

## THIN DIAMOND FILMS FOR SNS H<sup>-</sup> INJECTION STRIPPING

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### Abstract

We have investigated the preparation and testing of thin diamond foils for use in stripping the SNS H<sup>-</sup> Linac beam. A long useful lifetime for these foils is desirable to improve operational efficiency. Preliminary data presented at PAC 2001 indicated that diamond foils were superior to conventional evaporated carbon foils, exhibiting lifetimes approximately five-fold longer[1]. That work employed a fully supported diamond foil, a format that is not acceptable for the SNS application; at least two edges of the approximately 1x1 cm foils must be free standing to allow for beam rastering. Residual stress in a chemical vapor deposited (CVD) diamond foil results in film distortion (scrolling) when the film is released from its silicon growth substrate. We have attacked this problem by initially patterning the surface of CVD growth substrates with a 50 or 100 line/inch trapezoidal grating, followed by conformal diamond film growth on the patterned substrate. Then removal of the substrate by chemical etching produced a foil that possessed improved mechanical integrity due to its corrugation. The high nucleation density required to grow continuous, pinhole free diamond foils of the desired thickness (1  $\mu\text{m}$ , 350  $\mu\text{g}/\text{cm}^2$ ) was achieved by a combination of substrate surface scratching and seeding. A variety of diamond foils have been tested using the BNL 750 keV Radio Frequency Quadrupole H<sup>-</sup> beam to simulate energy loss in the SNS. Those include flat, corrugated, microcrystalline, and nanocrystalline foils. Foil lifetimes are reported.

### INTRODUCTION

Diamond thin films can be grown from the vapor phase by decomposition of methane in low pressure hydrogen. While the resulting films are polycrystalline, they exhibit many of the superb physical properties of natural diamond. We have prepared and tested diamond foils for use as the stripping foil for removing two electrons from the H<sup>-</sup> ions in the 1 GeV Linac beam at the Spallation Neutron Source (SNS).

Preliminary BNL data presented at PAC 2001 indicated that a diamond foil was superior to conventional evaporated carbon foils, exhibiting a lifetime approximately five-fold longer[1]. Any improvement in foil lifetime before failure will be an operational advantage for the SNS, which will be operated nearly continuously for users.

The SNS will require a foil size approximately 1 x 2 cm, with a thickness of about 1  $\mu\text{m}$  (350  $\mu\text{g}/\text{cm}^2$ ). An optimum design goal requires that an individual foil will

function for no less than about 200 hours. Multiple foils will be mounted on a 30-unit cassette changer to increase the overall facility operating time before new foils must be mounted. These foils can be supported mechanically by at most two edges, as the proton beam will be painted on and off the foil in both transverse directions. This latter criterion is particularly demanding because thin, polycrystalline diamond foils grown by chemical vapor deposition (CVD) are mechanically stable when affixed to their growth substrate, but curl dramatically when released due to stress in the foil. This stress is both intrinsic and thermal (stress produced by the large thermal expansion mismatch between diamond and the silicon growth substrate). We have attempted to overcome this mechanical instability problem by using two approaches: growth of nano-textured diamond and corrugation of diamond foils.

### FILM STRESS AND NANO-TEXTURED DIAMOND

Residual film stress for materials grown at elevated temperature is a well known and studied topic. Windischmann and co-workers [2] have determined the stress in microwave plasma CVD diamond films as a function of the methane concentration in the reagent gas and as a function of the deposition temperature. Both tensile and compressive stress was observed, depending on the growth conditions.

We feel that an approach that holds promise for stress averaging and film strengthening is the preparation of nanostructured diamond. Such films have the potential to provide adequate strength at the ca. 1  $\mu\text{m}$  thickness required. Several reports concerning nanocrystalline diamond, particularly from microwave-excited growth reactors, have appeared. Zhou and co-workers [3,4] discovered that the argon content of CH<sub>4</sub>/H<sub>2</sub>/Ar microwave discharges leading to CVD diamond films exerts a substantial effect on the particle size of these polycrystalline films. Nanocrystalline textured films, with grain sizes ranging from 3 to 50 nm, can result. More recently, similar results were obtained using a hot filament growth chamber [5].

### FOIL PREPARATION

Diamond films were grown using either a hot filament or a microwave reactor. The typical reagent gas mixture was 1 or 2% methane in hydrogen; the reactor pressure was maintained at 50 Torr, and the gas flow rate was 100 sccm. For nano-textured films, the input gas mixture was diluted with argon to create a 1/49/50 by volume

$\text{CH}_4/\text{H}_2/\text{Ar}$  mixture. The substrate temperature was set either by adjusting the microwave power or the substrate heater current in the microwave and hot filament reactors, respectively. The growth rate was about 0.5 to 1  $\mu\text{m}/\text{hr}$ . Greater thickness uniformity was achieved using the microwave reactor. The film thickness reported here is an estimate derived from the substrate mass change during growth, so is an average over the entire wafer surface. Films were characterized using SEM, TEM, surface profilometry, and micro-Raman spectroscopy. TEM analysis of our nano-textured diamond indicated that the typical particle size was 50 nm. A window was chemically etched in the substrate for accelerator beam foil lifetime testing using a mixture of 10:6:9 concentrated nitric: hydrofluoric:acetic acids.

Single crystal silicon wafers (100 orientation) were abraded using 0.1  $\mu\text{m}$  diamond paste before film growth to create nucleation sites. Diamond films prepared using the CVD method are polycrystalline with grain dimensions ranging from less than one to about ten micrometers. To a large degree, the grain size is determined by the substrate surface nucleation density, as diamond grows by development of crystalline nuclei (seeds) that enlarge with further growth until they merge. Thus the seeding process is critical for our application, as the nucleation density must be sufficient to result in a pinhole-free film even though the growth is terminated at a 1  $\mu\text{m}$  film thickness. Mechanical scratching of the substrate is commonly employed before growth in order to produce a high diamond nucleation density. We have extended that approach by first scratching with paste and then following with an ultrasonic bath wafer treatment in "Liquid Diamond", a concentrated slurry of 0.1  $\mu\text{m}$  diamond particles (GE Micron Products, Deerfield Beach, FL). The latter treatment loaded the surface scratches with diamond seeds. After the ultrasonic treatment, the wafer was rinsed, but not thoroughly cleaned, so as to leave behind surface seeds.

Corrugated diamond foils were prepared through the use of a photolithographic technique. A 100 silicon wafer was oxidized to produce a 400-500 nm oxide layer. That surface was spin-coated with a polymer photoresist. The resist was exposed to ultraviolet light through a metal-on-glass mask (50 or 100 lines per inch at 50% duty factor) at contact. The resist was developed and rinsed to leave protective resist lines on the oxide surface. The exposed oxide was removed in a brief buffered oxide etch (BOE; 10:1,  $\text{NH}_4\text{F}:\text{HF}$ ). The remaining resist was then stripped, and the wafer was etched in 25% tetramethyl ammonium hydroxide at 75  $^\circ\text{C}$  to produce surface trenches with approximately 45 $^\circ$  walls in the exposed silicon. The protective oxide lines were then stripped using BOE. This process resulted in a trapezoidal pattern on the silicon surface with trench depths of approximately 20  $\mu\text{m}$ . A conformal CVD diamond film was grown on this surface, and subsequently the silicon substrate was etched away to leave a corrugated foil. The sloping trench walls present a

thickness to a normal incidence ion beam that is ca. 50% greater than the nominal foil thickness, but the portion of the foil that corresponds to the walls is only 7% of the entire foil area (at 50 lines/inch corrugation). A schematic view of an L-bracket supported sample is shown in Figure 1; the foil corrugations are arranged in a diagonal orientation to pin the free foil corner. An image of an actual sample is also shown; the corrugation period is 50 lines/inch for this sample.

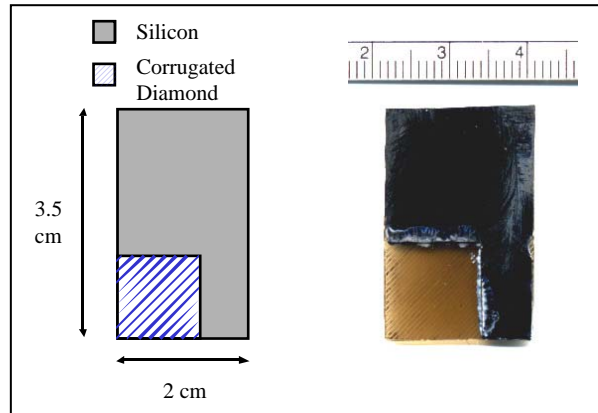


Figure 1. Schematic drawing and image of a corrugated foil test sample (50 Lines/inch). A cm scale is shown.

## FOIL TESTS IN THE BNL LINAC BEAM

The wafers were beam tested at Brookhaven National Laboratory, using the 750 keV H<sup>-</sup> Linac (6.7 Hz, 0.5 ms pulse). The beam was approximately circular, with a 3 mm diameter. A peak beam current of 2 mA was used for these tests so as to achieve the same energy loss in the foil as from the 50 mA, 1000-MeV SNS beam. Note that the SNS repetition rate is nine-fold higher than for the BNL Linac, and the foil lifetime in the SNS will be shorter. The test samples were 2 x 3.5 cm silicon coupons with a variety of window sizes: 7 mm round, 12x12 mm square ("window frame"), and 12x12 mm windows with L-bracket (two-edged) support. The total current was monitored behind the foil, and the lifetime was gauged by the time required for the current to drop to 90% of its initial value. However, tests were halted at about 130 hours, if the 90% current criterion had not been reached.

The test results are summarized in Table 1. Unfortunately our beam time for testing is limited, so the data are sparse at this time. However it can be seen that the lifetime for several of the foils exceeded 80 hours. The foils represented in Table 1 range from 1.0 to 1.9  $\mu\text{m}$  average thickness. Two foils (#4 and 5) were nanocrystalline (i.e., grown in the hot filament chamber with  $\text{CH}_4/\text{H}_2/\text{Ar}$  gas); the tests for both of these foils were terminated before the 90% criterion was reached. For comparison, foil #6 was microcrystalline; however, #6 was prepared with a smaller, round window and different

Table 1. Diamond foil lifetime test results for a 750 keV H<sup>-</sup> beam for a variety of diamond foils. The lifetime is defined as the time at which the downstream current decreased to 90% of the initial value. Foil # 1 was grown at a substrate temperature (ca. 900 °C) approximately 200 °C hotter than #2.

Foil Number	Growth Technique	Foil Structure	Reagent Gas Methane Content	Average Foil Thickness (μm)	Window	Measured Lifetime (Hr)
1	Microwave	Micro-	1%	1.9	12x12 mm	85.4
2	Microwave	Micro-	2%	NA	12x12 mm	16.4
3	Hot Filament	Corrugated, Nano-	1%	1.8	12x12 mm L-Bracket	60.0
4	Hot Filament	Nano-	1%	0.96	12x12 mm	>133
5	Hot Filament	Nano-	1%	1.1	12x12 mm	>120
6	Hot Filament	Micro-	1%	0.81	7 mm, Round	3.6

temperature maxima may have resulted for these foils. Foils #1 and 2 were grown in the microwave-powered chamber and were microcrystalline; the longer lived foil was grown at a substrate temperature (ca. 900 °C) approximately 200 °C hotter than the comparison foil. Foil #3 was nanocrystalline, corrugated at 100 lines/inch, and supported on only two edges; its observed lifetime was 60 hours.

The tested foils were characterized using SEM and Raman spectroscopy to ascertain beam-induced material alteration. A round, dark foil spot of the same size as the H<sup>-</sup> beam was observed. This region was typically wrinkled and damaged. Raman spectroscopic analysis showed clear evidence that a diamond-to-graphite conversion had occurred at the beam spot for both the nanocrystalline and microcrystalline foils. The sharp 1332 cm<sup>-1</sup> diamond phonon line disappeared, and new broad lines appeared at the positions of the D and G bands of graphite [6].

### CONCLUSIONS

To a large degree, corrugation of thin diamond films solves the curling problem for free standing foils. Flat foils scroll dramatically, while corrugated foils as large as 12 x12 mm only cup slightly. Our preliminary foil test results indicate that diamond foils with lifetimes greater than 100 hours can be prepared. It appears that nanocrystalline diamond exhibits a longer useful life than microcrystalline diamond for this beam stripping application. An L-bracket supported corrugated foil performed for 60 hours.

Future efforts will be focused on development of more reproducible diamond nucleation techniques,

improvements in corrugation geometry, and on further foil testing in the Linac beam.

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