Magnesium-intercalated graphene on SiC: highly n-doped air-stable bilayer graphene at extreme displacement fields

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We use angle-resolved photoemission spectroscopy to investigate the electronic structure of bilayer graphene at high n-doping and extreme displacement fields, created by intercalating epitaxial monolayer graphene on silicon carbide with magnesium to form quasi-freestanding bilayer graphene on magnesium-terminated silicon carbide. Angle-resolved photoemission spectroscopy reveals that upon magnesium intercalation, the single massless Dirac band of epitaxial monolayer graphene is transformed into the characteristic massive double-band Dirac spectrum of quasi-freestanding bilayer graphene. Analysis of the spectrum using a simple tight binding model indicates that magnesium intercalation results in an n-type doping of $2.1 \times 10^{14}$ cm$^{-2}$, creates an extremely high displacement field of 2.6 V/nm, opening a considerable gap of 0.36 eV at the Dirac point. This is further confirmed by density-functional theory calculations for quasi-freestanding bilayer graphene on magnesium-terminated silicon carbide, which show a similar doping level, displacement field and bandgap. Finally, magnesium-intercalated samples are surprisingly robust to ambient conditions; no significant changes in the electronic structure are observed after 30 minutes exposure in air.

Keywords: Graphene, extremely high displacement field, electronic structure, ARPES, air exposure
INTRODUCTION

Graphene, a single layer of $sp^2$ bonded carbon atoms [1], has an exceptionally high intrinsic electrical conductivity [2], yet is nearly 98% transparent to light [3] across a broad spectrum of wavelengths, making it attractive as a transparent conductor for a variety of applications.

Moreover, doping may be used to significantly modify graphene’s electrical and optical properties. Graphene’s conductivity can be tuned dramatically with doping [1], and in highly doped graphene achieved via chemical means [4,5] conductivity can often reach values near the intrinsic limit set by room temperature acoustic phonon scattering. Doping can be used to alter graphene’s workfunction [6], which can be exploited to make new types of electronic devices [7] or more efficient contacts to semiconductors [8]. Doping also alters graphene’s optical absorption properties. For example, Pauli blocking, where interband optical transitions for energies lower than twice the Fermi energy are forbidden, causes an increase in transparency, an effect which can be exploited for optoelectronic switching [9] or increased performance in transparent conductors [5,10]. In bilayer graphene, doping can produce a displacement field which opens a bandgap at the Dirac point, additionally altering the electronic and optical properties [11–17].

A variety of approaches have been used to tune graphene’s properties via doping, including field-effect gating [6], electric double layer gating [15,18], electrolytic gating [19], chemical substitution [20,21], adsorption [11,22,23], and intercalation [24–27]. Among these, chemical doping offers a simple, powerful approach to create highly-doped graphene layers which can be incorporated as transparent conductors, electrodes or optical elements in a wide variety of device structures. To be widely applicable, the chemical doping approach should result in a highly-doped graphene layer which is stable under processing conditions such as ambient exposure and high temperature. Several chemical doping approaches have been demonstrated to successfully produce stable highly p-doped graphene [28–31] with p-type carrier density exceeding $10^{14}$ cm$^{-2}$. Stable n-doped graphene is also desirable, particularly for applications requiring low work function (as compared to an increased work function in the case of p-doping). However the production of stable n-doped graphene has been more difficult, with only a few demonstrations [26,32,33]. In large part, difficulty in producing stable n-doped graphene is due to the highly reactive and air-unstable nature of n-type dopants. Despite this, highly air-stable, n-doped single-layer graphene was obtained by CsCO$_3$ [32] and ZnO [33] doping, attaining electron concentrations of $2.2 \times 10^{13}$ cm$^{-2}$ and
These values do not significantly exceed the natural doping found in epitaxial monolayer graphene (EMLG) on SiC [34], so achieving extremely high and stable n-doped graphene remains an open challenge.

Here, we use angle-resolved photoemission spectroscopy (ARPES) to demonstrate that magnesium intercalation of epitaxial monolayer graphene on 6H-silicon carbide (SiC) creates quasi-freestanding bilayer graphene on a magnesium-terminated SiC substrate (Mg-QFSBLG). Analysis of the electronic spectrum using a simple tight binding model indicates high n-doping (>2 × 10^{14} cm^{-2}). The exceptionally high displacement field produced by the charge transfer from the intercalated magnesium to graphene opens a large (0.36 eV) bandgap at the Dirac point. Moreover, the high level of n-doping is stable after heating to 350 °C, as well as 30 minutes of exposure to air. The electronic spectrum of the highly n-doped bilayer graphene is well described by a simple tight-binding model for bilayer graphene with displacement field. First principles density-functional theory (DFT) calculations corroborate that magnesium intercalation produces quasi-freestanding bilayer graphene with good agreement in doping level, Fermi energy, and bandgap to our experimental values.

METHODS

Epitaxial monolayer graphene samples of nominally sub-monolayer coverage were grown on a silicon face of a semi-insulating 6H-SiC substrate by silicon sublimation from the SiC, as described in Ref. [35]. Sample preparation, ARPES, and low-energy electron diffraction (LEED) measurements were carried out at the Toroidal Analyzer endstation at the Soft X-ray Beamline of the Australian Synchrotron. Samples were introduced to ultra-high vacuum (UHV, base pressure of 1 × 10^{-10} mbar), and annealed overnight at 500 °C. Sample cleanliness was confirmed by LEED and ARPES. A magnesium effusion cell was baked at 150 °C overnight and outgassed at 415 °C. Once the pressure reached 1 × 10^{-7} mbar, the effusion cell was inserted into the UHV preparation chamber. Magnesium (1/8 inch turnings, 99.95%, Sigma Aldrich) was intercalated following the recipe from Ref. [36]: Magnesium was evaporated for 25 min, with the magnesium cell held at 400 °C, and deposited on the graphene/SiC substrate held at room temperature in thickness of 188 Å, as determined by quartz crystal microbalance. Following the deposition, the graphene/SiC substrate was annealed at 350 °C for 30 min to facilitate magnesium intercalation under the graphene. For the air exposure experiment, after 30 minutes of air exposure, the sample was reintroduced to UHV and annealed at 350 °C for several hours prior to measurements.
Structural characterisation of the samples was undertaken using LEED (OCI™ 3 grid reverse view optics, 200 μm spot size) at room temperature, at energies between 56 eV and 200 eV, in-situ in the endstation used for ARPES. ARPES measurements used a toroidal-type angle-resolving endstation [37] at the Soft X-Ray Beamline of the Australian Synchrotron. All ARPES data was taken at room temperature and a photon energy ($h\nu$) of 100 eV using linearly polarised light at normal incidence to the sample, with a beam spot size of 100 μm × 60 μm. The binding energy ($E_{\text{Bin}}$) scale for all spectra are referenced to the Fermi energy ($E_F$), determined using the Fermi edge of an Au foil reference sample in electrical contact with the sample. The total energy and wavevector ($k$) resolution as determined by the spectrometer and beamline performance is estimated to be 100 meV and 0.2 Å⁻¹, respectively. The toroidal analyser permits all polar ($\theta$) emission angles (-90° to +90°) to be measured along a high-symmetry azimuth ($\phi$) of the surface containing $\bar{\Gamma}$ point. The unique geometry therefore allows for measurement of the Dirac cone along the $\bar{K} - \bar{\Gamma} - \bar{K}$ direction without the need for complex alignment of the spectrometer. A simple rotation of the sample in azimuth was then used to measure the Dirac point along the $\bar{A} - \bar{K} - \bar{A}$ direction. Using this latter method avoids the well-known intensity suppression of half of the Dirac cone seen when measuring along $\bar{K} - \bar{\Gamma} - \bar{K}$ using this polarization geometry [38] and provides a more robust means of determining the Dirac point and carrier velocities. The $\bar{A} - \bar{K} - \bar{A}$ measurement direction; however, exhibits a lower $k_{||}$ instrumental resolution than in $\bar{K} - \bar{\Gamma} - \bar{K}$ direction, resulting in momentum-broadened data. This is a result of the lower angular resolution of the instrument when scanning $k_{||}$ using $\phi$ compared to $\theta$ [37]. Data taken along the $\bar{K} - \bar{\Gamma} - \bar{K}$ direction can be found in the Supplementary Material, section 2.

First principles density-functional theory calculations were implemented using the Vienna ab initio Simulation Package (VASP) to calculate the electronic structure of Mg-QFSBLG [39]. The Perdew-Burke-Ernzehof (PBE) form of the generalized gradient approximation (GGA) was used to describe electron exchange and correlation [40]. A semi-empirical functional (DFT-D2) was employed to describe van der Waals interactions in the system [41]. The kinetic energy cut-off for the plane-wave basis set was set to 500 eV. We used a $9 \times 9 \times 1$ $\Gamma$-centered k-point mesh for sampling the Brillouin zone. The unfolded band structure and Fermi surface were obtained using the KPROJ program based on the $k$-projection method [42,43].
RESULTS AND DISCUSSION

Intercalation is a method commonly used to tailor the properties of graphene [24–27,44,45]. The choice of the intercalant is often governed by research on graphite intercalation, which has led to the creation of so-called graphite intercalation compounds [46,47]. However, magnesium does not intercalate graphite [48], and therefore is not expected to intercalate in the galleries between graphene layers. Remarkably, in the case of EMLG on SiC, magnesium intercalation was recently observed [36]. In this case, intercalation is possible due to the different chemical nature of the silicon-graphene interface, where the silicon is bonded to the first carbon layer, known as the buffer layer (Figure 1a). During the intercalation process, magnesium, rather than intercalating the graphene layer, goes under the buffer layer and sits on top of SiC [36], as shown in Figure 1b. Once magnesium is intercalated under the buffer layer, it effectively cuts the bonds between the carbon atoms in the buffer layer and silicon dangling bonds, thus turning the buffer layer into a free graphene layer, and by extension transforming EMLG into Mg-QFSBLG.

In order to confirm that EMLG is converted structurally to Mg-QFSBLG we use LEED. Figures 1c and 1d show LEED images before and after magnesium intercalation, respectively. Before intercalation, we observe the characteristic LEED pattern of EMLG, with $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ reconstruction relative to the graphene lattice and $(6 \times 6)$ reconstruction relative to the SiC lattice characteristic of the buffer layer (orange and blue circles, respectively, Figure 1c) in addition to the $(1 \times 1)$ graphene and $(1 \times 1)$ SiC spots (green and gray circle, respectively, Figure 1c). After intercalation, the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ spots are greatly reduced in intensity, and graphene $(1 \times 1)$ spots are significantly more pronounced than $(1 \times 1)$ SiC spots, indicating a reduced interaction with the substrate [34]. Additional $(\sqrt{3} \times \sqrt{3})R30^\circ$ spots with respect to the $(1 \times 1)$ SiC spots are visible (yellow circle, Figure 1d) after intercalation and are attributed to the formation of the magnesium silicide-like surface reconstruction under the graphene [36]. The first principles calculations support the interpretation that EMLG is converted to the Mg-QFSBLG heterostructure, shown in Figure 1b, with the energy of Mg-intercalated structure lower than the energy of crystalline Mg on epitaxial monolayer graphene by 1.18 eV. Additional LEED data and more details on the calculation of relative energies can be found in the Supplementary Material, section 1 and 5, respectively.
LEED itself, being a structural technique, cannot provide insight into the effect of magnesium intercalation on the electronic structure of graphene. To assess electronic structure changes, a more direct probe of the electronic structure is needed. One such probe is the ARPES technique, which can directly visualise the electronic structure of materials and give information about doping, bandgap, number of layers, and many-body interactions [49,50].

**Figure 1.** Magnesium intercalated epitaxial monolayer graphene. Sketch of a) epitaxial monolayer graphene on SiC and b) magnesium-intercalated quasi-freestanding bilayer graphene on SiC. Brown spheres: carbon; blue spheres: silicon; blue lobes: silicon dangling bonds; red spheres: magnesium. LEED image of epitaxial monolayer c) before and d) after magnesium intercalation. LEED images taken at 71 eV and 126 eV, respectively, on the same sample. Sample was remounted between the LEED measurements. Green circle: (1 × 1) graphene lattice; gray circle: (1 × 1) SiC lattice; orange circles: (6√3 × 6√3)R30° reconstruction relative to graphene and blue circles: (6 × 6) reconstruction relative to SiC arising from the buffer layer, yellow circle: (√3 × √3) reconstruction of SiC surface by magnesium.

Figure 2 shows ARPES measurements, before and after magnesium intercalation. Figures 2a and 2b, show the Fermi surface (spectral weight as a function of in-plane momentum at constant energy at the Fermi level) of clean (non-intercalated) EMLG and Mg-QFSBLG, respectively. Here, the unique
toroidal analyser geometry [37] enables the detection of a full hemisphere (i.e. a 180° photoelectron emission window), which samples a wide k-space, encompassing multiple Brillouin zones. The differences in the Fermi surfaces are easily seen: Prior to the intercalation (Figure 2a) the Fermi surface consists of an individual circular feature characteristic of the single Dirac cone of EMLG [51]. Following magnesium intercalation (Figure 2b), an additional feature develops and the Fermi surface now consists of a circular feature enveloped by a triangular one. This is consistent with the bilayer graphene structure [11]. Note that the absence of the intensity on one side of the Fermi surface contour in the bilayer graphene case is due to the A-B sublattice symmetry breaking [38,51,52].

Figures 2c and 2d show the band dispersion along the $\bar{A} - \bar{K} - \bar{A}$ direction, as indicated schematically in the inset of Figure 2c. This direction is perpendicular to the $\bar{K} - \bar{F} - \bar{K}$ high-symmetry direction, and is chosen because there are no changes in the graphene band intensity along this vector due to matrix-element effects. Before intercalation, Figure 2c, a single set of linearly dispersing bands is visible, as expected for EMLG. The Dirac point position and Fermi velocity of $v_F = (1.17 \pm 0.02) \times 10^6$ m/s, a value similar to typically reported Fermi velocity for EMLG on SiC [53,54], were obtained from the linear fit (black line, Figure 2c) to the band position values (blue markers) taken from the momentum distribution curves (MDCs). The Dirac point lies below the Fermi level, $E_F - E_D = 0.35 \pm 0.01$ eV, corresponding to a carrier density of $n = (7.3 \pm 0.4) \times 10^{12}$ cm$^{-2}$.

After intercalation, Figure 2d, two sets of bands are visible, as is expected for bilayer graphene. Red (blue) markers represent the conduction (valence) band position values obtained from the MDCs. These values were fitted to a tight-binding model, Eq. 1, overlaid in black, for bilayer graphene under a perpendicular displacement field, based on Refs. [11,12,55]:

$$
\varepsilon_\alpha(k) = \pm \left[\frac{\gamma_1^2}{2} + \frac{U^2}{2} + \left(\nu^2 + \frac{\nu_3^2}{2}\right)k^2 + (-1)^\alpha \sqrt{\psi}\right]^{1/2},
$$

where $\alpha=1,2$ is the band index, and

$$
\psi = \frac{1}{4} \left(\gamma_1^2 - \nu_3^2 k^2\right)^2 + \nu^2 k^2 \left(\gamma_1^2 + U^2 + \nu_3^2 k^2\right) + 2 \gamma_1 \nu_3 \nu^2 k^3 \cos 3\varphi
$$

and $\nu_3 = \sqrt{3a\gamma_3}/2\hbar$. Here $k$ is the wavevector, $\varphi$ is the azimuthal angle, $\nu$ is the band velocity, $U$ is the difference in the onsite Coulomb potential of two graphene layers, $\gamma_1 = 0.4$ eV is the out-of-plane nearest-neighbour interaction parameter, $\gamma_3 = 0.12$ eV is the out-
of-plane next-nearest neighbour interaction parameter, \( a = 1.42 \) Å is the lattice constant of graphene, and \( \hbar \) is reduced Planck's constant [11].

Figure 2. Electronic structure of graphene on SiC before and after magnesium intercalation. Constant energy surfaces taken at the Fermi level showing a) monolayer graphene Fermi surface and b) bilayer graphene Fermi surface following magnesium intercalation. Inset shows two times magnified area around a \( \bar{K} \) point. Band dispersion of c) monolayer graphene before and d) bilayer graphene after magnesium intercalation. Blue and red markers are extracted band positions from momentum distribution curves (MDCs). Overlaid in black is c) linear fit and d) tight-binding model for \( U = 0.87 \) V, defined in the Eq.1 of the main text. e) and f) are extracted MDCs from the grey shaded area in c) and d), respectively, showing two (four) bands as expected for monolayer (bilayer) graphene, Bands were averaged in a 50 meV window, taken 1.1 eV below extrapolated Dirac point. All data taken at \( h\nu = 100 \) eV and at room temperature.

From the fit, we obtain the band gap value of \( E_G = 0.36 \pm 0.01 \) eV, in agreement with theory [13], and \( v = (0.97 \pm 0.04) \times 10^6 \) m/s, same order of magnitude as in Ref. [11]. The tight-binding model includes an interlayer potential difference of 0.87 ± 0.06 V, yielding an extremely high displacement field of 2.6 ± 0.2 V/nm [56,57]. From the band parameters we obtain the Fermi wavevectors \( k_{F,1} = 0.24 \pm 0.01 \) Å\(^{-1}\) (outer band) and \( k_{F,2} = 0.09 \pm 0.01 \) Å\(^{-1}\) (inner band). We estimate the carrier densities as \( n_i = k_{F,i}^2/\pi \) for \( i = 1,2 \). Note that the first-order correction to the Fermi wavevector due to trigonal warping is zero along \( \bar{A} - \bar{K} - \bar{A} \) so this provides a good approximation even for the trigonally warped
obtained from the calculations is \(3\). 

The experimental band dispersion is shown in \(\text{Fig. 3c and 3d}\). The band gap \(E_F - E_D\) is \(1.07 \pm 0.07\) eV, corresponding to a Fermi level shift of \(0.72 \pm 0.08\) eV with respect to the EMLG. Figures 2c and 2f show MDCs obtained from the shaded areas (1.1 eV below the extrapolated Dirac point, bands averaged over a 50 meV binning window) in Figures 2c and 2d, which clearly indicate the presence of two (four) bands, as expected for monolayer (bilayer) graphene. The total carrier density in our system is significantly higher than in the previously reported air-stable n-doped graphene systems \([32,33]\), though higher densities have been achieved in vacuum for example by co-doping graphene by K and Ca \([27]\), or by Cs \([24]\) and Gd doping \([25]\).

The electronic structure of the magnesium-intercalated sample obtained by ARPES measurements can be compared with the first principles DFT calculations for a bilayer graphene system where magnesium atoms are sitting at the interface with the SiC substrate. The heterostructure is modelled using a \((\sqrt{3} \times \sqrt{3})\) SiC supercell and a \((2 \times 2)\) graphene supercell with one magnesium atom placed in between the two materials (Figures 3a and 3b). The lattice constant of SiC is unchanged while the graphene is stretched by 7.5%. We calculate the Fermi surface and electronic band structure of the system, Figure 3c and 3d. The calculated Fermi surface (Figure 3c) agrees well with our ARPES spectra, where two features are observed in the Fermi surface: A circular feature belonging to the top graphene layer (red contour lines), and a triangular one coming from the bottom layer (green contour lines). The DFT calculations also reproduce the experimental band dispersion as shown in Figure 3d. The band gap is 0.35 eV, which is in excellent agreement with experimental observations. The doping level obtained from the calculations is \(3.6 \times 10^{14}\) cm\(^{-2}\), somewhat larger than the
experimental value of $2.1 \times 10^{14}$ cm$^{-2}$, while the calculated Fermi energy relative to the Dirac point $E_F - E_D = 0.71$ eV is somewhat smaller than experimental value (1.07 eV). The differences are likely related to the artificial stretching of the graphene lattice by 7.5% which preserves the symmetry of the system but lowers the Fermi velocity by 10% relative to the true value [59].

Figure 3. First principles DFT calculations of magnesium-intercalated bilayer graphene. Model used in DFT calculations: a) side view and b) top view of the graphene/magnesium/SiC interface. Brown, orange and blue spheres indicate the positions of carbon, magnesium and silicon atoms. Only the topmost Si atoms of the SiC substrate are shown for clarity. c) Calculated unfolded constant energy slice at the Fermi level of magnesium-intercalated bilayer graphene. Red and green represent contribution from top and bottom graphene layer, respectively. d) Unfolded band dispersion of magnesium-intercalated bilayer graphene.

Highly n-doped graphene/SiC has previously been achieved by depositing or intercalating alkali and alkali-earth metals on graphene [11,25–27,60], however the
resulting systems are typically unstable when exposed to air. In our case, magnesium is buried between bilayer graphene and SiC, so it is conceivable that samples could survive air exposure. In order to test air stability, the magnesium-intercalated sample was taken out of UHV and exposed to air for 30 minutes.

**Figure 4.** Magnesium-intercalated epitaxial monolayer graphene before and after air exposure. Constant energy contour a) and band dispersion b) of magnesium-intercalated sample before (left) and after (right) 30 min air exposure. Data taken at $h\nu=100$ eV and at room temperature.

Figure 4 compares the electronic dispersion and Fermi surface measured by ARPES before and after 30 minutes air exposure. In contrast, no significant changes are observed in the area of the Fermi surface, the Fermi energy $E_F - E_D$, or the bandgap for our air exposed Mg-QFSBLG, within the experimental resolution. This degree of air stability is surprising for a surface layer and indicates that Mg-QFSBLG created by magnesium intercalation is relatively robust to ambient exposure, which is desirable for designing transparent conducting electrodes [5] with a low-work function. Note that the sample used for the air exposure experiment was a different sample (EMLG with nominally 1 monolayer coverage) than the one for which data is shown in Figure 1 and Figure 2 due to the experimental time constraints. Full LEED and ARPES characterisation of this sample can be found in the Supplementary Material, section 3 and 4, respectively.
CONCLUSIONS

We demonstrate that magnesium intercalation at the interface of SiC and the graphene buffer layer, transforms epitaxial monolayer graphene into quasi-freestanding bilayer graphene, as observed by LEED and ARPES. Once at the interface, magnesium acts as an electron donor and dopes graphene, shifting a Fermi level by 0.72 eV and resulting in an electron carrier density of $n = 2.1 \times 10^{14}$ cm$^{-2}$, proportionate to highest densities achievable with electrolytic gating ($4 \times 10^{14}$ cm$^{-2}$). Magnesium intercalation also creates an extremely high displacement field of 2.6 V/nm, comparable to the largest displacement fields (2.5–3.1 V/nm) obtained in dual gated bilayer graphene FETs. The field of 2.6 V/nm opens a bandgap of 0.36 eV, a value very close to $\gamma_1$ (out-of-plane nearest-neighbour interaction parameter) where the field induced bandgap is expected to saturate, and increases the splitting between the valence (conduction) bands of bilayer graphene. Despite this extremely high displacement field, the electronic structure of the Mg-QFSBLG can still be described with a simple tight-binding model that reproduces well both the bandgap opening and increase in the splitting between bands. First principles DFT calculations are in good agreement and reproduce the experimental band structure well, including the bandgap opening and the increase in the band splitting. An air exposure test shows that the Mg-QFSBLG samples are stable in air for up to 30 minutes, and are thermodynamically stable up to at least 350 °C, suggesting that magnesium-intercalated graphene could be a suitable candidate for application in transparent electrodes and organic opto-electronics.

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Magnesium-intercalated graphene on SiC: highly n-doped air-stable bilayer graphene at extreme displacement fields

Supplementary Material

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1. Low-energy electron diffraction (LEED) of magnesium intercalated quasi-freestanding bilayer graphene (Mg-QFSBLG)

Figure S1 shows low-energy electron diffraction of quasi-freestanding bilayer graphene (Mg-QFSBLG) formed by intercalation of epitaxial monolayer graphene (EMLG) with magnesium, taken at an electron energy of 71 eV. Graphene coverage was nominally sub-monolayer. This data is taken on the same sample as shown in the main text, Figure 1-Figure 3. The Mg-QFSBLG LEED (Figure S1) shows additional (√3 x √3) R30° spots relative to the SiC lattice; these spots are not visible for the EMLG sample at the same electron energy, see Figure 1c in the main text. The (√3 x √3) spots result from the interaction of magnesium with the SiC surface that causes reconstruction of the SiC. The (√3 x √3) spots are more visible at higher electron energy that is more bulk sensitive, such as 126 eV, as in Figure 1d, compared to the more surface sensitive energy of 71 eV, as in Figure S1.

Figure S1. Low-energy electron diffraction of magnesium intercalated quasi-freestanding bilayer graphene (Mg-QFSBLG) taken at the 71 eV. (√3 x √3) spots (yellow circle) arising from magnesium induced SiC reconstruction are less visible at this energy compared to more bulk sensitive energy of 126 eV. Green circle is graphene (1 x 1) spot, gray circle is SiC (1 x 1) spot and orange circles (6√3 x 6√3)R30° relative to the graphene are reconstruction arising due to the buffer layer.
2. Averaging angle-resolved photoemission spectroscopy (ARPES) data of Mg-QFSBLG taken along the K-G-K direction

When measuring graphene using linearly polarised light at normal incidence to the sample, an intensity suppression of half of the Dirac cone appears along the $\bar{K} - \bar{F} - \bar{K}$ direction due to a destructive interference between electrons coming from two sublattices of graphene [1]. In order to compare data taken along the $\bar{K} - \bar{F} - \bar{K}$ direction with the data taken along the $\bar{A} - \bar{K} - \bar{A}$ direction, where both branches of the Dirac cone are visible (but which due to the mode of acquisition in which $k_{||}$ is scanned using $\varphi$ instead of $\theta$, results in a lower momentum resolution), one needs both Dirac cone branches visible.

One way to obtain a full Dirac cone in this situation is by adding together the half cone data measured around the $\bar{K}$ and $\bar{K}'$ points; these can be summed together to produce a “full” Dirac cone, as shown in Figure S2. This is possible as although the $\bar{K}$ and $\bar{K}'$ points are inequivalent, they exhibit mirror symmetry in regards to the polarization effect and the intensity suppression is inverted for the two branches.

Note that this representation produces some artifacts; for example it exaggerates the effect of trigonal warping in the conduction bands (which are dominated by intensity from momenta along $\bar{K} - \bar{K}'$ direction) and suppresses the trigonal warping in the valence bands (which are dominated by intensity from momenta along $\bar{K} - \bar{F}$ direction).

Figure S3 shows ARPES data for Mg-QFSBLG, the same sample shown in Figure 1-3 of the main text, formed by intercalation of EMLG with magnesium, taken at the Toroidal Analyser Endstation, showing energy dispersion averaged along the $\bar{K} - \bar{F} - \bar{K}$. Dirac cones from inequivalent $\bar{K}$ and $\bar{K}'$ points are added together to reconstruct a “full” Dirac cone, that looks very similar to the data obtained along the $\bar{A} - \bar{K} - \bar{A}$ direction, including large splitting between inner and outer valence (conduction) band and the band gap (see Figure 2 of the main text), but with much higher intensity and k-resolution. Data was taken with a photon energy of $h\nu = 100$ eV and at room temperature.
Figure S2. Angle-resolved photoemission spectroscopy data along the high symmetry direction $\overline{K} - \overline{\Gamma} - \overline{K}$ of Mg-QFSBLG is averaged to create a “full” Dirac cone. a) Only one side of a graphene Dirac cone is visible along $\overline{K} - \overline{\Gamma} - \overline{K}$ . b) Data from $\overline{K}$ and $\overline{K'}$ point (left) is summed into a ”full” Dirac cone (right).
Figure S3. Angle-resolved photoemission spectroscopy data of a) EMLG and b) Mg-QFSBLG. Energy dispersion data is averaged along the $\bar{K} - \bar{\Gamma} - \bar{K}$ direction, shown in c).

3. LEED and ARPES of magnesium-intercalated quasi-freestanding graphene (2nd sample) upon exposure to air

An air exposure experiment was performed on a separate sample due to time constrains. The starting sample was nominally EMLG. Structural characterisation was done by LEED and electronic structure characterisation was done by ARPES, Figures S4-S5. No significant changes were observed in LEED and ARPES following air exposure.

After magnesium intercalation, EMLG is expected to be converted to Mg-QFSBLG. LEED data taken at 100 and 190 eV is shown in Figure S4. The $(\sqrt{3} \times \sqrt{3})$R30° spots relative to SiC are visible, indicating magnesium reconstruction of the SiC surface and formation of Mg-QFSBLG.

Fermi surfaces and ARPES data along $\bar{A} - \bar{K} - \bar{A}$ direction is shown in Figure S5. Following intercalation, second set of bands appear in ARPES, however, it is less clear than in the case of first Mg-QFSBLG shown in the Figure 2. The tight binding (TB) model for bilayer graphene under high displacement field is overlaid in dark gray in Figure S5d and S5f. The same parameters were used as in the TB model in the main text ($v_F = 0.97 \times 10^6$ m/s, $U = 0.87$ V).
Figure S4. LEED characterisation of second EMLG sample. Clean sample is shown in a), after magnesium intercalation in b) and after air exposure in c). Following magnesium intercalation, sample looks completely freestanding. No changes in LEED are observed following air exposure. Data taken at 100 eV (EMLG) and 190 eV (Mg-QFSBLG and air exposed Mg-QFSBLG) and room temperature. Green circle: (1 × 1) graphene lattice; gray circle: (1 × 1) SiC lattice; orange and blue circles (6√3 × 6√3)R30° relative to graphene and (6 × 6) relative to SiC reconstructions arising from the buffer layer; yellow circle: (√3 ×√3) reconstruction of SiC surface by magnesium.

Figure S5. Angle-resolved photoemission spectroscopy data on the second Mg-QFSBLG graphene sample, formed by magnesium intercalation of an EMLG sample. Constant energy surface taken at the Fermi level and energy dispersion along the $\bar{A} - \bar{K} - \bar{A}$ direction, shown
in the inset in b), for the clean sample, a) and b), magnesium-intercalated sample, c) and d), and air exposed magnesium-intercalated sample, e) and f), respectively. Insets in the Figure S5d and the Figure S5f show a region around the Fermi level where two sets of bands can be seen. Solid lines in b) are linear fit for the bandstructure of monolayer graphene, and solid lines in d), f) are a tight binding model of bilayer graphene using the same parameters as the main text.

4. Additional ARPES data of Mg-QFSBLG (2nd sample) averaged along the K-G-K direction

Figure S6 shows additional ARPES data for the second Mg-QFSBLG, the same sample shown in Figure 4 in the main text, and in Figures S4-S5. Data is showing energy dispersion averaged along the $\bar{K} - \bar{\Gamma} - \bar{K}$ direction, with “full” Dirac cone visible. Following magnesium intercalation, Figure S6b, two sets of bands are visible indicating a bilayer formation. Compared to the first Mg-QFSBLG sample, shown in Figure S3b, where bands are of comparable intensity, in this sample the outer conduction band and inner valence band are less intense. Reason for this discrepancy is currently unknown. Data taken with a photon energy of $h\nu = 100$ eV and at room temperature.

![Figure S6](image)

**Figure S6.** Angle-resolved photoemission spectroscopy data of a) pristine sample, b) sample after magnesium intercalation that formed Mg-QFSBLG and c) air exposed Mg-QFSBLG. Energy dispersion data is taken along the $\bar{K} - \bar{\Gamma} - \bar{K}$ direction.
5. First principles calculations of the energetics of Mg intercalation

The thermodynamic driving force for the conversion of EMLG on SiC to Mg-QFSBLG heterostructure shown in Figure 1b can be estimated by considering the reaction:

\[
\text{Monolayer graphene on SiC + Mg} \rightarrow \text{Mg-QFSBLG on SiC}. \tag{1}
\]

Our first principles calculations on models shown in Figure 3a, 3b indicate that this reaction is energetically favourable by 1.18 eV. In our supercell models, the energy of Mg-QFSBLG on SiC and monolayer graphene on SiC is $-291.44$ eV and $-288.98$ eV, respectively, and we have used the energy of crystalline Mg ($-1.28$ eV per atom) as the reference. In each case, the supercell consisted of 3 layers of $(\sqrt{3} \times \sqrt{3})$ SiC crystal along with $(2 \times 2)$ graphene layers.

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