PHYSICAL REVIEW B **73**, 085423 (2006)

Sub-bandgap photoenhancement of electron emission and discharging of hydrogenated and hydrogen-free diamond surfaces

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(Received 2 June 2005; revised manuscript received 13 December 2005; published 28 February 2006)

In this paper we report on the photoinduced enhancement of secondary electron emission and discharging of hydrogenated and hydrogen-free diamond surfaces subjected to continuous low energy electron irradiation. Diamon surfaces subjected to electron irradiation trap charges resulting in upwards surface band bending and consequent decrease of secondary electron emission. It is demonstrated that simultaneous electron irradiation and illumination of the diamond surfaces with sub-bandgap photons in the visible range enhances the secondary electron emission yield of diamond. For the hydrogenated diamond surfaces it is suggested that these effects are associated to a surface photovoltage effect which results in unpinning of the surface bands by photoexcitation of carriers and compensation of trapped surface charges. For the hydrogen-free diamond, discharging is most likely associated with photoexcitation of the trapped charges in midgap electronic states associated with surface reconstruction.

DOI: 10.1103/PhysRevB.73.085423 PACS number(s): 79.20.−m, 73.20.−r, 73.25.+i

I. INTRODUCTION

Diamond surfaces are good electron emitters due to the negative electron affinity (NEA) of its hydrogenated surface.[1–4] To realize the use of diamond in electron emission or detection devices the electronic stability of its surface under electron irradiation needs to be understood and hopefully controlled. Very important effects that may strongly influence the electron emission properties of hydrogenated diamond surfaces are band bending associated or not to surface charging.[5] We have recently reported the secondary electron emission (SEE) properties of hydrogenated diamond surfaces subjected to low energy electron irradiation.[6,7] It was determined that for incident electron energies, E_i, in the range of 5–20 eV and sufficiently low electron currents, the SEE decreases in intensity as a function of irradiation time, however, no net surface charging takes place.[6] For sufficiently large incident currents a net surface charge was found to build up as well.[7] It was found that the maximum decay rate and value of surface charging occurs for incident electron energies of ~9 eV.[6] This effect was explained by resonant electron trapping in the near-surface region of the hydrogenated diamond, charge compensation and consequent space charge distribution resulting in upward surface band bending.[6,7] The maximum cross section at incident electron energies of ~9 eV was associated with the excitation of a C-H$^-$ (ads) Feshbach anion resonance on the hydrogenated diamond.[8,9] It was found that by increasing the surface temperature the secondary electron emission intensity increases and less charging occurs.[7] This effect was associated to an increase of surface conductivity. The hydrogen-free diamond surface charges as a result of low energy electron irradiation more severely than the hydrogenated surface and no maximum in charging efficiency was measured as a function of incident electron energy. It was suggested that in this case surface charge trapping occurs through a mechanism of self-localization of secondary electrons, produced by the incident electron beam within the near-surface region, in surface electronic states of π symmetry associated with reconstruction.[6,7] As the incident electron beam energy increases so does the number of low energy secondary electrons excited through cascade processes and transported to the near-surface region (before escape) which may be trapped. This charging effect is different from the one observed when ion beam damaged diamond surfaces are subjected to electron irradiation.[10] In this case it was suggested that local defect states created by the ions get negatively charged when the surface is subjected to electron irradiation.

The influence of light illumination on the redistribution of charge at surface and interfaces—the so-called surface photovoltage (SPV) effect—has been known for a long time (Ref. 11 and references therein). Essentially in SPV a surface is illuminated with super- or sub-bandgap photons resulting in the production of photocarriers which move in the solid structure and interfaces under the influence of local electric fields.[12] Charge redistribution induced by the SPV was measured by Kelvin probe and lately by a combination of scanning probe methods.[13,14] A wealth of surface and interface phenomena can be induced by SPV-like charging of structural defects, impurities, adsorbates, and flatting of surface bands.[15] In this paper we report on a SPV effect associated with an externally trapped charge. The trapped surface charge results in upward band bending hindering electron emission while SPV flatten the surface band and results in its enhancement.

In this paper we report on the influence of sub-bandgap photon irradiation in the visible range on the SEE and electronic properties of diamond surfaces subjected to low energy electron irradiation. Both hydrogenated and hydrogen-free surfaces were investigated. It is reported that diamond surfaces can be discharged and its SEE properties can be enhanced and controlled by illumination with sub-bandgap light in the visible range. Finally a schematic model is suggested to explain the reported phenomena.

II. EXPERIMENT

Diamond films were deposited onto *p*-type doped silicon substrates using a methane/hydrogen gas mixture by the standard microwave chemical vapor deposition (MWCVD) method. The thickness of the films was ~10 μm with a characteristic microcrystalline size of 2 to 3 μm. After deposition the diamond films were further exposed to MW hydrogen plasma at the same substrate temperature, gas flow, and power as those used for the growth process. The surface composition and phase purity of the films were examined *ex situ* by various electron spectroscopies. The hydrogenation procedure results in a fully hydrogen-terminated surface as well as some incorporation of hydrogen in the subsurface region. This hydrogenation procedure results in NEA and *p*-type surface (or near surface) conductivity.[16–18] The hydrogen-free diamond film surfaces are prepared by annealing the diamond film to 1300 K for several minutes. This annealing process is known to result in desorption of most adsorbed hydrogen on the diamond film and produced a reconstructed surface.[19–22]

The apparatus for studying SEE (and ESD) was described in detail earlier.[8] In brief, it consists of a hemispherical electron monochromator as the electron gun, a hemispherical energy analyzer in line with a quadrupole mass filter for kinetic energy analysis and identification of desorbed ions and electrons. In our experimental setup when the radio frequency of the analyzer is not operative, which is the case of the present study, we collect all negative particles (H^- ions and electrons) of the same energy. For the hydrogenated diamond system H^- ions are produced with kinetic energy between 0 and a few eV, however, with an intensity of 2 to 3 orders of magnitude lower that the intensity of secondary electrons produced at the same energy. It is then reasonable to assume that the intensity of the negative particles collected when the radio frequency is not operative is entirely due to electrons.

The components are housed in an ultrahigh vacuum chamber (base pressure in the 10^{-11} mbar region) with a two-layer μ-metal shielding to block the Earth's magnetic field. The range of incident electron energies, E_i, was varied in the 6–20 eV range. The incident electron current was measured with a Faraday cup as a function of E_i. We estimate that the electron beam diameter was ~0.3 mm. The energy resolution of the electron beam at the target is estimated as 80 meV (full width at half maximum). The electron beam was oriented at 60° from the surface normal. The energy analyzer and quadrupole can rotate from 0° to 90° from the surface normal. In all electron emission and ESD experiments, the analyzer was positioned at 0° (i.e., normal to the sample surface). Prior to the electron emission experiments, the system was baked to 425 K and the sample was subsequently annealed to 900 K. This treatment results in desorption of any possible surface adsorbate impurities other than hydrogen such as oxygen and water molecules. The possibility that the electron irradiation results in a substantial depletion of chemisorbed hydrogen or electron beam-induced surface damage that may affect our results was examined repeatedly by measuring the H^- ion yield for incident electron energy of 9 eV in between experiments. By these alternating measurements the reproducibility of our results could also be verified. Also to avoid large exposures of a particular area to the electron beam, experiments were carried out on different areas of the sample surface.

The full electron emission curves were measured for a number of incident electron currents. The electron emission curves were measured from zero kinetic energy up to $E_i + 1$ eV, thus including the low energy secondary electrons up to the elastically backscattered primary electrons. The electron spectrometer optics was optimized to measure low energy electrons with an onset at zero kinetic energy.

Light illumination was performed using an external standard Xe incandescent lamp, operated at a power of 100 W and focused on the sample surface onto a spot of about 1 cm^2 through a quartz window. The distance between the light source and film was approximately 0.5 m. This illumination condition resulted in a broad spectrum ranging from the uv (~200 nm) to the IR. Using a set of low pass filters it was determined that light illumination in the visible range (above ~500 nm) is sufficient to induce the reported influence on the secondary electron emission. Following these results an experiment was carried out with a He-Ne laser for illumination which lead to the same type of results.

III. RESULTS

A. Hydrogenated diamond surfaces

The full electron emission spectra of the hydrogenated diamond films was measured as a function of incident electron beam energy, E_i, in the 6–20 eV range. The measurements were carried out using an incident electron current, I_e, of 8 nA while the surface was subjected or not to illumination. This incident current is defined as low current (LC) regime as no net surface charging occurs.[6] The electron emission curves without light illumination were previously published and are reported here again to show the influence of light illumination on these curves.[6,7] The main features in these curves are a broad low energy band associated with secondary electrons and a sharp peak at E_i associated with the elastically backscattered electrons. While the energy position of the elastically backscattered electrons does not change with surface charging the onset for secondary electron emission equals the net surface charging.

In Fig. 1(a) the full electron emission spectra for different incident energies with and without illumination are shown. In all cases the onset in electron emission was measured at ~0 eV. In Fig. 1(b) the electron emission intensity is plotted as a function of incident electron energies. To rule out the possibility that the enhancement in the electron emission is associated with photoemission, blank experiments were conducted. As expected no electron emission was detected when the surface was subjected to just photon irradiation within the visible range. The electron intensities were derived from Fig. 1(a) by calculating the integral intensity from zero electron energy up to 2 eV below the elastically backscattered

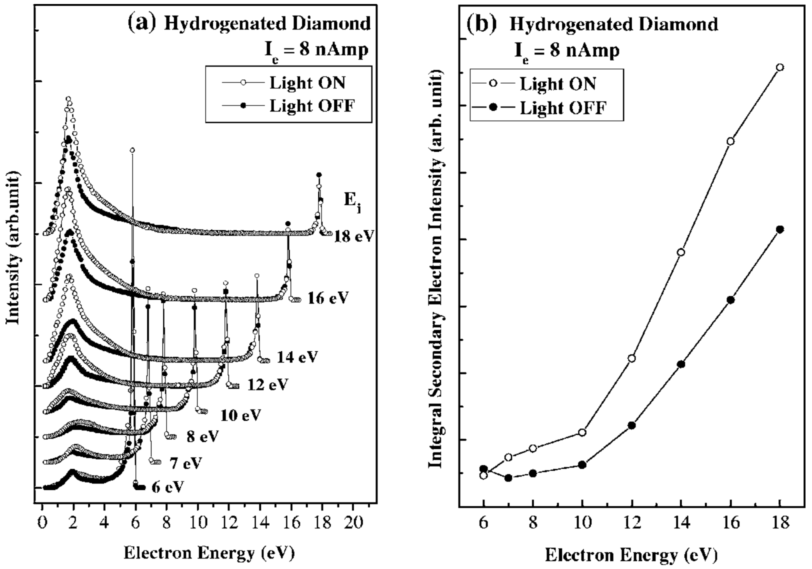

FIG. 1. (a) Full electron emission spectra for different incident energies with and without illumination. (b) Integral intensity of the low energy secondary electron emission band with and without illumination. The incident electron current is 8 nA. Hydrogenated surface.

peak. From this figure illumination results in an increases in secondary electron emission (SEE).

The influence of illumination on the decay of SEE was followed by monitoring the intensity of 1.6 eV secondary electrons with electron irradiation time from the moment the beam was switched on for different incident electron energies E_i. The results of these experiments are shown in Fig. 2(a). As observed from this figure the SEE intensity at 1.6 eV exponentially decays with electron irradiation time. From the intensity decay with time the exponential law was calculated and shown in Fig. 2(b) with and without illumination. The exponential law is defined here as the SEE decay factor. As observed from Fig. 2(b) the decay factor depends on E_i and is different for the surfaces subjected or not to illumination. From this figure it is seen that the decay factor for the unilluminated surface obtains a maximum value for $E_i \sim 9$ eV decreasing at higher and lower energies. Illumination of the surface results in a strong decrease in the decay factor for all incident energies.

The influence of the photon wavelength on electron emission was examined qualitatively by using a set of low pass filters. It was determined that sub-bandgap light (>500 nm) is sufficient to induce the observed effects. A more detailed study on the influence of photon wavelength and light intensity on the electron emission properties of diamond is being performed.

B. Hydrogen-free diamond surfaces

The SEE spectrum of the hydrogen-free diamond surfaces subjected to electron bombardment with different primary electron energies with and without light illumination were measured and are shown in Fig. 3(a). As previously reported the onset of the SEE for the hydrogen-free surface monotonically increases with incident electron energy [full circles in Fig. 3(a)] and this effect was already detected for low incident currents (LC regime), becoming very severe for higher electron currents.[6] In this case the effect of light illumination is very drastic resulting in that the onset for secondary electron emission occurs at nearly zero energy for all incident energies used in our experiments. In Fig. 3(b) the integral intensity of the secondary electron emission band, as derived from the data shown in Fig. 3(a), with and without illumination for the hydrogen-free surface are shown.

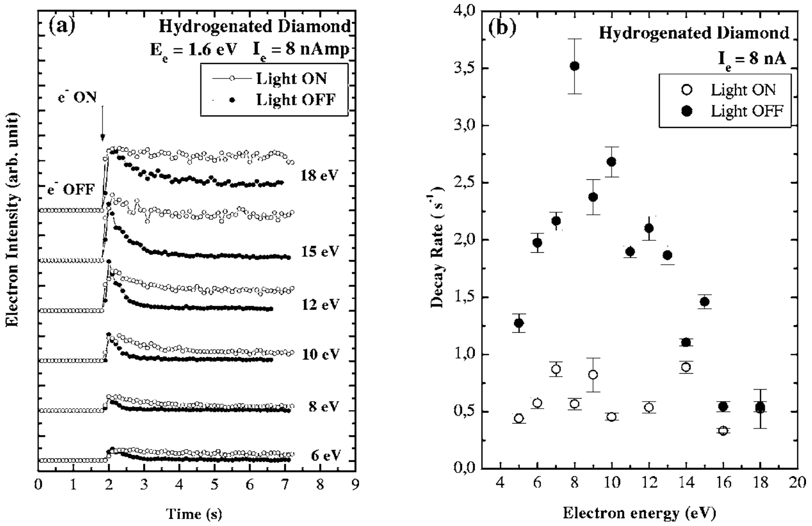

FIG. 2. (a) Decay of 1.6 eV secondary electrons as a function of electron irradiation time for different incident electron energies with and without illumination. (b) Decay rate factor calculated with and without illumination. The incident electron current is 8 nA. Hydrogenated surface.

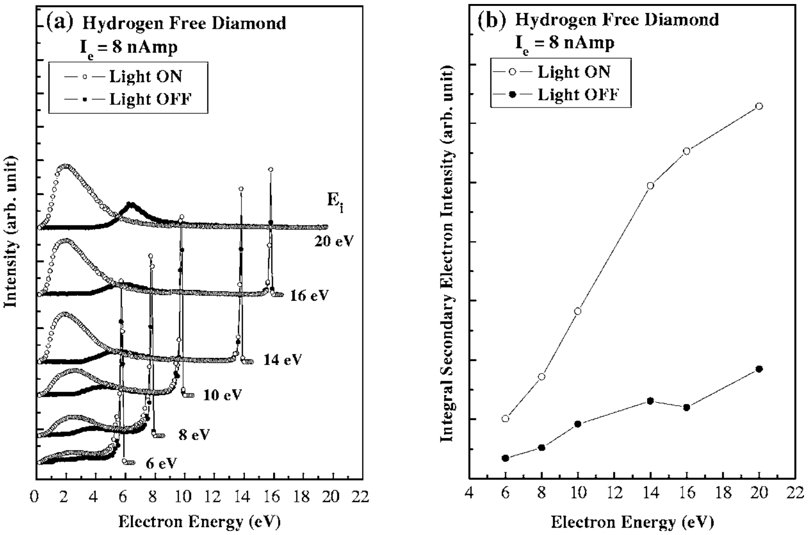

FIG. 3. (a) Full electron emission spectra for different incident energies with and without illumination. (b) Integral intensity of the low energy secondary electron emission band with and without illumination. The incident electron current is 8 nA. Hydrogen-free surface.

IV. DISCUSSION

Upwards band bending at the surface hinders the escape of low energy secondary electrons whose energy, upon arriving at the surface, lies between the bottom of the conduction band and the upwarded band bending value. This is expected to be the case when the vacuum level for the unperturbed surface lies below the conduction band minimum (CBM). The value of the surface barrier for electron emission is defined here as E_{sb} (sb stands for surface barrier).

A schematic representation of the hydrogenated diamond electronic structure is shown in Fig. 4(a). For the unperturbed hydrogenated diamond structure the surface bands naturally bend downwards. This is due to the charge distribution on the hydrogenated surface.[7] This surface displays NEA and *p*-type conductivity. In Fig. 4(b) a schematic representation of the surface bands of the hydrogen-free diamond surface is shown. In this case the surface displays positive electron affinity. The surface bands bend downwards due to the formation of π bonds associated with surface reconstruction. The hydrogen-free films are highly insulating.

The decrease in electron emission of the hydrogenated diamond surfaces subjected to low energy electron irradiation was shown to be associated with resonance electron attachment (REA) of incident electrons and formation of C-H(ads)$^-$ with a maximum cross section at ~9 eV.[8,9] Formation of a negative surface charge results in an upwards band bending or pinning of the surface band and for sufficiently large incident currents net surface charging also occurs.[7] Band bending and net surface charging depend on conductivity and are expected to be more pronounced at higher incident current and decrease with increasing temperature as the diamond conductivity increases. Indeed the influence of temperature on the SEE was examined and it was found that the overall SEE intensity increases with increasing temperature from 300 to 500 K.[7] A schematic representation of the surface bands of the hydrogenated diamond surface subjected to 9 eV electron irradiation at steady state is shown in Fig. 5(a).

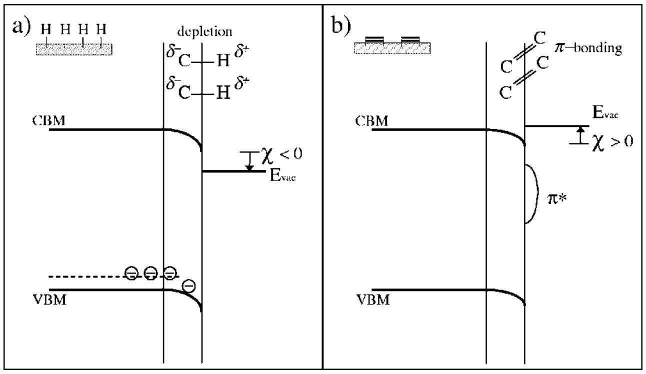

FIG. 4. Schematic representation of the hydrogenated diamond surface band structure: (a) unperturbed hydrogenated surface and (b) unperturbed hydrogen-free surface.

It is suggested in the present study that the effect of illumination on the electron emission of diamond surfaces is associated with reduction of the surface potential by lowering the band bending at the surface and decrease of net surface charging by photocarriers. This is a SPV effect in which the band bending is created by an externally trapped charge. These effects are discussed in detail below and described schematically in Fig. 5. Considering that the hydrogenated diamond surface displays *p*-type conductivity, then photon excitation with sub-bandgap light results in the production of holes which are expected to reduce the surface depletion layer created by resonance electron attachment and consequently reduce the band bending and neutralize the trapped charge.

From Figs. 1(b) and 2(a) light illumination results in an increase in the secondary electron emission as well as a reduction in the decay rate of secondary electrons. It is suggested that these effects are associated with the photoexcitation of acceptor states resulting in hole conductivity which compensates for the negative charge trapped at the surface. This is based on the fact that the influence of light illumination on the secondary electron emission occurs for sub-bandgap light (>500 nm) and that the hydrogenated diamond film surfaces display a *p*-type conductivity. The effect of photoirradiation on the electronic structure of the hydrogenated surface under electron irradiation is shown schemati-

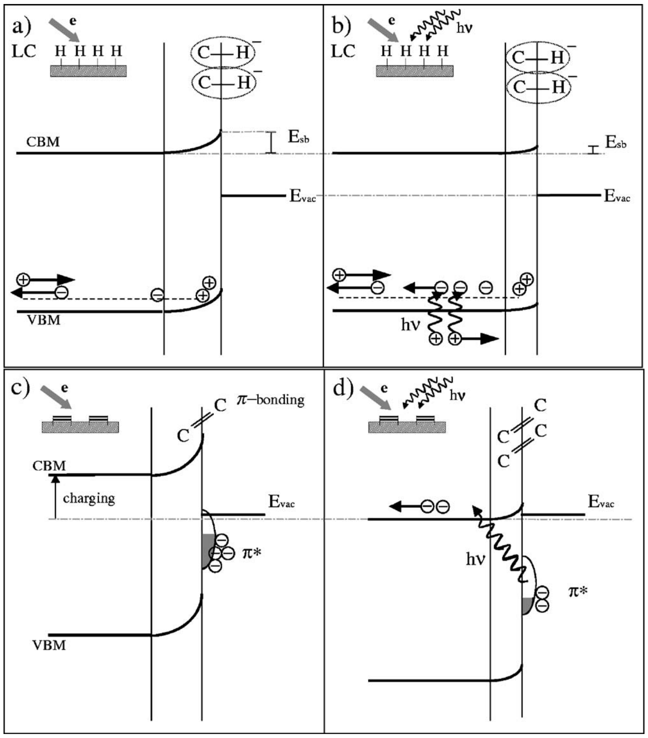

FIG. 5. Schematic representation of the surface bands under 9 eV electron irradiation with and without light illumination. (a) Hydrogenated surface under electron irradiation—LC regime: upwards pinning of the surface band, however, no net charging takes place due to efficient compensation; (b) hydrogenated surface under electron irradiation and light illumination—LC case: photoconductivity results in lowering of the surface band; (c) hydrogen-free surface under electron irradiation: upwards band bending at the surface and net surface charge; and (d) hydrogen-free surface under electron and light illumination: photoinduced excitation of the trapped surface charge results in neutralization.

cally in Fig. 5. As seen from this figure light illumination results in the production of *p*-type carriers resulting in an unpinning of the surface electronic structure, thus effectively reducing the surface barrier, E_{sb}, for electron emission. This consequently results in an increase of the secondary electron emission and a decrease in the decay rate of secondary electrons. As no net charging occurs the energy difference between E_{vac} and the CBM is similar to the unperturbed case.

For the hydrogen-free surfaces (after annealing to 1300 K) light illumination also results in elimination of the surface charge as determined by the onset in secondary electron emission and enhancement of electron yield [Figs. 3(a) and 3(b)]. For the hydrogen-free surface charge trapping under electron irradiation occurs in π bonds associated with surface reconstruction resulting also in upwards band bending and charging.[6] In this case charging is due to charge localization and is not limited by conductivity as the surface charges negatively. A schematic representation of the electronic structure of the bare diamond surface under electron irradiation without illumination is shown in Fig. 5(c). However, the influence of light illumination on the SEE intensity and onset is different from that offered for the hydrogenated surface. The difference being that the hydrogen-free surface does not display *p*-type conductivity and is highly insulating. It is suggested that in this case discharging occurs by photoinduced excitation of the trapped charge in the midgap π bonds associated with surface reconstruction to conduction band states from which neutralization through bulk conductivity may occur.

In summary, we have shown that sub-bandgap photon irradiation of hydrogenated and hydrogen-free diamond surfaces subjected to low energy electron irradiation results in an enhancement of electron emission and neutralization of surface trapped charge. For the hydrogenated surfaces the reported effect is suggested to be associated with a SPV whereas for the hydrogen-free surface charge neutralization is associated to direct photoinduced excitation of the trapped charge.

ACKNOWLEDGMENT

A part of this research was carried out with the financial support of the Technion Fund for Research and the Israeli Academy of Science and Arts.

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