ETCHING METHODS FOR IMPROVING SURFACE IMPERFECTIONS OF DIAMONDS USED FOR X-RAY MONOCHROMATORS

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ABSTRACT

In the last decade, diamond single crystals have become valuable monochromators for high-heat-load X-ray synchrotron beamlines. However, due to imperfections in the diamond, the rocking curves of diamond crystals are wider (e.g., 30%) than the theoretical values. Proper etching of the diamond can reduce the effects of imperfections. We explore four etching techniques using synthetic diamonds of type Ib and IIa. The diamond surfaces were variously treated by bombarding with ions, treating with a chemical solution, or using an atom-by-atom chemical machining process. Local variations of tilt and lattice parameter can be experimentally separated, and an improvement of the full width at half maximum (FWHM) of the rocking curve has been observed.

INTRODUCTION

Diamond single crystals have recently become popular with the synchrotron X-ray community [1, 2, 11-13] as high-heat-load X-ray monochromators [3-9]. Diamond monochromators can be produced in a variety of ways from naturally occurring or synthetically grown crystals. Naturally occurring diamonds are often used to create (110) and (111) oriented planes by sawing and cleaving [14]. Synthetic diamonds, on the other hand, are often created from (111) seed planes [2], or by chemical vapor deposition for (100) oriented diamonds. However when a diamond is created, surface tension and imperfections are produced. These factors affect the quality of the diamond and its performance as an X-ray monochromator. We explore methods of improving the diamond crystal for use as a monochromator.

In this investigation, (111) and (100) oriented type Ib and IIa diamond slabs, defined by the quality of their manufacturing, were used from Drukker International [15] and Harris International. The crystals were characterized with CuKα radiation from a rotating anode generator using the topographic test station (TTU) in the Optics Fabrication and Metrology Group of the Experimental Facilities Division of the Advanced Photon Source [16]. For the (111) oriented diamond samples, a silicon crystal cut at an asymmetry angle of 23° and set to the (220) reflection was applied as a monochromator while, for the (100) orientation, a silicon (531) monochromator was used.

The theoretical, ideal value for the full width at half maximum (FWHM) for the (111) diamond rocking curve in such a geometry is 5.8 arc-sec [6] and for the (400) rocking
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curve the FWHM should be 13.3 arc-sec. These values are based on the dynamical diffraction Darwin widths for perfect crystals and include a small wavelength dispersion contribution. The experimental values show that the actual FWHM’s are greater than the ideal calculated values due to near-surface tilt and stress distributions. Our purpose is to explore possibilities for improving the FWHM using some existing methods.

ETCHING PROCESSES

We investigate four methods for improving diamond crystals used as X-ray monochromators: (1) bombarding the diamond surface with high-energy oxygen and argon ions, (2) oxidation of the surface with KOH and Na₂O₂ at high temperature, (3) reactive radio frequency (rf) oxygen plasma etching, and (4) plasma deposition of SiOₓ compounds followed by abrasion.

LOW-ANGLE ENERGETIC ION SPUTTER ETCHING

In this technique, the diamond surface is sputter etched to smooth the surface and reduce stresses using low-angle energetic ions. Ions with energy on the order of 200 eV to 20 keV are used to impact the diamond surface near grazing incidence to selectively remove or sputter atoms of material from it.

A broad beam of gas ions for the sputter etching was produced by a Kaufman-type ion gun. A 3-cm-diameter gridded source was used, operated with an O₂ and Ar gas mixture, each flowing at 5 sccm into a cryo-pumped vacuum chamber. A tungsten filament was used to emit electrons and cause the ionization of the feed gas. The ionized atoms were extracted and focused onto the target by an acceleration grid. The gun potential was 1500 V, the internal discharge voltage was about 65 V and the beam current was 21 mA. At this discharge voltage, the beam was expected to consist of a mixture of Ar, O, and O₂ ions, both singly and doubly charged. The measured (Faraday cup) ion current normal to the beam was 0.39 mA/cm².

The specimen was bombarded by the ion beam at an angle of 12° and rotated 45° every 10 minutes to ensure uniform sputtering. The original diamond surface was chosen to be rough on both large and small scales. An area of the diamond that had both fine-scale roughness and a large raised feature was examined to determine the efficacy of this method.

An optical interference profilometer (Micro XAM) was used to generate three-dimensional images of the surface morphology of the diamond. Figure 1 shows an image from the Micro XAM of the diamond surface before sputter etching, with the vertical scale greatly exaggerated. Small-scale surface roughness, as well as a large projection 3 μm high and 70 μm in diameter was present. The specimen was sputter etched initially for 40 minutes and examined and then again for an additional 280 minutes. Figure 2 shows the effect of the sputter etching. After sputter etching for 40 minutes, Figure 2(a) shows that the small-scale roughness is largely eliminated, but the large feature appears
unaffected. After 320 minutes, Figure 2(b) shows the same area where some etching of the large feature is observed, but small-scale roughness has degraded.

During the etching process, a diamond and silicon witness were secured on a sample holder with silver paste. Approximately 4 µm of the silicon witness piece was removed by the sputter etching after 320 minutes. Since the etching rate of diamond is much less than for silicon, the large feature was relatively unaffected. Ion sputter etching is not an

![Figure 1. Diamond surface before sputtering. The large feature is 3 µm high and 70 µm in diameter.](image1)

![Figure 2. Diamond surface after sputter etching for (a) 40 minutes, and (b) 320 minutes. Note the reduction of fine-scale surface roughness and the slow erosion of the large feature after 40 minutes. After 320 minutes the surface roughness appears to increase with little change to the large feature.](image2)
effective technique for smoothing macroscopic irregularities. However, substantial small-scale smoothing was observed after 40 minutes. To achieve good overall smoothness, a combination of mechanical grinding followed by brief ion polishing may be used. The best results that were found using this method improved the FWHM of the rocking curve from 7.3 arc-sec to 6.4 arc-sec.

**CHEMICAL ETCHING USING Na$_2$O$_2$ AND KOH**

Chemical etching with a 4:1 mixture of potassium hydroxide (KOH) and sodium peroxide (Na$_2$O$_2$) was performed for several diamonds. Etching rates of diamonds exposed to molten KOH combined with Na$_2$O$_2$ at high temperatures have been measured and reported [10]. Potassium has the catalytic effect of breaking C-C bonds in the process of oxidation [14]. Etch rates in the range of 2 to 10 micron/hour for temperatures ranging from 650°C to 700°C were reported [10]. The oxidized layer was subsequently removed by washing the crystal in water.

The procedure for etching the diamond consists of first placing the specimen in an open stainless-steel jar and covering it with the solid mixture. Over the course of an hour, the temperature was raised to approximately 730°C in open air and maintained for another hour. The furnace was then slowly cooled, and the specimen removed and cleaned. Figure 3 shows X-ray topography (8 keV) CCD pictures of the diamond surface at the peak of the rocking curve before and after chemical etching. From these topographs, the entire diamond is clearly seen to be diffracting.

![Figure 3. CCD picture of diamond (111) (a) before chemical etching, and (b) after chemical etching.](image)

The greatest improvement of the FWHM of the rocking curve was from 8.2 arc-sec to 6.6 arc-sec. Figure 4 shows the rocking curve for a case showing similar improvement from 8.1 arc-sec to 6.7 arc-sec.
REACTIVE RF OXYGEN PLASMA ETCHING

An oxygen-bearing plasma etch was also investigated to determine its effectiveness at reducing the roughness of the diamond surface. It was expected that the oxygen-containing plasma would preferentially attack rough edges and points on the diamond surface. The reactive plasma was obtained using a Perkin-Elmer 2400 coating system equipped with an MKS/ENI OEM-25 radio-frequency plasma and a source gas consisting of 40% O₂ / 60% Ar by volume. The plasma composition was monitored by an Ametek Dycor Dymaxion mass spectrometer for CO, O₂, CO₂ to determine the status of the removal of carbon during the etching.

The diamond surface was observed after each etch cycle, pictures were taken of features on the diamond surface using an Olympus optical microscope, and profiles were taken using an ADE PhaseShift MicroXAM optical profilometer. Although a number of different sample fixturing configurations were tried, the results after etching did not show much improvement in the FWHM, but improvements were noted in the removal of surface imperfections. Despite a cumulative 15-20 hours of etching and the use of fixturing to generate a more intense plasma around the sample, insufficient material was removed from the surface. Limitations of the system likely prevented better results. In its current configuration, the maximum achievable bias voltage was −500 V, but significant sputtering does not generally take place below -1500 V. Although this limitation was known prior to testing, we believed that the chemical reactivity of the oxygen-containing plasma would allow removal of material at lower bias voltages due to the volatility of CO and CO₂.

Figure 4. Rocking curve for diamond (111) plane. Filled ellipses are data points corresponding to the original diamond surface. Empty ellipses correspond to the diamond surface after all treatments. The rocking curve improved from 8.1 to 6.7 arc-sec FWHM [19, 20].

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**THEORETICAL**
ABRASIVE ETCHING

Edge Technologies International (ETI) developed a patented and commercially available process [8, 12, 17, 18] that uses an atom-by-atom chemical-machining process to produce a super-smooth edge on single-crystal diamonds. The process removes atoms from the diamond and is capable of producing smooth cutting edges along the hard planes of the diamond's crystal structure.

Two diamond surfaces were tested and analyzed using this process. For the first diamond, a “snow-flake-like” pattern for the surface finish was produced after removal of about 12.5 microns and remained after an additional 12.5 microns was removed. However, this pattern did not cause additional broadening of the FWHM. For the second diamond, a similar surface pattern was noticed. After abrasive etching, the best-case FWHM improvement showed a reduction from 7.3 arc-sec to 6.6 arc-sec. Figure 5 shows a picture of the microscopic detail of the diamond surface before and after abrasive etching was performed.

![Figure 5. Microscopic picture of diamond (111) (a) before abrasive etching, and (b) after abrasive etching. The pictures show a gray-scale plot of surface roughness where the areas shown in black have no detectable surface roughness and areas shown in white have surface imperfections on the order of 100 nm.](image)

CONCLUSION

Four different methods of etching diamond single crystals were investigated. Application of chemical and ion sputter etching did improve the performance of the crystals by reducing their rocking curve widths and as a result improved the dispersion of the X-ray. It is expected that optimal improvement may occur by using a multi-step process consisting of these methods.
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