Below band-gap laser ablation of diamond for transmission electron microscopy

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ABSTRACT

A 248nm excimer laser was used to thin naturally occurring type 1 a diamond substrates at normal and glancing (22°) incidence. Perforation of a 250μm thick substrate was achieved in about 15 minutes at normal incidence. Whilst the substrate thinned at glancing incidence was found to have large electron-transparent areas, that thinned at normal incidence required additional argon ion milling to achieve electron transparency. X-ray photoelectron spectroscopy of the back surface of the diamond failed to detect any graphite or glassy carbon, confirming that damage due to laser ablation occurs only at the incident surface. Samples prepared using this technique imaged in the transmission electron microscope were observed to have retained the nitrogen platelets characteristic of such type 1a diamonds.

Recently, interest in diamond as a bulk substrate and as a coating materia has grown, for a variety of applications.[1] Transmission electron microscopy (TEM), both in the conventional and analytical modes, will continue to be an important technique'for the characterization of diamond based materials. 1 lowever, the main barrier to the widespread use of TEM as a characterization tool is the lack of a suitable technique to produce electron transparent thin foils in a controlled and timely manner. Natural diamond is the hardest substance known and consequently thinning of diamond has been a centuries-old problem, particularly among manufacturers of diamond jewelry. Traditionally the grinding and polishing of diamond is achieved with diamond-based abrasives and is a time. consuming process. Alternatively, argon ion milling[2], oxidation[3] in a furnace, and laser ablation[4] have been used as means of obtaining electron-transparent specimens. The furnace oxidation approach suffers from a lack of controllabili ty i n the desired area for TEM examination and possible surface structural modification, making the technique unsuitable for producing TEM specimens from homoepitaxial samples. Argon ion milling is a time-consuming process with a very low sputter rate of approximately 1 μm/hr[3]. Laser ablation has been attempted previously although only using radiation above the band gap (193nn1)4. 'l'his letter describes the results of an in-depth study of the laser ablation approach using below band-gap laser radiation with a view towards its applicability in producing TEM specimens from homoepitaxial samples without significantly damaging the epitaxial layers. The use of below band-gap laser radiation confines most of the energy of the laser pulse in the surface carbon layer formed during ablation and minimizes the absorption and consequent structural damage in the bulk of the diamond.

In this work, 2mm x 2mm x 0.25mm, (100) oriented, type 1a natural diamond substrates were used. The substrates were mounted in a copper holder in the as-received condition without the use of optically absorbent coatings. "]'binning was performed in air, using an excimer laser (Questek 2960) operated at 248 mn (KrF), at a pulse rate of 5Hz and with an output energy of 600mJ, at normal and glancing (22°) incidence. Although the

band-gap of natural diamond is around 5.48eV (226nm), a high concentration of nitrogen impurities in type 1a diamond lowers the uv absorption edge to 340nm.[5] The laser output was first reduced in size by passing the beam through a 3mm diameter aperture: the remaining 15mJ was focused on to the diamond substrate using a 30 cm focal-length fused-quartz lens. The substrate was placed near the focal point of the lens to produce an laser spot of approximately 300x500μm at normal incidence. The fluence at the center of this spot is estimated to be 20 J/cm^2.

Following laser thinning the resultant surface morphology was studied using scanning electron microscopy (SEM). TEM observations were conducted at 200kV. 'l'he diamond substrate thinned at glancing incidence could be imaged directly. However, the substrate thinned at normal incidence required the removal of the layer formed on the ablated surface of graphitic and amorphous carbon by argon ion milling at 5kV and 0.5mA for electron transparency. X-ray photoelectron spectroscopy (XPS) data were taken with a Surface Science Instruments SSX1 00-501 spectrometer **using** monochromatic Al K_α x-rays (1486.6 eV) with a beam of diameter 150μm or 300μm . Prior to XPS measurements, the diamond samples were degreased in hot trichloroethylene, acetone and methanol to minimize surface organic contaminants. The effects of sample charging during XPS data accumulation were minimized with the use of a low energy electron flood gun.

Low-magnification SEM micrographs of the the laser-thinned diamond substrates are shown in figure 1. The laser-exposed surfaces on both substrates are rough whereas the unexposed back surfaces retain their original surface polish. It was found that an absorbent coating was not necessary to initiate the laser-thinning process. A black surface layer, presumably a mixture of graphitic and amorphous carbon, forms very soon in the ablation process. This layer is consistent with the results from earlier furnace-oxidation studies of diamond which have shown the formation of a surface carbon (non-c] iamond) layer.[3] These studies determined that above 850°C a carbon (non-diamond) layer appeared on the (100) surface of the diamond. The formation of a surface carbon layer would reduce the

absorption depth of the laser radiation significantly and also have a lower thermal diffusivity than the underlying diamond, leading to localization of the laser pulse energy within the surface layer.[4,6] Rothschild *et, al.*[6] have proposed that thinning in such circumstances involves a sustained process of conversion of diamond to a graphite/amorphous carbon layer followed by evaporation or reaction of this layer with the ambient. However, unlike their etching method which used above band-gap 193nm laser radiation, this work uses a laser energy below the band gap of the diamond, with the bulk of the pulse energy being absorbed in the surface carbon layer thus minimizing absorption in the interior of the diamond. Although an optically absorbent coating was not used in the present study to initiate the thinning, such a coating could potentially be used with lasers having wavelengths in the optical transmission regime for diamond but within the absorption range for graphite or glassy carbon. The only requirement would be that the lasers have sufficiently high energy densities for sustaining the ablation process.

For the laser-thinning technique to be utilized in future TEM studies of homoepitaxial diamond layers, it is necessary to demonstrate that there is negligible damage in the form of graphitization to the back surface of the substrate. The presence of a surface graphite/amorphous carbon layer can be detected using XPS. Although both diamond and graphite contain only carbon and have C 1s core level XPS peaks at the same binding energy of 284.3 eV, the C 1s signals for these materials are distinguishable by their lineshapes and characteristic energy losses. Diamond is an insulator with a C 1s signal which is symmetric, while graphite is a semimetal whose C 1s signal exhibits a pronounced asymmetry on the high binding energy side and a characteristic energy loss peak at 291 eV which is absent in the signal from diamond.[7,8] Glassy carbon also exhibits spectral characteristics similar to those of graphite.[7] The diamond substrate laser-thinned at a glancing angle was selected for the XPS study. The C 1s signals from the samples measured in this work, including a virgin diamond crystal, consist of a single main peak with shoulders at both low and high binding energy. The only significant contaminant is O,

which is present at a level of -0.5- 1 monolayer assuming surface localization. Surface C-O or C-OH bonding may account for the high binding energy shoulder on the main C Is peak. Alternatively, the C 1s lineshape may indicate some differential charging of the sample surface. However, the 291 eV energy loss peak characteristic of graphite or glassy carbon was not observed, even near the spot where the laser had ablated completely through the sample. This result demonstrates that laser-induced heating does not damage the back surface of the diamond substrate in these experiments.

Figure 2 shows a TEM micrograph of a diamond substrate thinned at glancing incidence. This specimen contains large electron-transparent regions which exhibit thickness fringes. The substrate thinned at normal incidence however, required argon ion-milling at 12° for an hour following laser ablation to achieve electron transparency. Also, very small areas were available for observation as compared to the sample thinned at glancing angle, due the presence of steep sidewalls surrounding the perforated region. The presence of graphitic and amorphous carbon on the ablated surface of the diamond thinned at normal incidence was determined via electron diffraction. It was found that the graphitic and amorphous carbon layer could be removed by extended ion-milling. Figure 3 contains a diffraction pattern obtained from a <1211> oriented graphite particle found on the diamond substrate laser-thinned at normal incidence. Figure 4 contains a high magnification electron micrograph showing the presence of nitrogen platelets lying on {100} planes in the diamond thinned at normal incidence, which is characteristic of type 1a natural diamond. These results provide ample evidence for the viability of laser ablation as a TEM specimen preparation process.

In summary, a novel technique for the rapid thinning of diamond using below band-gap laser radiation is described. An optically absorbent surface carbon layer is formed during irradiation which then sustains the ablation process. XPS measurements were not able to detect damage in the form of graphitic/amorphous carbon formation on the unexposed side of the diamond substrate.

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LIST OF FIGURES

(a)
(b)
x35
1 mm

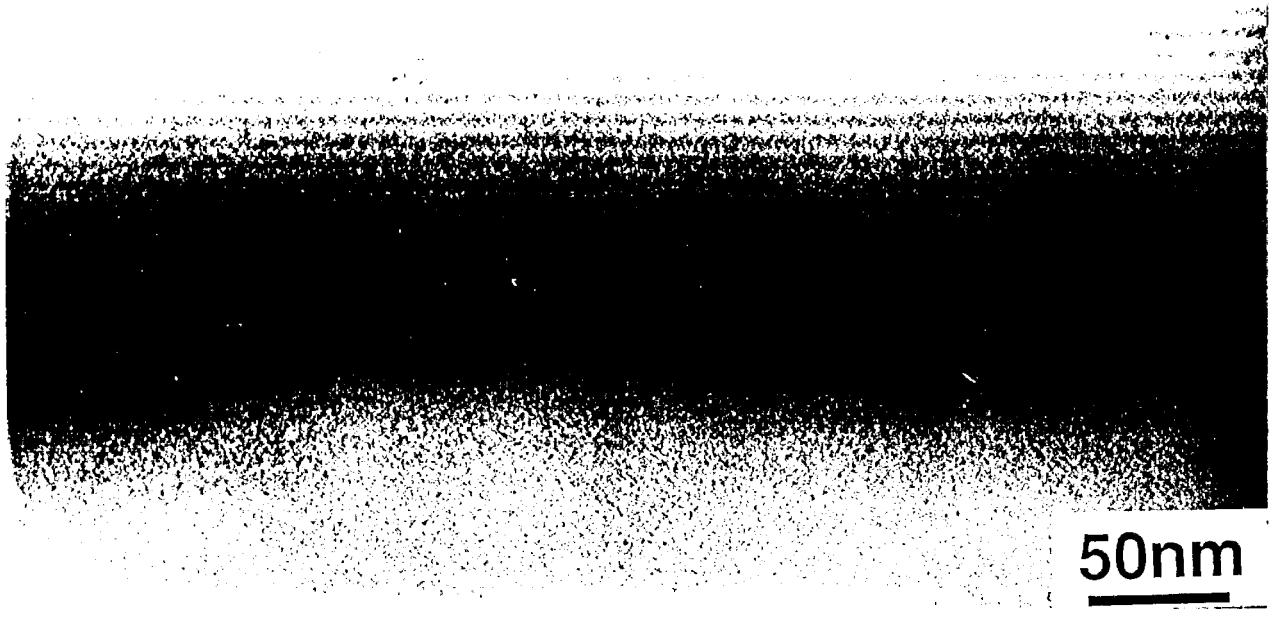
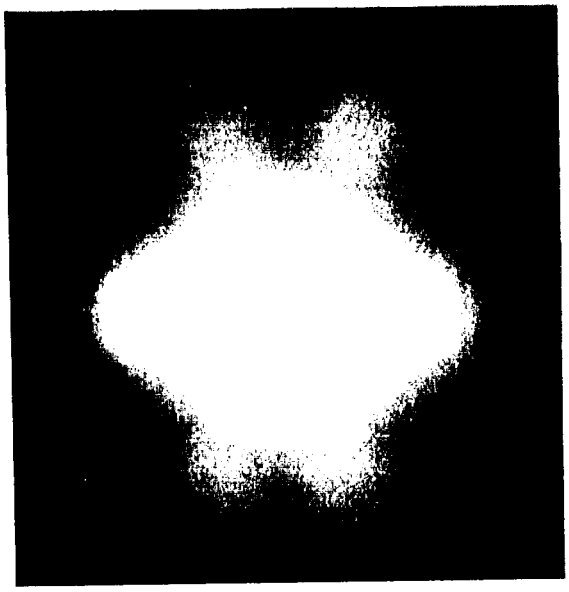


Fig. 2

(a)



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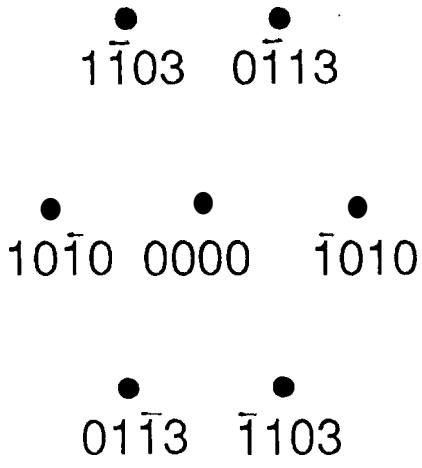

Fig. 3

Fig. 4