

1 Quasi Free-Standing Epitaxial Graphene Fabrication on 3C-SiC/Si(111)

2
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14 Abstract

15 Growing graphene on SiC thin films on Si is a cheaper alternative to the growth on bulk SiC, and
16 for this reason it has been recently intensively investigated. Here we study the effect of hydrogen
17 intercalation on epitaxial graphene obtained by high temperature annealing on 3C-SiC/Si(111) in
18 ultra-high vacuum (UHV). By using a combination of core-level photoelectron spectroscopy
19 (PES), low energy electron diffraction (LEED), and near-edge X-ray absorption fine structure
20 (NEXAFS) we find that hydrogen saturates the Si atoms at the topmost layer of the substrate,
21 leading to free-standing graphene on 3C-SiC/Si(111). The intercalated hydrogen fully desorbs
22 after heating the sample at 850 °C and the buffer layer appears again, similar to what has been
23 reported for bulk SiC. However, the NEXAFS analysis sheds new light on the effect of hydrogen
24 intercalation, showing an improvement of graphene's flatness after annealing in atomic H at
25 600°C. These results provide new insight into free-standing graphene fabrication on SiC/Si thin
26 films.

27 **Keywords:** epitaxial graphene, H-intercalation, free-standing graphene

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1. Introduction

Graphene grown on SiC, either bulk or thin films, is a promising platform for applications in electronics and sensing [1-5]. The growth of graphene directly on SiC eliminates the transfer step that is required to move graphene obtained by mechanical exfoliation or by CVD synthesis on metal to an insulating or semiconducting substrate [6, 7]. Compared to bulk SiC, SiC/Si thin films provide a cheaper and more versatile alternative for graphene fabrication, and a better integration with the standard microelectronic fabrication protocols, and since 2009 that M. Suemitsu et al. demonstrated epitaxial graphene growth on thin film 3C-SiC/Si, it attracted a lot of attention [8-16]. After annealing SiC to high temperature its topmost layer converts to an insulating carbon-rich layer with a $6\sqrt{3} \times 6\sqrt{3}$ R30° structure, and graphene grows on top of this layer by progressive sublimation of Si atoms [4, 17-20]. About 30% of carbon atoms in the interface layer (commonly called the buffer layer) are covalently bound to the substrate [21-23]. The presence of the buffer layer is suggested as the reason that significant doping ($\sim 1 \times 10^{13} \text{ cm}^{-2}$) is observed in graphene grown on SiC [24-28], which adversely affects the carrier mobility [22, 29]. Therefore, elimination of the buffer layer is necessary for growing graphene for device fabrication.

Breaking the carbon backbonds to silicon within the topmost layer of SiC and saturating them with some other species eliminates the buffer layer. Riedl et al [30] demonstrated that hydrogen intercalation can perform this function and decouple graphene from the substrate by penetrating between the buffer layer and the substrate and saturating the dangling Si bonds. This allows the carbon atoms in the buffer layer to establish a pure sp^2 bond which converts it to a graphene layer [30]. In this way it is possible to produce free-standing bilayer graphene from monolayer graphene grown on a bulk SiC (0001) [30]. Watcharinyanon et al [31] demonstrated by scanning tunnelling microscopy (STM) that hydrogen intercalation on monolayer graphene results in the creation of $(\sqrt{3} \times \sqrt{3})$ bilayer graphene islands which gradually expand and fully cover the surface [31]. Sforzini et al [32] further investigated the hydrogen intercalation of graphene grown on bulk 6H-SiC (0001) by measuring and calculating its adsorption height to evaluate the amount of interaction between graphene and its substrate. They concluded that free-standing graphene fabricated on SiC using H-intercalation has the lowest interaction with its substrate compared to a range of reported substrates such as Ir, Ni, Re and Co, suggesting that SiC is an ideal platform for graphene fabrication [32]. Furthermore, Yu et al [33] studied the effect of hydrogen intercalation on the

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1 electrical transport properties of graphene, demonstrating that this procedure is very effective in
2 improving the mobility of graphene fabricated on bulk 4H-SiC (0001). They also investigated the
3 effect of SiC crystal properties and reported that lower crystal quality leads to more interaction
4 between graphene and the substrate [33]. It has been also demonstrated that H-intercalation
5 improves the performance of field-effect transistors fabricated from epitaxial graphene on SiC [34-
6 36]. Some of these studies also demonstrated that the intercalation mechanism is reversible through
7 annealing [30, 31].

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8 So far the fabrication of free-standing graphene has been considered only on bulk SiC [30-33, 37-
9 42]; due to the technological importance of SiC/Si we explored the production of free-standing
10 graphene by hydrogen intercalation on 3C-SiC thin films on Si(111). We combine, for the first
11 time, synchrotron radiation near-edge X-ray absorption fine structure (NEXAFS) with core-level
12 photoelectron spectroscopy (PES) and low energy electron diffraction (LEED), with the aim of
13 obtaining a clear picture of the intercalation process on graphene grown on 3C-SiC/Si(111).

14 2. Experimental Details

15 A 1 μm thick 3C-SiC(111) layer grown on Si(111) was obtained from NOVASIC (France).
16 Chemical and mechanical polishing was performed on the samples (StepSiC[®] by NOVASIC
17 (France)), which reduced the surface roughness to ~ 1 nm [43]. The 3C-SiC/Si thin film is an
18 oriented epitaxial grown film on a single crystal of silicon which is P-doped and its resistivity is
19 1-10 $\Omega\text{-cm}$. The wafer was cut to the size of 12×2 mm². Prior to introduction into the UHV system
20 for graphene growth each sample was cleaned by 10' sonication in each of acetone, isopropanol
21 and deionised water, respectively.

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22 Synchrotron-based PES measurements were performed at the soft x-ray beamline at the Australian
23 Synchrotron. Samples were introduced into the UHV system at the beamline and annealed at 400
24 °C for several hours in order to remove contaminants. An optical pyrometer (IRCON Ultimax UX-
25 20P with emissivity = 0.9) was used to measure the sample temperature. PES measurements were
26 performed using a SPECS Phoibos 150 hemispherical analyser, operating at a pass energy of 10
27 eV.

28 An EFM-H atomic hydrogen source (FOCUS GmbH) was employed for atomic hydrogen
29 exposure operating at $P \sim 5 \times 10^{-6}$ mbar and 40 W power. Atomic hydrogen etching prior to

1 graphene growth is performed for all of the experiments, since has been reported to assist with
2 elimination of contamination and improving the surface flatness [16, 44, 45].

3 **The epitaxial graphene growth procedure we employed includes: inserting the sample into UHV**
4 **system, degassing the sample for several hours to eliminate the contamination at ~ 400 °C, atomic**
5 **hydrogen etching for about 30 minutes in order to further clean the sample and flatten the surface,**
6 **and final annealing for graphene growth at temperatures ranging from 1200 - 1250 °C for 5 - 10**
7 **minutes. The number of grown graphene layers is dependent on annealing time and temperature;**
8 **for further information in this regard please refer to [19, 46]. Based on this growth process on**
9 **similar substrate we expect terraces to be in a range of hundreds of nanometers [47]. H-**
10 **intercalation process on the grown graphene was performed for 30 minutes at ~ 600 °C.**

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11 **3. Results and Discussions**

12 **3.1 PES**

13 To investigate the chemical bonding changes during the H-intercalation experiment, the sample
14 was studied using core-level photoelectron spectroscopy (PES), **which is based on measuring the**
15 **energy distribution of the electrons emitted as a result of X-ray irradiation [48]. PES is a surface**
16 **sensitive technique and is very powerful in providing information about chemical state of the**
17 **compounds [49]. Fig. 1 shows C 1s and Si 2p core level spectrum measured during intercalation**
18 **at photon energies of 330 eV and 150 eV, respectively. The C1s spectrum are fitted with different**
19 **components: Si-C at ~ 283.6 eV, graphene at ~ 284.7, and buffer layer related components S1 and**
20 **S2 at ~ 285 eV and ~ 285.6 eV, respectively [17, 50, 51]. The Si 2p spectrum are fitted with two**
21 **spin-orbit split doublets (Si 2p_{3/2} and Si 2p_{1/2}) for Si-C at ~ 101.3 eV, Si-H at ~ 101 eV, buffer**
22 **layer at ~ 100.7 eV and Si at ~ 99.4 eV; the energies are given for Si 2p_{3/2} and the splitting of the**
23 **Si 2p_{3/2} and Si 2p_{1/2} components are 0.6 eV [30, 52]. The fits use a combination of Gaussian and**
24 **Lorentzian line shapes (Voigt), and the background was subtracted using the Shirley procedure**
25 **[52]; the graphene component was fitted with an asymmetric peak.**

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Commented [MAP7]: More info about PES. Referee3 Q6

26 **Fig. 1a shows the PES spectrum for the as grown graphene, which approximately corresponds to**
27 **a three-layer graphene sample; the graphene thickness was calculated using an equation based on**
28 **the differential cross sections and the inelastic mean free paths of electrons suggested by Rollings**
29 **et al [17, 53]. Here cross section of an atom refers the number of electrons excited per unit time**

1 divided by the number of incident photons per unit time per unit area and inelastic mean free path
2 of electrons is an average distance an electron can travel into a solid before scattering. Peaks (S1
3 and S2) related to the buffer layer are apparent in the C 1s region for the as-grown epitaxial
4 graphene (Fig. 1a). After exposure to atomic hydrogen, these peaks completely disappear,
5 indicating that H-intercalation has removed the interface layer (Fig. 1b) [30, 31]. The Si 2p
6 spectrum confirms the presence of Si-H bonds under the graphene layer (Fig. 1f), which originates
7 from Si atoms bonded to H as a result of H exposure [20, 30]. These are mainly the Si atoms at
8 topmost layer of the SiC substrate saturated by hydrogen bonding. The buffer layer component in
9 Si 2p spectrum also disappears after H-intercalation process (Fig. 1e and f).

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10 Closer look at the spectrum reveals that the graphene-related peak in C 1s region is shifted by ~
11 0.1 eV (Table S1) towards lower binding energies (Fig. 1b and 2a). The SiC component in Si 2p
12 region is also shifted ~ 0.4 eV to lower binding energies (Fig. 1f and 2b). These shifts in binding
13 energies are known to occur as a result of band bending induced by the hydrogen termination of
14 the surface of SiC [30, 54]. The shift observed here after H-intercalation of graphene on SiC/Si
15 thin film is less than the previously-reported value for graphene on bulk hexagonal SiC by Riedl
16 et al (~0.4 for graphene component and 1 eV for SiC one) [30]. We believe this is very likely to
17 stem from their difference in crystallography and defect density; we expect limited domain size
18 for SiC/Si epitaxial thin film and higher defect density compared to the bulk hexagonal one.

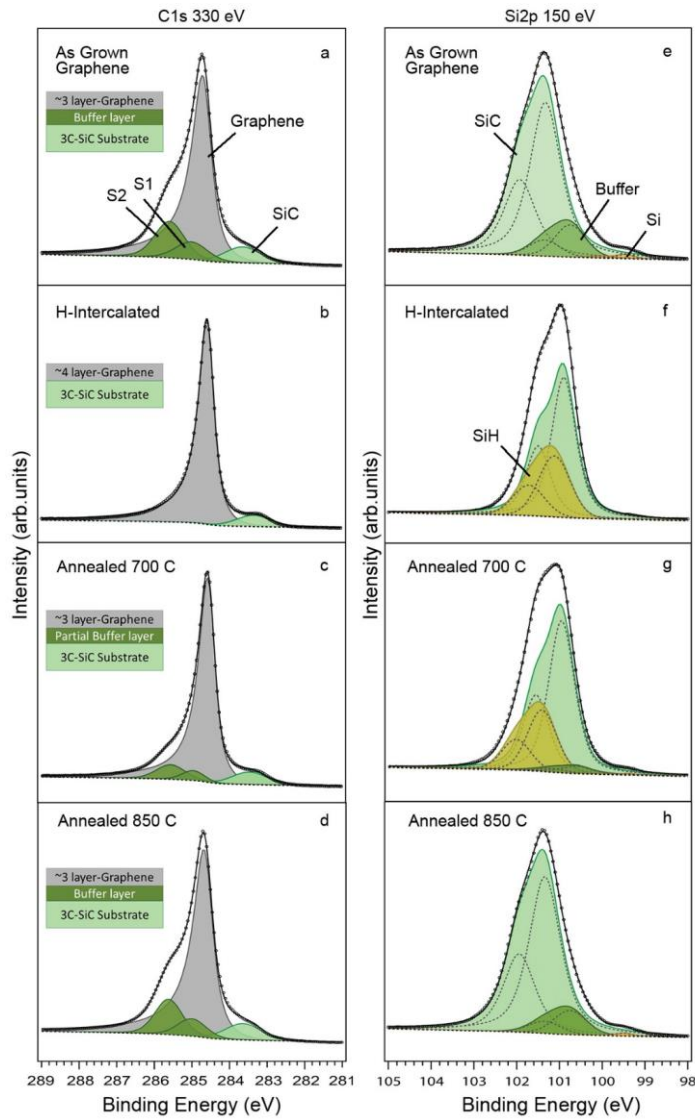
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19 After atomic H exposure, the intensity of the graphene peak increases, indicating that the carbon
20 atoms in the buffer layer, originally linked to the Si atoms, joined the graphene layer (Fig.1b). The
21 comparison of the peak intensity further confirms this, as the ratio of graphene-related spectral
22 weight to silicon carbide spectral weight, $R = \frac{I_{gr} + I_{S1} + I_{S2}}{I_{SiC}} \cong 12$, remains constant through the
23 intercalation. In this expression, I_{gr} , I_{S1} , I_{S2} , and I_{SiC} are intensities of the components related to
24 graphene, S1, S2, and SiC in C1s spectrum, respectively. Therefore, as a result of H-intercalation
25 procedure a ~ three-layer graphene converts into a ~ four-layer graphene. For H-intercalation effect
26 on PES data of monolayer and bilayer graphene samples please refer to the supporting information.

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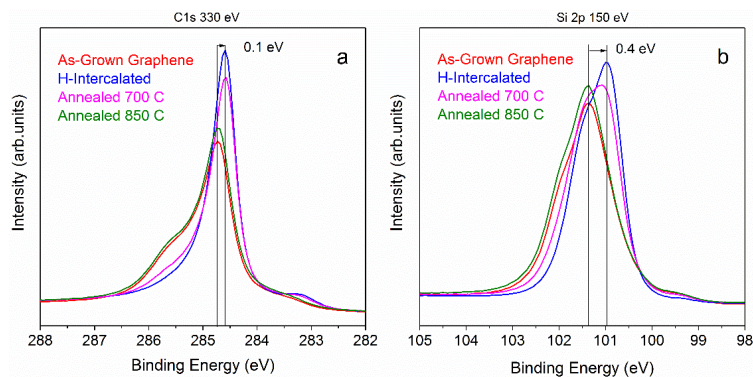
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 2 Fig. 1. C 1s core-level photoemission spectrum at 330 eV photon energy (a) as grown graphene
 3 (b) after hydrogen intercalation (c) after hydrogen desorption by annealing to 700 °C (d) after
 4 annealing to 850 °C. Si 2p core-level photoemission spectrum at 150 eV photon energy (e) as
 5 grown graphene (f) after hydrogen intercalation (g) after hydrogen desorption by annealing to 700
 6 °C (h) after annealing to 850 °C.

1 By annealing the H-treated sample in vacuum to 700 °C, the buffer layer is partially restored (Fig
 2 1c and g), due to the fact that the Si-H bonds are not stable at temperatures over 700 °C [30, 31].
 3 After further annealing the H-intercalated sample to 850 °C, the signatures of buffer layer fully
 4 recover to their original intensity (Fig. 1d and h). The shift in binding energies observed as a result
 5 of H-intercalation are also recovered after annealing to 850 °C (Fig. 2). H-intercalated samples
 6 were further studied after being exposed to air for 5 days and no significant change was observed
 7 (refer to SI). This indicates that the free-standing graphene prepared by this procedure is stable in
 8 air which is similar to free-standing graphene fabricated on bulk SiC [30, 31].



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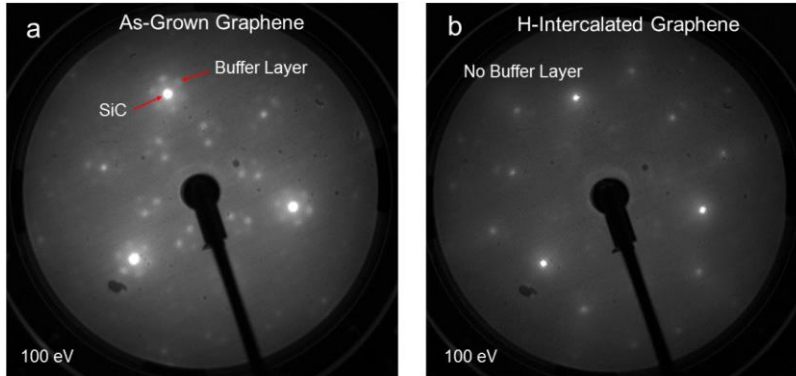
10 Fig. 2. Core-level photoemission spectrum of (a) C 1s at 330 eV photon energy, (b) Si 2p at 150
 11 eV photon energy

12 3.2 LEED

13 Fig. 3 shows the LEED patterns of the ~3 layer graphene sample before and after H intercalation.
 14 LEED is widely used for investigating the surface structure and is based on observing the diffracted
 15 electrons from the surface as a result of bombardment of the sample by a low-energy electron beam
 16 (typically in a range of 20-200 eV) [55]. Each of the three primary SiC spots are surrounded by
 17 six less intense superstructure spots that originate from the buffer layer (Fig. 3a) [7]. These spots
 18 originating from the $6\sqrt{3} \times 6\sqrt{3}$ interface layer vanish after exposure to hydrogen (Fig. 3b),
 19 suggesting the removal of the buffer layer. The LEED patterns of the sample are unchanged after
 20 being exposed to air for 5 days (refer to SI).

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2 Fig. 3. LEED pattern (a) after graphene growth (b) after H intercalation.

3 **3.3 NEXAFS**

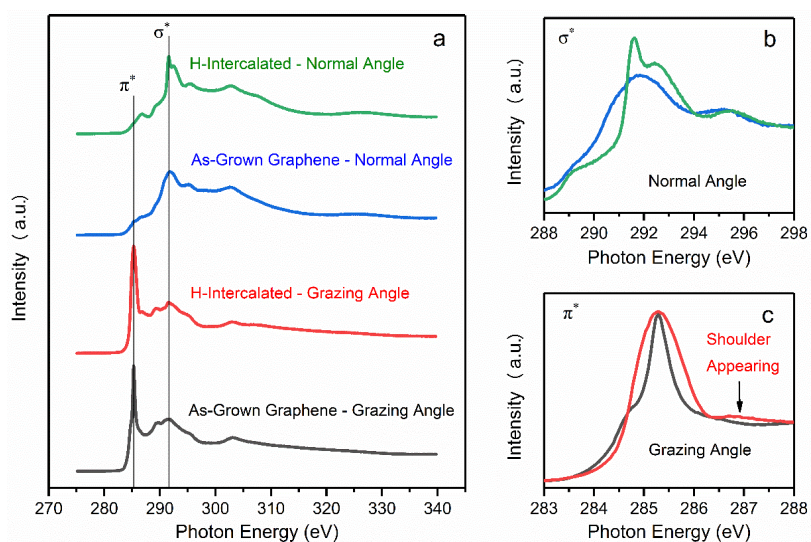
4 The unoccupied electronic states of graphene grown on a 3C-SiC/Si thin film were studied using
 5 near-edge x-ray absorption fine structure (NEXAFS) to further understand how the hydrogen
 6 intercalation affects the interface layer. Fig. 4 shows the carbon K-edge NEXAFS spectrum from
 7 monolayer epitaxial graphene grown on 3C-SiC/Si thin film. NEXAFS was acquired with two
 8 different incident angles of the synchrotron light with respect to the surface normal: 0° (normal)
 9 and 70° (grazing). The NEXAFS spectra are characterised by two main peaks at 285.3 and 291.6
 10 eV which correspond to transitions from the C1s core level to π^* and σ^* empty states respectively
 11 [56].

12 Varying the incident angle modifies the probability for different transitions for C1s. $1s - \pi^*$ has
 13 higher probability for the electric field vector perpendicular to the molecular plane, and $1s - \sigma^*$ is
 14 maximised for a parallel field [56]. As a consequence, the intensity of the σ^* peak significantly
 15 decreases at grazing angles, and the π^* transition has the opposite behaviour. NEXAFS was
 16 conducted on three different samples with different numbers of graphene layers: monolayer,
 17 bilayer and ~ 3 graphene layers.

18 Fig. 4 shows C1s NEXAFS spectrum for monolayer graphene before and after H-intercalation.
 19 The spectrum for the H-intercalated sample in the σ^* region is sharper (Fig. 4b) due to the lower
 20 interaction of the graphene layer with the substrate, which decreases its level of doping [57]. The
 21 intensity (calculated from the area under the peak) of the π^* band increases after H intercalation,

1 which is expected, due to the increase in sp^2 hybridization after the backbonds are broken.
 2 Hydrogen mainly breaks the backbonds between the buffer layer and the topmost layer of SiC
 3 substrate and saturates the dangling bonds at the interface. This changes the sp^3 nature of the
 4 backbonds and converts them to sp^2 of graphene, causing the intensity increase in the σ^* and π^*
 5 region of the NEXAFS spectrum. The π^* region shows also the appearance of a shoulder at higher
 6 photon energies (~287 eV), which can be linked to carbon atoms in substrate at the edges bonded
 7 to hydrogen atoms due to H-intercalation (Fig.7) [58-61].

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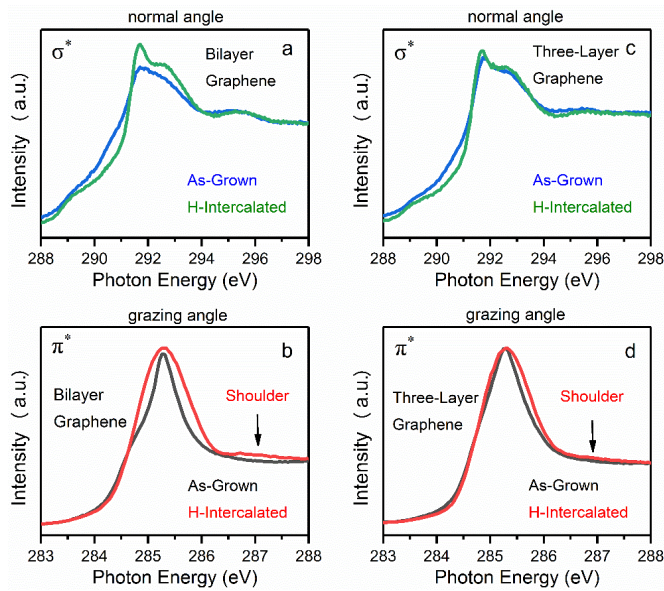


8
 9 Fig. 4. C 1s NEXAFS spectrum for monolayer graphene (a) full spectrum (b) σ^* peak region at
 10 normal incidence angle (c) π^* peak region at grazing incidence angle.

11 Fig. 5 shows NEXAFS data acquired from a bilayer and three layer graphene samples before and
 12 after H-intercalation. The σ^* region for the bilayer sample shows that the peak becomes sharper
 13 after intercalation, although this effect is less evident than in the monolayer case (compare Fig 4b
 14 and 5a). The increase in intensity of the π^* peak between H-intercalated and as grown samples is
 15 also observable, but to a lower extent compared to the monolayer sample (compare Fig 4c and 5b).
 16 The shoulder at 287 eV is still observable, but with lower intensity. For the three-layer graphene
 17 sample a significantly lower intensity change can be noted in both the σ^* and in π^* peaks as a result

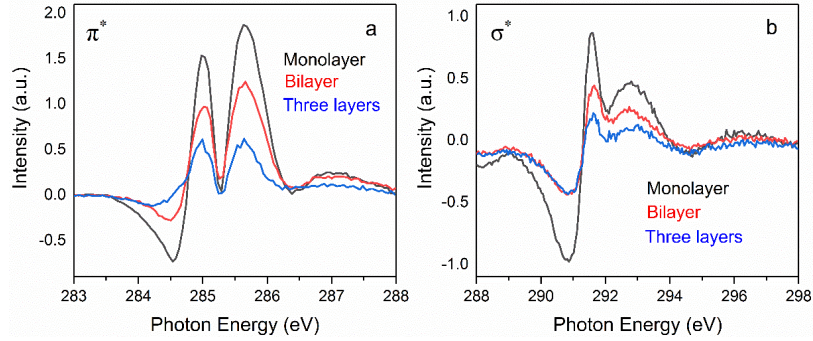
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1 of H-intercalation (Fig. 5c and d), and the shoulder at higher photon energies in π^* region is hardly
 2 noticeable (Fig. 5d).



3
 4 Fig. 5. C 1s NEXAFS spectrum for bilayer and three-layers graphene (a) σ^* peak region at normal
 5 incidence angle, for bilayer graphene sample (b) π^* peak region at grazing incidence, for bilayer
 6 graphene sample (c) σ^* peak region at normal incidence angle, for three-layer graphene sample (d)
 7 π^* peak region at grazing incidence angle, for three-layer graphene sample.

8 In order to enhance the details of this effect we calculated the differential spectra by subtracting
 9 the normalised NEXAFS spectrum before and after H-intercalation for the monolayer, bilayer and
 10 three-layers graphene (Fig.6). As expected the change in intensity is larger for the thinnest
 11 graphene sample, and by increasing the number of graphene layers the intensity change decreases
 12 significantly. In particular, the shoulder appearing at 287 eV is hardly noticeable for the sample
 13 with three graphene layers, indicating that this feature is definitely related to first layer of graphene
 14 formed on top of SiC, in agreement with our interpretation which assigns this feature to carbon
 15 atoms at the topmost layer of the substrate, bonded to hydrogen atoms [59].



1
 2 Fig. 6. C 1s NEXAFS differential spectrum made of H-intercalation spectrum –as grown graphene
 3 one (a) π^* peak region at grazing incidence angle full spectrum (b) σ^* peak region at normal
 4 incidence angle.

5 In order to further study the H-intercalation process, a dichroic ratio $DR = \frac{I_{\theta_1} - I_{\theta_2}}{I_{\theta_1} + I_{\theta_2}}$ is calculated,
 6 where I_{θ_1} and I_{θ_2} show the π^* peak region intensity which is extrapolated by integrating the area
 7 under the peak for normal incident angle ($\theta_1 = 0$) and grazing incident angle ($\theta_2 = 90$). The
 8 dichroic ratio is a measure for assessing the alignment of graphene, and is expected to equal to -1
 9 for a completely flat graphene and becomes 0 for a randomly oriented sample. [59]. H-intercalation
 10 improves the DR and makes the graphene flatter (Table 1). This increase in DR is smaller for the
 11 sample with more graphene layers (from -0.068 for monolayer to -0.026 for the three-layer one).
 12 This is due to the fact that most of the improvement in the orientation of graphene stems from
 13 elimination of the buffer layer after H-intercalation, and by increasing the number of the graphene
 14 layer, the contribution of the buffer layer to the signal becomes less significant.

15 Table 1. dichroic ratio (DR) calculated for the samples before and after H-intercalation.

Graphene condition	DR for As-grown	DR for H-intercalated	DR change
~ 1 layer	-0.542	-0.610	-0.068
~ 2layers	-0.545	-0.596	-0.051
~ 3 layers	-0.63	-0.663	-0.026

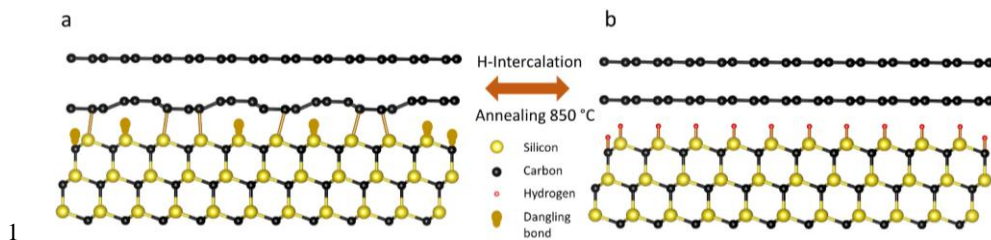


Fig. 7. graphical representation of H-intercalation (a) monolayer graphene formed with the buffer layer SiC (b) free-standing bilayer layer graphene fabricated as a result of the H-intercalation.

4. Conclusions

We demonstrated that hydrogen intercalation can eliminate the buffer layer at the interface between graphene and 3C-SiC/Si(111) thin films, producing free-standing graphene. The carbon atoms initially contained in the buffer layer create a new graphene layer and convert monolayer graphene into bilayer (Fig. 7). NEXAFS spectra indicate an increase in intensity of π^* and σ^* peaks, confirming a reduction of the substrate's effect on the graphene. The change in intensity due to H-intercalation in the π^* and σ^* regions decreases by increasing the number of graphene layers, indicating that the substrate contribution becomes less noticeable by NEXAFS for thicker graphene samples. Moreover, the free-standing graphene fabricated on the 3C-SiC/Si(111) thin film is stable in air. Finally, we demonstrated that the intercalation procedure is a reversible process, and that hydrogen desorbs as a result of heating the sample to 850 °C, resulting in the reformation of the buffer layer (Fig.7).

Acknowledgments

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Supporting Information

Quasi Free-Standing Epitaxial Graphene Fabrication on 3C-SiC/Si(111)

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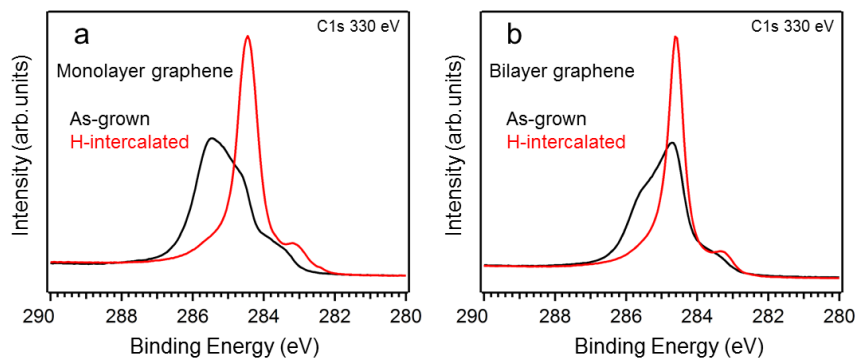


Fig. S 1. C 1s core-level photoemission spectrum at 330 eV photon energy before and after H-intercalation (a) monolayer graphene (b) Bilayer graphene.

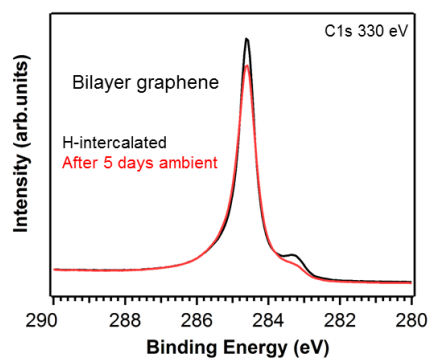


Fig. S 2. C 1s core-level photoemission spectrum at 330 eV photon energy for bilayer graphene after H-intercalation and being exposed to ambient conditions for 5 days.

Table S 1. Fitting results for the Core-level photoemission spectrum of binding energy (BE) position (± 0.2 eV), full-width at half-maximum (FWHM), and relative intensity (peak areas).

Condition	Component	Position	FWHM	Line shape	Intensity
Graphene	SiC	283.64	1.14	0.2	1.4E+05
	Graphene	284.76	0.8	0.95	1.3E+06
	Buffer	285	1	0.2	1.4E+05
	Buffer2	285.6	0.92	0.3	2.7E+05
H-Intercalated	SiC	283.35	1	0.2	1.5E+05
	Graphene	284.63	0.7	0.95	1.8E+07
	Buffer	-	-	-	0.0E+00
700 °C	SiC	283.4	1.1	0.2	1.4E+05
	Graphene	284.61	0.65	0.9	1.5E+06
	Buffer	285	0.7	0.2	7.2E+04
	Buffer2	285.57	0.9	0.3	1.4E+05
850 °C	SiC	283.64	1.13	0.2	1.6E+05
	Graphene	284.75	0.8	0.95	1.4E+06
	Buffer	285	0.9	0.2	1.3E+05
	Buffer 2	285.63	0.84	0.3	2.5E+05

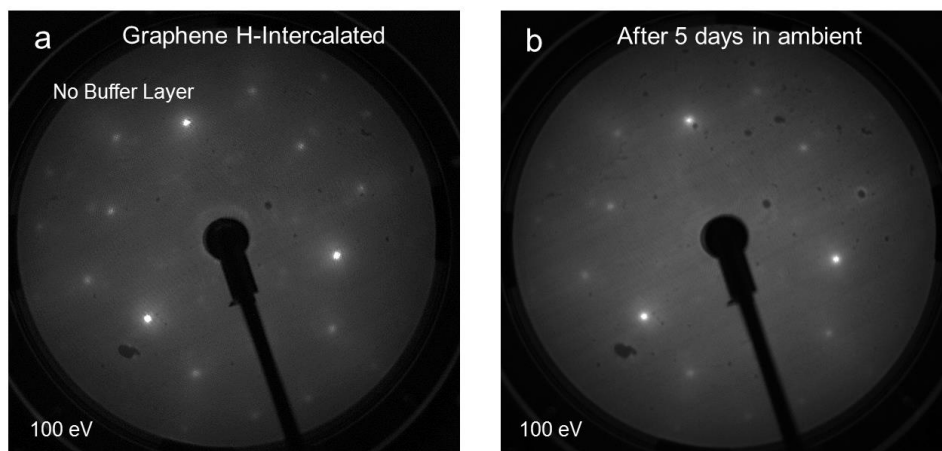


Fig. S 3. LEED pattern (a) after H-intercalation (b) after being exposed to ambient conditions for 5 days.

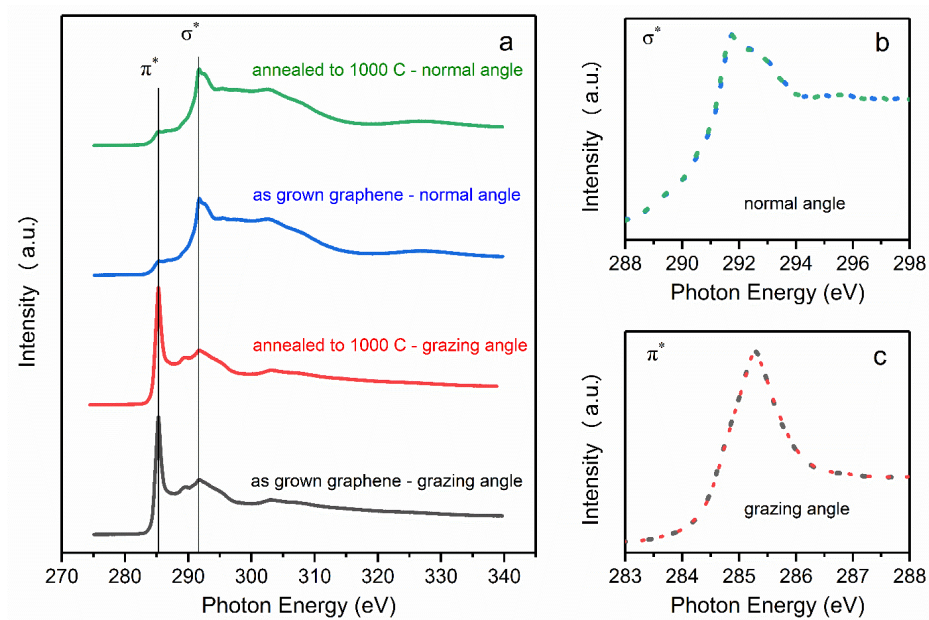


Fig. S4. C 1s NEXAFS spectrum after annealing to 1000 °C (a) full spectrum (b) σ^* peak region at normal incidence angle (c) π^* peak region at grazing incidence angle.

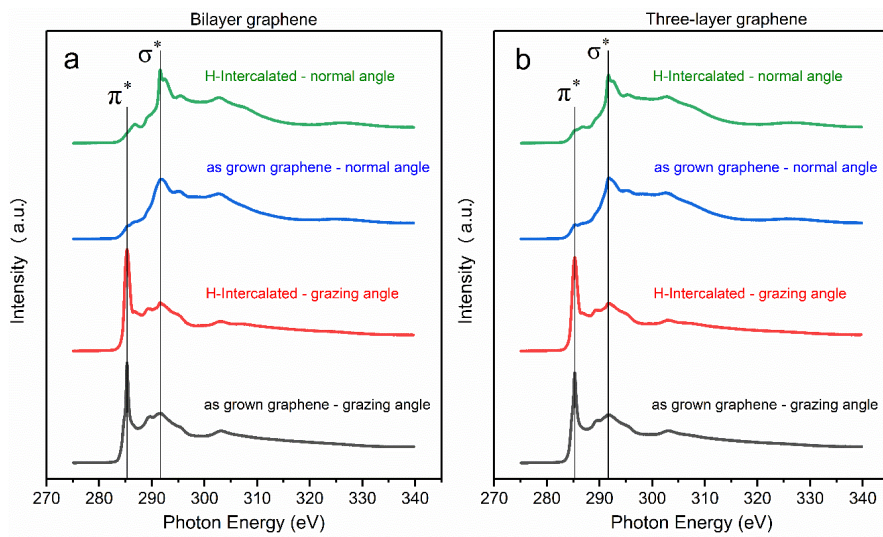


Fig. S5. C 1s NEXAFS spectrum before and after H-intercalation (a) bilayer graphene (b) three-layer graphene sample.