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Laser-assisted etching of diamonds in air and in liquid media

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Abstract. Etching with the help of a copper vapor laser (wavelength of 510 nm, pulse duration of 10 ns, pulse repetition rate of 8 kHz) of both synthetic diamond single crystals (HPHT) and diamond polycrystalline CVD films is studied in various surrounding media (air, H_2O, $(CH_3)_2SO$). Diamond samples are virtually transparent at this wavelength, and the coupling of laser radiation to diamond is via the formation of a thin graphitized layer at the diamond surface. The etching rate in liquid media is slightly higher than in air at otherwise equal conditions and is as high as $50\,\mu m/s$ for etching with a scanning laser beam. Raman spectra measurements carried out on diamond samples etched in air show the presence of glassy carbon on the surface, whereas for samples etched in a liquid the diamond peak at $1332\,cm^{-1}$ dominates with significantly lower intensity of the glassy carbon peak. Electroless copper deposition on the laser-etched features is studied to compare the catalytic activity of the diamond surface etched in air with that etched in liquids. Possible mechanisms responsible for the observed difference both in the structure of the etched area and in the electroless Cu deposition onto the surface etched in various media (air or liquids) are discussed.

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The use of diamond in electronic devices and sensors requires the elaboration of flexible techniques for the treatment of the diamond surface. This includes polishing, etching, and metallization of diamond surfaces, and laser treatment of diamond has been shown to be a versatile tool [1]. In particular, laser ablation of diamond surfaces is a good technique for etching, polishing, and activation for electroless metal plating. Laser ablation of diamond is accompanied by structural modification of the diamond, implying that a thin graphitized layer is formed at the diamond surface and around the ablated area. This layer can be eventually removed by 'laser cleaning'; that is, the irradiation of the graphitized surface in air at relatively low laser fluence [2]. Following this procedure, however, the ablated areas of diamond still contain significant amounts of glassy carbon. The presence of the graphitized layer on the laser-ablated diamond surface inexorably affects its properties, such as conductivity, hardness, etc. Moreover, the electroless metal deposition on the laser-ablated areas results in a 'metal–graphite' rather than a 'metal–diamond' interface [3, 4]. The purpose of this work is to compare the process of laser ablation (etching) of the diamond surface in various environments, such as air or liquids. Raman spectroscopy is used as a method sensitive to different types of carbon phases. It is shown that the laser-assisted etching of a diamond surface under a layer of liquid results in the formation of a 'clean' diamond surface containing almost no graphitic layer.

1 Experimental

Synthetic dielectric diamond crystals of 1 mm thickness and CVD diamond films (on Si substrates or free-standing) were used in the experiments. The method of diamond synthesis under high pressure and high temperature, and the properties of the crystals are described elsewhere [5]. Diamond films of 50–200 μm thickness were grown on Si substrates by dc arc discharge or a microwave plasma CVD technique. The substrate was subsequently etched, which resulted in the free-standing diamond films. The etching of the diamond surface was carried out in air with the help of a copper vapor laser (wavelength of 510 nm, repetition rate of 8 kHz, pulse duration of 10 ns). The laser radiation was focused on the diamond surface with the help of a microobjective into a 20 μm spot. For the laser etching of the diamond surface under liquid layer, the diamond samples were placed in a horizontal Teflon cell filled with the liquid, either distilled H_2O or dimethylsulphoxide $(CH_3)_2SO$ (DMSO). The thickness of the liquid above the diamond surface was typically about 1 mm. The diamond samples were placed on a computer-driven X-Y stage, permitting us to displace them under the laser beam with a scanning velocity ranging from 30 to 3000 μm/s. Raman spectra of the etched surface were recorded with the help of a cw Ar^+ ion laser at a wavelength of 514 nm. Electroless deposition of Cu was carried out on the etched areas by using a standard solution with formaldehyde as the reducing agent [6].

2 Results

A typical image of a diamond surface etched under a liquid layer is shown in Fig. 1. Typically, an air-etched diamond surface is covered by a layer of glassy carbon [2], whereas the liquid-etched diamond surface appears free of graphite, and no sputtered material around the etched areas is observed. This is confirmed by the difference in the conductivities of the etched areas: neither a liquid-etched (LE) surface, nor a virgin diamond surface, is conductive, whereas an air-etched (AE) diamond surface conducts well.

Raman spectra of AE and LE diamond surfaces are shown in Fig. 2, for which the etching was performed on the same face of a single diamond crystal. Note the absence of the diamond peak at 1332 cm^{-1} in the spectrum of the AE surface (graph 1), though the peak is well pronounced in the spectrum of the LE diamond surface (graph 2). The difference in the intensities of the Raman signals (from diamond and glassy carbon) means it would not be correct to compare the spectra in Fig. 2, since a much weaker signal from glassy carbon may be lost in the spectrum presented in graph 2. This is actually the case if both spectra are compared at the same intensity scale, and the weak graphitic band at 1580 cm^{-1} is observed in the spectrum of the LE diamond surface. The integral intensity of the graphitic band of the LE surface is about three times less than that of the AE surface. This, however, does not mean that the observed ratio of the integral intensities is a direct measure of the thickness of the graphitized layer formed under liquid or air etching, as only a top graphitic layer on the AE surface, completely absorbing the excitation light, could contribute to the Raman signal. Thus we can conclude that an ’almost clean’ diamond surface is formed by laser etching in liquid, keeping necessarily in mind that the laser-induced graphitic layer at the LE surface is at least three times thinner than that at the AE surface, which, in turn, promotes the low absorption of the excitation light at 514.5 nm and gives rise to a Raman spectrum characteristic of pure diamond.

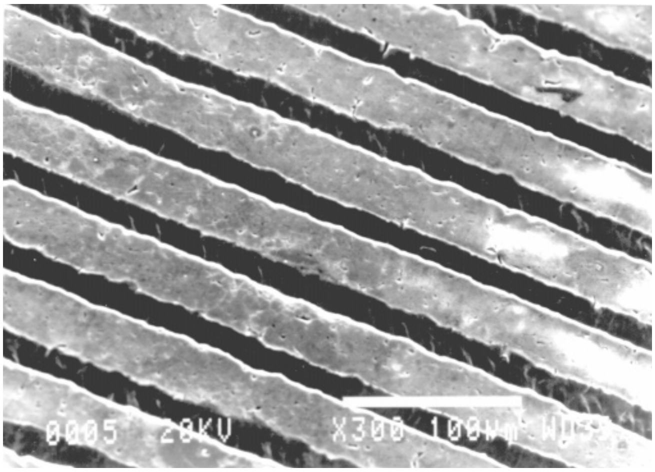

Fig. 1. Typical SEM view of a diamond surface etched under a layer of H_2O

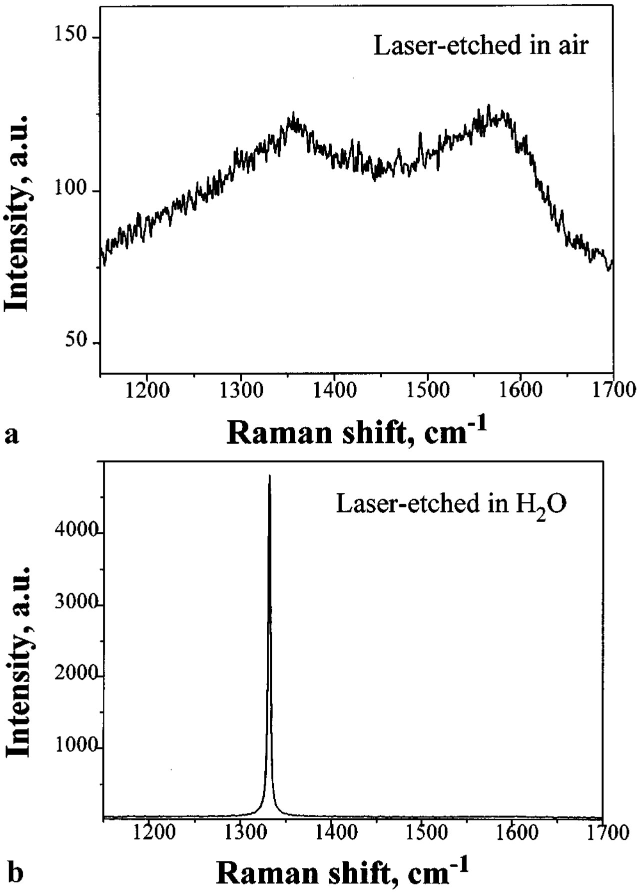

Fig. 2. Raman spectra of a diamond surface etched in air (1) and under a liquid layer (2)

The laser fluence required to start the etching of a diamond surface under a liquid is several times higher than that required for the etching in air. Or, the activation time of the etching of the diamond in liquid is several times higher than the activation time for etching in air under the same laser fluence. For instance, the delay in the etching of a diamond surface under a water layer is about several seconds at a laser fluence of 0.7 $\mathrm{J/cm}^2$, whereas for the etching of diamond in air the delay is less than 0.2 s. Once the etching has started, its rate is almost independent of the surrounding medium. Figure 3 shows the dependence of the groove depth on the scanning velocity of the laser beam. One can see that the etching rate in liquids is slightly higher than that in air. For a laser fluence of 18 $\mathrm{J/cm}^2$, the etching rate is as high as 50 $\mu\mathrm{m/s}$ at low scanning velocities, which corresponds to $\sim$ 600 Å per laser pulse. At higher scanning velocities, the etching rate in DMSO is about 0.1 μm per laser pulse, whereas in air the rate is twice as low. The decrease in the etching rate with depth can be explained by defocusing of the laser beam and by the change in the angle of incidence of the laser radiation in the relatively deep groove.

A diamond surface etched in air and then irradiated under a liquid layer is also free of the graphitic layer. Moreover, the areas with removed graphite are larger than the laser spot,

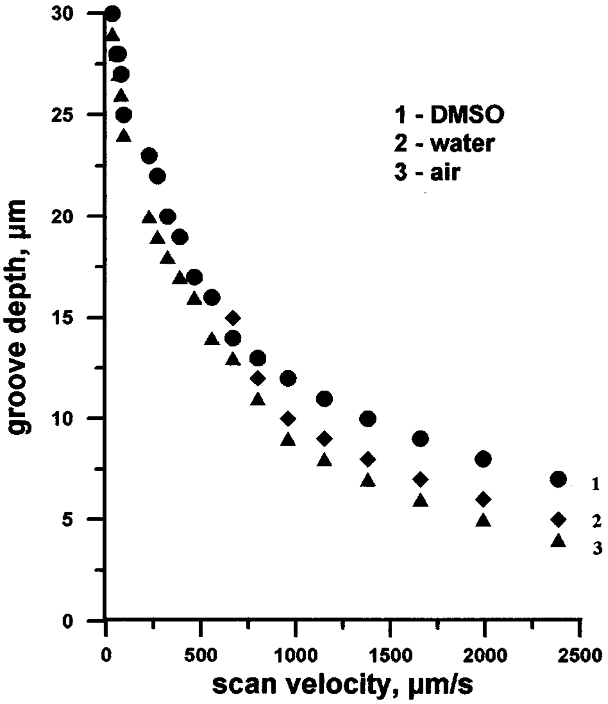

Fig. 3. Dependence of the groove depth etched in a CVD diamond film versus the scanning velocity of the laser beam. Surrounding medium: DMSO (1), H_2O (2), air (3). Laser spot size of 20 µm, laser fluence of 18.6 J/cm^2

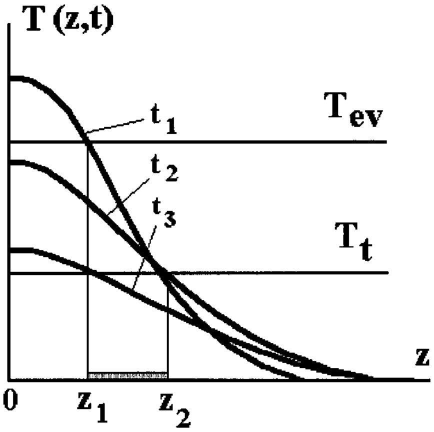

Fig. 4. Temperature distribution $T(z, t)$ for various moments in time $t_3 > t_2 > t_1$. T_{ev} and T_t are the temperatures of the graphite evaporation and diamond–graphite transition, respectively. $z = 0$ is the diamond surface before the laser pulse. The possible effect of surface cooling due to the evaporation is neglected

depending on the scanning velocity of the laser beam and laser fluence.

Electroless Cu deposition on a diamond surface etched under a liquid layer proceeds faster than on one etched in air. Typically, the deposition starts on LE features 40 min after the sample is dipped into the electroless solution at ambient temperature. The first traces of Cu deposition on AE features appear in 1 hour. This indicates a higher density of catalytic centers exposed to the electroless solution in LE samples. Also, AE features are surrounded by a significant amount of sputtered graphitic material, and electroless copper deposition proceeds on the sputtered material as well as in the etched areas.

3 Discussion

Let us consider the process of laser ablation of diamond in air with a series of laser pulses. The distribution of the temperature T for various moments in time $t_3 > t_2 > t_1$ is shown schematically in Fig. 4. Here T_{ev} is the temperature of graphite evaporation (about 4000 °C), and T_t is the temperature of the diamond–graphite phase transition (about 1500 °C). One may suggest that the graphitic layer will be evaporated to z_1 and the diamond will be transformed into graphite to z_2. So $\Delta z = z_2 - z_1$ is the thickness of the graphitic layer on the diamond surface left after the laser pulse. For a given value of laser fluence, the steady-state value of Δz can be found from the balance between the formation and evaporation of the graphitic film. Since $T_{ev} > T_t$, the graphitic layer remains on the diamond surface even for shortest laser pulse duration. $T(z, t)$ can be found from the heat diffusion equation, which is coupled to the equation of the graphite formation/evaporation, since the graphitic layer provides the coupling of copper vapor laser radiation to the transparent diamond.

One more process contributes to the decrease in Δz under the etching of diamond in the liquid: namely, the hydrodynamic impact of the liquid. Indeed, during the laser pulse a thin (~ 0.4 µm for H_20) layer of the liquid is heated via heat diffusion from the graphite layer. The temperature of this heated liquid layer is about of that of graphite surface, that is about 2000 °C, so the liquid is overheated. This layer of overheated liquid expands explosively, which causes pressure on the graphite layer and leads to the damage of the latter. In the first approximation, the pressure must be of order of the Young's modulus of the graphitic layer. For an absorption coefficient of graphite at 510 nm of 1.5×10^5, the 0.1-µm-thick graphite layer is heated up to the critical temperature of H_2O of 640 K at a laser fluence of ~ 4 mJ/cm^2. A graphite film of this thickness will be easily removed by the expanding liquid but the temperature rise in the film (~ 640 K) is not enough to increase significantly the thickness of the graphite layer. The absorption coefficient of the diamond surface at the laser wavelength is about 10 cm^{-1} [7], so there is no surface absorption of the subsequent laser pulse, and the etching stops. For higher laser fluences, the etching under liquid commences when the necessary thickness of the absorbing graphitic layer is gained, that is after a certain number of laser pulses. This is consistent with the higher value of laser fluence under which LE occurs and with the observed etching delay. The mechanism of explosive expansion of the overheated liquid explains why the areas with removed graphite layer are larger than the laser spot: the pressure wave propagates in the liquid in all directions. The removal of the graphitic layer by the fast expansion of a liquid is similar to that reported recently for laser-assisted etching of SiC ceramics [8]: all the products of its laser decomposition are removed from the areas etched under a liquid layer, thus leaving a SiC surface chemically identical to the virgin one. A more precise model of LE requires knowledge of the state equation of the liquid in the overcritical range of parameters.

Faster electroless deposition of Cu onto a diamond surface etched under a liquid confirms our previous observation that the graphitized layer screens the diamond surface from the plating solution, thus preventing the metal deposition. Laser ’cleaning’ of the graphitized surface as well as diamond etching under a liquid enhances the catalytic activity of the etched diamond for electroless metal plating. The I-V characteristics of the electroless metal contacts to the LE diamond surface are now under study.

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