Polymorphism of borophene on metal substrates

First-principles investigations of the formation of borophene on metal surfaces

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In Short

- Borophene
- Polymorphism
- Metal-substrate interactions
- First-principles calculations

Since the discovery of graphene by Andre Geim and Konstantin Novoselov in 2004, and their subsequent Nobel prize in 2010, various other two-dimensional materials (2DMs) have been successfully derived from different bulk solids, such as silicene, germanene, phosphorene, hexagonal boron nitride (h-BN), as well as transition metal dichalcogenides (TMDs). 2DMs consist of one atom thick sheets that exhibit physical and chemical properties different from their bulk counterparts. They are promising for next-generation nanoelectronics, energy storage and conversion devices. Neighbouring carbon in the periodic table, boron has also been of interest in this search for new 2DMs. The earliest mention of quasi-planar boron surfaces goes back to Ihsan Boustani in 1997 [1]. Following from previous studies on boron nanotubes, theoretical DFT studies on planar boron structures were conducted throughout the 2000s and predicted the existence of stable monolayer boron sheets with unusual electronic and mechanical properties [2]. The first experimental realisation of borophene was successfully performed in 2015 via molecular beam epitaxy on a Ag(111) surface [3].

A wide range of applications has been suggested for borophenes. These are primarily centered around energy conversion and storage, as well as gas capture and detection. Borophene is predicted to exhibit storage capacities exceeding those of graphene as electrode materials for lithium-ion and sodium-ion batteries. Borophene has also shown potential to be used for gas storage and capture, specifically for solid-state hydrogen storage by selectively doping the 2DM with alkali metals, as well as for fast, selective, and reversible charge-modulated CO_2 capture. Theoretical studies predict that borophene has capabilities for the detection of gases such as HCN and ethanol [4]. Through the incorporation of defects as well as formation of heterostructures with other 2DMs, this sensing ability can be potentially extended to other small gas molecules, such as carbon monoxide, nitrogen-oxides, and ammonia.

For over a decade, the polymorphism of borophene has been investigated both experimentally and theoretically. Experimental studies were first and foremost conducted on Ag(111), but also on Au(111), Cu(111), and Ir(111). The structure of 2D boron sheets has been found to be strongly influenced by external parameters such as the choice of metal substrate. The first synthesis of borophene on an Ir(111) surface was achieved in 2019 by directly exposing the surface to a flux of boron atoms at temperatures between 600 and 900 K, resulting in submonolayer quantities of boron in an organised, flat structure [5]. The deposited borophene was analysed by high-resolution scanning tunnelling microscopy (STM) and density functional theory (DFT) simulations, and thus, was identified as χ_6-type borophene, distinct from all planar boron allotropes reported earlier.

Recent computational efforts within our group focused on constructing and modelling borophene on Ir(111) surfaces. Initial tests were conducted on β_{12}-borophene due to its relatively smaller unit cell in comparison to the experimentally observed χ_6 phase. Figure 1 illustrates relaxed configurations of β_{12}-borophene on Ir(111). Additionally, we investigated χ_6-borophene stacked on an Ir(111) surface (Figure 2), employing structural arrangements and lattice parameters comparable to the theoretical model reported by Vinogradov et al. [5]

With this project, we will investigate the structural and electronic behaviour of various borophene polymorphs supported on an Ir(111) substrate, with a focus on understanding the intrinsic dependence of borophene structure and properties on the nature of the underlying metal surface. Borophene exhibits substrate-sensitive polymorphism, and therefore, the study aims to explore a diverse set of borophene phases. *Ab initio* molecular dynamics (AIMD) simulations will be utilised to assess the thermal and

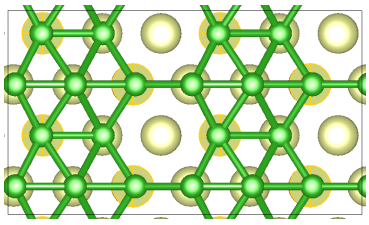

***Figure 1:** β_{12}-borophene above the Ir slab*

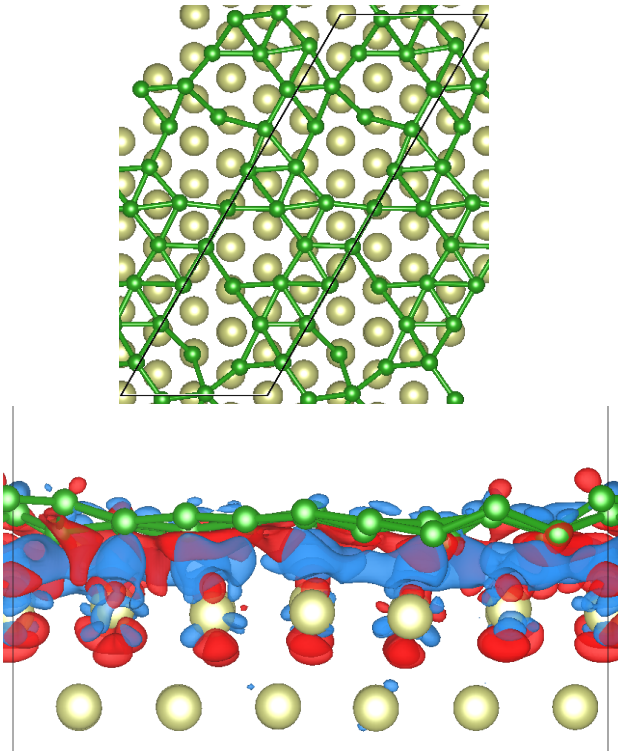

Figure 2: *χ_6-borophene adsorbed on a (2×6) supercell of Ir(111) (Top); Charge density difference for the stacked χ_6-system with an isosurface level of 0.005 e/Å^3. The accumulation of electron density is shown in blue, and the respective depletion of electron density in red (Bottom)*

configurational stability of selected stacked systems over multiple time-scales. Additionally, gas adsorption studies will be carried out to evaluate preferential adsorption sites for selected oxygen containing species, with AIMD used to interpret adsorption trajectories under finite-temperature conditions. The project will be conducted in tight collaboration with the experimental physical chemistry group led by Prof. Dr. Christian Papp (Freie Universität Berlin).

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https://www.bcp.fu-berlin.de/en/chemie/chemie/forschung/PhysTheoChem/agpaulus/index.html

More Information

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Project Partners

AG Papp at Freie Universität Berlin

DFG Subject Area

327-01, 327-02