

Remote epitaxial interaction through graphene

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42 **Abstract**

43 The concept of remote epitaxy involves a two-dimensional van der Waals layer covering the
44 substrate surface, which still enable adatoms to follow the atomic motif of the underlying substrate.
45 The mode of growth must be carefully defined as defects, e.g., pinholes, in two-dimensional
46 materials can allow direct epitaxy from the substrate, which in combination with lateral epitaxial
47 overgrowth could also form an epilayer. Here, we show several unique cases that can only be
48 observed for remote epitaxy, distinguishable from other two-dimensional material-based epitaxy
49 mechanisms. We first grow BaTiO₃ on patterned graphene to establish a condition for minimizing
50 epitaxial lateral overgrowth. By observing entire nanometer-scale nuclei grown aligned to the
51 substrate on pinhole-free graphene confirmed by high-resolution scanning transmission electron
52 microscopy, we visually confirm that remote epitaxy is operative at the atomic scale.
53 Macroscopically, we also show variations in the density of GaN micro-crystal arrays that depend on
54 the ionicity of substrates and the number of graphene layers.

55

56 **Teaser**

57 Remote epitaxy is studied to discern experimental cases where this unique growth mechanism is
58 operative.

59

60 **Introduction**

61 Remote epitaxy refers to epitaxy on the surface of a substrate covered by a two-dimensional
62 (2D) material, utilizing the partially screened electrostatic potential of the substrate to interact
63 indirectly with the adatoms during epilayer growth (1, 2). Without forming direct chemical bonds,
64 this remote interaction can lead to the well-aligned nucleation of an epilayer that follows the
65 orientation of the substrate. Moreover, as a 2D material is a layered van der Waals (vdW) material
66 free of dangling bonds, its weak bonding enables remote-epitaxial films to be detached at the 2D
67 layer interface by simple mechanical exfoliation with atomic precision (3). With the increasing
68 demand of freestanding membranes for both research and industry, the remote epitaxy community
69 has rapidly grown over the past few years (1–17). Various families of materials including III–V (1,
70 4–7), III–N (2, 8–11), and complex oxide (12–15) thin films have been grown and detached from
71 the substrate, and these films have served as fundamental building blocks for state-of-the-art devices
72 by overcoming the limitations of conventional epitaxy (1). Fields to which these films have been
73 recently applied include infrared photodetectors (18), vertically stacked micro-light-emitting-diodes
74 (LEDs) (19), heterostructured devices (20–22), and flexible electronics (12, 14, 23).

75

76 The mechanism of remote epitaxy has been investigated in numerous prior reports using
77 density functional theory (DFT) calculations and empirical observations (1, 3, 4, 9, 13). Nonetheless,
78 there has been a lack of studies that advise how to clearly distinguish the mechanism of epitaxy
79 among remote epitaxy, vdW (including quasi-vdW) epitaxy (24–28), and pinhole-based epitaxy (16,
80 17) as they all rely on 2D vdW materials for epitaxy and exfoliation. **Figure 1 (A–C)** shows
81 schematics of these three different epitaxial mechanisms and corresponding cross-sectional views,
82 and **Table 1** summarizes the main features of each mechanism (24–31), respectively. To confirm
83 the remote epitaxial growth mechanism, cross-sectional transmission electron microscopy (TEM)
84 images have been utilized to show the epitaxial relationship between epilayer and substrate across
85 2D interlayers in a direct way. Regardless, considering the difficulties of monitoring the growth in-
86 situ at a microscopic scale, and given the limited field of view in cross-sectional TEM images (which
87 is typically at the nanometer scale), the validity of remote epitaxy as an actual growth mode can be
88 questioned. Also, it is well-known that transferred graphene suffers from metallic or polymer
89 residues and wrinkles in addition to pinholes. These may affect the integrity of the graphene quality
90 during growth, making it prone to be damaged and create pinholes (32), in addition to already
91 existing ones that were created during transfer (15).

92 Recently, it has been reported that residual native oxides at the graphene-substrate interface
93 can vaporize during high temperature growth and generate additional pinholes unless they are
94 completely cleaned up (16). Thus, if oxidation at the surface cannot be prevented, a high
95 concentration of such pinholes could lead to epitaxial films predominantly formed by pinhole-based
96 epitaxy. One way to completely avoid such formation of residual native oxides would be to use
97 graphene directly grown on substrates for growth and our recent study proved that successful remote
98 epitaxy of single-crystalline GaAs can still occur on graphene “directly” grown on GaAs substrates
99 (33). Further, for the case of graphene transferred onto a substrate that may have many defects, the
100 following previous studies show that pinhole-based epitaxy cannot lead to single-crystalline films
101 for all substrate materials that have been studied. When attempting to perform remote epitaxy on
102 graphene-coated non-polar substrates such as Si or Ge, polycrystalline films were always formed
103 due to the failure of covalent field penetration (5) as shown in **Fig. 1D**. If pinhole-based epitaxy is
104 dominant, ionicity of substrates and epilayers should not determine the success of single-crystalline
105 formation on graphene-coated substrates. In fact, although evidence showing clear clues of remote
106 epitaxy have been embedded among different references (2, 4, 22, 38), dedicated studies that can
107 unequivocally verify the remote epitaxy mechanism have not been performed so far.

109 In this paper, we focus on clarifying whether remote epitaxy is truly occurring in a ‘remote’
110 sense through graphene. We start by establishing a system and growth conditions under which lateral
111 epitaxial overgrowth is minimal. The system is BaTiO₃ (BTO) and by growing it on a SrTiO₃ (STO)
112 substrate with patterned stripes of bare exposed STO adjacent to stripes covered by multilayer
113 graphene. We find that epitaxial BTO grows upward from the bare substrate and polycrystalline
114 BTO grows upward from the regions covered by the multilayer graphene. Having established
115 conditions inhibiting epitaxial overgrowth, we then grow nano-scale BTO islands (the widest
116 diameter being around ~30 nm) on a graphene-coated STO substrate to examine the alignment of
117 BTO nuclei with the substrate by TEM. Here the nuclei are sufficiently small that an entire nucleus
118 is in the field of view and nuclei free of pinholes can be studied. Nuclei atomically aligned to the
119 underlying substrate where the entire nucleus is separated by graphene from the substrate are
120 imaged, confirming the mechanism of remote epitaxy in the absence of pinholes under the entire
121 BTO nucleation site. Next, we grow GaN micro-crystal (μ C) arrays on epitaxial graphene directly
122 grown on SiC substrates. We grow monolayer to multilayer graphene to minimize the exposed
123 substrate area with pinholes by completely covering the surface of substrates. We confirm remote
124 interaction even through directly grown, bilayer graphene that completely seals the surface of the
125 substrates. Lastly, our studies reveal that growth on different substrate materials and under different
126 growth temperatures results in different nucleation density due to the different ionicity of the
127 substrates and varying diffusion length, respectively. This excludes the possibility of pinhole-based
128 epitaxy because the nucleation density will be determined by the density of pinholes, not by the
129 ionicity of the substrates or the growth temperatures, in pinhole-based epitaxy. From our systematic
130 approach to understand the unique characteristics of remote epitaxy, we verify remote epitaxy as a
131 distinct epitaxy mechanism from pinhole-based and vdW epitaxy.

132

133 **Results**

134 **Growth on nanopatterned graphene to emulate pinhole-based lateral epitaxial overgrowth**

135

136 In order to clearly distinguish the case between pinhole-based lateral epitaxial overgrowth
137 and remote epitaxial growth, we intentionally created periodic nanopatterns on graphene on which
138 we epitaxially grew materials. The graphene was patterned with various combinations of line widths
139 (50–200 nm) and pitches (200 nm–2 μ m) by etching away designated regions of graphene with
140 electron-beam lithography (EBL) (33) as in **Fig. 2A** and **fig. S1A**. As shown in **Fig. 2B**, when the
141 width and period of the pattern was 100 and 200 nm, respectively, the growth of GaAs on patterned
142 graphene on Ge substrates was found to form a smooth surface with perfect single-crystallinity by

143 lateral epitaxial overgrowth. Moreover, several other epitaxial lateral growths of III–V single-
144 crystalline films have been demonstrated through nanopatterned graphene (33). Thus, the possibility
145 of defect-seeded lateral overgrowths cannot be completely excluded for an attempt of remote epitaxy
146 of III–V materials. Nevertheless, in lateral epitaxial overgrowth, surface topography and
147 crystallinity of epilayers are largely determined by the geometry and density of exposed areas. As
148 pinholes in graphene form in random places and sizes with non-uniform densities over local areas
149 in real cases, this will make it extremely difficult for pinhole-based epitaxy to exhibit the same
150 features as remote epitaxy, not to mention the reproducibility of clean exfoliation. Unless the 2D
151 layers have a high pinhole density, the most probable case might be a co-existence of the pinhole-
152 based and remote epitaxial growth mechanism when forming an epilayer (16, 17, 35).

153

154 Meanwhile, if nucleated islands do not laterally overgrow, then pinhole-based epitaxy would
155 not lead to the formation of completely single-crystalline epilayers. By the experiment described
156 next, we established that the conditions we use for the growth of the perovskite BTO by molecular-
157 beam epitaxy (MBE) involve minimal lateral epitaxial overgrowth. The experiment involved the
158 deposition of BTO onto a patterned, graphene-coated STO substrate. Here multilayer graphene was
159 used to be assured of polycrystalline BTO nucleation on the region of the STO substrate covered by
160 the multilayer graphene. From the perspective of the remote epitaxy mechanism, sufficiently thick
161 multilayer graphene will block the potential of the underlying substrate. From the perspective of the
162 pinhole epitaxy mechanism, the probability of a pinhole making its way through a thick graphene
163 layer is lower than through a thin graphene layer, resulting in a lower density of pinholes as the
164 thickness of the graphene layer is increased. From both perspectives, deposition of BTO on
165 multilayer graphene is expected to yield polycrystalline nucleation. Our expectation for a system
166 devoid of lateral epitaxial overgrowth is thus for the film to nucleate and grow polycrystalline on a
167 non-patterned, multi-layer graphene region, whereas the patterned, or substrate-exposed region will
168 result in a single-crystalline film. In the schematics of **Fig. 2C**, the epilayer colored in red represents
169 the single-crystalline region of film growth and the light pink represents the poly-crystalline region.

170

171 As representatively shown in **Fig. 2C**, a scanning electron microscopy (SEM) image
172 captures the surface of a 50 nm thick BTO film grown on an STO substrate coated by patterned
173 multilayer graphene. Distinct surface morphologies are observed that corresponds to the patterning
174 of the multilayer graphene. BTO grown on a multilayer graphene region exhibits a rough
175 polycrystalline surface, while BTO grown on the bare substrate region free of graphene exhibits a
176 smooth single-crystalline surface (see electron backscattered diffraction (EBSD) and a cross-

177 sectional TEM image in **fig. S1B** and **Fig. 2D**, respectively, for crystallinity). We did not observe
178 any single-crystalline BTO regions crossing the multilayer graphene stripes for any combinations
179 of line widths and periods used in this study. In **Fig. 2D**, we observe vertically formed single-
180 crystalline regions that stand out by bright contrast, showing no signs of lateral epitaxial overgrowth
181 to the nearby region. The insets in the enlarged image show selected area electron diffraction
182 (SAED) patterns at each region confirming the crystallinity (**Fig. 2E**). An annular bright field
183 scanning transmission electron microscopy (ABF-STEM) image in **Fig. 2F** captures the interface of
184 a polycrystalline region grown on trilayer graphene (shown as dark lines; see **fig. S2** for more
185 images). In order to confirm whether lateral epitaxial overgrowth may take place once we grow
186 thicker, we also grew a 500 nm-thick film. **fig. S3** shows polycrystalline BTO dominating over
187 single-crystalline regions, confining the single-crystalline BTO into a cone-shape, which still does
188 not show lateral epitaxial overgrowth.

189

190 Observing direct growth through pinhole by TEM

191 For a further discussion, we intentionally tracked pinholes on the epitaxial BTO films grown
192 on graphene-coated STO and studied crystallographic alignment of the obviously pinhole-seeded
193 nuclei. **Fig. 3A** shows an example of an actual pinhole and its effect on BTO growth. Direct epitaxy
194 occurred at local pinholes approximately 12 nm apart; however, these regions did not merge together
195 nor induce nicely aligned single-crystalline epilayers in the nearby region. Rather, the epilayers are
196 rotated in-plane, possibly due to strain caused by interaction between layers grown directly from the
197 substrate and layers nucleated on top of graphene. Therefore, in this system involving negligible
198 lateral epitaxial overgrowth, we see no evidence of unintentionally formed pinholes acting as the
199 main source of nucleation responsible for the overall epitaxial orientation of the final film.

200

201 To demonstrate a complete picture of remote epitaxy, we then grew 50 nm-thick BTO films
202 on 1–2 monolayer (ML) graphene-coated STO substrates using similar growth condition. The
203 quality of the film was confirmed by X-ray diffraction (XRD) as shown in **fig. S4**. The STEM
204 images in **fig. S5A, B** and **fig. S5 (C-E)** show remote epitaxial growth of BTO on STO coated by
205 monolayer and bilayer graphene, respectively, with lattice alignments following that of the substrate
206 in both cases. ABF-STEM images (**fig. S5B, E**) clearly show the number of graphene layers at the
207 interface. We also note that perfect single-crystalline BTO growth on monolayer graphene by
208 remote epitaxy has already been reported, successfully demonstrating the ability to peel off the BTO
209 film (13). Having identified an epitaxial system with minimal lateral epitaxial overgrowth poises us

210 to directly probe the mechanism of remote epitaxy. For a better, and direct clarification, we now
211 show the formation of lattice-aligned BTO nuclei in the following section.

212

213 **Growth of BTO nuclei without pinholes**

214 So far, assessment of successful remote epitaxy has been mostly limited to empirical
215 observations by examining the crystallinity of the epilayer and confirming its exfoliation after
216 growth. Previously reported cross-sectional TEM images representative of remote epitaxy, have
217 typically shown an enlarged local area at the interface to confirm the presence and thickness of a
218 2D layer as well as the crystallinity of both the epilayer and the substrate. Due to their limited field
219 of view, those images were subject to major concern on the possibilities for deliberately avoiding
220 or cropping nearby pinhole-based epitaxy regions that may have led to single crystalline epilayers
221 by lateral epitaxial overgrowth.

222

223 The mechanism of remote epitaxy can be firmly established by studying small BTO nuclei
224 grown on STO substrates covered by bilayer to trilayer graphene. We grew BTO films with an
225 average thickness of 3 unit cells on bilayer to trilayer-graphene covered STO for close observation
226 at the nucleation stage. Here we chose BTO for demonstration as it is relatively easier to control the
227 growth at the unit-cell level compared to III–V or III–N materials that have a faster growth rate as
228 well as longer diffusion lengths that would result in a more sparse and larger nuclei. The cross-
229 sectional STEM image on one of these islands in **Fig. 3B-D** shows a completely ‘floating’ island of
230 BTO on bilayer graphene, with the lattice aligned to the underlying STO substrate. Conventional
231 TEM specimens are about 30–50 nm thick along the beam direction, resulting in images showing
232 projection of materials within such thicknesses. The widest diameter of these BTO islands was
233 measured to be 27.78 nm on average (with a standard deviation of 8.99 nm). The STO substrate and
234 the BTO islands are viewed along the [100] zone axis. Due to the symmetry of the <100> BTO
235 directions, the extent of the island along the beam direction is comparable to the lateral extent of the
236 island. Therefore, the size of the BTO islands in this study makes it possible to encapsulate the entire
237 volume of the nuclei within the TEM specimen as in **Fig. 3B**, which completely eliminates possible
238 ambiguities in confirming the mode of epitaxy. As a side note, **Fig. 3C, D** is focused on the substrate,
239 not the island. This focus difference implies that the thickness of the nucleated island along the
240 electron beam is smaller than the thickness of the TEM specimen, as depicted in **Fig. 3B** and **fig. S6**. Due to the use of non-uniform multilayer graphene (small bilayer graphene regions mixed in
241 trilayer graphene) mentioned previously, most nuclei were randomly aligned due to quasi-vdW
242 epitaxy on thick graphene (density of total nuclei is approximately $(4.6 \pm 0.9) \times 10^{10} \text{ cm}^{-2}$).

244 Nonetheless, observation of nuclei aligned to the substrate lattice (density of aligned nuclei is
245 approximately $(1.2 \pm 0.7) \times 10^9 \text{ cm}^{-2}$) that could be observed at the bilayer graphene region showing
246 no signs of pinholes, signifies the remote epitaxy mechanism in action.

247

248 Considering the cost and expertise required for microscopic analysis (i.e., TEM),
249 macroscopic observation can be beneficial as it requires minimal processing of the material. Another
250 method for determining the mode of epitaxy is to grow spatially separated nano- or micro-crystals.
251 We can then macroscopically investigate the nucleation density and crystallographic orientation
252 influenced by the graphene thickness and the kinds of substrate materials (i.e., ionicity). This
253 approach is particularly useful for materials having fast growth rates which makes it hard to control
254 the size of nucleated islands down to a few nanometer scale. Also, it can benefit the study of
255 materials that prefer lateral epitaxial overgrowth (e.g, GaAs and GaN) where observations of the
256 growth mode can become difficult once they overgrow and form a planar film. In the next section,
257 we demonstrate how we can indirectly verify the mode of epitaxy with GaN micro-crystal (μC)
258 arrays that allows better visual and quantitative comparison by probing the unique characteristics of
259 remote epitaxy that are distinct from other epitaxy mechanisms.

260

261 **Effect of the number of graphene layers on remote epitaxy**

262 Performing epitaxial growth on varying thicknesses of graphene can lead to different
263 crystallographic orientation and nucleation density of the epilayer, clearly distinguishing the modes
264 of epitaxy. Given the characterizations of each growth modes in **Table 1**: (1) For remote epitaxy,
265 the nucleation density will decrease due to decreased penetration of electrostatic field from the
266 substrate. When the penetrated electrostatic field is too weak, the orientation of μC arrays will
267 become random, regardless of the underlying substrate. On the other hand, (2) for vdW epitaxy, the
268 nucleation density, and crystallographic orientation should be similar for all graphene thicknesses
269 owing to the short-range nature of the vdW attraction (36). (3) For pinhole-based epitaxy,
270 crystallographic orientation of μC arrays should always be uniformly aligned to the substrate. Also,
271 the exfoliation of μC arrays from the substrate may damage the substrate, leaving the fracture
272 footprints on the substrate. Based on such distinctive expectations among each epitaxial mechanism,
273 we expect the types of growth modes to be clearly distinguished as the graphene thickness increases.

274

275 To minimize pinholes in graphene, we prepared templates by directly growing graphene on
276 SiC substrates instead of transferring graphene. The graphene layers were formed directly on SiC
277 surface by graphitization of SiC, allowing fully “sealed” SiC with residue-free, clean graphene

278 layers to be achieved (37). Also, the number of graphene layers were controlled by adjusting
279 annealing conditions. **Figure 4 (A–C)** are SEM images of GaN μ Cs grown on single layer graphene
280 (SLG)-, bilayer graphene (BLG)-, and multilayer graphene (MLG, three layers or more)-formed SiC
281 substrates via metal-organic chemical vapor deposition (MOCVD). The number of graphene layers
282 was corroborated by Raman spectroscopic measurements (**fig. S7**). GaN μ Cs grown on a SLG/SiC
283 substrate showed long-range homogenous orientation of hexagonal pyramidal {1011} facets of μ Cs
284 over the entire substrate surface. This indicates that GaN μ Cs were epitaxially grown on SLG/SiC
285 substrates (**Fig. 4A**). For the case of epitaxy on BLG/SiC, we were still able to observe perfect
286 crystallographic alignment of GaN μ C to the SiC substrate, even though the SiC was covered by
287 directly grown bilayer graphene (see **Fig. 4B**). More importantly, the growth density of the epitaxial
288 μ Cs was notably reduced with an increase in the graphene thickness from SLG to BLG, due to
289 attenuation of electrostatic potential from SiC substrate. (**Fig. 4D**). The average density was
290 measured to be $(8.4 \pm 1.4) \times 10^5$ and $(8.5 \pm 1.3) \times 10^3 \text{ cm}^{-2}$ for SLG and BLG, respectively.

291

292 Without presuming the involvement of remote epitaxy, the change in nucleation density is
293 surmised to depend on pinhole formation mechanism, which remains inadequately understood. If
294 mechanical transfer or growth of an additional graphene layer is disrupted by pre-existing pinholes
295 at the bottom layer, pinholes may be vertically extended from bottom-most graphene up to the
296 topmost graphene, resulting in similar number of pinholes regardless of the graphene thickness.
297 However, the substantial decrease in nucleation density from SLG/SiC, BLG/SiC, to MLG/SiC
298 suggests we can rule out this possibility. Instead, the number of pinholes should decrease with an
299 increase in number of graphene layers, given that the pinholes can be completely concealed unless
300 they are identically aligned in each layer. As we are using directly grown graphene instead of
301 manually transferred ones, BLG/SiC is expected to have extremely lower pinhole density compared
302 to that of manually twice-transferred graphene. Based on our hypothesis, the aligned GaN μ Cs
303 grown on directly grown BLG/SiC supports remote epitaxy mechanism in action.

304

305 Moreover, if vdW interactions from graphene dictated the epitaxy, the use of SLG and BLG
306 would have exhibited similar growth densities. For the case of MLG/SiC, we observed the loss of
307 remote epitaxial interaction between μ Cs and substrates by the random alignment of μ Cs (**Fig. 4C**
308 and **fig. S8**) and a much lower density ($(2.9 \pm 0.8) \times 10^3 \text{ cm}^{-2}$) under the same growth conditions. This
309 also corroborates with ref.(11), where remote epitaxial growth of GaN was shown to fail for trilayer

310 graphene-covered SiC due to a substantial decrease in the penetration of electrostatic field from SiC.
311 These findings effectively rule out both the vdW and pinhole-based epitaxy.
312

313 Another distinguishable feature of remote epitaxy involves an easy and clean peelability of
314 the epilayer enabled by the non-covalent, weakly bound remote epitaxial interface. The exfoliation
315 of GaN μ Cs was performed by the polymeric encapsulation–mechanical exfoliation technique using
316 adhesive tape (9, 38). Prior to exfoliation, polyimide (PI) was spin-coated to fill the gaps between
317 μ C arrays. Here, the PI filler can mechanically support the μ Cs by forming a film, thereby allowing
318 exfoliation of the μ Cs without geometric collapse of random arrays during the exfoliation process.
319 Then, the PI-encapsulated μ C film was delaminated from the substrate using a thermal release tape.
320 As shown in the SEM image of **Fig. 4E**, GaN μ C arrays were nicely released, maintaining the film
321 form without any fracture or loss of μ C arrays. Furthermore, the substrate surface after exfoliation
322 was also found to be clean and smooth after exfoliation, without any spalling marks or substrate
323 damage (**Fig. 4F** and **fig. S9**). Such a result is unexpected for the case of pinhole-based epitaxy. This
324 complete separation signifies the remote epitaxial character of GaN μ Cs epilayer.

325

326 **Effect of the substrates with different ionicity and temperature on remote epitaxy**

327 The potential fluctuation on the graphene surface induced from the substrate depends not
328 only on the graphene thickness but also on the ionic character (i.e., ionicity) or polarity of underlying
329 compound substrate materials (2, 39, 40). In this regard, we additionally investigated the effect of
330 bonding ionicity of the substrate to show the characteristics of remote epitaxy by comparing the
331 growth density of GaN μ Cs using graphene-coated Al_2O_3 and GaN substrates. The ionicity can be
332 calculated using the Pauling's equation below, which is calculated as the electronegativity difference
333 of bonded atoms:

$$334 \quad \text{Ionicity \%} = [1 - \exp(-0.25 \times (X_A - X_B)^2)] \times 100$$

335 where X_A and X_B are electronegativity values of atom A and atom B, respectively. According to the
336 equation, the ionic character percentage for Al_2O_3 ($X_{\text{Al}}: 1.6$, $X_{\text{O}}: 3.5$) and GaN ($X_{\text{Ga}}: 1.8$, $X_{\text{N}}: 3.0$) are
337 calculated to be 59.4% and 30.2%, respectively. From this result we estimate a higher growth density
338 on Al_2O_3 substrates than on GaN substrates.

339 To empirically demonstrate the effect of the ionicity of the substrate materials, remote
340 epitaxy of GaN μ Cs was carried on CVD-grown graphene-coated *c*-plane $\text{Al}_2\text{O}_3(0001)$ and *c*-plane

341 GaN(0001) substrates at diverse growth temperature conditions of 900, 950 and 1000 °C by
342 MOCVD. SEM images in **Fig. 5A, B** display surface morphologies of remote epitaxial GaN μ Cs
343 grown on graphene/Al₂O₃ and graphene/GaN, respectively. As marked with orange arrows in
344 **Fig. 5A, B**, homogeneous in-plane ordering of hexagonal sidewall {1010} facets of vertical μ Cs was
345 observed over the entire surface of the substrates despite the use of a poly-domain CVD-graphene
346 layer with a typical domain size of 5–25 μ m. This indicates that GaN μ Cs form an epitaxial
347 relationship with the underlying single crystalline Al₂O₃ and GaN substrates across the graphene.

348 Cross-sectional STEM images of remote epitaxial interfaces of GaN μ C/graphene/Al₂O₃ and
349 GaN μ C/graphene/GaN clearly display structural discontinuity due to the existence of graphene
350 between the GaN μ Cs epilayer and the substrates (i.e., Al₂O₃ and GaN) (**fig. S10A, B, E and F**). It
351 should be noted that, in our remote epitaxy experiments, we specifically employed graphene-coated
352 N-polar GaN substrate. Otherwise, graphene/Ga-polar GaN substrate would be thermochemically
353 decomposed under the high growth temperatures required for growing GaN μ Cs in MOCVD, thus
354 precluding successful remote epitaxy (41). The non-covalent remote epitaxial GaN
355 μ C/graphene/Al₂O₃ and GaN μ C/graphene/GaN interfaces allowed exfoliation of the μ Cs epilayer
356 from substrates by thermal release tape (**fig. S11**). The atomic-resolution STEM images and
357 selective-area electron diffraction (SAED) patterns obtained from substrates and GaN μ C reveal
358 well-defined remote epitaxial relationships of (0001)[1010] _{μ C} || graphene || (0001)[1120]_{Sapphire} (**fig.**
359 **S10C, D**) and (0001)[1010] _{μ C} || graphene || (0001)[1010]_{GaN} (**figs. S10G, H**).

360 The nucleation densities of remote epitaxial μ Cs on two different substrates were
361 quantitatively measured, as shown in **fig. 5C**. Interestingly, although the GaN μ Cs were grown on
362 the same graphene surface under the same MOCVD growth conditions, even in the same batch, the
363 average nucleation density of GaN μ Cs grown on graphene/Al₂O₃ was consistently higher than that
364 on SLG/GaN for all growth temperatures. This trend is associated with the difference in the
365 electrostatic interaction from the underlying substrate across graphene. Also, as shown in the SEM
366 images in **Fig. 5A,B**, and statistically analyzed in **Fig. 5C**, the density of μ Cs decreased by
367 increasing the growth temperature on both Al₂O₃ and GaN templates, which indicates increased
368 diffusion length of adatoms on graphene at higher temperatures. For pinhole-based epitaxy, since
369 the nucleation density will only depend on the density of pinholes for each prepared template, there
370 should be no clear trend of growth densities for different substrates or growth temperatures. Hence,
371 these results corroborate our hypothesis that remote epitaxy on substrates with higher ionicity can

372 exert a stronger electrostatic force through the graphene layer and attract more adatoms to the
373 graphene surface, resulting in a higher density formation of μ Cs formed.

374

375

376 **Discussion**

377 In conclusion, direct and indirect evidence reveals that remote epitaxy is a distinct epitaxial
378 mechanism. This conclusion arises from selecting a materials system that does not exhibit lateral
379 epitaxial overgrowth, by mimicking pinhole-based epitaxy utilizing patterned graphene, and by
380 varying growth conditions to observe the unique characteristics of remote epitaxy. Meanwhile, our
381 results highlight the importance of the quality and number of graphene layers required for
382 conducting remote epitaxy, which otherwise can unintentionally induce pinhole epitaxy or lead to a
383 failure of remote epitaxy. Strict measures (28) should be followed to guarantee the quality of the
384 transferred graphene and to avoid damage.

385

386 The degree of damage caused in 2D layers seems to be highly dependent on growth methods
387 and conditions for different materials system. As directly grown pristine graphene on SiC can be
388 supplied easily, remote epitaxy of III-N materials has been successful and most widely studied. On
389 the other hand, only a handful of oxide growths have been reported to date as oxygen, oxygen
390 plasma, or ozone required in the growth process as well as harsh growth conditions can easily
391 deteriorate 2D layers. We have experienced that high temperature growth of oxides by pulsed-laser
392 deposition (PLD) leads to a larger area of damage in 2D, making oxides that can be grown at lower
393 substrate temperatures such as spinels or garnets more suitable for PLD. For perovskites which
394 require growth temperature above 600 °C, MBE seems to be a better option, particularly for
395 perovskites like STO and BTO that grow readily in O₂ rather than needing oxygen plasma or ozone.
396 The effect of growth methods and the range of temperature on graphene damage should be
397 systematically studied to understand the limits and to seek improvements that can be made for
398 performing better remote epitaxy (20, 42). Recently, direct growth of graphene on several oxide
399 substrates of interest (43) have been demonstrated, allowing consecutive remote epitaxial growth of
400 films in the growth chamber under high vacuum. Additionally, remote epitaxy has been performed
401 on transition metal dichalcogenides (TMDs) which demonstrates all aspects of remote epitaxy we
402 have discussed so far (14, 44). Such advances are moving towards establishing remote epitaxy as a
403 more robust mechanism by eliminating previously discussed scientific ambiguities. Overall, we
404 hope this paper can serve as a guideline for researchers on distinguishing the differences among 2D

405 assisted epitaxy modes and to make remote epitaxy the dominant epitaxial mechanism when it is so
406 desired.

407

408

409 **Materials and Methods**

410 **Preparation of graphene templates for oxide growth**

411 Graphene grown on SiC was transferred onto STO substrates using a dry transfer method. After
412 graphene was transferred onto the substrate, the graphene was patterned at nanoscale by various
413 types of lithographic methods, including e-beam lithography, interference lithography, and stepper
414 lithography. More details on the graphene transfer method (5, 28) and process for graphene
415 patterning can be found in previous references (33).

416

417 **MBE Growth of BTO**

418 BTO thin films were deposited on (001)-oriented SrTiO_3 substrates partially or fully covered by
419 graphene layers by reactive molecular-beam epitaxy in a Veeco GEN10 chamber at a background
420 pressure of 1×10^{-6} Torr O_2 . The STO substrates were prepared with a TiO_2 -termination following
421 the procedure established by Koster *et al.* (45), with the graphene coating applied after this
422 termination procedure. Source materials of elemental barium in a low-temperature effusion cell and
423 titanium from a Ti-Ball® (46) were used to synthesize BTO using the growth method illustrated in
424 Barone *et al.* (47). *In-situ* monitoring of the half-order streaks appearing along the [110] azimuth in
425 the reflection high-energy electron diffraction (RHEED) pattern allowed for calibration of the
426 source fluxes for deposition of stoichiometric BaTiO_3 . After the sources were calibrated, graphene-
427 coated substrates were heated in ultra-high vacuum to growth temperatures in the 850–970 °C range,
428 measured by a thermocouple that is near, but not in contact with the substrate. From optical
429 pyrometer measurements, the true temperature of the substrate is about 100 °C cooler. To protect
430 against graphene damage, the O_2 oxidant was supplied with a background pressure of 1×10^{-6} Torr
431 controlled by a feedback loop to a motorized VAT series 590 variable leak valve after the substrate
432 temperature was reached. As soon as the O_2 background pressure of 1×10^{-6} Torr was reached, the
433 shutters to the barium and titanium sources were simultaneously opened for a predetermined time
434 to grow a targeted thickness of BTO. In the case of the 3-unit cell thick BTO film, a measurement
435 of the time taken to complete one unit cell of BTO during the RHEED oscillation calibration was
436 found to be 29 s. The 3-unit cell thick BTO film was grown by co-deposition of barium, titanium,

437 and O₂ for three times this duration (a total of 87 s) immediately following the calibration of the
438 source fluxes. All films were cooled in the same pressure of O₂ in which they were grown until the
439 substrate temperature was below ~200 °C, at which point the O₂ was turned off and the films were
440 transferred out of the growth chamber. RHEED was conducted using a Staib electron gun operating
441 at 13 keV and 1.3 Å. X-ray diffraction data was collected using a PANalytical Empyrean X-ray
442 diffractometer with Cu K α_1 radiation.

443

444 **Substrate preparation of graphene/SiC substrates and remote epitaxy of GaN μ C arrays**

445 Remote epitaxy of GaN μ C arrays were conducted on SLG, BLG, and MLG directly grown on SiC
446 substrates. Wafers with a size of 0.9 × 0.9 cm² were prepared from 4-inch on-axis semi-insulating
447 4H-SiC (0001) (Cree Lighting). Then they were pre-treated in Nano-strip solution for 15 min. For
448 graphitization, these wafers were loaded into a Model 1000-4560-FP30 (Thermal Technology LLC),
449 and surface cleaning and anisotropic step-bunching were performed under hydrogen atmosphere. Si
450 sublimination was conducted under an Ar pressure of 1 atm at 1800 °C for 5 and 10 min for BLG
451 and MLG, respectively. A stressor layer composed of Ni, which applies a tensile stress, was
452 deposited via plasma sputtering with a Rocky Mountain Vacuum Tech Intelsi-L series multi-
453 function PVD system for exfoliation of epitaxial graphene layers. Then a thermal release tape was
454 placed on the Ni stressor, causing the graphene to be mechanically exfoliated from the SiC surface
455 and thereby revealing pseudographene, which we denote as SLG in this work. MOCVD growth of
456 GaN μ Cs was conducted on a 2-inch wafer using a closed-coupled vertical showerhead reactor
457 (SYSNEX, Marble 180), facilitated by the Metal-organic Compounds Materials Core Facility
458 Center for Advanced Materials Application. Trimethyl-gallium (TMGa) and NH₃ gas were
459 introduced as precursor reactants for Ga and N, respectively, with a high-purity H₂ carrier gas. The
460 GaN μ Cs were grown using the precursors TMGa and NH₃ with flow rates of 6 and 2000 sccm,
461 respectively, at 1000 °C for 10 min.

462

463 **Substrate preparation of graphene/Al₂O₃ and graphene/GaN substrates and remote epitaxy 464 of GaN μ C arrays**

465 Remote epitaxy of GaN μ C arrays was performed on graphene-coated Al₂O₃ (0001), and N-polar
466 GaN (0001) substrates via MOCVD. The graphene was synthesized on copper foil using chemical
467 vapor deposition method, which produced poly-domain single layer graphene. Then, the graphene
468 was transferred onto the Al₂O₃ and N-polar GaN substrates by wet transfer technique using a
469 poly(methyl-methacrylate) as a supporting layer (48). For the MOCVD growth of GaN μ Cs, TMGa

470 and NH₃ gas were introduced as precursor reactants for Ga and N, respectively, with high-purity H₂
471 carrier gas. The GaN μ Cs were grown using the precursors of TMGa and NH₃ with the same flow
472 rates of 15 sccm at 900, 950, and 1000 °C for 10 min.

473

474 **Exfoliation of μ C arrays**

475 The GaN μ Cs was exfoliated by utilizing the polymeric encapsulation–mechanical exfoliation
476 technique using sticky tape (37). For the exfoliation of GaN μ C arrays, gaps between μ Cs were
477 filled with PI using spin-coating method to support the μ C arrays. The PI layer was then dried at
478 120 °C for 2 min and cured at 300 °C for 5 min on a hot plate. The PI encapsulation layer allowed
479 to exfoliate GaN μ Cs overlayer without geometric collapse by mechanically supporting the μ C
480 arrays. The PI-encapsulated μ C arrays were exfoliated from the substrates using a thermal release
481 tape.

482

483 **Electron microscopy characterization of materials**

484 SEM imaging and preparation of TEM specimens were performed using an FEI Helios 660 focused
485 ion beam (FIB) with beam voltage and current of 30 kV and 80 pA, respectively and then lowered
486 to 5 kV and 68 pA for final thinning. Carbon was first deposited by electron-beam evaporation to
487 protect the film and additional platinum was deposited with an ion beam to minimize FIB milling
488 damage. Atomic scale STEM images were acquired using a Thermo Fisher Scientific (TFS) Themis
489 Z G3 aberration-corrected scanning transmission electron microscope at a beam voltage of 200 kV.
490 HAADF-STEM and ABF-STEM images were acquired with a convergence angle of 80–200 mrad
491 and 10–30 mrad, respectively. To determine the nuclei density, we counted the as-grown crystals
492 using SEM in a given unit area. It was postulated that all nuclei, larger than a critical size would
493 overcome the activation energy barrier, attracting more adatoms and subsequently growing into
494 crystallites large enough to be visible in SEM. At least 10 different areas were examined to guarantee
495 the statistical reliability of the average number density and its standard deviation. To improve the
496 statistical accuracy, we utilized particle analysis program ‘Image J’.

497

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723 supplementary materials.

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Tables and Figures

	Remote Epitaxy (1, 4, 28)	van der Waals Epitaxy (29-31)	Pinhole-based Epitaxy (16, 17)
All three epitaxy involves 2D layers as interlayers			
Concept	<ul style="list-style-type: none"> Epitaxy influenced by substrate bonding ionicity/polarity through lattice-transparent ultrathin 2D van der Waals interlayer 	<ul style="list-style-type: none"> Epitaxy based on van der Waals interacting force from the substrate surface (e.g., graphene or other 2D van der Waals layers) 	<ul style="list-style-type: none"> Epitaxy based on direct nucleation through pinholes in 2D layer completed by lateral overgrowth
Nucleation from	<ul style="list-style-type: none"> Attracting force given by partially penetrated bonding ionicity/polarity of the substrate No chemical bonds are formed at the interface Surface potential on 2D layer resembles that of underlying substrate, driving the nucleation and epitaxial growth aligned to the underlying substrate 	<ul style="list-style-type: none"> Van der Waals interaction from 2D substrate holds adatoms arranged in the lattice pattern of the substrate without chemical bonds Either the overlayer or the substrate surface having dangling bonds or reconstructed dangling bonds leads to epitaxy establishing a quasi-van der Waals interaction between epilayer and the substrate (quasi-vdW epitaxy) 	<ul style="list-style-type: none"> Chemical bonds on exposed surface of substrate through holes in 2D layer Adatom adsorption preferentially on the substrate rather than 2D layer Selectivity of adatom adsorption
Characteristics	<ul style="list-style-type: none"> van der Waals interaction from 2D layer but also forms a stronger interaction with the substrate via penetration of substrate ionicity/polarity Strain from lattice mismatch but significantly reduced Epilayer lattice aligns with the underlying substrate, irrespective of 2D layer in-plane orientation Applicable regardless of crystallinity/polarity of the vdW interlayers, but directly affected by their thickness Atomically precise exfoliation enables substrates to be reusable 	<ul style="list-style-type: none"> van der Waals interaction at the interface Epilayer lattice alignments do not necessarily follow the underlying substrate, but follow the crystal structure of the 2D layer Applicable to largely lattice-mismatched materials Easy exfoliation 	<ul style="list-style-type: none"> Direct covalent bonding on substrate Local strain from lattice mismatch Lateral overgrowth of the material is required for growing a film structure Epilayer lattice aligns with the substrate Precise control of pinhole location and density are required for uniform film growth and exfoliation Exfoliation may lead to fracture damage of the substrate

Table 1. Summary of three different epitaxy mechanisms Concepts and characteristic features for remote, van der Waals, and pinhole-based epitaxy are summarized in the table.

Fig. 1 Schematics of three different mechanisms of growth upon an intervening van der Waals layer nominally covering a substrate surface. 3D schematics show the growth mechanism of (A) remote, (B) Quasi- van der Waals, and (C) pinhole-based epitaxy methods. vdW epitaxy refers to epitaxial growth on a dangling-bond-free substrate via weak van der Waals interaction between grown materials and the substrate. (B), therefore, is a quasi-vdW epitaxy where conventional bulk material with initial dangling bonds (usually 3D materials) are grown on a vdW substrate, which corresponds to the examples shown in our study. The grown epilayer exhibits incommensurate in-plane lattices and the alignment follows the underlying vdW surface as shown. Cross-sectional view depicted below highlights the differences among these mechanisms. (D) Summary of various materials showing the effect of polarity on remote epitaxy. Non-polar substrates such as Si, Ge leads to polycrystalline epilayers, while polar GaAs can induce remote epitaxy of a single crystalline GaAs film. The polarity of the film also matters, as shown by polycrystalline Ge grown on graphene-covered polar GaAs substrate.

Fig. 2 Oxide growth on patterned Graphene (A) Graphene is patterned using electron beam lithography, with width and period as defined in the schematics. An example of patterned graphene on a SrTiO_3 substrate with dark (graphene) and bright stripes (openings) is shown in the SEM image. Expectation and actual results for epilayer growth of materials with different diffusion lengths are shown in Fig. 2(B, C). (B) GaAs grown on patterned graphene with width and period of 100 and 200 nm, respectively, shows a smooth surface as a result of lateral overgrowth of nucleation sites from the openings. (C) Plan-view SEM image of BaTiO_3 grown on patterned graphene of width 200 nm and period of 800 nm shows a different surface morphology correlated to the pattern. Bare substrate region leads to smooth surface while multi-graphene region results in a rough surface of BaTiO_3 . (D, E) Cross-sectional HAADF-STEM image of BaTiO_3 grown on patterned graphene with a width of 100 nm and 800 nm period shows crystallinity of each region more clearly. The distinguishable contrast reveals single (bright) and poly (dark) crystalline region. Insets in (E) show SAED patterns for each region confirming its crystallinity. (F) The white-boxed region in (E) is enlarged to show tri-layer graphene under poly-crystalline domains. A set of three red lines indicating each graphene layer on the left, serves as a guide to the eye. Scale bar in (A-C) is 2 microns.

757 **Fig. 3 TEM images of pinhole-based epitaxy and remote epitaxy of BTO grown on gr/STO** **(A)** Example
758 of an area showing direct growth through pinholes. Direct growth regions are denoted with red arrows. They
759 do not show lateral growth leading to single-crystalline film aligned to the substrate, instead, we can observe
760 domains with in-plane rotation. The schematic in the right shows simplified domains to aid understanding.
761 **(B)** The schematic depicts the encapsulated nuclei within the sampled TEM specimen. TEM images are
762 acquired perpendicular to the cross-section, where the electron beam direction is denoted by a white cross.
763 **(C), (D)** shows simultaneously taken HAADF- and ABF-STEM images of remote-epitaxially formed island
764 without any pinholes, respectively. The atomic alignments of the island follow the bottom substrate lattice.
765 Bi-layer graphene without pinholes can be observed from **(D)**.

766 **Fig. 4 Influence of graphene thickness on remote epitaxy of GaN μ Cs.** Plan-view SEM images of remote
767 epitaxial GaN μ Cs grown on **(A)** SLG-, **(B)** BLG-, and **(C)** MLG-grown SiC substrates. **(D)** Plot of growth
768 density of μ Cs as a function of number of graphene layers. SEM images of **(E)** bottom side of exfoliated PI-
769 encapsulated GaN μ Cs and **(F)** substrate surface after the exfoliation process.

770 **Fig. 5 Influence of substrate with different ionicity and growth temperatures on remote epitaxy GaN**
771 **μ Cs.** Plan-view SEM images of GaN μ Cs grown on graphene-coated **(A)** Al_2O_3 and **(B)** N-polar GaN
772 substrates under growth temperature conditions of 900, 950, and 1000 °C. Orange arrows indicate the in-
773 plane orientation of {1010} sidewall facets of μ Cs. **(C)** Comparison of growth density of GaN μ Cs grown
774 on graphene/ Al_2O_3 (red columns) and graphene/GaN substrates (blue columns) at 900, 950, and 1000 °C.
775 The growth density of μ Cs grown on graphene/ Al_2O_3 at 900, 950 and 1000 °C were $(5.7\pm0.5)\times10^6$,
776 $(3.7\pm0.6)\times10^6$, and $(1.4\pm0.1)\times10^6 \text{ cm}^{-2}$, respectively. The growth density of μ Cs grown on graphene/GaN at
777 900, 950 and 1000 °C were $(3.8\pm0.8)\times10^6$, $(1.6\pm0.2)\times10^6$, and $(1.1\pm0.1)\times10^6 \text{ cm}^{-2}$, respectively.

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