Acta Materialia* 126(Supplement C) (2017) 272-279.
- [29] M. Vangari, T. Pryor, L. Jiang, Supercapacitors: Review of Materials and Fabrication Methods, *Journal of Energy Engineering* 139(2) (2013) 72-79.
- [30] S.O. Kasap, *Principles of electronic materials and devices.*, McGraw-Hill, Boston, 2006.
- [31] K.C. Kao, *Electrical Aging, Discharge, and Breakdown Phenomena.*, *Dielectric Phenomena in Solids — With Emphasis on Physical Concepts of Electronic Processes*, Academic Press, San Diego, 2004, pp. 515–572.
- [32] Y. Cao, J. Shen, C. Randall, L.-Q. Chen, Effect of Ferroelectric Polarization on Ionic Transport and Resistance Degradation in BaTiO₃ by Phase-Field Approach, *Journal of the American Ceramic Society* 97(11) (2014) 3568-3575.