

DFT+VTST investigations of (100)–(2×1):H diamond surfaces by means of first-principle calculations

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Radical attack and recombination are thought to play an important role in the atomic-scale mechanisms driving the growth of diamond. Unfortunately, accurate *ab-initio* calculations of the growth mechanisms are scarce^{1,2}. This work presents an analysis of the reactions involving hydrogen and methyl radicals on a (100) H-passivated diamond surface.

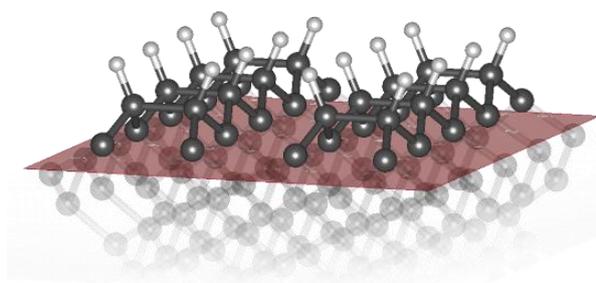


Figure 1 – *Ab-initio* calculations are performed on slab containing more than 200 atoms.

The reactions we investigate include migration of a lone hydrogen on a non-passivated surface³ and of single and double vacancies on a H-passivated surface³, along with the study of the growth steps that create a nucleation seed on the surface⁴. Calculations are carried out considering a diamond surface modelled by means of a thick slab (11 layers containing each 16 atoms, Fig. 1).

To provide an even bigger picture of the growth, we identified an ensemble of reactions that can etch the said seed (Fig 2).

One of the main features of a chemical reaction is its energy profile along the minimum energy pathway. It reveals either a tight or a loose transition state (TS), *i.e.*, the presence or absence of an energy barrier. To identify the minimum energy path (MEP) we use the nudged elastic band method for barrierless reaction (Fig 4), and the climbing nudged elastic band method otherwise (Fig 4). These methods rely on a set of intermediate configurations, also known as images, between reactants and products. Each image is assumed to be connected with the two closest ones via fictitious springs. Then a subtle combination of the forces exerted by the fictitious springs and the potential energy surface (PES) ensures that the ensemble of images converges towards the MEP.

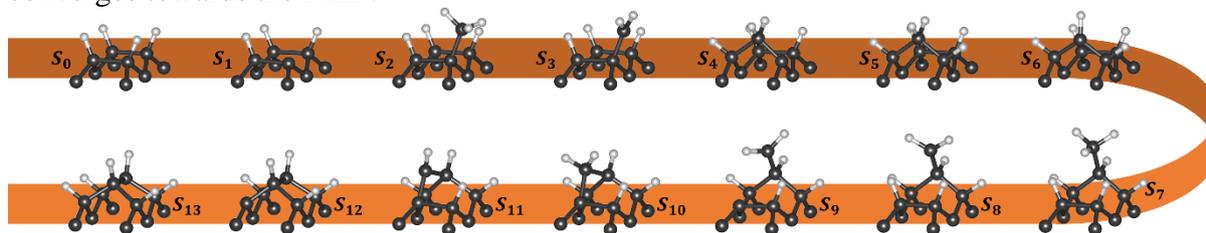


Figure 2 – Sequence of stable intermediate steps⁴ between a flat surface (S_0) to a nucleation seed (S_{13}).

Calculations of the energies and forces were carried out using the VASP implementation of the density functional theory. According to the transition state theory (TST), if the energy profile reveals an energy barrier, the calculation of the reaction rate is unambiguous as it only requires

the vibrational spectra of the reactants, products, and of the maximum energy image along the MEP.

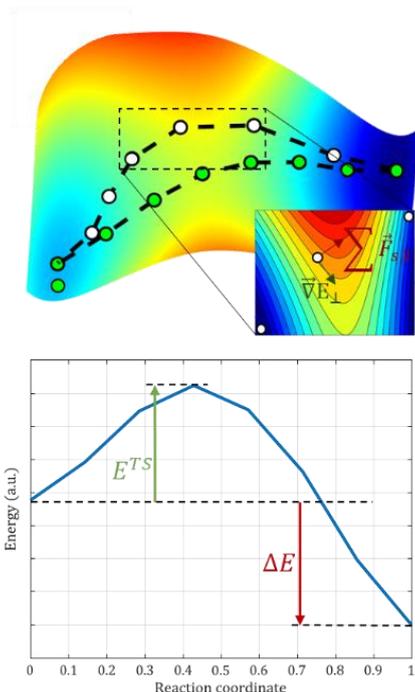


Figure 3 – Example of a tight TS on top of the MEP, whose position is only determined by the PES.

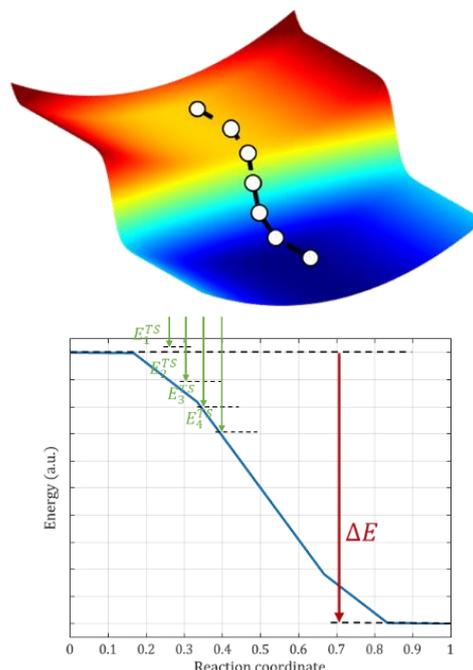


Figure 4 – Barrierless reaction containing a loose TS whose position is moving with temperature.

Then, one can compute the partition functions, zero-point energies and tunnelling coefficient to determine the exponential pre-factor for any given temperature:

$$k(T) = \kappa(v^{TS}, E^{TS}) \left(\frac{k_B T}{\hbar} \right) \frac{Q^{*TS}(T)}{Q^I(T)} \exp \left(- \frac{[E^{TS} - E^I]}{k_B T} \right)$$

For barrierless reactions, the approach slightly differs. We also use TST, but in its variational form. Briefly, all images along the MEP are possible transition states (TS). As such, we perform the TST calculation assuming each point to be the TS. For a specific temperature, variational TST states that the TS is the one that minimises the reaction rate:

$$k(T) = \min_{\bar{r} \in \text{MEP}} \left\{ \left(\frac{k_B T}{\hbar} \right) \frac{Q^{*TS}(T)}{Q^I(T)} \exp \left(- \frac{[E^{TS} - E^I]}{k_B T} \right) \right\}$$

Using multi-scale methods (*e.g.*, kinetic Monte-Carlo), these reaction rates have great potential to provide insights into the best conditions to grow single crystal diamond: temperature, pressure, and radical densities in the reactor influence both the rate and quality of the growth. The approach used in this work can be generalised to other crystallographic orientations of diamond and even to other semi-conductor surfaces.

References

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