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

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We have worked on 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. When an UV laser beam impinges on the diamond surface with a single shot having enough fluence it induce a local graphitization ($T > T_g \sim 700^oC$) causing a bump on the surface profile due to the density difference between diamond and graphite (ρ_{diamond}=3.5 g/cm^3, $\rho_{\text{graphite}} = 1.9\, g/cm^3$), 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 ($T_S = 4000^oC$) and ablate away, giving rise to the formation of a crater in the irradiation zone.

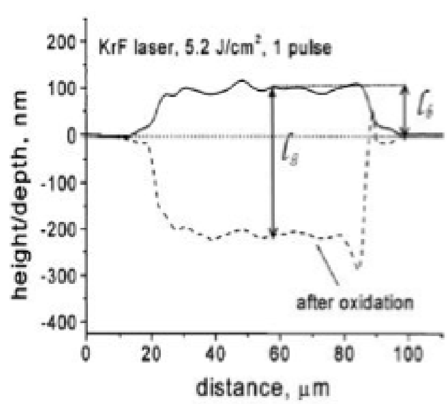

Figure 1. Lateral profile of a diamond film irradiated by a single excimer laser pulse: the continuous line represents the swelling (bump) while the dashed line shows the depletion (crater) after an oxidation reaction (the Figure is taken courtesy from [1]).

In our 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.

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 [2] 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 $10{\times}10{\times}0.25$ 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.

Experimentally we have realized two different geometries of graphite structures: (i) spots with different number of laser pulses and variable laser fluence, and (ii) strips with several up-and-down laser scan cycles and changeable laser fluence. A preliminary series of investigations with a digital microscope have allowed us to discriminate the graphitic structures of most interest to the set objectives. More precisely, we have selected *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 strips. All the selected graphitic structures have been realized at the fluence of 5 and 7 J/cm^2.

The graphitic structures have been characterized by means of micro-Raman Spectroscopy using an InVia Raman Microscope with an Ar+ laser (λ=514.5 nm) for the structural information, then with an Atomic Force Microscopy (AFM) Park System Xe-70 AFM in non-contact mode for the morphological investigations, and finally by means of a method based on the Transmission Line Model (TLM) for the electrical measurements.

The first result is about the micro-Raman spectra of the spot test structures made with N=1 pulse and a fluence of F=5 and 7 J/cm^2: we have obtained only the graphite phase (peak at 1580cm^{-1}) without evidence of any diamond phase (peak at 1332 cm^{-1}), while the latter 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 graphite 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 two graphite peaks (1580cm^{-1} and 1350 cm^{-1}) also the diamond peak appeared, which was not visible for fluence of F=5 J/cm^2. We have 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.

Subsequently the height (and depth) of the spot test structures were measured by AFM. In particular, we have considered the structures realized at the fixed fluence value F=5 J/cm2, 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), respect to the diamond flat surface assumed as reference level. This is in agreement with the previous investigation with micro-Raman spectra. The trend is almost linear and this is in agreement literature with the data [1].

Moreover, in order to determine the resistivity of the graphitic structures, the thickness of

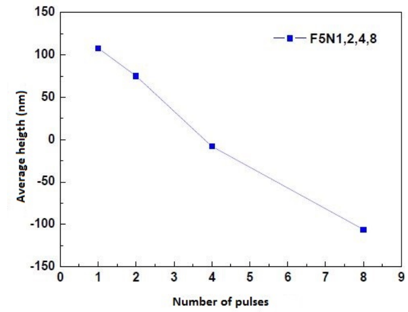

Figure 2. Trend of the average graphitic structure heights for spots realized at a fixed of fluence F=5 J/cm^2 with respect to the number of pulses N=1, 2, 4 and 8.

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 lg according to the relation:

$$l_g = |l_b| + |l_h| \ , \tag{1}$$

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^{o}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 Fig. 3.

Strisce	R_P (Ω/cm)	t (cm)	w (cm)	ρ (Ω*cm)
F5C6	1,38E+05	1,81 E-05	30 E-04	7,5 E-03
F5C8	1,63E+05	1,7 E-05	30 E-04	9 E–03
F7C6	0,590 E+05	1,69 E-05	40 E-04	4,0 E–03
F7C8	0,63 E+05	2,26 E-05	40 E-04	5,5 E-03

Figure 3. 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).

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

$$l_g = \frac{\rho_d}{\rho_d - \rho_g} l_b \tag{2}$$

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 values [1]. In Figure 4 we show the example of AFM pictures of the graphitic strip structure before and after thermal annealing.

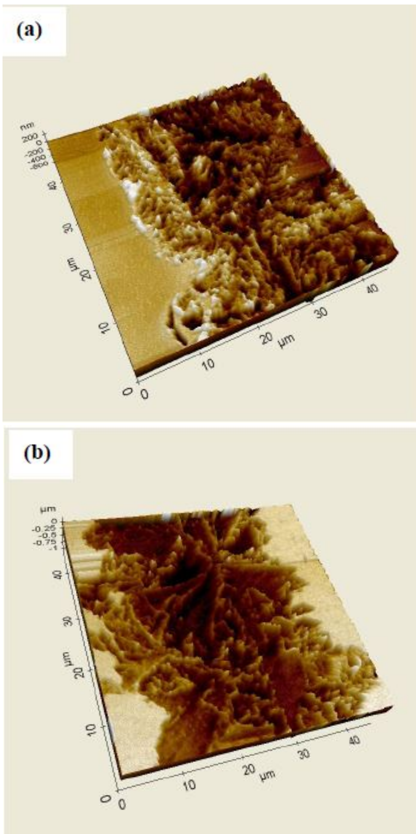

Figure 4. AFM images of the graphitic strip structure realized at fluence of F=7 J/cm^2 and laser up-and-down scans C=8 before (a) and after (b) the thermal annealing.

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). The estimated resistivity ρ values, are reported in Fig. 3 and the results are consistent with those expected for graphite $\rho = 10^{-3} - 10^{-4}\,\Omega$ 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 $\rho = (4.0 \pm 0.8) \times 10^{-3}\,\Omega$ cm, in good agreement with values reported in the literature [1,2].

Therefore, in this work 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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