Two-Dimensional Transition Metal Honeycomb Realized: Hf on Ir(111)

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S *Supporting Information*

ABSTRACT: Two-dimensional (2D) honeycomb systems made of elements with d electrons are rare. Here, we report the fabrication of a transition metal (TM) 2D layer, namely, hafnium crystalline layers on Ir(111). Experimental characterization reveals that the Hf layer has its own honeycomb lattice, morphologically identical to graphene. First-principles calculations provide evidence for directional bonding between adjacent Hf atoms, analogous to carbon atoms in graphene.

Calculations further suggest that the freestanding Hf honeycomb could be ferromagnetic with magnetic moment μ/Hf = 1.46 μ_B. The realization and investigation of TM honeycomb layers extend the scope of 2D structures and could bring about novel properties for technological applications.

KEYWORDS: *Honeycomb lattice, hafnium, epitaxial growth, STM*
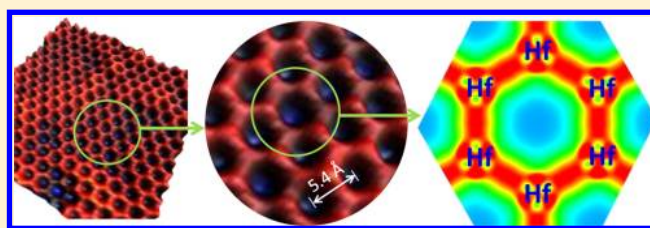
The novel properties of graphene's honeycomb structure[1−4] have spurred tremendous interest in investigating other two-dimensional (2D) layered structures beyond graphene. This includes, for example, hexagonal boron nitride[5−7] and silicene.[8−12] Almost exclusively, however, the reported 2D honeycomb materials are made of elements with p-orbital electronic structure. The 2D honeycomb structures made of elements with d electrons are still rare, although there are many more transition metal (TM) elements than the ordinary main-group honeycomb elements in the first-two rows of the Periodic Table. Generally, the TM elements have rich many-body physical behaviors and coordination chemistry properties; many of them also exist as spin-polarized magnetic ions. Hence, it is highly desirable to fabricate 2D honeycomb structures of the TM elements for drastically enhanced and/or novel electronic, spintronic, and catalytic activities.

In the present work, therefore, we challenge the conventional wisdom that honeycomb structure can exist only in elements that bear great chemical similarity to carbon. We report that honeycomb structure of TM elements can also be fabricated with totally uncharted physics and chemistry in particular for Hf on Ir substrate. Low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) measurements reveal that despite the triangular planar structure of the substrate Hf forms its own honeycomb structure with Hf−Hf nearest neighbor distance remarkably close to that of bulk Hf. Electronic structure calculation further reveals direct bonding

of covalent character between the nearest neighbor Hf atoms, as reflected in the calculated total charge density.

Experiments were performed in an ultrahigh vacuum (UHV) system with base pressure in the range of 10^{-10} mbar, equipped with an STM, a LEED apparatus, an Ar^+ sputtering gun, a Hf evaporator, and so forth. The Ir(111) sample was cleaned by several cycles of Ar^+ ion sputtering followed by annealing at around 1473 K until sharp 1 × 1 diffraction spots in the LEED pattern and clean surface terraces in the STM images were obtained. Hafnium, evaporated from the electron-beam evaporator, was deposited at room temperature. The Hf flux is set at 10 nA. The deposition time varies depending on the intended Hf coverage. The sample was subsequently annealed until a well-ordered structure was observed. (See details in the Supporting Information.) The STM and LEED techniques were combined to characterize the structural and physical properties of the Hf/Ir system. First-principles calculations were performed using the projector augmented wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP).[13,14] The generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) was used for the exchange and correlation interaction between electrons.[15] Periodic slabs with four layers of (4 × 4) Ir(111) were used as the substrate, plus one layer of Hf and a vacuum of 12 Å

wide. All atoms were fully relaxed except for the bottom Ir layer, until the net force on each atom was less than 0.01 eV/Å. The energy cutoff for the plane-wave basis set is 400 eV, and the k-points sampling is $3 \times 3 \times 1$. To simulate the STM images, we used the Tersoff-Hamann approach.[16]

More specifically, we deposited Hf atoms at room temperature, which form nanoclusters on the Ir substrate (details can be found in Figure S1 in Supporting Information). With follow-up annealing at 673 K, a well-ordered structure is observed, as shown in Figure 1 (more can be found in Supporting
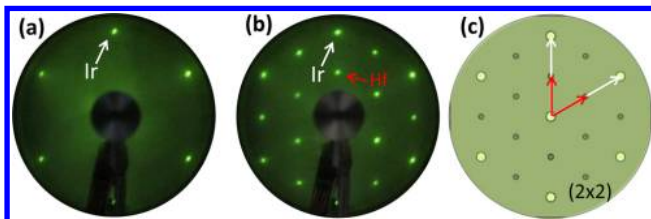

Figure 1. LEED patterns obtained on Ir(111). (a) Clean Ir(111) substrate. The six spots originate from the 6-fold symmetry of the Ir(111) substrate. (b) Sample with Hf annealed at 673 K. The additional diffraction spots due to Hf form a (2×2) superstructure. The patterns in (a) and (b) are obtained at electron beam energies of 68 and 70 eV, respectively. (c) Sketch of the ideal diffraction pattern of the (2×2) superstructure on Ir(111), where the reciprocal lattice vectors of Ir and Hf are indicated by the white and red arrows, respectively.

Information Figures S2 and S3). The structural information of the sample was first characterized by LEED. Figure 1a shows a typical LEED pattern, in which the six bright spots can be assigned to as-prepared clean Ir(111) substrate of 6-fold symmetry. After the deposition of Hf followed by annealing, additional diffraction spots appeared, as indicated by the red dashed-line arrow in Figure 1b, which signals that a new superstructure of Hf origin has emerged. It has the (2×2) pattern with respect to the Ir(111) substrate. Figure 1c shows a theoretical diffraction pattern for the (2×2) superstructure on Ir(111). Comparison between Figure 1b,c reveals remarkable agreement between the two. The LEED data thus suggest the formation of a well-ordered network of Hf adlayer with a periodicity twice that of Ir(111).

To gain understanding of this Hf superstructure in real space, we carried out an STM study. Figure 2a shows a typical STM image, which reveals a continuous 2D lattice of honeycomb structure. The orientation of the honeycomb lattice is parallel to the close-packed $[1\bar{1}0]$ direction of the Ir(111) lattice, in agreement with the LEED results, where the reciprocal vectors of the Ir spots are in line with those of the Hf spots (see Figure 1b). Figure 2b is a zoomed-in image in which perfect honeycomb structure can be clearly resolved. Combining the STM results with the LEED patterns, we conclude that well-ordered Hf honeycomb with a (2×2) superstructure has formed on Ir(111).

Figure 2c shows a height profile of the honeycomb lattice along the blue line in Figure 2b. It indicates a 5.40 Å periodicity of the honeycomb lattice, which is consistent with the value deduced from the (2×2) spots in the LEED pattern (5.40 Å $\approx$ 2×2.71 Å, where 2.71 Å is the lattice constant of the Ir(111)). From this periodicity, we determine the distance between two adjacent Hf atoms in the 2D plane to be $(5.40/\sqrt{3})$ Å = 3.12 Å. This value is very close to the Hf−Hf distance of 3.19 Å on the (0001) facet of bulk Hf. Half of the value, 3.12 Å/2 = 1.56

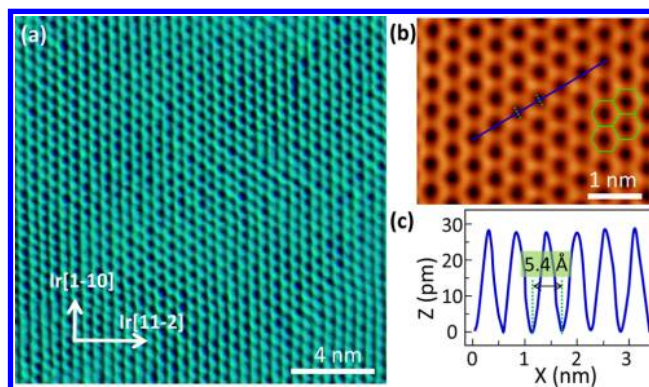**Figure 2.** STM images and height profile of Hf layer formed on Ir(111). (a) The topographic image ($U = -1.0$ V and $I = 0.8$ nA) shows a well-ordered pattern. The close-packed directions of Ir$[1\bar{1}0]$ and $[11\bar{2}]$ are indicated by the white arrows. (b) The close-up image ($U = -0.7$ V and $I = 0.16$ nA) shows the honeycomb lattice of the Hf adlayer. (c) A height profile taken along the blue line in (b), revealing the periodicity of the honeycomb lattice (5.4 Å between holes).

Å, is also within the range of the proposed covalent radii for Hf, which are between 1.44 and 1.75 Å. In other words, the Hf atoms are the nearest neighbors, rather than disjointed adatoms on Ir(111).

To confirm the experimental observations, we conducted density functional theory (DFT) calculations. For isolated Hf adatoms on Ir(111), we considered three atomic sites, the face-centered cubic (fcc), hexagonal close-packed (hcp), and vertically above an Ir substrate atom (atop), as the building units of the honeycomb lattice. Table S1 in Supporting Information shows that Hf binding to the atop site is the weakest; relative to the atop site, the binding energies of the hcp and fcc sites are 1.54 and 1.28 eV/Hf, respectively. Next, we mixed the hcp, fcc, and atop sites to obtain three honeycomb structures in Figure S5 in Supporting Information. Not surprisingly, the fcc/hcp mixing is 0.45 and 0.36 eV/Hf lower in energy than the atop/fcc and atop/hcp mixings, respectively.

Figure 3a shows a top view of the atomic structure for the fcc/hcp mixing on Ir(111), whereas Figure 3b shows the corresponding simulated STM image for bias = -1.5 V. The honeycomb structure is clearly seen in the STM image as marked by the green hexagon. Figure 3c shows the corresponding experimental STM image. The overall features are in remarkable agreement with the simulated results in Figure 3b. Figure 3d shows a side-view of the calculated atomic structure. It reveals that the Hf honeycomb is flat with a height variation between the fcc and hcp sites $\leq$0.03 Å.

A key issue here is whether Hf forms its own honeycomb lattice. While both the experimental STM images in Figures 2b and 3c and the measured Hf−Hf distance strongly suggest so, more evidence comes from the calculated charge distribution in the Hf layer. Figure 4 shows the total charge density in the Hf honeycomb plane. It reveals the formation of direct Hf−Hf bonds and thus explains why the Hf does not simply follow the Ir triangular lattice. Another issue is whether Hf forms the honeycomb with Ir (in other words, forming surface alloys). Our calculations reveal that a honeycomb made of only Hf is energetically more stable than a honeycomb with Hf−Ir mixing. (Table S3 and Figure S6 in Supporting Information provide detailed results from the calculations.) Therefore, both experiment and theory suggest the existence of a continuous
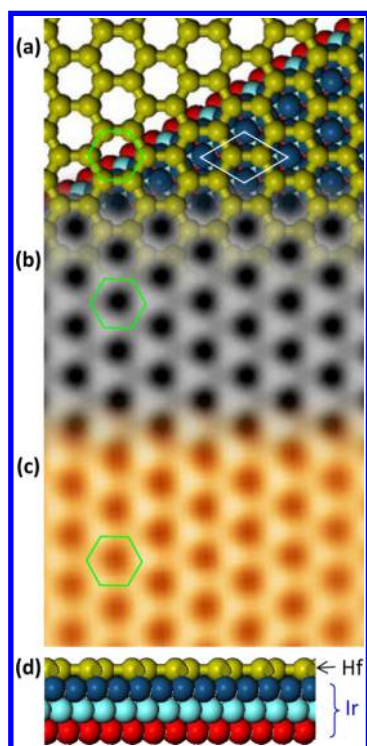
Figure 3. Atomic configuration of Hf honeycomb lattice on Ir(111). (a) Top view of the calculated atomic structure. Half of the Hf atoms are on the fcc sites (vertically above the red Ir balls), while the other half are on the hcp sites (vertically above the cyan Ir balls). For clarity, some of the substrate atoms are removed. The white rhombus denotes the Ir(111)-(2 × 2) unit cell. (b) DFT-simulated STM image (−1.5 V). The Hf honeycomb is highlighted by the green hexagon. (c) Atomically resolved experimental STM image (−1.5 V, 0.1 nA) showing features identical to those in (b). (d) Side view of the relaxed atomic structure in (a), showing a planar Hf layer on an Ir(111) surface.
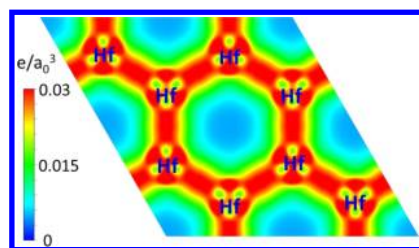

Figure 4. The 2D charge density in the Hf plane on Ir(111) substrate. Hf−Hf bonds are clearly seen and they are responsible for the observed honeycomb structure.

single-layer Hf film with honeycomb structure, supported on the Ir(111) substrate. The name of this material may be coined as "hafnene", as a special case of possible metalenes.

Furthermore, we observed the formation of a second Hf honeycomb layer on top of the first one upon increasing the Hf coverage (details can be found in Figure S2 in Supporting Information). This could be important, as it suggests that the existence of the Hf honeycomb structure does not necessarily depend on the binding to the Ir substrate. Thus there comes a question that whether the single-layer Hf honeycomb structure could readily be separated from the substrate. It has not been possible so far, and even if separated, the freestanding film may not be stable. However, there may be other ways to isolate the Hf honeycomb structure from the substrate without strongly

perturbing its physical properties or its physical integrity, for example, by intercalation. In light of the above analysis and the fact that freestanding honeycomb structures usually hold essential properties for technological applications, we have calculated the band structures of a freestanding Hf honeycomb.

Figure 5 shows the band structures for (a) spin-up and (b) spin-down states. They reveal that the freestanding Hf
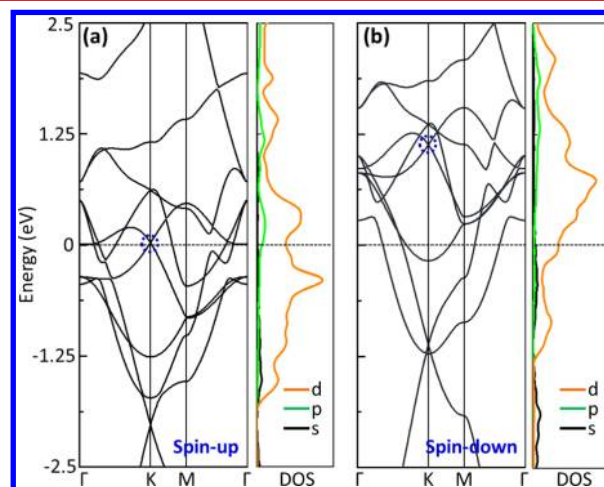

Figure 5. Band structures of freestanding Hf honeycomb. Spin-up (a) and spin-down (b) states along with their partial densities of states (DOSs). Dotted cycles denote the positions of the Dirac cones near the Fermi level (set at E = 0).

honeycomb is metallic and strongly spin-polarized (and hence ferromagnetic), with a magnetic moment of 1.46 μB/Hf. The density of states (DOS) plots show the presence of a large number of d states near the Fermi level, which could be utilized for catalytic reactions.[17] Dirac cones also exist in this system. Because of the localization of the wave functions in the 2D plane, which increases exchange coupling between electrons,[18] the Dirac cone for the spin-down states is about 1 eV higher in energy than that for the spin-up states.

What's more, it is necessary to note that the observation of Hf honeycomb on Ir(111) is not an isolated case. A similar honeycomb structure has also been fabricated on Rh(111) substrate. Detailed data can be found in Figure S7 in Supporting Information, which reveal that the two have qualitatively identical charge distributions and band structures.

In summary, we report here the first examples of TM honeycomb structures. The LEED and STM studies reveal highly ordered Hf lattices on Ir and Rh substrates. Our analyses conclude that the Hf honeycomb forms a lattice of its own. Interesting ferromagnetism, high density of d states at the Fermi level, and large spin-splitting of the Dirac cones are theoretically predicted for a freestanding Hf honeycomb structure. Given the rich electronic, magnetic, and catalytic properties of TM elements in general, and the insufficiency of knowledge of their 2D structures, further realization and investigation of TM single layers are highly desirable. As the TM honeycomb structures provide a new platform to investigate hitherto unknown quantum phenomena and electronic behaviors in 2D systems, we expect them to have broad application potential in nanotechnology and related areas.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Supporting Information and figures regarding the sample preparation and characterization; detailed discussions about DFT calculations and hypothetical surface alloys. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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