Grain-boundary-induced strain and distortion in epitaxial bilayer MoS₂ lattice

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Abstract

Grain boundaries between 60° rotated and twinned crystals constitute the dominant type of extended line defects in two-dimensional transition metal dichalcogenides (2D MX₂) when grown

on a single crystalline template through van der Waals epitaxy. The two most common 60° grain boundaries in MX_2 layers, i.e., β - and γ -boundaries, introduce distinct distortion and strain into the 2D lattice. They impart a localized tensile or compressive strain on the subsequent layer, respectively, due to van der Waals coupling in bilayer MX_2 as determined by combining atomic resolution electron microscopy, geometric phase analysis and density functional theory. Based on these observations, an alternate route to strain engineering through controlling intrinsic van der Waals forces in homo-bilayer MX_2 is proposed. In contrast to commonly used external means, this approach enables localized application of strain to tune electronic properties of the 2D semiconducting channel in ultra-scaled nanoelectronic applications.

Owing to their unique optical and electronic properties, two-dimensional (2D) transition metal dichalcogenides (MX_2 , with M a transition metal, and X a chalcogen) have garnered significant interest in the past decade for applications in next-generation nanoelectronics. Molybdenum disulfide (MoS_2) is the most investigated member of the MX_2 family. In its bulk form, MoS_2 has a layered structure in which individual Mo atoms are covalently bound to S atoms within a single layer; while the individual layers are coupled by a weak van der Waals interaction. MoS_2 is an n-type semiconductor with a layer-dependent bandgap ranging from 1.2 to 1.9 eV. The band gap decreases with the number of layers and evolves to a direct band-gap in a single layer due to 2D-confinement^{1–3}. Apart from this layer thickness dependence, 2D MX_2 optoelectronic properties are strongly influenced by changes to the atomic arrangement, such as polymorphism,^{4,5} stacking differences,^{6–9} presence of grain-boundaries^{10–14} and strain.^{15–21}

Introducing lattice strain in atomically thin materials emerges as a promising route to modify a wide range of their properties including electrical,^{15,16} optical,^{17–19} magnetic²⁰ and catalytic.²¹

Whilst strain in 2D layers is most commonly achieved through external means, intrinsic strain due to van der Waals coupling has only recently been reported where a mirror twin boundary is shown to exert an average strain of 1.6% in bilayer MoSe₂.²² Such exerted strain can lead to a direct-to-indirect-bandgap transition, in which, the bandgap reduces with the applied tensile strain until a semiconductor-to-metal transition occurs at $\sim 11\%$ according to first principle calculations.^{23,24} As a result, characterizing the strain and interlayer interactions in two-dimensional materials is not only critical for gaining further insight into their properties, but also holds the key to unlock the potential of materials with specifically tailored properties.

Throughout the last decade, several techniques have been developed to fabricate MX₂ of single to few-layer nature, including exfoliation and vapor-phase deposition. The former is either mechanical or liquid-phase based, while the latter relies either on a physical or chemical deposition approach. Chemical vapor deposition (CVD) is by far the most promising road to synthesize high-quality, wafer-scale, uniform layers, which is a crucial requirement for the development of any semiconductor manufacturing technology. Often, MX₂ layers are grown by CVD on amorphous substrates (SiO₂, Al₂O₃)^{25–27} which do not afford any control over the in-plane orientations of the growing crystal domains. As a result, these randomly oriented domains often meet to form dislocation-rich grain boundaries²⁸ that ultimately hamper the device performances. In contrast, the deposition on single crystalline substrates such as sapphire,^{29–31} mica,³² or other 2D materials³³ enables epitaxial seeding with crystal domains developed along a preferential orientation and reduces significantly the density of dislocations at grain boundaries. In a single layer of MX₂, certain grain boundaries dominate the boundary structures due to the absence of inversion symmetry, particularly grain boundaries that occur between 60° rotational twinned crystals. While a translational mismatch could be present between grains with the same orientation, it can also be

relaxed through their sliding on ultra-flat crystalline substrate, resulting in a well-stitched, defect-free boundary.³⁴

In this work, we investigate the morphology of MoS₂ layers grown on two-inches sapphire substrates using the molybdenum hexacarbonyl and dihydrogen sulfide metal organic CVD (MO-CVD) precursors. During the growth, the MoS₂ crystals develop a preferential in-plane orientation and form therefore a representative system to study inevitable disorder events in such an epitaxial system. In this paper, we focus only on the case of the dominant 60° twin boundaries, keeping in mind that other boundaries and dislocations can also occur in a reduced occurrence. Using a combination of scanning transmission electron microscopy (STEM), geometric phase analysis (GPA) and density functional theory (DFT), we find that the occurrence of two types of twin boundaries, β or γ , introduces either a lattice expansion or a compression respectively, which is reduced in a bilayer system due to the van der Waals coupling occurring with the second pristine layer. Such coupling induces tensile or compressive strains on the pristine layer in the region located above the corresponding grain boundary (GB). Interestingly, recent studies demonstrated the formation of a high density of β -GB in MBE grown MoSe₂,³⁵ whereas the γ -GBs are known to form under an e-beam exposure in a bilayer MoS₂, leading to the formation of inversion domains.³⁶ The insights into the mechanism of strain transfer due to interlayer interactions in presence of such twin boundaries is expected to provide alternative routes to engineer strain in these layered systems.

Results and discussion

Types of 60° twin boundaries in MoS₂

Figure 1 (a,c) shows Annular Dark Field (ADF) – STEM images of 60° twin boundaries along with the structure of the corresponding DFT optimized models. Both these GBs are symmetric along the zig-zag direction and consist of 4|4-fold rings highlighted with blue in both GB models. The β -GB is parallel to the zig-zag direction (termed 4|4P) in which, the S atoms at the boundary are 4-fold coordinated. On the other hand, the γ -GB consists of shared zig-zag edges (4|4E) in which the S site remains 3-fold coordinated.³⁷ Unlike the β -GB, where the S positions consist in projection of two S atoms, a γ -GB consists of only one S atom in projection, which results in a 5-fold coordination of the Mo at a γ -GB. The local stoichiometry at the GB is however the same for both GBs and S-deficient compared to pristine MoS₂. While a γ -GB is found exclusively along the zig-zag direction and is atomically sharp, a β -GB can move in the armchair direction aided by 8 membered rings (marked in Fig. 1b with green octagons). β -GBs can therefore exist in several other directions apart from zig-zag, allowing their formation between rough/faceted edges of merging grains, which is partly responsible for their seeming abundance relative to γ -GB. Moreover, previous theoretical studies^{38,39} have shown that β -GB has a lower formation energy compared to the γ -GB, which is consistent with our experimental observations. It however must be noted that other factors such as the edge structure of the grains, their interactions with the underlying mismatched sapphire and related local strain effects may also influence the relative abundance of these GBs. We also observe some instances of GBs which switch between β and γ structures along the zig-zag direction. Fig. S1 shows such a transition. Since the two GBs are related by a shift of a half unit cell vector along the GB direction, a dislocation is found in this transition region when the columns of S atoms switch from a double to single occupancy, forming a distorted 4|4 structure.

Figure 1: Atomic structure of 60° twin GBs. High magnification ADF-STEM images of β and γ GBs along with their corresponding DFT optimized structures (a,c). Low magnification ADF-STEM images of both GBs (b,d) highlighted by the dashed lines where the green octagons mark the 8-membered rings in a β -GB.

Due to the hexagonal symmetry of the underlying sapphire template, the orientation of growing domains is controlled to a great extent through a van der Waals epitaxy. However, the lack of inversion symmetry in a monolayer MoS₂ implies that growing domains with 0° rotation between them can get stitched without any defects,³⁴ whereas domains that are 60° twins always result in a grain boundary (GB). Therefore, in highly epitaxial MoS₂, the GBs are overwhelmingly dominated by 60° twin boundaries. Although theoretical studies have predicted more than ten types⁴⁰ of possible boundaries between 60° twins, the two most frequently reported boundaries in MoS₂ are β and γ GBs. Several studies^{37,38} predicted that the presence of both types of GBs introduces mid-gap states, which results in a semiconductor to metal transition at the GB.

Figure 2: ADF-STEM images of β (a) and γ (b) GB in a bilayer MoS₂. (c) Geometric models of β and γ GB illustrating the five stacking constructions that can be built for bilayer MoS₂ by translating the top layer in the armchair direction. In the bottom layer, Mo atoms are colored purple and the S atoms are yellow while in the top layer they are blue and orange respectively. The colors indicate their DFT based stability from reference⁴¹: stable (green), meta-stable (orange) and unstable (red). The top-most is the most stable configuration.

Next, we investigate the bilayer configuration. Fig. 2 (a,b) shows HAADF-STEM images of a β and a γ GB. The lattice pattern on the left-hand side consists of hexagonal rings which correspond

to the AA' (2H) bilayer stacking, while the reduced contrast on the right-hand side is attributed to the AB (3R) stacking. In order to transform an AA' stack to AB (or the equivalent inverted BA stacking), one of the layers should undergo a 60° rotation operation, with a lattice site acting as a rotation axis. When the second layer with an AA' stacking grows across both a β or a γ GB, it results in AB stacking on the other side (Figure 2c top). In fact, five stacking orders are possible through the translation of the top layer over the GB along the armchair direction. This is depicted in Fig. 2c, where a simple 2D model of the 2 GBs is made using the necessary symmetry operations and overlaid with a continuous strip of MoS₂. This is translated over a distance $\frac{1}{\sqrt{3}}\mathbf{a}$ along the armchair direction, where $\mathbf{a}$ is the MoS₂ lattice parameter. Among the five possible stackings, the first principle simulations suggest that the AA' and AB (or BA) are most energetically favorable with a weak difference in total energy.^{22,41} The other models are either meta-stable (AB') or unstable (AA, A'B). As a result, the most favorable configuration is one where the AA' and AB stackings are separated by a β or γ GB, which is consistent with the most common formation observed in our films. The other stacking configurations can however still occur for twisted layer configurations which are virtually absent in this study.

GB induced distortion and strain in bilayer MoS₂

The presence of any grain boundary introduces distortion to the MoS₂ lattice due to a local rearrangement of atoms and changes in bond lengths, which in turn depend on the type of grain boundary present. This lattice distortion can be measured using geometric phase analysis (GPA) by selecting the appropriate $\mathbf{g}$ -vectors (reciprocal lattice vector) which fulfil the condition $\mathbf{g} \cdot \mathbf{v} = \mathbf{n}$, where $\mathbf{n}$ is an integer number and $\mathbf{v}$ is the displacement vector between the Mo and S sublattices. It was previously shown that the unfulfillment of this criterion leads to severe artefacts⁴². For 2H-MX₂, this condition is fulfilled for the {11-20} spots where $\mathbf{n} = 4$. Notably, selecting any set of

non-collinear spots among this family results in the same strain profiles. On the contrary, selecting any of the $\{10-10\}$ spots results in a non-integer $\mathbf{n}$, which leads to different strain maps depending on the selected spot which is illogical. (See supplementary Fig. S2 and related text for more details and examples).

The β - and γ -boundaries introduce distinct distortion and strain into the 2D lattice, which imparts a localized tensile or compressive strain on the subsequent layer, respectively. From the GPA strain maps of a β -GB in a monolayer MoS_2 , we observe that the localized lattice clearly expands as evidenced by the narrow red region in the ϵ_{xx} map (Fig. 3a). In contrast, a γ -GB introduces a localized lattice compression along the GB (Fig. 3c). In order to obtain an aligned stacking order across the GBs using a simple geometrical model (as shown in Fig 2c), the Mo-Mo spacing in a β -GB and the Mo-S planar spacing in a γ -GB must be equal to the Mo-S spacing, i.e. to $(\frac{1}{\sqrt{3}}\mathbf{a})$, in a MoS_2 unit cell. The lattice expansion is confirmed by measuring the Mo-Mo spacing in β -GB on the ADF images using a 2D gaussian fitting procedure,⁴³ which measures ~~approaches~~ 0.275 ± 0.003 nm. This is significantly larger than the Mo-S planar spacing $(\frac{1}{\sqrt{3}}\mathbf{a})$ of 0.188 ± 0.006 nm measured away from the boundary. This shows that the MoS_2 lattice relaxes itself at the β -GB. Since at γ -GB's only single sulfur atoms are present, they show only weak contrast on the ADF images and hence do not allow an accurate measurement of the spacing. Therefore, instead in this case we compare the Mo-Mo spacings across the GB. The Mo planes are separated by 0.268 ± 0.003 nm across the GB and 0.279 ± 0.002 nm away from it, clearly confirming that the MoS_2 lattice contracts at the γ -GB.

Intriguingly, the strain at the GB reduces noticeably when going from a single to a bilayer MoS_2 , as determined from the GPA maps and strain profiles of either GB in Fig. 3e. The reference $\mathbf{g}$

vectors in GPA are chosen by selecting a region away from the boundary, which is assumed to be strain free. We obtain a similar strain profile when mapping the strain in a larger image, where the GB passes from a monolayer to bilayer region, as shown in Fig. S3. Here the selected reference is the same for mono and bilayer regions.

Figure 3: ADF-STEM images and corresponding GPA strain maps of β and γ - GB in a monolayer (a,c) and bilayer (b,d) along with the strain profiles (e) extracted from the center of the ϵ_{xx} maps, integrated over a width of 2 nm in each case.

Next, we gain further insights into the GB induced distortion in both mono- and bilayer MoS_2 through DFT calculations. The input models for these calculations are formed through transformations similar to the ones illustrated in Figure 2c. The morphology of the β -GB model in a monolayer is built by using a mirror symmetry operation with the mirror plane being the S atoms present at the zig-zag edge. On the other hand, the γ -GB model is formed by a similar mirror operation, followed by a translation of $\frac{2}{\sqrt{3}} \mathbf{a}$ along the armchair direction and another $\frac{1}{2} \mathbf{a}$ translation in the zig-zag direction. The monolayer models are then compared with the DFT relaxed models

for β - and γ -GB, respectively (Figure 4 (a,b)). The resulting formation energies ($E_f = E_{GB} - E_{pristine}$) are shown in Fig. S4 for all GB models. As expected, the formation energy of the β -GB is lower than of the γ -GB, which agrees with the trend reported by Hong *et al*.³⁸ This is also maintained for the case of a bilayer system.

The geometric β -GB model of a monolayer has a Mo-Mo distance of 0.181 nm in the 4-members ring, which is equal to the Mo-S planar separation ($\frac{1}{\sqrt{3}} \mathbf{a}$, where $\mathbf{a} = 0.313$ nm for a geometrically relaxed pristine monolayer MoS_2). The Mo-Mo distance increases to 0.258 nm after relaxation due to the repulsion between opposing Mo atoms. The Mo-S planar separation in γ -GB, however, reduces to 0.123 nm causing a compression of the lattice.

In a bilayer system, such a distortion (being either an expansion or a compression) at the GB leads to an intermediate/misaligned stacking order on the other side of the GB, when one side is perfectly AA' stacked. This is illustrated by setting a pristine MoS_2 lattice under the geometrically relaxed monolayer models of β and γ -GB on Fig. 4 (a,b). Such misaligned stacking orders are only rarely observed experimentally at second layer grain edges, an example of which is shown in Fig S5. Instead, we typically observe a sharp transition going from AA' to AB across both β and γ GB's. Moreover, the geometrically relaxed bilayer models (Fig. 4 (c,d)) have an aligned stacking on both sides of the GB.

Hence, in bilayer MoS_2 , the lattice of the continuous top layer (i.e., the one without GB) is straining itself to accommodate the expansion or contraction due to the presence of a β or γ -GB in the bottom layer respectively. When comparing the GPA strain profiles of either GB's in a bilayer to the one in a monolayer, the strain at the GB is noticeably reduced (Fig. 3e). This indicates that the GB distortion is suppressed in a bilayer system due to the interlayer interaction with the

subsequent layer, wherein the tendency to form low-energy stacking registries on both sides of the GB causes a compression (or expansion) of the β (or γ) GB, respectively. This also suggests that a strain transfer process takes place between the interacting layers.

To verify the occurrence of this strain transfer, we compared the morphology of both β - and γ -GB in the mono- and bilayer models as optimized by DFT. GB distortion profiles are obtained by analyzing the $\{10-10\}$ spacings across the boundary relative to the spacing in relaxed MoS₂ (Fig. 4e). For this purpose, the S and Mo sublattices are used for the β -GB and γ -GB respectively as these are continuous across the interfaces. The suppression of the GB distortion in a bilayer is evident for both GBs by the reduction of the peak heights. Moreover, up to 3 nm of the neighboring lattice on both sides of the GBs experiences strain due to the top layer.

Figure 4: First-principle simulation results: Crystal structures of β (a) and γ (b) GB as built (top) and after geometry relaxation (bottom) for a MoS₂ monolayer. A second MoS₂ sheet is overlaid on the monolayer structures to illustrate the resulting misaligned stacking on right hand side of the

boundary if a second continuous layer is grown over the relaxed monolayer models. The morphologies of the β and γ structures, as obtained by DFT, in both GBs in a bilayer are illustrated in figures c and d, respectively. For comparison of the strain evolution relevant distances across the GB are indicated in the geometrical model and after the DFT relaxation for monolayer and bilayer systems. Distortion profiles of the GB containing layer in a mono and bilayer derived from the $\{10\text{-}10\}$ spacing in the sublattices (e). Strain profiles of the top pristine layer for both GBs (f).

As the top layer suppresses the GB distortion in the bottom layer, it experiences in turn strain in the opposite direction (i.e. tensile for β -GB and compressive for the γ -GB). This strain can be determined by comparing the $\{10\text{-}10\}$ spacing in the top layer of both DFT optimized bilayer models to the reference one ($\frac{\sqrt{3}}{2}\mathbf{a} = 0.271$ nm). The strain in the top layer peaks at +1%, immediately above the GB for the β -GB bilayer model and at -0.8% for the γ -GB, which in both cases reduces when moving away from the GB (Fig. 4f). These observations confirm that a strain transfer process takes place between the interacting layers in a bilayer configuration due to the van der Waals coupling.

Figure 5: Decomposition of the Density of States (DOS) obtained for pristine structures (a) after geometric relaxation, where purple and yellow illustrate the contributions from the Mo and S atoms, respectively. The position of the Fermi levels is indicated by dotted lines. Spatially varying local DOS (LDOS) plotted for both β and γ -GB as a function of distance from the GB (b). Note that the energy range is different in the monolayer and bilayer models to focus on the bandgap. The zero is set at the position of the Fermi level.

Finally, to understand the influence of these GBs on the electronic properties of a mono and bilayer system, their density of states (DOS) is evaluated for pristine MoS₂ and GB containing models as illustrated in Fig. 5. The pristine models show a PBE bandgap close to 2 eV for monolayer and ~ 1 eV for bilayer within which no additional states are present. On the other hand, the models containing GB clearly show mid-gap states in all cases. The γ -GB in a monolayer has a distinct state signature close to the conduction band, whereas the β -GB has two states, with one close to the conduction band and another one close to the valence band. γ -GB in a monolayer appears to have some band bending to lower energies on either side of the GB. We attribute this effect to the strain induced by the buckling at the GB (see Fig. S6). Notably, the valence bands are raised into the bandgap and undergo a splitting in both bilayer GB models. Due to the strain in a bilayer, the bandgap is reduced slightly at the GB and gradually approaches the nominal level further away from the GB. Therefore, a 1D GB in a single layer exerts a localized 2D strain on the subsequent layer, thereby influencing electronic transport not only within the GB layer, but also in the adjacent layers.

Conclusions

We investigated the structure of two typical 60° twin GBs, β and γ , found in an epitaxially grown MoS_2 bilayer. In any bilayer MX_2 , the presence of either of these boundaries in one of the layers leads to a change in the stacking order from an AA' to AB alignment across the GB. A simple and efficient strain mapping using GPA is demonstrated, wherein the importance of selecting the correct g-vectors on the resulting strain map is discussed. The GB distortion is suppressed in a bilayer due to the van der Waals coupling of the forces between the two layers, leading to a strain transfer to the pristine layer on top and to the lattice on either side of the GB. While the β -GB induces a tensile strain of $\sim 1\%$, the γ -GB induces a compressive one peaking to $\sim -0.8\%$ in the pristine layer. Electronic structure calculations show the impact of the GB in mono and bilayer systems, which leads to the introduction of mid-gap states and to the lowering of the bandgap. These insights into the interlayer interactions in presence of such twin boundaries may provide alternative routes to engineer both tensile and compressive strain locally in these layered systems. This approach enables the application of localized strain to tune the electronic properties of the 2D semiconducting channel in ultra-scaled nanoelectronic applications.

Experimental Methods

MoS₂ templated growth: MoS_2 is deposited by MOCVD in a 200 mm MOCVD reactor connected to an ASM Polygon8200 platform. The deposition method is similar to the one described by Chiappe *et al.*³¹ Molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$) and dihydrogen sulfide (H_2S) are used as the Mo and S precursors, respectively, while N_2 acts as the inert carrier gas. Prior to the MoS_2 growth, the 2-inches c-plane sapphire substrate is annealed in a furnace under O_2 ambient at 1175°C for 60 minutes, and then ex-situ transferred to the MOCVD reactor. During the MOCVD process, the sapphire substrate is heated under N_2/H_2 until it reaches the deposition temperature of

1000°C. After a stabilization period, the Mo(CO)₆ precursor is sent into the chamber preceded by H₂S. The total pressure is maintained at 20 Torr and a H₂S/Mo ratio of $\sim 1.2 \times 10^4$ is set during the growth. A post-deposition anneal treatment is then applied at 1000°C and 90 Torr in N₂:H₂S ambient. This results in a closed monolayer MoS₂ with second- and third-layer islands as shown in Fig. S7.

Sample transfer and TEM analysis: The CVD MoS₂ is transferred from the sapphire growth substrate onto a TEM grid using ultrasonic delamination in warm water using a method similar to the one reported by Chiappe *et al.*³¹ The samples are spin coated twice with 3% Poly(methyl methacrylate) in anisole (PMMA A3), once at 1000 rpm followed by another at 3000 rpm. After each coating, these samples are baked at 120°C for 2 mins. This results in approximately 150 nm PMMA thickness. Subsequently, a frame of thermal release tape with a window slightly bigger than a standard TEM grid is attached to the top of the sapphire/MoS₂/PMMA stack. This stack is then placed in a beaker containing water maintained at 80°C for 20 minutes, then immersed in an ultrasonic bath for 5 minutes to facilitate the MoS₂ delamination. Using tweezers, the frame with suspended PMMA/MoS₂ is detached from the sapphire and placed on top of a TEM grid followed by PMMA removal in acetone overnight. The TEM grid is then rinsed in isopropyl alcohol several times, air dried and inserted into the TEM shortly after the preparation. Transmission electron microscopy is carried out in a TFS Titan G² 60-300 operated at 120 kV to minimize beam damage. The ADF-STEM images are acquired with a convergence angle of 23 mrad and a STEM detector ranging from 25 to 153 mrad. The atomic resolution images are filtered using a band-pass filter to remove the amorphous contributions mainly from the PMMA residues. GPA is carried out using the Strain++ program⁴⁴ using a mask size roughly equal to $\frac{1}{2}$ reciprocal lattice parameter.

DFT simulations: First-principle calculations are carried out using the exchange-correlation functional developed by Perdew, Burke and Ernzerhof revised for solids (PBEsol)⁴⁵ combined with Goedecker–Teter–Hutter (GTH)⁴⁶ pseudo-potentials, as implemented in the CP2K package.⁴⁷ Calculations were performed for both monolayer and bilayer MoS₂ with either a β or γ -GB. In order to avoid edge effects, the MoS₂ nanoribbon models are created with a $20\sqrt{3} \times 1$ unit cell with the long direction in the armchair direction in which the GB is set at the center with an additional 1 nm of vacuum to prevent interaction of dangling zig-zag edges with their periodic images. Similarly, 1 nm of vacuum is added along the z-direction to preserve the 2D nature of the material. A plane-wave kinetic energy cut-off of 250 Ry is used to expand the wave functions and van der Waals corrections using the DFT-D3 Grimme formalism were included. Monkhorst k-point schemes of $4 \times 1 \times 2$ and $4 \times 1 \times 1$ were used to sample the Brillouin zone of the monolayer and bilayer, respectively. Atomic energies are calculated using the self-consistent energy-force method (SCF) with a double- ζ polarization basis-set using a convergence threshold of 1×10^{-6} . The atomic coordinates are fully relaxed using LBFGS optimizer until a maximum atomic force criterion of $0.00045 \text{ bohr}^{-1} \text{ hartree}$ is reached while the cell is constrained in the z direction to prevent self-interaction.

Supporting Information Available: Discussion on artefacts due to wrong g-vector selection on GPA strain maps. Formation energies of the two grain boundaries in mono- and bilayer. Other STEM images including low magnification overview of the sample and atomic resolution STEM images of a transition from β to γ -GB and stacking at edges of bilayer islands. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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TOC Figure