Photocatalytic reduction of nitrogen to ammonia on diamond thin films grown on metallic substrates

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Abstract

Recent studies have demonstrated that boron-doped diamond can act as a solid-state source of electrons in water when illuminated with above-bandgap light. Excitation of electrons to diamond's conduction band leads to facile emission of electrons into water; the resulting solvated electrons are potent reducing agents able to initiate many chemical reactions such as the reduction of N_2 to NH_3 and the reduction of CO_2 to CO. Here, we report investigations of the photocatalytic activity of diamond thin films grown on Mo, Ni, and Ti substrates. Our results show that in each case, there is a maximum in the photocatalytic activity that occurs just when the diamond coalesces into a contiguous film, then decreasing as the film becomes thicker. These results suggest that electron emission arises in part from excitation of electrons in the metal substrate, followed by injection into the conduction band of the diamond film. More detailed studies on films grown on niobium show that at the open-circuit potential the films have a downward band-bending of ~ 0.3 V, which is favorable for barrier-free electron emission. Our result suggests that metal-diamond heterostructures may provide a scalable approach to achieving difficult photocatalytic reactions.

1. Introduction

It has long been known that the H-terminated surface of diamond has negative electron affinity [1]. One consequence of NEA is that when diamond is illuminated with ultraviolet light at wavelengths shorter than ~ 225 nm (corresponding to diamond's bandgap of 5.5 eV), it becomes a facile emitter of electrons [1-6]. We recently showed that boron-doped diamond can act as a solid-state source of solvated electrons in water when illuminated with ultraviolet light, and that the resulting solvated electrons can initiate novel energy-intensive reactions such as the reduction of nitrogen (N_2) to ammonia [7] and the selective reduction of CO_2 to CO [8]. The ability to perform these and other electrochemical reduction reactions in aqueous media presents an opportunity to initiate new types of chemistry in more energy-efficient manner. For example, the critical step in the synthesis of NH_3 from N_2 is the formation of the N_2H , which requires more than 3 eV of energy [9]. Solvated electrons have sufficient energy to initiate these and other high-energy species.

While the use of diamond as a solid-state emitter is promising, the efficiency is low because diamond has a large, indirect bandgap, leading to relatively weak optical absorbance even for photons with energies above the 5.5 eV bandgap. In typical materials, photoemission is a strongly surface-localized process as illustrated in Fig. 1a. In this case, illumination with ultraviolet light promotes electrons to excited electronic states, from which they are then directly emitted. In materials with NEA, a second process becomes possible in which light is absorbed in the *bulk* of the material to create electrons in the conduction band; these electrons can relax to the conduction band edge, diffuse to the surface and be emitted into a very intense, narrow distribution of electrons readily detected in photoemission measurements as an "NEA peak". Yet, for photons in the energy range of 5.5 - 6.5 eV (where water remains transparent), diamond's absorption remains weak, limiting its efficiency.

In principle a third process is feasible, using diamond films grown on a metallic substrate [10, 11]. In

Fig. 1. Schematic illustration of photoemission processes. a) conventional surface photoemission, b) bulk photoemission from NEA materials, and c) metal-assisted NEA photoemission, in which a metal substrate is excited and injects electrons into the diamond film. In each case electrons can be emitted into vacuum or into aqueous media.

this case, light impinging on the sample excites the metal, which then injects electrons into the diamond conduction band. Following diffusive transport through the film, electron emission should occur. This “metal-assisted NEA photoemission” has several attractive aspects. For example, if electron emission can be initiated from the underlying substrate, then the diamond film does not need to be optically thick and just needs to serve as a chemically resistant coating. Furthermore, diamond thin film growth can be achieved in a more scalable manner compared with bulk diamonds. The present work demonstrates that diamond thin films grown on several different metallic substrates have the ability to reduce nitrogen to ammonia, although only niobium provides high stability under the harsh experimental conditions involved. From electrochemical measurements

we establish the band alignments in water, revealing downward band-bending under open-circuit conditions. These studies provide new insights into the energetics and practical application of diamond thin films as photocatalysts.

2. Experimental Details

We investigated diamond thin films grown on three different metals: niobium (Nb), molybdenum (Mo), and titanium (Ti). These metals were chosen because Nb and Ti are used extensively as diamond substrates in water purification via electrochemical oxidation of water [12, 13], while Mo has also been used as a diamond substrate for thermionic emission [10, 11]. The three metal substrates here all have similar work functions of 4.1 eV for Ti [14], 4.2 eV for Mo [14], and 4.3 eV for Nb [15]). Consequently, we anticipate the photon energies of > 5.3 eV ($\lambda < 234$ nm) should be capable of injecting electrons into diamond's conduction band. Through our own experimentation, we found Nb was the only substrate out of the three that could withstand all experimental conditions of extensive exposure to intense ultraviolet light and water without excessive oxidation through pinholes. Therefore, in later sections of the paper dealing with the effect of surface termination, we concentrate on diamond films grown on Nb. The substrates were seeded by polishing with 0-2 μm and then 0-0.1 μm diamond particles. The diamond thin films were grown using microwave plasma enhanced chemical vapor deposition in a modified AsTex system. Films were nucleated for 10 minutes using 200 standard cubic centimeters per minute (sccm) H_2 and 2 sccm CH_4 at a power of 1000 W. For diamond growth, the power was reduced to 800 W and the CH_4 flow rate was decreased to 1 sccm. Growth times used vary from 10 minutes to 10 hours. After growth, a 10 minute etching phase was done with hydrogen alone before ramping the power down. A pressure of 48 torr was used in all phases. Hydrogen termination was also carried out in the same chamber at 600 W in a hydrogen atmosphere with pressure set to 48 torr for 1 hour to ensure the diamond had NEA.

SEM: Scanning electron microscopy (SEM) was carried out using a Leo Gemini Supra 55 VP with an acceleration voltage of 5 kV. To best capture film morphology, an SE2 detector was used for imaging. Each sample was characterized at different magnifications for every substrate and growth time used. SEM was also used to characterize the film thicknesses by using cross-sections of the diamond films at an angle of 15° .

Photoelectron spectroscopy: To measure the NEA on the diamond as well as the position of the valence band, we used ultraviolet photoemission spectroscopy (UPS) to characterize the energy distribution of electrons emitted when the sample was illuminated with light (21.2 eV photon energy) from He(I) resonance lamp (Vacuum Generators, Inc.). A DC power source was used to create the He plasma with a current of 40 mA at an internal lamp pressure of 120 torr. While under irradiation, a -10 V bias was applied to the diamond films. The electrons emitted perpendicular to the surface plane were detected by directing them into a hemispherical energy analyzer (Phi) with a microchannel plate array and 16-channel detector. Using the same detection system, X-ray photoemission spectroscopy (XPS) was also performed using a monochromatized Al K_{α} electron source (1486.9 eV) at a take-off angle of 45° from the surface normal. Analysis of the oxygen coverage used the equation $n = \frac{I_O}{I_C} \frac{S_C}{S_O} \rho_C \lambda \cos(\theta)$ where n is the number of O atoms per unit area of the surface, I_O and I_C are the XPS peak areas of O and C, respectively; S_C and S_O are the atomic sensitivity factors for C and O, ρ_C is the density of carbon atoms in bulk diamond, λ is the inelastic mean free path of the emitted C(1s) electrons in diamond, and θ is the angle of collection with respect to the surface normal. We used an inelastic mean free path of 1.8 nm based on experimental measurements in nanocrystalline diamond [16].

Flat-band potential measurements: Electronic properties of the sub-surface band-bending region were characterized using Mott-Schottky analysis. The interfacial impedance was characterized as a function of electrochemical potential using a Solartron 1287 potentiostat with a 1260 Gain-phase analyzer. The cell consisted of a 1 M KCl electrolyte, a Ag/AgCl reference electrode, and a Pt counter-electrode. Complete plots of complex impedance vs. frequency were measured at various potentials. An example Bode plot is shown in the Supplementary Information. These measurements showed that at frequencies near 1 kHz the total impedance at all potentials was dominated by the interfacial capacitance. This frequency is commonly used for the characterization of diamond surfaces in aqueous solutions [17]. This complex impedance was then measured at 1 kHz while scanning the potential at a scan rate of 10 mV/s. The complex impedances were analyzed using an equivalent circuit consisting of a depletion layer

capacitance in parallel with a charge transfer resistance, and with this combination in series with the solution resistance. This simple model is often referred to as a simplified Randles model [18]. Mott-Schottky data are presented in the conventional form as plots of $1/C^2$ vs. potential based on the Mott-Schottky Equation: $\frac{1}{C_{SC}^2} = \frac{2}{N_A e \epsilon_0 \epsilon_S} \left[E - E_{FB} - \frac{kT}{e} \right]$ where E is the applied potential, E_{FB} is the flat-band potential, C_{SC} is the capacitance of the semiconductor space-charge region, e is the electron charge, ϵ is the dielectric constant of the diamond, ϵ_s is the permittivity of free space, k is Boltzmann's Constant, and T is the absolute temperature.

Ammonia Yield: Ammonia yield experiments were carried out using a 450 W high-pressure Hg/Xe lamp (Osram, model 6278) mounted in an Oriel lamp housing located 10 inches from the samples was used as the source of light. A water absorptive filter was used to eliminate infrared radiation. Pure N_2 (Airgas research grade, 99.9997% minimum purity) gas was passed through a Johnson Matthey IG-70XL PureGuard catalytic purifier and slowly bubbled for 1 hour through the reaction vessel, which contained 18.0 MΩ water (Barnsted NanoPure) with 0.01M of high-purity (Alfa Puratronic, 99.9955%) Na_2SO_4 . After saturation of the reaction vessel with N_2 , the cell was sealed and exposed to the light for 4 hours. The reaction vessel has an H-cell configuration with the diamond electrode contained in one compartment and a second compartment containing a platinum electrode immersed in a 0.03M solution of 250:1 KI/KI₃ in water. The solutions in the two compartments are connected through a glass frit that provides electrical contact between the solutions but prevents mixing, and an external wire connects the diamond and Pt electrodes. A bias of -0.3 V vs. the open circuit potential was applied to help encourage oxidation reactions on the Pt counter-electrode and help eliminate the possibility of corrosion of the diamond electrode by reaction of the valence band holes with water. For oxygen termination of the diamond films, the diamond samples were exposed to these same conditions for 16 hours instead of 4 hours.

The production of ammonia was measured using the indophenol blue method [19]. Reagents were purchased from Sigma-Aldrich in the highest available purity. A 2 ml aliquot of solution was removed

from the reaction vessel. To this solution was added 0.100 ml of a 1M NaOH solution containing 5% salicylic acid and 5% sodium citrate (by weight), followed by addition of 20 μ l of 0.05M NaClO and 20 μ l of an aqueous solution of 1% (by weight) Na [Fe(NO)(CN)₅] (sodium nitroferricyanide). After 1 h, the absorption spectrum was measured using a Shimadzu 2401PC ultraviolet-visible spectrophotometer. The formation of indophenol blue was determined using the absorbance at a wavelength of 700 nm. Absolute calibration of the method was achieved using ammonium chloride solutions of known concentration as standards.

3. Results

3.1. Ultraviolet photoemission spectroscopy

We used ultraviolet photoemission spectroscopy (UPS) to demonstrate our H-terminated diamond thin films have negative electron affinity [1, 20]. Fig. 2 shows UPS spectra of a diamond thin film that was grown for 1 hour on a Nb substrate and was then hydrogen-terminated. An equivalent sample that was oxygen-terminated is also shown. These spectra were obtained using an identical alignment of the UPS system and calibrated such that 0 eV represents the Fermi Energy for both spectra. The H-terminated sample shows a very strong increase in emission at high binding energy with a width of ~ 1 eV, followed by a rapid plunge to zero. Such a large peak at high binding energy is characteristic of materials with negative electron affinity and arises from

Fig. 2. UPS spectra of diamond grown on niobium for 1 hour. 0 eV is the Fermi energy for each spectrum. The inset shows a 200X magnified view of the region near the Fermi energy, with extrapolated lines to define the valence-band edge.

electrons that are excited in the bulk, relax to the conduction band edge, and are then emitted into vacuum from the conduction band edge. In accordance with previous studies, we refer to this large peak as an “NEA peak” [1]. The full-width at half-maximum of ~ 1 eV is larger than the value of ~ 0.5 eV reported on single crystals [1], but is comparable to previous reports on polycrystalline diamond samples [21]. which have also shown that the shape and width of the NEA peak depend on the distribution of crystal faces present in the film and on the sample preparation [21].

After the diamond surface was terminated with oxygen; this sample shows comparable intensity at binding energies from 0 to 12 V, but lacks the intense emission of the H-terminated diamond film at larger binding energies near 16 eV. Closer examination of the region near the Fermi energy (Fig. 2, inset) shows that the H-terminated sample has a valence band edge at 0.85 V below E_F and the O-terminated sample is at 1.35 V below E_F . This dramatic reduction in total emission intensity upon oxidation further establishes that only the H-terminated sample exhibits NEA.

3.2: Photocatalytic measurements of Ammonia Yield

While the UPS experiments show that the diamond thin films are capable of emitting electrons into vacuum, direct measurement of electrons emitted into water is challenging. To characterize electron emission into water, we use the formation of NH_3 from N_2 as a proxy for direct detection of the electrons. Formation of

Fig. 3. a) Steps in forming NH_3 from N_2 . b) Ammonia yield produced during 4 hours of illumination from diamond samples grown for the indicated lengths of time on Mo, Ti, and Nb. c) Thickness of the diamond films grown on each substrate as measured by SEM cross-sectional images.

NH₃ from N₂ has an energy barrier of 3.1 eV due to the high energy of the N₂H intermediate [9, 22]. We showed previously [7] that under the conditions of these experiments, reduction of N₂ to NH₃ takes place via a pathway (see Fig. 3a) in which (1) electrons are excited to the diamond conduction band, (2) the conduction band electrons are emitted into water and surrounded by water molecules to form aqueous “solvated” electrons e⁻_(aq) [23], (3) the solvated electrons react with protons (H⁺) to form neutral hydrogen atoms H• and (4) these hydrogen atoms react with dissolved N₂ gas to form N₂H, the critical intermediate in NH₃ production. Once formed, N₂H will spontaneously continue adding protons until it forms NH₃. Solvated electrons play a key role in the third step (e⁻_(aq) + H⁺ → H•) and therefore the formation of NH₃ can be taken as a proxy for the formation of solvated electrons. In aqueous solution, H⁺ ions lost during this reaction will be immediately replenished by the spontaneous dissociation of water via H₂O → H⁺ + OH⁻; while some change in pH may occur, under the conditions of our experiments this effect is small. Furthermore, in previous work we investigated the pH dependence of this reaction and showed that NH₃ production is only modestly dependent on pH because the reaction to form NH₃ competes with the bimolecular reaction 2H⁺ + 2e⁻ → H₂ [7].

In order to test how the thickness of the diamond film influenced the electron emission, we investigated the ammonia yield from diamond films that were grown for different lengths of time on the Nb, Mo, and Ti substrates. In each case, after growth of diamond for the indicated length of time we removed the sample from the growth chamber, placed the sample in contact with N₂-saturated water, and illuminated with Hg/Xe lamp for 4 hours. After the 4 hr illumination time, we characterized the total yield of NH₃ produced, giving the results shown in Fig. 3b. For each metal, the ammonia yield shows a maximum for diamond films grown for a specific length of time, approximately 60 minutes on Nb and 30 minutes on Mo and Ti. In general, films on Nb shows slightly lower yields than those grown on Mo and Ti, but only the films grown on Nb were able to withstand the rigors of additional experiments described below.

3.3. Evolution of film structure with increasing growth time

To understand why the ammonia yield depends on diamond film thickness, we characterized the diamond films at different stages of growth via SEM. To measure the film thicknesses, we partially removed the diamond films from the growth substrates and measured the thickness using SEM. Attempts to determine film thickness via ellipsometry were not reproducible. Fig. 3c shows the thicknesses measured at different growth times, with the actual images shown in the Supplementary Information. Over the range of growth times investigated the films have thicknesses ranging from several hundred nanometers to 1 micron. Initially, diamond on Nb has a quicker growth rate than diamond growth on Mo or Ti, but after nucleation is complete, diamond growth rates equilibrate on all substrates since the thicknesses of samples become similar at higher growth times.

Fig. 4. SEM images of the diamond films grown on niobium for different lengths of time. a) 10 minutes; b) 30 minutes ; c) 1 hour.

Fig. 4 shows SEM images of diamond films grown on niobium for different lengths of time. These images, in conjunction with cross-sectional images (not shown) confirm columnar growth of microcrystalline diamond, in agreement with previous studies [24]. After 10 minutes of growth the surface is primarily still niobium; after 30 minutes diamond particles can be observed but they have not coalesced; after 60 minutes the particles have coalesced into a continuous film. Additional SEM images obtained on Mo and Ti are shown in Supplementary Information. For Mo and Ti, the nuclei appear to coalesce into a continuous film after ~30 minutes of growth. Differences in carbon diffusivity into the each of the metal substrates could be responsible for the changes in morphology evolution observed in the SEM images. Based on the thickness data in Fig. 3c, these growth times correspond to a diamond film thickness of about 160 nm for Mo, 210 nm for

Ti respectively, and 360 nm for Nb. Comparing the ammonia yield data (Fig. 3c) with the SEM images (Fig. 4 and Supplementary Information) indicates that for all three substrates, the maximum ammonia yield occurs when growth conditions yield the thinnest possible completely coalesced film.

3.4. The Effect of Oxygen Termination

A unique aspect of photocatalysis on diamond surfaces is the strong dependence of electron emission

Fig. 5. Comparison of H-terminated and O-terminated samples. a) C(1s) and O(1s) XPS spectra of diamond film grown on Nb for 1 hour; spectra are shown for “as-grown” sample (H-terminated) and after immersion in water with exposure to UV light for 16 hours (“O-terminated”); b) Ammonia yield of diamond grown on Nb for 1 hour after H-termination (red) and O-termination (blue).

on surface termination. Many previous reports have shown that H-terminated surfaces yield negative electron affinity with electron emission, while oxygen-terminated surfaces are poor emitters.[25] Indeed, our own experimental data in Fig. 2 show that oxidation dramatically reduces electron emission into vacuum. To establish whether this trend also holds for electron emission into water, we measured ammonia yields from diamond films exposed to various oxidizing treatments. We found that illuminating water-immersed diamond samples for long periods of time (typically 16 hours or more) led to significant surface oxidation. Fig. 5 shows C(1s) and O(1s) XPS data from a H-terminated diamond and from a sample that was oxidized by this process. In agreement with prior work by McFeely and co-workers, the symmetrical shape of the C(1s) peak reveals the presence of mostly diamond on the surface, as expected after the 10 minute etching phase we conducted after diamond growth [26]. For

bulk characterization of the diamond film, a typical Raman spectrum of our diamond thin films showing the presence of diamond, graphitic carbon, and disordered carbon is given in the Supplementary Information. XPS analysis of the O(1s) peaks yielded oxygen coverages of 0.7 ± 0.3 atoms/nm² on the H-terminated sample and 9.4 ± 1.0 atoms/nm on the O-terminated sample. Fig. 5b shows the ammonia yield from H-terminated and O-terminated samples. The ammonia yield data show very pronounced differences in ammonia yield, with the O-terminated sample yielding no detectable NH₃. These data show that there is a strong correlation between the presence of NEA in vacuum emission experiments and the ability to reduce N₂ to NH₃ when in contact with N₂-saturated water.

3.5. Band positions at the diamond-water interface

To establish the overall band alignments in the aqueous matrix, we used electrochemical measurements to determine the open-circuit potential (E_{OC}) and the flat-band potential (E_{FB}). For H-

Fig. 6. Mott-Schottky plots of the diamond surface after hydrogen termination (red) and after oxygen termination (blue) by exposure to UV light in water.

terminated diamond, we found the open-circuit potential to be 0.00 ± 0.02 V vs. Ag/AgCl. Figure 7 shows a Mott-Schottky plot of a H-terminated diamond film grown on Nb for 1 hour, and the same sample after oxygen-terminating the surface. The sigmoidal shape of the curve shows that both samples are p-type. The H-terminated sample has a flat-band potential of $+0.31$ V vs. Ag/AgCl; since the open-circuit potential was 0.00 V, this indicates that under open-circuit conditions the sample has a downward band-bending of 0.31 V. This downward bend bending is expected in

nominally undoped diamond films due to electron accepting defects in the diamond [27], and the equilibration of charge across the electrochemical interface with the Ag/AgCl reference electrode. Once

the surface is oxygen terminated, a similar open circuit potential of -0.02 V vs. Ag/AgCl is maintained, but the flat-band potential increases to +0.59 V vs. Ag/AgCl, indicating a downward band-bending of 0.57 V under open-circuit conditions.

4. Discussion

The above experiments reveal several important facts. First, the data in Fig. 3 shows that the ability of photoilluminated diamond to emit electrons and thereby initiate reduction of N_2 to NH_3 is maximized at a thickness of ~ 250 nm. The data in Fig. 3 and in Supplementary Information shows that as the films are grown, there is an evolution in the surface morphology from an incomplete diamond film to a complete faceted film with the coalescence of the film approximately coinciding with the maximum in electron emission yield. Finally, the electron emission is highly sensitive to the nature of the surface termination, illumination with UV light in water leads to gradual conversion of the H-terminated surface into an O-terminated surface that has positive electron affinity, greatly reduced electron emission in vacuum, and greatly reduced ability to initiate reduction of N_2 to NH_3 .

4.1 Absorption of light in diamond thin films grown on metallic substrates

The experiments reported here deal almost exclusively with illumination with a broadband UV source that includes light at wavelengths shorter than ~ 225 nm, corresponding to 5.5 eV. These photons have energies exceeding the bandgap of the substrate metals and the ability to excite electrons across the bandgap of diamond. At early stages of diamond film growth, electron emission can arise either directly from excitation of the substrate metals (e.g., excitation of electrons from states just below the Fermi energy to free-electron final states, as in classical photoemission) or by exciting electrons to diamond's conduction band. Previous studies of metals have provided evidence for electron emission from metals into water.[28-30] However, solvated electrons adjacent to metal surfaces are expected to have short lifetimes because the electrons in water are immediately adjacent to a continuum of empty states of the metal, leading to rapid recombination of the electron back into the metal. In contrast, once electrons are

emitted from diamond into water, the electrons in water have energies within the forbidden bandgap of diamond, so there are no degenerate states available for recombination.

4.2 Excitation of diamond vs. injection from metallic substrate

One question that arises is whether the UV excitation occurs within the diamond film, or whether it occurs by excitation of electrons in the metal film that are then injected into the diamond conduction band. Transport in diamond is complicated by the presence of strongly bound neutral excitons that can diffuse relatively long distances [4]. In single-crystal samples Cui and co-workers reported an upper limit of 5 μm for the exciton diffusion length, but reported much longer electron diffusion lengths of $L_e \sim 200 \mu\text{m}$ for free electrons in the conduction band [31]. In polycrystalline thin films, however, we anticipate much shorter carrier lifetimes and therefore much smaller electron diffusion lengths [32, 33]. For example, Yater and co-workers [34] observed that in CVD diamond thin films, strong reductions in electron mobility allowed conduction-band electrons to travel only much shorter distances, $<1.5 \mu\text{m}$. Based on this and other previous work [32, 33], we anticipate that electrons are likely to be able to traverse the distances of $\sim 250 \text{ nm}$ associated with the films investigated here. Since diamond's NEA places its conduction band 1 eV higher than the vacuum level, it should require photon energies of $E_{\text{photon}} = \phi_{\text{metal}} + 1.0 \text{ eV}$ to inject electrons from the metal substrate into diamond's conduction band. As noted above, all three metal substrates here all have similar work functions of 4.1 eV for Ti [14], 4.2 eV for Mo [14], and 4.3 eV for Nb [15]). Therefore, for photons with energy of $> 5.3 \text{ eV}$ ($\lambda < 234 \text{ nm}$) can inject electrons into the conduction band of the diamond from the metal substrate.

Since diamond is an indirect bandgap semiconductor, its optical absorption increases slowly as the photon energy increases above the 5.5 eV bandgap energy. Robins and co-workers determined the optical properties of diamond films grown by microwave chemical vapor deposition [35]. Under the conditions of our experiments (0.5% methane concentration), Robin's data yields an extinction coefficient $\alpha \sim 0.5 \times 10^4 \text{ cm}^{-1}$ at 213 nm. Combining this value with our typical film thicknesses of $t = 300 \text{ nm}$

(approximately 1 hour growth time) yields $\alpha t = 0.15$. Assuming that the transmitted light decays as $I = I_0 \exp^{-\alpha t}$ and neglecting reflection losses, these results indicate that 85% of the incident light at 213 nm penetrates through to the underlying substrate and only 15% is absorbed by the diamond film. Quantitative measurements of the quantum yield from niobium metal yielded values of 1×10^{-4} at 248 nm and 2.8×10^{-4} at 193 nm, with an applied field of 1 MV/cm [36]. In comparison, the absolute photoelectron yield from bulk diamond samples at 200 nm was reported to be 3×10^{-3} , rising steeply at shorter wavelengths [37]. Metallic substrates have lower photoemission quantum efficiency than bulk diamond. However, for diamond films that are optically thin (e.g., sufficiently thin that most of the incident light is transmitted rather than being absorbed), the number of electrons injected from the metal should be able to surpass the number of electrons created by absorption within the thin diamond film. In addition, metals may provide the opportunity to extend the wavelength range beyond the bandgap of diamond for suitable band alignment at the metal-diamond interface. While relatively little is known about the probability of exciting an electron from the metal substrates into the diamond film via an internal photoemission process, optical excitation of metallic substrates has been used as a way to enhance diamond emission into vacuum [38].

4.3 Band Alignments at the Diamond-aqueous Interface

To achieve facile electron emission, the C-H surface dipole of H-terminated diamond must be accompanied by a downward band-bending in the sub-surface space-charge region. From the information gained in the Mott-Schottky plots in Fig. 7, we develop an estimate of band alignments at the diamond-water interface. We measured an open-circuit potential of 0.00 ± 0.02 V vs. the Ag/AgCl reference electrode for H-terminated diamond, thereby establishing that the sample's Fermi energy is at 0.0 V vs. Ag/AgCl. Since $E_{\text{Ag/AgCl}} = 0.22$ V vs. E_{SHE} (the standard hydrogen electrode) and E_{SHE} lies at 4.44 ± 0.02 V below the vacuum level [39], this establishes that the Fermi level of our sample lies 4.66 eV below the vacuum level, while the Mott-Schottky measurements show that under open-circuit conditions the bands

are bent downward by 0.31 V at the surface compared with the bulk. These results are important because the downward band-bending establishes that under open-circuit conditions electron emission is favorable.[17] This result is similar to that reported by Bechter, et al. whose Mott-Schottky data yielded downward band-bending of 120 mV under open-circuit conditions.[17] While we do not know the exact position of the Fermi level with respect to the valence band edge, prior studies have shown that for nominally undoped diamond films like those investigated here, the valence band is typically 0.75-0.85 eV above the valence band due to defects in the bulk materials.[27, 40]. Taken together, these data are sufficient to draw an approximate energy level diagram as shown in Fig. 7. We note that these data suggest that the conduction band of diamond may be slightly lower than the vacuum level; however, even in this case electrons can be emitted in a barrier-free manner in water. Previous studies have shown that water can be treated like an amorphous semiconductor, with electrons injected into water going first in a continuum of states that comprise the conduction band of liquid water [41]. The conduction band edge of water edge lies ~ 1.1 eV below the vacuum level, as depicted in Fig. 7 [41]. Electrons in the water conduction band are similar to those in an amorphous semiconductor and are transiently in a delocalized state [41]; over times scales of ~ 1 ps the water molecules polarize around the electron to form the much

Fig. 7. Band alignment diagram of the diamond-water interface.

more localized solvated electron $e^-_{(aq)}$ which has lifetimes on the order of microseconds in the absence of other aqueous species such as H^+ or O_2 [42, 43].

Previous studies have reported that equilibration of diamond with air-

saturated electrolyte solutions results in upward band-bending under open-circuit conditions [44-47] and have attributed this in part to reversible equilibration between diamond and the O_2/OH^- redox couple of water [47]. However, our work involves two important differences. First, our samples are nominally undoped with the Fermi level position likely controlled by graphitic impurities, instead of being boron-doped. Secondly, while the previous studies were performed using water in equilibrium with air, our studies are all performed in electrolytes that were extensively purged with N_2 . Purging with N_2 to eliminate dissolved O_2 and other dissolved gases may change the electrostatic equilibration of the diamond surface with the adjacent water phase and is expected to enhance the ability of solvated electrons to reduce N_2 to NH_3 by eliminating the parasitic reaction of solvated electrons with O_2 to form the superoxide radical O_2^- [48].

While this work shows that the solvated electron emission may be enhanced by the absorption of light at the substrate, it opens up the possibility of using shorter wavelengths of light if the substrate is carefully chosen as has been reported by Koeck [11]. Our work also shows that a loss in H-termination during the course of the experiment has detrimental effects on its use as a photocatalysis, which caused a loss of positive charge near the diamond's surface. Therefore, the solvated electron emission can be further enhanced by the application of a proper bias to overcome changes in charge accumulation near the diamond's surface due to oxygen termination or to prevent oxygen termination of the surface from occurring. Research into diamond as a UV photodetector has led to the creation of device structures that can increase the amount of electrons emitted into vacuum if a significant bias is applied [49-51]. Use of a sacrificial oxidant may also be promising in prevention of the oxygen termination of the surface during its use as a photocatalyst [52].

5. Conclusion

Our results show that undoped diamond films as thin as 200 nm grown on metal supports can effectively catalyze the reduction of N_2 to NH_3 . Due to diamond's very weak optical absorbance in the 190-225 nm region, our data suggest that a significant part of the electron emission arises from electrons

excited in the underlying metals and then injected into the thin diamond film. Due to the relatively short lifetime and small diffusion coefficient for electrons in diamond, the optimal diamond thickness corresponds to the thinnest coating that can completely cover the underlying metal substrate. Future studies using different metals may provide a pathway for enhancing the yield and extending it to longer wavelengths. Our studies show that H-termination of the diamond surface is essential to achieve good electron emission and N_2 reduction, suggesting that the favorable surface dipole that results in good emission in vacuum is also important in achieving facile electron emission into water.

Prime Novelty Statement

In this manuscript we report on the factors that influence the use of diamond thin films on metallic supports (Niobium, molybdenum, and titanium) as photocatalysts for the reduction of N_2 (nitrogen) to NH_3 (ammonia). In recent work, we demonstrated a completely new approach to photocatalysis using diamond's unique electron emission capabilities to initiate extremely difficult reactions such as the reduction of N_2 and of CO_2 ; the work reported here provides additional insights into the mechanisms of electron emission and provides insights into possible ways to increase the efficiency of the process.

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Graphical abstract