

Photoelectron emission from B-doped diamond (111) into water vs. vacuum: the role of surface states

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While photoelectron emission from diamond into vacuum has been widely studied, electron emission into water and other non-vacuum environments is much less well understood, particularly when using sub-bandgap excitation sources. The emission of electrons in aqueous environments is of great interest the field of chemistry because electrons in water are potent reducing agents, able to facilitate extraordinarily difficult reactions such as the reduction of CO₂ and the formation of NH₃ from N₂. Here, we report investigations of electron emission from H-terminated and O-terminated single-crystal B-doped diamond (111) surfaces into vacuum and into water using above-bandgap and below-bandgap excitation sources. In these studies, we use multiple excitation sources including convention He(I) resonance lamps (21.2 eV photon energy), diode laser as discrete near-UV wavelengths, and a laser-driven Xe-arc lamp coupled to a high-throughput UV monochromator, providing continuous tunability of the incident photon energy.

When using typical UV excitation sources such as He(I) resonance lamps (21.2 eV energy), the energy distribution of emitted electrons shows two clear peaks. One peak is attributed to direct emission from electrons in the conduction band, while a second peak at lower kinetic energy, arises from electrons that pass into a surface state associated with the H-termination of the diamonds surface. This C-H midgap state is important as it provides a way to emit electrons from diamond using sub-bandgap photons. Using discrete diode laser sources, sub-bandgap excitation show primarily one peak arising from the direct excitation from bulk states into the C-H antibonding surface state. H-terminated diamond(111) surfaces that were exposed to ozone for durations of 1 second to 21 minutes show continuously varying amounts of oxidation. In vacuum, even partial oxidation of the surface leads to a dramatic decrease in the electron emission yield.

We also performed corresponding studies of H-terminated B-doped diamond(111) in water. In this case, the energy distribution of emitted electrons cannot be measured, but the total photocurrent can be used as a proxy. Somewhat surprisingly, oxidation of the surface does not shut off electron photocurrent in water, even for sub-bandgap excitation. We interpret this as a reflection of the fact that oxidation leads to C=O surface states that lie in the bandgap at energies below the vacuum level.

In this talk we will discuss experiments aimed at a fundamental mechanistic study of electron emission and the role of surface states in facilitating electron emission using sub-bandgap excitation.