Excimer laser processing of chemical vapour-deposited diamond fibres

G. MEADEN, P. G. PARTRIDGE
Interface Analysis Centre, University of Bristol, Bristol BS2 8BS, UK

S. E. JOHNSON, R. J. LADE, E. D. NICHOLSON, M. N. R. ASHFOLD
School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

Excimer laser radiation (XeCl, $\lambda = 308$ nm and ArF, $\lambda = 193$ nm) has been used both to cut chemical vapour-deposited diamond-coated tungsten wires (diamond fibres) of diameter $\leqslant 200$ μm and to smooth and profile the diamond surface. The effects of ablation and localized heating in the focal volume on the diamond and the tungsten core are described, and compared with results obtained for a Nd:YAG laser. The laser fluence and/or intensity, beam homogeneity and angle of incidence were identified as key parameters in ultraviolet laser-induced ablation of diamond-coated wires and fibres. Surface smoothing may lead to increase fibre strength.

1. Introduction

It has long been recognized that natural diamond has exceptional hardness and elastic modulus values, as well as outstanding thermal conductivity, chemical inertness and optical transparency over a large frequency range [1, 2]. The more recent development of laboratory synthetic methods, based on chemical vapour deposition (CVD), for producing films of polycrystalline diamond without seriously compromising these remarkable mechanical, thermal and optical properties, suggests many possible applications. Some (e.g. inserts for cutting tools, heat spreaders, infrared and X-ray windows) are now starting to be realized commercially; others are still at the development stage. Diamond-coated wires, fibres and meshes [3–9] are one example in this latter category: they may be used, for example, as reinforcement in stiff, lightweight composite materials [9, 10], as chemically inert sensors (thermal or, if suitably doped, electrochemical [11]), and in nanoscale grinding of ceramics [12, 13].

The exceptionally high hardness, elastic stiffness and low strain to fracture of diamond, combined with its chemical inertness, makes cutting and machining CVD diamond films difficult and expensive with conventional tools, and slow even with ion beams. However, such diamond films exhibit significant absorption at the ultraviolet (UV) wavelengths characteristic of excimer lasers, and pulsed photon absorption can lead to high local temperatures and evaporation or ablation in thin surface layers. Several groups have demonstrated that laser ablation offers one possible route to machining and profiling CVD diamond films [14, 15] and preliminary studies have been reported of the use of a Nd:YAG laser for sectioning and for surface smoothing CVD diamond-coated tungsten wires [9, 16, 17]. Compared with Nd:YAG and CO_2 lasers, excimer lasers offer the advantage of less heating of the work piece [18]. In this paper we describe the sectioning, smoothing and profiling of CVD diamond films using an excimer laser, and discuss the advantages of using such high-intensity, short-wavelength radiation for such applications.

2. Experimental procedure

The monofilament diamond fibres used in this work were prepared by CVD on to 20–125 μm diameter tungsten wires using a purpose-designed hot-filament reactor (Thomas Swan and Co. Ltd) and standard process conditions: 1% CH_4 in H_2, a gas flow rate of 200 standard $cm^3\,min^{-1}$, a tantalum filament maintained at 2100 °C and a gas pressure of 20 torr. Radiative heating from the hot filament and hydrogen atom recombination on the growing surface ensured that the fibres were maintained at ~ 900 °C during deposition. The tungsten cores were abraded with 1–3 μm diamond powder prior to deposition to enhance nucleation; typical radial growth rates were ~ 1 μm h^{-1} over a sample length of 135 mm.

Two different Lambda–Physik excimer lasers were used. One was a Lextra 200 laser, operating on XeCl (308 nm), the focused output of which was used for full and partial sectioning of a number of CVD diamond-coated tungsten wires, and a number of preliminary surface smoothing studies. The second was a Compex 205 laser, operating on ArF (193 nm); this was used more extensively as a means of smoothing the surface of the as-grown CVD diamond-coated wires. A pair of dichroic mirrors in a periscope arrangement was used to lower the height of the output of the Compex

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laser to match that of the sample manipulator. The respective laser outputs were rectangular in cross-section and were focused using a two-lens combination comprising, first, a spherical fused silica lens (focal length 250 mm) and then a cylindrical lens (focal length 195 mm) of the same material, separated by $\sim$110 mm in order to produce a line focus some 80 mm beyond the centre of the second lens.

For the sectioning studies in air, the fibres were mounted vertically and orthogonal to the line focus using an optical mount and a semi-permanent fixative. Laser pulse energies in the range 240–400 mJ were employed, at a repetition rate of 10 Hz. The effects of laser fluence and intensity were investigated by positioning the fibre at, and at various distances beyond, the position of optimal focusing, whilst the effect, if any, of the local atmosphere was investigated (crudely) by directing a jet of gas into the cutting zone using a pipette attached to a gas cylinder via a length of rubber tube. Oxygen and argon were used, so that possible physical and chemical effects could be distinguished. The same focusing arrangement was used for the smoothing studies, but in these latter experiments the fibres were mounted axially, aligned with the line of focus, on the end of a stepper-motor-driven lead-screw. This rotated (1 rev $\min^{-1}$) and advanced the sample with a helical pitch of 1 mm. The minimum length of the line focus was $\sim$5 mm; smoothing was attempted at and beyond the focus in order to allow variation in the incident focal line width, and hence the fluence. The laser-processed samples were examined using scanning electron microscopy (SEM) and laser (632.8 nm) Raman spectroscopy.

3. Results

3.1. Laser Cutting

Fig. 1 shows a 100 μm deep, $\sim$45° included angle, V-shaped cut made in a diamond fibre mounted in air at the focus of the XeCl laser output. Evidence of ablation (i.e. material removal) and localized melting of the exposed tungsten core in the focal region is clearly evident. Some of the ablated tungsten has condensed on the diamond surface at distances tens of micrometres from the cut, whilst the resolidified molten material appears as irregular filaments attached to the core, as shown at A in Fig. 1. The ablated diamond surface, inclined to the incident beam at B, was smooth. The simple V-profile of this cut compares favourably with the more jagged multiple V-profile obtained in earlier work using the focused third harmonic output of an Nd:YAG laser equipped with unstable resonator optics [16, 17]. From the depth of the cut, an "effective" (composite) cut rate of $\sim$0.5 μm pulse^{-1} or 5 $\mu m\, s^{-1}$ can be obtained, some ten times faster than that achieved using the (admittedly lower power) Nd:YAG laser [16, 17]. The etch rate increases linearly with the incident fluence ($J\, cm^{-2}$) [19]. Positioning the fibre a few millimetres beyond the point of optimum focusing resulted in a wider, less aggressive cut (Fig. 2), and suggested the possible use of excimer laser radiation for smoothing the rough faceted surface of the CVD diamond-coated fibre.

Longer exposure to the XeCl laser radiation under the imperfectly focused condition can lead to cuts with flat bottoms and almost vertical faces as shown in Fig. 3. In almost all cases where "out-of-focus" cuts of this type were made, and the cut penetrated into the tungsten core, some cracking of the diamond coating was observed at the periphery of the cut. The energy supplied by the laser can cause ablation, but also local heating and possible melting (of the tungsten). Ablation is favoured by high peak intensities. Thus the relative importance of these various processes will depend on the intensity of the incident radiation, and on factors like the absorptivity and thermal conductivity of the sample, and can therefore be a fairly sensitive function of position within the laser beam. "Out-of-focus" conditions correspond to lower peak intensities, which will tend to favour heating and, if heat transport is not too efficient, local melting. Such behaviour was evident in the SEM image shown in Fig. 1, but is much more obvious in the "out-of-focus" cut shown in Fig. 3. The laser causes significant, but very localized, heating. Thermal conduction results in

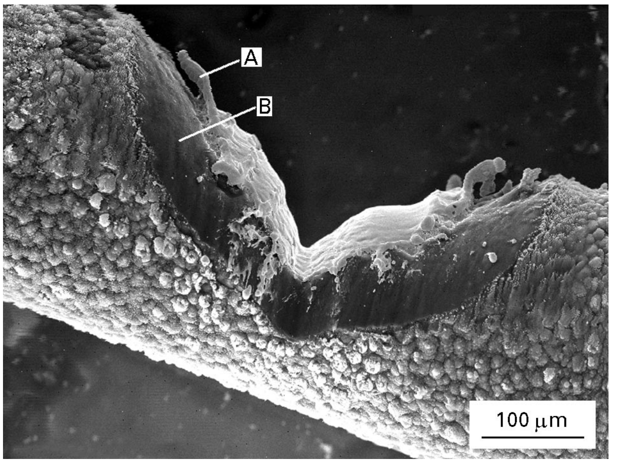

Figure 1 SEM image of a partial cut through a diamond-coated tungsten wire, achieved using 200 pulses of focused XeCl laser radiation (308 nm, 10 Hz repetition rate, $\sim$350 mJ pulse^{-1}).

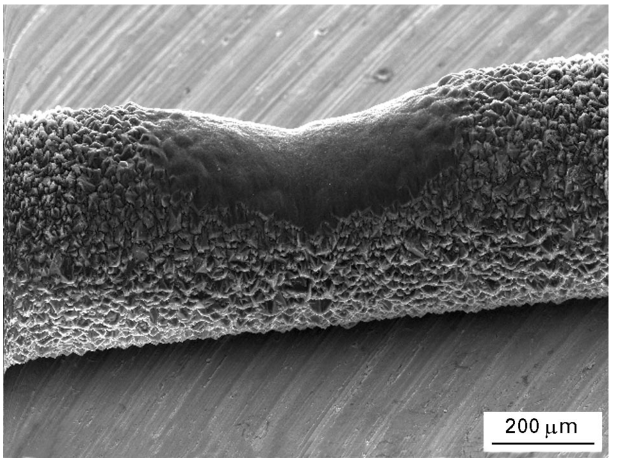

Figure 2 SEM image showing the effects of exposing a diamond-coated tungsten wire to 100 × 350 mJ pulses of XeCl laser radiation at a repetition rate of 10 Hz. The fibre in this case was positioned about 10 mm beyond the point of optimal focussing.

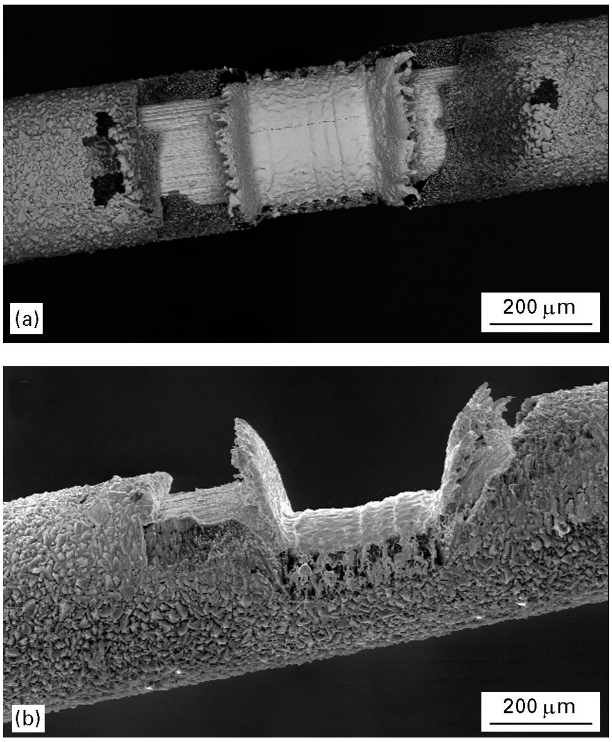

Figure 3 (a) Top and (b) side views of a flat-bottomed "trench" cut in a CVD diamond-coated tungsten wire using 200×350 mJ pulses of XeCl laser radiation (10 Hz repetition rate), with the fibre positioned a few millimetres beyond the point of optimal focusing. (a) A back-scattered electron image showing atomic number contrast, which serves to highlight the difference between tungsten (bright) and diamond (darker).

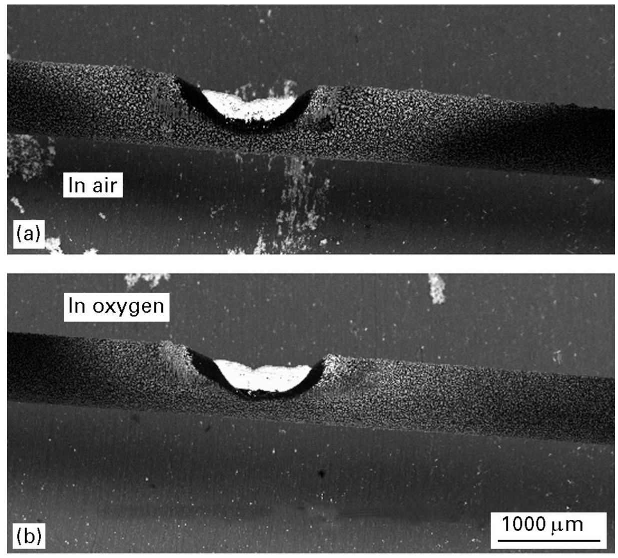

Figure 4 Back-scattered SEM images of CVD diamond-coated tungsten wires exposed to 100×350 mJ pulses of XeCl laser radiation (10 Hz repetition rate) using similar focusing conditions to those in Fig. 1, (a) in air, and (b) with a jet of oxygen directed at the ablation zone.

rapid freezing after cessation of each pulse, and the build-up of "lips" at each side of the cut (Fig. 3). If the accompanying transient thermal expansion and contraction of the core sets up local stresses, these may be relieved by local spalling of the diamond coating.

Directing jets of gas on to the cutting area was found to have little or no effect on the cutting rate, or on the amount of sputtered material that deposited around the cut (see Fig. 4, for example), though in both cases some evidence for a reduction in the amount of tungsten deposited on the neighbouring diamond surface or on the "lips" is apparent, suggesting that the gas jet may improve the efficiency with which ablated material is transported from the focal region. The feed direction of the gas jets had no discernible effect, and EDX analysis showed no evidence for any tungsten oxide either on the cut surface or in the very thin sputtered deposit around the cutting zone.

3.2. Laser smoothing

Laser smoothing is faster than alternative mechanical methods and increases with angle of incidence [18, 20, 21]. Smoother surfaces and lower surface temperatures have been reported for excimer lasers than with Nd:YAG lasers [18]. The feasibility of using excimer laser radiation to smooth diamond fibres uniformly over a length of several centimetres was investigated. It was found that the most uniform surface smoothing was achieved with a fibre mounted parallel to a slightly out-of-focus focal line, where the focal stripe was ~ 5 mm long and ~ 1 mm wide (i.e. some five times wider than the diameter of the coated fibre). Such a tolerant arrangement is clearly less than optimal in terms of efficient photon utilization. However, it ensured the fibre remained within the laser beam under constant ablation conditions during large fibre displacements, and was insensitive to small errors in the parallelism of the fibre and the focal stripe and to the lack of rigidity of the leadscrew.

In these experiments, 380 mJ pulses of ArF (193 nm) laser radiation were used together with a stepper motor rotation speed of 1 rev $\min^{-1}$. Given a lead screw pitch of 1 mm and focal stripe length of 5 mm, it follows that any point on the fibre surface will be in the focal region for five complete revolutions. For half that time, however, it will be in the laser shadow. For the remaining time when it is illuminated, the angle of incidence of the incoming radiation will vary from 90°, through 0°, and ultimately back to 90°. Thus a single smoothing "pass" takes 5 min to complete, but only involves 2.5 min of (mainly) near grazing incidence irradiation.

The SEM images displayed in Fig. 5 show how the surface topology of the CVD diamond coating evolves as a result of one, two and three smoothing passes. It is clear that the highest points and edges are ablated preferentially; facets associated with some of the least exposed surface crystallites persist after two smoothing passes (c). The overall loss of material is small, as indicated by the SEM images in Fig. 6. These show cross-sections of unsmoothed as-deposited and of three-times smoothed parts of the same fibre; the diamond coating thickness (~ 35 µm) is reduced by just a few per cent. The crack at the diamond/tungsten core interface, clearly evident in these images, was caused by the mechanical cutting of this fibre. Such damage is avoided by laser cutting.

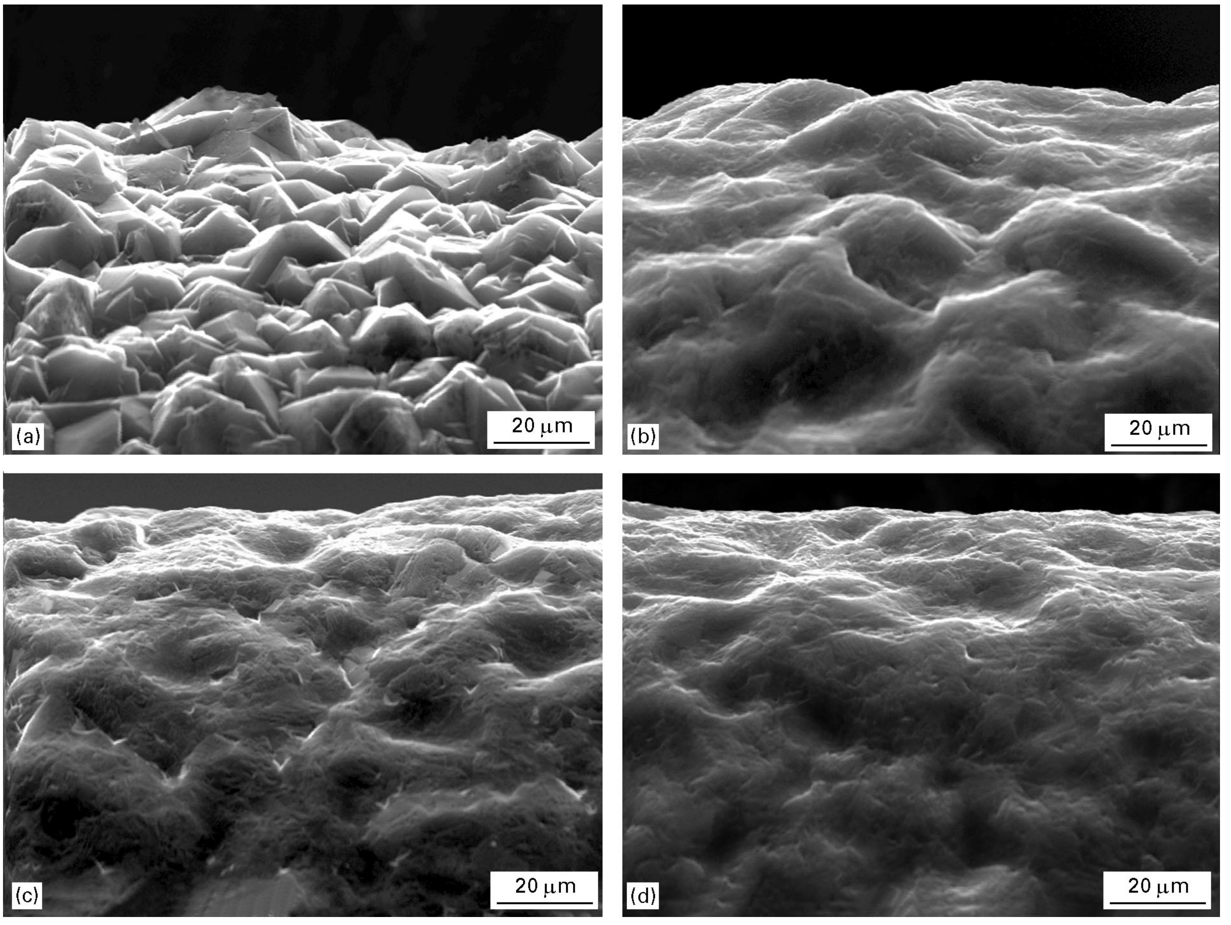

Figure 5 SEM images of the surface of CVD diamond-coated tungsten wire, (a) as-deposited, and after (b) one, (c) two and (d) three smoothing passes using 380 mJ ArF laser pulses as described in the text.

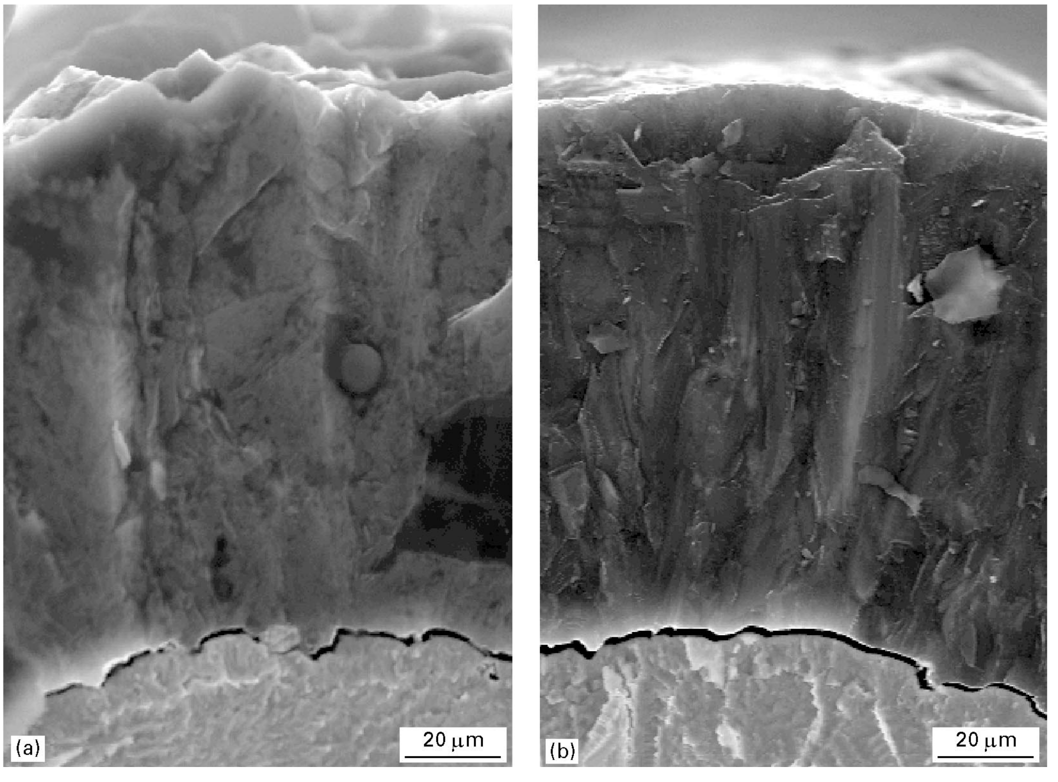

Figure 6 SEM images showing cross-sections through (a) as-grown and (b) three times smoothed portions of the same CVD diamond- coated tungsten fibre. The crack at the diamond/tungsten core interface was introduced during mechanical sectioning.

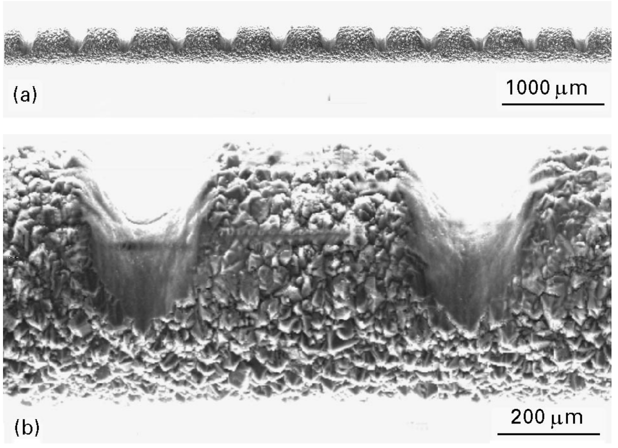

Figure 7 A grooved diamond fibre surface produced using XeCl laser ablation to make a series of partial cuts: (a) 3.5 mm length of fibre, (b) detail showing grooves spaced ~ 0.3 mm apart, with typical depths ~ 60 μm, full widths ~ 100 μm and with the cut faces inclined $\sim 25^\circ$ to the vertical.

These SEM images illustrate the advantage of laser ablation for both smoothing and cutting such hard diamond fibres. Laser Raman and Auger spectroscopy of the fibre surface, before and after smoothing, gave results very similar to those reported in earlier investigations of Nd:YAG laser processing of CVD diamond [16, 17], which indicated the presence of a sub-micrometre thick surface layer of non-diamond carbon. The origin of this non-diamond carbon is not clear. The laser may provide sufficient peak energy for local surface reconstruction. Alternatively, the thin surface layer may form by redeposition from the gas phase as in amorphous carbon deposition during pulsed laser ablation of dense graphite targets [22, 23].

3.3. Laser profiling

Excimer laser radiation can be used to profile CVD diamond surfaces [15, 19]. Fig. 7 shows SEM images of laser-cut grooves in the surface of a diamond fibre. This was achieved by excimer laser ablation (XeCl, 308 nm, 350 mJ pulse^{-1}) of a CVD diamond-coated tungsten wire (70 μm film thickness on a 50 μm diameter core). Under optimal focusing conditions, 600 laser shots were sufficient to cut through the fibre completely, whilst 150 shots did not quite penetrate through to the tungsten core. Thus the grooves were produced by making a partial cut in just the diamond skin of the fibre using 150×350 mJ pulses, translating the fibre ~ 300 μm and repeating the ablation process. Similar (~ 50 μm deep) V-shaped teeth produced by ArF laser ablation of CVD diamond films on flat substrates, have been reported [19].

4. Discussion

The incident laser wavelength, the fluence and/or intensity, the beam homogeneity and the beam angle of incidence have all been identified as key parameters in laser surface processing of diamond fibres. The use of laser radiation for cutting grooves in flat diamond films has been widely reported [15, 19]. Laser-assisted chemical etching of poor quality diamond films (produced by a d.c. arc discharge) using a low-power continuous wave Ar^+ laser in air or O_2 has been reported, with etching rates of ~ 50 μm s^{-1} [15], but more powerful lasers were required in order to ablate good quality films. Ralchenko *et al.* [19] found that the ambient gas atmosphere had little effect on the etch rate of CVD diamond films when using pulsed lasers, in agreement with the present results using a jet of O_2.

Previous workers [19–21] have shown that ArF laser smoothing of flat CVD diamond surfaces increased with angle of incidence, θ, and that by working at $\theta \simeq 80^\circ$, the surface roughness, R_a, value could be reduced from 1–3 μm to about 0.1–0.3 μm [20, 21]. However, shadowing caused by surface facets can result in surface ripples aligned in the plane of incidence, which prevents further reduction in the R_a value [20]. The rippling effect can be alleviated by reciprocating the film, and an R_a value of 33 nm was then obtained [20]. In the present experiments, because the fibre spends more time exposed to near grazing irradiation and is subjected to both rotation and displacement, the present fibre processing conditions should favour low surface roughness values.

This demonstration of efficient, uniform surface smoothing of CVD diamond-coated wires and fibres has implications for their mechanical properties and hence for diamond fibre-reinforced composites. Although high fibre elastic modulus values have been obtained [6], the fibre strength is much lower than current SiC fibre strengths. This may be caused by the rough diamond surface, and may be improved by smoothing. The production of a thin non-diamond surface film appears inherent in laser processing of diamond, but it has been reported [19] that it can be minimized by cleaning at a reduced fluence or by hot acid etching, and can be almost eliminated by annealing in O_2 at 400 °C.

5. Conclusion

Diamond-coated wires and fibres can be cut, smoothed and profiled using focused UV radiation from a pulsed excimer laser. The quality of the surface cuts, at an ablation rate of ~ 5 μm s^{-1}, were superior to those obtained with a Nd:YAG laser. The high quality surface smoothing obtained was attributed to processing under rotation and displacement conditions, combined with a high angle of incidence for the laser beam during fibre rotation.

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