Supporting Information: Influence of the underlying substrate on the physical vapor deposition of Zn-Phthalocyanine on graphene[†]

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S1: Graphene before ZnPc deposition

In order to better understand the impact of graphene on the ZnPc morphology, the various graphene systems have been images using SEM. Figure S1 shows low and high magnification images of graphene as grown on Cu (Fig. S1a-b) and graphene transferred onto SiO_2(Fig. S1c-d), Si (Fig. S1e-f), and sapphire (Fig. S1g-h). Even after transfer, graphene maintains its planarity (i.e. ripples and wrinkles) induced by the step-bunching of the Cu surface during graphene growth.

SEM imaging does not seem to provide more insight into the role of the underlying substrate on the ZnPc growth.

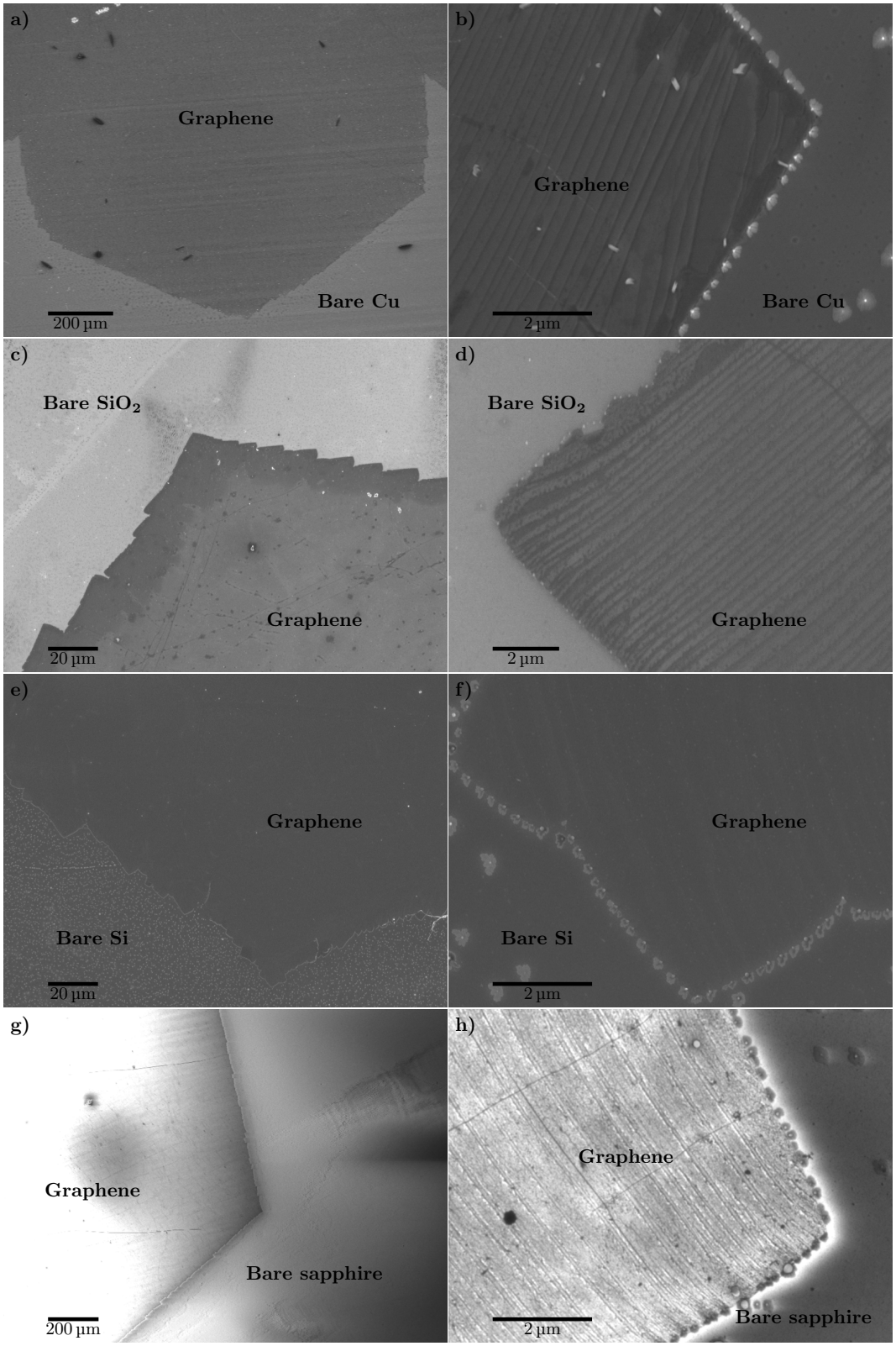

Figure S1: low-magnification (**left column**) and high magnification (**right column**) SEM images showing graphene on various substrates after annealing the samples at 250°C for 20 min in the ZnPc PVD system.

S2: Effect of the stacking order of multilayer graphene

The ZnPc crystallinity and morphology are found to vary with the number of graphene layers but also with their relative twist angle or stacking order. To show such phenomenon, ZnPc has been deposited on a graphene sample transferred onto SiO_2/Si with twin multi-layer domains, that is, multilayer domains exhibiting different twisting angles/stacking orders while emerging from one single nucleation site.

Figure S2 shows multi-layer graphene domains with the second layer exhibiting two different in-plane orientations. While the orientation of the first (top) layer remains the same within the span of the SEM images (given that millimeter-size single-layer crystals of graphene were grown), there are two different orientations emerging from the same nucleation center for the second layer (denoted A and B in Figs. S2a and S2b). Such a change of orientation can be easily observed at the edges and by noting the distinct ZnPc morphology differences.

During the CVD process, additional C species can produce additional layers under the first top layer. Such ad-layers are either turbostratic/twisted (see regions denoted by A) or somewhat oriented with the first layer to form AB stacked graphene (see regions denoted by B). It is well known that the graphene electronic structure strongly depends on the twisting angle/stacking order. The electronic coupling between adjacent graphene layers is typically characterized as either weak or strong depending on if the layers are twisted or AB-stacked, respectively.

The change of ZnPc morphology is attributed to a change in the electrostatic field screening of the substrate by graphene and a change in the number of carbon atoms available to interact with ZnPc molecules impinging on the top surface. The strong electronic coupling in AB-stacked multi-layer graphene most likely facilitates the transfer of electrostatic dipoles

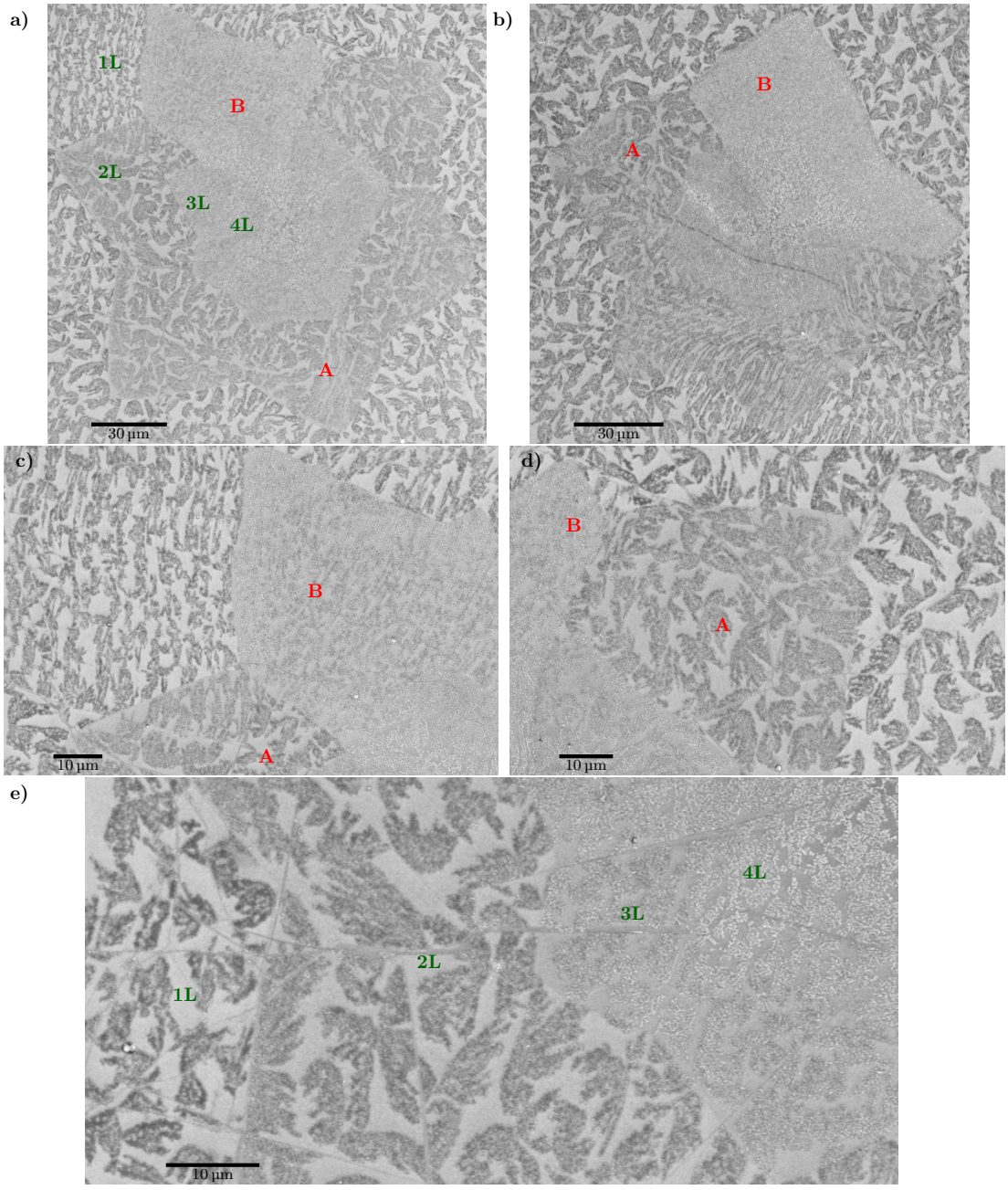

Figure S2: **a-b)** Large area SEM images showing entire multilayer graphene domains transferred onto SiO_2 after the deposition of ZnPc using a source temperature of 400°C, a substrate temperature of 250 °C and a deposition duration of 30s. **c-e)** Higher magnification SEM images of (a). "A" and "B" regions refer to two different orientations for the second layer of graphene.

and less efficiently screens the substrate-induced electrostatic doping. On the other hand, ZnPc molecules impinging on AB-stack multilayer graphene can interact more with the C atoms of the second layer (as they sit right underneath the aromatic rings of the first top layer) compared with those of twisted multilayer graphene.

Figure S3 shows another example of ZnPc crystallites grown on multilayer graphene for which the second layer exhibits different in-plane orientations depending on the nucleation center (as shown by the orientation of the edges). When considering the effect of bilayer graphene, the bilayer domain on the right side of Fig. S3 seems to have a less prominent effect on the ZnPc morphology compared to the bilayer on the left side of Fig. S3 which is rotated by an angle in the 24-36°range (based from edge orientation).

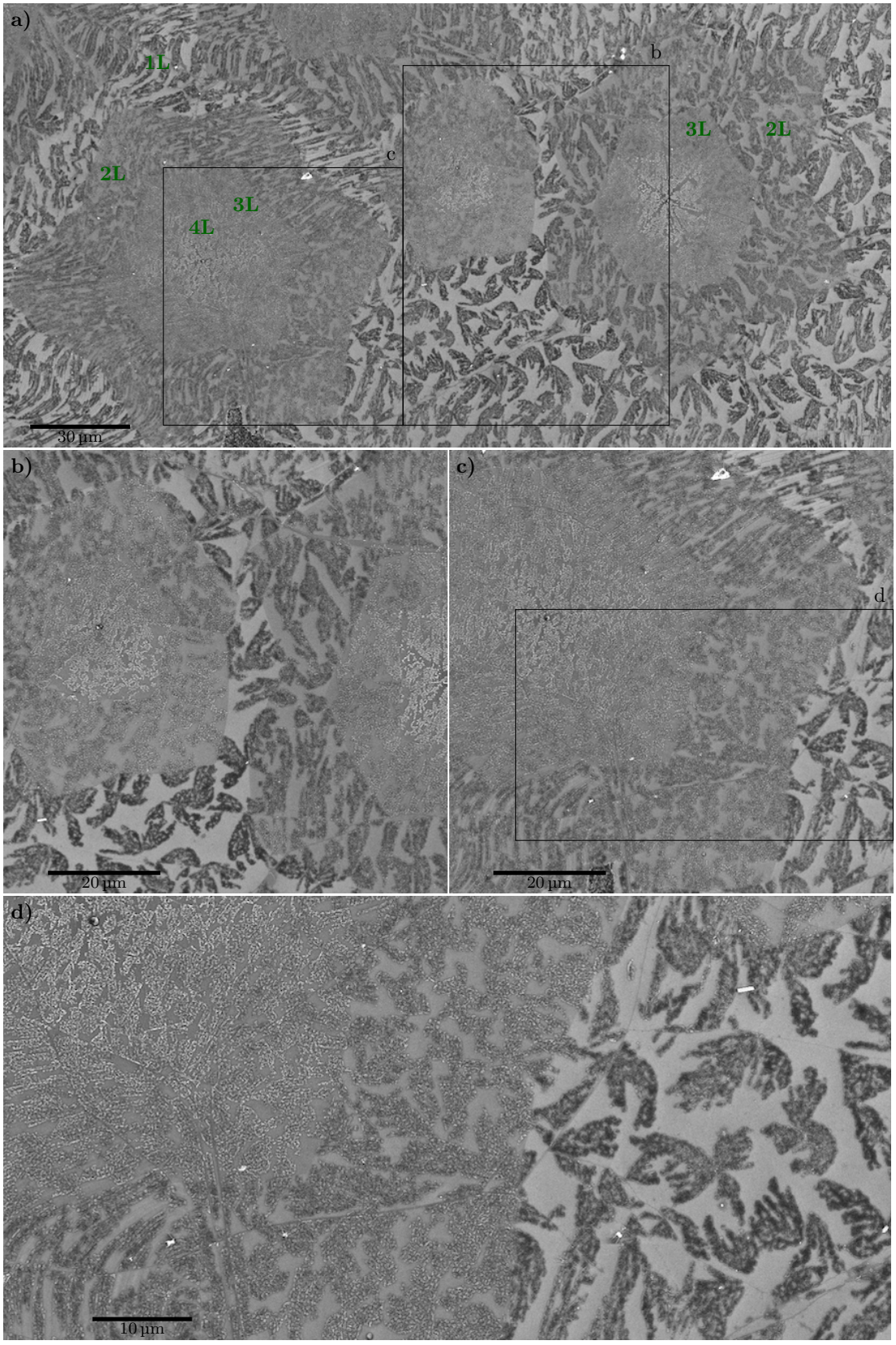

Figure S3: **a)** Large area SEM image showing multilayer graphene domains transferred onto SiO_2 after the deposition of ZnPc using the same conditions as for the samples shown in Fig. S4. **b-d)** Higher magnification SEM images of the domains in (a).

S3: Effect of the graphene ripples on the ZnPC growth

During the CVD growth, graphene mimics the surface morphology of the Cu catalyst. Cu foil, which is the most widely used catalytic template for CVD process, is typically polycrystalline. Depending on the thermal treatment, the CVD atmosphere composition, and the Cu foil thickness, the Cu grains can reach a lateral size exceeding a few hundreds of micrometers. The step bunching is mainly governed by the Cu grain crystalline orientation and by the thickness of the graphene growing on its top. Figure S4a shows a large SEM image of ZnPc deposited on single-layer graphene. The color contrast stems from a slight change in ZnPc morphology caused by a change in the orientation and dimensions of graphene ripples. As discussed in the manuscript, the presence of ripples impedes the surface diffusion and modifies the arrangement of ZnPc molecules into crystalline islands.

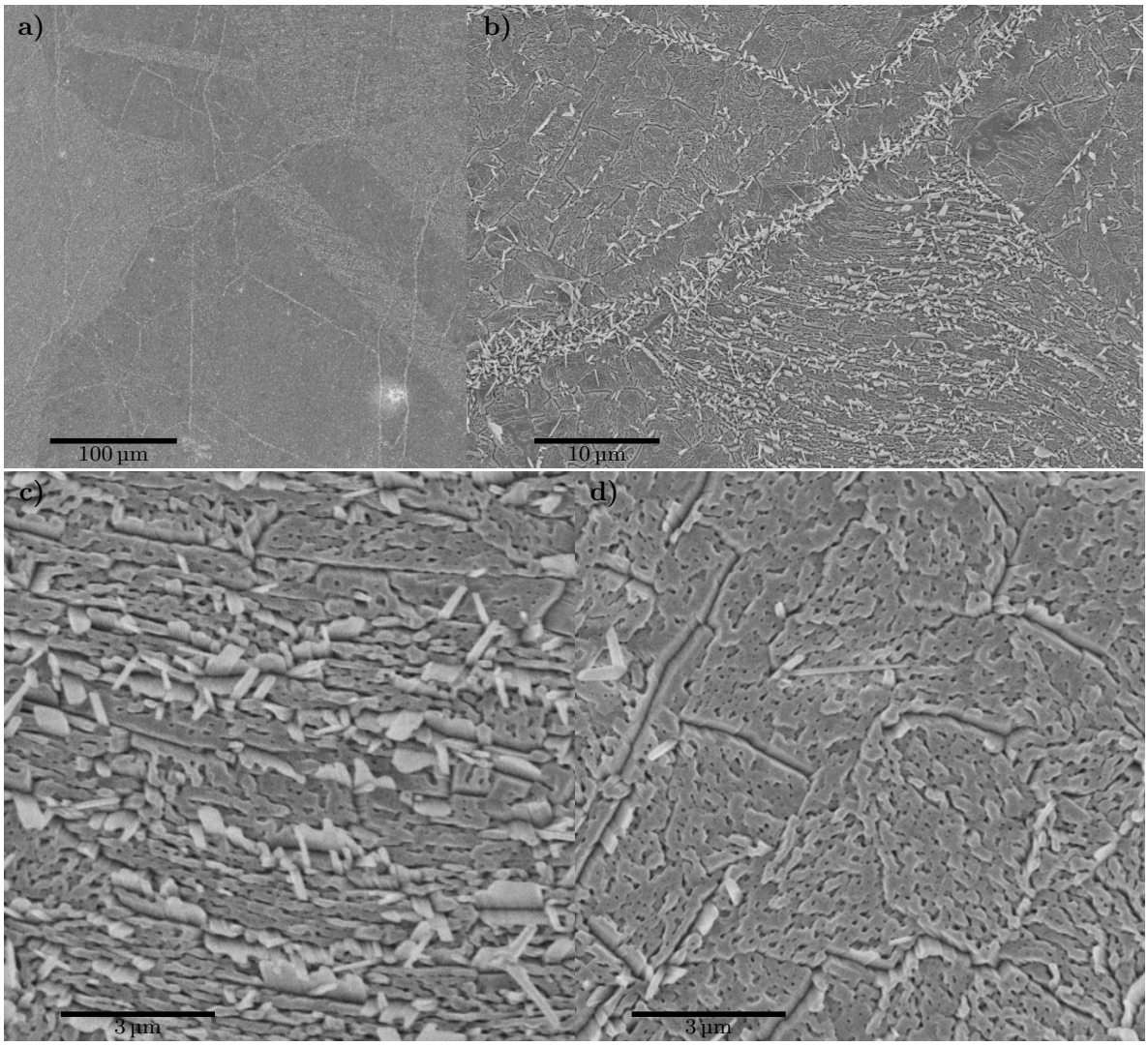

Figure S4: **a)** Large area SEM images showing ZnPc deposited on single-layer graphene transferred onto sapphire after the deposition of ZnPc using a source temperature of 450°C, a substrate temperature of 250 °C and a deposition duration of 30s. **b-d)** Higher magnification SEM images of (a).