High Throughput Screening of Substrates for Synthesis and Functionalization of 2D Materials

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ABSTRACT

Several two-dimensional (2D) materials have been synthesized experimentally, but many theoretically predicted 2D materials are yet to be synthesized. Here, we will review a density-functional theory based framework to enable high-throughput screening of suitable substrates for the stabilization and functionalization of 2D layers. A Materials Project based open source python tool, MPInterfaces, based on this framework, is being developed to automate the search of suitable substrates as well as to characterize their effect on the structural and electronic properties of 2D materials. Lattice-matching, symmetry-matching, substrate surface termination, configuration sampling, substrate induced structural distortion and doping estimation algorithms are being developed and will be described in this article. This computational tool will be employed to identify suitable substrates for scores of technologically relevant 2D materials, leading to acceleration of their synthesis and application, and more efficient use of experimental resources.

Keywords: Materials Genome Initiative, Substrates, 2D Materials, Functionalization, Growth, Density-Functional Theory

1. INTRODUCTION

Following the discovery of graphene, a whole new class of materials, two-dimensional (2D) materials, has emerged and many 2D materials like BN, MoS$_2$, ZnO, SnS$_2$, and WSe$_2$ have already been experimentally synthesized. 2D materials research is expanding at a fast pace. Every month there are a number of theoretical and experimental works reporting synthesis, growth, structural characterization, and property measurements of 2D materials. Potentially, there are many more 2D materials with different structures and composition awaiting discovery.

The reduction in dimensionality makes the properties of these 2D materials very different from those of their three-dimensional (3D) counterparts. For instance, pristine graphene differs from graphite withstanding strains exceeding 20 %, as opposed to an elastic strain of up to 0.1 % for graphite. Single-layer ZnSe exhibits a remarkable photocurrent density of 2.14 mA/cm$^2$, about 200 times higher than the value for bulk ZnSe and an incident photon-to-current efficiency (IPCE) of 42.5 % compared to 0.25 % of the bulk counterpart. At the same time, the 2D materials identified so far provide a large range and variety of properties, from large band-gap insulators to the very best conductors, the extremely mechanically strong to the soft and fragile, and the chemically active to the very inert. The unique properties of 2D materials invite applications in nano-electronics, bio-sensing, photo-catalysis, drug delivery, nano-mechanical sensors, and so on.

Despite their unique and novel properties and applications, many theoretically predicted 2D materials are yet to be synthesized. Majority of un-synthesized materials are expected to require suitable substrates to stabilize their formation energies. In fact, 2D materials are always metastable and not in the true thermodynamic ground states due to the omnipresent dispersion interaction, resulting in an unfavorable formation...
energy which reduces when two layers are brought together. The commercialization of these 2D materials is impeded by the lack of synthesis methods which can mass produce, large area, high quality (low-defect) and reproducible films of 2D materials. Substrate assisted synthesis techniques, such as chemical-vapor deposition and molecular-beam epitaxy, promise scalable growth of electronic-grade films enabling commercialization of novel 2D devices.

In this proceeding, we describe a density-functional theory (DFT) based framework for enabling high-throughput screening of suitable substrates for the stabilization and functionalization of 2D layers. In section 2 we present an overview of this strategy and demonstrate how using this computational strategy, we have already identified several transition and rare-earth metals, metal oxides and metal diborides that enable the synthesis of 2D group-III-V materials and 2D MoS$_2$ by sufficiently reducing their formation energies and making them thermodynamically stable on these substrates. In addition, we will discuss how these substrates can functionalize the structural and electronic properties of the materials due to their interaction at the interface.

Further, in response to the Materials Genome Initiative (MGI), we are developing a Materials Project based python tool, MPInterfaces, based on this strategy, to automate, thus accelerate, the search of suitable substrates as well as to characterize their effect on the structural and electronic properties of these high-performance 2D materials, which will be discussed in section 3. The algorithms for automated lattice-matching, symmetry-matching, substrate surface termination, configuration sampling, substrate induced structural distortion and doping estimation are being developed and will be discussed in section 3. This computational tool will be employed to identify several suitable substrates for scores of technologically relevant 2D materials. Such a high-throughput computational screening of substrates is a powerful tool in rapidly predicting promising substrates and eliminating unlikely candidates, allowing for more efficient use of experimental resources and accelerating possible applications of 2D materials.

2. COMPUTATIONAL SYNTHESIS

Over the last decade, a variety of methods have been developed to synthesize 2D materials. The most widely used methods include mechanical exfoliation, chemical vapor deposition (CVD), liquid-phase exfoliation, and molecular beam epitaxy (MBE) and have been adapted to produce other 2D materials. These methods allow a wide choice in terms of quality and have a range of cost of production. The most widely used method of synthesis for van der Waals bonded materials, such as graphene, is mechanical exfoliation which provides excellent quality samples but lacks in scalability. In contrast, substrate assisted methods such as, the CVD method, are better suited for scalable growth without compromising the quality of flakes.

Computational description of synthesis of 2D materials is a challenging problem and has received considerably less attention than the prediction of the structure and properties of 2D materials. Considering the different growth methods, a variety of mechanisms are possible for the growth of 2D materials, which makes theoretical studies very difficult. Different synthesis methods involve different mechanisms, heavily depending on synthesis conditions like precursors, temperature, pressure in reaction chamber, gas flow-rate, substrate quality, nucleation sites like substrate step edges etc., to name a few. Despite the advancement in the resources for simulations, most theoretical studies only focus on a specific issue in 2D materials growth, and a unified growth mechanism at the atomic level is still not available due to the complexity of the problem. From the point of view of accelerating the discovery of theoretically predicted but experimentally unrealized 2D materials, and thus engaging their superior properties in practical applications, a predictive computational method is imperative for finding a starting point for laboratory synthesis of these 2D materials.

Ab-inito methods like density functional theory (DFT) are known to predict structural, electronic and magnetic properties of solid-state materials with an excellent agreement with experimental measurements and can be used to provide a description of the thermodynamics of 2D materials synthesis. The deposition of 2D materials on substrates can be approximated as a two-step process,

1. the creation of 2D flakes from the 3D counterpart; which requires an energy equivalent to the formation energy, $E_{\text{vac}}$. The formation energy of an isolated free-standing 2D material, $E_{\text{vac}}^f$, is defined with respect to the energy, $E_{3D}$, of bulk counterpart, $E_{\text{vac}}^f = E_{2D}/N_{2D} - E_{3D}/N_{3D}$, where $E_{2D}$ denotes the energy of
isolated 2D material, $N_{2D}$ and $N_{3D}$ are the number of atoms in the unit cell of the 2D and bulk structure, respectively; and

2. the placement of 2D flakes on a substrate surface which results in an attractive or repulsive interaction between the two surfaces that can be quantified as the binding energy, $E_b = (E_{2D} + E_S - E_{2D+S})/N_{2D}$, where $E_{2D+S}$ is the energy of strained 2D material adsorbed on the substrate, $E_S$ the energy of the substrate, and $E_{2D}$ the energy of isolated unstrained 2D material. Note that this definition of binding energy naturally accounts for the lattice-mismatch between a substrate and a 2D material.

The successful stabilization and synthesis of 2D material is feasible when the formation energy of the 2D materials is overcome by the binding energy resulting from the adsorption on a substrate. In other words, the formation energy of the adsorption, $E_{ads}^f = E_{vac}^f - E_b$, becomes negative, indicative of a spontaneous and exothermic deposition of the 2D material on a substrate. The substrates modify the structural and electronic properties of 2D materials and this can be studied effectively using DFT as well. This substrate screening approach helps in finding a starting point for the laboratory synthesis of 2D materials.

Figure 1 shows a flow chart of the steps involved in the DFT-based search of substrates which can enable growth of 2D materials. These steps are briefly listed and explained below.

1. **2D Material Structure and Formation Energy**: As an input, we need the 2D materials structure and formation energy, $E_{vac}^f$. Bulk material properties and structure are well documented in databases but 2D materials structure should be carefully checked for instabilities and closely competing phases.

2. **Epitaxially Matched 2D Materials and Substrates**

Figure 3(a-c) show the different surfaces of Cu, exemplifying that different surfaces of materials can have different lattice constants and symmetries. While Cu(100) has a square surface, Cu(110) has a tetragonal lattice, and Cu(111) has a hexagonal lattice. For epitaxial growth, the potential substrate surfaces should exhibit the same symmetry as the 2D materials and have a close lattice match with the 2D material. An epitaxial growth maximizes interactions between the two surfaces due to the decrease in the repeat length of the coincident atoms. Also, a small lattice-mismatch is favorable to minimize loss of energy due to strain. While non-epitaxial growth can also reduce the formation energy for lattice-mismatched systems, these can result in hundreds of atoms in the simulation cell, which is computationally expensive for a high-throughput DFT search. Lattice-matched and symmetry-matched substrate surfaces can be identified for...
Input translation vectors of the 2 materials
\[ R_1 = a_1 + a_2 + a_3, \]
\[ R_2 = b_1 + b_2 + b_3. \]

Select planes for both materials and define translations vector on the 2D planes of two materials, \[ R_1 = \vec{a}_1 + \vec{a}_2, \] \[ R_2 = \vec{b}_1 + \vec{b}_2, \] where \( \vec{a} = c, i + d, j \) and so on

Cell reduction, using scheme in Fig. 2 of Zur et al.

Compute area of primitive cells, \( A_1 \) & \( A_2 \)
\[ A_1 = a_1 \times a_2, \]
\[ A_2 = b_1 \times b_2. \]

Find, \( r_1 \) & \( r_2 \), such that \( r_1 A_1 \sim r_2 A_2 < A_{\text{max}} \)

Find all unit cells with area \( r_1 A_1 \& r_2 A_2 \), using eq 2.3, 2.4, 2.5, 2.6 of Zur et al.

Reduce all supercells

Compute dimensions of all cells, i.e. if \( R_1 = \vec{a}_1 + \vec{a}_2 \), find \( |\vec{a}_1|, |\vec{a}_2| \) and \( \alpha = \cos^{-1} \left( \frac{\vec{a}_1 \cdot \vec{a}_2}{|\vec{a}_1||\vec{a}_2|} \right) \)

Find supercells of the two materials whose dimensions match within a few percent

Create individual supercells and superimpose them post rotation

Figure 2. The robust algorithm of Zur et al.\textsuperscript{43} for the epitaxial lattice-matching and symmetry-matching of any two surfaces for all rotations; within a given lattice mismatch and within a given surface area of the resultant cells.

Figure 3. A substrate can have different lattice constants and symmetries on its various surfaces. For example, (a) Cu(100) has a square symmetry, (b) Cu(110) has a tetragonal symmetry and (c) Cu(111) has a hexagonal symmetry. Some substrates have complex surface reconstructions, for example, \( \beta\text{-}2\times 4\)-GaAs (001) has a dimer reconstruction. (d) Side view and (e) top view of the surface reconstruction in \( \beta\text{-}2\times 4\)-GaAs (001) surface.

Epitaxial growth using simple mathematical models, such as the one used in our previous work\textsuperscript{37} or more efficient algorithms such as that of Zur et. al.\textsuperscript{43}

Polar substrate surfaces are prone to complex reconstructions and these must be taken into account for any simulations. For instance the \( \beta\text{-}2 \times 4\)-GaAs(001) surface has a complex dimer reconstruction.\textsuperscript{44} Surface terminations of multi-component substrates must be considered for a comprehensive sampling of the substrate surfaces. Also, 2D materials can be placed on a substrate surface in more than one non-equivalent configurations and these should be identified by comparing the Wyckoff positions of the surface atoms of each material.

3. The binding energy, \( E_b \), of 2D materials on lattice- and symmetry-matched substrate surfaces is computed. If the adsorption energy, \( E_{\text{ads}}^f = E_{\text{vac}}^f - E_b \), is less than zero, the 2D material is stable on the substrate. Thus the substrate can be used for the spontaneous and exothermic deposition of the corresponding 2D
High-Throughput Substrates Search for 2D Materials

Lattice & Symmetry Matching at Arbitrary Rotation

Creation of Coincidence Lattices

Creation of Input Files

Submission to Computing Resources

Analysis and Post-processing

Storage in Database

Surface Reconstructions

Wyckoff Positions for Configurational Sampling

Structural Relaxation

Energy Computation

Electronic Structure

2D Material and Substrate Structure from Databases

Figure 4. A schematic representation of the steps involved in high-throughput computational screening of substrates for the synthesis and functionalization of 2D materials.

material.

4. Post-adsorption on substrate, the electronic and structural properties of 2D materials are expected to change and should be investigated to identify charge doping, semiconducting to metallic transition, mobility enhancement, structural distortion etc. induced by the interaction of 2D materials with substrate.14, 24, 25

Using this computational strategy we have identified several transition-metal, rare-earth-metal, high-κ dielectric oxide, and refractory-diboride substrates that sufficiently reduce the formation energies of 2D group-III-V materials and 2D MoS₂, making them thermodynamically stable on these substrates.14, 24, 25 Additionally, these substrates lead to variable amount of doping of the 2D III-V materials depending on the differences in the work functions of the 2D materials and the substrates. We observed large adsorption energies and strong doping of the 2D III-V materials which indicates that the predicted metal substrates can provide good electrical contact to enable transport measurements and electronic applications.14, 24, 25 We demonstrated that substrates not only help in synthesis but they also help in functionalization of 2D materials; allowing patterned growth, variable doping, and modification of electronic structure.14, 24, 25

3. HIGH-THROUGHPUT SCREENING STEPS

An efficient high-throughput computational screening relies largely on robust automation of all the steps, starting from the generation of input files to analysis after runs. Figure 4 shows a broad classification of the steps involved in the automation of steps involved in the computationally intensive substrate searches for 2D materials. The first step in the automation of substrate searches is to obtain the optimized bulk structures from which the substrate surface , and if unknown, the 2D material's structures can be carved out.14, 24, 25 There are many available high-throughput resources such as the Materials Project, 26 and AFLOWLIB45 that facilitate search and automatic import of well optimized bulk structures from their databases. In this work we use exclusively the resources and structures provided by the Materials Project database. The second and the most important step is the identification of epitaxially matched super-lattices of the 2D material and the substrate. This involves
computation of the minimal coincident lattice between the 2D material and the substrate. This is achieved by employing the afore-mentioned algorithm by Zur et. al as shown in the flowchart in Figure 2. After identifying the coincident lattice, the only other degree of freedom that is left to be optimized is the positioning of the lattice-matched 2D material with respect to the substrate, which is efficiently tackled by identifying the Wyckoff positions of the surface atoms.

The above two steps: the automatic import of structural data of bulk materials from a publicly available database, and the generation of all possible compatible 2D/substrate interface configurations are combined to create a high-throughput framework for the screening of a vast array of 2D material/substrate interfaces and is implemented in the python package MPInterfaces. This open source package (https://github.com/henniggroup/MPInterfaces) makes an extensive use of the publicly available and well tested open source tools provided by the Materials Project (https://github.com/materialsproject), to interface with their database and to set up high-throughput workflows in a robust and efficient manner. The Materials Project packages such as pymatgen and the FireWorks are particularly suited for structure manipulations and for the setup and submission of the DFT workflows for the calculation of formation energies, adsorption energies and electronic properties. In addition to the tools for interface creation and DFT analysis, work is also in progress to setup a local database tuned specifically for 2D materials and other interfaces such as nanoparticles capped with ligands.

Currently, MPInterfaces is being used to find suitable substrates for 42 2D materials useful for photoconversion and nano-electronic applications. Namely, 3 group-III monochalcogenides (AX, with A = In and X = S, Se, Te), 12 group IV-monochalcogenides (BX, with B = Ge, Sn, Pb and X = O, S, Se, Te), and the 27 metal dichalcogenides (MX$_2$, M = Ti, V, Cr, Mn, Fe, Co, Ni, Ta, W and X = S, Se, Te).

4. CONCLUSIONS

In summary we present a unified DFT based atomic level picture of deposition of 2D materials on substrates. This framework enables high-throughput screening of suitable substrates for the stabilization and functionalization of 2D layers. A Materials Project based open source python tool, MPInterfaces, based on this framework, is being developed to automate the search of suitable substrates as well as to characterize their effect on the structural and electronic properties of 2D materials. Lattice-matching, symmetry-matching, substrate surface termination, configuration sampling, substrate induced structural distortion and doping estimation algorithms are being developed. This computational tool will be employed to identify suitable substrates for scores of technologically relevant 2D materials, leading to acceleration of their synthesis and application, and more efficient use of experimental resources. While, our work helps in finding a starting point for the laboratory synthesis of 2D materials, several pieces of the puzzle such as temperature, pressure, deposition rate of precursors, and effect of defects remain to be worked on.

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