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UV laser induced changes to morphological, optical and electrical properties of conductive nanocrystalline diamond films

Maxim S. Komlenok [a,b], Anna M. Zaniewski [c,*], Evgeny V. Zavedeev [a,b], Vitaly I. Konov [a,b], Franz A.M. Koeck [c], Robert J. Nemanich [c]

[a] Natural Sciences Center, General Physics Institute, Vavilova 38, Moscow 119991, Russia
[b] National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoye shosse 31, Moscow 115409, Russia
[c] Department of Physics, Arizona State University, Tempe AZ 85287-1504, USA

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ABSTRACT

The possibility of laser induced variation of optical and electrical properties of conductive nanocrystalline diamond (CNCD) films has been demonstrated. The films were produced by microwave plasma chemical vapor deposition (MPCVD) from CH_4:H_2:N_2 gas mixtures. The films were irradiated in air with 20 ns pulses of an ArF excimer laser ($\lambda = 193$ nm). It was found that low laser pulse intensity (~0.05 J/cm^2), well below film surface graphitization (~0.3 J/cm^2) and nanoablation (~0.08 J/cm^2) thresholds, induces changes of the film properties. The effect requires multiple pulsed irradiation and results in a decrease of the film electrical conductivity, which is accompanied by optical bleaching of the diamond film absorption.

1. Introduction

Conductive nanocrystalline diamond (CNCD) films have great potential as a new material for electronic devices, e.g. as field electron emitters for displays and as thermionic emitters for energy conversion applications [1,2]. Such films can be produced by microwave plasma chemical vapor deposition (MPCVD) synthesis with the addition of nitrogen to the traditional CH_4:H_2 based gas. The films show electrical conductivity with n-type character [3]. The nitrogen incorporation has been shown to be largely in the grain boundaries [4], and theoretical studies have indicated that n-type character is expected [5]. Prior reports [4,6] have suggested that a concomitant increase in sp^2 bonded grain boundaries may present the largest contribution to the increased electrical conductivity. The actual conductivity mechanism is a topic of study, but a model of combined localized states and hopping conductivity and extended π-bonding states and band conductivity has been able to describe the conductivity over a range of temperature and N concentration [7–9].

Laser-based modification of materials allows for versatile patterning and scalability, and is a widely used tool for nano and microprocessing films and surfaces (see e.g. [10]). However, this approach is less developed but under intensive study for diamond films [11,12]. For example, recently it has been demonstrated that laser nanoablation is an effective technique for ultra precise removal of single, poly and nanocrystalline (all non-conductive) diamond samples, which are irradiated in air [13, 14]. In this work, we present a new technique for laser induced nanostructuring of CNCD films which manifests itself at laser pulse intensities below the laser nanoablation threshold. We are not aware of prior experimental data for such laser induced effects with diamond material [15].

2. Experiment

CNCD films were deposited on mirror polished 25 mm diameter conductive silicon (001) substrates (P-doped, n-type, 0.01 Ω-cm, from Virginia Semiconductor) using N_2:H_2:CH_4 gas mixtures by MPCVD [1]. The films were prepared with a N_2 gas phase concentration greater than 20%, which corresponds to a [N] concentration of $\sim 2 \times 10^{20}$ cm^{-3} and a resistivity of ~0.1 Ω-cm [8,9]. The initial film thickness was ~150 nm. For laser processing, the samples were mounted on a holder attached to a translation stage. An ArF excimer laser (wavelength of 193 nm, pulse duration of 20 ns and a repetition rate of 50 Hz) was used for sample irradiation at ambient atmospheric conditions. The beam was focused on a rectangular aperture to establish the exposed area of the sample surface. The laser pulse fluence, E, was varied from 0.05 to 5 J/cm^2. The film properties were analyzed before and after laser treatment. Surface morphology was investigated by standard (Carl Zeiss, Axiotech 25 HD) and white light interferometric (Zygo, New View 5000) optical microscopes as well as scanning probe microscopes (NT-MDT, NTEGRA Solaris, Asylum MFP3D). We utilized a micro-Raman spectrometer (Jobin Yvon, LabRAM HR800) with an

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[*] Corresponding author.

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excitation wavelength of 488 nm to determine the type of carbon bonding present. The spatial uniformity of the film conductivity was measured with an Asylum atomic force microscope operated with a conductive diamond nanoprobe.

3. Results and discussion

We have found that at low laser fluence ($E = E_o \approx 0.05$ J/cm^2), which is below the nanoablation threshold for CNCD films, pulsed laser exposure can induce changes to the optical and electrical properties of the diamond film without evident crater formation. To observe such changes of material properties, multiple (pulse number $N > 10^4$) laser pulses are needed. Using an optical microscope, one can visually observe the difference in color of the irradiated regions of the sample (bright image on the left side in Fig. 1a) and the initial unprocessed regions of the film (right side in Fig. 1a). The corresponding atomic force microscope images of the film surface morphology prior to and after multiple pulsed laser irradiation exposures ($E_o \approx 0.05$ J/cm^2 and $N = 3 \cdot 10^4$ pulses) are presented in Fig. 1b. It is evident that the film surface shows a similar morphology before and after the laser irradiation. The size and distribution of nanoprotrusions and nanopores remain the same. Moreover, the average surface roughness does not change and equals to $R_a \approx 30$ nm. Therefore, we can conclude that laser induced variation of the CNCD film surface morphology, which can influence light scattering, is not responsible for the observed optical effect.

Raman spectra before and after laser treatment at $E = E_0$ are presented in Fig. 2. The different scans represent different regions on the sample. The silicon line from the substrate is clearly visible at 520 cm^{-1}, and all of the spectra have been normalized to the intensity of this line. Vibrational modes of sp^2 bonded carbon D (1360 cm^{-1}) and G (1590 cm^{-1}) and second order Raman features around 2700–2900 cm^{-1} are evident [16]. The broad background has been attributed to defect related luminescence [17]. The relative intensity and the shape of the carbon lines remain essentially unchanged, but the relative intensity decreases by about 50% after laser irradiation ($E = E_0$, $N = 3 \cdot 10^4$). The absolute intensity of the 520 cm^{-1} Si substrate signal increases by about 30% while the absolute intensity of the sp^2 related features decreases by about 30%. Consequently, the two effects contribute approximately equally to the observed relative change in the ratio of the silicon substrate line intensity, I_{si}, to that of the D and G peaks, $I_{D(G)}$. We note that both the bleaching and the strong decrease of the sp^2 signal after laser treatment, have occurred while the thickness of the film is essentially unchanged. Evidently, the decrease in the optically absorbing sp^2 bonded content can account for the film bleaching effect.

The differences in optical properties of the initial and laser treated films may be explained by the laser induced variation of carbon phases and their ratio [18]. There are two effects that could be considered: 1) surface oxidation, and 2) redistribution of the hydrogen in the film.

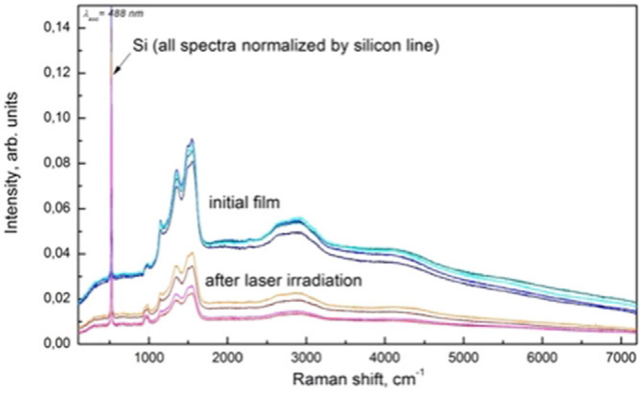

Fig. 2. Raman spectra of diamond film before and after laser irradiation. All spectra normalized to the 520 cm^{-1} silicon line.

First we estimate the surface temperature due to the laser pulse process. For a diamond film in ambient air, surface graphitization is known to occur at a temperature $T_g \approx 800$ °C. The fluence range employed in our experiments was varied from 0.05 through 5 J/cm^2, and the ablation rate was observed to decrease by more than 2 orders of magnitude at a fluence of $E \approx E_g \approx 0.3$ J/cm^2, which is typical for this change of the mechanism of the diamond film ablation [14]. High-rate ablation results from evaporation of a graphitized surface layer, and low-rate etching (nanoablation) is characterized by laser-induced oxidation of the initial material. Therefore, we can use this threshold value to estimate the surface temperature at $E = E_0$. We assume a linear relationship between temperature and laser power which assumes that the optical properties are constant in this range. Then the estimated temperature at $E = E_0$ is found to be $T_0 \approx T_g(E_0 / E_g) \approx 130$ °C. We note that this is a conservative but realistic approach since the optical absorption decreases slightly during the measurements. At this low temperature one would not expect significant film oxidation that could lead to the removal of a significant quantity of the film. Prior research has shown that low intensity pulsed illumination with UV radiation can induce oxidation of carbon nanodots [18] and of highly oriented pyrolytic graphite [19]. Consequently, the UV illumination can induce oxidation of small clusters or surface atoms of sp^2 bonded carbon. The optical properties of the structures can be changed and/or the reacted atoms can be chemically removed as CO or CO$_2$ from the surface and intergranular space. As a result fewer sp^2 bonded carbon atoms remain on the film surface. Considering the film porosity and the high optical absorption of the sp^2 phase, the low intensity UV illumination could account for the diamond film bleaching by oxidization of sp^2 clusters not only at the thin surface layer, but throughout the film thickness.

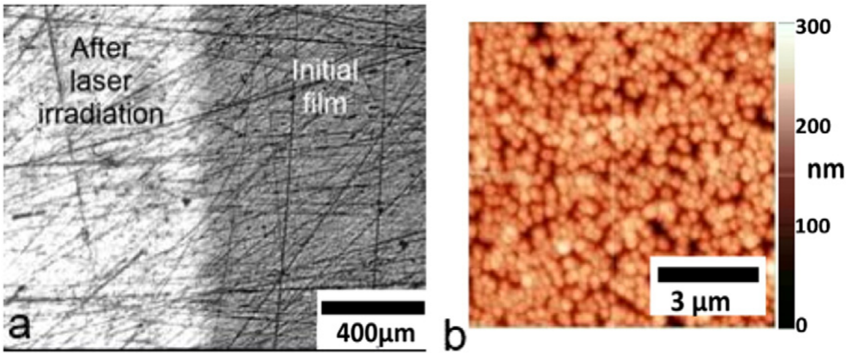

Fig. 1. Images of CNCD film from (a) an optical microscope and (b) an AFM. The left part of both images corresponds to the film after laser irradiation with a fluence of 0.05 J/cm^2 and $N = 3 \cdot 10^4$ pulses.