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Electrochemical Patterning of Amorphous Carbon on Diamond

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ABSTRACT

The ability to pattern ion-implantation damaged or other nondiamond carbon on a diamond substrate is useful for fabricating a variety of devices. We accomplished such patterning by an unmasked implantation into a diamond substrate followed by photolithography and a selective electrochemical etch. The use of a high resistivity medium coupled with applied biases over 50 V permitted etching without requiring contact between the substrate and an electrode. Many electrolytes gave etches that exhibit high selectivity for nondiamond carbon over both diamond and dielectrics such as photoresist. Optical, electrical, and Raman spectroscopic measurements elucidate the effects of the etch on the implanted diamond surface.

Damage from ion-implantation causes insulating diamond to swell, become opaque, and to have a conductive surface.[1] Selective removal of this damage allows the formation of surface features having many potential uses. The ability to define patterns of nondiamond carbon on diamond allows the fabrication of many robust optical, electrical, and mechanical devices. High resolution pattern definition could enable fabrication of durable visible light optics and x-ray phase plates. The resistivity of the damaged material is low enough to make it useful as an interconnect material for diamond-integrated circuits. Controlled reduction of the damaged layer thickness should make it possible to fabricate semitransparent electrodes for opto-electronic devices.

Many techniques exist to etch diamond and nondiamond carbon, but they suffer from inadequate selectivity. Reactive ion etching (RIE) etches both diamond and damaged diamond or nondiamond carbon, albiet with somewhat different rates.[2,3] In addition, it damages the diamond surface during etching, making it undesireable for electrical device fabrication. Hot acids such as mixtures of sulfuric and chromic acid are used to remove nondiamond contaminants from the diamond surface.[1,4] However, these acids attack metals and photoresists at comparable rates, making them unsuited for patterning applications.

Because nondiamond carbon is generally more conductive than either diamond or photoresist and is known to be electrochemically oxidizable[5] we explored the capability of electrochemical techniques to selectively remove it. We found that under conditions of high applied voltage and low conductivity media, it can be removed with good selectivity over both diamond and photoresist at room temperature. Unexpectedly, it was observed that no electrical contact is required between substrate and electrodes to obtain etching. In this paper, we present the results of attempts to pattern the damage caused by ion-implantation into diamond with electrochemical etchants using several different electrolytes. Optical, electrical, and micro-Raman results all tend to confirm that high selectivity was achieved and that the electrochemical etch removes roughly as much damaged material as a typical boiling acid etch.

Experimental

The electrochemical etching technique was explored by ion-implanting, etching, and characterizing a variety of diamonds with and without a photoresist etch mask. Polycrystalline diamond on silicon was used to test the effect of certain etchant systems before attempting to etch single-crystal samples. Single-crystal substrates used for these experiments are summarized in Table I. Substrates labelled as SUMI are from Sumitomo Electric (Westerville, Ohio) and synthesized by high-pressure, high-temperature techniques. Those labeled MG, MSM, and DD are natural diamonds obtained from Dubbeldee Harris Corporation (Mount Arlington, New Jersey). Some substrates were used for multiple experiments. Multiple experiments are distinguished by appending a hyphen and an experiment number to the substrate name. All of these samples are (100) oriented and were implanted with 4×10^{16} cm^{-2} of C^+ at 40 keV. Some substrates were implanted without masking and others were implanted using a metal contact mask to define 100×3000 μm implanted stripes and implanted quadrants. After implantation, some of the samples were spin coated with 1 μm of Shipley 1400-26 Novolac photoresist and patterned using photolithography. Prepared substrates were etched using either an aqueous solution of sulfuric and chromic acid or the electrochemical (EC) method.

The EC etching system consists of a solvent, an electrolyte, two electrodes, and a glass holder to orient the substrate to be etched. For all experiments, electrodes were graphite rods 0.5 cm in diame-

Table I. List of diamond substrates used in etching experiments. Stripe and quadrant implants were defined using metal contact masks during the implant. Uniform implants were accomplished with no mask. Etch conditions are abbreviated as EC: electrochemical etch, either directional (D) or non-directional (N) and with surfacant (S); acid: boiling sulfuric/chromic etch. Numbers under the comment heading indicate the amount of swelling (+) caused by the implant and depth of etch pit (–) below the virgin diamond surface.

Sample name	Implant conditions	Etchant	Comments
SUMI4-1	Stripes	EC-D	+600/–700 Å
SUMI4-2	Uniform	EC-D, N	PR mask, scribed features
SUMI5	Stripes	EC-D	+600/–900 Å
MSM5-1	Stripes	acid	+500/–600 Å
MSM5-2	Uniform	EC	PR mask, photolith, +/–1200 Å
MSM7	Uniform	EC-D	Unmasked
DD6	Three quadrants	EC-NS	IIb substrate, dots
MG1	Uniform	EC-N	IIa substrate, dots

ter. Spacing between electrodes varied from 1 to 4 cm. Generally, 2 cm of electrode was immersed in the solvent. Platinum-iridium wire and platinum gauze were tested as electrode materials but no significant change in etch characteristics was observed. Applied voltages ranged from 50 V, the lowest voltage at which etching was apparent, to over 300 V. Except where noted, commercially available distilled water (obtained from Deer Park Company of Deer Park, Maryland) was used as a solvent. Ammonia was also found to work, but it does not have any apparent advantage over water and is more difficult to work with. Concentrated sulfuric acid also produced etching but caused excessive damage to the carbon electrodes.

Two classes of electrolytes were added to distilled water to modify the etch characteristics. Simple electrolytes such as chromic and boric acids were used in sufficient concentrations to allow approximately 100 mA of current flow with 150 V of bias. It was believed that the etch rate is controlled by the dissolution of potentially hydrophobic products from the substrate, so a combination of cationic and anionic surfactants was also tested. A few grams of sodium dodecyl sulfate (SDS) dissolved in 100 ml of distilled water was added a drop at a time to 100 ml of distilled water until bubbling oxygen formed a foam on the solution surface. Benzylalkonium chloride (BAC) was then slowly added until the gas bubbles stop foaming on the water surface.

Two geometries were used for the EC method: a directional geometry and a nondirectional geometry. During early experiments, it was observed that etching proceeded from the substrate edge closest to the cathode. The nondirectional etch was performed by orienting the damaged film to face the cathode to encourage uniform etching perpendicular to the substrate surface. The directional etch was performed by orienting the substrate face perpendicular to both electrodes and allowing the etch to progress across the film. In only one experiment was the substrate in electrical contact with an electrode.

Following the etch, the samples were rinsed in acetone and distilled water and then examined by micro-Raman spectroscopy, contact surface profilometry, optical density measurement, and current-voltage measurement. In Raman spectroscopy, the radiation from an Ar^+ laser operating at 514.5 nm was focused through a microscope onto the sample surface. The minimum spot size was approximately 1 μm. Scattered radiation was analyzed with a triple-pass monochromator and a CCD detector. Optical density measurements were made using a white light microdensitometer with 5 μm aperture. All electrical measurements were made using a combination of tungsten probes on the etched side of the substrates and an indium contact to the backside.

Results

Results are discussed in the order in which experiments were performed. First, a single implanted sample was etched in boiling acid to serve as a point of comparison for the EC technique. EC results progress from unpatterned etches in distilled water to patterned etches in various electrolytes.

MSM5 was used to establish the characteristics of the acid etch for comparison to the EC method. Surface profile measurements prior to etching MSM5-1 showed a 500 Å rise at the implant border. Etching in acid was followed visually. The dark implanted stripes showed no apparent change for 15 min, at which time they appeared to become lighter and slightly pink. After about 30 min, no dark areas were observable. The surface profile measurement was repeated and showed that a 600 Å etch pit was created in the implanted regions. Also, a 100 Å tall ridge existed at the implant border. Electrical probing demonstrated that the pit bottoms were more conductive than the virgin diamond surface and that the surrounding ridge was even more conductive. Quantitative results were hindered by the nonhomogeneous resistivity and unmeasured probe spacing. Further etching for several hours gave no detectable change in surface profile or observable reduction in conductivity.

The EC etch technique was explored using the synthetic substrates SUMI4 and SUMI5. We attempted to etch the stripes on SUMI4-1 individually by contacting a selected stripe with a steel anode biased at 50 V while the sample was immersed in ammonia with a graphite cathode present. The selected stripe etched and formed a pit around the anode within a few minutes. However, the noncontacted stripes also etched, suggesting that this technique could be used to pattern isolated conducting regions on a uniformly implanted substrate.

SUMI5 was then used to evaluate the etch rate of a noncontacted sample. It was etched in ammonia between two graphite electrodes in the directional geometry with a bias of 60 V and electrode spacing of approximately 2 cm. Significant etching was observed in 1 h as determined visually by the change from opaque to transparent in the implanted region. The sample was then evaluated using Raman spectroscopy and surface profile measurements. The implanted region was 600 Å higher than the virgin diamond before etching. Completely etched areas on SUMI5 were 900 Å deep, but the deepest etched region observed (after etching all dark areas away) on SUMI4 was only 700 Å. Ridges with heights 200 to 300 Å above the virgin surface were observed at all stripe borders. Raman spectra, shown in Fig. 1 confirm the disordering effects of the implantation and the removal of the nondiamond material by the etch. Fully etched areas gave spectra essentially indistinguishable from the virgin surface. The implanted but unetched region had a much weaker 1332 cm^{-1} peak, while the 1500 cm^{-1} feature characteristic of amorphous carbon developed substantial intensity. The spectra exhibited a gradually increasing diamond peak as the illumination spot moved from the unetched area to the etch pit bottoms and a correspondingly decreasing amorphous carbon signal. In all cases, the 1332 cm^{-1} peak FWHM remained at the instrumental resolution of 4 cm^{-1}. The etched, optically clear areas exhibited variable but increased conductivity compared to the virgin surface even though the Raman spectra from fully etched areas gave no indication of increased damage. These results are consistent with observations by previous workers that Raman spectroscopy is insufficiently sensitive to detect low concentrations of damage in diamond.[6]

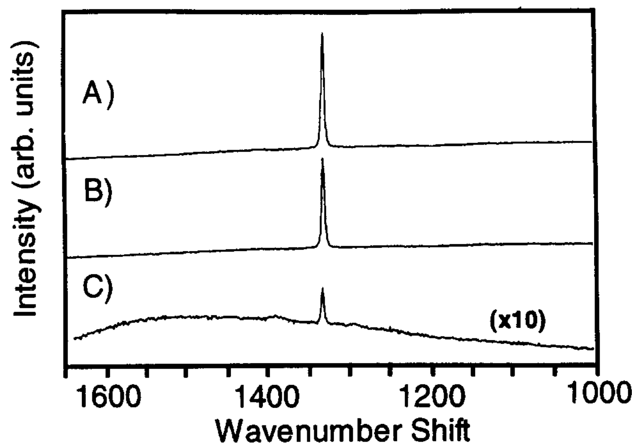

Fig. 1. Raman spectra from SUMI4 after implantation and etching: (A) the original surface, (B) implanted and etched, (C) implanted only.

The etch profile was further explored by directionally etching MSM7 for 1.5 min at 160 V in distilled water. The resulting etch profile was evaluated by optical density measurement. Because the substrate is transparent and the total surface height changes by less than 2000 Å over a distance of several hundred microns, this technique is more helpful than surface profilometry, even though the profilometry is capable of higher resolution and is easier to understand. A typical edge is shown in Fig. 2. A smooth optical density gradient was observed over a 400 μm distance before reaching a plateau. If the damaged layer had a homogeneous composition, then the optical density would be proportional to its thickness. However, as we discuss below, the implanted area is likely to be heterogeneous.

We first demonstrated the ability to mask the etch with SUMI4-2. It was given a uniform implant. A line was defined by coating with photoresist and mechanically removing a 0.3 mm stripe of the resist. Nondirectional etching with slow movement of the cathode for 55 min in distilled water gave the surface profile shown in Fig. 3. Etching occurred only in the areas exposed to the solution. 600-750 Å of material was removed near the pattern boundaries but only 450 Å had been removed near the center, indicating that the etch began at the boundaries and proceeded inward.

The ability to pattern with this technique was further explored with MSM5-2. It was uniformly implanted and then patterned with Novolac resist by conventional photolithography. The small sample size made photolithography difficult but several bar and cross patterns were produced. The sample was then etched in distilled water giving the result shown in Fig. 4. The distribution of etched and unetched features was controlled by electrode placement. When the corner of the sample nearest the cathode was etched, the cathode was moved nearer to the adjacent corner to allow it to etch. Etched features were 1200 Å deep (measured from the bottom of

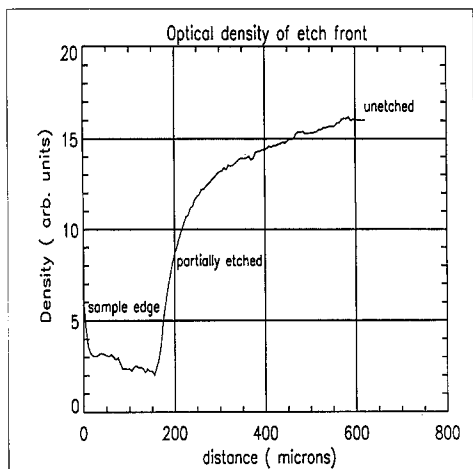

Fig. 2. Etch front profile as characterized by optical density. The fully etched area (0-150 μm) appears optically clear. The transition to unetched density occurs over a 400 μm distance. For a homogeneous absorbing material, the optical density is proportional to the material's thickness.

the etched region to the top of the swollen, implanted area rather than to the virgin surface) with vertical edges in contrast to the tapered edge profile obtained with MSM7. Within the uncertainty of the measurement, the EC method etched as deeply as the boiling acid procedure previously used on this sample. In some areas, the etch undercut the photoresist-covered diamond as much as 5 μm beyond the resist edge, resulting in a tapered optical density profile. Raman spectra showed increased amorphous carbon in the optically clear regions where no photoresist undercutting had occurred while the areas in which undercutting had occurred exhibited Raman spectra similar to the unimplanted diamond.

A scanning electron microscopic micrograph of a vertical edge as measured by profilometry is shown in Fig. 5. The bottom of the etch pit exhibits small (≈25 nm diam) bumps of unknown origin. It is unclear if this roughness occurs in all samples, or whether it can be eliminated. The profile is not truly vertical but exhibits undercutting. This undercutting is consistent with the presence of a relatively undamaged and nonconductive diamond layer above a heavily damaged and more conductive region assuming that the etch rate increases with conductivity.

After the above results had been obtained, experiments were conducted on implanted CVD diamond on silicon in an attempt to increase the etch rate. This material is not expected to etch exactly like the single-crystal material due to possible preferential etching at grain boundaries and an altered electric field profile at the surface due to the highly conducting silicon substrate. However, relative effects of electrolyte composition could be observed. The

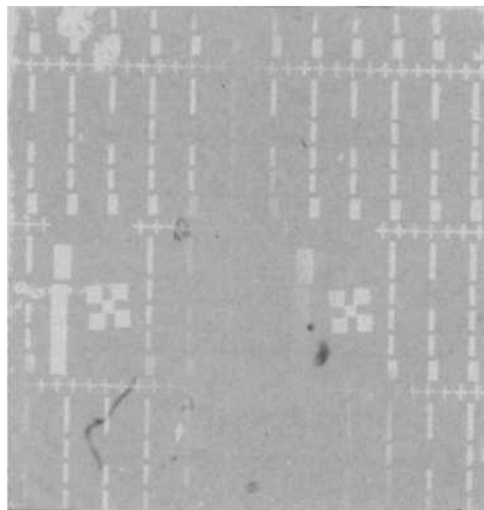

Fig. 4. Optical transmission micrograph of patterned open windows in an amorphous carbon field on a 3 × 3 mm substrate. Well-etched features are observed in the two top corners of the sample. Undercutting is seen on the right edge of the sample.

chromic acid solution described previously made the implanted surface darker and hydrophilic after 10 s of exposure. After 60 s, all dark material was removed and interference fringes characteristic of the virgin diamond film could be seen. No apparent etching of the photoresist occurred although undercutting was prevelant. Addition of boric acid produced no change in properties. The surfactant solution similarly increased etch rates and made the nondirectional etch more uniform across the substrate but it sometimes also attacked the photoresist. This result is very surprising since the photoresist is nonconductive and is not attacked by these surfactants until voltage is applied. The photoresist damage does not appear to be due solely to undercutting and subsequent mechanical removal. Even when Novolac resist was attacked, PMMA on silicon appeared to resist the etch. The BAC seemed to be "used up" as current flow increased after it was added and then slowly decreased until it was replenished. Too much BAC caused a white, passivating material to form on the substrate and electrodes. The original reason for testing the surfactants cannot be validated but the effect of the surfactant addition is certainly dramatic.

Further patterning trials were performed on DD6 and MG1 by creating an array of 100 μm diam dots on 225 μm centers. Prior to island definition, one quadrant of DD6 was completely etched in distilled water, leaving it transparent but slightly darker than the virgin quadrant. SDS/BAC was used in the DD6 etch during island definition. The Novolac resist was attacked, as evidenced by vigor-

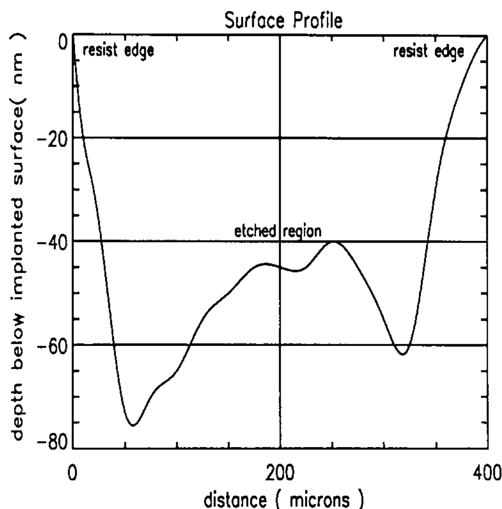

Fig. 3. Surface profile measurement of partially etched feature in implanted synthetic diamond.

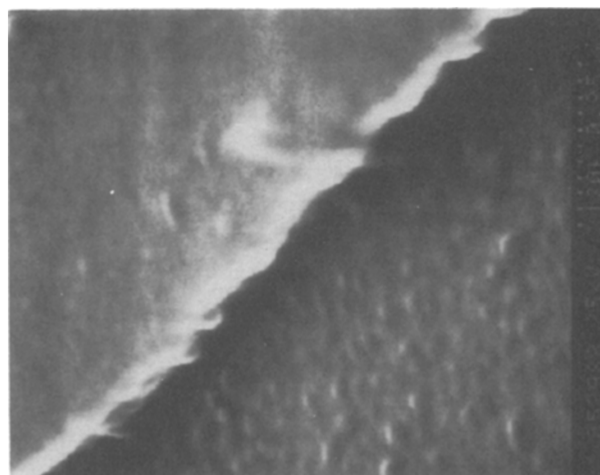

Fig. 5. SEM photograph of an etched edge. The area in lower right of photo is fully etched. The unetched region is in the upper left. Increased surface roughness is noted in the etched region and a small amount of undercutting is apparent.

ous bubbling on the photoresist and pattern damage, but several well-defined dots were nonetheless produced. MG1 was etched in pure distilled water and gave good pattern definition.

Current-voltage (*I-V*) curves were obtained on MG-1 between islands and across various spans of etched areas. All *I-V* curves were approximately ohmic, but there was no consistent resistivity between different areas. Island to field current at 300 V ranged from 10 μA to 1 mA for different islands. Island to island currents at 100 V ranged from 10 to 20 μA with no apparent dependence on island separation. We speculate that the current flow is controlled by a semitransparent conductive layer of varying thickness left after etching. Results on DD-6 were similar to those from MG-1. Current between probes on the etched field varied between 0.5 and 5 μA at 50 V for fixed probe separation. This is in contrast to two points on the virgin surface which gave about 100 pA at 50 V. *I-V* curves between a back-side indium contact and an island were rectifying but were similar to results obtained from indium to etched field.

Conclusion

We have demonstrated a simple, selective electrochemical etch for the removal of damaged diamond and amorphous carbon from an implanted diamond substrate. The etchants explored can remove all the implantation damage observable by Raman spectroscopy but do not restore the surface of type IIa diamond to its preimplant resistivity. More needs to be learned about the etch mechanism and techniques for controlling the etch selectivity and absolute etch rates. The observation that photoresist was attacked by the surfactant solution is surprising but also encouraging since it indicates that certain dielectrics may be etchable with variants of this technique. Further investigation into the selectivity of this etch system on boron-implanted diamond is indicated to determine if isolated p-type regions can be made this way.

Acknowledgments

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Comparison of Tantalum and Rhenium Filaments in Diamond CVD Using Selective Carbon-13 Labeling

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ABSTRACT

Heterogeneous carbon scrambling at the hot-filament in thermally assisted diamond chemical vapor deposition has been investigated through isotopic labeling studies. Films were produced using acetone, preferentially labeled at either the methyl or carbonyl carbon, and ^{13}C incorporation was determined from the shift of the first-order diamond one-phonon band in the Raman spectra. A comparison of the effects of carbide-forming materials, such as tantalum, and non-carbide formers, such as rhenium, is made. Results indicate that heterogeneous scrambling is limited in the rhenium case, which may prove useful in selective isotopic labeling studies. This study demonstrates the importance of heterogeneous reactions at the hot-filament and thus, has important implication for the modeling of these systems.

Hot-filament chemical vapor deposition (CVD) has been used extensively to produce diamond films at low-pressure.[1-6] One of the reasons cited for choosing this technique is the simplified gas-phase chemistry with respect to plasma systems. Species measurements have shown that the gas-phase concentrations of many carbon species in a typical hot-filament CVD environment, such as C_2H_2, CO, and CH_4, approach those calculated at equilibrium for the filament temperature and reactor pressure.[7-9] In addition, there has been extensive kinetic modeling of the gas-phase chemistry within these systems.[10-18] While these homogeneous reactions have been explored in some detail, little information is available concerning the heterogeneous chemistry within the system. Of particular interest are heterogeneous reactions at the hottest surface in the reactor, the filament, which is often a carbide-forming refractory metal, such as tantalum or tungsten. Metals which do not form carbides, such as rhenium, have also been used successfully for filaments in diamond deposition. Comparison of these types of materials by selective isotopic labeling of the carbon source may shed light on the importance of heterogeneous reactions at the hot-filament.

Selective isotopic labeling has been used successfully to study the kinetics of combustion systems.[19,20] In many systems, however, the application of this technique is limited by rapid homogeneous gas-phase or heterogeneous surface reactions which scramble or rearrange carbons from different sites in various species. Such scrambling is often rapid between hydrocarbon species.[21] However, this type of scrambling is not necessarily complete under all conditions. Chu *et al.* have shown that in cases where only partial scrambling occurs, selective isotopic labeling can be used to gain insight into the kinetics of diamond formation.[21,22]

The heterogeneous chemistry at carbide-forming filaments is a particularly interesting method by which carbon labels may scramble. If this type of reaction proceeds to a significant extent, the results of labeling studies may differ from those found in systems using method which do not form carbides. This has important implications for the modeling of hot-filament CVD where, to date, such reactions have not been considered.

Heterogeneous chemistry at the filament has been examined using hot-filament deposition under the operating conditions shown in Table I. Acetone was used as the carbon source, introducing the effects of oxygen on both the homogeneous and heterogeneous chemistry in the system. The acetone was selectively labeled at either the methyl or carbonyl carbon, as in previous work.[9] Acetone was chosen as the carbon source because it is expected to readily yield methyl radicals and CO. Although selectively labeled hydrocarbons in the gas-phase are expected to scramble completely in