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Graphitization wave in diamond induced by uniformly moving laser focus

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Laser beam tightly focused inside single-crystal diamond allows conducive microstructures to be fabricated via local phase transition of diamond to graphite. An extended modified region is formed in diamond due to propagation of so called laser-induced graphitization wave, which occurs immediately after the optical breakdown and propagates towards the laser beam even though the position of the laser focus is fixed. This paper is the first to consider the behavior of the graphitization wave when the laser focus uniformly moves towards the laser, which results in the formation of conductive wires of unlimited length in diamond. It has been found that there is an initial transitional period in the wire growth, during which velocities of the laser focus and the wire front are equalized owing to the change in the distance between them. After stabilization of the graphitization front velocity, the axial fluence at the front of the growing wire also reaches a constant value. It has been found that the stable laser fluence at the wire front is practically independent of the laser pulse energy, but it grows with increasing velocity of the laser focus. Such increase finally leads to violation of the physical criterion of the continuous wire growth, since the axial fluence at the wire front becomes higher than the diamond breakdown threshold. It has been shown that the minimal fluence providing propagation of the graphitization wave in diamond can be used to predict the lateral wire dimension.

1. Introduction

Diamond has a number of unique properties, such as a high mechanical hardness, wide band gap, high thermal conductivity, radiation resistance, optical transparence in a wide spectral range (from UV to MW), and high charge carrier mobility [1,2]. Laser-induced transformation of diamond into the sp^2 phase is another remarkable property of diamond [2]. Specifically, laser radiation tightly focused on the face of a diamond crystal causes the formation of a thin uniform layer of nanocrystalline graphite on the diamond surface [2,3]. On the other hand, owing to the high transparency of diamond, laser radiation can be focused inside the diamond crystal at an arbitrary depth, and the phase transition occurs about the focal plane at a sufficient laser fluence [4]. If the laser focus is translated through the crystal, a conductive region of an unlimited length can be formed inside the dielectric [5]. The techniques of laser microstructuring of bulk diamond developed to date allow obtaining modified regions of various shapes ranging from wires to complex 3D microstructures [5–9]. Most attention is currently paid to wire-shaped laser-induced microstructures, the interest in which is stimulated by the challenging issue of designing 3D diamond detectors of radiation [6,7,9–18], photonic crystals [9,19], solar cells [20], and waveguides [21].

Optical breakdown induced inside a diamond crystal by short laser pulses above a certain fluence threshold (F_{opt}) due to diamond ionization and nonlinear light absorption is accompanied by local phase transition [4]. As a result, a highly absorptive seed of sp^2 carbon is formed inside diamond and then isotropically grows during several subsequent laser pulses until its size becomes comparable with the beam waist diameter [2]. The following pulses initiate phase transition in the adjacent diamond layer, which leads to formation of a continuous wire-like modified region extending towards the laser beam. As the modified region front moves away of the focus, the fluence at the front gradually decreases. The graphitized region grows until the fluence at its front reaches a certain limit (F_{gr}), which is considerably lower than the diamond breakdown threshold [4]. This spontaneous extension of the continuous modified region, occurring as long as the fluence (F) at its front satisfies the condition $F_{gr} \leq F < F_{opt}$, is referred to as a

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laser-induced graphitization wave [22]. If the focal plane is moved through the crystal towards the laser, the graphitization wave can unlimitedly propagate in diamond. This propagation of the graphitization wave is generally used for fabrication of graphitized wire-shaped microstructures in diamond.

The formation of the conductive graphitized wires inside diamond has been observed at various processing parameters, including laser wavelength (from UV to MW), pulse duration (from femtoseconds to nanoseconds), pulse energy, and laser focus velocity [5–7,9,11,14,19]. The last two parameters are usually optimized to improve the morphological and conductive characteristics of the graphitized wires. For instance, at low laser focus velocities and high pulse energies, the wires become split into several thin filaments, which leads to a lower wire conductivity [5,9]. On the other hand, when laser focus velocity exceeds some threshold, the formation of broken wires is observed, which indicates that the continuous propagation of the graphitization wave becomes impossible [9]. The physical mechanism of these experimental effects still remains unclear. Moreover, the relationship between the processing parameters and specifics of laser-induced wave propagation under the moving laser focus conditions has been never studied before. This also applies to another important parameter, laser energy distribution at the front of the graphitization wave, which influences both the graphitization wave velocity [22] and characteristics of structural transformations at the wave front.

Here, in order to study the behavior of the graphitization wave in the case of the moving laser focus, we obtained a set of laser-induced wires inside diamond at different pulse energies and laser focus velocities. Two parameters of the graphitization wave, the front velocity and the laser fluence at the wave front, were determined. In addition, we estimated the relationship between the wire diameter and the laser energy profile at its front.

2. Experiments

The experiments were performed with a 1.1 × 1.2 × 5 mm single-crystal CVD diamond sample purchased from Innovative Plasma Systems GmbH. An amplified mode-locked Ti:sapphire laser (Spectra Physics) with a repetition rate of 1 kHz generating 140-fs pulses at a wavelength of $\lambda = 800$ nm was used as a laser source. The laser beam focused by an aspheric lens (NA = 0.09) was perpendicular to the (1 0 0) face of the sample mounted on an XYZ translation table (Fig. 1) The Gaussian radius of the laser spot (at an intensity of $1/e^2$) was evaluated as $\omega_0 = 2.5$ µm on the basis of imprints made at different pulse energies on the metal-coated glass target. In the experiment, a 20× objective lens was set perpendicular to the laser beam for observing the process of diamond microstructuring, which was recorded by means of a CCD camera (Fig. 1). The video records were used for measuring the velocity of the wire front.

A set of laser-induced wires was formed inside the diamond crystal at different pulse energies ($E = 98$–331 nJ) in the following way. Laser radiation was initially focused far behind the rear side of the crystal, so as to cause the optical breakdown precisely at the rear side of the crystal. Then, the sample was moved along the beam (the Z axis) away from the laser at a constant velocity ($v = 1$–30 µm/s). Note that the velocity of the laser focus movement inside diamond (v_f) exceeds that of the sample scanning by a factor of 2.4 owing to the high refractive index of diamond (n = 2.4). Below, we will consider only the velocity of the laser focus movement in the diamond sample.

As the sample uniformly moved away of the laser, the laser focus came closer to the rear side of the sample, with the fluence at the rear side gradually growing until it reached the threshold for diamond optical breakdown. Then, the optical breakdown occurred precisely at the rear side of the crystal and an extended graphitized region began to grow towards the laser. A typical dependence of the velocity of the growing wire front on its length is shown in Fig. 2. Immediately after the diamond breakdown, the velocity of the wire front exceeds that of the laser focus. There is an initial transitional period during which the wire front velocity decreases until it becomes comparable with v_f. After that, the front velocity of the growing wire only slightly fluctuates around the stable level, which is equal to v_f. The mechanism of the velocity equalization will be discussed in detail in 3.

Equalization of the velocities means that the laser focus and wire front move synchronously now; i.e., the distance between them remains constant during subsequent wire growth. In order to determine this distance, we turned off the laser radiation and simultaneously shut off the sample scanning, which caused practically immediate stopping of the wire growth. Thus, we fixed the spatial positions of both the modification front and the laser focus inside the diamond. The system of visualization used in our experiment allowed us to determine the final position of the wire front which corresponds to the right edge of the wire in Fig. 3. In order to determine the position of the laser focus at the moment of the process stop the following procedure was conducted. We shifted the crystal at ~10 µm perpendicularly to the laser beam (along the Y axis). Then, keeping the laser focus fixed, we irradiated the

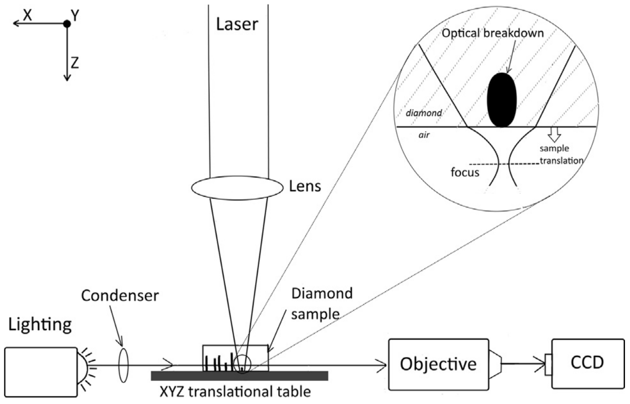

Fig. 1. A schematic of the experimental setup used for microstructuring of diamond sample. The inset shows the moment of the optical breakdown at the rear side of the diamond crystal in more detail.

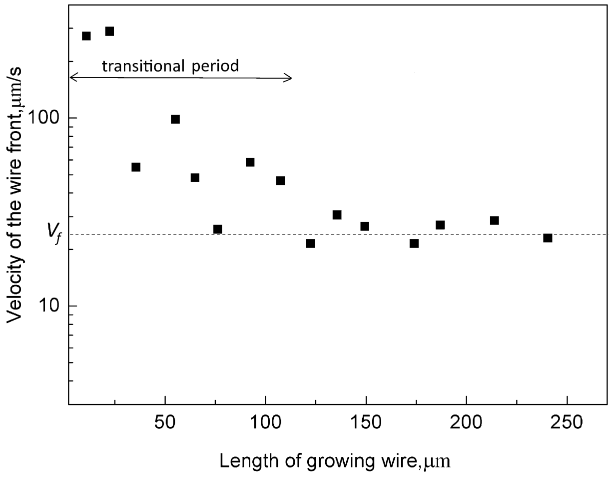

Fig. 2. Dependence of the velocity of the growing wire front on its length (E = 331 nJ, $v_f = 24$ µm/s).