

## CH<sub>2</sub> group migration between the H-terminated 2×1 reconstructed {100} and {111} surfaces of diamond

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### ABSTRACT

Various possible routes for the migration of a CH<sub>2</sub> group between the H-terminated 2×1 reconstructed {100} surface and the H-terminated {111} surface of diamond have been explored using a hybrid quantum mechanical/molecular mechanical method. The calculated energies suggest that movement of such surface bound species across step edges should be a facile process under typical diamond growth conditions, and that such migrations are significant contributors to the observed morphologies of diamond grown by chemical vapor deposition methods.

### INTRODUCTION

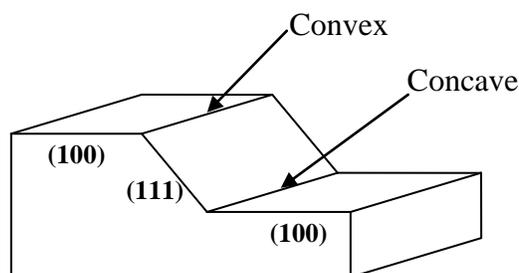
Chemical vapor deposition (CVD) techniques for growing diamond films from an activated hydrocarbon/hydrogen gas mixture are now well established [1,2]. Activation of the gas mixture – with, for example, a hot filament, or in a microwave plasma – results in H<sub>2</sub> dissociation and production of H atoms. These H atoms react with the hydrocarbon source gas via a series of addition and/or abstraction reactions, creating a wide variety of carbon containing species – both radicals and stable molecules. Gas phase H atoms can also abstract surface terminating H atoms (*i.e.* from surface C–H bonds), thereby creating temporary radical sites on the growing diamond surface. The most probable fate of these radical sites will be re-termination by another gas phase H atom, but occasionally they will bond with an incident carbon-containing radical (*e.g.* a CH<sub>3</sub> radical). Subsequent H atom abstraction (creating a pendant CH<sub>2</sub> group), surface rearrangement and addition steps result in eventual incorporation of the incident carbon atom into the diamond lattice.

Migration of surface bound carbon radical species on the 2×1 {100} surface [3-7] and on the {111} surface [8] have both been studied previously. In both instances, migration requires that the pendant CH<sub>2</sub> group reacts with an adjacent surface radical site, forming a (strained) ring; subsequent re-opening of this ring results in, either, reversion to the starting configuration, or movement of the CH<sub>2</sub> group along the diamond surface by one carbon atom. Such migrations have been advanced as making an important contribution to the smooth surface morphology that is often observed in diamond samples grown by CVD [5]. Migration from one diamond surface to another (*i.e.* across a step edge) has received less attention, but may also be important in determining the morphology of as-grown CVD diamond. The aim of the present study is to investigate the energetics of migration between the H-terminated 2×1 reconstructed {100} and the {111} surfaces of diamond.

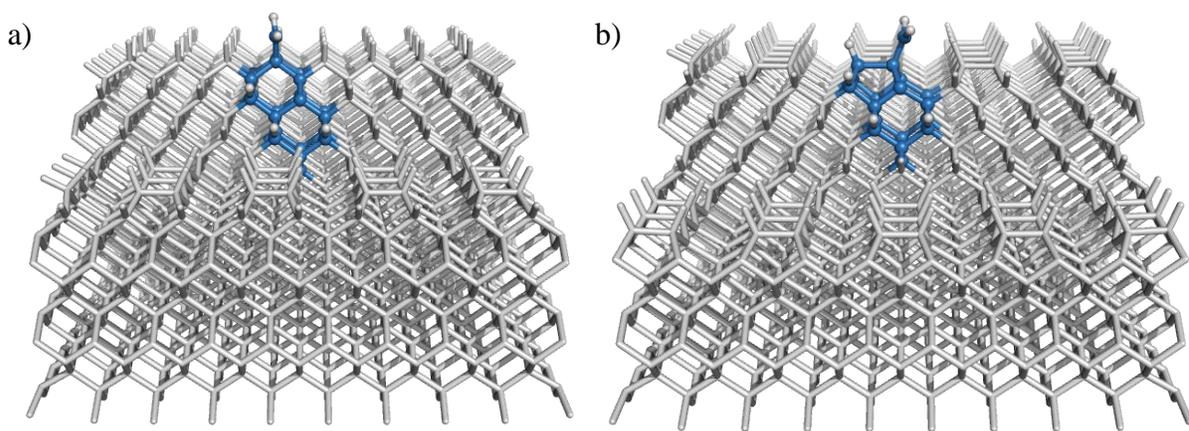
## THEORY

The present calculations employ hybrid quantum mechanical/molecular mechanical (QM/MM) methods. The calculations were performed using the QoMMMa program [9,10]; calculations for the QM region were performed using Jaguar 5 [11], while the MM region was modeled using TINKER [12]. The geometry of the QM region was optimized using the B3LYP density functional with the 6-31G(d) basis set. The MM region was described using the MM2 protocol. As in the previous studies [7], the starting species for migration involve a pendant  $-\text{CH}_2$  group, and a neighboring radical site, and hence have two unpaired electrons. The final species also have two unpaired electrons, whereas the intermediate strained-ring systems have closed-shell electronic structures. All reported energies are provided relative to the triplet electronic state of the starting species, described using an unrestricted DFT ansatz. The corresponding open-shell singlet, again modeled with an unrestricted ansatz, lies within  $\sim 10 \text{ kJ mol}^{-1}$  in energy of the triplet. The transition states for ring-opening and closing were studied using unrestricted DFT, with the ring-closed species described using restricted closed-shell DFT.

Two principal types of step edge can be formed by juxtaposing a  $\{111\}$  surface between two  $2 \times 1 \{100\}$  surfaces. These are henceforth termed convex and concave, as illustrated in fig. 1.



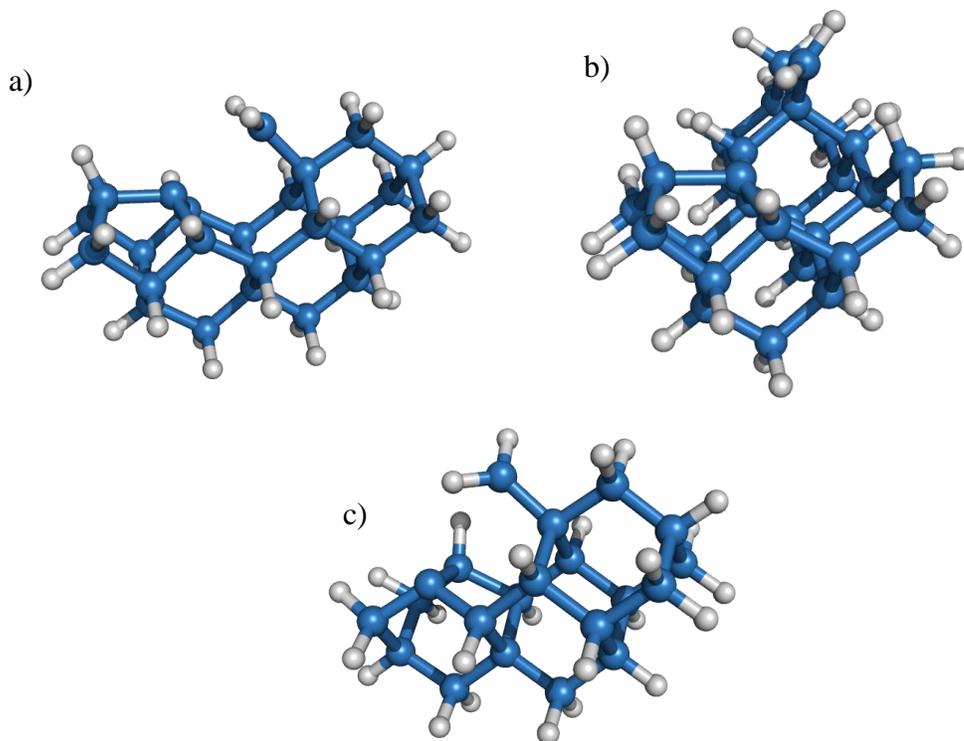
**Figure 1.** Illustration of the two step edges created between the  $\{100\}$  and  $\{111\}$  surfaces.



**Figure 2.** Models used to simulate the convex step edge between the  $2 \times 1 \{100\}$  and  $\{111\}$  diamond surface: a) dimer rows perpendicular b) dimer rows parallel to the step edge. The region treated with MM methods is shown in grey, while the blue region in this illustration is treated using QM.

Two models have been used to describe the convex step edge between the  $2\times 1$  H-terminated  $\{100\}$  and the H-terminated  $\{111\}$  surfaces. Both are based on suitably modified versions of the  $5\times 9\times 4$  slab (defined in terms of the numbers of C–C dimer bonds) used in our earlier studies of  $\text{CH}_3$  addition to the  $2\times 1$   $\{100\}$  diamond surface [7]. These differ in the relative orientations of the dimer rows on the upper  $2\times 1$   $\{100\}$  surface, which can be either parallel or perpendicular to the step edge as shown in fig. 2.

There are two possible types of intersection between the  $\{111\}$  and  $\{100\}$  surfaces at the concave step-edge. Given that for one of these topologies, there are two distinct routes from the  $\{111\}$  surface leading down to the  $\{100\}$  surface, we needed to consider three possible pathways for migration across the concave step-edge. The corresponding QM regions are shown in fig. 3.



**Figure 3.** QM regions used in QM/MM studies of three different pathways by which a  $\text{CH}_2$  group might migrate from a  $\{111\}$  face to a  $2\times 1$   $\{100\}$  terrace at a concave step-edge.

Note that these QM regions are considerably larger than most considered in our earlier migration study [7] and, at this stage, we have only determined approximate transition states for the various  $\text{CH}_2$  migration processes by calculating the energy of the system along a specified reaction coordinate. The system is held close to the desired value of this reaction coordinate using a harmonic constraint. QM and MM energies calculated for each value of the reaction coordinate are combined and the transition state identified as the maximum energy along this curve. All QM/MM energies reported are in  $\text{kJ mol}^{-1}$  relative to the triplet diradical starting species.

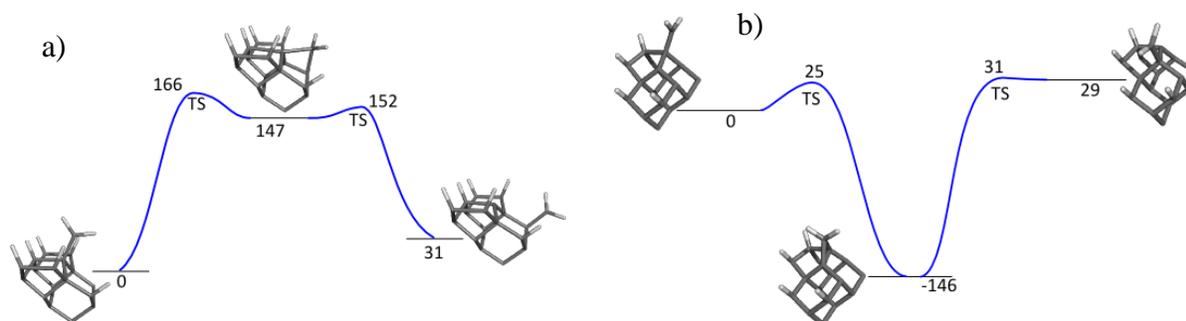
## RESULTS AND DISCUSSION

Migration of a CH<sub>2</sub> group on the diamond surface starts with the abstraction of a surface hydrogen species from a carbon atom adjacent to the radical group of interest. The CH<sub>2</sub> group can then move between the radical sites via a ring closing and subsequent ring opening mechanism. The present calculations start with a pendant CH<sub>2</sub> group adjacent to a surface radical site (*i.e.* the earlier H abstraction steps have been skipped) and attention is focused on the ring closing / ring opening sequence that enables migration of the CH<sub>2</sub> group.

### Convex step edge

As fig. 2 showed, two different scenarios for CH<sub>2</sub> migration between the upper 2×1 {100} surface and the {111} surface can be envisaged, wherein the dimer rows are respectively perpendicular (fig. 2(a)) or parallel (fig. 2(b)) to the step edge. The minimum energy pathway for the former scenario is found to proceed via a 4-member ring intermediate, lying 140 kJ mol<sup>-1</sup> higher in energy than the starting configuration (*i.e.* with the CH<sub>2</sub> group at the edge of the 2×1 {100} surface) and 109 kJ mol<sup>-1</sup> higher than that of the structure that results after the CH<sub>2</sub> group has successfully migrated to the {111} surface. Transition states were located for the movement from the 2×1 {100} surface to the 4-member ring, and from the {111} surface to the 4-member ring. These were found to lie at 166 kJ mol<sup>-1</sup> and 121 kJ mol<sup>-1</sup>, respectively, indicating that formation of this 4-member ring intermediate is likely to be the rate limiting step for these migrations. The starting, intermediate and final structures are depicted along with the relevant energy profile for migration in fig. 4(a).

QM/MM calculations for migration of a pendant CH<sub>2</sub> group from a 2×1 {100} surface with the dimer rows aligned parallel to a convex step edge identify a 3-member ring intermediate that lies lower in energy than either the initial 2×1 {100} or the fully migrated {111} structures – by, respectively, 146 kJ mol<sup>-1</sup> and 175 kJ mol<sup>-1</sup>. Low energy transition states have been located for the movement of the CH<sub>2</sub> between the 3-member ring structure and either the {100} or {111} surface.



**Figure 4.** Energy profiles for the migration of a CH<sub>2</sub> group from the 2×1 {100} surface to the {111} surface. a) dimer rows perpendicular to the step edge b) dimer rows parallel to the step edge. Energies shown are in kJ mol<sup>-1</sup> and are defined relative to the initial structure with the migrating CH<sub>2</sub> group located on the 2×1 {100} surface.

## Concave step edge

Migration of a CH<sub>2</sub> group from the {111} surface to the 2×1 {100} surface via a concave step edge can proceed via three different routes, as implied by the different QM regions displayed in fig. 3. The dimer rows on the receiving 2×1 {100} surface may be either perpendicular (fig. 3(a)) or parallel to the step edge. The latter case allows further variety, since the migrating CH<sub>2</sub> group can approach from either between the dimer chains (fig. 3(b)) or from the middle of a dimer (fig. 3(c)). These different pathways are henceforth referred to as P1, P2 and P3, respectively. Optimized geometries and energies for the CH<sub>2</sub> group located on the {111} surface, on the 2×1 {100} surface and in a bridging ring geometry have been calculated for each of the three pathways. The calculated energy differences, defined relative to the initial structure with the pendant CH<sub>2</sub> group located on the {111} surface, are shown in Table 1.

**Table 1.** Relative energies of the fully migrated structure with the CH<sub>2</sub> group on the 2×1 {100} surface ( $\Delta E_{\{100\}}$ ), and of the 3-member bridging ring intermediate ( $\Delta E_{\text{ring}}$ ), respectively, defined with respect to the initial structure with the pendant CH<sub>2</sub> group located on the {111} surface. The calculations are at the B3LYP/6-31G(d):MM2 level of theory, and the quoted energies are in kJ mol<sup>-1</sup>.

Pathway	$\Delta E_{\{100\}}$	$\Delta E_{\text{ring}}$
<b>P1</b>	-99	-363
<b>P2</b>	-33	-119
<b>P3</b>	-60	-171

Pathways P2 and P3 proceed via similar energy intermediate 5-member ring structures, which enable facile transfer of the CH<sub>2</sub> group from the {111} surface to the 2×1 {100} surface, and vice versa. The energy minimum associated with the 6-member ring bridging structure in pathway P1 is much deeper, however, suggesting that once a migrating CH<sub>2</sub> group reaches this bridging position between the 2×1 {100} and {111} surfaces it is very likely to remain fixed at this location – *i.e.* to incorporate into the diamond lattice at the step edge, in accord with the earlier conclusions from Frenklach *et al* [6].

## CONCLUSIONS

QM/MM computational methods have been used to explore the migration of a surface bound CH<sub>2</sub> species between the 2×1 {100} and {111} surfaces of diamond at two different step edges. The resultant energies suggest that migration of a CH<sub>2</sub> group between these surfaces will be a reasonably facile process at typical substrate temperatures ( $T_{\text{sub}} \sim 1000\text{-}1400$  K), and that such migrations are thus likely to be a significant factor in determining the observed morphologies of as-grown CVD diamond.

## ACKNOWLEDGMENTS

We are grateful to EPSRC, for the reward of a research grant and studentship, and to Element Six Ltd. for financial support.

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