Effects of Surface Treatments on Secondary Electron Emission from CVD Diamond Films

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Secondary electron emission (SEE) properties of polycrystalline diamond films grown by chemical vapor deposition (CVD) were measured. The total secondary yield ($\sigma$) from as-grown samples was observed to be as high as 20 at room temperature and 48 while heating at 700 K in vacuum. Electron-beam-activated, alkali-terminated diamond films have shown stable values of $\sigma$ as high as 60 when coated with CsI and similarly high values when coated with other alkali halides. Diamond coated with BaF$_2$ had a stable $\sigma$ of 6, but no enhancement of the SEE properties was observed with coatings of Ti or Au. Hydrogen was identified to give rise to this effect in as-grown films. However, electron beam exposure led to a reduction in $\sigma$ to values as low as 2. Exposure to a molecular hydrogen environment restored $\sigma$ to its original value after degradation, and enabled stable secondary emission during electron beam exposure. Atomic hydrogen and hydrogen plasma treatments were performed on diamond/Mo samples in an attempt to increase the near-surface hydrogen concentration which might lead to increased stability in the secondary emission. Raman scattering analysis, scanning electron microscopy, and Auger electron spectroscopy (AES) confirmed that hydrogen plasma and atomic hydrogen treatments improved the quality of the CVD diamond significantly. Elastic recoil detection (ERD) showed that heating as-grown diamond targets to 700 K, which was correlated with an increase in $\sigma$, removed contaminants from the surface but did not drive hydrogen from the diamond bulk. ERD showed that the hydrogen plasma treatment produced an increase in the hydrogen concentration in the near-surface region which did not decrease while heating in vacuum at 700 K, but no improvement in the SEE properties was observed.

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1. Introduction and Background

Interest in technological applications of diamond has shifted recently from wear-resistant coatings to electronics due to the negative electron affinity (NEA) of natural diamond, coupled with the relative ease of fabrication of conductive diamond films grown by chemical vapor deposition (CVD). It is also well established that the diamond surface is terminated with hydrogen, which may give rise to NEA in natural diamond and some well-oriented CVD diamond films. This present work is a continuation of measurements of the secondary electron emission (SEE) from diamond on Mo, Si, Ti, AlN, and Pd which began several years ago and indicates that diamond may be suitable in many secondary emitter applications due to its high total secondary yield ($\sigma$).

Devices which utilize secondary emitters include cross-field devices such as magnetrons, cross-field amplifiers (CFA), traveling-wave tubes (TWT), electron multipliers and photomultiplier tubes (PMT). Such devices are essential in radar, intelligence gathering, space communications, and night vision glasses. Materials used presently in secondary emitter applications may have values of $\sigma$ as high as 4, but generally fall between 2 and 3. Many devices which rely on SEE operate in an evacuated environment (10$^{-9}$ Torr), or often in the presence of a background with a partial pressure of 10$^{-6}$ Torr. In many instances the background is oxygen, but hydrogen would be desirable if it would enhance or not lead to degradation of the secondary electron emitting surfaces.

Hydrogen was identified to be responsible for the high values of $\sigma$ from as-grown CVD diamond films. Total secondary yields as high as 27 from diamond/Mo and as high as 48 from diamond/Pd were measured in vacuum during heating to 700 K. The total secondary yield was observed to degrade as a function of fluence under continuous exposure to an electron beam due to electron-induced desorption of hydrogen. Subsequent exposure to a molecular hydrogen partial pressure of 1.0 $\times$ 10$^{-6}$ Torr for approximately 20 min restored $\sigma$ to its original value. The total secondary yield from diamond/Mo was stable at 12 during continuous electron beam exposure, in the presence of a molecular hydrogen partial pressure of 1.0 $\times$ 10$^{-6}$ Torr. The total secondary yield from diamond/Pd was observed to be stable at 25 during exposure to a continuous beam of electrons at 1 keV while heating at 700 K which produced a hydrogen background pressure of 1.0 $\times$ 10$^{-6}$ Torr.

High stable secondary emission ($\sigma$ = 25–45 @ 1500 eV) in ultrahigh vacuum (UHV) was achievable by coating CVD diamond with an alkali-halide thin film and activating the surface by electron beam exposure. The activation produced a halogen-free surface (as observed with AES) which was terminated by ~1 monolayer of the alkali metal, and was reproducible using different alkali-halide overcoatings. These electron-beam-activated, alkali-terminated (EBAAT) diamond surfaces showed no degradation of $\sigma$ after long-term electron beam exposure when CsI was used as the overcoating, and promising results with little degradation when NaCl or KCl was used. The EBAAT surface was stable to temperatures exceeding 120°C and when exposed to air for several months.

Emission from EBAAT diamond films has been observed to decrease in the presence of Ar at pressures exceeding 1.0 $\times$ 10$^{-7}$ Torr when under exposure to a primary electron beam with current density less than 1 mA/cm$^2$. The decrease in $\sigma$ is not permanent, and is probably due to impurity atoms contaminating the EBAAT surface. The effect can be
reversed by either an increase in primary current density or a decrease in pressure. However, for this reason the EBAAT diamond is not necessarily as desirable as the hydrogen-terminated diamond for specific applications. Also, NEA observations from diamond coated with thin films (submonolayer and monolayer coverages) of Ti and Co suggest that these or other materials may produce high stable $\sigma$ and allow operation at higher temperatures. These considerations were the motivation for this work.

2. Experimental Procedure

SEE measurements were conducted in a UHV chamber with a base pressure of $1.0 \times 10^{-10}$ Torr. The experimental setup has been described previously. The samples tested were p-type diamond films on Mo and Si substrates, ranging from 1 $\mu$m to 20 $\mu$m in thickness, grown by hot filament (HF) and microwave plasma (MP) CVD. Total secondary yield vs. primary beam energy ($E_{\text{primary}}$) was measured for all samples, where $E_{\text{primary}}$ ranged from 100 eV to 3 keV in 50 eV increments. To investigate the effects of beam exposure on $\sigma$, each sample was exposed to the electron beam for up to 72 h at current densities ranging from 50 mA/cm$^2$ to 10.0 mA/cm$^2$. The beam diameter ranged from 0.12 to 0.25 mm. The current density was held constant during each experiment and the data were normalized by comparing the fluence dependence of each sample. In all cases the data were collected every 5 s while the primary beam energy was held constant in the range 1.0 to 1.5 keV.

Each as-deposited sample was tested prior to any hydrogen treatment, after which each sample was subjected to a molecular hydrogen treatment, an atomic hydrogen treatment, a hydrogen plasma treatment, or a combination of these. The SEE measurements were repeated on the treated samples.

Scanning electron microscopy (SEM), Raman scattering analysis, and Auger electron spectroscopy (AES) were used to determine the effects of the hydrogen treatments on the diamond samples. Rutherford backscattering spectroscopy (RBS) was used to investigate the purity of the diamond bulk, and elastic recoil detection (ERD) was used to characterize bulk and near-surface hydrogen concentrations in the diamond samples, as-grown and after hydrogen treatments. ERD was also used to detect changes in the hydrogen concentrations during heating at 700 K, which might be responsible for the increase in $\sigma$ observed previously. AES was used to investigate changes in the shape of the carbon peak from CVD diamond/Si due to ionic bombardment, indicating graphitization of the diamond surface.

BaF$_2$ coatings, 30 nm thick, were resistively evaporated onto diamond targets in a diffusion-pumped high-vacuum system with a base pressure of $2 \times 10^{-4}$ Torr. Thin coatings of Ti and Au, ranging from < 1 monolayer to 30 nm in thickness, were vacuum-deposited from a resistively heated source onto diamond targets in a turbopumped preparation chamber attached to the main UHV test chamber and separated with a gate valve. SEE properties of these samples were measured as described above. Thin CsI coatings were deposited onto representative diamond samples from the depositions used for Ti and Au coatings, and the targets were used as control samples to ensure that diamond films from different depositions had similar SEE properties.
3. Experimental Results

SEE measurements from as-grown samples have been discussed previously[^9] and some results will be included here for comparison. Figures 1 and 2 show σ vs. \( E_{\text{primary}} \), and σ vs. fluence data from representative CVD diamond targets, respectively. No differences in the SEE results have been observed to arise from the different deposition techniques (HFCVD and MPCVD). \( \sigma_{\text{MAX}} \) from as-grown samples nominally occurred between 1000 and 1500 eV, and ranged from 10 to 20 as seen in Fig. 1. As-grown CVD diamond/Pd had \( \sigma_{\text{MAX}} \) of ~20 at 1400 eV, and \( \sigma_{\text{MAX}} \) of 48 at 3 keV while being heated in vacuum at 700 K. \(^{10}\)

EBAAT diamond/Mo had \( \sigma_{\text{MAX}} \) of 50–60 at 3 keV at room temperature. \(^{13,18}\)

Figure 2 shows that σ decreased from untreated samples under electron beam exposure in vacuum, independent of the type of hydrogen surface treatment. Stable SEE (σ = 12) was observed from as-grown diamond/Mo in a hydrogen atmosphere of \( 1.0 \times 10^{-6} \) Torr while exposed to 1 keV electron beam (not shown). \(^{9b}\) It was noted that at the values of hydrogen partial pressure and current density necessary for stable σ, the hydrogen molecules impinged on the diamond surface at the same rate as energetic electrons. \(^{9a}\) The increase in σ from
Fig. 2. Total secondary yield ($\sigma$) vs. fluence from CVD diamond at 1 keV: (△) as-grown on Mo; ( ) heated in vacuum at 700 K (Mo); (◆) heated in vacuum at 700 K (Pd); (□) after atomic hydrogen treatment (Mo); ( ▽ ) after hydrogen plasma treatment (Mo).

diamond/Mo while heating is seen from all diamond targets and is probably due to initial desorption of surface contaminants. This effect was not observed in the other curves because data collections began after initial beam exposure.

Stable $\sigma > 25$ from diamond/Pd was also observed when the sample was heated in vacuum at 700 K (cf. Fig. 2) while the target was exposed to 1 keV electron beam.$^{10}$ At this temperature the Pd substrate provided a hydrogen background pressure of $1.0 \times 10^{-6}$ Torr, which was sufficient to replenish the surface hydrogen desorbed by the electron beam. After sufficient heating, hydrogen stored in the Pd substrate was depleted and $\sigma$ decreased with the same behavior seen in the as-grown films (cf. Fig. 3). Figure 3 shows that stable SEE ($\sigma = 20-45$ @ 1500 eV) was readily observed from alkali-halide-coated diamond films in UHV, independent of the primary beam current.$^{12,13,18}$

Barium is well known for lowering the work function of W and Mo, thereby enhancing emission in thermionic cathodes.$^{19,20}$ To investigate possible enhancement of secondary emission from Ba on CVD diamond, thin BaF$_2$ films were deposited on diamond. It was assumed that a monolayer coverage could be produced by electron beam exposure similar to the EBAAT process, which might lower the work function of the diamond surface. As
is seen in Fig. 3, \( \sigma \) vs. fluence from BaF\(_2\)-coated diamond showed a behavior similar to that of EBAAT samples. However, the maximum value of \( \sigma \) never exceeded 6 at 1.5 keV in samples of diamond/Si coated with 30 nm BaF\(_2\). Csl-coated diamond films from the same diamond-coated Si wafers used with BaF\(_2\) had values of \( \sigma > 30 \) under the same operating parameters.

The fluence dependence of \( \sigma \) from diamond in vacuum during exposure to an electron beam, shown in Fig. 2, has been observed in all as-grown CVD diamond targets tested, independent of the current density or the substrate material. It was observed previously that energetic primary electrons induced hydrogen desorption from the diamond surface, which resulted in lower \( \sigma \) (cf. Fig. 2).

The Auger carbon peaks from an as-grown diamond surface, before and after Ar ion sputtering at 2kV, are shown in Fig. 4. Before sputtering the signature Auger diamond peak was observed. After sputtering for 6 min the diamond structure was destroyed, as indicated by the shape of the Auger carbon peak. Ion bombardment using oxygen at 2kV, and hydrogen to as low as 200 V, produced the same change in the carbon peak from CVD diamond targets. This graphitization of the diamond surface due to ion bombardment is responsible for the reduction in \( \sigma \) to that of ordinary carbon observed when diamond targets
Fig. 4. Auger carbon peak from as-grown diamond/Si (top curve) and after Ar ion sputtering at 2kV for 6 min (bottom curve), indicating a graphitic structure.

were sputtered with Ar, O\textsubscript{2} and H\textsubscript{2} with energies $\geq 200$ V\textsuperscript{111}.

The increase in $\sigma$ from 12 to 27, shown in Fig. 1, from diamond/Mo heated in vacuum at 700 K, was originally thought to be due to hydrogen diffusing from the bulk\textsuperscript{9,112}. However, this is not observed to occur below 1200 K\textsuperscript{123}. ERD analysis of the as-grown diamond/Mo samples at room temperature showed an average hydrogen concentration of 2.0 atomic percent in the near-surface region as compared to 1.0 atomic percent present in the bulk, as illustrated by the solid curve in Fig. 5. The dashed curve shows the same sample 60 min after heating at 700 K, where the surface peak disappeared. Figure 5 shows that the hydrogen concentration in the bulk was unaffected at these temperatures. The curve in Fig. 5 shows the same sample after it was removed from vacuum, then reintroduced 96 h later. The surface peak reappeared, suggesting that this peak is due to contaminants adsorbed onto the surface during exposure to air. The increase in $\sigma$ due to heating observed previously\textsuperscript{9,111} was a result
Fig. 5. ERD spectra from CVD diamond target showing hydrogen concentration: (solid line) as-grown, before heating; (dashed line) after heating at 700 K for 60 min; ( ) room temperature, after reexposure to air for 96 h.

of the removal of surface contaminants, not an increased surface concentration of hydrogen. Although the width of the hydrogen peak in the near-surface region in Fig. 5 corresponds to a thickness of 200 nm, we believe the contamination layer is significantly thinner, ~10-20 nm. The apparent thickness was probably a result of the surface roughness of the CVD diamond film. Using a stylus profilometer with a radius of curvature of 12.5 μm, we were able to assign a lower limit of 150 nm to the surface roughness of the diamond used in this work.

Figure 6 shows σ vs. $E_{\text{prim}}$, from a representative diamond/Mo sample, as-grown and after hydrogen plasma treatment. Both the hydrogen plasma and atomic hydrogen treatments led to a significant reduction in σ. In the case of atomic hydrogen treatments (not shown), $\sigma_{\text{max}}$ from the as-grown sample was reduced from 12 to 4. Subsequent exposure to molecular hydrogen, or heating in hydrogen, oxygen or vacuum environments to as high as 900 K was unsuccessful in reversing the reduction in σ.

It was clear from SEM images, and the associated Raman and Auger spectra (not shown),
that hydrogen plasma and atomic hydrogen treatments improved the quality of diamond. The ERD spectra in Fig. 7 show that the hydrogen plasma treatment led to a significant enhancement in the near-surface hydrogen peak as compared to the as-grown samples, unlike the atomic hydrogen treatment which did not result in any increase in the near-surface hydrogen concentration. However, as described above (cf. Fig. 6), the reduction in $\sigma$ resulting from the hydrogen treatments was irreversible by heating or molecular hydrogen exposure. These data suggest that these treatments alter the surface and increase the work function, regardless of the increase in the near surface hydrogen concentration due to the hydrogen plasma.

Most metals exhibit $\sigma_{\text{max}}$ at primary beam energies between 0.6 and 1 keV. Measurements from as-grown CVD diamond indicate that $\sigma_{\text{max}}$ occurs between 1 and 1.5 keV. The total secondary yield vs. $E_{\text{primary}}$ curves from EBAAT diamond using Cs1 and the diamond/Pd during heating shown in Fig. 1 are atypical since $\sigma_{\text{max}}$ has not been reached at 3 keV. These data suggest that emission is being generated below the surface in these materials, since the deeper-penetrating, higher-energy electrons appear to lead to an increasing number of secondaries. No measurements were made above 3 keV to determine $\sigma_{\text{max}}$ from these samples. It is likely that this behavior was not observed in the as-grown films due to the desorption of hydrogen by the electrons striking the surface before penetrating into the bulk. This would decrease $\sigma_{\text{max}}$ and hence, increase the work function which would prevent...
electrons generated deeper in the diamond from escaping to vacuum.

The SEE data obtained from the as-grown diamond after hydrogen treatments show that the surface structure is critical to the secondary emission. Also, $\sigma$ vs. fluence data from EBAAT diamond during heating ($T > 150^\circ$C) or at elevated pressures ($1.0 \times 10^{-6}$ Torr Ar, not shown) show the EBAAT surface to be highly sensitive to impurity concentrations and temperature. Multiple Ti and Au depositions were made onto two diamond/Mo films to investigate the possibility of other emission-enhancing surface coatings which may have the benefit of withstanding higher temperatures.

The depositions were performed in a preparation chamber without disrupting vacuum, and the vacuum during depositions never exceeded $5 \times 10^{-7}$ Torr. CsI was deposited in the same way on a diamond target as those used with the metal overlayers to ensure that the diamond had potential for highly stable SEE. The total secondary yield measured from the CsI-coated control sample was stable and exceeded 30 at 1500 eV. Figures 8 and 9 show multiple scans of $\sigma$ vs. fluence from diamond/Mo coated with Ti and Au, respectively, with the overlayer thicknesses starting from < 1 monolayer and increasing in multiple monolayer
Fig. 8. Total secondary yield ($\sigma$) vs. fluence from CVD diamond/Mo after successive depositions of Ti.

Fig. 9. Total secondary yield ($\sigma$) vs. fluence from CVD diamond/Mo after successive depositions of Au.
increments. The overlayer materials were chosen based on emission-enhancing effects reported in the literature. Ti/diamond has been reported as a NEA material, and thin Au films have been reported to stabilize field emission from CVD diamond films. With each successive deposition \( \sigma_{\text{max}} \) was reduced, until the SEE behavior became that of the overlayer material.

The apparent temporary recovery in the data from diamond coated with 0.4- and 1.0-nm-thick Au films is probably due to mobile gold atoms under electron beam exposure. As the surface was exposed and locally heated, Au atoms might gain sufficient energy to "hop" out, revealing a previously unexposed diamond surface. Thereafter the data follow the normal behavior for hydrogen-terminated diamond. This behavior was observed at every point tested on the diamond coated with 0.4- and 1.0-nm-thick Au. It was not observed after the Au thickness exceeded 1.0 nm.

4. Conclusions

High SEE has been observed from CVD diamond films grown on various substrates. In as-grown films the effect is due to surface hydrogen which is unstable under exposure to an electron beam. Alkali-halide coatings on the diamond films lead to highly stable emission in UHV after the surface is activated by electron beam exposure. No differences in SEE properties have been observed between samples grown by HFCVD or MPCVD. The SEE properties appear to have little or no dependence on the substrate material, except in the case of Pd substrate where heating induces a continuous flow of hydrogen from the Pd onto the diamond surface, which stabilizes \( \sigma \). Thin BaF\(_2\) coatings provided some enhancement in the stability of \( \sigma \) but \( \sigma_{\text{max}} \) was considerably lower than those for EBAAT surfaces or even as-grown films.

ERD showed that heating untreated samples at 700 K cleaned the surface, which led to an increase in \( \sigma \). The bulk hydrogen concentration was observed to remain unchanged at this temperature.

Hydrogen plasma and atomic hydrogen treatments led to a significant, irreversible reduction of \( \sigma \) from CVD diamond/Mo targets. Raman scattering Analysis, SEM, and AES showed that the diamond surface was improved significantly by the treatments. ERD showed that hydrogen plasma treatment led to a significant increase in the near-surface hydrogen concentration. However, \( \sigma \), which is highly surface-sensitive, decreased after the hydrogen treatments. This implies that SEE is dependent on surface hydrogen and is not affected by the near-surface hydrogen concentration. The \( \sigma \) vs. \( E_{\text{primary}} \) data from EBAAT diamond coated with CsI show higher emission at higher primary energies, indicating that electrons generated deeper within the bulk drift to the surface and are emitted into the vacuum. However, the data from as-grown films indicate that the surface properties ultimately determine the SEE properties from CVD diamond.

Although Ti on diamond has been observed to be a NEA material when Ti is \( \leq 1 \) monolayer thick, no SEE enhancing effect was observed when thin layers were deposited on diamond. The same results were observed with thin Au films.
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