

Targeted Dy intercalation under Gr/SiC for tuning its electronic band structure

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Abstract

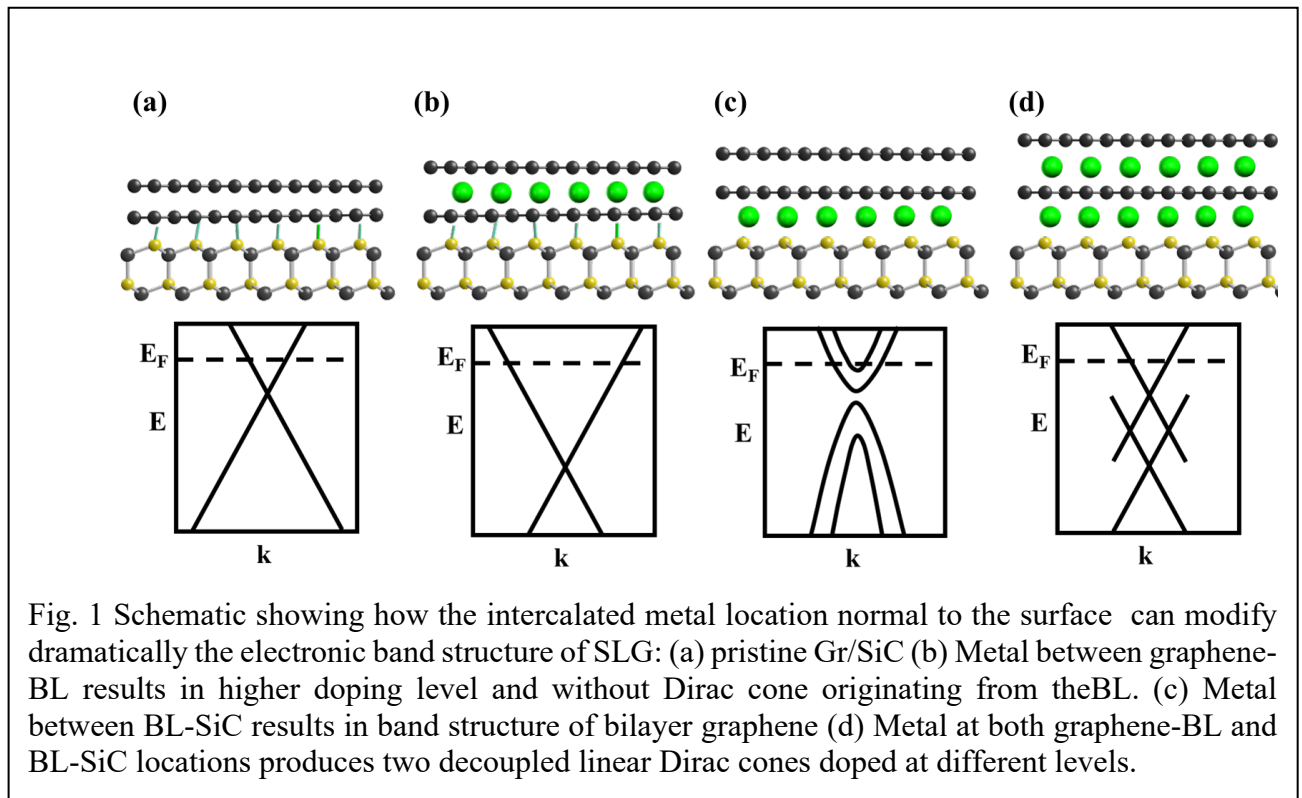
Metal intercalation of graphene is a promising method to tune its electronic band structure and generate novel electronic and topological phases. The tuning depends critically on the ability to bond the intercalated atoms at pre-designed, sub-surface interlayer locations because the emerging band structure depends on metal location. We have studied Dy intercalation under single layer graphene (SLG) on SiC using Spot Profile Analysis-Low Energy Electron Diffraction (SPA-LEED) and Scanning Tunneling Microscopy (STM). The experimental work is complemented with Density Functional Theory (DFT) analysis. Because different diffraction spots originate from different sub-surface interlayer regions, it is possible to identify changes in the intercalation location by monitoring the spot intensity as function of growth conditions. DFT calculations of the chemical potential as a function of intercalated Dy coverage, support the variation of the stability of the intercalated phase at different intercalated locations. The preferred location is confirmed from STM studies showing the removal of the 6×6 moiré corrugation at the preferred location, observed at higher Dy coverage.

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I Introduction

Graphene intercalation is a robust, routine method to modify graphene's electronic properties and grow 2-d quantum materials, with targeted band structure. The interest in intercalation has been growing steadily, either of elemental quantum materials or heterostructures, as is well-documented over different types of materials[1-4]. Different properties can be controlled, ranging from 2-d superconductivity[5,6], heterostructure magnetization[7], spin band polarization[8], correlated electron physics in rare earth layers[9]. Metal intercalation has been used both in epitaxially grown graphene on SiC (Gr/SiC) and in graphene grown on metals. Intercalation offers advantages in building heterostructures because of the intercalated metal-graphene proximity, the uniform confined spaces the intercalated metal is bonded to and the tuning of the strength and type of metal-graphene interaction based on the atomic structure of the selected metal. The coverage and potential ordering of the intercalated phase can add a new length scale in the graphene Hamiltonian, similar to the longer length scale introduced by Moiré superlattices in stacked heterostructures. The interlayer location and coverage of the intercalated metal are control parameters to realize a wealth of theoretically predicted electronic phases[1-4]. For Gr/SiC, several sub-surface interlayer locations are possible, depending on the initial graphene layer (i.e., zero or buffer layer-graphene (BL), single-layer-graphene (SLG), bilayer graphene (BLG)). For SLG shown in fig. 1(a), three different locations of a metal under graphene can be realized as shown schematically in figs.1(b-d). Depending on the intercalation location, the system can transform into BLG or highly doped SLG or two decoupled graphene SLG layers shifted in energy. The number of bands, band gap, effective mass, density of states, the Fermi level can be tuned continuously, if it is possible to control reliably the intercalated metal phases. This can be done with systematic control of the growth conditions (temperature, deposited amount, annealing time). One also needs reliable characterization tools and protocols to validate the targeted atom location and the anticipated electronic effects. Experimental work has confirmed in numerous studies how the band structure can be modified dramatically by intercalation. Decoupling from the substrate has been shown with hydrogen intercalation[10]; controlling the doping at different sub-surface locations with Yb intercalation[11]; using Ga, In, Sn intercalation to modify and protect electronic properties of the confined layers, including 2-d superconductivity[6]; controlling the size of the induced band gap in graphene by Eu intercalation at different locations [12].

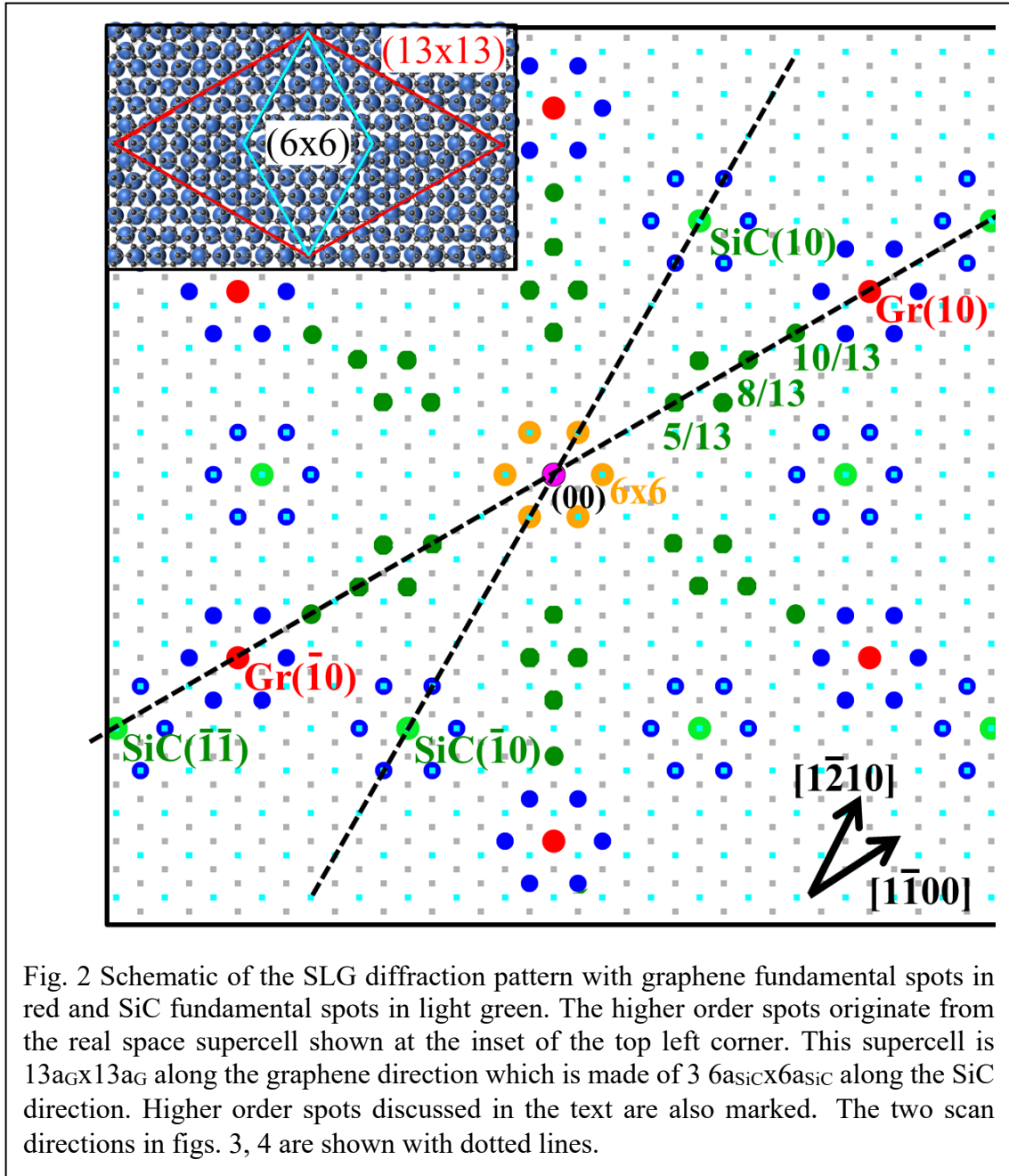
Dy is a good candidate to realize topological phases because of its high atomic number Z . Spin-orbit coupling effects are expected to produce an effective magnetic field and the spectra to show sharp Landau levels of a 2-d electron gas [13]. Split polarized bands are possible with a large band gap ~ 200 meV and a realization of the Quantum Hall Spin Effect (QHSE) state [8,14] at finite temperatures. Ideal location of intercalated Dy under SLG to see topological effects is for the metal to be between BL-SiC to form BLG. A different application of intercalated Dy is based on using the hard magnetic properties of Dy; especially if it is intercalated at the top location between graphene-BL it will demonstrate an outstanding prediction in nanomagnetism, i.e., a spring nanomagnet[15]. If a soft magnetic element like Fe is deposited on top of the intercalated Dy the soft layer can transform to a hard, atomically thin magnetic layer of high coercivity, because of the interaction with the high Dy magnetic moment.



Most of the intercalation work in the literature has been performed under the BL where only one location is possible. It is important to carry experiments on thicker graphene with more available intercalation locations and therefore more possibilities to grow novel electronic phases. Only recently the same system was studied (Ca/Gr/SiC) in different experiments with the same initial phase, i.e. BLG, because the intercalated Ca was found to be a superconductor. There are three

possible Ca intercalation locations: between the two top graphene layers or between graphene-ZLG or between ZLG -SiC. All three locations were identified as possible intercalation locations from these recent experiments. Initially Ca was found to be between the two top graphene layers using ARPES, LEED and STM[16] which was later confirmed with diffraction and transport measurements[17]. A recent study using positron scattering and the dependence of the intensity vs normal component of the momentum transfer found that Ca intercalates between graphene-ZLG [18]. Another study using XPS, LEED and STM found Ca intercalation between ZLG-SiC[19]. STM on separate graphene islands grown on SiC of different thickness found that Ca always intercalates under the top layer[20]. A more recent study has concluded that two of the three possible sites must be occupied at the same time, i.e., between graphene-BL and BL-SiC using structural techniques and ARPES [21]. This very wide range of conclusions about the intercalated metal location will lead to very different band structures and needs to be resolved, so the origin of Ca superconductivity can be identified unambiguously.

Surface diffraction is a powerful technique to study metal intercalation because one can obtain statistical information about the lateral and vertical atom distribution. Since the technique samples a sub-millimeter size probed area, it can ensemble average over the mesoscale if different intercalated phases coexist. Surface X-ray has been used in hydrogen intercalation studies of BL, by combining structural and spectroscopic techniques, to identify the atom distribution and chemical nature of the BL-SiC interface[22]. In a different study pristine Gr/SiC was studied with X-ray reflectivity to measure the density and bonding of the carbon atoms in the BL and deduce that the BL is incommensurate with the graphene layer on top[23].



In the current work using high resolution electron diffraction (SPA-LEED), DFT and STM, we show how changes in the location of intercalated Dy under SLG can be controlled by tuning the growth parameters (temperature, coverage, time). A detailed protocol is followed that results in the unique identification of the intercalated metal location. Different locations under graphene give rise to distinct diffraction spots, shown schematically in fig. 2. Changes in the spot intensities measure whether a metal has intercalated in the location generating the spot. For example, the SiC(10) spot originates from the region between BL and SiC and the 6x6 and 5/13

spots measure the area of the BL[10]. After Dy deposition the system is annealed to higher temperatures over predetermined time intervals. From the Gr(10) intensity drop we deduce that up to 1050° C Dy occupies the graphene-BL region, but after further annealing to 1200° C Dy bonds in the BL-SiC region. This conclusion is reached from the recovery of Gr(10) and the extinction of SiC(10) spots. Using SPA-LEED to determine the intercalated metal location from quantitative intensity measurements adds more capabilities to conventional LEED, that commonly relies on visual inspection of the diffraction pattern. Ideally it would be desirable to be able to carry I-V measurements with LEED to determine the exact coordinates of all type of atoms present on the surface[24]. Unfortunately the complexity of the $6\sqrt{3}\times 6\sqrt{3}$ unit cell is too high. Just for pristine SLG it involves the top four layers of the graphitized substrate with a total of 558 atoms; the complexity of the unit cell will further increase after metal intercalation and the different possibilities for the metal to intercalate. At this stage the determination of the structure of such large unit cell is prohibitively costly and has not been completed yet[24].

DFT calculations verify that the most stable location for Dy with increasing coverage switches from the graphene-BL to the BL-SiC region; and that the corresponding interlayer spacing increases considerably to accommodate the intercalated metal. The conclusion is confirmed with local STM images that show that the 6×6 superstructure is completely removed as the Dy bonds between BL-SiC (after stepwise annealing and increasing Dy coverage). The 6×6 moiré superstructure with period ~ 1.84 nm is observed for pristine Gr/SiC as a coincidence lattice at the BL-SiC interface.

Such intercalation protocol can be applied with any quantitative diffraction probe and can settle incompatible conclusions about the intercalation location. More importantly it provides a robust methodology to grow on-demand, targeted electronic phases. The metal atoms can be directed to specific interlayer locations, as required by the theory predicting the novel electronic phases.

II Experiment

Experiments were performed in UHV with pressure $\sim 5 \times 10^{-11}$ Torr. The growth of high quality graphene on 4-H SiC(0001) was carried out at high temperatures to desorb Si while C diffuses and forms large uniform domains[25]. By flashing within 1200°-1400° C for short 15 seconds graphene of different thickness can form, starting with the BL and finishing with the trilayer[26]. Spot profiles along different directions are used to deduce the initial graphene

thickness. The current surface was prepared at 1300° C and is more than 90% SLG as deduced from quantitative analysis of the 00 and Gr(10) spots, (and their corresponding Bell-Shaped-Components (BSCs)). These paradoxically broad diffraction features were shown to be markers of high quality graphene[27]. Dy was deposited with a flux rate of $\sim 1/60$ ML/min at room temperature for a total of ~ 2 ML. Annealing was carried out using e-beam heating with temperature calibration based on the well-known Pb/Si(111) phase transitions[28].

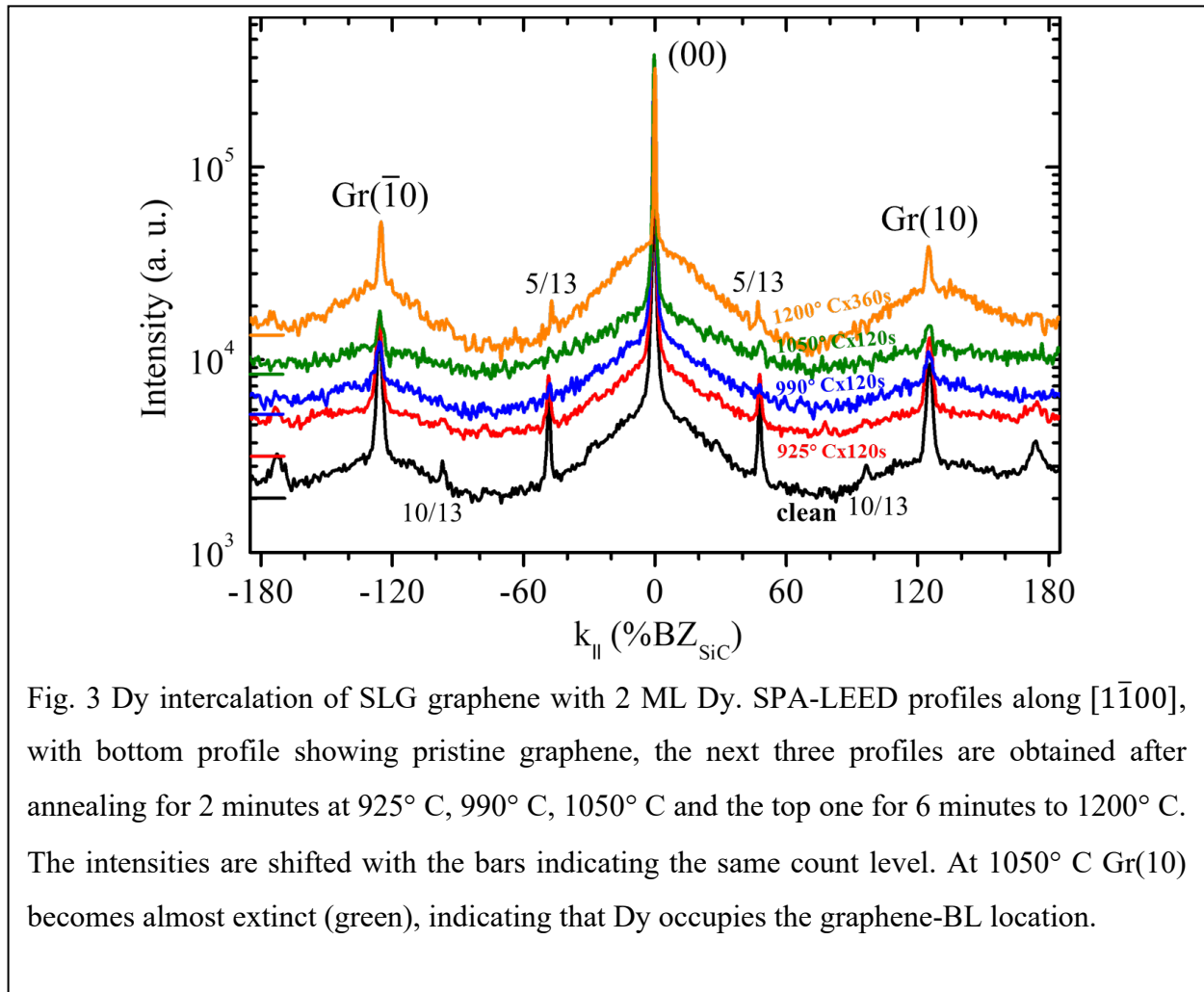


Fig. 3 Dy intercalation of SLG graphene with 2 ML Dy. SPA-LEED profiles along $[1\bar{1}00]$, with bottom profile showing pristine graphene, the next three profiles are obtained after annealing for 2 minutes at 925° C, 990° C, 1050° C and the top one for 6 minutes to 1200° C. The intensities are shifted with the bars indicating the same count level. At 1050° C Gr(10) becomes almost extinct (green), indicating that Dy occupies the graphene-BL location.

The instrumental resolution is less than $\sim 0.3\%$ of the Brillouin Zone (BZ) (or the coherence length is larger than ~ 300 nm.) Since the spots are measured simultaneously using the difference of spot intensity from their clean surface values, the assignment of intercalated metal location is complete and self consistent. The difference from the clean spot intensity is a measure of the intercalated amount. $E=194\text{eV}$ was used to probe with higher sensitivity deeper in the surface. STM provides mainly information about the 6×6 superstructure of ~ 1.84 nm period. It is used to

deduce that the most stable metal intercalation site is BL-SiC, since the 6×6 periodicity is globally removed after annealing to the higher temperature.

III Results

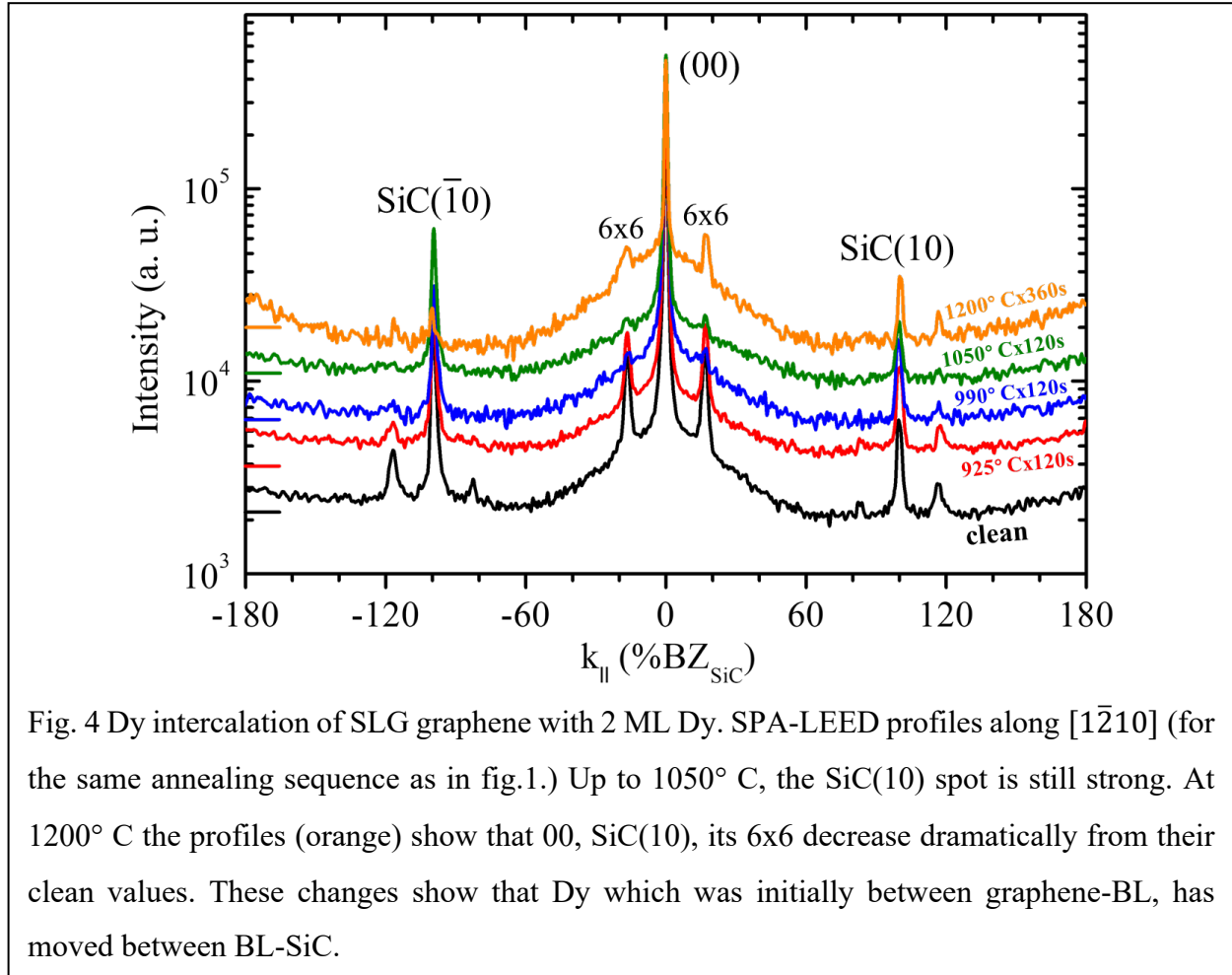
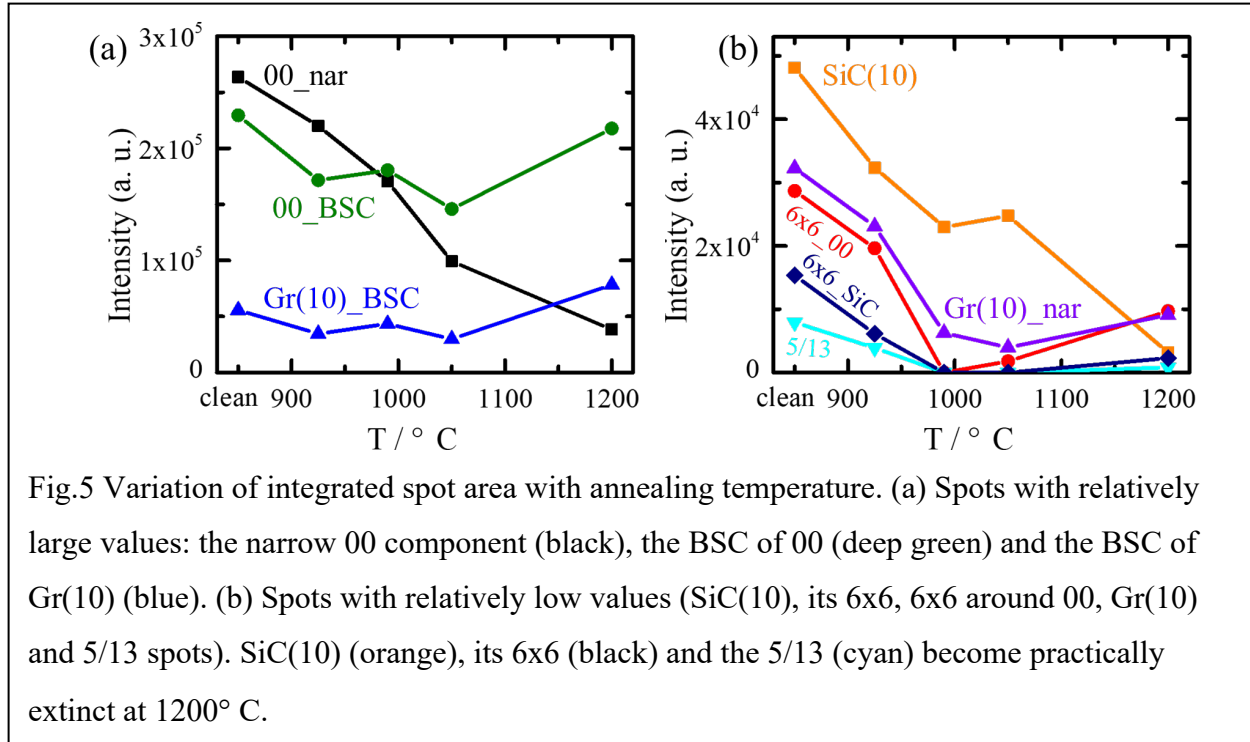


Fig. 4 Dy intercalation of SLG graphene with 2 ML Dy. SPA-LEED profiles along $[1\bar{2}10]$ (for the same annealing sequence as in fig.1.) Up to 1050°C , the SiC(10) spot is still strong. At 1200°C the profiles (orange) show that 00, SiC(10), its 6x6 decrease dramatically from their clean values. These changes show that Dy which was initially between graphene-BL, has moved between BL-SiC.

Diffraction Fig. 3 shows results for Dy intercalation of SLG graphene after annealing 2 ML Dy deposited at room temperature. For rare earth metals higher temperatures are needed to overcome the high kinetic barriers of intercalation[29]. The profiles are along $[1\bar{1}00]$ (the Gr(10) direction), with the bottom profile corresponding to pristine graphene, the next three after annealing for 2 minutes at 925°C , 990°C , 1050°C and the top one after annealing for 6 minutes to 1200°C . The intensities are shifted for clarity with the bars to the left indicating the same count level. The 00 and Gr(10) show also the BSCs around each spot, which are affected less with annealing. As seen at 1050°C the Gr(10) becomes almost extinct (green), indicating that Dy atoms occupy mainly the graphene-BL location. Fig. 4 shows the corresponding profiles along $[1\bar{2}10]$

(the SiC direction) for the same annealing sequence. Up to 1050° C, the SiC(10) is still strong. But at 1200° C the profiles (orange) show that some spots increase substantially compared to the spots at 1050° C (Gr(10), the two BSCs around 00 and Gr(10)) while others (00, SiC(10), its 6×6) decrease dramatically from their clean surface values. These changes imply that Dy which was initially between graphene-BL has moved between BL-SiC; so the Gr(10) intensity increases while the SiC(10) intensity decreases as Dy atoms bond on top of SiC.



Spot profile fitting was used for quantitative analysis, deducing the variation of the integrated areas, the Full-Width-Half-Maxima (FWHM), the peak intensities with annealing temperature. These metrics have quantitative information about the location and coverage of the intercalated metal. For the fits, Lorentzian functions with an exponent of 3/2 (LRZ-3/2) were used. Some of the fits are shown in figs. S1-S4 Supplementary Materials[30]. Table I shows the extracted integrated areas for the spots along $[1\bar{1}00]$ and table II shows the analogous parameters along the $[1\bar{2}10]$ direction. These quantitative fits follow the spot dependence with annealing as described qualitatively in the previous paragraph. The results are plotted in fig.5(a) showing the spots which have relatively large value: the narrow 00 component along $[1\bar{1}00]$ (black), the BSC of 00 along $[1\bar{1}00]$ (deep green) and the BSC of Gr(10) (blue). The narrow 00 component drops continuously while the two BSCs have only small variation. Fig. 5(b) shows intensities of spots with relatively

low values (the SiC(10), its 6×6, the 6×6 around 00, Gr(10) and 5/13 spots). The Gr(10) (purple) and the 6×6 around 00 (red) recover partially towards their pristine values. The other three spots SiC(10) (orange), its 6×6 (black) and the 5/13(cyan) become practically extinct at 1200° C. The most spectacular variation is the one from SiC(10) and its 6×6 which drop by an order of magnitude; in conjunction with the Gr(10) increase this confirms the Dy transfers to BL-SiC.

Table I

Integrated areas for the listed spots as a function of annealing temperature along the $[1\bar{1}00]$ direction. Lorentzian functions with exponent 3/2 (LRZ-3/2) were used for the fits.

Annealing step	E / eV	Constant Background	Specular		Gr($\bar{1}0$)	
			Narrow	Broad	Narrow	Broad
Pristine	194	1900	2.6×10^5	2.3×10^5	3.2×10^4	5.6×10^4
925° C × 120 s	194	2600	2.2×10^5	1.7×10^5	2.3×10^4	3.5×10^4
990° C × 120 s	194	1900	1.7×10^5	1.8×10^5	6.3×10^3	4.3×10^4
1050° C × 120 s	194	1900	9.9×10^4	1.5×10^5	4.0×10^3	3.0×10^4
1200° C × 360 s	194	1500	3.8×10^4	2.2×10^5	9.1×10^3	7.8×10^4

Table II

Integrated areas for the listed spots as a function of annealing temperature along the $[1\bar{2}10]$ direction. Lorentzian functions with exponent 3/2 (LRZ-3/2) were used for the fits.

Annealing step	E / eV	Constant Background	Specular		Left 6×6 of (00)	SiC ($\bar{1}0$)	Left 6×6 of SiC($\bar{1}0$)
			Narrow	Broad			
Pristine	194	1900	3.9×10^5	2.3×10^5	2.9×10^4	4.8×10^4	1.5×10^4
925° C × 120 s	194	2600	3.2×10^5	1.7×10^5	2.0×10^4	3.2×10^4	6.1×10^3
990° C × 120 s	194	1900	2.4×10^5	1.9×10^5	/	2.3×10^4	/
1050° C × 120 s	194	1900	1.4×10^5	1.5×10^5	1.8×10^3	2.5×10^4	/
1200° C × 360 s	194	1500	6.3×10^4	2.2×10^5	9.7×10^3	3.2×10^3	2.3×10^3

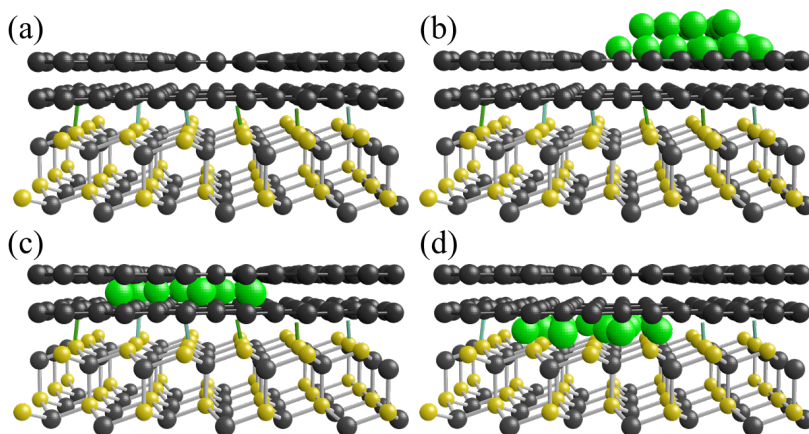
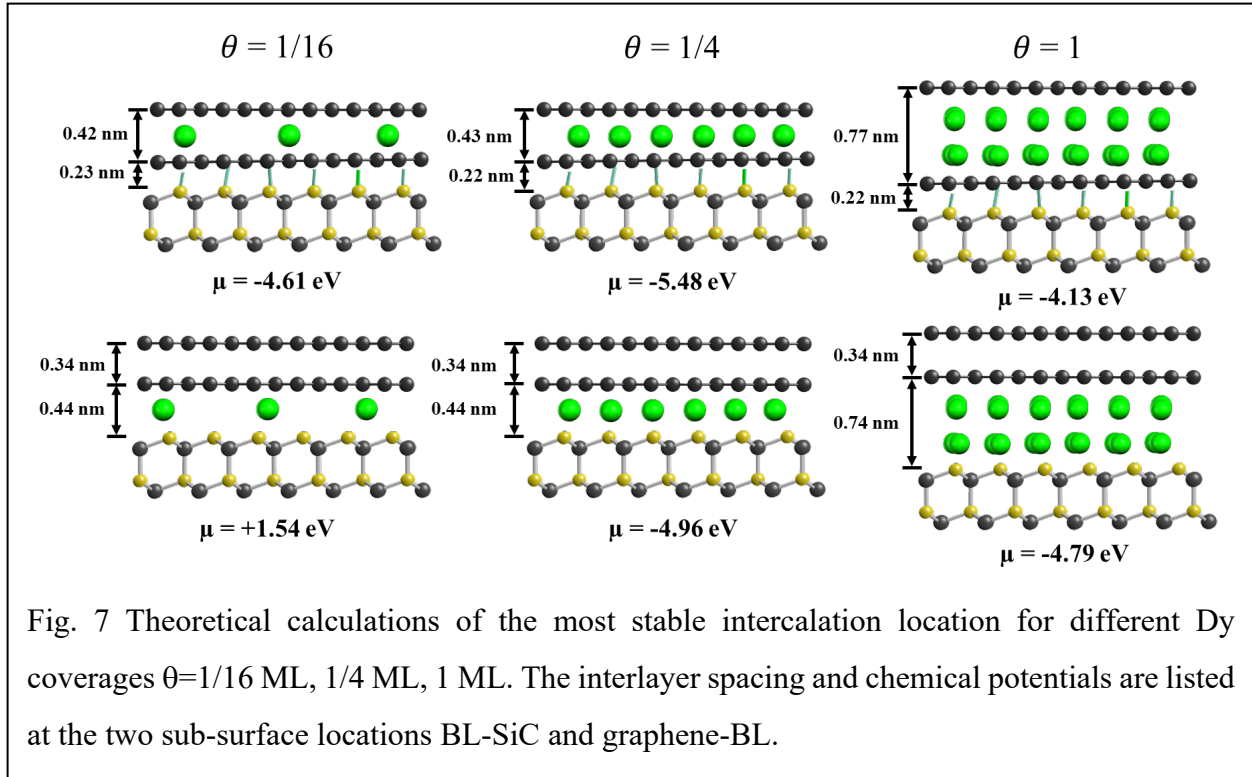


Fig. 6 (a-d) Schematic of the different steps in the experiment: (a) pristine SLG; (b) after deposition of Dy; (c) after annealing to 1050° C with Dy between graphene-BL; and (d) after annealing to 1200° C with Dy between BL-SiC.

Fig. 6 (a-d) shows schematically the different steps in the experiment: starting from pristine SLG (fig.6(a)), after deposition of Dy on top (fig.6(b)), after annealing to 1050° C with Dy between graphene-BL (fig.6(c)) and after annealing to 1200° C with Dy between BL-SiC (fig.6(d)). These results show that intercalation is mostly a kinetic process with controllable locations for the intercalated metal, depending on growth conditions. The different Dy intercalated phases, can be used to tune the intercalated Dy band structure.



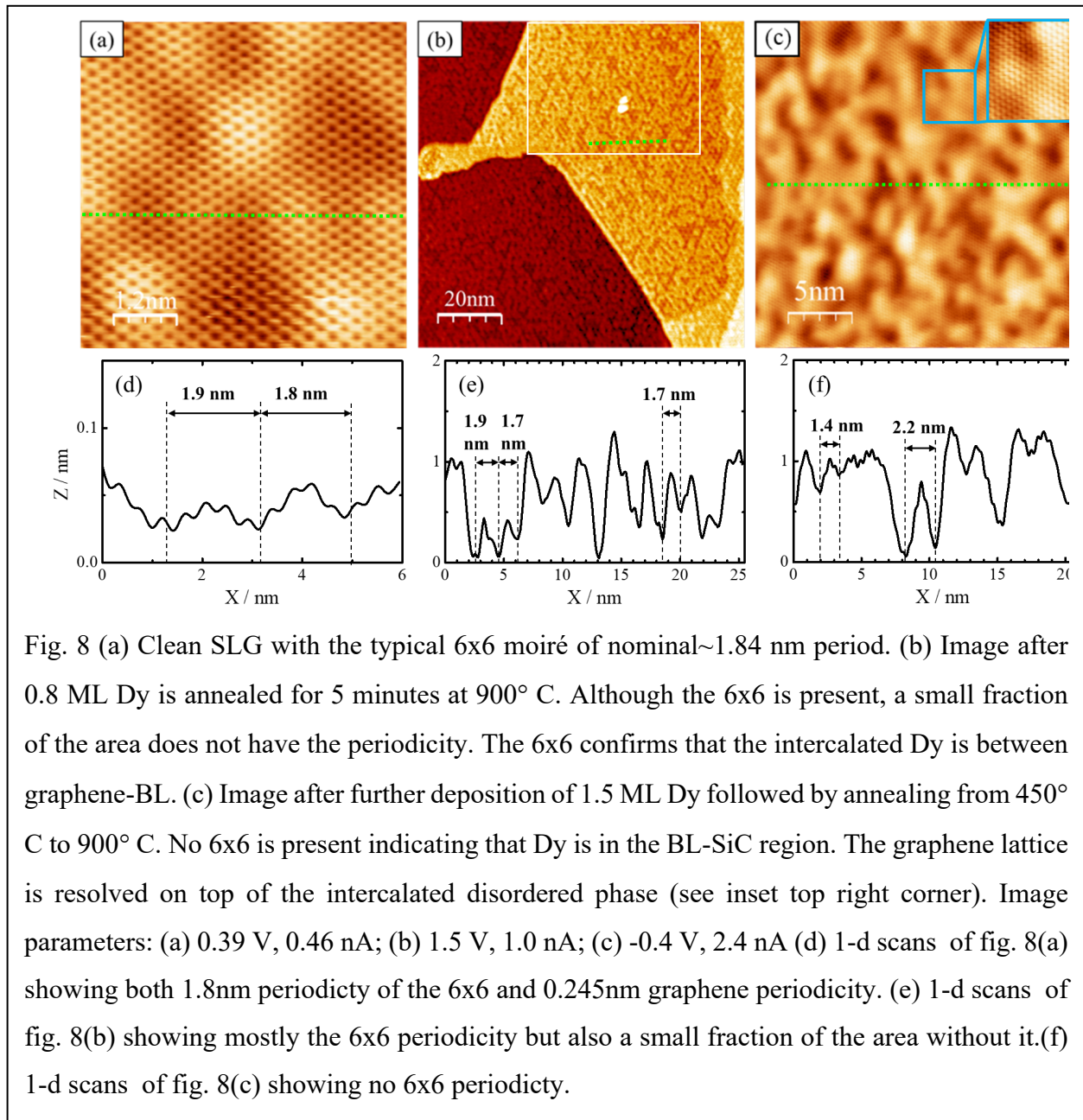
Theoretical analysis Calculations have been performed to determine Dy adsorption energetics over different types of steps present on SLG separating graphene and BL regions[29]. Such steps are likely places for Dy deposited on top to move below graphene. The stability of the intercalated phases and location of the intercalated metal were studied for different Dy coverages $\theta=1/16$ ML, $1/4$ ML, 1 ML. But no discussion was made in connection to experiments as the ones described in this work; especially to identify the trend of the intercalated metal location as a function of Dy coverage. Three bonding sites were tested: on top, within graphene-BL and within BL-SiC. Results are shown in fig. 7 with both the calculated interlayer spacing and the corresponding chemical potentials listed at the two sub-surface locations. The spacings of pristine graphene are 0.23 nm for BL-SiC and 0.33 nm for graphene-BL.

For $\theta=1/16$ ML the most stable site is between graphene-BL with a chemical potential $\mu=-4.61$ eV; the corresponding spacing increases to 0.42 nm[29]. For $\theta=1/4$ ML the two locations become comparable ($\mu=-5.48$ eV for graphene-BL and $\mu=-4.96$ eV for BL-SiC) and again the intercalation location increases to 0.44 nm while the location without Dy keeps its pristine value. This result is consistent with the earlier conclusions that the BL-SiC is preferred at 1200° C, since the experiments were carried out at high Dy coverage. The calculations are based on the widely

used ($2\sqrt{3}\times 2\sqrt{3}$)R30° unit cell (in the theoretical literature[29]) to model the BL $6\sqrt{3}\times 6\sqrt{3}$ unit cell present in Gr/SiC; for $\theta = 1/4$ ML 4 Dy atoms are bonded within the unit cell. For even higher coverage $\theta=1$ ML (16 Dy atoms bonded within the $2\sqrt{3}\times 2\sqrt{3}$ unit cell ,i.e., much larger compression) the BL-SiC becomes the most stable location ($\mu=-4.79$ eV); but because of the large compression Dy forms a bilayer and the interlayer spacing more than doubles to 0.74 nm. Although such high coverage will not be attained for the intercalated Dy, the DFT results suggest a monotonic decrease of the chemical potential with coverage. The BL-SiC location becomes the most stable site and its interlayer spacing continuously increases with θ . (Ge intercalated in Gr/SiC has two different intercalated phases, n-doped with 1 ML and p-doped with 2ML forming a p-n-junction[31]). The n-doped phase with 2 ML coverage is a likely realization of the phase predicted for $\theta=1$ ML in fig. 7 with the double intercalated layer and the very large increase of the interlayer spacing. The interlayer spacing increase at the metal location is also seen in other DFT studies of metal intercalation in Gr/SiC. Both the experimental and theoretical results listed demonstrate that besides intercalation controlled mainly by kinetics, the competition between elastic and electronic energies plays a role to define the most stable location, within the confined spaces in the interior as analyzed in ref. [32]. This competition accounts for the larger interlayer spacing with increasing metal coverage.

STM The change of intercalation location observed in the diffraction experiments and in the calculations at finite coverage is confirmed in STM experiments of SLG intercalation shown in fig.8. A similar Dy deposition experiment was performed as before with the initial surface morphology shown in fig. S5(a) over the mesoscale. A line scan in fig.S5(b) shows that the step heights separating adjacent terraces are multiples of 0.25 nm: the step height of SiC. This implies that the grown graphene layer is homogeneous draping SiC steps of differing heights. The initial Dy morphology after deposition is seen in fig.5(c). Fig.8(a) shows clean graphene with both the graphene lattice and the typical 6×6 corrugation of ~ 1.84 nm period defect-free. As discussed changes in the intercalated phase are induced from variations in the controlled parameters (coverage, time, temperature, etc.). The previous theoretical prediction of fig.7 about intercalated phase stability can be tested with STM. The STM provides local images and there might be a distribution of intercalated phases present on the surface after annealing; especially of coexisting phases with similar energetic stability. But the coverage which is uniformly deposited across the whole surface is a better parameter to control the uniformity of the intercalation outcome. Fig.8(b)

shows a typical image of the surface after smaller amount 0.8 ML Dy deposition and stepwise annealing for 30 minutes from 450° C to 900° C. No Dy islands are on top indicating that Dy has moved below SLG. 1-d scan for pristine surface



is seen in fig.8(d) with both the graphene lattice of lattice constant 0.245nm and the 6x6 periodicity ~1.8nm clearly visible. 1-d scan for the phase of fig. 8(b) is seen in fig. 8(e). Although the ~1.8nm periodicity is present indicating that there are still 6x6 domains there is still large modulation of the amplitude of the 1-d scan and a small fraction of linear

segments without the 6x6 periodicity. The presence of 6x6 confirms that the intercalated Dy is not between BL-SiC, as also deduced previously from the strong 6x6 spots in the diffraction profiles colored green in figs. 1, 2. A small fraction of Dy atoms within BL-SiC could be responsible for the lower amplitude between the regions with strong 6x6 intensity. Fig. 8(c) shows the outcome covering globally the surface after further deposition of 1.5 ML Dy; followed again by gradual heating over the same temperature range 450° C to 900° C. No sign of the 6x6 remains demonstrating that all the intercalated Dy has now moved in the BL-SiC region. This is also confirmed in the 1-d scan of fig. 8(f). The graphene lattice is clearly resolved on top of this disordered intercalated Dy phase (seen at the inset of fig. 8(c)), which further supports that the phase is below graphene and homogeneous. The stepwise deposition and stepwise annealing of Dy is needed so the already intercalated Dy moves in the interior away from the entry portals and additional Dy entering the portal can complete the more uniform intercalated phase within BL-SiC as shown in fig.8(c).

In addition figs. 9(a-c) shows the autocorrelation of the previous images figs. 8(a-c) which provide further support about the changes in the intercalated surface for different growth conditions. Figs. 9(d-f) show 1-d scans marked with green dotted lines in the autocorrelation images figs.9(a-c). In fig. 9 (d) the very regular 1.8nm periodicities of the 6x6 and 0.245nm of pristine graphene are seen. In fig.(e) periodicities close to the 6x6 periodicity (1.7nm, 1.8nm, 1.9nm) of the 0.8ML Dy phase are seen but of reduced amplitude. As discussed earlier a small fraction of disorder is generated by Dy atoms starting to occupy the BL-SiC location. In fig. 9(f) after the additional 1.5ML Dy deposition and annealing to 900° C the 1.8nm periodicity is absent indicating full intercalation at the higher coverage. The regularity of the 6x6 phase is a sign whether the buffer layer-SiC interlayer location is occupied by intercalated Dy.

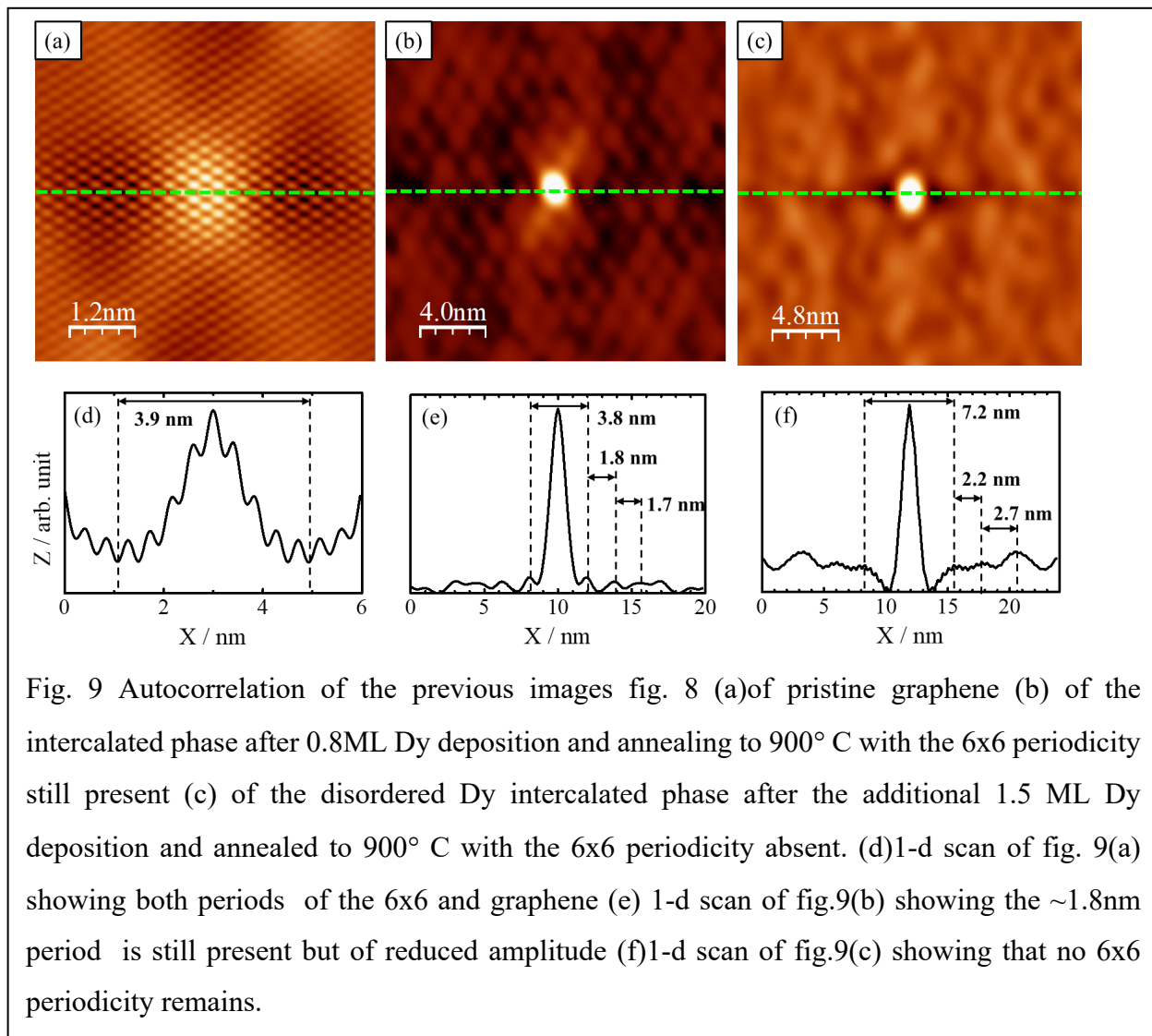


Fig. 9 Autocorrelation of the previous images fig. 8 (a) of pristine graphene (b) of the intercalated phase after 0.8ML Dy deposition and annealing to 900° C with the 6x6 periodicity still present (c) of the disordered Dy intercalated phase after the additional 1.5 ML Dy deposition and annealed to 900° C with the 6x6 periodicity absent. (d) 1-d scan of fig. 9(a) showing both periods of the 6x6 and graphene (e) 1-d scan of fig.9(b) showing the ~1.8nm period is still present but of reduced amplitude (f) 1-d scan of fig.9(c) showing that no 6x6 periodicity remains.

IV Discussion.

The previous results have shown how the intercalation location can change with annealing or increasing coverage and how the new location can be identified unambiguously with complementary diffraction, STM and DFT techniques. Such characterization is relevant to more recent intercalation studies, since there is growing interest to use a wider range of deposited metals and/or initial graphene phases. As discussed in the introduction Ca intercalation in BLG was found to be a 2-d superconductor. This is the only system that many different studies have been performed for the same metal and the same initial graphene surface[16-21]. Unfortunately all three intercalation locations for BLG were identified as possible sites; and even joint occupation of the

two deeper locations has been deduced in the latest publication[21], which raises the number of intercalation possibilities even more. This and similar conflicting identifications should be resolved quickly and robustly; otherwise different band structures and inconsistent 2-d physical mechanisms for the superconductivity will be deduced from experiments. Part of this disagreement is related to using video LEED only qualitatively from the visual inspection of the spots, which also depends on contrast settings of the detector camera. Using the variation of all the spots and measuring their intensities quantitatively as in the current work can remove the ambiguity. The Ca studies have also demonstrated the increase of interlayer spacing at the Ca intercalation location analogous to the Dy results; in ref. [19] the spacing of the BL-graphene was found to be 0.42 nm and in ref. [18] the spacing between BL-SiC was found to be 0.47 nm .

Besides the Ca controversy, the growing intercalation literature shows other systems where different locations or intercalated phases have been identified, which further points to the value of quantitative diffraction. When ZLG was used as the initial graphene phase, there is only one location for the metal to bond, so it is not possible to have inconsistent assignments in metal location. However when thicker graphene was used and the same metal was deposited different intercalation locations were identified. We briefly list several systems in the literature which show resolving conflicting identifications is a more general challenge. Although ZLG-SiC is the most stable location expected from the majority of experiments and DFT calculations, this is not always the extracted intercalation location.

When SLG was used as the initial surface and Au was intercalated at 850° C [33] it was found that the intercalation location was between graphene-ZLG and not ZLG-SiC as found in [34,35]. In the Au intercalation experiments under SLG two coexisting intercalated phases were identified: a phase with intercalated clusters and a phase with moiré ($2\sqrt{3}\times 2\sqrt{3}$)R30° pattern (located between graphene and BL). Au intercalation of the BL (despite only one possible intercalation location) has shown two differently doped Au phases: a p-doped (1/3 ML) phase and an n-doped (1ML) phase. Similar experiments with Co intercalated at 400° C have reached the same conclusion about graphene-ZLG as the bonding location [36] and not ZLG -SiC as in [37, 38]. Tb intercalates at 600° C in SLG but both graphene-ZLG and ZLG-SiC locations were found to be occupied jointly[39]; Rb intercalated at -190° C in BLG (with three possible singly-occupied locations as in the Ca experiments) bonds between first and second graphene layers as expected for alkali metal intercalation of graphite [40]; Eu intercalates at 300° C under SLG at both locations

depending on temperature, i.e., between graphene-ZLG at 120° C and between ZLG-SiC at 300° C[12].

In the current Dy intercalation experiments we have varied the growth conditions from RT to higher temperature, so it is possible to capture all the intercalated phases that form, including metastable ones. Predominantly intercalation is determined by kinetics, i.e., by the energetic barriers that control the transfer of the deposited atoms to sub-surface locations. These barriers include adatom diffusion on top to reach the entry portals and surface diffusion within the inner spaces that controls adatom spreading and aggregation to form sub-surface structures. It is more common in the literature to deposit an initial large amount of the metal of interest, followed by one-step annealing to sufficiently high temperature, searching for the absence of the 6x6 spots that indicates occupation of the BL-SiC location. This is usually complemented by XPS that gives information about the transfer of atoms below, but with limited sensitivity to the intercalation location, especially for thicker graphene. Such one-step annealing might bypass phases that are kinetically easier to form and are favored at lower temperatures.

In the literature Gd intercalation has been studied under the BL[9]. It is remarkable that the growth conditions to intercalate Gd are analogous to the ones used in the current Dy experiments, although the initial surface in the two experiments is different, i.e., BL vs SLG. After Gd deposition annealing to 800° C-1200° C results in uniform disordered intercalated layer without the 6x6 periodicity. Clearly surface diffusion in two systems is comparable, since relative high temperatures are needed to induce structural changes in the distribution of the intercalated atoms. On the other hand comparison with other rare earth metals shows that for these metals the temperatures atoms transfer below are much lower Yb(250° C)[11] Tb (600°)[39] Eu (120°-300° C)[12]; most likely because the interaction between these metals and C atoms is much weaker than the interaction of Dy, Gd with C atoms.

In ref.[9] Gd doping of the BL was sufficiently high to reach the Van Hove singularity at the M point, resulting in an intercalated phase of strong homogeneity and stability. Flat bands developed which were confirmed in theoretical studies. Novel ordered electronic states driven by electronic correlations and high density of states at the M point are expected to form in such systems. A different study [41] using high resolution STM/STS maps of Gd intercalation under bilayer graphene (with three intercalation locations possible) has also shown similar high doping for the lower two bands (with Gd occupying the BL-SiC and graphene-BL locations). The dI/dV

maps provide both the phase morphology (from topographic images) and the local density of states (from STS spectra). A uniform high coverage $\sim 2\text{ML}$ Gd phase intercalated at 1200°C under BLG was grown. This Gd phase has analogous growth procedure and is morphologically similar to the Dy phase shown in fig.8(c). Since unusual high level doping were seen for Gd intercalation in the two experiments under BL[9] and BLG[41], one should expect that Dy intercalated under SLG should also have high doping levels reaching the M point. Correlated electron physics and flat bands should be expected for Dy. Using SLG as the initial substrate, only two bands will be present and heavily doped. The interaction between the two linear bands at the points they cross can lead to non-linearities in the energy dispersion, potentially can open large energy gaps and change the electron effective mass. Analogous electronic effects related to the crossing of linear bands were shown in several earlier studies of SLG [39,42]; but the linearity of the band dispersion was attributed to the presence of a fraction of AA regions within the normal AB stacked regions, which partially results in sample electronic inhomogeneity. Since by controlling both the Dy coverage and annealing temperature, the dopant location can be tuned gradually between graphene-BL to between BL-SiC, this eventually will change the massless linear Dirac cones to massive parabolic bilayer bands.

Examining the tables I,II of the spot intensities and fig.5 in more detail we can follow how changes of other spots can clarify further the intercalation process. The narrow component of the 00 spot over the full annealing range decreases by a factor of 5 from its clean value; while as noted, the BSC increases by a factor of 1.5. The 00 spot has contribution from any type of disorder at all graphitized layers, probed at the relative high electron energy of 194eV ; while the BSC to be discussed further below originates from the top layer as implied by electron confinement and is not sensitive to deeper defects.

Concerning the Gr(10) spot and its BSC they have lower integrated areas than the corresponding ones of the 00 spot by factor of ~ 10 ; while the corresponding FWHM of the Gr(10) is larger by factor of 3 than the FWHM of the 00 spot. (FWHM values are listed for the four profiles shown in the supplementary materials.) This can be related to the presence of different types of orientational graphene domains because graphene has 3-fold symmetry. These domains are separated by antiphase domain boundaries and can be abundant on the surface as imaged by LEEM with their lateral sizes smaller than 100nm [45]. Because the Gr(10) wavevector has non-zero parallel momentum transfer it is sensitive to the finiteness of the domains and the intervening

domain boundaries. The 00 spot has no parallel momentum transfer and is not sensitive to lateral domain boundaries. It can explain why it is stronger and with smaller FWHM than the Gr(10) spot. The complexity of the BL-SiC interface with the structure of the $6\sqrt{3}\times 6\sqrt{3}$ large supercell still not determined, is also seen from the way different 6x6 spots behave with annealing. As seen from table II, the 6x6 spots surrounding the SiC spot become extinct with annealing at 1200° C and the transfer of Dy between BL-SiC; while the 6x6 spots surrounding the 00 spot still have finite intensity. This shows that other factors control how these 6x6 spots are generated, which results in non-equivalent spots depending on the adjacent fundamental spot i.e., whether the 00 or the SiC(10).

The behavior of the different diffraction spots with annealing can also shed more light on the origin of the Bell-Shaped-Component (BSC). There is need for routine diagnostic tools, especially to confirm the thickness uniformity of 2-d materials. We have demonstrated that the BSC is a very strong broad background in surface electron diffraction from graphene[27]. The Full-Width-at-Half-Maximum (FWHM) can be unusually large $\sim 50\%BZ$, but paradoxically it is a very useful marker of high-quality graphene. This diffuse intensity follows the Bragg component as a function of electron energy; which is the opposite of what expected in normal interference scattering when the diffuse intensity should be anticorrelated to the Bragg peak. The BSC has been present in numerous graphene studies over the last ~ 25 years but totally ignored by the community [27]. At least three different systems (Gr/SiC, Gr/Ir(111) and h-BN)[27,43] were studied quantitatively with similar large FWHM $\sim 50\%BZ$ of the BSC. In addition in all three systems the BSC integrated intensity is at least one order of magnitude larger than the Bragg component integrated intensity, which points to a strong and universal mechanism generating the BSC. A plausible origin of the BSC is electron confinement within a uniform graphene layer (or in other 2-d materials) that causes a spread in their normal wavevector component [44]. This spread is transferred to the parallel component of the diffracted electrons via strong interaction between graphene electrons and incident beam electrons.

The Dy annealing experiments at 1200° C of figs. 3, 4 show that after Dy is transferred in BL-SiC, although the Gr(10) spot increases it does not fully recover to its initial value for the clean surface; on the other hand the BSC returns back to its pristine value. This suggests that the Gr(10) spot is sensitive both to the top graphene layer and the BL (which almost has the same crystalline structure as graphene but different band structure). Dy below BL after annealing to 1200° C can

lower the Gr(10) intensity. On the other hand the BSC most likely is only sensitive to the graphene layer (as implied by the confinement model and because the pure BL layer shows no BSC). This explains why the BSC recovers to its pristine value after 1200° C, since its intensity is not affected by Dy atoms intercalated under the BL. It most likely implies that the BSC is a stronger marker of graphene thickness uniformity than the Gr(10) spot.

As mentioned the intercalated Dy between graphene-BL will be a candidate to realize a spring magnet, i.e., a structure with a layered hard magnet in contact with layered soft magnet, both structures grown as ultrathin films. The proposal has been in the literature for sometime and discussed in ref.[15]. Such concept requires growing on the nanoscale with the proximity of the two layers critical to maximize the exchange interaction, that causes the high coercive field of the hard magnet to increase the coercivity of the soft magnet. Growing Fe film on top of intercalated Dy under graphene fulfills the proximity condition and adds chemical passivation to the Dy layer, because it is covered by graphene on top. In addition the single layer thickness of the soft magnetic layer avoids one major challenge, i.e. magnetization twisting for thickness comparable to the domain wall width of the soft layer. Magnetic heterostructures based on graphene intercalation have been already implemented in the literature demonstrating strong interaction between the orbitals of the intercalated metal and the orbitals of the metal on top. A Co-Gr-Fe heterostructure was grown on Gr/Ir(111) with Co below and Fe on top[7]. XMCD shows that the Fe film has opposite magnetization from the intercalated Co thus the heterostructure can be used as antiferromagnetic filter, ideal for spintronics. In a different study an intercalated magnetic layer in contact with topological insulator thin film has generated novel magnetic topological phases in the composite system[46].

Besides magnetic effects it was shown that the interaction between the sub-surface metal layer and the deposited metal on top is sufficiently strong to affect other atomistic processes, such as nucleation and surface diffusion on top. Studies were performed on mixed substrate of intercalated and non-intercalated regions. Eu island nucleation was preferred on non-intercalated than intercalated regions of Gr/Ir(111)[47]. In ref.[48] Dy adatom random walk diffusion was changed to biased random walk diffusion transferring deposited atoms to the intercalated areas under Gr/SiC. Using ARPES and theoretical modeling was another way to account for changes of the band structure after K deposition at low temperature on BL[49]. For this non-intercalated system a higher fraction of K is adsorbed on top than at the interior interfaces which generates

charge asymmetry and opens a large energy gap. But no change of metal location with potentially tunable electronic phases was shown, as in the current intercalation studies.

V Conclusions

It is important to control metal intercalation of Gr/SiC, especially if the initial surface is thicker than BL because different intercalation locations are possible. The emerging band structure depends on the sub-surface metal location, so control of the intercalation location provides a way to generate a wealth of electronic phases. Using Dy intercalation under SLG as a prototype, we show from quantitative analysis of the diffraction spots with annealing, that the metal intercalation location can be controlled from graphene-BL to BL-SiC. DFT calculations show that as the Dy coverage increases, the preferred intercalation site is BL-SiC, with a corresponding large increase in the interlayer spacing. The preference for BL-SiC as the intercalated site is further supported from STM studies that show the 6×6 becomes extinct with gradual annealing and increasing Dy coverage, confirming that Dy prefers the BL-SiC location. This intercalation protocol can be applied in other experimental systems to control metal intercalation in a similar way and show how a novel class of 2-d electronic materials can be generated via predictive and targeted intercalation.

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Supplementary materials

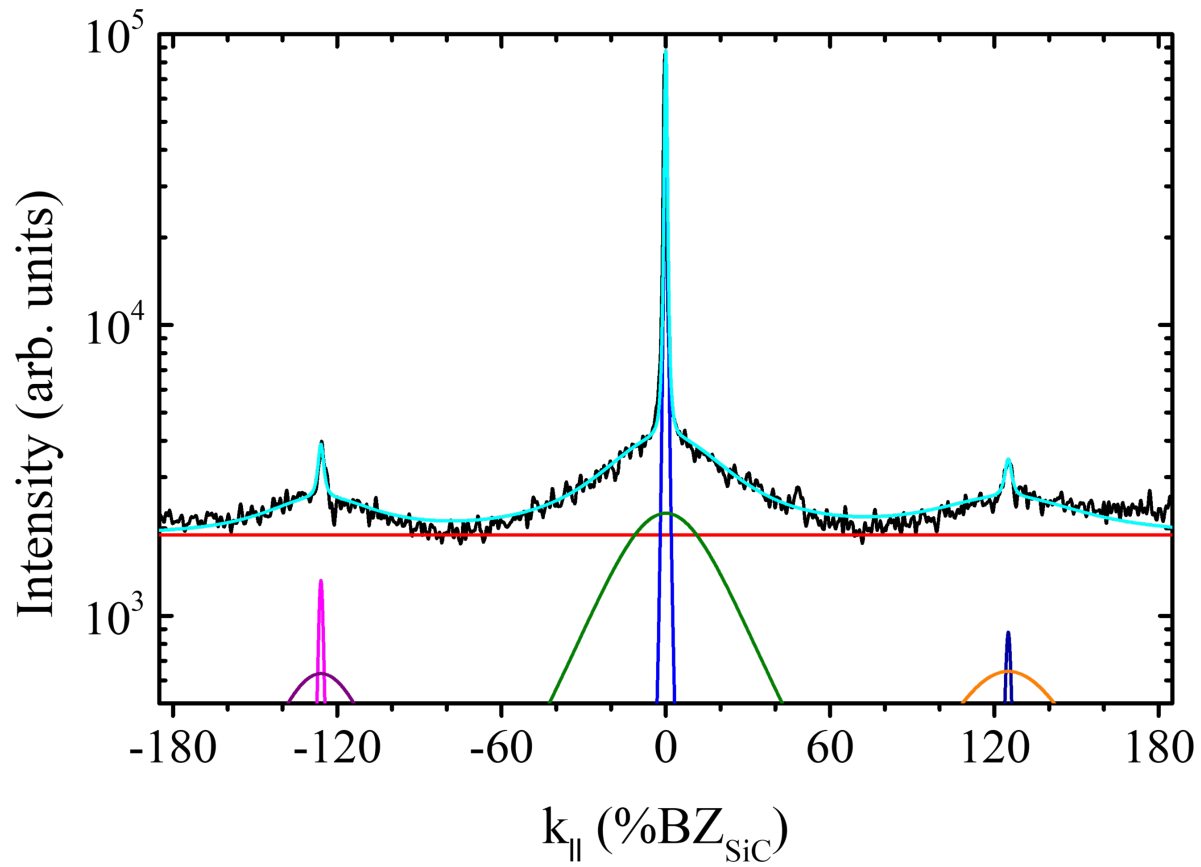


Fig. S1 Fitting of profile along $[1\bar{1}00]$ after annealing at $1050^{\circ}C$ for 2 min. The FWHM of the narrow 1.2%BZ of the BSC 48%BZ and the integrated area of the narrow component 1.4×10^5 and of the BSC 1.5×10^5

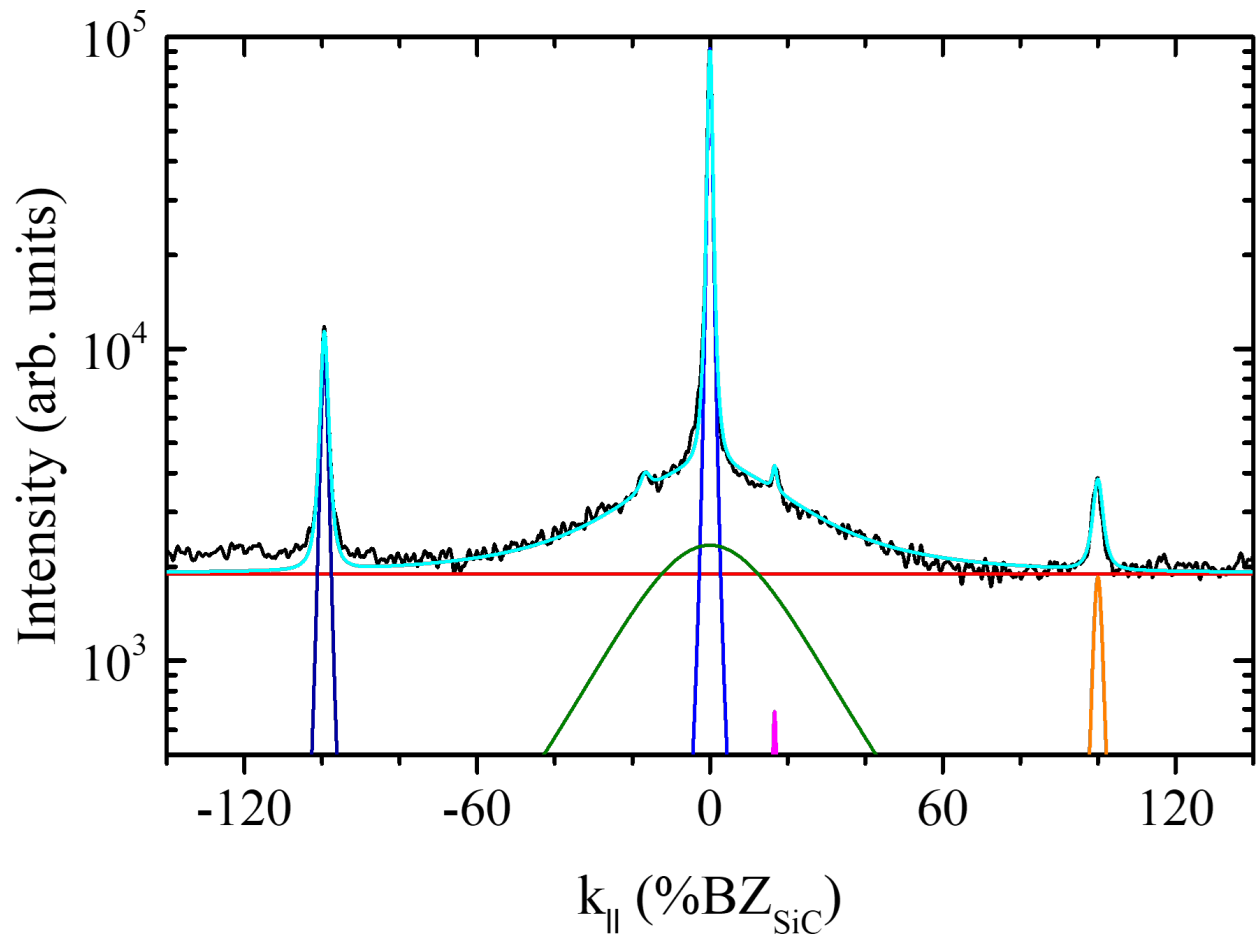


Fig. S2 Fitting of profile along $[1\bar{2}10]$ after annealing at 1050°C for 2 min. 0.9 50 100 145 The FWHM of the narrow 0.9 %BZ of the BSC 50%BZ and the integrated area of the narrow component 1×10^5 and of the BSC 1.5×10^5

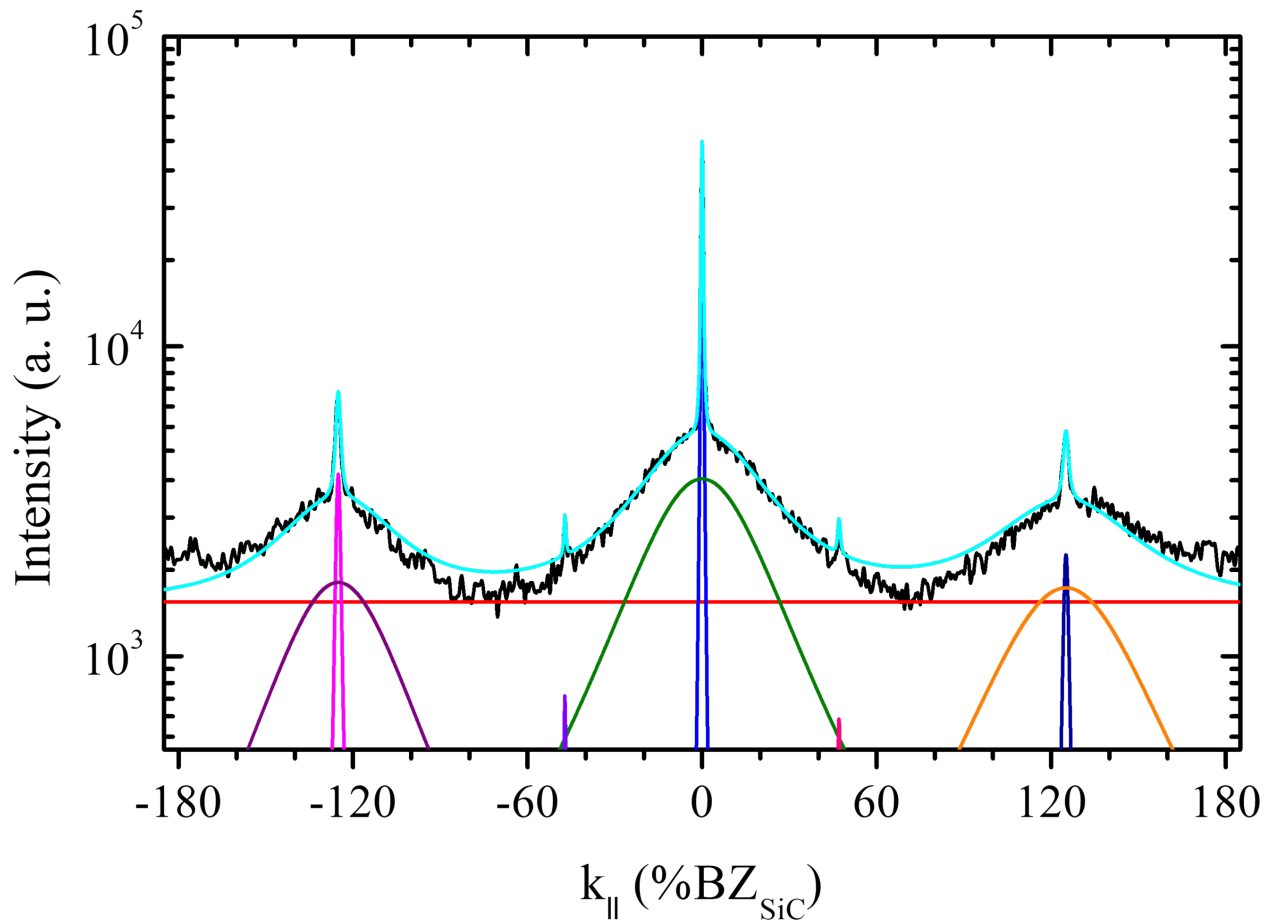


Fig. S3 Fitting of profile along $[1\bar{1}00]$ after annealing at 1200°C for 6 min. 1.03 48. 62 215
 The FWHM of the narrow component is 1.0%BZ of the BSC is 48%BZ and the integrated area of the narrow component is 0.6×10^5 and of the BSC is 2.2×10^5

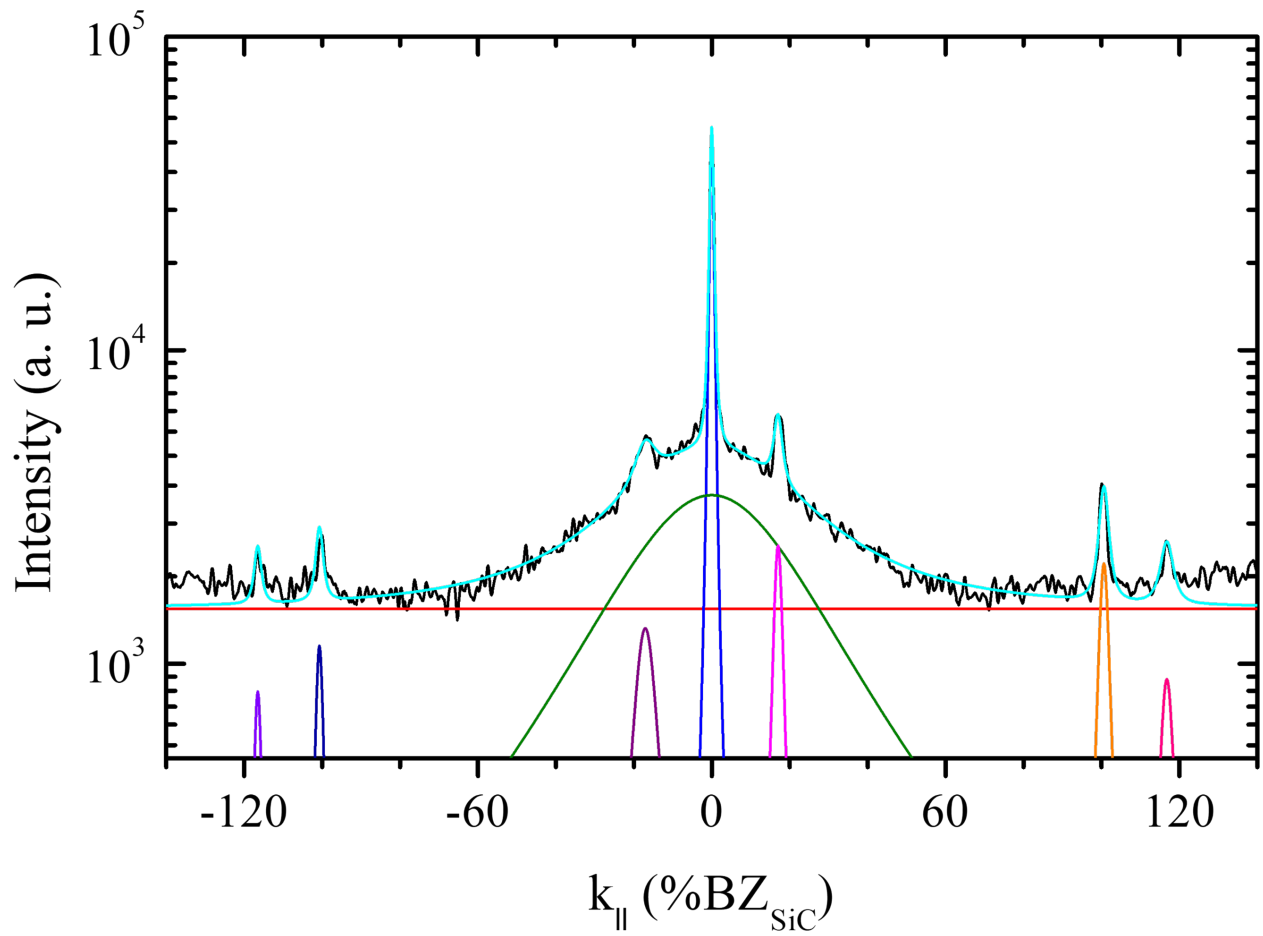


Fig. S4 Fitting of profile along $[1\bar{2}10]$ after annealing at 1200°C for 6 min. 1.3 48 62 215 The FWHM of the narrow component 0.7%BZ of the BSC 44%BZ and the integrated area of the narrow component is 0.4×10^5 and of the BSC 2.2×10^5

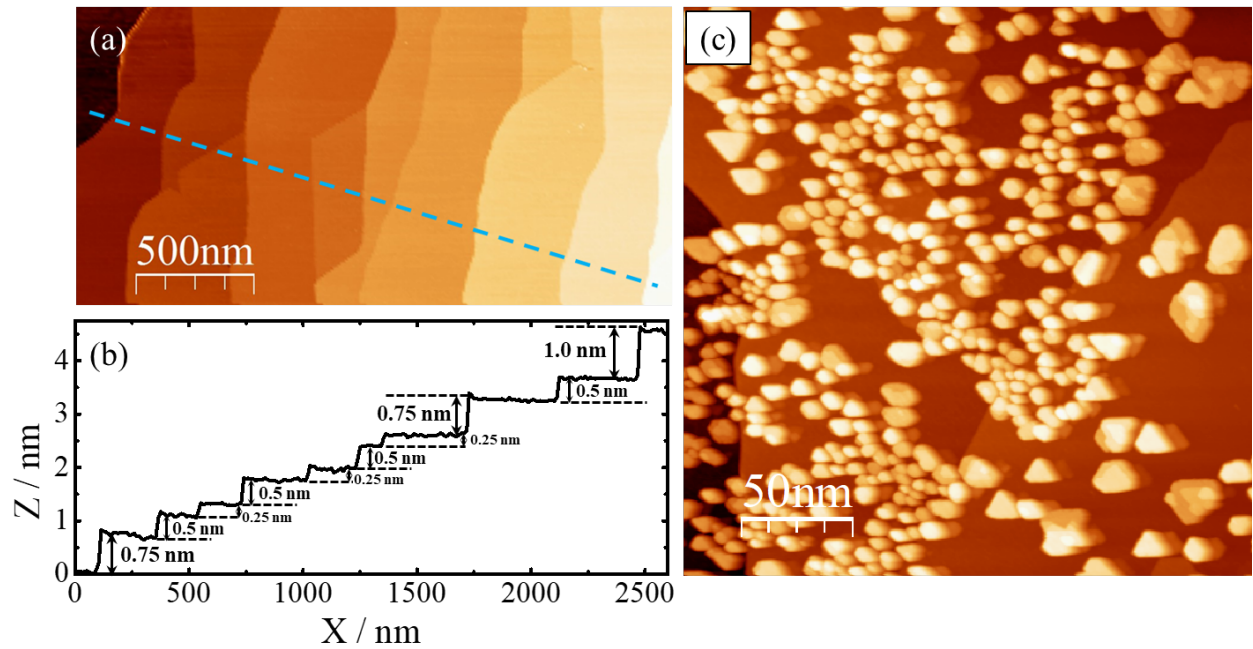


Fig. S5 (a) Initial large area of pristine graphene. The step heights are multiples of 0.25 nm indicating homogenous graphene domains. (b) Graphene area with Dy islands after deposition of 2.3ML at room temperature. Heating these phases to the different temperatures results in a range of intercalation phases with Dy intercalated at different sub-surface locations.