Supporting Information Available

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

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Hf Deposition. Hf atoms are deposited by electron-beam evaporator to Ir(111) substrate at room temperature. The Hf flux is 10 nA during the deposition. The Hf coverage is adjusted by varying the deposition time. At this deposition flux, one monolayer (ML) Hf honeycomb corresponds to a deposition time of 40 minutes. After annealing, we estimate the coverage by counting the percentage of Hf-covered surfaces.

Annealing. The sample is heated until a well-ordered superstructure is observed by in-situ LEED measurement. The corresponding annealing temperature is 573 K. Identical superstructures to those in Figs. 1 and 2 are observed at temperatures between 573 K and 773 K.

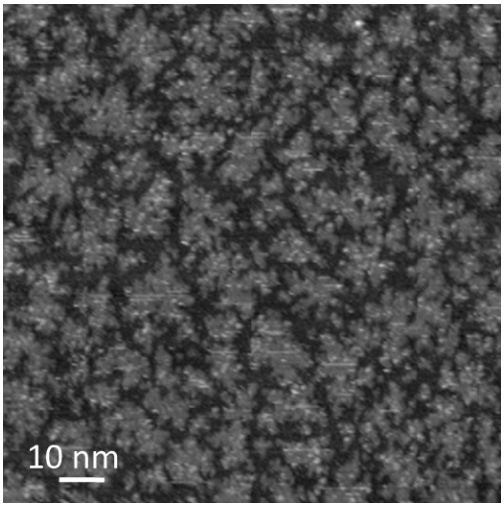

Figure S1. An STM image of Hf-deposited sample before annealing. It shows that Hf atoms form nanoclusters at room temperature. The deposition time is 40 minutes. This is the same sample given in Figures 1 and 2 of the main text after annealing.

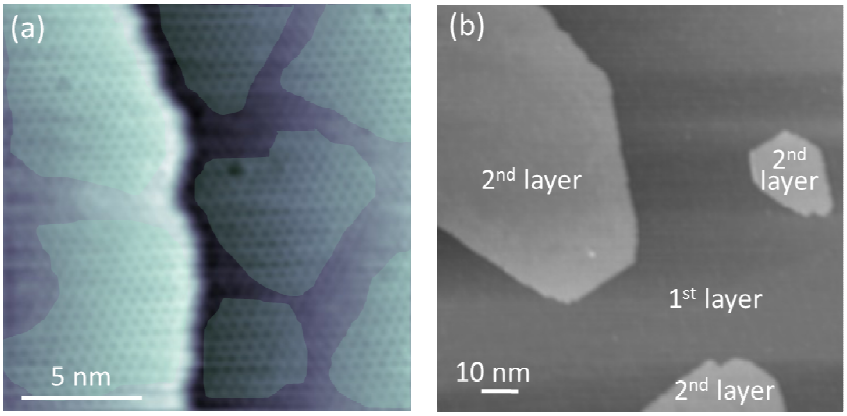

Figure S2. STM images of Hf samples after annealing. The deposition time is (a) 25 mins and (b) 50 mins. The apparent coverage of Hf honeycomb is (a) 0.65 ML and (b) 1.3 ML, respectively. In (a), for clarity, the honeycomb covered areas are highlighted in pea-green. In (b), both the first and second layers show identical structures.

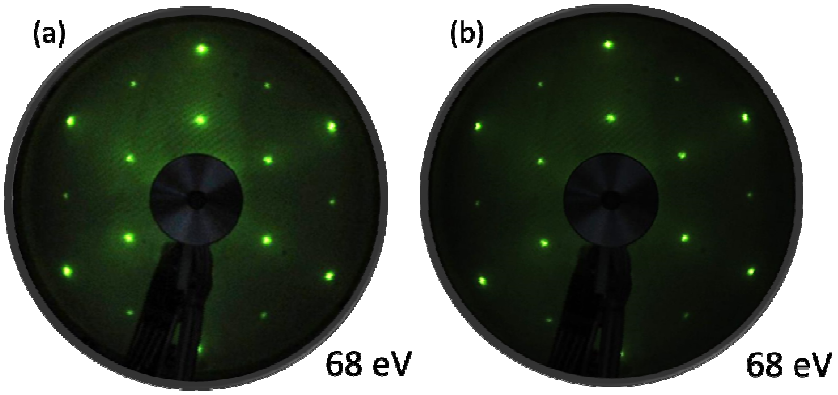

Figure S3. LEED patterns of Hf superstructure on Ir(111). The samples are annealed at (a) 573 K and (b) 773 K, respectively. An identical (2x2) superstructure is observed.

Energetics of Hf on Ir(111)

On the Ir(111)-(2×2) surface (see Fig. S4), there are three ways to place Hf, either on (a) *atop*, (b) *fcc*, or (c) *hcp* sites, while preserving the threefold rotational symmetry. A combination of any two sites here will result in the Hf honeycomb structure. This leads to three different arrangements of the Hf honeycomb on Ir(111): (a) *atop* + *fcc*, (b) *atop* + *hcp*, and (c) *fcc* + *hcp*, as shown in Fig. S5.

Formation enthalpies of single Hf atom and Hf honeycomb on the three sites are calculated as follows:

$$\Delta H_f = E(Hf/Ir) - E(Ir) - n_{Hf}\mu_{Hf}(solid)$$

where $E(Hf/Ir)$ is the total energy of Hf on Ir substrate and $E(Ir)$ is the total energy of the substrate. n_{Hf} is the number of Hf atoms deposited and μ_{Hf} is the energy of the Hf bulk metal. The results are summarized in Tables S1 and S2, respectively.

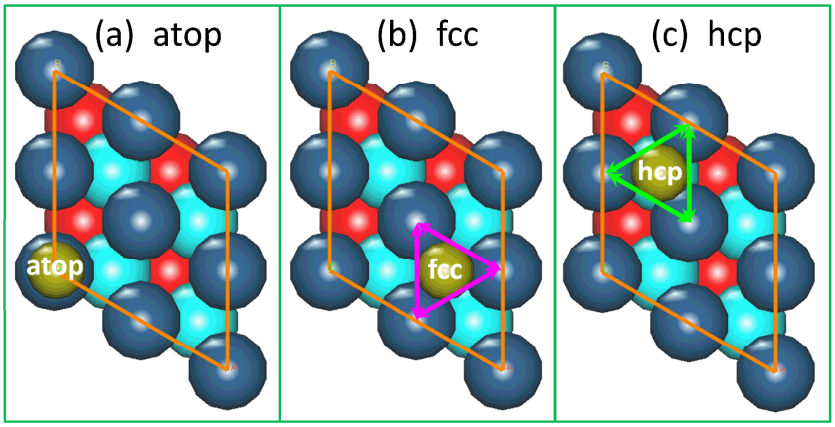

Figure S4. Hf on Ir(111). (a) *atop* site, (b) *fcc* site, and (c) *hcp* site. Red, cyan, and blue balls represent Ir atoms in the first three layers of Ir(111)-(2×2). Yellow balls are Hf atoms.

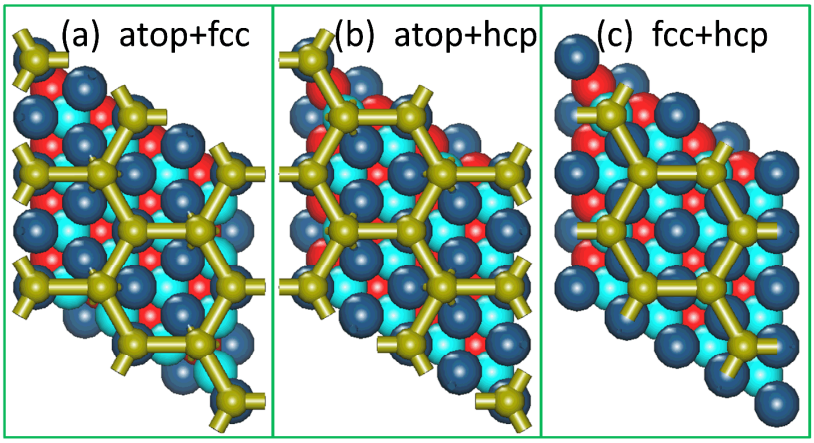

Figure S5. Three different arrangements of Hf honeycomb with respect to Ir(111). Hf atoms at (a) *atop* and *fcc* sites, (b) *atop* and *hcp* sites, and (c) *fcc* and *hcp* sites.

Table S1. Formation enthalpy of single Hf atom on Ir(111).

Hf occupied site	**Formation enthalpy (eV/Hf)**
atop	+0.56
fcc	-0.72
hcp	-0.98

Table S2. Formation enthalpy of a layer of Hf honeycomb on Ir(111).

Hf honeycomb at different sites	Formation enthalpy (eV/Hf)
atop + fcc	-0.12
atop + hcp	-0.21
fcc + hcp	-0.57

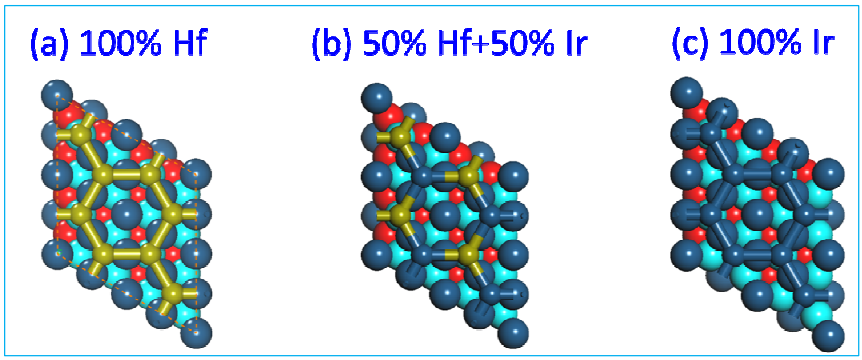

Figure S6. Models of honeycomb lattices with different Hf-Ir mixing: (a) 100% Hf; (b) 50% Hf + 50% Ir; and (c) 100% Ir.

Table S3. Formation enthalpy of honeycomb structures on Ir(111). Lower energy signals better stability.

Honeycomb component	Formation enthalpy (eV/atom)
(a) 100% Hf	-0.57
(b) 50% Hf + 50% Ir	-0.26
(c) 100% Ir	+1.76

Table S3 shows the formation enthalpy of honeycombs with different amount of Ir. It reveals that pure Hf honeycomb is energetically more stable than either pure Ir or mixed Hf-Ir honeycomb structures.

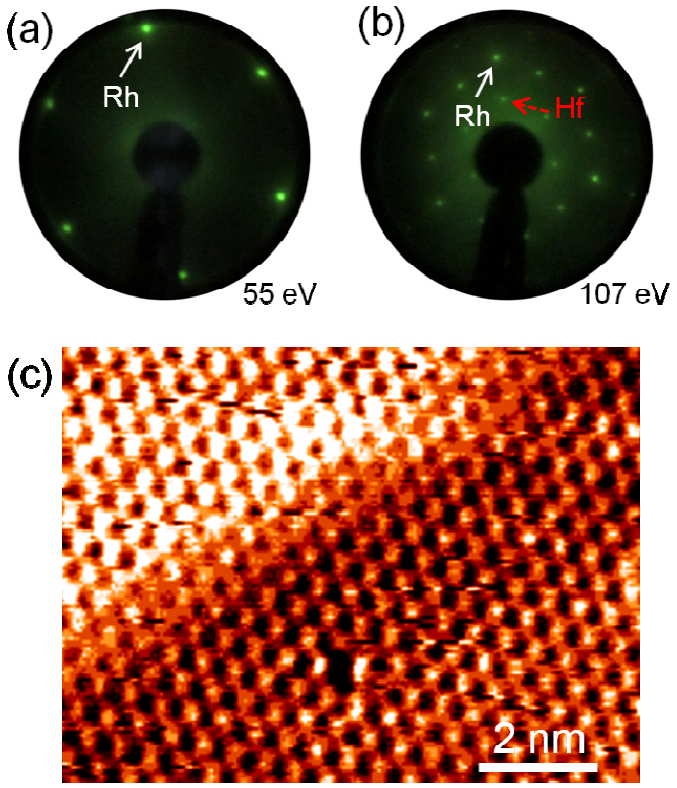

Figure S7. LEED patterns and STM image of Hf on Rh(111). (a) The six spots in the absence of Hf originate from the six-fold symmetry of the Rh(111) substrate. (b) The additional diffraction spots due to Hf form a (2×2) superstructure. The diffraction spots resulting from Rh and Hf are indicated by the white and red arrows, respectively. The patterns in (a) and (b) are obtained at electron beam energies of 55 eV and 107 eV, respectively. (c) The STM image (U = -2.0 V and I = 0.3 nA) showing the honeycomb lattice of Hf adlayer on Rh(111).