

Carbon Dimer Deposition on Diamond (111) Surfaces From Molecular Dynamics Simulations

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Introduction

Spectroscopic investigations of various atmospheres appearing in diamond film synthesis suggest evidence for carbon atoms, dimers or trimers. The monatomic and triatomic species are mostly associated with flames and arc jets (1-3), whereas dimers are thought to be prevalent in the microwave decomposition of buckminsterfullerenes (4). For the purposes of diamond deposition process development, it would be helpful for understanding the contributions of the different species to the growth process. The ultimate goal for these investigations would be improved processes and improved process models where large-length or long-time scale phenomena are based on small-length or short-time scale submodels.

In the near-term, the types of insights gained are: (1) Suggestions for new reaction mechanisms, (2) Focus for more complex investigations and (3) Estimates of elementary reaction rates when no others are available. One source for gaining these insights derives from estimating the probabilities of various events through molecular dynamics (MD) simulations with a Brenner potential (5) on cells with periodic boundary conditions. As reported previously (6), at 1200 K atomic carbon will not add to a pristine diamond (111) surface. However, it will add to radical sites with a 15 % probability.

Results

Here we focus only on carbon dimers. Preliminary investigations, both experimental and numerical, indicate that carbon dimers react vigorously with diamond surfaces even when radical sites are not present on the surface. The present investigation provides evidence that among the most prevalent events on a pristine, hydrogen-terminated diamond (111) surface at 1200 K include insertion of a dimer between a surface carbon atom and a surface hydrogen atom, abstraction of a surface hydrogen atom to form an acetylenic radical and substitutions or displacement of a surface hydrogen atom by the dimer. The reactive probability for carbon dimers on this surface at 1200 K is approximately 80 %. The individual categories of events occur with roughly equal probability.

Note that other events may be possible, but for two reasons they are not observed: (1) They are much less probable and therefore difficult to observe with MD simulations or (2) The Brenner potential does not properly describe some reaction paths. At this time it is impossible to discern if either case occurs.

In addition we can estimate the reaction barrier height from the trajectories. We do this by periodically recording the potential energy of the system. The barrier appears as a hump in the plot of potential energy versus time. From these plots we estimate that the reaction barriers are: (1) 0-0.2 eV for insertion; (2) 0.2-0.5 eV for abstraction; and (3) 0-0.2 eV for substitutions. Unfortunately with this method, it is not possible to identify clearly the transition state configuration. Other techniques are

required, perhaps in conjunction with using cluster models.

Conclusions

The present simulations support the experimental assertion that carbon dimers react easily with diamond surfaces. We find at least two reaction channels, insertion and substitution, whereby dimers add to the surface with low (~0.2 eV) barriers. The third reactive channel abstracts hydrogen atoms from the diamond surface which creates radical sites that other species might react with.

It is very tempting to wonder if, even in small amounts, carbon dimers are having a large influence on diamond growth. One can equally imagine controlling nucleation density by controlling the near-surface concentration of carbon dimers during the synthesis.

Perhaps the most important aspect of this work is that, with some of the key reaction channels identified by MD simulations, it may be possible to apply more quantitative methods, such as high-level configuration interaction calculations or the most sophisticated density functional calculations, for evaluating the kinetics of these and related systems. The type of model that one would want to use for this purpose is probably a transition state theory approach.

References

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