

# Adsorption and Thermal Evolution of Nitrogen Species on Diamond Surfaces

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Layer-by-layer construction of diamond devices for spin-sensing calls for atomistic understanding of the nitrogen species on diamond surfaces.[1] As motivated by recent spectroscopic measurements (e.g., X-ray photoelectron spectroscopy, high-resolution electron energy loss spectroscopy and temperature-programmed desorption) on diamond surfaces impacted by N<sub>2</sub> plasma,[2] we conducted density functional theory simulations to gain atomistic details into the adsorption and thermal evolution of the resulted nitrogen species, as below.

1. **Diamond(001)**. We find that nitrogen plasma attacks the C=C dimers on the pristine diamond(001), forming nitrogen-dimers in a horizontal configuration, h-N<sub>2</sub>(ad).[3] The formation of h-N<sub>2</sub>(ad) is capable of resolving some discrepancy in the literature. the desorption of N<sub>2</sub>(ad) on pristine diamond(001) follows a concerted process with a barrier of 0.91 eV. By contrast, there emerges a new state of nitrogen-dimers in a vertical configuration, v-N<sub>2</sub>(ad), in addition to h-N<sub>2</sub>(ad). [4] Consequently, the desorption of N<sub>2</sub>(ad) is altered into a stepwise fashion, giving an overall barrier of 2.36 eV.
2. **Diamond(111)**. On bare domains of diamond, as represented by the models of C(111)-2x1 and graphite-like C(111), N<sub>2</sub>(ad) is identified as major surface species; the desorption of N<sub>2</sub>(ad) proceeds on both models via a concerted process of breaking two C-N bonds.[5] By contrast, there is evidence of formation of (NH)<sub>2</sub>(ad) via the insertion reaction of N<sub>2</sub> plasma on hydrogenated domains of diamond, as represented by the models of C(111)-2x1-H and C(111)-1x1-H. Interestingly, contrasting dynamics of desorption of (NH)<sub>2</sub>(ad) are presented on these two models; that is, via sequential breaking of two C-N bonds on C(111)-2x1-H, and via concerted breaking of both C-N bonds on C(111)-1x1-H.[6]

## References

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## Supplementary Pages (Optional)

Dear PCSI Organizer,

As an assistant professor of chemistry at Guangdong Technion-Israel Institute since 2018, I look forward to opportunities to be exposed to the wide community of surface science. Your favorable consideration of this abstract (particularly into **updated talks**) will be greatly appreciated.

In what follows, I further elaborate on our work on surface engineering of diamond.

Kai Huang

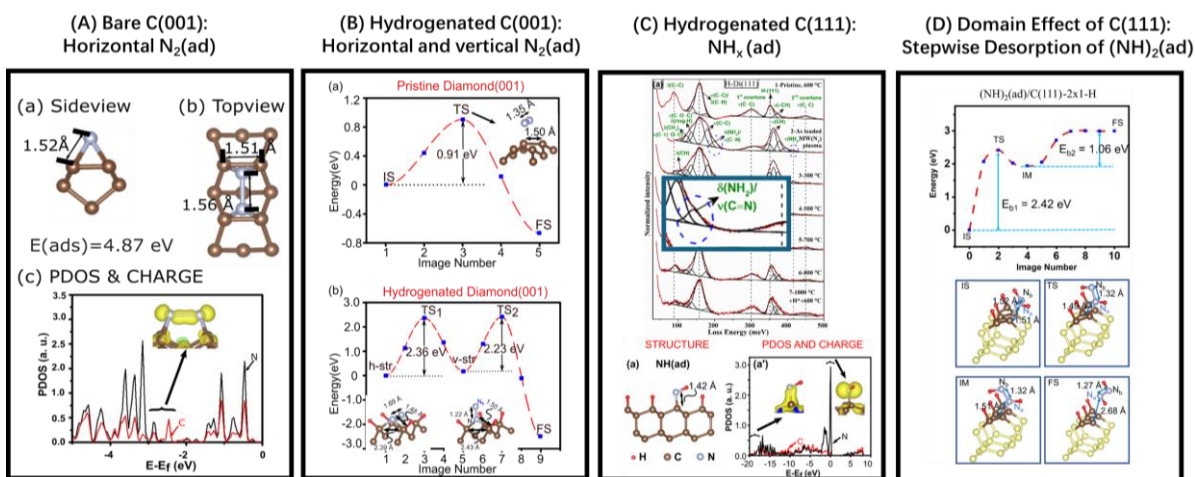
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### Surface Engineering of Diamond

Diamond is a wide bandgap semiconductor material of excellent physical and chemical properties. Engineering of diamond surfaces by chemical termination is an effective way to broaden its functionality. Due to its high stability, the termination of diamond surfaces often requires harsh treatments. For example, controlled termination of diamond surface by nitrogen has been demonstrated by recent work from the Hoffman group (collaborator) using  $N_2$  plasma and  $N_2^+$  ions; the involved microscopic mechanism on diamond surfaces is not yet clear.



**Figure 1** Atomistic mechanism into surface engineering of diamond by nitridation. (A) Horizontal nitrogen dimers,  $h-N_2(ad)$ , are formed on the bare diamond(001). (B) On the hydrogenated diamond(001), both horizontal and vertical nitrogen dimers,  $h-$  and  $v-N_2(ad)$ , are formed. (C) By contrast, there is evidence of formation of nitrogen-hydrogen species,  $NH_x(ad)$ , on hydrogenated diamond(111). (D) On diamond(111), nitrogen species exhibit diversity in surface behaviors, arising from the co-existence of domains of differing termination and reconstruction, e.g., the stepwise desorption of  $(NH)_2(ad)$  from C(111)-2x1-H.

As sketched in Figure 1, we conducted atomistic simulations by DFT to study the nitridation of diamond surfaces of a variety of facets, terminations and reconstructions. *Our work is unique in modeling the impact of the activated nitrogen source (e.g. N<sub>2</sub> plasma) as the chemisorption of a gaseous N<sub>2</sub> that has overcome the barrier when approaching the diamond substrate.* The resulting adsorbed nitrogen species are further evaluated in both static (e.g., composition and bonding) and dynamical (e.g., pathway of desorption, barrier height) aspects. This is in contrast to the conventional notion that nitrogen is introduced into the *bulk lattice* of diamond by an activated nitrogen source. Research highlights are given below.

- (a) In Figure 1A, we show the formation of a horizontal nitrogen dimer, *h*-N<sub>2</sub>(ad) on *bare* diamond(001), forming a termination layer of nitrogen of half monolayer in either p(2x2) or c(4x2) superstructures. The facile interchange of these two superstructures reconciled the controversy of the reported p(2x1) pattern by low energy electron diffraction in the literature. (*Langmuir* **2021**, 37, 6248)
- (b) On the *hydrogenated* diamond(001), by contrast, we show the formation of both horizontal and vertical nitrogen dimers, *h-* and *v*-N<sub>2</sub>(ad). As in Figure 1B, the thermal stability of nitrogen dimers on *hydrogenated* diamond(001) is enhanced compared to that on *bare* diamond(001), due to the conversion of *h-* to *v*-N<sub>2</sub>(ad). (*J. Phys. Chem. C* **2021**, 125, 28157)
- (c) On *hydrogenated* diamond(111), we show the formation of *nitrogen-hydrogen species* (shown in Figure 1C), in contrast to our findings of *nitrogen dimers* on *bare/hydrogenated* diamond(001). (*Appl. Surf. Sci.* **2022**, 600, 154085)
- (d) We show that the observed diversity of surface nitrogen species on diamond(111) originates from domains of a variety of surface terminations and reconstructions, as represented by N<sub>2</sub>(ad) on the *bare* (2x1) and graphite-like surfaces, and N<sub>2</sub>H<sub>2</sub>(ad) on the hydrogenated (2x1) and (1x1) surfaces. (showcased in Figure 1D, *J. Chem. Phys.* **2024**, 160, 214713)

Our on-going work is shifted to the nitrogen species in the subsurface region of diamond, as suggested by our collaborator's recent experiment using surface bombardment by low energy N<sub>2</sub><sup>+</sup> ions. For the representative N<sub>1</sub> interstitials of a variety of configurations, we find that the relative stability at the subsurface of hydrogenated diamond(001) is altered significantly from the bulk. We will elucidate the underlying mechanism using an analysis based on the density-of-states and local/partial charge.