

## Supplementary information

### Discovering atomistic pathways for supply of metal atoms to graphene surface from methyl-based precursors

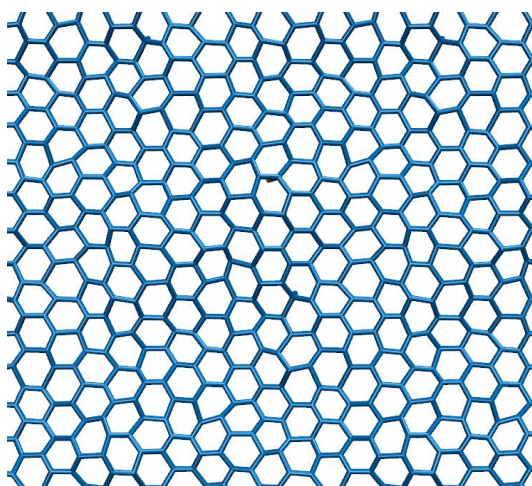
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**Figure S1.** Plan view of zero-layer graphene on SiC (0001) after 10 ps exposure to a temperature of 3500 K in an atmosphere of TMI<sub>n</sub> and H<sub>2</sub>. The dynamic bonds have maximum length of 1.9 Å.



#### Results of AIMD simulations of TMI<sub>n</sub> on defect-free self-standing graphene

To complement the results presented in the main text, we carry out additional AIMD simulations to probe the reactivity of TMI<sub>n</sub> precursors (in absence of H<sub>2</sub> gas) on self-standing defect-free graphene. The results provide an understanding of TMI<sub>n</sub> reactions on top-layer graphene which, due to weak interactions with the underlying zero-layer graphene, can be described as self-standing carbon monolayer. These simulations follow the procedure detailed in our previous AIMD study, which was dedicated to TMAI-precursor reactions with self-standing graphene [Ref. R1] and hence offer a qualitative comparison between the reactivity of TMI<sub>n</sub> and TMAI. Note that, at variance with simulations of TMI<sub>n</sub> on graphene/SiC, reactions of TMI<sub>n</sub> with self-standing defect-free graphene are modelled at a temperature of 4300 K. A higher temperature is motivated by the lower reactivity of defect-free graphene in comparison to graphene on SiC (part of zero-layer graphene C atoms form bonds with underlying Si atoms). As explained in our previous work [Ref. R1], stability of the graphene sheet at such high temperature – which is however lower than the melting point predicted for graphene (4500 K [Ref. R2]) – is ensured by (i) imposing structural parameters which correspond to an equilibrium interatomic spacing at temperatures lower than graphene's melting point and (ii) preventing occurrence of long-wavelength vibrations – that destabilize graphene at temperatures > 3500 K [Ref. R3] – via use of relatively small supercells (6 × 6 graphene unit cells = 72 carbon atoms).

We carried out three independent simulations (named as **Simulation#S1**, **#S2**, **#S3**), for a total simulated time of ≈90 ps that corresponds to 900 thousand AIMD ionic steps (the timestep is 0.1 fs). All three simulations ultimately lead to production of atomic Indium adsorbed on defect-free graphene. Our observations are described below.

**Simulation#S1.** A neutral In adatom forms on graphene after three consecutive methyl-group eliminations from the TMI<sub>n</sub> precursor. The first methyl elimination occurs at a simulation time ( $t_{\text{sim}}$ ) of ≈18 ps, directly after the sixth collision of TMI<sub>n</sub> with the graphene layer. The two subsequent methyl-elimination events require significantly shorter times, as they take place at  $t_{\text{sim}}$ =19.2 and 20.4 ps.

Accordingly, four additional TMIn/graphene collisions activate the dimethyl-indium  $\rightarrow$  methyl-indium + methyl reaction, while just one extra collision is sufficient to trigger dissociation of methyl-indium in a  $\dot{\text{C}}\text{H}_3$  radical gas molecule and an isolated electrically neutral indium adatom on graphene. Hence, AIMD results indicate that the activation energy required for removal of methyl groups decreases with decreasing coordination of the central In atom.

It is important to note that, despite an elevated temperature of 4300 K, the In monomer does not desorb, but resides and diffuses on the graphene surface for the remaining simulation time (additional 16 ps). During this timeframe, the In monomer bonds with a H adatom (which, in turn, had detached from a methyl molecule, see description below) to form an indium-hydride ad molecule. This ad molecule re-dissociates into In and H adspecies after  $\approx 1$  ps.

Other relevant reactions revealed by **Simulation#S1** are summarized as follows. The 1<sup>st</sup>-eliminated methyl group adsorbs on graphene. However, during collision with the surface, the ad molecule loses a H atom, thus leaving a  $\dot{\text{C}}\text{H}_2$  double radical group on graphene. The H atom flies away from the surface and attaches with the 2<sup>nd</sup>-eliminated  $\dot{\text{C}}\text{H}_3$  radical, thus forming a methane molecule. Subsequently, the 3<sup>rd</sup>-eliminated methyl group bonds with the  $\dot{\text{C}}\text{H}_2$  ad molecule to form an ethene ( $\text{H}_2\text{C}=\text{CH}_2$ ) gas molecule and a hydrogen adatom, which temporarily bonds with the In monomer (see previous paragraph). Then, the ethene molecule flies proximate to the H adatom: the  $\text{H}_2\text{C}=\text{CH}_2$  / H interaction induces temporary formation of a highly-reactive  $\text{H}_3\text{C}\dot{\text{C}}\text{H}_2$  radical molecule. Indeed, the  $\text{H}_3\text{C}\dot{\text{C}}\text{H}_2$  transition-state quickly evolves into  $\text{H}_2$  and  $\text{H}\dot{\text{C}}=\text{CH}_2$  radical gas molecules.

To summarize, relevant products of **Simulation#S1** are an electrically neutral In adatom, as well as  $\text{CH}_4$ ,  $\text{H}_2\text{C}=\text{CH}_2$ , and  $\text{H}_2$  gas molecules.

**Simulation#S2.** The first methyl elimination event occurs at the third collision of TMIn with graphene, at  $t_{\text{sim}}=9.0$  ps. While the  $\dot{\text{C}}\text{H}_3$  radical flies away from the surface, dimethyl-indium remains adsorbed on graphene for  $\approx 5$  ps. Then, the  $(\text{CH}_3)_2\text{In}$  molecule desorbs from the surface and reacts with the  $\dot{\text{C}}\text{H}_3$  radical in the gas phase. The reaction produces ethane ( $\text{C}_2\text{H}_6$ ) and methyl-indium gas molecules. During an accidental re-approachment of ethane and methyl-indium (both still in the gas phase), the In atom of  $\text{CH}_3\text{In}$  “steals” a hydrogen atom from the ethane molecule. The reaction produces  $\text{HInCH}_3$  and a  $\text{H}_2\dot{\text{C}}\text{CH}_3$  radical. After  $\approx 1$  ps, an intramolecular proton-transfer reaction drives  $\text{HInCH}_3$  dissociation into atomic In and  $\text{CH}_4$  gas. However, the indium atom rapidly attaches to the (still vicinal)  $\text{H}_2\dot{\text{C}}\text{CH}_3$  radical to form a  $\text{InCH}_2\text{CH}_3$  gas molecule which remains stable for  $\approx 1$  ps. Excitation of a bending vibrational mode brings the In atom and  $\text{CH}_3$  group of the  $\text{InCH}_2\text{CH}_3$  molecule close to each other. This induces proton transfer from  $\text{CH}_3$  to In, ultimately leading to formation of ethene and indium-hydride gas molecules. Finally, indium-hydride lands on graphene, where it quickly dissociates into In and H monomers. The In adspecies remains on graphene for the remaining simulation time ( $\approx 1$  ps).

To summarize, relevant products of **Simulation#S2** are In and H monomers, as well as methane, ethane, and ethene gas molecules.

**Simulation#S3:** In this case, the second collision between TMIn and graphene induces concerted detachment (and desorption) of all methyl groups ( $t_{\text{sim}}=2$  ps). Conversely, indium remains on the surface as adatom. Furthermore, we observe methyl/methyl association in the gas phase, with consequent formation of ethane ( $\text{C}_2\text{H}_6$ ). However, due to bending of the C–C bond, the ethane molecule spontaneously evolves into  $\text{H}_2\text{C}=\text{CH}_2 + \text{H}_2$  gases. A stochastic collision between ethene and the 3<sup>rd</sup>-eliminated  $\dot{\text{C}}\text{H}_3$  radical in the gas phase liberates a H atom and produces a  $\text{CH}_3\dot{\text{C}}\text{H}\dot{\text{C}}\text{H}_2$  double radical. A collision between the H atom and the In monomer causes desorption of an indium-hydride molecule. However, this species re-adsorbs on graphene and splits into H and In monomers. We note that In resides as adatom on graphene during major part of the entire simulation (24 ps). Eventually, the H atom reacts with the  $\text{CH}_3\dot{\text{C}}\text{H}\dot{\text{C}}\text{H}_2$  radical which, after several intramolecular reactions, produces a  $\text{C}_2$  addimer and a H adatom on graphene as well as one methane and two  $\text{H}_2$  gas molecules.

### Comparison of TMIn vs TMAI reactivities

To conclude the supplemental information section, it is worth underlining qualitative differences in the reactivity of TMIn with that of TMAI on defect-free graphene. The results for TMAI (obtained in the same conditions of temperature and gas pressures) are described in our previous study [Ref. R1]. **Simulations #S1, #S2, and #S3** of this work provide estimate for the average number of collisions required for TMIn to undergo the first transformation due to interaction with defect-free graphene at 4300 K. AIMD results show that total of 11 collisions (sum of number of collisions with the graphene surface prior to TMIn dissociation) activates the three first reactions of TMIn. This corresponds to an average number of collisions of 3.7 to trigger the initial transformation of TMIn. At parity of gas pressures (same volume of the vacuum region in TMAI and TMIn simulations), 13 collisions with graphene are necessary to initiate the two initial TMAI transformations. This provides an average of 6.5 collisions required to activate the first TMAI transformation.

The average number of collisions translates into an effective reaction rate at the corresponding gas pressure and temperature, and thus suggests higher reactivity of TMIn vs TMAI. However, even assuming that our estimates of average number of collisions are

accurate for a temperature of 4300 K, it cannot be ruled out that the relative reactivity (rate for the 1<sup>st</sup> transformation of the precursor) of TMI<sub>n</sub> vs TMAI changes for temperatures decreasing to actual experimental conditions.

#### References

- (R1) D. G. Sangiovanni, G. K. Gueorguiev, and A. Kakanakova-Georgieva, Ab initio molecular dynamics of atomic-scale surface reactions: insights into metal organic chemical vapor deposition of AlN on graphene, *Phys. Chem. Chem. Phys.*, 2018, **20**, 17751.
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- (R3) A. Fasolino, J. H. Los, M. I. Katsnelson, Intrinsic ripples in graphene, *Nature Materials*, 2007, **6**, 858.