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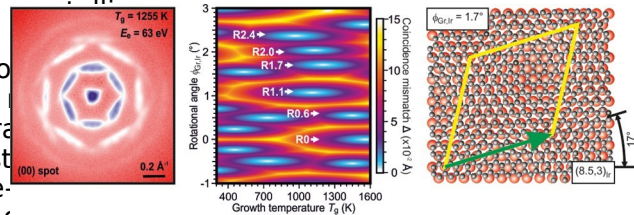
Temperature-Controlled Rotational Epitaxy of Graphene

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ABSTRACT: When graphene is placed on a surface, the periodic structures within the layers and moiré superlattices form. Small lattice rotations of the two materials in contact strongly modify the moiré pattern, upon which many electronic, vibrational, and chemical properties depend. While precise adjustment of the relative orientation in the degree- and subdegree-range is not easily achieved via careful deterministic transfer of graphene, we report on the spontaneous reorientation of graphene on a metallic substrate, Ir(111). We find that selecting a substrate temperature between 1530 and 1000 K during the growth of graphene leads to distinct relative rotational angles of 0° , $\pm 0.6^\circ$, $\pm 1.1^\circ$, and $\pm 1.7^\circ$. When modeling the moiré superlattices as two-dimensional coincidence networks, we can ascribe the observed rotations to favorable low-strain graphene structures. The dissimilar thermal expansion of the substrate and graphene is regarded as an effective compressive biaxial pressure that is more easily accommodated in graphene by small rotations rather than by compression.

KEYWORDS: *graphene, strain-relief, moiré, iridium, thermal expansion*



In most future applications, graphene will have to be supported either by a substrate or another two-dimensional (2D) material.¹ Since the lattice parameters of the graphene and the neighboring materials are usually different, lateral modulations in the stacking configuration will result. These modulations are described as moiré lattices, and their properties are determined by the rotational angle, which also defines the resulting strain state of the graphene.^{2–4} Controlling the moiré pattern's structural parameters constitutes a major yet important challenge⁵ since the parameters of the moiré pattern cause fundamental changes to the

control the properties of the 2D material. We use high-resolution low-energy electron diffraction to study the moiré patterns formed between graphene and Ir(111). In comparison to local probes, diffraction is excellently suited to determine the angular distribution of rotated domains, as it averages over a large surface area. In earlier studies of graphene on Ir(111), large angles of rotation have been found at different growth temperatures, which have been studied extensively

past.^{16,17} In contrast, here we report distinct rotational angles of 0° , 60°

36 properties of graphene. Known examples for the
influence of
37 the moiré pattern are the amplitude and energy
range of moiré-
38 induced electronic mini-gaps,^{6,7} superlattice
Dirac cones⁸ in

39 graphene, the energy range of Van Hove
singularities in twisted
40 bilayer graphene,^{9,10} the Hofstadter
butterfly spectrum in
41 graphene on hexagonal boron nitride,^{11,12}
and correlated
42 electron phenomena in twisted bilayer
graphene.^{13–15} In all
43 these examples, the interaction between
graphene and the
44 support is sufficiently weak to maintain the
graphene's genuine
45 2D properties, while it can be shown that the
properties are
46 modified by the presence of the
moiré superstructure.
47 Here, we address the question whether
engineering of the
48 moiré pattern in a high-quality epitaxially
grown graphene or
49 2D related material through manipulation of
the rotational
50 angle is possible. Such engineering might
provide a strategy to

0.6°, ±1.1°, and ±1.7° as the growth temperature
decreased⁶¹
from 1530 to 1000 K. We explain the observed
rotational⁶²
angles within a basic model describing the 2D
in-plane⁶³
coincidence of the substrate and graphene lattice.
Justified by

the results of Hattab et al.,¹⁸ our model accounts for
the⁶⁴
65

varying lattice parameter of Ir(111) compared to
an essentially⁶⁶ constant graphene lattice
parameter, as the growth temperature⁶⁷
changes. The distinct thermal behavior of the two
materials⁶⁸ effectively imposes a biaxial
pressure exerted on the graphene⁶⁹ layer,
which induces a rotation rather than
compression. This⁷⁰

has lately been referred to as rotational epitaxy.¹⁹
71

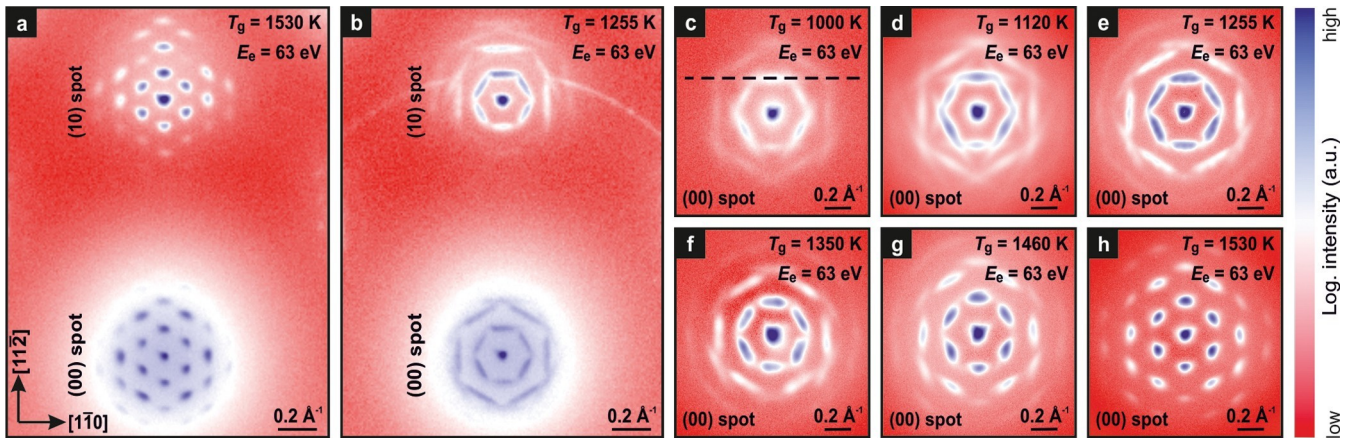


Figure 1. Room-temperature SPA-LEED patterns at different growth temperatures T_g for $E_e = 63$ eV. (a,b) Overview patterns for growth at 1530 and 1255 K, respectively. (c-h) Close-up patterns of the (00) spot at different growth temperatures between 1000 and 1530 K with subtracted background to reveal details of each spot. In (c) the direction of the line profiles shown in Figure 2a is marked by the dashed black line.

72 Experimental Section. Preparation of
 73 samples and experiments were performed in an ultrahigh
 vacuum (UHV)
 74 chamber with a base pressure of 1×10^{-10}
 mbar. The UHV
 75 chamber is equipped with a chemical vapor
 deposition reactor
 76 for preparation. Spot profile analysis—low
 energy electron
 77 diffraction (SPA-LEED) was used for
 characterizing the
 78 orientation of the graphene layer.
 SPA-LEED provides
 79 superior resolution in terms of reciprocal space
 and signal-to-
 80 noise ratio in comparison to conventional
 optical LEED
 81 systems.^{20,21} A well-oriented Ir(111) substrate
 was prepared by
 82 repeated sputter annealing cycles until the
 full width at half-
 83 maximum (FWHM) of the diffraction spots was
 limited by the
 84 instrumental resolution of $\sim 1\%$ Brillouin zone.
 On the Ir(111)
 85 surface, graphene layers were grown using
 thermal catalytic
 86 decomposition²² of ethylene (C_2H_4) at a
 pressure of 5×10^{-6}
 87 mbar and substrate temperatures between
 1000 and 1530 K
 88 (reached using electron bombardment of the
 backside of the
 89 sample). The sample temperature was
 determined using an
 90 Impac IGA 10 infrared pyrometer. The
 decomposition of C_2H_4
 91 is only effective in the presence of bare
 Ir(111) so graphene
 92 growth is self-limited²² to a single layer. Under
 the conditions
 93 used here, the surface is completely covered
 with graphene
 94 after less than 1 min of exposure with C_2H_4 .

$k_{\text{moiré}} = k_{Gr} - k_{Ir}$.^{2,3,24} The position of the moiré spots
 is thus strongly dependent on even very small
 variations of the graphene lattice parameter¹⁷
 or rotations^{25,26} the moiré spots act as a
 “magnifying glass” to detect strains and rotated
 domains. Figure 1b shows the same segment
 of the reciprocal space after preparation of
 graphene at a lower temperature of 1255 K. It
 is known that at such low growth temperatures
 graphene forms large-angle rotational domains
 on the surface,^{16,17,27,28} and these domains
 are reflected in a faint ring of diffracted
 intensity, which is centered around the (00)
 spot and intersects the (10) spot. Also, unlike
 in Figure 1a, the moiré spots in Figure 1b
 are substantially elongated, similarly
 observed by Usachov et al.²⁹ Figure 1c-h
 shows the temperature dependence of the
 spot elongation around the (00) spot. With
 an increasing growth temperature, the

elongated character is progressively lost.

130

SPA-LEED

95 probes a surface area of the order of 1
 mm², and thus, the
 96 diffraction pattern is averaged across
 this surface area. All
 97 SPA-LEED patterns and line profiles were
 recorded at room
 98 temperature, after the sample has been
 cooled down from
 99 growth temperature.

f1 100 Results and Discussion. Figure 1
 shows SPA-LEED

101 patterns at an electron energy of $E_e = 63$

eV. Figure 1a,b show sections of the reciprocal space including the (00) spot and the first integer order spot (10) for growth at 1530 and 1255 K, respectively. In Figure 1a the graphene layer is not rotated with respect to the Ir substrate (R0 phase); still, both Ir(111)

integer order spots are surrounded by distinct satellite spots that arise from the moiré pattern of the graphene layer and the Ir(111) substrate.^{17,23} The spot spacing between the satellites is determined by the lattice parameter difference of graphene and Ir of ~10%.^{17,18} These moiré spots are clearly observed up to fourth order in the false-color plot, reflecting the long-range order of the epitaxially grown graphene on the Ir(111) substrate. The positions of the moiré spots can be determined as a function of the graphene and Ir(111) unit cell vectors as

Figure 2 summarizes an analysis of the first order moiré spots surrounding the (00) spot, along the dashed black line shown in Figure 1c. Figure 2a shows a stack of line profiles recorded after growth at different temperatures. The profiles have been vertically shifted, and the growth temperature increases from bottom to top. The features marked “B” and “C” in the profiles simply originate from intersections with other first and higher-order moiré spots and do not warrant further discussion. We will instead discuss the central features “A” and “R0”, which provide new information about the morphology of the graphene layer. With increasing growth temperature these features become sharper. At intermediate growth temperatures of 1255–1350 K not only a broadening of “A” is observed but also a fine structure of two or three distinct and distinguishable diffraction peaks can be identified.

These peaks each correspond to small-angle rotations with respect to the Ir(111) lattice (amplified by the aforementioned “magnifying glass” effect), meaning the graphene layer comprises small-angle rotational domains.

The intensity profiles of the moiré spots in Figure 2a reflect the angular distribution function of rotated domains in the graphene layer. Figure 2d illustrates the relevant angles and lattice vectors that result in the formation of rotated moiré patterns. For each rotated domain, the rotational angle $\phi_{Gr,Ir}$ relative to the Ir substrate can be determined with extremely high accuracy from the experimental splitting of the first order moiré spots ($\delta k_{[112]}, \delta k_{[1\bar{1}0]}$) relative to the (00) spot. The

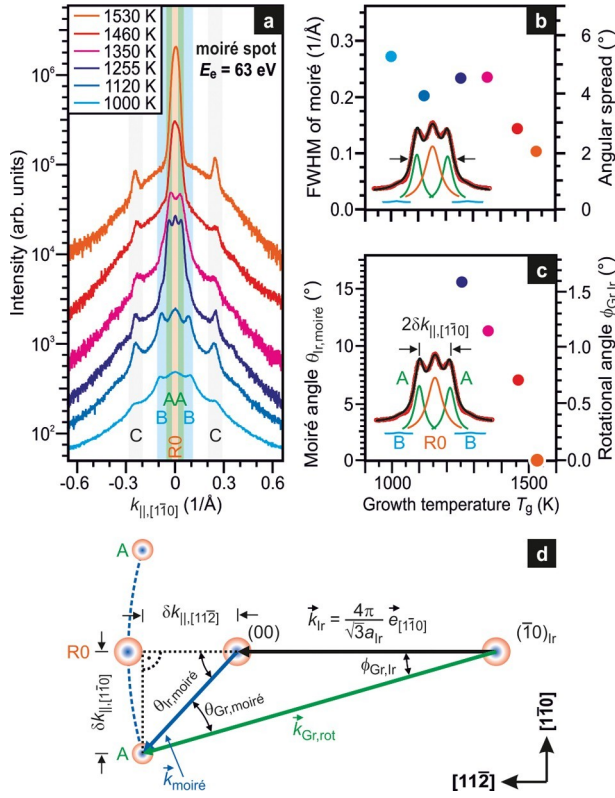


Figure 2. Moiréspot analysis. (a) High-resolution SPA-LEED line profiles reflecting the angular distribution of rotated domains. The line profiles have been recorded for different growth temperatures T_g and were taken along the elongated direction of the first order moiré spots of the (00) spot as marked in Figure 1c. (b) fwhm of the entire moirépeaks “R0” and “A” at different temperatures. (c) Observed rotational angle $\phi_{Gr,Ir}$ and moiréangle $\theta_{Ir,moiré}$ as a function of graphene formation temperature. (d) Schematic diagram of the reciprocal lattice vectors of rotated graphene $k_{Gr,rot}$ and Ir k_{Ir} along with the rotational angle $\phi_{Gr,Ir}$ and the moiréangles $\theta_{r,moiré}$ and $\theta_{Gr,moiré}$ with respect to Ir(111) substrate and graphene, respectively (the positions of the spots are shifted for better visibility).

158 experimental values of $\delta k_{\parallel,[110]}$ can be extracted directly from
 159 Figure 2a. The moiréangle $\theta_{Ir,moiré}$ can also be derived by
 160 considering the two triangles in Figure 2d as

$$\tan \theta = \frac{\delta k_{\parallel,[110]}}{\dots} = \sin \phi_{Gr,Ir}$$

is present at 1530 K, resulting in a high-quality well-ordered ¹⁷⁵ graphene layer without additional ¹⁷⁶ rotated domains.

The rotational angles $\phi_{Gr,Ir}$ of the components of the “A” ¹⁷⁷ feature are determined using eq 2 (see Figure 2c). Fitting the ¹⁷⁸ line profiles in Figure 2a with Gaussian peaks, we are able to ¹⁷⁹ extract distinct rotational angles for growth temperatures of ¹⁸⁰ 1255 and 1350 K. For the growth at 1255 K, we observe three ¹⁸¹ peaks at $\phi_{Gr,Ir} = \pm 1.7^\circ$ and $\phi_{Gr,Ir} = 0^\circ$, respectively, while for ¹⁸² the growth at 1350 K, we only observe two peaks at $\phi_{Gr,Ir} = \pm 1.83^\circ$ ¹⁸³ without any contribution of the R0 phase. The line ¹⁸⁴ profile of the graphene layer grown at 1460 K does not show ¹⁸⁵ distinct peaks. Instead, the central part of the moiréspot is ¹⁸⁶ significantly broadened in comparison with the other growth ¹⁸⁷ temperatures. This broadening suggests that the moiréspot ¹⁸⁸ actually consists of three overlapping contributions, wherein ¹⁸⁹ there is a coexistence of small-angle rotated domains with $\phi_{Gr,Ir}$ ¹⁹⁰ $= \pm 0.6^\circ$ and $\phi_{Gr,Ir} = 0^\circ$. For a graphene formation temperature ¹⁹¹ of 1530 K, we finally find the R0 phase only. We note that for ¹⁹² lower growth temperatures (1120 and 1000 K), we do not ¹⁹³ observe any rotational angles between the intersections “B” ¹⁹⁴ from other first order moiréspots except the R0 phase. ¹⁹⁵ Nonetheless, from the SPA-LEED patterns at 1255 K shown ¹⁹⁶ in Figure 1b,e, we know that domains with larger rotational ¹⁹⁷

angles must be present. ¹⁹⁸

To explain the observed rotational angles and their ¹⁹⁹ monotonic decrease with increasing growth temperature, we ²⁰⁰ performed a simple 2D in-plane coincidence site lattice (CSL) ²⁰¹ analysis without concerning substrate-graphene interaction ²⁰² and graphene lattice undulation: we constructed rigid graphene ²⁰³ and Ir lattices with the appropriate lattice parameters. The ²⁰⁴ simulation cell consisted of 10×10 graphene unit cells and a ²⁰⁵ larger Ir(111) lattice. The thermal expansion of the Ir lattice ²⁰⁶ parameter^{32,33} was considered for elevated formation temper- ²⁰⁷ atures. In the relevant growth temperature range between 1000 ²⁰⁸ and 1550 K, the Ir lattice parameter increases by 0.4%. We ²⁰⁹ modeled the graphene layer using the commonly accepted ²¹⁰ value of $a_{Gr} = 2.465 \text{ \AA}$ for unstrained graphene,³⁴⁻³⁶ which is, ²¹¹ just like graphite,^{37,38} temperature independent³⁹ in the ²¹² temperature range considered here. We then rotated the ²¹³ graphene layer with respect to the Ir(111) lattice around a ²¹⁴ high-symmetry site in small increments of 0.01° while keeping ²¹⁵ the vertical distance between the graphene plane and the Ir ²¹⁶ surface constant. Based on the work by Merino et al.⁴⁰ we refer ²¹⁷ to the minimum value of the distance between all the C and Ir ²¹⁸

$$161 \quad \frac{a_{Ir}(T)}{a_{Gr}} \cos \phi_{Gr,Ir} = \frac{a_{Gr}}{a_{Ir}(T)} \cos \theta_{Ir,moiré} \quad (1)$$

162 where $a_{Ir}(T)$ and a_{Gr} are the lattice parameters
of Ir(111) and

163 graphene, respectively. From Figure 2d we also derive $\theta_{Ir,moiré} = \phi_{Gr,Ir} + \theta_{Gr,Ir}$

164 For small angles $\phi_{Gr,Ir}$ and $\theta_{Ir,moiré}$, eq 1
simplifies to

$$165 \quad \phi_{Gr,Ir} \approx \theta_{Ir,moiré} - \frac{a_{Gr}}{a_{Ir}(T)} \tan \theta_{Ir,moiré} \quad (2)$$

167 To further analyze the moiré spots, we first
discuss the
168 overall fwhm of the “A” feature as a whole
(see Figure 2b). Our
169 fit includes the $\phi_{Gr,Ir} = 0^\circ$ component (R0
phase) and the two
170 side peaks. This fwhm is a measure of the
overall spread of the
171 angular distribution of the rotated domains. A
decrease of the
172 fwhm is observed for increasing growth
temperatures,
173 indicating a reduction of the angular
distribution of the
174 rotational angles $\phi_{Gr,Ir}$. Eventually, only the
oriented R0 phase

except the atoms at the high-symmetry site at the
219 origin of rotation) as the coincidence mismatch Δ ,
which is a 220
function of the rotational angle. Despite the
simplicity of the 221

definition of Δ , we can nevertheless determine the
occurrence 222
of several preferential orientations $\phi_{Gr,Ir}$ versus
growth 223
temperature by varying the Ir surface 224
lattice parameter.

225 The result of the simulation is shown in Figure 3a
where the 226
coincidence mismatch Δ is color-coded as a function
of the 226

growth temperature and the rotational angle $\phi_{Gr,Ir}$.
White areas 227
reflect minima of Δ of the stable
rotational 228

unstable configurations. Within the analyzed
temperature 230 regime, small-angle rotational
domains R0, R0.6, R1.1, R1.7, 231 R2.0, and R2.4
are found. All these represent local minima of 232 Δ
across a few 100 K. For 1530 K the minimum at
 $\phi_{Gr,Ir} = 0^\circ$ 233 marks a simple coincidence ratio of
10 graphene unit cells on 234 nine Ir(111) unit cells
(10:9). Decreasing the growth 235 temperature to
1460 K, we find two primary minima (see 236 curve
at 1460 K of Figure 3b), which indicate the
coexistence 237

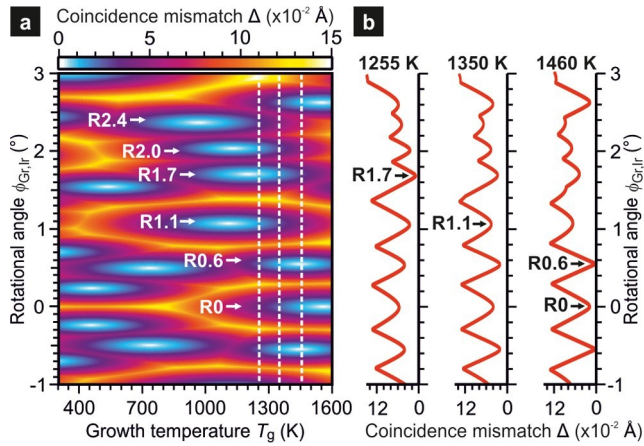
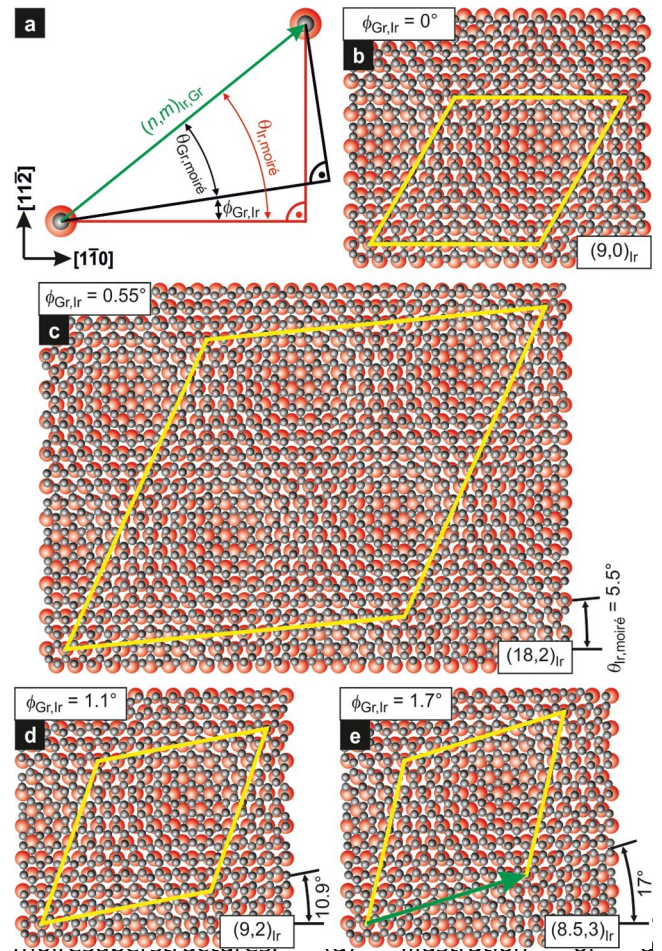


Figure 3. Coincidence site lattice analysis. (a) Two-dimensional representation of the coincidence mismatch Δ as a function of the rotational angle $\phi_{Gr,Ir}$ and the growth temperature. White color indicates the vanishing of Δ and denotes the existence of a coincidence site within the simulated lattice. Blue, red, and yellow colors indicate increasing values of Δ , indicative for conditions, where the graphene and Ir lattices do not exhibit coincidence lattice sites without straining the graphene layer. (b) Stability curves that correspond to coincidence phases with an angular orientation that accumulate the minimum value of Δ for specific temperatures.



coincidence situation where graphene (gray balls) and Ir(111) substrate (red balls) describing coincidence vector $(n,m)_{Ir,Gr}$ along with the rotational angle $\phi_{Gr,Ir}$ and the moiré angles $\theta_{Ir,moiré}$ and $\theta_{Gr,moiré}$: (b–e) Moiré superstructures for small rotational angles $\phi_{Gr,Ir}$ (calculated by eq 2), which read 0° , $+0.6^\circ$, $+1.1^\circ$, and $+1.7^\circ$ for panels b–e, respectively. $(n,m)_{Ir,Gr}$ is exemplarily shown in (e) for the R1.7 phase with $n_{Ir} = 8.5$ and $m_{Ir} = 3$ as the green-colored arrow.

$$\epsilon_c = 1 - \frac{9}{4} \frac{\sqrt{n_{Gr}^2 + 3m_{Gr}^2}}{\sqrt{n_{Ir}^2 + 3m_{Ir}^2}}$$

238 of two phases of differently rotated domains (R0 and R0.6),
 239 with the R0.6 phase being dominant. This result from the
 240 model nicely matches the experimental observation. At 1350 K
 241 the simulation in Figure 3b shows four prominent minima at
 242 rotational angles $\phi_{Gr,Ir}$ that correspond to the R0.6 phase for
 243 the deepest minimum, and the R0, R1.1, and R1.7 phases for
 244 the other minima. In SPA–LEED we only observe the R1.1
 245 phase at this temperature. Further decrease of the growth
 246 temperature results in an increase of Δ for the R0 phase, such
 247 that other rotated domains (R0.6, R1.1, and R1.7) become
 248 more favorable. Particularly at 1255 K we obtain the minimum
 249 Δ for the R1.7 phase consistent with the observations made by
 250 SPA–LEED in Figure 2c.
 251 A real space model of the oriented R0 phase with 10:9
 252 coincidence ratio of the graphene and Ir lattices is sketched in
 253 Figure 4b, while the commensurate rotated R0.6, R1.1, and 10
 254 R1.7 phases are shown in Figure 4c–e. While the graphene
 255 lattice is only rotated by a small rotational angle $\phi_{Gr,Ir}$, the
 256 moiré pattern exhibits a larger rotational angle $\theta_{Ir,moiré}$. As

257 indicated in Figure 4a the moiré magnification also works in

By evaluating eq 3, we arrive at $\epsilon_c = 0.27\%$ (as compared to the unstrained R0 commensurate real space.³⁰ In the following we will discuss the case of the

R1.7 phase shown in Figure 4d as an example for all other rotational phases. It is coincident with a lateral translational vector of $n_{Ir} = 8.5$ Ir atom distances a_{Ir} along the [110]-direction and $m_{Ir} = 3$ Ir atomic row distances

$a_{Ir, row} = (\sqrt{3}/2)a_{Ir}$ along the perpendicular [112]-direction.

Hence, the length of this so-called coincidence vector $(n, m)_{Ir}$ is

given by $\sqrt{n^2 + m^2} \cdot a_{Ir}$, which corresponds to the

higher-order commensurate (HOC) structure

$Ir(\sqrt{79} \times \sqrt{79})$ with respect to the Ir(111) substrate and $Gr(\sqrt{97} \times \sqrt{97})$ with respect to the graphene lattice.⁴¹ This

R1.7 coincidence structure of an unstrained graphene layer

with $a_{Gr} = 2.465 \text{ \AA}$ fits to the Ir lattice only if the Ir lattice

parameter is reduced by

structure). For 1255 K, we indeed find a relative change of the Ir lattice parameter in comparison to 1530 K of

$$\epsilon_L = 1 - \frac{a_{Ir}(1530 \text{ K})}{a_{Ir}(T)} \quad (4)$$

which is $\epsilon = 0.23\%$. Thus, the R1.7 phase becomes more

favorable compared to the R0 phase because the graphene layer is less strained when it is rotated. Table 1

summarizes the considerations of coincidence vector, rotational angle, and

strain for the observed small-angle rotated domains.

Our simulations suggest that, given Ir's thermal expansion,

the R0 phase can only fulfill the coincidence of every 10th graphene unit cell on top of every ninth unit cell of the Ir(111) substrate at a particular growth temperature of 1530 K. Lower growth temperatures and maintaining an unstrained graphene lattice parameter result in a rotation of the graphene layer with

Table 1. Small-Angle Rotational Domains for Graphene on Ir(111)^a

phase Ir	coincidence vector (<i>n,m</i>) _r		higher-order commensurate (HOC) structure	Moiré angle $\theta_{Ir,moiré}$	rot. angle $\phi_{Gr,Ir}$	relative change ϵ_L of Ir lattice parameter	relative coincidence mismatch ϵ_c	exp. growth temp. T
	<i>i</i> = Gr	<i>i</i> =						
R0	(10,0)	(9,0)	$Gr(10 \times 10)/Ir(9 \times 9)$	0°	0°	–	–	1530 K
R0.6	(20,2)* (18,2)*		$Gr(\sqrt{403} \times \sqrt{403})$ $/Ir(\sqrt{327} \times \sqrt{327})$	5.5°	0.55°	0.06%	0.09%	1460 K
R1.1	(10,2) (9,2)		$Gr(\sqrt{103} \times \sqrt{103})$ $/Ir(2\sqrt{21} \times 2\sqrt{21})$	10.9°	1.07°	0.15%	0.34%	1350 K
R1.7	(9.5,3) (8.5,3)		$Gr(\sqrt{97} \times \sqrt{97})$ $/Ir(\sqrt{79} \times \sqrt{79})$	17.0°	1.70°	0.23%	0.27%	1255 K
R2.0	(18.5,7)*	(16.5,7)*	$Gr(379 \times 379)/Ir(309 \times 309)$	23.4°	2.36°	–	0.33%	–
R2.4	(8,4)		$Gr(93 \times 93)$ $\times \sqrt{19} \times \sqrt{19}$ $/Ir(2\sqrt{19} \times 2\sqrt{19})$			–	0.44%	–

^aCalculated coincidence vectors, HOC structure, Moiré and rotational angles, relative change of the Ir lattice parameter ϵ_L with respect to 1530 K, relative coincidence mismatch ϵ_c , and experimental growth temperature. The calculated results are compared to the HOC values using density functional theory based on first-principle calculations by Meng et al.⁴¹ Asterisk (*) signifies the second order coincidence vector coordinates as shown exemplarily for the R0.6 phase in Figure 4c with a larger unit cell.

286 respect to the Ir(111) lattice to adopt other
 287 commensurability
 288 conditions. The tendency of forming rotational
 289 coincidences is
 290 a resemblance of the so-called rotational
 291 epitaxy that was
 292 introduced by Novaco and McTague⁴² to
 293 account for similar
 294 small-angle rotations observed at first in 2D
 295 lattices of noble
 296 gas atoms deposited on graphite¹⁹ and, later
 297 on, in many other
 298 systems including layers of alkali atoms or
 299 molecules on metal
 300 or graphite surfaces.^{43–45} In these systems, the
 301 driving force for
 302 the rotation was the joint effect of (i) the
 303 increase of the
 304 adsorbate density at the 2D lattice (in our
 305 case an effective
 306 biaxial compressive stress) and (ii) the
 307 repulsion within the
 308 constituents of the lattice, forbidding
 309 excessive compressive
 310 strain. In the case of the self-limited growth of
 311 graphene grown
 312 at different temperatures on the Ir(111)
 313 surface, the amount of
 314 C atoms in the graphene layer does not
 315 change in absolute
 316 numbers but as a relative with respect to
 317 the Ir substrate.
 318 Indeed, the negligible thermal compression
 319 of the graphene
 320 lattice parameter in comparison with that of
 321 Ir(111)^{32,33,38,39}
 322 effectively corresponds to an increase of the
 323 relative C atom
 324 density on Ir(111) as the growth
 325 temperature decreases, in
 326 other words, the buildup of an effective biaxial
 327 compressive

rotations rather than by compressions of the
 graphene lattice. 327 Within our coincidence site
 328 lattice model, we are able to 328 reproduce our
 329 experimental results, and we find robust locking
 330 conditions of the rotated graphene with
 331 minima in the stability 330 curve for the distinct
 332 commensurate small-angle rotational 331

phas
 es. 332
 As our model is only sensitive to the strongest
 333 coincidence 333
 of C atoms in graphene with atoms of the topmost
 334 layer of the
 metal substrate, the at least locally, must
 335 binding,⁴⁹ exhibit 335
 covalent contributions instead of being only of the
 336 van der Waals type. Anticoincidence sites,
 337 however, naturally also exist 337 in the
 338 moiré lattice, and there the graphene-Ir atom
 339 distance is 338
 typically larger by 0.1–1 Å.^{23,36,46} From the
 340 robust rotational 339
 locking conditions, we are furthermore able to
 341 estimate the 340 lattice parameter of relaxed
 342 graphene on Ir(111) at the 341 investigated
 343 growth temperatures. Considering the general
 344 assumption of small or negligible thermal
 345 expansion of 343 graphene, we can conclude the
 346 room temperature lattice 344 parameter
 $a_{Gr}/Ir(111) = 2.465 \pm 0.003 \text{ \AA}$ for relaxed 345
 graphene on
 Ir(111). 346

307 stress. The resulting strain is relieved
308 through the observed
309 small-angle rotations rather than
310 accommodated through
311 isotropic compression.
312 Summary and Conclusions. During growth
313 of graphene
314 on Ir(111), islands with a variety of
315 rotational angles are
316 formed. Large-angle rotations on various
317 substrates were
318 already reported several years ago^{16,40,48,49,52}
319 and are believed
320 to be formed due to kinetic limitations.⁵¹
321 Here, we report a
322 new class of small-angle rotations at distinct
323 angles of $\pm 0.8^\circ$,
324 1.1° , and $\pm 1.7^\circ$. While some of these have
325 been predicted by
326 density functional theory,⁴¹ there was
327 no experimental
328 evidence for their existence until now. The
329 presence of the
330 particular angles we observe in the
331 present study can be
332 explained by strain minimization between the
333 graphene layer
334 and the Ir(111) substrate. As the growth
335 temperature is
336 decreased, the Ir lattice parameter shrinks while the
337 graphene lattice parameter remains almost constant.⁴⁷ We
338 argue that the
339 significant reduction of the substrate's lattice
340 parameter during
341 growth at lower temperature imposes a biaxial

The existence of rotated domains with robust
locking 347 conditions for graphene on Ir(111) is
similar to 2D lattices of 348 noble gas or alkali
atoms at the surface of graphite or metals, 349
where increasing adatom density resulted in
increasing 350 compressive strain and a series
of distinctly rotated 351 domains.^{19,43–45} This
was referred to as rotational epitaxy.⁴² 352 In
our version of rotational epitaxy, however, it
is not a 353
changing adatom density but the effective
biaxial stress 354

imposed by the substrate that 355
causes the effect.
Our study emphasizes the important role of the
substrate's 356

temperature-dependent lattice parameter
resulting in the 357 formation of small-angle
rotated domains. Depending on the 358
interaction strength between the substrate and
any epitaxially 359 grown 2D materials,⁵⁰ we
would expect the formation of 360

similar thermodynamically stable small-angle rotational
domains to be inevitable. However, the 36
rotational epitaxy 2
presented here may provide a route to achieve 36
particular 3
orientations in stacks of 2D materials, which 36

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383 Notes

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