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REACTIVE SPUTTER-THINNING OF LARGE DIAMONDS WHILE PRESERVING EXCELLENT CRYSTALLINE PERFECTION*

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Abstract: Production of monochromatic bremsstrahlung beams for high-energy physics at SLAC required thin slabs of (100) face diamond crystals with high crystalline quality. The starting material was selected to have double-crystal spectrometer /1/ rocking curves less than 20 seconds of arc in width. A radio-frequency sputtering process using argon-2% oxygen is described which has produced 7 mm-square diamond slabs 48 μm thick, with a uniformity of a few percent, from starting material 10 times the finished thickness. Etching rates of 45 μm/day are routinely obtained. Details of sputtering system design and process parameters are given, as well as their effect on etch rate and thickness uniformity. Double-crystal spectrometer rocking curves are shown to indicate the effect of sputtering and the final inert gas annealing step in maintaining the 20 arc-second rocking curve. Effects of annealing on electron-beam-induced radiation damage will also be demonstrated.

INTRODUCTION

Diamond crystals have been used to produce monochromatic bremsstrahlung beams /2, 3, 4, 5/ at the Stanford Linear Accelerator Center. The monochromatic photons are produced as a spike of narrow angular spread (sitting on the broad bremsstrahlung background) at specified angles with respect to the incident electron beam direction, and the diamond crystal planes. The monochromatic photon beam is obtained by collimation about the spike direction. In order not to wash out the spike, the diamond crystal must be both of high crystalline perfection and of a thickness (50 μm) such that multiple scattering of the incident electrons is small with respect to the spike width. Since conventional sawing and lapping techniques can only produce slabs of the order of 700 μm thickness, a reactive rf sputter-thinning and inert-gas annealing process were developed for production of 50 μm diamond slabs.

SPUTTERING APPARATUS AND PROCEDURES

A small, relatively simple rf sputter-thinning system was constructed, with the rf voltage applied between ground and the target electrode while the latter is allowed to assume a negative dc voltage determined by the discharge parameters. Figure 1 shows a schematic of the system which was constructed in a short length of 15-cm diam Pyrex glass pipe. The cathode electrode consists of a 6.3-cm diam, water-cooled copper cylinder insulated (by P.T.F.E.) from a coaxial ground electrode which has a 6 mm radial spacing to the cathode. (The close spacing prevents discharges from the side or back of the cathode.) A 2.5 mm-thick insulating platen (initially quartz, later 99% alumina) with the same diameter as the cathode was thermally sinked to it with silicone vacuum grease. The planar copper anode (12.7 cm diam) was spaced 3.7 cm from the cathode. A copper magnet coil surrounded the chamber and produced a 150 gauss axial magnetic field at the target, in order to increase the discharge intensity. The 3 MHz transmitter, operated at a plate input power of 500 watts, was matched to the discharge by a π-section filter from its 300-ohm, floating link output. The applied rf voltage measured during sputtering was about 5 kV peak-to-peak, while the negative dc bias voltage on the cathode was about 1.2 kV, and the chamber pressure was 2×10^{-2} Torr (2.7 Pa) of 98% A, 2% O_2 gas.

The sputtering system attained base pressures of about 1×10^{-7} Torr (1.3×10^{-5} Pa), produced by a 750 ℓ/sec diffusion pump fitted with a baffle and throttling gate valve. During sputtering, the throttle valve was adjusted for a pressure ratio of about 70, thus maintaining a substantial gas flow and high gas purity in the sputtering chamber.

The samples to be thinned were placed on the platen, within a 1-cm radius of the center. Within this circle, the etching rates were

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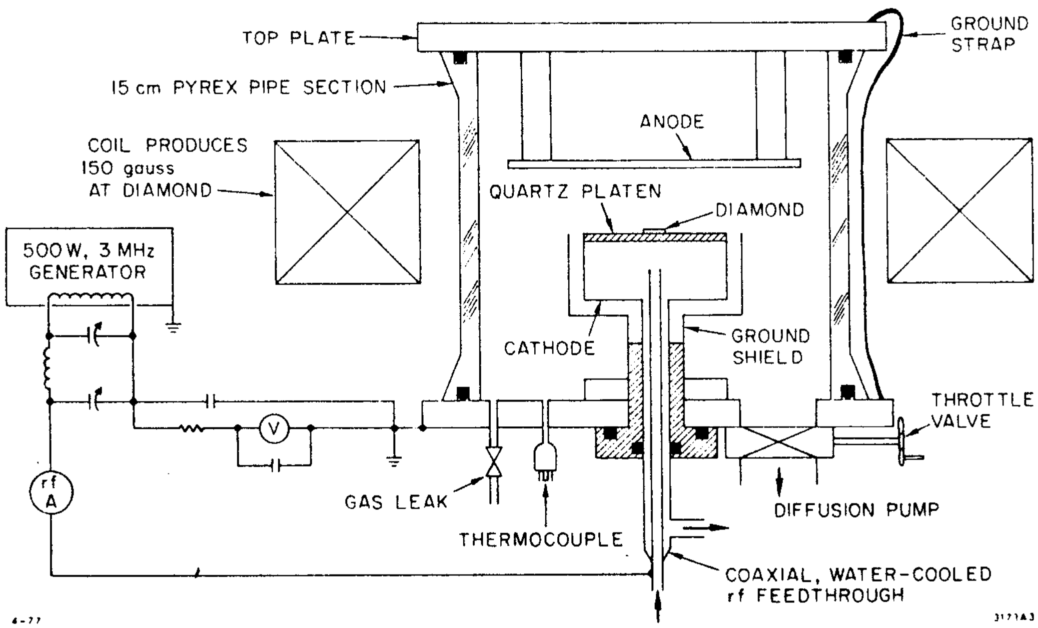

Fig. 1--Schematic of dc biased rf sputtering system.

uniform to within one or two tenths of a percent. The samples were carefully heat-sinked with silicone vacuum grease, taking great care that no grease contact the upper surface to be thinned. Initially, with pure argon as the sputtering gas, low etch rates were observed for the diamond, while erosion rates on the quartz platen were so high as to require frequent platen replacement. Addition of 2% O_2 to the argon not only increased the diamond sputtering rate, but also had the salutary effect of reducing the erosion rate of the platen. As is evident from Table I, which shows the effect of oxygen addition on

TABLE I

Sputter-etching rates, in μm/day, of various dielectrics for two gas compositions

Material	Pure Argon	Argon + 2% O_2
Diamond	16	43
Pyrex	58	19
99% Alumina	--	33
Quartz	81	23

etching rates of various materials, the diamond thinning rate is increased by a factor 2.7. The quartz erosion rate is reduced by a factor 3.6, which considerably exceeds the factor 2.3 previously reported /6/ at a comparable oxygen partial pressure.

With 2% O_2, 50 μm-thick diamonds could conveniently be produced from available starting slabs in two sputtering runs, each about one week long. After the first half of estimated running time, the thinned diamond was removed, cleaned in solvent, lapped lightly on a piece of diamond-impregnated boxwood, and measured with a micrometer. The diamond was then greased to the platen with the previously unsputtered face up, in order to produce in both faces equal stresses from the radiation damage /7/ due to ion bombardment and trapping. These stresses were observed to bow (and ultimately crack) glass sections thinned from one side only. The length of the second and final run could be adequately calculated from the results of the first.

Although the thinnest diamond produced to date was 48 μm, it is believed that a 25 μm section could easily be prepared. In order to handle even the 48 μm section, great care is required lest the crystal be cracked. Most of the crystal handling is accomplished with a flat-ended tube connected to a vacuum pump. This 1.5 mm-diam tube provides adequate force to lift and hold the thin sections, although stamp collectors' tweezers are used when absolutely necessary. Breaking the vacuum releases the crystal from the end of the tube.

ROCKING CURVES AND ANNEALING OF SPUTTERING DAMAGE

As has been mentioned in the introduction, the thin diamond crystals must possess high crystalline perfection in order not to broaden the angular spike of monochromatic photons. In order to make quantitative evaluations of diamond quality, the stones were studied with a double-crystal x-ray spectrometer /1/ at the National Bureau of Standards. Initially, only those diamonds were selected which had no visible flaws. Next, the natural octahedrons were sawed apart on the (100) plane. Rocking curves of the (111) faces of the resulting square pyramids were obtained, in reflection, by using CuKα radiation and silicon (220). Requiring full width at half maximum (FWHM) better than 20 arc-seconds caused rejection of 90% of these crystals. The surviving diamonds were then slabbed parallel to the (100) plane, and mechanically ground and polished to a thickness of about 700 - 1000 μm. Rocking curves were then obtained for these sections, using CuKα radiation with a silicon (331) reference crystal in reflection and the diamond 220 planes in transmission. The rocking curves were obtained using all of the diffracted radiation from the crystal, as is done with topographs. The crystals were mounted with wax along a fraction of one edge (which occasionally produced some strain in the sputter-thinned sections).

After sputter-thinning, transmission rocking curves of the slabs were again obtained. Figure 2 shows one such curve for the 48 μm diamond after sputtering. The 96 arc-second

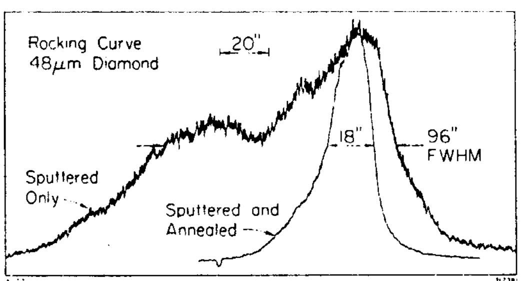

Fig. 2--Transmission rocking curves for 48 μm diamond: (1) As sputtered, (2) Sputtered and annealed for 4 hours at 950°C.

(96") FWHM clearly indicates a crystal highly strained by radiation damage from the sputtering process, since the FWHM was less than 20" before sputtering. The diamond in Fig. 2 was annealed in flowing argon for 4 hours at 950°C to produce the 18" FWHM curve.

ANNEALING OF HIGH-ENERGY ELECTRON RADIATION DAMAGE

Unfortunately for crystalline perfection, use of these thin diamonds involves passage of an intense multi-GeV electron beam through the crystal for long periods of time. As is well known, these electrons displace atoms from their lattice sites, and in so doing also produce vacancy-interstitial pairs whose net effect is to increase the crystal volume and strain it locally. As long as the vacancy sites are quite dilute, i.e., few di-vacancies are formed, this damage can frequently be thermally annealed. Figure 3 shows a 30" FWHM

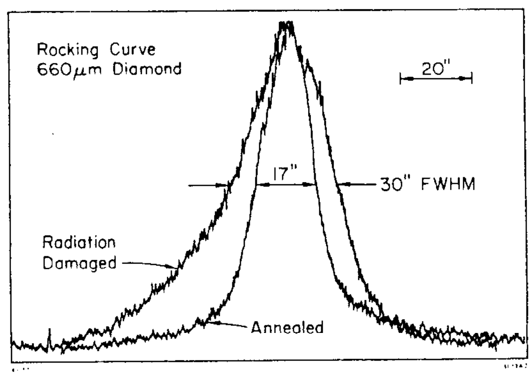

Fig. 3--Transmission rocking curves for 660 μm diamond: (1) Radiation damaged (10^{13} rad). (2) Annealed for 4 hours at 600°C followed by 4 hours at 950°C.

rocking curve for a 660 μm diamond slab which had been damaged by roughly 3×10^{19} electrons passing through an 0.1 cm^2 area, giving a dose of about 10^{13} rad. After annealing in argon at 600°C for 4 hours, the FWHM had fallen to 22" (not shown), and after a further 4 hours at 950°C the FWHM was 17", as shown in Fig. 3. Heating to 1100°C in argon did not further improve the rocking curve, and slight surface graphitization was observed, which could easily be removed by rubbing the crystal on a diamond-impregnated boxwood lap.

DISCUSSION

The apparatus and procedures described have demonstrated that 7 mm-square diamond slabs of 48 μm thickness can be produced from starting material 10 - 15 times thicker, while preserving a finished thickness variation of 2% through the use of rf sputtering with 98% argon, 2% oxygen. Recent results /8,9/, showing mass etch rates a factor 7 higher than this work for graphite in pure oxygen, merit investigation, particularly to see whether the required etch rate uniformity exists over the dimensions of the crystal to be thinned.

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