Quantum Simulations on Dynamical Heterogeneous Catalysts

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In 2020-2021, we carried out theoretical investigation of chemical processes at surfaces and interfaces, oxidative etching process of diamond [1], multi-scale simulation of Cu adatom diffusion on Cu surfaces [2], formic acid adsorption in polymeric form and decomposition on Cu(111) [3], oxygen vacancy induced metal-insulator transition of $LaNiO_3$ thin film over SrTiO3 [4].

In this report, we report the oxidative etching process of the diamond (100) surface [1]. Diamond possesses a unique combination of superlative properties that makes it an attractive material for several novel applications. Of all semiconductors, diamond has the highest dielectric breakdown field, saturated electron drift velocity, and thermal conductivity which make it an ideal material for next-generation electronics that will outperform current systems in terms of operating frequency and power handling capacity. In addition, diamond's wide band gap, optical transparency, chemical inertness, hardness, and low thermal expansion have led to a number of specialized photonics applications including spacecraft window, optoelectronic microlens, photodetector, high energy particle detector, UV and infrared LED, and Raman laser. Diamond has color centers that functions as bright single photon source (SPS) at room temperatures and can be potentially implemented in quantum metrology and quantum information science.

At present, a theoretical study that investigates the entire oxidation process, starting from the adsorption of gas phase O_2 up to the desorption of CO and etching of the surface, has never been done. This kind of study is necessary to develop a comprehensive knowledge of diamond oxidation mechanism. For this reason, van der Waals-corrected density functional theory simulations of the oxidation of the C(100) surface have been performed.

Density functional theory (DFT) calculations have been performed using STATE code package (Simulation Tool for Atom TEchnology) with generalized gradient exchange-correlation functional (GGA) based on the work of Perdew, Burke and Ernzerhof (PBE). Semi-empirical van der Waals correction was implemented. Core electrons were treated using ultra-soft pseudopotentials. Wave functions were expanded using plane-wave basis with wave function and augmentation charges cutoff of 36 Ry and 400 Ry, respectively.

We simulated the succeeding desorption of CO up to the complete etching of the top C layer. The reaction paths and optimized structures are shown in Fig. 1. Following the desorption of the first CO, there are two possible locations where the second CO could desorb, the adjacent CO_{bridge} towards the $[01\bar{1}]$ direction where O is on top site and the CO from the adjacent ether group towards the [011] direction. The former and the latter have $E_{barrier}$ of 4.53 eV and 3.62 eV, respectively. Succeed-

ing CO desorptions along [011] (Fig. 1 B-E) all have lower E_{barrier} compared to [01$\bar{1}$], suggesting a preferred etching direction. The calculated desorption activation energies vary between 1.01 - 4.68 eV. Initial desorption of CO along a given row in [011] direction has the highest desorption activation energy (reaction A$\to$ B and E $\to$ F), while succeeding energy barriers are lower (Fig. 1 A-E, E-I). Analysis of the reaction path geometries shows that for these two reactions, the initial CO desorption proceeds by the near-simultaneous breaking of two CO_{bridge}-C bond. The point defect left by the initial desorption allows the next CO_{bridge} to break one bond with second layer C and form CO on top (CO_{top}) structure. The non-simultaneous bond breaking reduces the heat released by the reaction and the desorption activation barrier. This suggests that the point defect functions as nucleation point for CO desorption along [011] direction. This nucleation function was first proposed by John et al. based on their observation that the surface roughness of diamond (100) did not increase even after removal of over 5300 atomic layers, suggesting that the removal rate of rows of atoms is more rapid than the removal rate of layers. Our work is the first theoretical study to support their prediction.

In summary, we performed density functional theory calculations with van der Waals corrections to elucidate diamond oxidation mechanism on the atomic-level which could lead to insights that will advance the improvement of nascent nanofabrication technologies. We developed a comprehensive theory of oxidative etching of the diamond (100) surface, from the adsorption of gas phase O_2, including details of metastable adsorption states, intersystem crossing, and induced surface dereconstruction, to the desorption of CO and CO_2, complete etching of the top surface layer and its subsequent stabilization.
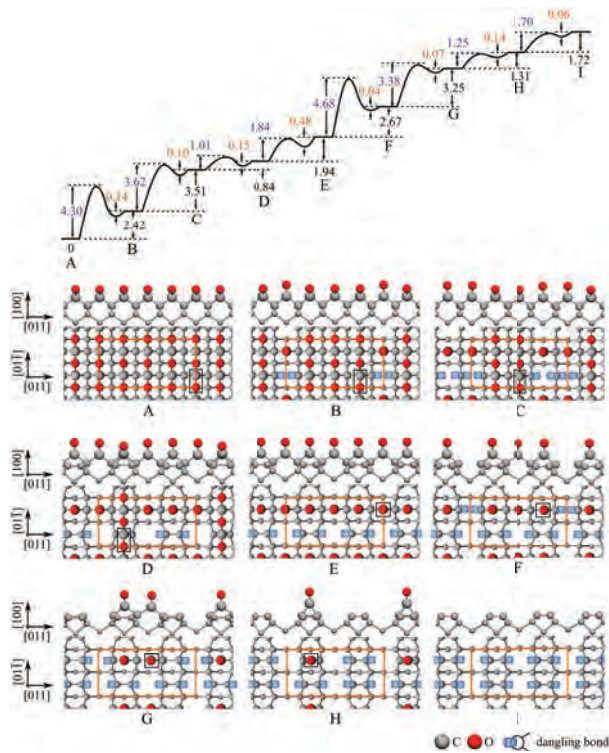

Figure 1: Etching of the top-layer atoms of C(100)-(1 $\times$ 1): O_{bridge} surface through successive CO desorption. The heat of reactions and activation energies in electron-volts are shown in black and blue texts, respectively. Physisorption energies of CO are shown in orange text. Grey and red spheres correspond to carbon and oxygen atoms, respectively, while the dangling bonds are represented by blue cylinder.

References

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