



Infrared wavelength-selective photodesorption on diamond surfaces

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Abstract

We report first studies of photodesorption from diamond films using the Vanderbilt Free-Electron Laser at two infrared wavelengths: 3.5 μm , corresponding to localized absorption by C–H bonds at grain boundaries, and 5 μm , corresponding to two-phonon absorption by the bulk diamond. At 3.5 μm , we observe two photodesorption thresholds at fluences well below the onset of ablation. In contrast, at 5 μm , a single photodesorption threshold is identified at a fluence which is close to the second fluence threshold, observed at 3.5 μm . These experiments shed light on the physics of wavelength selective desorption through non-electronic channels. © 1998 Elsevier Science B.V.

PACS: 79.20.La; 78.70 – g; 68.35.Ja

Keywords: Photoablation; Photodesorption; Diamond; Vibrational excitations; Impurities; Semiconductor

1. Introduction

Mechanisms responsible for incident-photon induced heavy-particle emission from surfaces below the ablation fluence threshold is a topic of intense interest [1]. In order to elucidate this issue, we have initiated a comprehensive study to compare the dynamics of energy deposition into localized surface excitations vs. bulk excitations using the Vanderbilt

Free-Electron Laser (VFEL). In this paper, we report first results. Ablation and desorption of wide-band-gap materials can occur through multiphoton electronic excitation or through vibrational excitation. The electronic route to desorption and ablation is better understood [2] than is the vibrational route. There have been relatively few investigations of vibrational excitations, mainly because a powerful broadly tunable infrared source has not been readily available. The unique capabilities of the VFEL, allow these kinds of experiments to be performed.

The VFEL was used to probe vibrationally resonant processes via time-of-flight mass spectrometry, and strong wavelength dependence of cluster emission was found [3].

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Another study of the formation of ablation craters demonstrated that the fluence threshold for large-scale photoablation of diamond films decreases approximately three-fold when the laser is tuned to resonance with the $3.5\text{ }\mu\text{m}$ C–H stretch [4].

However, the intensities required to produce visible surface damage are also strong enough to produce plasma breakdown. We call the event ablation when plasma is formed in the plume, and UV light is detected. In this case, laser–plume interactions complicate the analysis of particle-emission dynamics. To study a system free of these complications, we investigated the near-threshold desorption of atoms and clusters from a diamond film at the $3.5\text{ }\mu\text{m}$ C–H stretch resonance and at the $5\text{ }\mu\text{m}$ two-phonon bulk absorption resonance. By tuning the laser from impurity to bulk absorption bands, we changed the local or non-local nature of the energy deposition. With this first experiment, we examine differences in fluence thresholds at these two wavelengths.

2. Experiment

The sample used in this experiment was a polycrystalline diamond film, approximately $10\text{-}\mu\text{m}$ thick, deposited on a $500\text{-}\mu\text{m}$ silicon substrate. The film was grown by the microwave plasma-assisted chemical vapor-deposition (CVD) process [5]. The as-grown films contain relatively large amount of hydrogen, approximately one hydrogen atom per one hundred carbon atoms [6]. The absorption spectra of CVD diamond films show a sharp increase centered around $3.5\text{ }\mu\text{m}$, corresponding to the C–H stretch absorption, and a broader feature showing approximately the same absorption around $5\text{ }\mu\text{m}$, corresponding to a two-phonon bulk absorption [7].

The VFEL delivers infrared light tunable from $2\text{ }\mu\text{m}$ up to $10\text{ }\mu\text{m}$. The temporal structure of the beam consists of a train of typically $2\text{--}5\text{ }\mu\text{s}$ long macropulses. The macropulse repetition rate is variable up to 60 Hz . The macropulses in turn consist of approximately 1 ps long micropulses separated by 350 ps . Depending on wavelength, the full macropulse energy varies between 30 and 200 mJ , which corresponds to a power of order $1\text{--}10\text{ MW}$ during the micropulse.

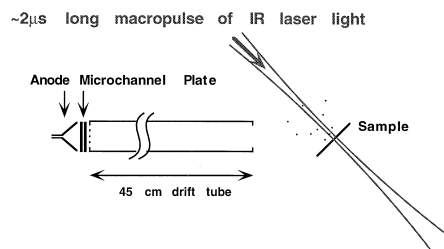


Fig. 1. Experimental schematic. The sample is a hydrogen-rich CVD diamond film, approximately $10\text{ }\mu\text{m}$ thick on silicon substrate. The pressure during the experiment is in the low 10^{-9} Torr range.

The sample was mounted in an ultrahigh vacuum chamber maintained in the low 10^{-9} Torr range by a sputter-ion pump. Because the samples are chemically stable in air, no special surface preparation was performed. Desorbed positive ions or metastable neutrals can be measured with our current time-of-flight (TOF) setup. Our TOF spectrometer consists of a 45-cm shielded drift tube and a chevron microchannel plate (MCP) detector. There was no accelerating grid nor extraction voltage, and the drift tube was maintained at ground potential when the data presented here were taken. The front and rear surfaces of the MCP were maintained at -2200 V and -200 V , respectively, and anode was at ground potential. The analog signal on the anode is integrated with a fast integrator. The integrator output was captured by a digitizing oscilloscope and stored on a computer. In this configuration, only the number and the velocity distribution of the particles as they leave the diamond surface were measured. A schematic setup of the experiment is shown in Fig. 1. Each TOF spectrum corresponds to a single $2.5\text{-}\mu\text{s}$ FEL macropulse incident on a fresh spot on the sample. A fast IR photoelectromagnetic detector (BSA Techn., PEM-L) is used to generate a start-pulse for the detection electronics from a small portion of the laser pulse. The laser pulse energy incident on the sample is measured using a second beam-splitter and a pyroelectric joulemeter (Molelectron J4-09).

3. Results and discussion

Figs. 2 and 3 show typical TOF spectra for $3.5\text{-}\mu\text{m}$ and $5\text{-}\mu\text{m}$ laser pulses, respectively, at different

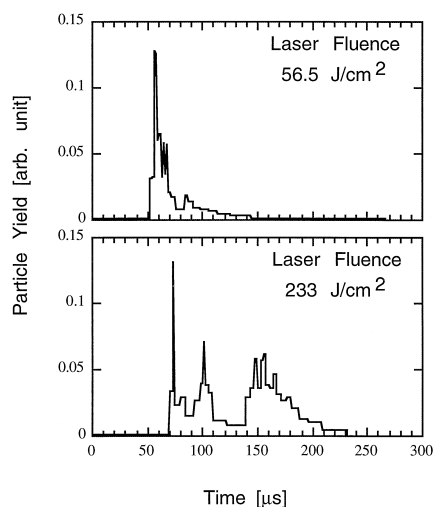


Fig. 2. Typical TOF spectra taken at 3.5 μm wavelength.

fluences. These curves are the numerical derivatives of the acquired integrator output.

Sample positions relative to the focal point of the laser were the same for both wavelengths. The laser spot diameters are estimated to be 75 and 80 μm at wavelengths of 3.5 and 5 μm , respectively. This choice simplifies the analysis by providing similar conditions for the two wavelengths, under the assumption that the beam profiles are the same for a given pulse energy.

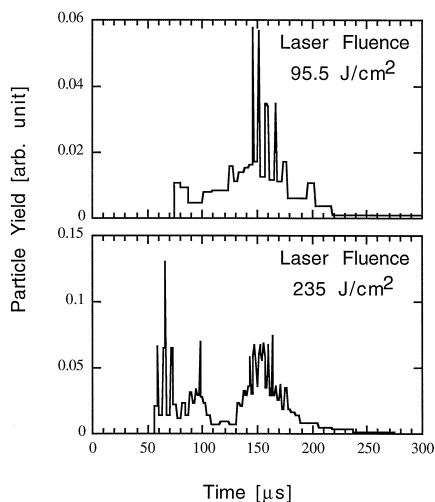


Fig. 3. Typical TOF spectra taken at 5 μm wavelength.

The laser-material interaction possesses several distinct time scales for energy transfer, corresponding to different stages in the energy redistribution. Cooling of the vibrationally excited molecule is thought to take of the order of tens of picoseconds [8]. Although the diamond is a good thermal conductor, thermal diffusion will not carry any significant amount of energy away from the irradiated area in a time less than about 1 μs [9]. On this time scale, energy can be removed from the irradiated spot only by desorption of particles or by radiation. To develop a more detailed picture of the energy transfer, one must take into account the temporal structure of the laser macropulse. However, for this initial comparison, we simply took the macropulse fluence as a measure of the deposited energy. These measurements were taken with macropulse widths of about 2.5 μs at both wavelengths.

The TOF spectra shown in Figs. 2 and 3 are typical of all spectra taken in this experiment at fluences below the ablation threshold. The ablation threshold is identified to be at a fluence (above 200 J/cm^2) where a prompt signal is observed, which we attribute to photon emission associated with plasma formation in the ablation plume.

The desorbed species cannot be identified with the current experimental configuration. In order to investigate the charge of the desorbed species, we varied the bias on the drift tube from 0 V to 450 V. The spectra do not change significantly with the bias, which suggests that the desorbed species are mostly metastable neutrals. Qualitatively, the TOF spectra show most particles arriving in two distinct time windows, which are shifting in time as a function of fluence.

If we assume that the kinetic energies of all particles are centered around the same value, then the mass ratio of the two groups of particles is approximately 1:3. This ratio does not give a good match to the mass ratio of the possible desorbed species considering the constituent atoms of the diamond film. According to this assumption, the groups most likely consist of a variety of larger molecules with slightly different masses. Or it is also possible, that different species desorb via different mechanisms and do not have the same kinetic energies. Future experiments will attempt to determine the species desorbed from the surface.

More information can be obtained by comparing the integrated particle yield for the two wavelengths vs. laser fluence. Figs. 4 and 5 show the total particle yield as a function of the laser fluence at wavelengths of $3.5\ \mu\text{m}$ and $5\ \mu\text{m}$, respectively.

The total yield vs. fluence at $3.5\ \mu\text{m}$ (Fig. 4) shows two desorption thresholds: the first corresponds to a very sharp increase of the yield at $20\ \text{J}/\text{cm}^2$. The second is around $100\ \text{J}/\text{cm}^2$, where the particle yield starts to slowly increase. The total yield vs. fluence plot at $5\ \mu\text{m}$ (Fig. 5) is different. It suggests one desorption threshold between 70 and $80\ \text{J}/\text{cm}^2$.

At fluences above $200\ \text{J}/\text{cm}^2$, we observe yields several times greater than the last points shown here at both wavelengths. At these fluences we also observe immediate response from the detector, indicating that UV light was emitted from the plume. These data are not considered here in detail because ablation events complicated by the presence of plasma plume are outside of the scope of this investigation.

The comparison between Figs. 4 and 5 indicates that energy absorbed at the C–H vibration frequency produces desorption with the same yield at less than one-third of the fluence than energy absorbed in the bulk two-phonon band. There was no absorption measurement taken on the sample used in this experiment, but a typical as-grown CVD diamond film has similar relative absorbance at the two studied wavelengths [6,7], showing strong hydrogen content. The difference in the thresholds suggests that energy channeled through a particular route can cause bond breaking more efficiently.

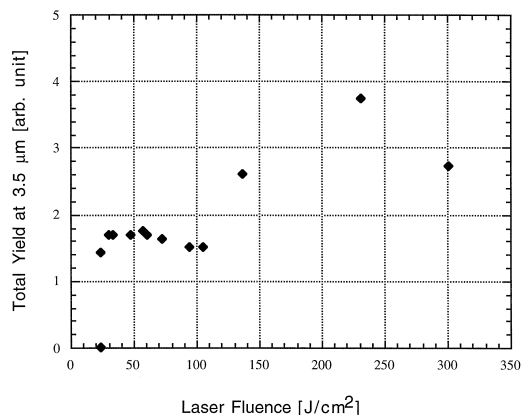


Fig. 4. Total particle yield vs. laser fluence at $3.5\ \mu\text{m}$ wavelength.

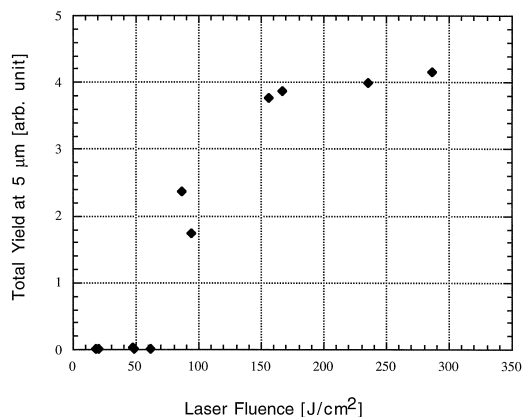


Fig. 5. Total particle yield vs. laser fluence at $5\ \mu\text{m}$ wavelength.

It is reasonable to conjecture that the first sharp threshold is associated with the presence of hydrogen in the diamond film. Previous studies conclude that hydrogen is located mainly at the surfaces and grain boundaries of the diamond [6,10]. It seems plausible that depositing energy locally on the surface leads more readily to particle desorption. Clearly, desorption caused by the delocalized bulk excitation requires more energy, as shown in these preliminary experiments.

4. Conclusion

Photodesorption from diamond films induced by strong infrared radiation has been investigated at wavelengths of $3.5\ \mu\text{m}$ and $5\ \mu\text{m}$ at fluences below the onset of ablation. Our initial results show that the energy absorbed at the C–H vibration frequency results in desorption from the diamond film with same yield at significantly lower fluences than energy absorbed in the bulk two-phonon band. Our results indicate the presence of wavelength selective desorption processes through non-electronic channels. To better understand the role of the hydrogen impurity in the microscopic processes leading to ablation, we will perform experiments using diamond samples with lower hydrogen concentration and other systems such as silicon, and we will identify the desorbed species.

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