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Nearly-free-electron system of monolayer Na on the surface of single-crystal $HfSe_2$

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The electronic structure of a single Na monolayer on the surface of single-crystal $HfSe_2$ is investigated using angle-resolved photoemission spectroscopy. We find that this system exhibits an almost perfect "nearly-free-electron" behavior with an extracted effective mass of $\sim 1m_e$, in contrast to heavier masses found previously for alkali-metal monolayers on other substrates. Our density-functional-theory calculations indicate that this is due to the large lattice constant, causing both exchange and correlation interactions to be suppressed, and to the weak hybridization between the overlayer and the substrate. This is therefore an ideal model system for understanding the properties of two-dimensional materials.

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Understanding and controlling electrons in reduced dimensions, for example, at the interfaces between disparate semiconductors, underpins modern electronic devices [1–4]. In recent years, this has found renewed prominence through the study of electrons naturally confined in atomically thin layers, such as in graphene or monolayer transition-metal dichalcogenides, opening prospects to achieve novel functionality such as ultrafast electronic [5], spintronic, or valleytronic devices [6–11]. To progress towards these goals, it is critical to understand the behavior of electrons in two-dimensional (2D) solids, and the influence of many-body interactions between them.

Angle-resolved photoemission spectroscopy (ARPES) is a powerful tool to achieve this. It directly measures the electronic structure of materials, and can provide valuable information on carrier masses and the interactions between electrons in the system. This has been applied to numerous two-dimensional (or quasi-two-dimensional systems), including surface states of noble metals (e.g., Cu [12,13], Ag and Au [14,15]), semiconductors [16–20], and metal oxides [21,22], and alkali metals grown as two-dimensional layers on metallic substrates [23–28]. Despite many of these systems being generally considered weakly interacting, there is hardly any example of a system which displays true nearly-free-electron behavior manifested by a parabolic band dispersion with an effective carrier mass $m^* = 1m_e$). For example, even for an alkali metal, in the cases of Na monolayers on Cu(111) [24] and Ni(100) [25] surfaces, the effective mass was reported to be at least 30% heavier than the bare electron mass. This was attributed to a hybridization between the Na-derived electronic states and those of the underlying substrate. Moreover, exchange interactions can even lead to a lowering of the effective mass below unity [29,30], making achieving true free-electron-like behavior very rare. In this Rapid Communication, we show how just such behavior is manifested in a single Na layer stabilized on a semiconducting $HfSe_2$ substrate. We attribute this to particularly weak hybridization with the substrate due to a large out-of-plane lattice constant, and to a particularly weak exchange and correlation interaction.

$1T$-$HfSe_2$ single crystals, which we use as a substrate, were grown using the flux method. This compound crystallizes in the CdI_2 structure with a hexagonal unit cell with in-plane and out-of-plane lattice constant of $a = 3.74$ Å and $c = 6.14$ Å [31,32], respectively [see Fig. 1(a)]. To obtain a clean surface, the crystal was cleaved in ultrahigh vacuum at a pressure better than 4×10^{-11} Torr. ARPES measurements were performed immediately after cleaving, and following the deposition of sodium (Na) on the sample surface from a SAES alkali-metal source. The measurements were performed at beamlines 4.0.3 and 10.0.1 of the Advanced Light Source (USA) using Scienta R4000 hemispherical electron analyzers. Photon energies were set to be in the range between 50 and 80 eV. The sample temperature was maintained at between 40 and 80 K throughout the experiment.

Figures 1(b) and 1(c) show ARPES data measured after Na atoms were deposited on the cleaved surface of single-crystal $HfSe_2$ for 5 min. A dispersive band with a parabolic shape is clearly observed. By fitting momentum distribution curves (MDCs) of this parabolic band, we extracted the effective mass to be $m^* = (1.00 \pm 0.04)m_e$, which is within error identical to the free-electron mass. The corresponding Fermi surface has a circular shape, again consistent with a free-electron gas. From this measured Fermi surface, we extract a surface carrier density from the Luttinger area, $n_{2D} = k_F^2/2\pi = 8.72 \times 10^{14}$ cm^{-2}. We also note the possible presence of a second smaller band near E_F marked by an arrow in Fig. 1(b) (see Fig. S1 in the Supplemental Material [33]

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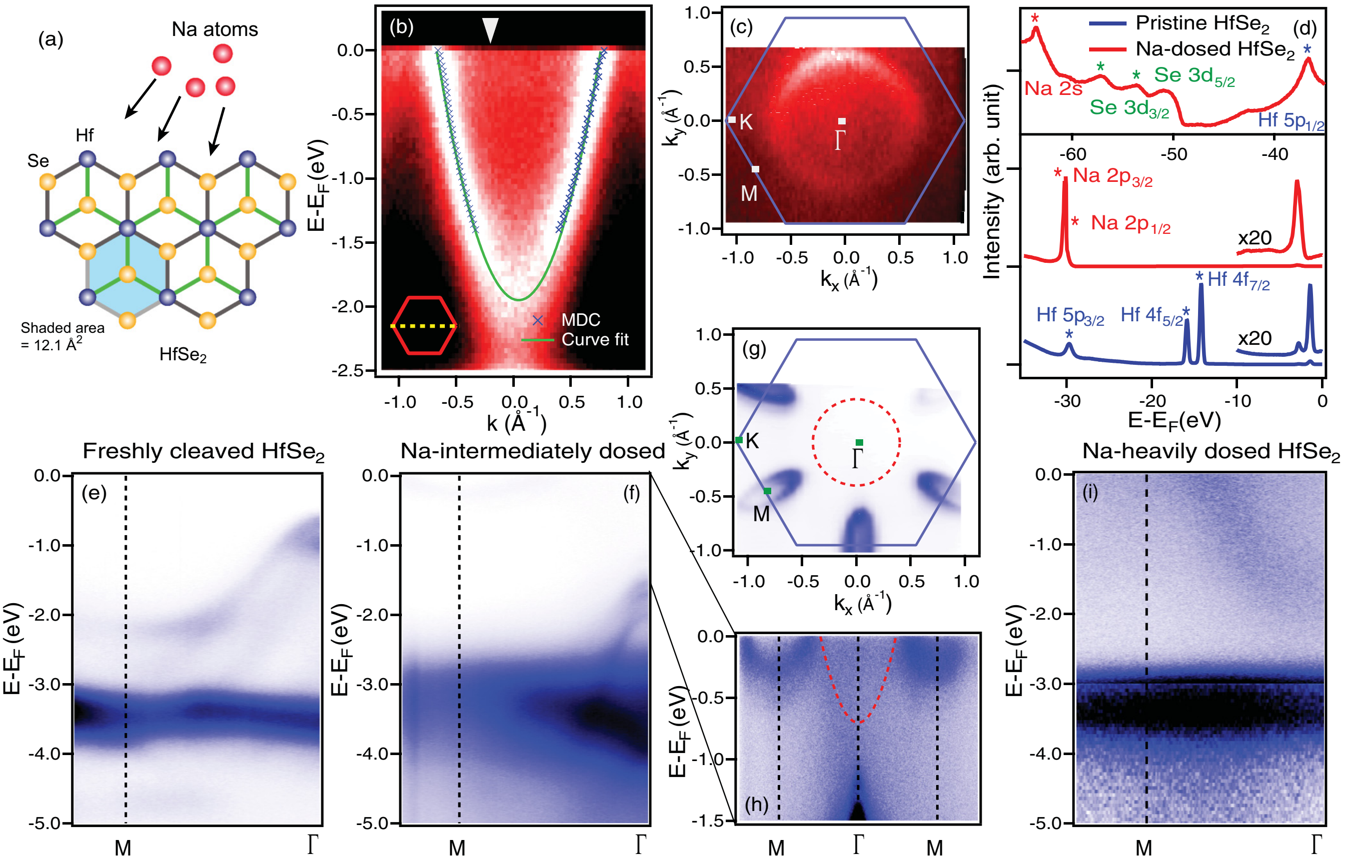

FIG. 1. (a) The atomic structure of HfSe$_2$ surface (top view). (b) Parabolic band dispersion of heavily evaporated Na atoms on the surface of HfSe$_2$. (c) Corresponding Fermi surface map of the band in (b). (d) Angle-integrated photoemission spectra of freshly cleaved and Na heavily evaporated HfSe$_2$, showing the core levels of Hf and Na (photon energy = 50 and 80 eV, respectively). (e), (f), and (i) show the valence bands of freshly cleaved, intermediately dosed (2 min of dosing), and heavily dosed HfSe$_2$ (5 min of dosing), respectively. (h) shows the zoom-in data of the HfSe$_2$ band dispersion in (f), as indicated; the dashed line shows a faint Na band dispersion. (g) shows the Fermi surface map of intermediately dosed HfSe$_2$; note that this map is a different sample with similar dosing.

for higher contrast); this may be due to a possible intercalation of a small fraction of Na atoms into the first van der Waals gap in HfSe$_2$, similar to the case of MoS$_2$ [18].

Our observations of a dispersive band and a clearly defined Fermi surface are indicative of a uniform and well-ordered metallic layer atop our semiconducting HfSe$_2$ substrate. To estimate the Na coverage, we perform additional measurements for shorter Na deposition times. As shown in Figs. 1(e)–1(h), after depositing Na on the surface for 2 min, the HfSe$_2$ valence bands present in the freshly cleaved material [Fig. 1(e)] are still clearly visible, but shifted to a higher binding energy concomitant with filling of the HfSe$_2$-derived conduction band states (charge transfer from the Na to the HfSe$_2$ populates the conduction band with carriers). The total electron density extracted from the Luttinger area of these conduction band pockets is estimated to be around 3.8×10^{14} cm^{-2}. Assuming a constant deposition rate, and assuming that each Na donates one electron, this would give a Na coverage of 9.4×10^{14} atoms cm^{-2} for the 5 min deposition. This is very close to the experimentally extracted Luttinger count identified from the heavier dose above, implying that the results shown in Figs. 1(b) and 1(i) are from approximately 1.1 monolayers (ML) of Na on HfSe$_2$.

This is further confirmed by comparing the angle-integrated core-level spectra before and after Na evaporation, as shown in Fig. 1(d). Before evaporation, Hf ($4f_{5/2}$ and $4f_{7/2}$) peaks can be clearly observed at a binding energy of around 14–17 eV [32,34]. After the heavy Na evaporation, Na ($2p_{3/2}$ and $2p_{1/2}$) peaks at ~30 eV binding energy become pronounced [35] while the spectral weight of the Hf $4f$ peaks is almost completely suppressed. This confirms a uniform coverage of the Na overlayer. Additional Hf- and Se-derived core levels are still observed at higher binding energies [e.g., between 35 and 60 eV, Fig. 1(d)]. Due to the extreme surface sensitivity of photoemission performed at these photon energies, these results (i.e., suppression of intensity for HfSe$_2$ bands at both the Fermi level and at higher binding energy) are entirely consistent with a single monolayer coverage of Na.

We now turn to our key observation that this Na monolayer hosts carriers with an effective mass so close to that of a free electron. In particular, this can be contrasted with similar systems such as a single monolayer of Na on Cu(111) where the measured effective mass has been determined to be as heavy as $1.3m_e$ [24]. This was suggested as a possible result of hybridization with the Cu substrate. We note that, in that case, the much smaller in-plane lattice constant of Cu(111)

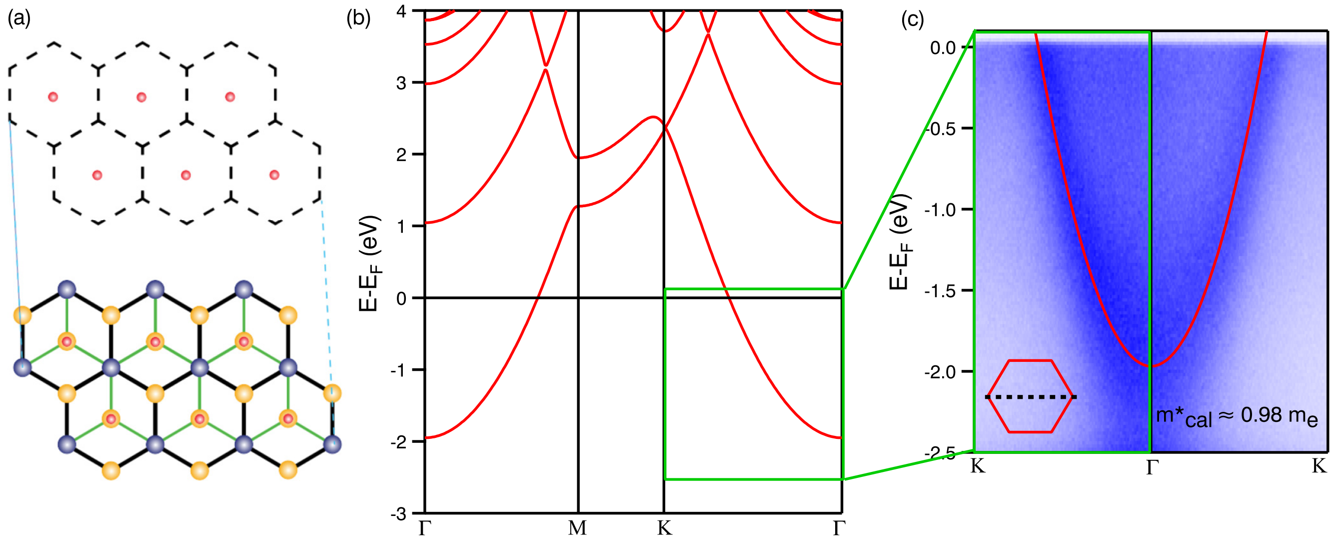

FIG. 2. (a) Atomic structures of monolayer Na on HfSe$_2$ (below) and bare monolayer Na (above) which is used for calculating the band structure in (b). (c) shows the zoom-in bands in the indicated box on top of the experimental data from Fig. 1(a).

(2.21 Å [36]) as compared to bulk sodium ($a = 3.77$ Å) may cause a greater overlap of the wave functions of Na and Cu, implying such a hybridization can easily occur. Here, however, the in-plane lattice constant of the substrate (HfSe$_2$; $a = 3.74$ Å) is very similar to that of the Na lattice. Moreover, HfSe$_2$ is a layered material, dominated by weak van der Waals bonding between layers as in other transition-metal dichalcogenides [18,37,38]. As such, hybridization between the Na- and HfSe$_2$-derived states can be expected to be substantially weaker.

Based on this assumption of such a weak interaction, we perform first-principles calculations of the band structure of an isolated Na monolayer (see Fig. 2). The calculations were carried out within the framework of density functional theory with projector augmented wave potentials (PAW) [39] as implemented in the VASP code. The Perdew-Burke-Ernzerhof (PBE) approximation is used for the exchange correlation terms [40,41]. The electron wave functions were described using a plane wave basis set with an energy cutoff of 520 eV. To calculate the 2D electronic band structures of the Na monolayer, a periodic slab of monolayer Na[001] ($P6_3/mmc$ hexagonal structure) with 20 Å vacuum spacing between layers to prevent interlayer interactions was used. The positions of Na atoms were relaxed until the Hellmann-Feynman forces become less than 0.001 eV/Å [42] while the in-plane cell vectors are kept at the theoretical relaxed bulk value $a =$ 3.76 Å (experiment 3.77 Å) which is approximately the same as the HfSe$_2$; this should therefore be a reasonable representation of our situation realized experimentally, as previous low-energy electron diffraction (LEED) studies show that Na overlayers form commensurate with the underlying substrate [e.g., Cu(111) and Ru(0001) [43–45]]. For k-space integrations, we used the Monkhorst-Pack scheme [46] with $11 \times 11 \times 1$ k-point sampling.

The calculated bands are shown in Fig. 2(b). These show a clearly dispersive band, which has an effective mass, $m^*_{\mathrm{cal}} \approx 0.98 m_e$. This is in excellent agreement with our ARPES data, as shown in Fig. 2(c), where the calculations are overlaid on the data. This suggests that the larger lattice constant of this substrate as compared to previously investigated examples could be key in stabilizing the free-electron-like behavior in a

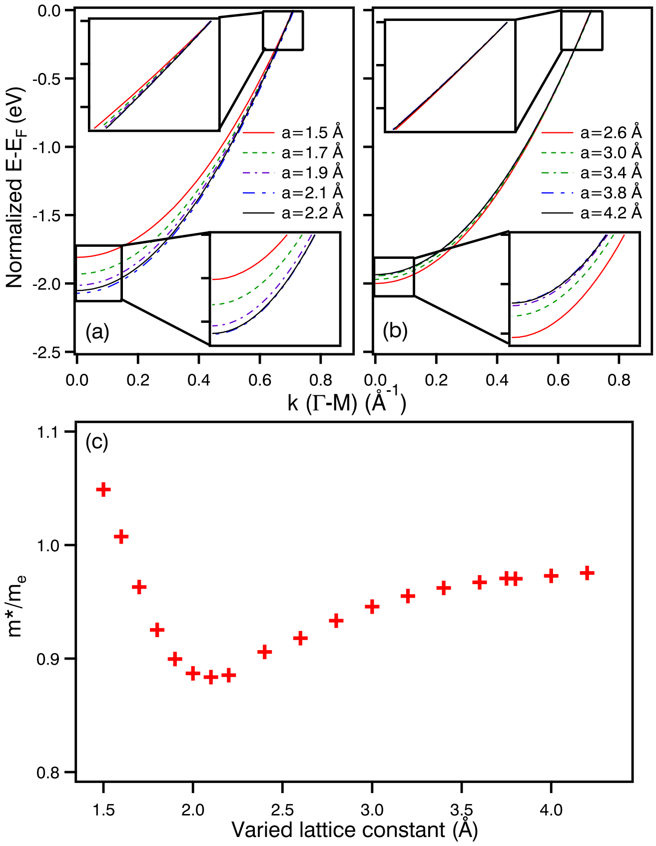

FIG. 3. (a) and (b) show calculated band dispersions of bare monolayer Na with various lattice constants between 1.5 and 4.2 Å. The insets show the zoom-in bands at the Fermi level and the band bottoms. (c) shows the effective masses extracted from the calculations in (a) and (b).

monolayer of Na. We note, also, that the high carrier densities can be expected to lead to very strong electronic screening, and, as such, the exchange interaction (which can make the effective mass lighter) will remain small in comparison to the kinetic energy. This is in contrast to other two-dimensional electron gases (2DEGs) stabilized in much more poorly screening materials, such as at the interfaces/surfaces of oxides and low-doped dichalcogenides [19,29,30]. We note that, as the lattice constant is reduced in our calculations (Fig. 3), and where screening can be expected to become less efficient, the effective mass of an isolated layer of Na can indeed become smaller than 1. At the smallest values, below 2.1 Å, however, an increase in correlation energies cause the correlation term to dominate over exchange, leading to a steep increase in the effective mass.

Our findings show that, even for a simple model system of an alkali-metal single layer, there is a possibility to engineer band structures via a judicious choice of material substrates. In other words, a two-dimensional material cannot be considered in isolation. Its electronic structure can be influenced directly, via hybridization with the supporting medium, but also via many-body effects, e.g., by balancing and controlling the ratio of the exchange and correlation energies both to each other and to the kinetic energy. Understanding the fundamentals of this process will be key to designing desired properties in two-dimensional materials, e.g., negative electronic compressibility [19] and fast band-gap renormalization [47,48]. Here, we show that by using a transition-metal dichalcogenide semiconductor as a support for a metallic Na single layer, we demonstrate that it is possible to minimize both of these effects, realizing the unusual situation of an almost ideal nearly-free-electron system with $m^* \sim 1m_e$.

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Data underpinning this publication can be accessed at http://personal.sut.ac.th/worawat/PRB2016a/.

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