Electronic Supplementary Material (ESI) for Nanoscale.

Two-dimensional honeycomb hafnene monolayer: stability and magnetism by structural transition

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Phonon dispersion of flat hafnene

Flat structure of hafnene has large imaginary frequencies in the Brillouin zone and this demonstrates the structural instability of the flat structure.

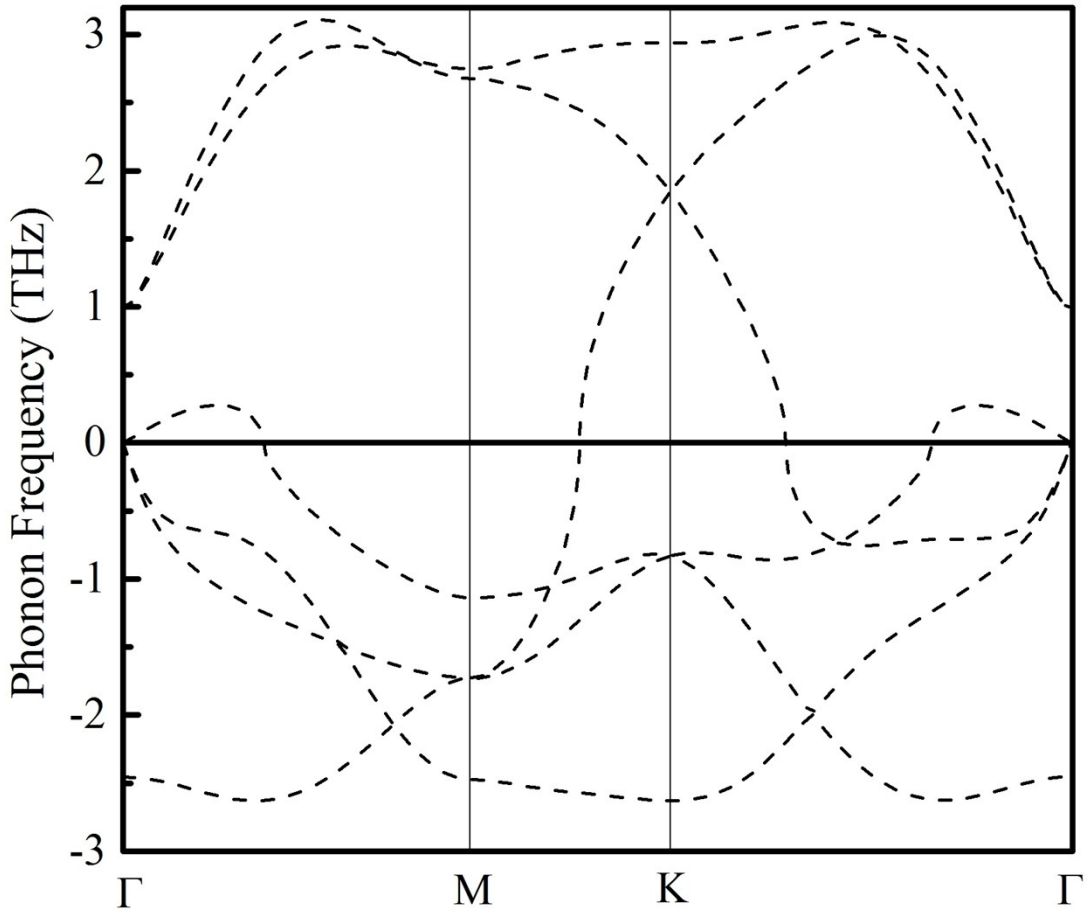

Fig. S1 Phonon dispersion of flat layer.

Hafnene on Ir(111) substrate

Experimentally grown epitaxial hafnene honeycomb lattice on the clean Ir (111) surface at room temperature indicates a planar structure. Thus on Ir (111) substrate, PL as well as HB structure is studied to find out the most stable Hf in the presence of Ir substrate.

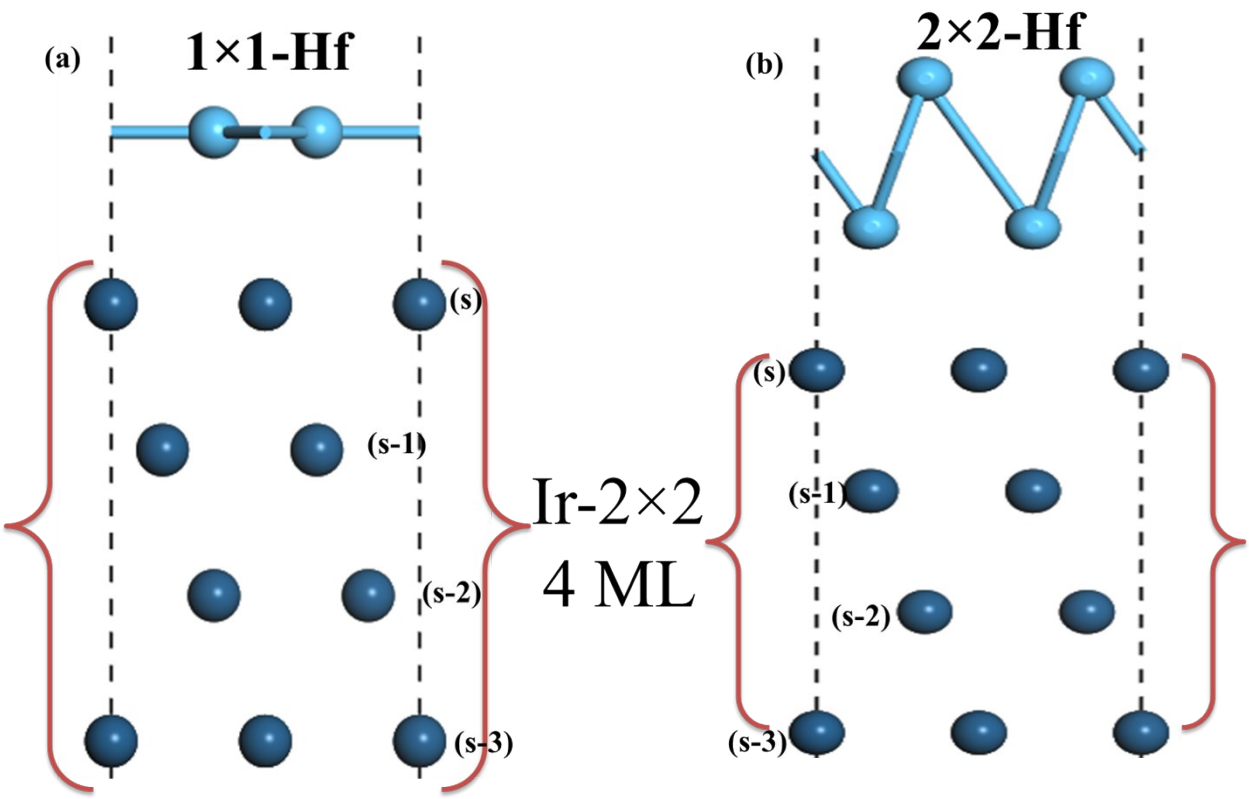

Fig. S2 Schematic illustrations of Hf/Ir(111): (a) side view of (1×1) FL Hf on Ir(111) and (b) side view of (2×2) HB Hf on Ir(111). Cyan and hague-blue balls represent Hf and Ir atoms, respectively.

Different arrangements of honeycomb Hf with respect to Ir (111)

On the Ir (111)-(2×2) surface, there are three ways to place Hf on Ir. Here, we have Top site where Ir is directly on top of Surface (s) Ir. In Hcp site, Hf atom is on top of (s-1) Ir layer while Fcc site where Hf atom is placed on top of (s-2) layer of Ir. A combination of any two sites here will result in the Hf honeycomb structure.

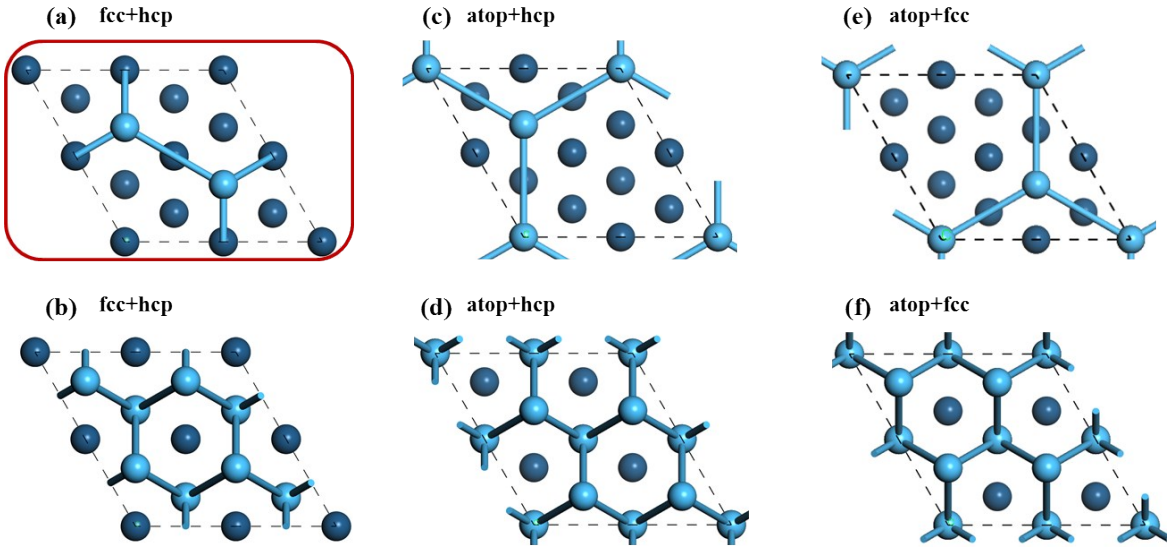

Fig. S3 Three different arrangements of Hf honeycomb on Ir(111) substrate. Upper panel: Top view of FL Hf on Ir substrate while lower panel is top view of HB Hf on Ir. (a, b) fcc+hcp site (c, d) atop+fcc (e, f) atop+hcp site. Structure within red boundary is most stable structure.

DOS of Hf/Ir(111) system

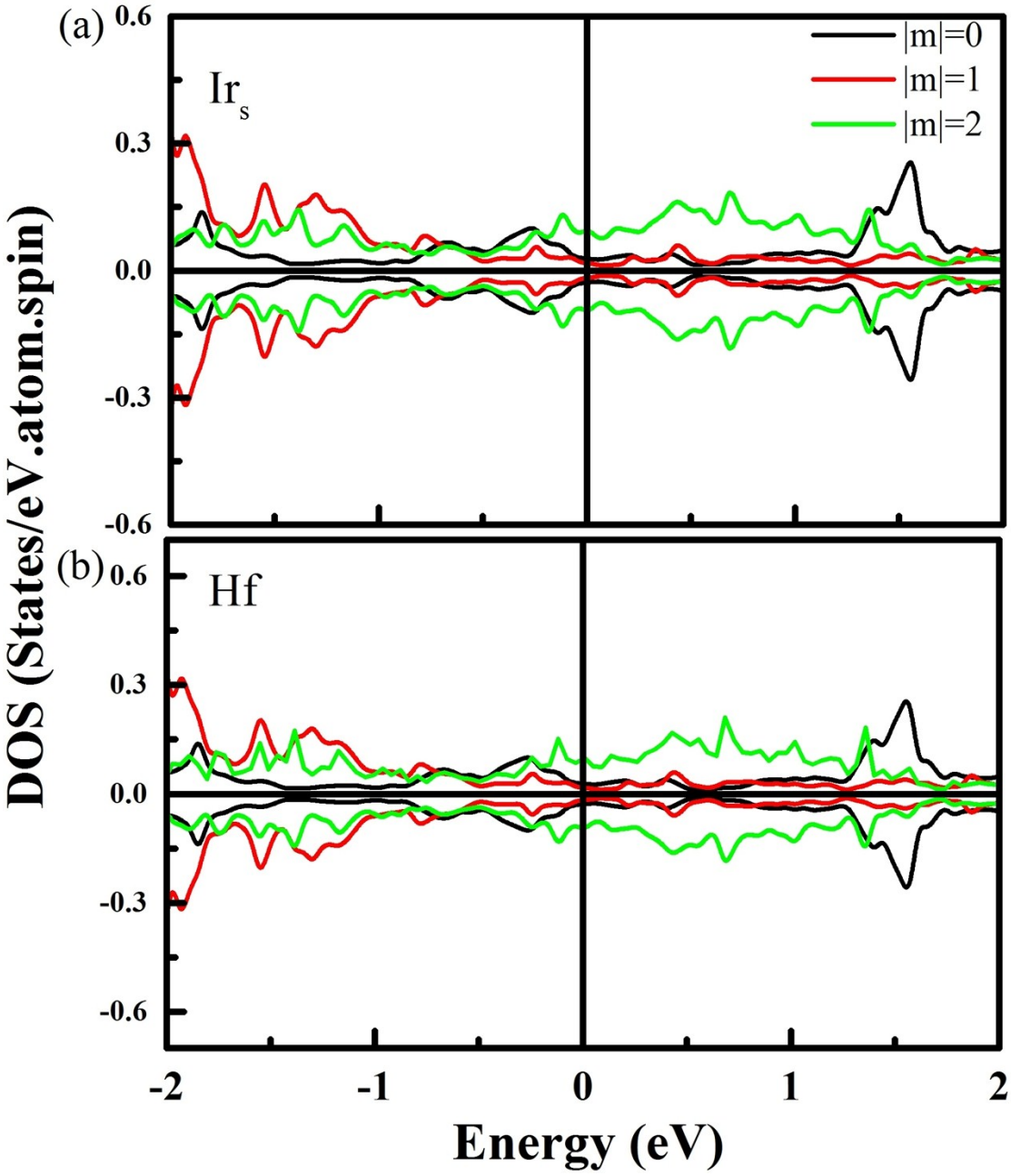

Fig. S4 Calculated mdos of (a) Ir surface (b) Hf on Ir(111) substrate.

BN (ML) adsorption on Ir(111) substrate

Table 1 shows the adsorption energy and structural parameter for six possible BN configurations on Ir(111). The adsorption energy is defined as

$$E_{ads} = E_{BN/Ir(111)} - E_{Ir(111)} - E_{BN}$$

Here $E_{BN/Ir(111)}$ and $E_{Ir(111)}$ are the total energies of the Ir(111) surface with and without the BN layer, respectively while E_{BN} stands for the energy of a clean BN layer.

TABLE SI: Adsorption Energy Eads, (in eV) & Buckling Height BH in BN layer (in Å) for six different configurations on Ir(111) substrate.

System	B-top, N-hcp	N-top, B-hcp	B-top, N-fcc	N-top, B-fcc	B-hcp, N-fcc	N-hcp, B-fcc
Eads	-0.068	-0.342	-0.066	-0.491	-0.068	-0.067
BH	0.002	0.14	0.002	0.14	0.001	0.001

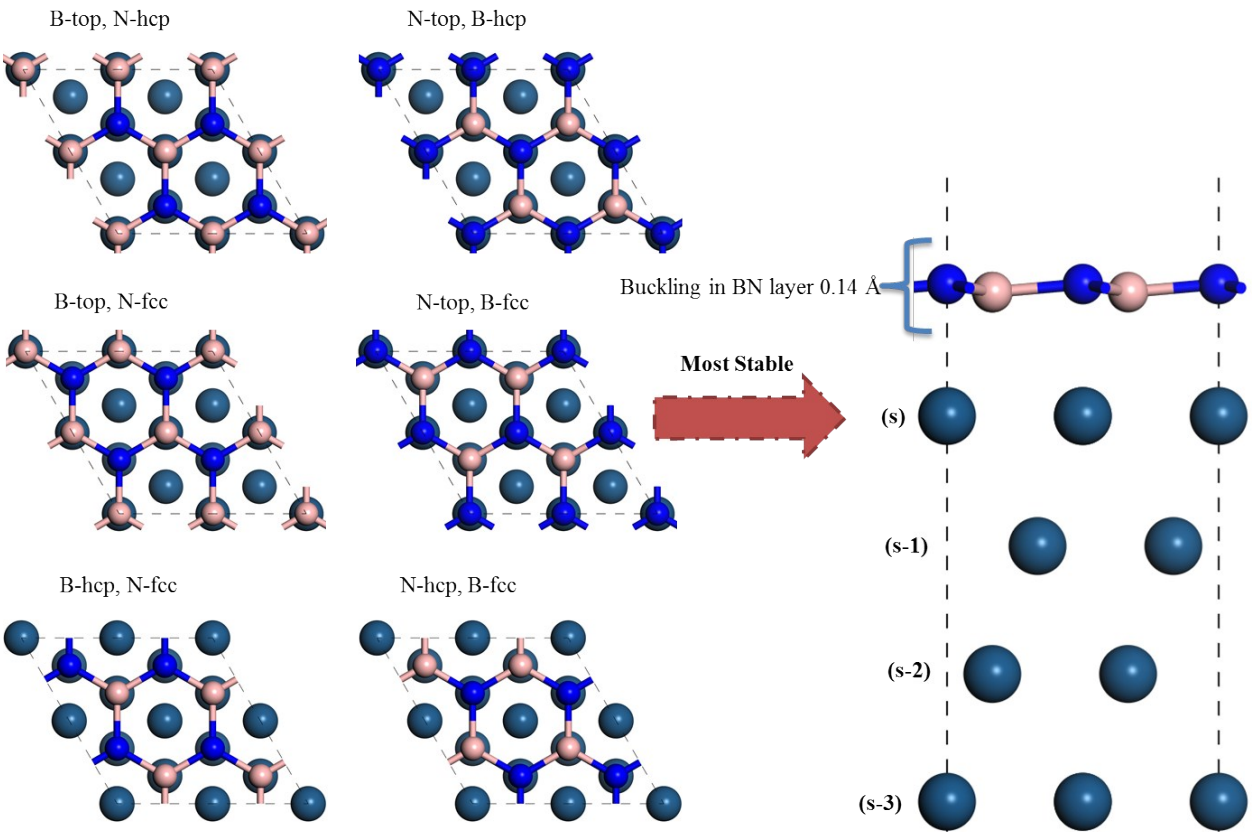

Fig. S5 Schematic illustration of BN on Ir(111) substrate. Right panel: Top view of six different sites of BN on Ir(111) surface. Left panel: Side view of most stable (N-top, B-fcc) configurations. Cyan and hague-blue balls represent Hf and Ir atoms, respectively while dark-blue and pink balls represent the N and B atoms in BN.

Hafnene (ML) on BN/Ir(111) system

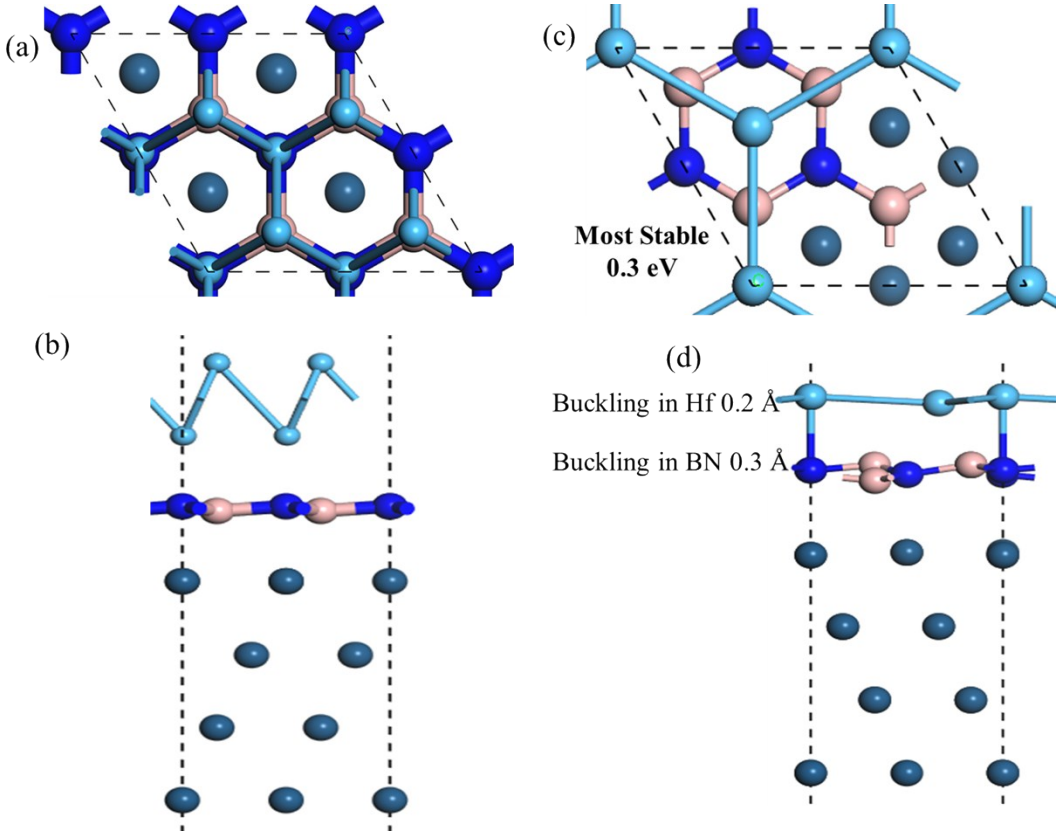

Fig. S6 Schematic illustration of HB and slightly buckled Hafnene on BN/Ir(111). (a) Top view of HB (b) Side view of HB Hf Hafnene (c) Top view of most-stable slightly buckled Hf (d) Side view of most-stable slightly buckled Hafnene. Cyan and hague-blue balls represent Hf and Ir atoms, respectively while dark-blue and pink balls represent the N and B atoms in BN.

Realization of high-buckled (HB) Hafnene on BN substrate

HB structure is stable in the free-standing form and this HB isn't easy to produce on substrate especially metallic substrate like Ir(111). we anticipated that this HB structure can be grow on the insulator substrate such as BN where the hybridization between substrate and Hf layer wouldn't be too strong.

Keeping this in mind, we have used insulator h-BN as a substrate to grow Hf. We have calculated the formation energy of HB and as well as FL structure.

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

We have found that HB hafnene is extremely stable on BN having negative formation energy of 3.5 eV/Hf while the FL structure is highly unstable with positive formation energy. Hence, on behalf of formation energy, we deduce that if one can use an insulator substrate like BN then it is likely to grow a HB hafnene structure.