Defect-mediated, thermally-activated encapsulation of metals at the surface of graphite

Yinghui Zhou [a, **, 1], Ann Lii-Rosales [a, b, *, 1], Minsung Kim [a], Mark Wallingford [a], Dapeng Jing [a], Michael C. Tringides [a, c], Cai-Zhuang Wang [a, c], Patricia A. Thiel [a, b, d, ***]

[a] The Ames Laboratory, Ames, IA 50011, USA
[b] Department of Chemistry, Iowa State University, Ames, IA 50011, USA
[c] Department of Physics & Astronomy, Iowa State University, Ames, IA 50011, USA
[d] Department of Materials Science & Engineering, Iowa State University, Ames, IA 50011, USA

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ABSTRACT

We show that 3 metals — Dy, Ru, and Cu — can form multilayer intercalated (encapsulated) islands at the graphite (0001) surface if 2 specific conditions are met: Defects are introduced on the graphite terraces to act as entry portals, and the metal deposition temperature is well above ambient. Focusing on Dy as a prototype, we show that surface encapsulation is much different than bulk intercalation, because the encapsulated metal takes the form of bulk-like rafts of multilayer Dy, rather than the dilute, single-layer structure known for the bulk compound. Carbon-covered metallic rafts even form for relatively unreactive metals (Ru and Cu) which have no known bulk intercalation compound.

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1. Introduction

Intercalation in bulk layered materials has long been recognized as a way to alter and tune the transport and magnetic properties of a *bulk* compound over a wide range [1]. However, intercalation at *surfaces* of *bulk* layered compounds has received very little attention, despite the fact that it presents attractive possibilities. For example, intercalation could be an opportunity to tailor transport, catalysis, magnetism, or friction properties at the surface while also protecting the intercalated material. Indeed, this rationale has motivated the scientific community to examine intercalation beneath supported graphene closely [2,3], but it has rarely extended its scope to the surfaces of *bulk* layered materials.

Graphite is a particularly attractive layered material because it is cheap, abundant, and robust. It is the focus of the present work, together with elemental metals as intercalants. Certain elemental metals are known to form bulk graphite intercalation compounds (b-GICs), which consist of single, dilute layers of intercalant separated by one or more graphene sheets. b-GICs are particularly well-known for the alkali metals and alkaline earths, such as Li, Cs, and Ca [1]. For Cs, surface intercalation on graphite has been observed, and the structure is the same as in the b-GIC of Cs [4]. For other types of metals, there are no reports of surface intercalation on graphite to our knowledge, despite numerous investigations of metals deposited on graphite [5]. In this work we investigate one rare earth metal (Dy), and two metals that represent late transition metals (Ru, Cu), with the goal of determining whether experimental conditions can be found that enable surface intercalation. It is thus noteworthy that b-GICs are known for some rare earths, including Dy, but not for transition metals [6,7].

We show that two specific conditions are required. First, defects must be introduced on the graphite terraces prior to metal deposition. Second, the metal must be deposited at temperatures well above ambient. This results in multilayer metallic islands that are embedded in the graphite surface, but they are so much different from b-GICs that "encapsulated" may be a better descriptor than

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"intercalated".

The idea of introducing defects derives from an earlier study of the alkali metal Cs on graphite, where Büttner et al. [4] ion bombarded a graphite surface. When Cs was then deposited at room temperature and annealed, Cs formed bulk-like intercalation structures in the surface region. The authors proposed that bombardment-induced defects could serve as portals for surface intercalation of Cs, but only if defects exceeded a certain minimum size related to the number of missing carbon atoms. In the present work, we adopt part of their approach—ion bombardment prior to metal deposition—but their approach of subsequent annealing *to* elevated temperature is ineffective for these metals. Instead, deposition *at* elevated temperature is required. The fact that ion bombardment is part of the process means that it may eventually be possible to pattern the active defects and hence fix the locations of the encapsulated nanostructures.

2. Experimental and computational details

Our experiments were performed in an ultrahigh vacuum (UHV) chamber with base pressure 2×10^{-11} mbar, and equipped with scanning tunneling microscopy (STM). Commercial samples of highly-oriented pyrolytic graphite (HOPG; ZYB grade) were used as substrates for metal deposition. These are expected to have a high degree of perfection along the [0001] direction (perpendicular to the graphene sheets) but to contain micron-size rotational domains within the sheets [8]. The clean pristine surface was prepared by tape-cleavage in air, followed by transfer into UHV and then annealing at 800 K for 20 min. The ion-bombarded graphite surface was prepared with subsequent 3 keV Ar^+ bombardment for 30 s followed by annealing at 900 K for 2 h to remove embedded Ar. Details about metal deposition and STM methods are available in the Supplementary Data.

First-principles calculations were based on density functional theory (DFT), as implemented in the VASP package [9,10]. The projector-augmented wave (PAW) method [11] was used where 4*f* electrons of Dy were kept frozen in the core. Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was adopted [12]. A plane-wave basis set with energy cutoff 400 eV was used. Dispersion forces were included using the DFT-D3 method [13]. We employed slab geometries, and included sufficient vacuum regions (>1.8 nm) to prevent unwanted interaction between the periodic slabs.

Two types of configurations were analyzed for Dy: One chosen to mimic the known b-GIC, and a denser configuration to approximate a raft of metallic Dy. The b-GIC-like configuration is a $(\sqrt{3} \times \sqrt{3})R30°$ ($\sqrt{3}$ for short) unit cell of Dy. For this we used 11 AB-stacked graphene layers where the stacking of adjacent layers was set to be AA upon intercalation (consistent with the b-GIC structure), and $15 \times 15 \times 1$ *k*-point meshes. For the denser Dy configuration, we used 5 or 7 graphene layers in the slab, depending on the number of Dy layers, and $8 \times 8 \times 1$ *k*-point meshes.

3. Experimental results

Large-scale STM images (Fig. 1a) show that the pristine graphite surface has atomically flat terraces, hundreds of nanometers wide. The atomic order of graphite is resolved at higher magnification (Fig. 1b), with the expected atomic spacing of 0.247 ± 0.003 nm (bulk value: 0.246 nm [14]). In contrast, many defects are present after Ar^+ ion bombardment as described in Sec. 2. Fig. 1c shows a typical STM image of such a surface, with defect density 0.020 ± 0.003 nm^{-2}. Moreover, the well-known [15] $(\sqrt{3} \times \sqrt{3})$ *R*30° superstructure can be observed surrounding many defect sites, extending several nanometers from the center of each defect,

as shown in Fig. 1d.

Dy was deposited onto these two types of graphite substrates *at* 800–850 K in UHV. On the pristine graphite surface, at this temperature, Dy forms some large faceted islands on the terraces, and heavily decorates the step edges (Fig. 2a). In contrast, on the ion bombarded surface, ion-induced defects act as effective trapping sites for Dy and promote the nucleation of Dy clusters on top of graphite terraces (Fig. 2b). These Dy clusters show smaller footprints and higher density compared with those on pristine graphite. In addition to the surface Dy clusters on the ion bombarded surface, there exists another type of island with a specific height of 0.61 ± 0.03 nm (averaged over 54 islands). Examples are encircled in Fig. 2b.

If, instead of being deposited *at* 800–850 K, Dy is deposited on the ion bombarded surface at 300 K and then annealed *to* 800 K, the result is much different. Fig. 2c shows the result of deposition of Dy on the bombarded surface at 300 K, which produces small Dy clusters. Heating this surface to 800 K causes the small clusters to coarsen, as shown in Fig. 2d, but does not produce the 0.6 nm features. They also fail to appear upon heating to this temperature if the graphite surface is initially pristine, as shown by data in the Supplementary Data. Therefore, deposition must be carried out at elevated temperatures on the ion-sputtered surface, to form the special 0.6 nm islands.

In STM images (Fig. 3a and b), the 0.6 nm islands are characterized by a flat top, though they often emanate from the base of a taller Dy cluster. The islands often exhibit a faceted shape consistent with hexagonal symmetry, together with a hexagonal moiré pattern having periodicity 1.49 ± 0.10 nm, as shown in Fig. 3a', b'. The presence of the moiré indicates that the islands are atomically-well-ordered. Islands lacking these two features − moiré and hexagonal shape − presumably are more disordered. More STM images, produced in different experiments with comparable experimental parameters, are given in the Supplementary Data to demonstrate the robustness of these results.

Superimposed on the moiré is a hexagonal arrangement of features with lateral spacing of 0.247 ± 0.005 nm, which serves to identify this as the atomic graphite lattice. This spacing is distinct from the Dy interatomic spacing in a (0001) plane of bulk Dy, 0.359 nm. The graphite lattice is continuous over the edge of the island, as illustrated in Fig. 3(c', c''). The transition region between the substrate and the island is about 1 nm wide.

We propose that the 0.6 nm features are islands of Dy, covered by one or more layers of graphene. The moiré is evidence that the Dy is dense (close-packed), which is supported further by the frequent hexagonal footprint. Given that the interplanar spacing between close-packed layers of bulk Dy is 0.283 nm, the measured thickness of 0.6 nm indicates that multiple Dy layers are involved.

To confirm the role of ion bombardment-induced defects in the surface intercalation, we vary the defect density by changing bombardment time and energy. We find that the density of the 0.6 nm islands depends strongly on the defect density, confirming that the defects play an important role. Furthermore, the intercalated island density is consistently a small fraction (~1%) of the corresponding defect density, indicating that only a small fraction of defects is active in promoting intercalation. Following Büttner et al. [4], we propose that the active defects are entry portals that satisfy a minimum size requirement, hence accounting for the small ratio of 0.6 nm islands to total defects. The requirement of elevated temperature may reflect an activation barrier for passage of metal atoms through the portals, as suggested by Büttner et al. [4] The requirement of *deposition* at elevated temperature, rather than annealing, then indicates that this process can be blocked if Dy islands form at the portals, which