Realization and characterization of graphitic contacts on diamond by means of laser

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Abstract

This work deals with the realization and characterization of integrated graphitic contacts on diamond by means of laser irradiation (graphitization), in order to obtain good quality ohmic electrodes for nuclear radiation detectors to be used in high energy physics experiments. Unlike the conventional method used for the electrode production, which requires numerous steps and very well controlled environmental conditions, this alternative technique presents many advantages: the contacts are realized in air at room temperature in a single step. In this study, the characteristics of several graphitic structures realized on a diamond surface by changing the radiation-matter interaction parameters have been evaluated in order to define the best experimental conditions to create graphitic electrodes with low resistivity. The obtained results are promising: contacts perfectly adherent, with good charge collection properties, stable and resistant to ionizing radiation.

Introduction

Diamond is a widely investigated material due its unique properties. It has record values of hardness, thermal conductivity, and carrier mobility [1]. In addition, diamond is an excellent insulator, chemically inert, biocompatible, resistant to ionizing radiations, and transparent in the NUV, visible, IR and MW spectral regions. All these extraordinary properties together with the availability ty to have commercial CVD polycrystalline diamond films and substrates, pave the way to different innovative applications such as 2D dosimeters for advanced medical therapy, particle tracking, beam monitoring and luminosity measurement for high energy physics, neutron detection for nuclear physics, and bio and chemical sensors for applied physics.

Traditionally, diamond detectors are designed as solid-state ionization chambers in two main configurations: with electrodes front and back or interdigitated on the same surface [2]. When a charged particle or a photon with energy above the diamond bandgap (5.5 eV) passes through the material, it produces ionization and creates electrons-hole pairs. The generated charge carriers are separated by an electric field applied through the electrodes and collected by them using an external circuit which makes possible to reveal the photoconductive current.

The first step to obtain a good diamond detector is the realization of electrical contacts that should be simultaneously ohmic, stable, perfectly adherent, reproducible, and also resistant to ionizing radiations and with a good charge injection. The conventional technique to fabricate electric contacts on diamond is by metal layers deposition, consisting in many complex process steps: surface cleaning, carbide formation (with Cr or Ti), thermal annealing, metal contact layer deposition (with Au or W), strip and pixel patterning with mask or lithography. Here we report on an alternative technique, which allows to realize ohmic contacts in a single process step: the laser-induced graphitization of diamond.

When an UV laser beam impinges on the diamond surface, it induces a localized heating of the material due to electrons thermalization, which can allow to overcome the potential barrier of the diamond-graphite transition at T>Tg≈700°C in air [1]. As a result, irradiating the diamond surface with a single shot having enough fluence permits to induce a local graphitization causing a bump on the surface profile due to the density difference between diamond and graphite ($\rho_{diamond}$=3.5 g/cm^3, $\rho_{graphite}$=1.9 g/cm^3), as schematically shown in Figure 1. If the laser fluence is sufficiently large, a part of the graphite material can even heat up to the sublimation temperature (T_S=4000°C) and ablate away, giving rise to the formation of a crater in the irradiation zone.

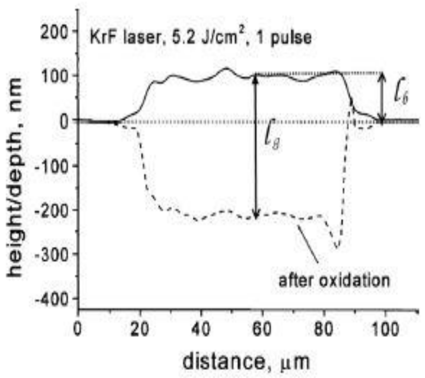

Figure 1: Lateral profile of a diamond film irradiated by a single excimer laser pulse: the continuous line represents the swelling (bump) due to local graphitization induced by the concentrated laser beam energy, the dashed line shows the depletion (crater) after an oxidation reaction (the Figure is taken courtesy from [1], [4]).

In this study, the characteristics of several graphitic structures realized on a diamond surface by changing the radiation-matter interaction parameters have been evaluated in order to define the best experimental conditions to create low resistive graphitic electrodes. The realized graphitic structures have been characterized by morphological, structural and electrical investigations.

Experimental set-up

The surface of a “thermal grade” CVD polycrystalline diamond sample has been irradiated by means of an ArF excimer laser beam (Lambda Physik LPX305i, λ=193 nm), with 20 ns long pulses, 10 Hz repetition rate and 20×10 mm^2 initial beam transverse size. The experimental set-up [3] included also an attenuator to modulate the pulse energy, and an optical system, composed of a circular diaphragm with variable aperture and a 15×UV objective lens.

The CVD diamond sample, with dimensions 10×10×0.25 mm^3, was placed on a holder, which was fixed to a x-y handling stage controlled by two 1D step motors with micrometric resolution, in order to produce the wanted graphitic structures. The sample was laser irradiated in air and at room temperature.

In order to study the physical evolution of the graphite phase and search for the best parameters to create electrical contacts, we realized two different geometries of graphite structures: (i) spots with different number of laser pulses (N=1, 2, 4, 8, 25, 40, 50 and 100) and variable laser fluence (F=2, 5 and 7 J/cm^2), and (ii) strips with several up-and-down laser scan cycles (C=1/2 (only one laser scan), 1, 2, 6, 8, 10 and 12) and changeable laser fluence (F=2, 3, 5 and 7 J/cm^2). Both graphitic structures were characterized by means of Micro-Raman Spectroscopy, Atomic Force Microscope, and electrical measurements to obtain structural, morphological and electrical information, respectively.

In particular, for micro-Raman Spectroscopy a Renishaw InVia Raman Microscope was employed. An Ar+ laser (λ=514.5 nm) was focused by a 50× optical objective (Leica, Germany) to a spot of 1 µm diameter on the sample surface; the backscattered light was collected by the same objective and analyzed by a microscope equipped with a holographic Notch filter (cut-off at 100 cm^{-1}), a 1800 lines/mm diffraction grating and a thermoelectrically cooled RenCam CCD detector. The resolution was 0.5 cm^{-1} in the wavenumber range from 100 to 8000 cm^{-1}. Raman spectra were taken in the center of every graphitic structure.

For the morphological investigation an Atomic Force Microscopy (AFM)Park System Xe-70 AFM in non-contact mode was used, using a tip of silicon nitride with radius of curvature <10 nm. The scans were performed on 20x20 μm^2 areas at a frequency of 0.6 Hz, obtaining 3D images with subnanometric resolution.

The resistivity of the graphitic strips was evaluated employing a method based on the Transmission Line Model (TLM), which makes use of a series of contacts with increasing separation d to evaluate the dependency of the total resistance R_T on the distance d and hence the resistivity. The contacts were performed by using two probes with tungsten tips of 40 µm in diameter hooked to two micromanipulators for handling long 3D. The voltage was applied by the DC source (Yokogawa 7651 programmable DC source) while the current, amplified by the preamplifier (FEMTO, model DLCPA -200), was recorded with a digital multimeter (Agilent HP34410). The data allowed us to verify theand the low resistivity of the graphitic structures.

Results and discussion

A preliminary series of investigations with a digital microscope, later confirmed by Micro-Raman analysis and nanometer scale microscopy, allowed to prove that graphitic structures realized with laser fluence lower than 3 J/cm^2 and with a low number of laser pulses for spot are quite not homogenous with clear evidence that the irradiated area did not undergo graphitization. Instead, rather uniform graphitic structures over the whole irradiated area were induced with laser fluence values of 5 and 7 J/cm^2 also with a low number of pulses (including one single spot). For this reason, these last values were employed to make the graphitic test structures discussed in this work. More precisely, we made *spot graphitic structures* with a limited number of laser pulses N=1, 2, 4 and 8, to circumscribe the ablation effect, and *strip graphitic structures* (length equal to 1 mm) with 6 and 8, up-and-down laser scan cycles (C) to have defined strip boundaries. Several Raman spectra, acquired on CVD diamond samples, are discussed in the literature in which the broad peak at 1580cm^{-1} (G peak) is associated to the graphite impurity (allotropic forms of carbon), and the sharp peak at 1332 cm^{-1} (d peak) to the diamond real phase [5]. The ratio between the intensities of the two peaks indicates how much of each carbon phase is present onthe surface. For completeness, it is worth mentioning that the graphite presence is also accompanied by the occurrence of two other features of disorderly graphite: the peaks at 1350 cm^{-1} (D peak) and at 2700 cm^{-1} (2D peak). The micro-Raman spectra of all the spot test structures made with N=1 pulse and a fluence of F=5 and 7 J/cm^2 displayed only the graphite phase without evidence of any diamond phase, while the d peak is clearly present for lower laser fluences. This means that in our experimental conditions the laser fluence threshold to create a bump of graphite, at least thick as the micro-Raman sampling depth (50 nm for λ=514.5 nm), is of 5 J/cm^2. Moreover, in the case of diamond irradiation with only one pulse (N=1), the G peak intensity increased with the fluence, indicating more presence of graphite. For the spots realized with N=2 pulses and a fluence of F=7 J/cm^2 in addition to the D and G peaks also the d peak appeared, which was not visible for fluence of F=5 J/cm^2. We concluded that for N=2 pulses and at the fluence of F=7 J/cm^2 the ablation phenomena began to be in competition with the graphitization phenomenon. Similarly analysis were made for the strip test structures and only the ones created with a fluence of F=7 J/cm^2 and C=6 up-and-down scans had the graphite component without any diamond phase, this is the ideal condition for a good electrical contact.

In order to better characterize the laser induced structures, the height (and depth) of the spot test structures with respect to the diamond flat surface, assumed as reference level, were measured by AFM. In particular, we considered the structures realized at the fixed fluence value F=5 J/cm^2, but with a variable number of pulses (N=1, 2, 4 and 8) to study the evolution from the graphitization to the ablation phenomena. Figure 2 shows the evolution of the average spot height as a function of the number of pulses, which turns out to be positive for N=1 and 2 and negative for N=4 and 8 (crater formation). This is in agreement with the previous investigation with micro-Raman spectra. The trend is almost linear and this is in agreement literature data [1].

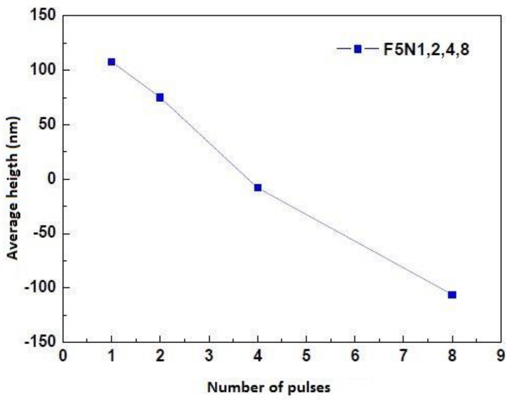

Figure 2: Trend of the average graphitic structure heights for spots realized at a fixed of fluence F=5 J/cm^2 with respect to the number of pulses N=1, 2, 4 and 8.

Moreover, in order to determine the resistivity of the graphitic structures, the thickness of the laser induced structures has been estimated. Knowing the average height l_b (bump height) with respect to the not irradiated diamond surface, and measuring, by AFM, the depth l_h (hole depth) of the graphitized structures (Fig. 1) it is possible to determine the thickness l_g according to the relation:

$$l_g = |l_b| + |l_h| (1),$$

where the length values are negative if they correspond to surfaces lower than the reference one (for this reason we consider their modules). To measure l_h an annealing treatment in air at 600 °C for 150 min was performed, in order to remove the graphitic layers by means of oxidation reaction [1]. The estimated thickness values for the graphitic strips are reported in Table 1.

Table 1: Value of the length (l), width (w), thickness (t) and resistivity (ρ) of graphitic strip structures realized at different irradiation fluencies (F=5 and 7 J/cm^2) and laser up-and-down scans (C=6 and 8).

Strip	l (cm)	w (cm)	t (cm)	ρ (Ω*cm)
F=5,C=6	1 E-01	30 E-04	1.81 E-05	7.5 E-03
F=5,C=8	1 E-01	30 E-04	1.7 E-05	9 E-03
F=7,C=6	1 E-01	40 E-04	1.69 E-05	4.0 E-03
F=7,C=8	1 E-01	40 E-04	2.26 E-05	5.5 E-03

The thickness estimated for the graphitic spots obtained with N=1 can be compared with the theoretical prediction described by Konov [1]:

$$l_g = \frac{\rho_d}{\rho_d - \rho_g} l_b (2).$$

For the spots realized with only one pulse (N=1) at the laser fluences F=5 and 7 J/cm^2 the measured experimental values of the graphitic layer thickness are (181±7)nm and (210±16)nm, respectively, in reasonable agreement with the theoretical calculated values. Figure 3a and 3b report the AFM pictures of the graphitic strip structure realized at fluence of F=7 J/cm^2 and laser up-and-down scans C=8 before and after thermal annealing respectively.

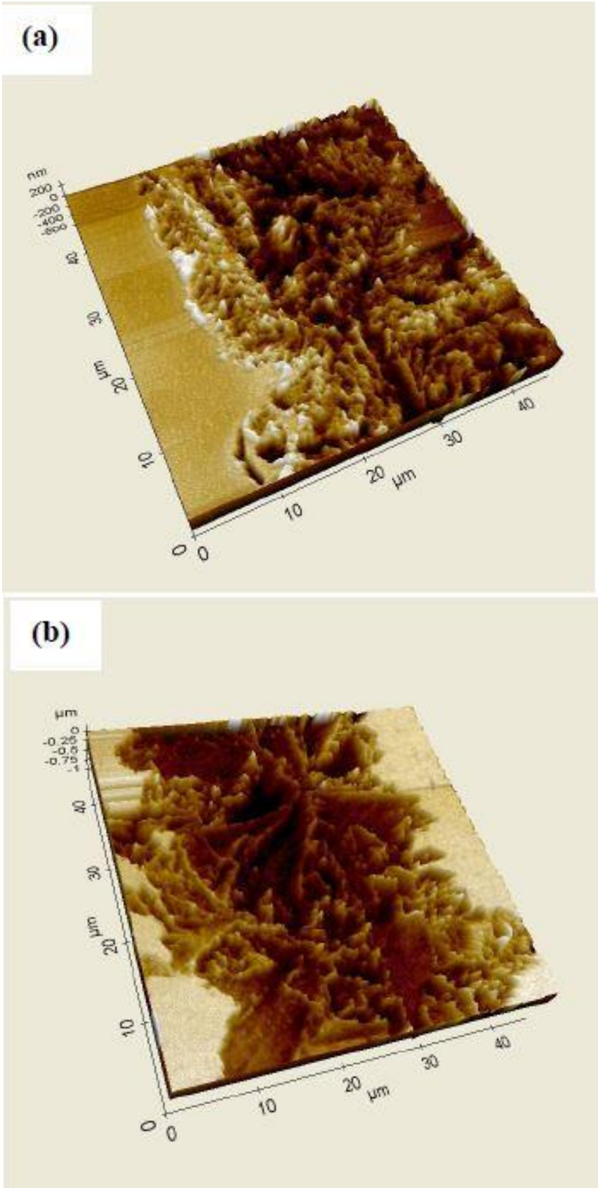

Figure 3: AFM images of the graphitic strip structure realized at fluence of F=7 J/cm^2 and laser up-and-down scans C=8 before (a) and after (b) the thermal annealing.

Finally, the ohmic nature of the graphitic strips was verified by the linearity of the measured I-V curves, while their resistivity has been determined by means of the Transmission Line Model (TLM) [6], measuring the resistance among contacts placed at an increasing distance d along the strip. This approach allows to remove the series resistance R_C of the probe electric contact and estimate the electrical resistivity ρ from the formula:

$$R_T = 2R_C + \frac{\rho}{tw} d (3),$$

where R_T is the total resistance, R_C is the resistance of the probe contact, ρ, t and w are the resistivity, the thickness and the width of the graphite strip, respectively, and d the distance between probe tips. By plotting R_T as a function of the distance d, the resistivity of the graphitic strips was evaluated by the slope of a linear fit based on equation (3). A good linearity of resistance dependence on contact separations was always found, confirming the goodness and homogeneity of the graphitization process.
The estimated resistivity values are reported in Table 1 and the results are consistent with the one expected for graphite $\rho=10^{-3}$-$10^{-4}\Omega\times$cm. In particular, the strip structure realized at fluence of F=7 J/cm^2 and laser up-and-down scans C=6 is characterized by $\rho=(4.0\pm0.8)10^{-3}\Omega\times$cm, in good agreement with values reported in the literature [1], [3], [7].

Conclusions

The feasibility of the fabrication technique of ohmic contacts on "detector grade" CVD diamond by means of laser graphitization has been demonstrated in recent years by our group. The first particle detector realized with this technique has been successfully tested with particle beams. Here a methodology has been developed to characterize extensively the diamond-graphite contacts through micro-Raman, AFM and TLM investigations, in order to put on solid bases the earlier pioneering results. We applied the methodology to several test graphitic structures, such as spots and strips, characterizing them structurally, morphologically and electrically. The physical evolution of the diamond to graphite transformation has been determined as a function of laser fluence, number of pulses and number of up-and-down scanning cycles. The comparison between theoretical predictions and experimental measurements for spots realized with one laser pulse (the only case where predictions were available) was satisfactory. In addition, the graphitic layer thickness and electric resistance were measured, obtaining values for the electrical resistivity consistent with natural graphite.

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