Confined monolayer Ag as a large gap 2D semiconductor and its many-body interactions with high-density Dirac electrons.

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2D materials have intriguing quantum phenomena that are distinctively different from their bulk counterparts. Recently, epitaxially synthesized wafer-scale 2D metals, composed of elemental atoms, are attracting attention not only for their potential applications but also for exotic quantum effects such as superconductivity. By mapping momentum-resolved electronic states using time-resolved and angle-resolved photoemission spectroscopy (ARPES), we reveal that monolayer Ag confined between bilayer graphene and SiC is a large gap (> 1 eV) 2D semiconductor, consistent with GW-corrected density functional theory. The measured valence band dispersion matches DFT-GW quasiparticle band. However, the conduction band dispersion shows an anomalously large effective mass of 2.4 m0 that we attribute to interactions with high-density Dirac electrons in a bilayer graphene capping layer.
The capability to synthesize materials with atomic layer precision has enabled many scientific discoveries and advanced technologies, exemplified by the discovery of graphene and its derivatives\(^1\text{--}^4\). Epitaxial metal layers have also inspired discoveries of several novel quantum effects in the ultra-thin regime\(^5\text{--}^8\) although their investigations are often limited to ultra-high-vacuum environments unless the surface is properly protected and stabilized, e.g. by a capping layer\(^9\). Recently, a novel intercalation method was developed in which confined metal layers can be realized between a SiC substrate and a bilayer graphene (BL-Gr) capping layer which prevents oxidation of the confined epitaxial metals\(^10,11\). More intriguingly, such a confined metal layer may harbor novel electronic properties\(^12,13\). For example, density functional theory (DFT) predicted that silver- and indium-monolayer (MLs) are narrow gap semiconductors due to their hybridization with the underlying SiC\(^14\). Indeed, recent ARPES investigations of intercalated Ag monolayer revealed the existence of a valence band maximum (VBM) below the Fermi level\(^15\). Because excited states are not accessible using static-ARPES, it is not known what the bandgap is, whether it is a direct or indirect gap, or what the excited-state energy-momentum dispersions are.

Here we report ARPES and time-resolved ARPES (trARPES) investigations of the electronic structures of both occupied and unoccupied states in the confined Ag-ML between a SiC substrate and BL-Gr. We find that the confined Ag-ML is indeed an artificial 2D semiconductor with a surprisingly large bandgap (~ 1 eV). Theory predicts this bandgap correctly when quasiparticle effects were accounted for (without the inclusion of graphene layer) using GW calculations on top of mean-field DFT results. The valence band dispersion is found to be consistent between the experiment and DFT-GW calculations. However, the conduction band dispersions differ substantially. The experimental effective mass is found to be a factor of 2.6 larger than the theoretical prediction. Moreover, the energy at the M point is revealed to be only 0.14 eV higher than the conduction band minimum (CBM) at the Γ point, in stark contrast to a predicted value of 0.6 eV in DFT-GW calculations. These unusual features demonstrate a massive renormalization of the conduction band dispersion. Considering the high electron density in BL-Gr measured to 2
be \( \sim 4 \times 10^{13}/\text{cm}^2 \) with the Dirac point \( \sim 0.6 \text{ eV} \) below the Fermi level, we attribute the extraordinary band renormalization to the strong coupling between the conduction band electrons in Ag-ML and the intersubband plasmons in the BL-Gr layer. These results highlight a novel strategy of electronic band engineering in the ultimate 2D limit.

The atomic structure of the confined metal monolayer and the experimental setup are illustrated in Fig. 1a. At the thermodynamic ground state, the Ag monolayer assumes the lattice constant of SiC with surface Ag atoms projecting vertically onto the second topmost layer of C sites in the SiC substrate; the next most stable Ag registry (Ag projecting onto the topmost C sites) is higher in energy by +8 meV per Ag. Both configurations are realistic and considered in theory discussions later. The bilayer graphene protects the confined epitaxial Ag from oxidation, allowing sample transport under ambient conditions. The confined growth of metal monolayers using epitaxial graphene as a template has been described previously \(^{10}\). The same procedure is used in this study to intercalate Ag atoms between the bilayer graphene and SiC substrate. All samples are cleaned.

**Figure 1 Monolayer Ag atomic structure and surface characterization.** (a) Schematics of the experiments and the atomic structure of intercalated Ag between bilayer graphene and SiC. (b) Low energy electron diffraction (LEED) images were acquired before and after Ag intercalation. (c) STM topography (top) and its real space fast Fourier transform (FFT) image (bottom). (d) Brillouin zones of monolayer Ag and bilayer graphene.
in the ultra-high-vacuum (UHV) chamber (pressure \(< 1 \times 10^{-10} \text{ mbar}\)) by overnight annealing at 220 °C. A thoroughly cleaned sample exhibits a sharp graphene 1×1 LEED pattern co-existing with another pattern consistent with the SiC lattice constant (Fig. 1b). The commonly observed sharp $6\sqrt{3} \times 6\sqrt{3}R30^\circ$ patterns for pristine BL-Gr on SiC become a fuzzy ring, suggesting a decoupling of BL-Gr and SiC due to Ag intercalation. STM studies, however, still exhibit a quasi $6\times6$ superstructure superimposed on the graphene 1×1 lattice (Fig. 1c), consistent with the Ag monolayer following the SiC lattice constant. Based on this structural information, the surface Brillouin zones (BZs) for BL-Gr and Ag-ML and their orientation relationship are shown in Fig. 1d. The valence band dispersion is mapped out using static-ARPES with $h\nu = 21.2$ or $40.8$ eV. The conduction band structure is mapped out using trARPES. The photon energy of the pump pulse is tuned from 1.5 to 3.2 eV. The probe pulse has a fixed photon energy of 6 eV restricting accessible unoccupied states in the BZ within \(\pm 0.2 \text{ Å}^{-1}\) near the $\Gamma$ point.

**Figure 2** Occupied and unoccupied electronic structures of monolayer Ag. (a, b) Occupied band dispersions along with the high symmetry points. (c, d) Second derivative images of (a) and (b) respectively. (e) Unoccupied structure of the monolayer Ag along the $\Gamma - K$ direction. (f) The effective mass was determined from EDC fittings from (e). (g) DFT-GW calculated band dispersion superimposed with acquired experimental images. The experimental conduction band dispersion near the $\Gamma$ point (upto $k_{\parallel} = 0.2 \text{ Å}^{-1}$) is marked by a red curve. The energy location at the $\bar{M}_{Ag}$ point is marked by a red bar. The grey dashed line is just a guide to eyes connecting the experimental data points near $\Gamma$. 

The band dispersions for the occupied states of Ag monolayer are obtained along two major directions, $\Gamma - K_{Ag}$ and $\Gamma - M_{Ag}$. The raw data using 21.2 eV photon energy is shown in Fig. 2a and 2b respectively, and the second derivative enhanced spectra are shown in Fig. 2c and 2d. The valence band maximum (VBM) is identified at $K_{Ag}$ with a binding energy of $\sim 0.45$ eV below $E_F$. At the saddle point $M_{Ag}$, a local maximum is identified as $M_v \sim -1.25$ eV. Near the $\Gamma$ point, the SiC band structure is also observed with SiC$_{VBM}$ located around $-1.8$eV. The same band dispersion acquired with different photon energy (40.8eV) can be found in Fig. S1. We note that our VB mapping result is very similar to that reported recently for ML-Ag confined between ML-Gr and SiC$^{15}$, except for the absolute energy relative to the Fermi level.

The CBM, as revealed by trARPES using 3 eV pump photons, is located at $\Gamma$ with the energy position at $\sim 0.56$ eV above $E_F$ (Fig. 2e). The peak position does not show probe power dependent, indicating the absence of space charge effect (Fig. S2). Moreover, the possibility that this state is due to the imaging potential is ruled out by performing pump photon energy dependence (Fig. S3). The conduction band dispersion is mapped out from $k_\parallel = 0$ to $k_\parallel = 0.2$ Å$^{-1}$. The measured conduction band dispersion allows us to determine an effective mass of $2.4 \pm 0.3 m_0$ (Fig. 2f). The acquired occupied/unoccupied band dispersions reveal an indirect gap of 1.01 eV, a value significantly larger than the earlier DFT prediction of 0.2 eV$^{14}$.

To better capture this large bandgap feature, we carried out GW corrections to the DFT calculation (see details in Methods) and superimposed the results on the experimental observation as shown in Fig. 2g. To make the DFT-GW calculations computationally feasible, the graphene cap is excluded, which simplifies the computation cell to a minimal SiC surface unit cell. The calculation predicts a bandgap value of $\sim 1.15$ eV, consistent with the experimental observation. Moreover, the valence band dispersion from the DFT-GW calculations agrees well with the experimental results.
By contrast, the calculated conduction band dispersion clearly differs from the experimental observation. The GW quasiparticle band dispersion near CBM yields an effective mass of $0.94 m_0$, a factor of 2.6 lighter than the experimental estimate. Moreover, as discussed further below, while the GW calculation shows that the conduction band energy at $M_{Ag}$ is $\sim 0.6$ eV above the CBM, the experiments indirectly determines it to be only $0.14$ eV above the CBM. Thus, one can conclude that the conduction band energy-momentum dispersion is dramatically renormalized.

![Figure 3 Indirect bandgap determination at $M_{Ag}$ point and ultrafast decay of CBM.](image)

(a) CB intensity versus pump photon energy. 4mW pump power was used for the measurements. (b) Pump power dependence of CB intensity at different pump photon energies. Linear and quadratic dispersions reflect one-photon absorption (1PA) and two-photon absorption (2PA) processes at each photon energy respectively. (c) Photoelectron intensity versus energy and time delay. The CBM intensity distribution was represented with white dots. (d) Schematic of 1PA and 2PA process at different critical points. Near the photon energy of 1.95eV, electrons at $M_{Ag}$ point are excited directly via the 1PA process to the CB. On the other hand, the smaller photon energies can also excite the electrons to $\Gamma$ point CB via 2PA, resulting in lower photo-excitation density than the 1PA process.
To gain further insight, trARPES is carried out as a function of the pump photon energy. Fig. 3a shows the photoelectron intensity near the CBM as a function of pump power for four different pump photon energies. The quadratic dependence on the pump power clearly shows two-photon absorption (2PA) processes for $h\nu = 1.5$ and 1.7 eV. On the other hand, for $h\nu = 1.95$ and 2.9 eV, only the one-photon absorption event is involved. Fig. 3(b) shows the photoelectron intensity near the CBM vs. pump energy at a constant incident pump fluence of ~ 85μJ/cm$^2$. The plot shows that as the $h\nu_{pump}$ drops below 1.95 eV, the excitation efficiency to the conduction band quickly decreases, consistent with the existence of a threshold of $h\nu \approx 1.95$ eV for transition from 2PA to 1PA process. Fig. 3c shows the delay time dependence of photoelectron intensity at the CBM which exhibits a gaussian intensity distribution. This implies that the excited states in the CB decay rapidly at a time scale shorter than our upper limit of a time resolution (FWHM ~ 400fs). Such rapid decay is likely due to interactions with the high electron density in the bilayer graphene.

As the direct gap at the $\Gamma$ point is ~ 2.35 eV, it is not surprising that excitations to the CB using $h\nu = 1.5$ and 1.7 eV require two-photon absorption (and for that matter, one photon absorption for $h\nu = 2.9$ eV) (see Fig. 3d). What is surprising is that only one photon absorption is involved for $h\nu = 1.95$ eV which is smaller than the direct gap at the $\Gamma$ point. We noted that $\bar{M}$ is a saddle point, representing the existence of a van Hove singularity with a high density of state (DOS). This suggests that 1.95 eV absorption involves the VB to CB excitation at $\bar{M}$. This conjecture will place the conduction band $\bar{M}$ point at an energy location of 0.7 eV above the Fermi level, which is only 0.14 eV above the CBM. By contrast, the calculated quasiparticle bands shows an energy difference of 0.6 eV. Given that the effective mass is renormalized by a factor of 2.6 from GW results, it is reasonable to expect the $\bar{M}$ point energy to be lower than the GW results (dashed lines in Fig. 3d). All experimental evidence points to the fact that the conduction band electronic structure is massively renormalized. This point will be discussed further after we discuss the electronic structures of BL-Gr in this hybrid structure.
Shown in Fig. 4a are $E$ vs. $k$ mappings for a series of k-space segments perpendicular to the $\Gamma - \bar{K}_{Gr}$ direction. The zoomed-in image of the band mapping at $\bar{K}_{Gr}$ is shown in Fig. 4b. One can see a gap opening at the Dirac point (DP) due to the lattice symmetry breaking along the c-axis creating a vertical electric field $^{16,17}$. The splitting between the coupled Dirac bands in BL-Gr is observable with two Fermi wavevectors, $k_{F,1} = 0.11 \pm 0.01 \text{Å}^{-1}$ and $k_{F,2} = 0.03 \pm 0.01 \text{Å}^{-1}$. The energy separation for the two Dirac bands above the DP is $\sim 0.36$ eV. The Fermi velocity $v_F$, fitted at $k_{F,1}$, is $0.55 \times 10^6 \text{cm/s}$, about half of the Dirac velocity of the unperturbed Dirac cone in single-layer graphene. The Dirac electron density, $n_s$, is related to the Fermi wavevector by $n_s = k_F^2/\pi$, from which we calculate an electron density of $\sim 4 \times 10^{13}/\text{cm}^2$. The BL-Gr electronic structure is consistent with previously reported results for the same density $^{16}$. 

Figure 4 High electron density in the bilayer graphene and plasmon-induced effective mass enhancement. (a) Dirac cone dispersions were acquired along the $\Gamma - \bar{K}_{Gr}$ direction. (b) Zoomed-in Dirac cone at $\bar{K}_{Gr}$ point. (c) Schematic Dirac band dispersions derived from (b). Two Fermi wavevectors and Dirac point were identified. (d) Energy shift of “dressed” states which leads to flattening of band dispersion.
We now discuss the anomalously large mass renormalization of conduction band observed using trARPES. Band renormalization of 2D semiconductors in proximity to the graphene or graphite layers has been intensively investigated recently. Such a renormalization effect is often attributed to dielectric/Coulomb screening from graphitic substrates\textsuperscript{18–22}. In our case, the measured bandgap size is 0.15 eV smaller than the DFT-GW result (1.15 eV). The difference can be attributed to screening from graphene layers, which was not explicitly included in the GW calculations. However, such a dielectric/Coulomb screening effect leads primarily to rigid band shifts, and cannot explain the anomalously large effective mass observed in the conduction band. We note that trAPRES probes the excited state spectrum and is subjected to different kinds of many-body interactions. It has been reported that excitonic effect can influence the apparent dispersion\textsuperscript{23,24}. However, such an effect occurs when the exciton population is considerably higher than free carriers and manifests at a longer time scale. Thus, it cannot explain the observed phenomenon. A totally new mechanism is needed to explain the anomalously large effective mass in the CB observed using tr-ARPES, which we discuss below.

As shown in Fig. 4c, the high density electrons occupy two Dirac bands with two Fermi wavevectors $k_{F,1} = 0.11 \text{Å}^{-1}$ and $k_{F,2} = 0.03 \text{Å}^{-1}$, supporting \textit{inter-subband plasmonic modes} with $\vec{q}$ values between $k_{F,1}$ and $k_{F,2}$\textsuperscript{25}. This facilitates a large phase space for interactions with quasiparticles in the 2D semiconductor conduction band. We attribute the large mass renormalization to such interactions via a process that is analogous to the electron-phonon polaron mass enhancement, with the lattice phonon modes replaced by BL-Gr inter-band plasmons. In this process, the semiconductor conduction band energy at momentum $\vec{k}$ is shifted down in energy due to dressing by excited states in which an inter-band plasmons with wavevector $\vec{q}$ is excited in the bilayer graphene and the conduction band momentum is shifted from $\vec{k}$ to $\vec{k} - \vec{q}$. Such a “dressed state” has a negative energy shift relative to the undressed state with $\Delta \varepsilon_k \sim - \sum_q \frac{v_{k,q}^2}{\varepsilon_k^2 - \varepsilon_k + \hbar \omega_{p1}(\vec{q})}$.
where \( V_{k,q} \) depicts the coupling to the virtual state. A conceptual understanding of mass enhancement is described below (full calculations of coupling matrix elements will be described elsewhere). Note that for the inter-subband plasmon mode, \( \hbar \omega_{pl}(q) \sim 0.36 \text{ eV} \) which is insensitive to the \( q \) value. On the other hand, \( \varepsilon_{k-q} - \varepsilon_k \) is a negative value whose magnitude increase on an average with increasing wavevector \( \mathbf{k} \) (see Fig. 4d). Thus, the denominator decreases with a larger \( k \). This yields a more negative \( \Delta \varepsilon_k \) at a larger \( \mathbf{k} \) value, leading to a less dispersive quasiparticle dispersion and a heavier effective mass.

In summary, by combining ARPES and trARPES to probe momentum resolved quasi-particle dispersions for both the equilibrium and excited states, we reveal that a confined Ag monolayer between SiC and BL-Gr is an artificial 2D semiconductor with an indirect band gap of 1 eV. In addition, we show that the equilibrium quasi-particle dispersion in the valence band dispersion is well captured by the DFT-GW calculation. On the other hand, the excited state dispersion in the conduction band is dramatically different, exemplifying by an anomalously large effective mass (a factor of 2.6 enhancement). We attribute this massive renormalization effect to many-body interactions between the conduction band electrons in this 2D semiconductor and high-density Dirac electrons in BL-Gr, leading to “plasmon-polaron dressed” quasi-particle states. Such novel many-body interactions have important implications in low dimensional quantum devices.
Methods

Experimental details

ARPES/ 6eV-trARPES measurements

Scienta R3000 hemisphere analyzer was used to collect the photoemission spectra for both static-ARPES and 6eV-trARPES measurements. The static ARPES measurements were carried out with a Helium lamp using He I-α (21.2eV) and He II-α (40.8eV). During the helium lamp measurements, the pressure was better than $6 \times 10^{-10}$ Torr. The 6eV-trARPES measurements were performed using probe pulse (206nm) and pump pulse (826–387nm). The pressure was maintained below $8 \times 10^{-11}$ Torr. The fundamental 1030nm pulses from a Carbide laser of Light conversion were used for the 5th harmonic generator (HIRO) and Orpheus-HP optical parametric amplifier (OPA) to generate the pump and probe pulses at 100 kHz repetition rate. All measurements were performed at room temperature. The pump-probe cross-correlation width was estimated as 400 fs (FWHM) via the fastest photoemission dynamics. The incident fluence was ~85μJ/cm².

Computational details

DFT-GW calculations were based on the Ag/SiC structure described in the main text. Additional DFT calculations were performed for structures with Ag projecting onto the topmost C sites and onto the topmost Si sites, where M point energies were 0.47 and 0.80 eV relative to the CBM respectively, neither smaller than that of the main Ag/SiC structure we considered 0.45 eV. This excludes the possibility that the small M point energy could be due to a thermodynamically competing Ag surface phase. In all DFT-GW calculations, we employ an 18×18×1 k-point grid and a truncated Coulomb interaction. We employ the extrapolar technique to achieve convergence for all quasiparticle band energies within 0.05 eV. Extrapolar energy of 2.0 Ha was extracted from systematic convergence studies, allowing accelerated convergence at a plane-wave energy cutoff of 10 Ha and 100 empty bands for the evaluation of the dielectric matrix and self energies. The calculated static dielectric matrix was extended to finite frequencies using the Godby–Needs-generalized plasmon-pole model. All calculations are performed using the ABINIT code.
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Contributions

W.L., J.A.R., and C.K.S. conceived the experiment. W.L. carried out trARPES/ARPES measurements. Y.W. and V.C. performed DFT-GW calculations. R.M., C.D., and J.A.R. prepared the sample. M. L. performed STM measurements. W.L. created a platform for 6eV trARPES and UHV investigation with participation of H.K., T.N.N., and B.F. under joint supervision of C.K.S. and X.L.. A.H.M. proposed the theoretical model. W.L., C.K.S., and A.H.M analyzed the data. W.L. and C.K.S. wrote the manuscript with substantial contributions from all the authors.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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Supplementary information

Confined monolayer Ag as a large gap 2D semiconductor and its many-body interactions with high-density Dirac electrons.

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Figure S1 Occupied electronic band structure of 2D metal (Gr/Ag/SiC) acquired with 40.8eV photon energy. (a, b) Band dispersions obtained by static-ARPES along $\Gamma - K_{Ag}$ and $\Gamma - M_{Ag}$ respectively. (c, d) Second derivative images of (a) and (b).

Figure S2 6eV probe pulse power dependence at CBM. The intensity stands for photoelectron counts per second obtained by the electron analyzer. Below $I=23,000/s$, no space charge effect was observed. All data of this work was taken with the probe power below $I=9,000/s$. 
Figure S3 Pump photon energy dependence at CBM. The fact that the CBM peak position does not change on the different pump photon energy excludes a possibility of observing image potential states which can be excited by a 6eV pulse and detected by a pump pulse. In this case, the peak position changes depending on the pump photon energies.